

Measurement of Toxic and Related Air Pollutants

TECHNICAL REPORT DATA

1. REPORT NO. 600/R-94/136		2.	
4. TITLE AND SUBTITLE Measurement of Toxic and Related Air Pollutants, 1994		5. REPORT DATE Aug, 1996	
		6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Bruce W. Gay, Jr., and Robert G. Fuerst, EPA R.K.M. Jayanty, RTI		8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Atmospheric Research and Exposure Assessment Laboratory Office of Research and Development US Environmental Protection Agency Research Triangle Park, NC 27711		10. PROGRAM ELEMENT NO. GC1A1E	
		11. CONTRACT/GRANT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Research and Exposure Assessment Laboratory Office of Research and Development US Environmental Protection Agency Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Proceedings, 5/2-6/94	
		14. SPONSORING AGENCY CODE EPA/600/R-94/136	
15. SUPPLEMENTARY NOTES EPA Author Papers received individual Agency clearance			
16. ABSTRACT <p><i>The 1994 United States Environmental Protection Agency/Air and Waste Management Association International Symposium: Measurement of Toxic and Related Air Pollutants was held in Durham, North Carolina on May 2-6, 1994. The four day technical program consisted of 210 papers presented in twenty four sessions plus a poster session with twenty papers. Individual sessions concentrated on recent advances in the measurement and monitoring of toxic and related air pollutants. The program consisted of sessions on air pollutants measurements of the OAQPS Enhanced Ozone Program, the Mount Mitchell Global Climate Change Program, the NC O₃ State Implementation Plan, Russian Air Pollution Studies, and general papers.</i></p> <p><i>Measurement and monitoring research efforts are designed to anticipate potential environmental problems. Research supports regulatory actions by developing an in-depth understanding of the nature of processes that impact compliance with regulations and evaluates the effectiveness of health and environmental protection through the monitoring of long-term trends. EPA's Atmospheric Research and Exposure Assessment Laboratory is responsible for research and development of new methods, techniques and systems for detection, identification and characterization of pollutants in emission sources and in indoor and ambient environments. The Laboratory has the responsibility of implementation of a national quality assurance program for air pollutant measurement systems, and supplying technical support to Agency regulatory programs and to state and local agencies.</i></p> <p><i>The A&WMA provides a neutral forum where professionals skilled in environmental matters share technical information about air pollution measurement and control. This year (1994) was the 14th consecutive year of holding the symposium and the 9th year of its co-sponsorship with the A&WMA.</i></p>			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/ OPEN ENDED TERMS	c. COSATI
18. DISTRIBUTION STATEMENT <u>Release to Public</u>		19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 1073
		20. SECURITY CLASS (This Page) Unclassified	22. PRICE

Proceedings of the 1994 U.S. EPA/A&WMA
International Symposium

*MEASUREMENT OF TOXIC
AND
RELATED AIR POLLUTANTS*

Jointly sponsored by the
U.S. EPA Atmospheric Research and Exposure Assessment Laboratory
Air & Waste Management Association

**VIP-39
Measurement of Toxic and
Related Air Pollutants**

Proceedings of the U.S.EPA/A&WMA International Symposium
Durham, North Carolina
May, 1994

Report Number EPA/600/R-94/136

Publication Policy

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PREFACE

The 1994 United States Environmental Protection Agency / Air & Waste Management Association International Symposium: Measurement of Toxic and Related Air Pollutants was held May 2-6, 1994 in Durham, North Carolina. This annual symposium is co-sponsored by the United States Environmental Protection Agency (USEPA), Atmospheric Research and Exposure Assessment Laboratory (AREAL) of Research Triangle Park, North Carolina and the Air & Waste Management association (A&WMA) of Pittsburgh, PA.

The four-day technical program consisted of 210 papers presented in twenty-four sessions plus a poster session with twenty papers. Individual papers focused on recent advances in the measurement and monitoring of toxic and related air pollutants in indoor and outdoor atmospheres. The program consisted of sessions on air pollution measurements of the OAQPS Enhanced Ozone Program, the Mount Mitchell Global Climate Change Program, the NC O₃ State Implementation Plan, Russian Air Pollution Studies, and Particles Studies, Quality Assurance and General Papers.

Courses offered in conjunction with the symposium were taught by experts in the field of air pollutant monitoring and focused on basic sampling and analytical methodology. Exhibits were on display from over sixty instrument development and consulting services. The keynote address was presented by Dr. George Hidy of the Electric Power Research Institute.

Measurement and monitoring research efforts are designed to anticipate potential environmental problems. Research supports regulatory actions by developing an in-depth understanding of the nature and processes that impact compliance with regulations and evaluates the effectiveness of health and environmental protection through the monitoring of long-term trends. EPA's Atmospheric Research and Exposure Assessment Laboratory is responsible for research and development of methods, techniques and systems for detection, identification and characterization of pollutants in emission sources, and in indoor and ambient environments. The Laboratory has the responsibility of implementation of a national quality assurance program for air pollutant measurement systems, and provides technical support to Agency regulatory programs and to state and local agencies.

The A&WMA provides a neutral forum where professionals skilled in environmental matters share technical information about air pollution measurements, monitoring techniques, and pollution control. This year (1994) was the 14th consecutive year of the EPA symposium and the 9th year of its co-sponsorship with the A&WMA.

Bruce W. Gay Jr. (EPA)
Robert G. Fuerst (EPA)
R.K.M. Jayanty (RTI)

SESSION 1:

**PREDICTING VOC EMISSION RATES
AIR QUALITY MODELS, DEPOSITION**

Model Predicted VOC Emission Rates Based on Measured Concentrations and Meteorological Data

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ABSTRACT

Two methods of estimating VOC emission rates from a single point source were field tested by the University of Kansas, in cooperation with Region VII of the U.S.EPA and Kansas State University. Both methods use path-integrated VOC concentrations and a form of the Gaussian dispersion equation. The methods differ in their use of meteorological data: Model 1 uses means of wind speed and wind direction for the duration of the test period; Model 2 uses one-minute means of those variables. Correlations between measured and estimated emission rates were significant at the 0.01 level for all compounds released. Based on all canister data, Model 1 provides 8% and 10% increases in mean estimation accuracy over the direct application of the integrated Gaussian equation (Equation 2) for 1,1,1-TCA and toluene, respectively; Model 2 provides 5% additional increases in both cases. Based on data from only those tests during which the assumptions used to derive the integrated Gaussian expression were violated, Model 1 provides a significant increase in estimation accuracy over Equation 2; Model 2 provides a significant additional increase: differences in Equation 2 and Model 2 predictions were significant at the 0.001 level for both 1,1,1-TCA and toluene. Model performance was also evaluated as a function of atmospheric stability: estimation accuracy generally increases and variability decreases as stability increases; Model 2 provides greater increases in accuracy over Model 1 as conditions become more unstable.

INTRODUCTION

The University of Kansas (KU) has assisted Region VII of the U.S.EPA in the development of a volatile organic compound (VOC) monitoring capability during the last several years¹. As a part of that work, KU and Region VII have field tested and refined a whole-air sampling and analysis method. In addition, KU has assisted in the field testing of an open-path Fourier Transform Infrared spectroscopic (FTIR) method developed by Kansas State University (KSU) and Region VII². Results have shown both methods to be viable for ambient air VOC monitoring.

In order to extend the capabilities of the two methods, KU, in cooperation with KSU and Region VII, is field testing techniques that use VOC measurements and meteorological data to estimate the emission rate³. The study is divided into three phases, which consist of field testing the emission rate models (1) using only a single point source, (2) using multiple point sources to simulate an area source during, and (3) at selected actual VOC sources. Data collection for Phase 1 was completed in July, 1993. Analysis of these data provide an assessment of the performance of the emission rate models; of particular interest were the applicability and relative accuracy of the models as a function of downwind distance and atmospheric stability. Because of space constraints, model performance as a function of distance is not discussed in this paper^{4,5}.

MODEL DESCRIPTION

The emission rate models being evaluated for the single-point-source case in Phase 1 are based on the premise that integration of the Gaussian dispersion equation in the crosswind direction results in an expression for the emission rate as a function of the path-integrated concentration³. The models differ in their use of meteorological data: Model 1 uses values for wind speed and wind direction that are averaged over the duration of the test period; Model 2 employs one-minute means of those variables, with one-minute dispersion estimates then summed over the test period^{4,6}.

During Phase 1, the effective emission height and the measurement height are both approximately two meters. With the source and receptors very near ground level, the applicable form of the Gaussian dispersion equation is as follows^{7,8}:

$$C(x,y) = (Q/\pi\sigma_y\sigma_z u) \exp[-1/2(y/\sigma_y)^2], \quad (\text{Equation 1})$$

where $C(x,y)$ is the concentration at (x,y) , x and y are the downwind and crosswind distances to the receptor, respectively, Q is the emission rate, σ_y and σ_z are horizontal and vertical dispersion coefficients, respectively, and u is the mean wind speed.

Integrating Equation 1 with respect to y , from $y=-\infty$ to $y=+\infty$, and rearranging yields:

$$Q = [(2\pi)^{1/2}/2] C_y \sigma_z u, \quad (\text{Equation 2})$$

where C_y = crosswind path-integrated concentration.

This method should produce a reasonably accurate value for the emission rate, given an accurate value of the crosswind path-integrated concentration and the satisfaction of assumptions made in the development of the above equations.

The integration of Equation 1 involved an assumption that x (and, consequently, σ_y and σ_z) was held constant. Therefore, the path-integrated concentration must be determined for a path normal to the mean wind direction. In addition, the integration was from $-\infty$ to $+\infty$; thus, all of the plume constituents at the measurement height must pass within the boundaries of the sampling network. Because of fluctuating winds, those assumptions are often violated, and in those cases the direct application of Equation 2 will not yield an accurate emission rate.

Meteorological data can be used to overcome this problem. Consider Equation 1 in a rewritten form: $Cu/Q = (1/\pi\sigma_y\sigma_z) \exp[-1/2(y/\sigma_y)^2]$. Summation of Cu/Q values for evenly spaced points along the measurement path yields a relationship between path-integrated concentration, wind speed, and emission rate for a given stability class and sampling network orientation:

$$\Sigma\{(1/\pi\sigma_y\sigma_z) \exp[-1/2(y/\sigma_y)^2]\}/n = \Sigma(Cu/Q)/n \approx C_y u/Q.$$

Values for $C_y u/Q$ can be calculated under the ideal-case conditions used to derive Equation 2 and summed across the path to yield $(C_y u/Q)_I$. Values can also be calculated using the measured wind direction data from the test period and summed to yield $(C_y u/Q)_M$.

The ratio of these two values can be used as follows: $C_{yI} = C_{yM} (C_y u/Q)_I / (C_y u/Q)_M$ where C_{yI} is the path-integrated concentration that would be observed under the ideal-case conditions and C_{yM} is the measured path-integrated concentration. C_{yI} can then be used in Equation 2 to more accurately estimate the emission rate. $(C_y u/Q)_M$ can be determined either by using means of wind speed and wind direction for the entire test period, or by using one-minute means of those variables, then summing over the test period. These two methods of determining $(C_y u/Q)_M$ give rise to the two emission rate models alluded to previously⁴.

EXPERIMENTAL METHODS

In order to meet the objectives of Phase 1, data were collected at several downwind distances, and under a variety of stability conditions. Although the choice of sampling days provided a generally similar synoptic weather framework from test day to test day, the effect of stability was examined by selecting the timing of test periods within a given day. Data were collected at downwind distances of 50, 100, 150, and 225 meters. The dimensions of the sampling network were adjusted along with downwind distance in an attempt to place a large percentage of the plume within the path during as many test runs as possible. Because of space constraints, a detailed methodological description, including study site characteristics, VOC plume generator

capabilities, meteorological data collection, and VOC sampling and measurement protocol, is not given here^(4,5).

RESULTS AND DISCUSSION

Overall Model Performance

Performance of Equation 2, Model 1, and Model 2 for 1,1,1-trichloroethane (1,1,1-TCA), toluene, and for a third data set that includes all other compounds released, is shown in Table 1. Results displayed are based on canister-derived path-integrated concentrations and on FTIR measurements. It should be noted that the third data set was collected using only one downwind distance and in one series of tests during three consecutive days in a previous field study⁹; therefore, it is not representative of the same range of conditions as are the 1,1,1-TCA and toluene data sets. Sample size and the mean and standard deviation of the estimation accuracies are shown (estimation accuracy is expressed as a percentage of the measured emission rate). Also shown in Table 1 are the correlations between the measured and estimated rates, as well as the level at which these coefficients are significant. Outliers were removed prior to analysis according to Dixon¹⁰.

Based on the canister data, Model 1 provides an increase in mean estimation accuracy for both 1,1,1-TCA and toluene over the direct application of Equation 2; Model 2 provides an additional increase. The standard deviations are approximately 30% for both compounds and all three prediction techniques. Model 2 provides the highest correlation with measured values for both compounds, but all correlations are significant at the 0.01 level. Little difference among the prediction techniques is seen in the "other compounds" data set.

Based on the FTIR data, mean estimation accuracy increases from Equation 2 to Model 1 to Model 2 for both 1,1,1-TCA and toluene. However, this increase is accompanied by a slight increase in variability and a slight decrease in correlation with measured values. All correlations are significant at the 0.01 level. Once again, little difference among the prediction techniques is seen in the "other compounds" data set. For both 1,1,1-TCA and toluene, canister data produced a higher mean estimation accuracy than did FTIR data.

Model Performance versus Atmospheric Stability

The sensitivity of the models to atmospheric stability can be explored by examining Table 2, which shows results for tests conducted under Class A, B, C, and D stability conditions, based on canister data for releases of 1,1,1-TCA. It is apparent that emissions were somewhat better predicted under more stable atmospheric conditions, and that the estimation variability decreased, both for results from any one model and among models, from Class A to Class D; correlations with measured values were also higher under more stable conditions. These trends are especially apparent for Equation 2.

Model 1 provides large increases in estimation accuracy over Equation 2 for Classes A and B. Model 2 provides additional large increases: Model 2 mean accuracies are at least 25 percent higher than those for Equation 2 in both cases. These large increases in estimation accuracy are accompanied by little change in variability and slight increases in correlation with measured values. Less difference among the three prediction techniques is seen for Class C; Models 1 and 2 provide slight increases in mean accuracy and slight decreases in variability. For tests conducted under Class D stability conditions, increases in estimation accuracy provided by Models 1 and 2 are accompanied by slight increases in variability and slight decreases in correlation with measured values.

Results for Class C stability can be studied more closely by examining Figure 1, which shows estimated versus measured emission rates for each of the three predictive techniques. Although correlation of Equation 2 estimations with measured values is high, Model 1 and Model 2 plots show less scatter and conform more closely to a line with slope of 1 and an intercept of 0.

Model Performance Under Conditions Where Assumptions Were Violated

Equation 2 was derived under two assumptions: (1) the path-integrated concentration must be determined for a path normal to the mean wind direction; and (2) all of the plume constituents at the measurement height must pass within the boundaries of the sampling network. In cases where those assumptions are violated, the direct application of Equation 2 will not yield an accurate emission rate. Model 1 and Model 2 were evaluated to determine the extent to which this problem can be overcome through the use of meteorological data. (Assumption 1 was considered to be violated if the mean wind direction was 15 degrees or more different from the network centerline direction. Assumption 2 was considered to be violated if less than 95% of the plume constituents at the measurement height passed within the sampling network, based on the meteorological data.)

Canister data for 1,1,1-TCA releases were divided into two subsets, one containing tests in which all assumptions used to derive Equation 2 were met, and one containing tests in which one or more assumptions were violated. Note that assumptions were violated during all tests conducted under Class A or Class B stability conditions. Figure 2 shows 95% confidence intervals for the mean percent accuracy for emission estimations from Equation 2 and Models 1 and 2 for both subsets. For the assumptions met subset, very little difference is seen among the three predictive techniques, each producing a mean percent accuracy of approximately 80 percent. Examination of results for individual tests reveals that when all assumptions are met, estimations are virtually equal for the three techniques for most tests.

For the assumptions violated subset, large differences among the techniques are seen. The mean percent accuracy for Equation 2 was less than 60 percent; Model 1 mean accuracy was above 70 percent; Model 2 was near 80 percent, virtually equal to those produced by all three techniques for the assumptions met subset. In addition, Figure 2 shows results from paired comparisons t-tests among the three predictive techniques. Those tests show that for all pairwise comparisons, results differed significantly at the 0.01 level or below.

Canister data for 1,1,1-TCA releases conducted under Class C stability conditions were divided in the identical manner as that described in the preceding paragraph. Figure 3 shows 95% confidence intervals for the mean percent accuracy. As in the previous case, very little difference is seen among the three predictive techniques for the assumptions met subset, with mean percent accuracies near 85 percent in all cases. For the assumptions violated subset, Equation 2 produced a mean accuracy of approximately 52 percent; Model 1 produced an increase to approximately 63 percent; Model 2 produced only a slight additional increase. Also shown in Figure 3 are results from paired comparison t-tests among the three techniques. Significant ($\alpha < 0.01$) differences were seen between the results produced by Equation 2 and Model 2. As would be expected from the similarity of their means, little significance is seen in the differences between Models 1 and 2. The differences between Equation 2 and Model 1 are not highly significant, due to the large variability in Model 1 results for this subset.

CONCLUSIONS

During Phase 1 of this study, two models that estimate VOC emission rates from a single point source, using path-integrated concentrations and meteorological data, were evaluated. The performance of Model 1 (which uses meteorological data averaged over the entire test period) and Model 2 (which uses one-minute means of meteorological data) are compared to the direct application of Equation 2 (the integrated Gaussian dispersion equation). Results reported in this paper yield the following conclusions:

- Based on both canister and FTIR data, VOC emission rates estimated by all three predictive techniques produced highly significant correlations ($\alpha < 0.01$) with measured rates for all compounds released. Overall, and for each data subset, Model 2 produced the highest mean percent accuracies of the three techniques.

- Model performance was sensitive to atmospheric stability. Estimation accuracy generally increased, and variability decreased, as atmospheric increased. Model 2 provided greater increases in accuracy over Equation 2 and Model 1 as conditions became more unstable, and it provided the most accurate emission estimates overall.
- For tests in which the assumptions used to derive Equation 2 were met, Models 1 and 2 produced virtually equal emission rate estimations as did the direct application of Equation 2. In the case of canister data, all three techniques produced mean accuracies of approximately 80 percent for both 1,1,1-TCA and toluene; FTIR data produced somewhat lower mean accuracies.
- For tests in which the assumptions were violated, Model 1 produced an increase in estimation accuracy over the direct application of Equation 2; Model 2 produced a statistically significant ($\alpha < 0.01$) further increase. A higher percentage of tests in which assumptions were violated was associated with decreasing atmospheric stability.

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Table 1. Results for All Compounds

Canister	1,1,1-TCA			Toluene			Other Compounds		
	EQ2	M1	M2	EQ2	M1	M2	EQ2	M1	M2
n	55	55	55	51	51	51	22	22	22
Mean	66.1	74.5	79.6	71.9	81.5	86.4	67.7	68.2	69.2
StDev	27.5	28.4	28.3	28.7	32.3	31.5	18.1	18.4	19.6
r/p	.766/.01	.767/.01	.776/.01	.773/.01	.747/.01	.781/.01	.911/.01	.909/.01	.903/.01
FTIR									
n	53	53	53	32	32	32	16	16	16
Mean	62.3	67.3	72.0	64.7	66.6	71.9	74.8	75.1	76.5
StDev	21.8	22.1	25.3	32.9	33.2	36.9	19.1	19.1	20.4
r/p	.798/.01	.783/.01	.741/.01	.846/.01	.855/.01	.841/.01	.901/.01	.899/.01	.889/.01

Table 2. Results by Stability Class

1,1,1-TCA Canister	Class A Stability			Class B Stability			Class C Stability			Class D Stability		
	EQ2	M1	M2	EQ2	M1	M2	EQ2	M1	M2	EQ2	M1	M2
n	8	9	8	10	10	10	24	24	24	13	13	13
Mean	44.0	60.4	69.9	63.9	78.6	90.4	71.1	75.3	76.2	72.1	78.7	83.5
StDev	37.4	42.8	42.8	25.9	32.0	29.5	24.7	20.8	20.0	22.2	28.3	30.4
r/p	.492/n.s.	.591/n.s.	.596/n.s.	.797/.01	.757/.01	.825/.01	.867/.01	.905/.01	.916/.01	.798/.01	.689/.01	.672/.01

r - correlation coefficient p - level at which r is significant (n.s. indicates not significant at the 0.05 level.)

Figure 1. Measured Versus Estimated Emission Rates (1,1,1-TCA, Canister Data)

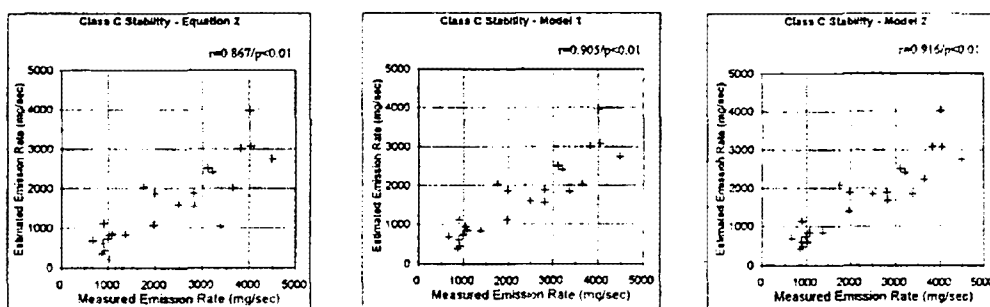


Figure 2. Model Discrimination
Canister Data, 1,1,1-TCA, All Stability Classes

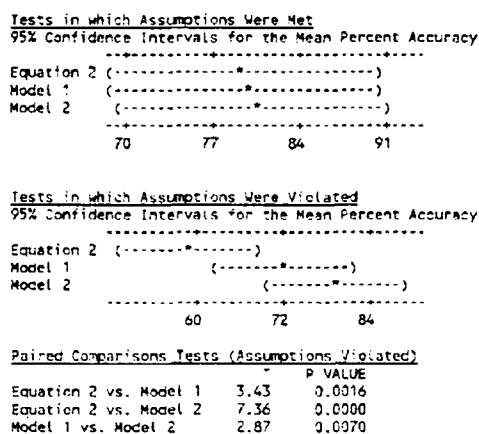
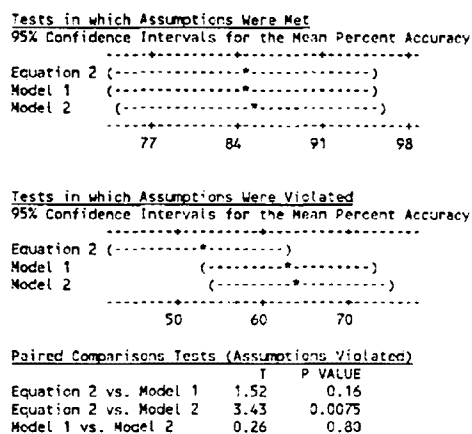


Figure 3. Model Discrimination
Canister Data, 1,1,1-TCA, Stability Class C



APPROXIMATION OF THE MAXIMUM IMPACT ON AIR QUALITY FROM AREA SOURCE EMISSIONS

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ABSTRACT

Atmospheric dispersion models for the estimation of ambient air quality impacts as a function of radial distance and azimuthal direction require representative meteorological data. Maximum radial concentrations (direction independent) are somewhat insensitive to meteorological data. To simplify the dispersion modeling process, screening models which do not require representative meteorological data have been developed. No such screening model is available for the estimation of maximum annual concentrations resulting from area source emissions.

The cost of representative meteorological data and the cost of dispersion modeling cannot be justified for many of the activities at Superfund sites. Many Superfund air pathway analyses can be satisfied with direction independent maximum concentrations.

Modeling (ISCST2) results which utilized 27 different meteorological data sets for various sizes of area sources were utilized to develop empirical equations for the approximation of maximum 1-yr, 24-hr, 8-hr, 3-hr and 1-hr concentrations. The required input data for these equations are: area size, distance to the receptor, and the emission rate. Development and testing of these equations is the subject matter of this paper.

BACKGROUND:

Atmospheric dispersion models for the estimation of ambient air quality impacts as a function of radial distance and azimuthal direction require representative meteorological data. Superfund air pathway analyses, for purposes of risk assessment, for purposes of determining the need for air emission controls, and for purposes of determining the necessity to monitor ambient air usually can be determined by the maximum radial concentration

(azimuth-independent). Maximum radial concentrations are somewhat insensitive to variations in meteorology and can be estimated using boilerplate meteorological data (the SCREEN model). The SCREEN model estimates maximum 1-hour radial concentrations. Factors which are used for the conversion of short term SCREEN values to longer averaging times are not applicable to SCREEN estimates for area sources.

The purpose of this study was to develop a method for the approximation of area source impacts for averaging times of 1-year, 24-hr, 8-hr, 3-hr, and 1-hour.

A paper¹ presented at the 1991 Annual Meeting of the Air & Waste Management indicated the need for on-site meteorological data to do dispersion modeling as needed for PSD permits. Observation of the results in this paper indicated that the estimations (using National Weather Service or on-site meteorological data) of the maximum radial long term concentrations did not differ by more than a factor of two.

The Air/Superfund Program of the Office of Air Quality and Standards in 1992 investigated^{2,3,4} the need for representative meteorological data for estimating emission impacts as needed for toxic air pollutant Air Pathway Analyses (risk assessment) at Superfund sites. Those studies indicated that representative meteorological data was not needed when approximations within a factor of two are acceptable.

The study report⁴ titled "Generation of Concentration Factors and Nomographs for Superfund Point and Area Sources" resulted in concentration factors for six sizes of area sources. Each factor is specific to area size, concentration averaging time, receptor distance, and meteorological data set. An approximation of the concentration is made by multiplying the factor by the emission rate. By selection of the factors which represent the median of the meteorological data sets, a best estimate is made. Best estimates are generally well within a factor of 2 of the concentration estimates for the meteorological data sets which have the best and worst dispersion.

In order to simplify and to expand the use of these factors, equations (regression) were developed mathematically.

DEVELOPMENT OF EQUATIONS:

Regression analyses on the study data⁴ revealed that the data from the study for each averaging time-area source size combination could be represented by the general formula (power relationship):

$$C_t = a(L/D)^b$$

where:

- C_t = concentration in $\mu\text{g}/\text{m}^3$ per $\mu\text{g}/\text{s}\cdot\text{m}^2$;
- L = the square root of the size of the area source;
- D = the distance in meters from the center of the source to the receptor;
- a & b are constants derived from the study modeling results.

Equations for approximation of the maximum 1-year concentrations from each of the six area source sizes were developed and are presented in Table 2.

Table 2. Maximum 1-year concentration in ug/m³ per ug/s-m² if D is in meters.

$C_t = a (L/D)^b$	
$C_{1-yr} = 1.157 (1/D)^{1.8629}$	$r^2 = 0.9989$
$C_{1-yr} = 1.379 (50/D)^{1.6362}$	$r^2 = 0.9996$
$C_{1-yr} = 1.499 (100/D)^{1.5885}$	$r^2 = 0.9997$
$C_{1-yr} = 1.584 (150/D)^{1.5542}$	$r^2 = 0.9997$
$C_{1-yr} = 1.752 (300/D)^{1.4888}$	$r^2 = 1.0000$
$C_{1-yr} = 1.908 (500/D)^{1.4228}$	$r^2 = 0.9999$

Inspection of the equations in Table 1 indicated that the constants a and b are closely related to the size of the area (L). Accordingly, the equations which are area size specific can be combined mathematically into the following equation which is not area size specific:

$$C_t = a(L/D)^b \quad \text{where: } r_a^2 = .9960 \text{ \& } r_b^2 = .9855$$

$$C_{1-yr} = 7.87 (L^{.141}) (L/D)^{2.0068 + .0521 \ln(L)}$$

Equations for approximation of the maximum 24-hr, 8-hr, 3-hr, and 1-hr concentrations were similarly developed and are listed below:

$$C_{\max, 24-hr} = 6.1 (e^{0.0009L}) (L/D)^{(2.3 - 0.27 \ln L)} (E_f)$$

$$C_{\max, 8-hr} = 14 (L/D)^{(2.3 - 0.30 \ln L)} (E_f)$$

$$C_{\max, 3-hr} = 14 (e^{0.0015L}) (L/D)^{(2.3 - 0.34 \ln L)} (E_f)$$

$$C_{\max, 1-hr} = (12 + 0.12L) (L/D)^{(0.82L)} (E_f)$$

where:

- $C_{\max, \text{xxx}}$ is the annual, 24-hr, 8-hr, 3-hr, or 1-hr maximum concentration in ug/m³ at the receptor distance D in meters from the center of the area;
- L is the square root of the source area in meters and is >25 and <1000 meters;
- D is the receptor distance, in meters, from the center of the area source and $L/2 < D < 2$ kilometers;
- E_f is the annual emission flux rate in ug/m²-s; and
- a is $e^{(-0.0057L)}$.

An additional equation was developed for approximation of

the maximum annual concentrations. Inspection of the original study data revealed that impacts from the six area sources were nearly equal at receptors which are at a distance equivalent to the square root of the respective area size. It was also found that by dividing these concentrations by the concentration at the center of the respective area sources, the range of the ratios differed by only about 10%. Using the average values of these ratios for receptor distances up to 8 area source diameters, the following relationship was developed:

$$C_{\max, 1\text{-yr}} = 0.584 \left((L^{1.737}) / (D^{1.536}) \right) (E_i) \quad r^2 = .9999$$

EXAMPLES:

Approximate the maximum annual concentration from a 2500 square meter area source with an emission flux rate of 1 ug/m²-s at the receptor which is 100 meters from the center of the area source.

$$\begin{aligned} \text{Using equation: } C_{\max, 1\text{-yr}} &= .787 (L^{1.41}) (L/D)^{2.0068 - .0921 \ln(L)} (E_i) \\ &= .787 (50^{1.41}) (50/100)^{2.0068 - .0921 \ln(50)} (1) \\ &= 0.44 \text{ ug/m}^3 \text{ per ug/s-m}^2 \end{aligned}$$

$$\begin{aligned} \text{Using equation: } C_{\max, 1\text{ yr}} &= 0.584 \left((L^{1.737}) / (D^{1.536}) \right) (E_i) \\ &= 0.584 \left((50^{1.737}) / (100^{1.536}) \right) (1) \\ &= 0.44 \text{ ug/m}^3 \text{ per ug/s-m}^2 \end{aligned}$$

note: 0.46 is report⁴ value

Approximate the maximum 8-hr concentration from a 2500 square meter area source with an emission flux rate of 1 ug/m²-s at the receptor which is 100 meters from the center of the area source.

$$\begin{aligned} C_{\max, 8\text{-hr}} &= 14 (L/D)^{(2.3 - 0.30 \ln L)} (E_i) \\ &= 14 (50/100)^{(2.3 - 0.30 \ln 50)} (1) \\ &= 6.4 \text{ ug/m}^3 \text{ per ug/s-m}^2 \end{aligned}$$

note: 6.0 is the report⁴ value

EQUATION TESTING:

In order to demonstrate the validity of the equations, a

comparison of formula derived values (this paper) to dispersion-model derived values⁴ was made and presented in Table 2. The values in the table were generated by dividing the difference between the two values by the dispersion-model derived values⁴ and multiplying the quotient by 100 to convert the value to percent difference from the dispersion-model derived value⁴.

Except for the 1 x 1 meter area source, none of the values are greater than 25% and are generally below 10%. This variation is insignificant since the approximations are meant to be only within a factor of 2. It should be noted that the 1 x 1 meter area source was not used to derive the equations.

TABLE 2. Percent difference from modeled results.

<u>50² meter² area size</u>		<u>receptor distance in meters</u>							
	<u>50</u>	<u>100</u>	<u>150</u>	<u>200</u>	<u>300</u>	<u>400</u>	<u>500</u>	<u>750</u>	<u>1000</u>
1-year	1	3	0	3	9	14	16	25	30
24-hour	12	6	6	8	9	7	5	1	1
8-hour	25	4	1	2	2	1	2	9	12
3-hour	11	5	12	15	14	13	11	4	1
1-hour	1	2	6	9	8	2	5	22	34

<u>100² meter² area size</u>		<u>receptor distance in meters</u>							
	<u>100</u>	<u>150</u>	<u>200</u>	<u>300</u>	<u>400</u>	<u>500</u>	<u>750</u>	<u>1000</u>	
1-year	2	0	1	1	4	6	12	13	
24-hour	4	1	3	2	2	2	1	2	
8-hour	11	6	5	5	5	6	10	13	
3-hour	5	4	0	5	5	4	2	4	
1-hour	6	6	3	5	9	9	2	8	

<u>150² meter² area size</u>		<u>receptor distance in meters</u>							
	<u>150</u>	<u>200</u>	<u>300</u>	<u>400</u>	<u>500</u>	<u>750</u>	<u>1000</u>	<u>1200</u>	
1-year	4	1	0	1	2	5	6	5	
24-hour	2	1	1	5	5	5	6	6	
8-hour	2	1	1	1	5	2	5	6	
3-hour	3	2	1	2	3	5	3	0	
1-hour	8	9	3	4	8	8	1	6	

<u>300² meter² area size</u>		<u>receptor distance in meters</u>							
	<u>300</u>	<u>400</u>	<u>500</u>	<u>750</u>	<u>1000</u>	<u>1200</u>	<u>1500</u>	<u>2000</u>	
1-year	6	2	2	0	1	1	3	5	
24-hour	1	1	3	4	4	3	2	1	
8-hour	15	14	12	12	12	12	13	12	
3-hour	2	1	0	4	8	9	8	2	
1-hour	3	0	2	7	9	8	3	11	

<u>500² meter² area size</u>		<u>receptor distance in meters</u>							
	<u>500</u>	<u>750</u>	<u>1000</u>	<u>1250</u>	<u>1500</u>	<u>1750</u>	<u>2000</u>	<u>2250</u>	
1-year	7	2	2	5	6	7	9	10	
24-hour	3	1	1	1	2	3	4	5	

8-hour	0	2	3	2	1	1	2	3
3-hour	2	2	3	4	5	5	5	3
1-hour	1	0	4	5	5	4	2	1

	<u>1² meter² area size</u>		<u>receptor distance in meters</u>		
	5	10	20	40	100
1-year	9	6	20	100	150
24-hour	65	80	87	91	95
8-hour	67	82	89	92	95
3-hour	79	90	94	96	97
1-hour	26	57	159	375	998

CONCLUSIONS:

Using the developed equations, it is practical and possible to approximate the exposure factors for risk evaluations of Superfund remediation actions. Such approximations can also be used to identify pollutants of concern, to determine ambient monitoring priorities and to determine the need for emission controls.

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AIRCRAFT MEASUREMENTS OF THE TRANSFER VELOCITIES OF GASES AND
AEROSOLS ACROSS LAKE MICHIGAN SURFACE DURING THE SUMMER

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Abstract

On June 18, 1992 our instrumented aircraft made a constant altitude flight over lake Michigan near the Chicago shoreline and about 50 km downwind of it. We use the eddy correlation method to calculate the fluxes of CO_2 , O_3 , water vapor and aerosols in the diameter range of 0.1 to 3.0 μm . The fluxes near the shoreline were found to be significantly higher than those in the middle of the lake. The turbulence intensities, as measured by $\epsilon^{1/3}$, were $2.92 \pm 0.75 \text{ cm}^{2/3}\text{s}^{-1}$ and $1.34 \pm 0.39 \text{ cm}^{2/3}\text{s}^{-1}$ near the shoreline and mid-lake respectively. We feel that fluxes we measured near the shoreline were representative of those at the surface of the lake, because of the strong turbulence we experienced during our measurement. However, we cannot assume the same for the fluxes measured at mid-lake.

The fluxes near the shoreline for O_3 and aerosols were directed toward the surface and corresponding to transfer (deposition) velocities of 0.15 cm s^{-1} and 0.86 cm s^{-1} , respectively. For CO_2 , and water vapor, the fluxes were directed upward and corresponding to transfer velocities of 0.04 cm s^{-1} and 0.54 cm s^{-1} , respectively.

Our west to east constant altitude flight, starting from Chicago, over the lake showed that turbulence, as measured by $\epsilon^{1/3}$, decayed slowly along the flight track. The O_3 concentration steadily increased from 39 ppb to about 52 ppb as the air moved away from the shoreline.

1-Introduction

From spring to the end of summer the temperature of the Great Lakes can be as much as 20°C cooler than the surrounding land (Eichenlaub 1979). The temperature difference between the lake's surface and the air above it can be as much as 5.0 to 10°C . Air advected over the cooler lake becomes very stable and dry deposition and diffusion will be insignificant. Miller et al. (1977) showed that a plume emitted from Oak Creek, south of Milwaukee, WI remained intact after it travelled 120 km across Lake Michigan. However, turbulent air advected over the lake will have to travel some distance from the shoreline before it becomes stable. The length of the travel depends upon prevailing meteorological condition such as air water temperature difference, and wind speed. Alkezweeny et al. (1977) measured vertical profiles of O_3 downwind of Milwaukee over the lake in August and found the advected air did not become stable until it travelled 20 to 50 km from the shoreline. This means that atmospheric input of pollution to the lake surface can be substantial even under such stable conditions.

2-DESCRIPTION OF THE MEASUREMENTS

The measurements were made using the University of North Dakota Cessna Citation Aircraft. The aircraft was instrumented to measure meteorological parameters, concentrations of aerosols and several trace gases. The aerosol size distributions were measured using the Particle Measuring System (PMS) passive cavity aerosol spectrometer probe (model PCASP-100X). The sampling time of this instrument is 0.25 s, and it covers the size range from 0.1 to 3.0 μm in diameter. The probe was mounted under the wings. The ozone concentrations were measured using the eosin-Y ozone analyzer manufactured by Scintrex. This instrument relies on a highly specific chemiluminescent reaction between the eosin-Y and ozone and has a response time of less than 1.0 s. The CO_2 and water vapor concentrations were measured using a nondispersive infrared instrument manufactured by Li-Cor. It has a response time of less than 0.1 s.

The horizontal and vertical winds were calculated from the data collected from a Rosemount Gust probe Model 858AJ, A Rosemount Model 102 temperature probe, and an LTN-76 Inertial Navigation System (INS). The calculation was made using the method described by Lenschow (1972)⁴.

The sampling altitude was maintained at about 300 m above the lake. Three segments of the flight will be presented (Fig. 1). The first was downwind of Chicago about 7 to 8 km from the shoreline between $42^\circ 13'/87^\circ 46'W$ and $41^\circ 54'/87^\circ 34'W$ (pass A), the second was an west-east route between $42^\circ 8'/87^\circ 39'W$ and $42^\circ 7'/86^\circ 54'W$ (pass B), the final segment was in the middle of the lake across the wind between $42^\circ 38'/86^\circ 58'W$ and $42^\circ 50'/87^\circ 18'W$ (pass C). During the flight the aircraft measured wind at the sampling altitude averaged about 12 m s^{-1} and was occasionally as high as 18 m s^{-1} , from about 250 to 260° .

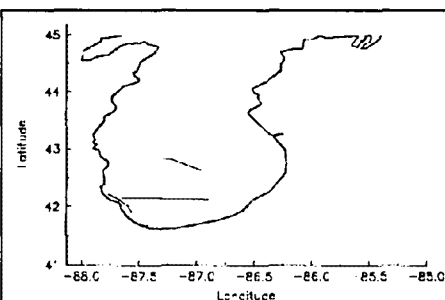
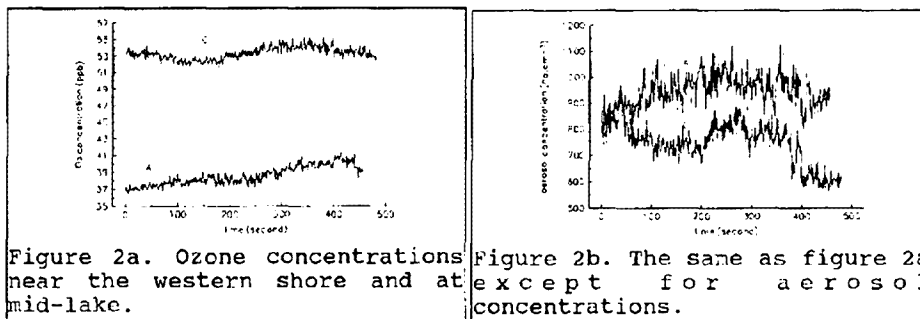


Figure 1. The aircraft sampling route over lake Michigan.

3-RESULTS AND DISCUSSION

Figure 2a and 2b show the concentrations of O_3 and aerosols



along pass A and pass C. Although the average O_3 concentration have increased from less than 39 ppb to about 53 ppb during transport, the average aerosol concentration actually decreased from 943 to 746 # cm⁻³ (Table 1).

Table 1: Averages of parameter levels measured over lake Michigan

parameter	near Chicago	mid-lake
CO_2 (ppm)	351±1	352±1
O_3 (ppb)	39±1	53±1
aerosols (#cm ⁻³)	943±69	746±81
aerosol mean diameter (μm)	0.21±0.01	0.23±0.01
water vapor (g kg ⁻¹)	10.7±0.2	11.2±0.2
turbulence (ε ^{1/3})	3.92±0.88	0.80±0.23
temperature (°C)	22.4±0.2	20.3±0.1
wind speed (m s ⁻¹)	12±1	13±1
wind direction (°)	258±6	262±3

Alkezweeny et al. (1977)³ and Alkezweeny (1980) used an instrumented aircraft and boats to study the formation and transport of ozone and sulfate aerosols over Lake Michigan. Although ozone formation was detected in all their daytime flights, no sulfate aerosol formation was found when the initial ozone concentrations were below 30 ppb. Furthermore, in that study the correlation coefficients between O_3 and aerosol concentrations for the data collected near the shoreline and mid-lake were 0.14 and 0.15 respectively. However, we have found a correlation coefficient of 0.755 for measurements taken on June 13, 1992 downwind of Chicago where the O_3 concentrations were between 65 and 100 ppb.

Since aerosol formation in urban plumes is dominated by HO reactions with SO_2 and NO_2 and ozone formation is dominated by HO₂ reaction with NO , the ratios of HO/HO₂ should differ from days with

different upwind levels of reactive species and meteorological conditions. When O_3 concentrations are high HO's sinks are suppressed and thus more HO molecules become available for the oxidation of SO_2 and NO_2 .

The fluxes of aerosols, water vapor, O_3 , and CO_2 were calculated using the eddy correlation method. The vertical wind, W , and the pollutant concentrations, S can be represented by the following equations:

$$W = \bar{W} + W' \quad (1)$$

$$S = \bar{S} + S' \quad (2)$$

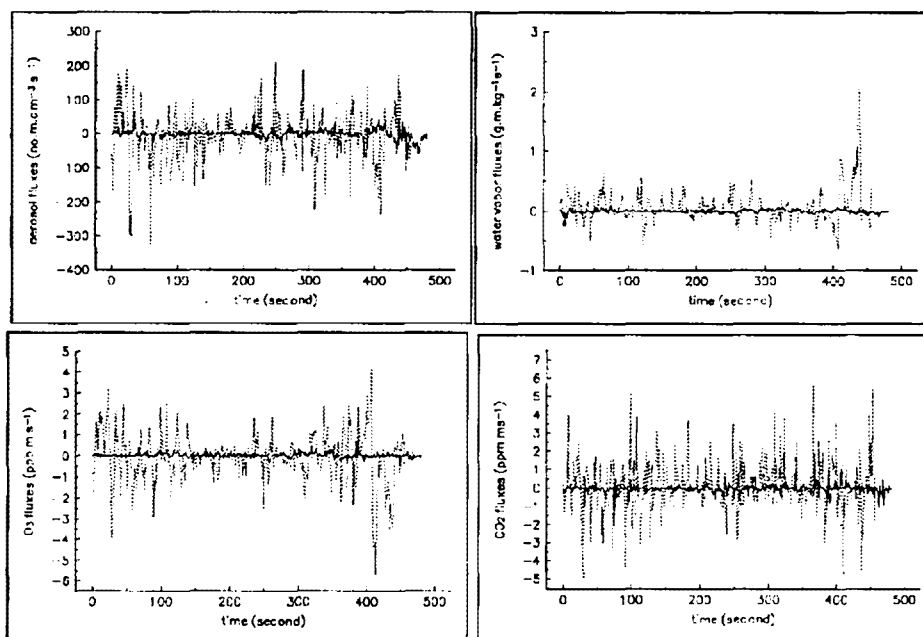


Figure 3. Fluxes of aerosols, ozone, water vapor, and carbon dioxide near the shoreline, pass A, dotted lines, and at mid-lake, pass C, solid lines.

the total flux is:

$$\overline{WS} = \bar{W} \cdot \bar{S} + \overline{W'S'} \quad (3)$$

the bar denote averages over a period of about 8 minutes and the primes denote deviations from the means. The first term in equation (3) represents the flux due to the mean flow and the

second term, the covariances between fluctuations of the vertical wind velocity and S , represents the vertical turbulence flux. Figure 3 shows the variation of the covariance along pass A and pass C for O_3 , CO_2 , water vapor, and aerosols. The figure shows that $W'S'$ near the shoreline is more than an order of magnitude larger than in the middle of the lake for all the gases and aerosols. In Fig. 4 we show the changes in the turbulence intensity in the subrange as measured by $\epsilon^{1/3}$, along pass B.

It is clear that as the air travels further over the lake it will continue to sense the cooler temperature below.

We have calculated the transfer velocity, V from the following equation:

$$V = \frac{\overline{W'S'}}{\bar{S}} \quad (4)$$

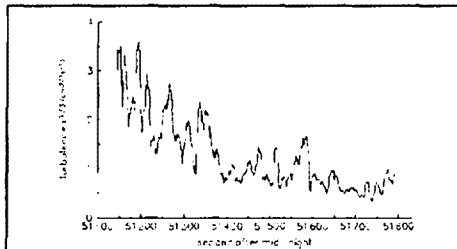


Figure 4a. Turbulence intensity along the B-sampling route.

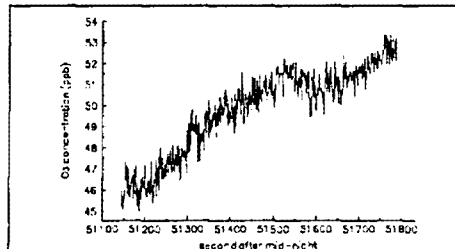


Figure 4b. The same as figure 4a except for ozone concentrations.

where the bar denotes time averages over about 8.0 minutes. A positive V values indicate emission, negative values deposition, and they are called deposition velocities.

The transfer velocities of O_3 , water vapor, CO_2 , and aerosols during pass A, 7.5 km from the shoreline are -0.15 , 0.54 , 0.038 , and -0.856 cm s^{-1} respectively, and in mid-lake during pass C, are 0.045 , 0.003 , -0.006 , and -0.226 cm s^{-1} .

There are not many aircraft measurements of the transfer velocities of the above species over water. Lenschow et al. (1982)⁴ used the eddy correlation method from aircraft, to measure the vertical fluxes of ozone over the North Pacific Ocean. They reported deposition velocities between 0.050 to 0.063 cm s^{-1} . These values are much lower than the 0.15 cm s^{-1} we measured. Earlier aircraft measurements of Lenschow et al. (1981)⁷ 100 km northeast of Denver CO showed a deposition velocity of 0.47 cm s^{-1} . Wesely et al. (1981)⁸ measured the ozone deposition velocity over Lake Michigan using eddy correlation from a tower about 25 km southeast of Chicago. They reported values between 0.008 to 0.045 cm s^{-1} . Their values are still lower than ours. It should be noted that

their measurements were made during northeasterly winds with speeds between 3.0 to 6.5 ms^{-1} . These values are much lower than the wind speeds during our measurements which were in excess of 10 ms^{-1} with a maximum of 18 ms^{-1} . Furthermore, under their northeasterly wind conditions the air traveled long distances over the cooler water and may have become more stable.

Wesely et al. (1982)⁹ also measured the transfer velocities of CO_2 at the Lake Michigan site they used for the ozone flux measurements. They reported a deposition velocity of (negative transfer velocity) 0.00102 cm s^{-1} . This is in contrast to our finding in which we measured an upward flux near the shoreline. Their measurements were made at wind speeds of 3 to 10 m s^{-1} which were much lower than ours. Although this value is about six times what we measured at mid-lake, at least it has the same sign. The positive value of our V is supported by result of a vertical profile of CO_2 we made on June 7, 1992 near the eastern shore of Lake Michigan across from Muskegon, MI. During the measurement a temperature inversion was present at about 700 m msl. A definite change in the CO_2 concentrations was observed across the inversion; the concentrations below were 2 to 4% higher than above. Upstill-Goddard et al. (1990)¹⁰ measured the transfer velocity of CO_2 from two small lakes in upland SW England from a boat using an SF_6 tracer. The measurement was carried out at wind speeds between about 2 to 13 ms^{-1} . Their upward transfer velocities are in the range of 0.003 to 0.007 cm s^{-1} , the higher values were associated with higher wind speeds. Our shoreline value of 0.006 cm s^{-1} obtained during the mid-lake flight is within their range. Our upward transfer velocity of 0.038 cm s^{-1} is in agreement with the results of the Heidelberg circular wind tunnel study (Jahne et al., 1979)¹¹.

Our aerosol deposition velocities are 0.86 cm s^{-1} near the shoreline and 0.23 cm s^{-1} at mid-lake. Wesely et al. (1982)⁹ used a nephelometer to measure aerosol loading and to determine the aerosol deposition velocity. This instrument measures the light scattering from aerosols in the accumulation mode, which is the same size range as our instrument. They reported a deposition velocity of 0.5 cm s^{-1} which is between our two values. Our upward transfer velocity for water vapor, 0.54 cm s^{-1} near the shoreline is in a very good agreement with wind tunnel study of Liss (1983)¹².

We are confident that our transfer velocities during pass A, near the shoreline are representative of those near the lake's surface because of the strong turbulence we experienced during the flight. We have recorded an average value for $\epsilon^{1/3}$ of $3.92 \pm 0.88 \text{ cm}^{2/3} \text{ s}^{-1}$. MacCready (1964)¹³ proposed turbulence scales of $1.5 < \epsilon^{1/3} < 3.5$ and $3.5 < \epsilon^{1/3} < 8.2 \text{ cm}^{2/3} \text{ s}^{-1}$ for moderate and heavy turbulence, respectively. This value is also about what we found during our flight over land at mid-day in the presence of convective activity, and very well vertically mixed air as indicated by the vertical profiles of O_3 and aerosols. However, at mid-lake the averaged value of $\epsilon^{1/3}$ was $0.80 \pm 0.23 \text{ cm}^{2/3} \text{ s}^{-1}$; such a value is found above the mixed layer, and in the $\epsilon^{1/3}$ range values of 0.0 to 1.5 $\text{cm}^{2/3} \text{ s}^{-1}$ which is considered as light turbulence (MacCready 1964)¹³. If the air had stabilized then the surface layer might have decoupled from the layers above the surface. In

this case our computed transfer velocities would not be representative of the lake-surface values. However, the values of $\epsilon^{1/3}$ we measured on this day are still much larger than what we measured at the same location one week earlier under northwesterly wind. On that day the air had spent a much longer time over the cool water and had enough time to stabilize. Therefore, our result may still represent transfer velocities for this particular wind speed. The positive transfer velocity of ozone might have been caused by more intense photochemical reaction near the surface than at our flight level because reflection from the surface enhanced the UV light intensity. Furthermore, lake temperatures near the shoreline may have been much warmer than mid-lake. The cooler temperature may have influenced the transfer velocities and possibly caused the CO_2 transfer velocity to be negative (deposition).

The data in Table 1 also agree qualitatively with the transfer velocity calculations. For instance, the average mixing ratios of CO_2 and water vapor are higher at mid-lake than near the shoreline; which is consistent with the measurements of positive transfer velocities near the shoreline. The increase in the CO_2 mixing ratio only about 0.28% compared with to about 4.67% for water vapor. Our calculations show that near the shoreline the transfer velocity of water vapor is about 14.21 times that of CO_2 , which is similar to the 16.68 value for the ratio of the percentage increase in the water vapor mixing ratio to the percentage increase of CO_2 between the shoreline and mid-lake. The reduction in the aerosol concentrations also indicated deposition as our calculation showed negative transfer (deposition) velocity. As expected the temperature of the air decreased by about 2.1 °C. The wind speed also increased as the air moved over smoother surface and it was deflected to the right as a result of the Coriolis force.

4-CONCLUSION

We have used the eddy correlation method to determine the transfer velocity of gases and aerosols over Lake Michigan downwind of Chicago. Our result shows downward transfer velocities (deposition) of 0.15 and 0.86 cm s^{-1} for O_3 and aerosols in the size range of 0.1 to 3.0 μm in diameter and upward transfer velocities of 0.04 and 0.54 cm s^{-1} for CO_2 and water vapor about 7.5 km from the shoreline. At mid-lake much lower transfer velocities were measured. The turbulence intensity, in the subrange, was found to decrease as the air traveled over the cooler water.

Even during summertime where the air is generally stable over the lake, deposition close to the upwind side of the lake cannot be ignored. The deposition will be enhanced and may be extended deeper into the lake surface under high wind conditions.

5-ACKNOWLEDGMENTS

This work was supported by the US Environmental Protection Agency through Cooperative Agreement CR-816010-01-0 to the University of North Dakota. While this work was supported by the EPA, it has not been subject to Agency review and therefore does not necessarily reflect the views of the Agency, no endorsement should be inferred.

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Development of the Operational Multiscale Environment Model with Grid Adaptivity (OMEGA) and its Aerosol Transport and Diffusion Model (ATDM)

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ABSTRACT

The Operational Multiscale Environment Model with Grid Adaptivity (OMEGA) is a new atmospheric simulation system that merges state-of-the-art computational fluid dynamics techniques with a comprehensive nonhydrostatic equation set. OMEGA is based on an unstructured triangular prism grid that permits a horizontal grid resolution ranging from 100 km down to 1 km, and a vertical resolution ranging from a few tens of meters in the boundary layer to 1 km in the free atmosphere. OMEGA contains an embedded Aerosol Transport and Diffusion Model (ATDM) that permits the high-resolution simulation of the advection and diffusion of either Eulerian or Lagrangian parcels.

OMEGA is naturally scale spanning, and its unstructured grid allows the addition or subtraction of grid elements at any point in space. This capability allows the model to readily adapt its grid to fixed surface or terrain features and land/water boundaries. The implications for the ATDM are that enhanced grid resolution can be provided in localized regions such as emission sources and receptor locations, or in the vicinity of a dust, smoke, or chemical cloud.

INTRODUCTION

Atmospheric processes are inherently scale-interactive. Current operational atmospheric simulation systems (Hoke *et al.*, 1989, Mesinger *et al.*, 1988), however, are scale-specific and have a limit to their resolution imposed by a fixed rectangular grid structure. This constraint limits the resolution of both the input boundary conditions and the resulting atmospheric simulation including the accurate forecast of the dispersal of gases and aerosols.

Adaptive grid refinement has been identified as an area of atmospheric model development that shows promise for providing selectively enhanced resolution for scale-interactive problems (Koch, 1993). Although a few groups have implemented adaptive grid techniques in nonhydrostatic, nested atmospheric models (Dudia, 1993; Skamarock and Klemp, 1992), these efforts still employ refinements to rectangular-based gridding schemes.

The Operational Multiscale Environment model with Grid Adaptivity (OMEGA) is a new nonhydrostatic atmospheric simulation system, based on an unstructured grid (AGARD, 1992), that makes possible a continuously varying horizontal grid resolution ranging from 100 km to 1 km, and a vertical resolution from a few tens of meters in the boundary layer to 1 km in the free atmosphere.

OMEGA was conceived to advance the capability for predicting the dispersion of hazardous releases. Embedded within the model are both Eulerian and Lagrangian aerosol and gas transport algorithms. These algorithms are being developed to permit the high-resolution simulation of the advection and diffusion of either grid-based aerosols or Lagrangian parcels.

This paper provides a short overview of the OMEGA/ATDM simulation system followed by two applications that demonstrate the system's unique grid generation and adaptation capabilities and their implications for the transport and diffusion of effluents.

OMEGA MODEL DESCRIPTION

OMEGA uses a fully nonhydrostatic equation set for its dynamics. The fundamental equation set for OMEGA is slightly different from that used in most atmospheric models because of the requirements for a completely flux-based system that conserves mass, momentum, and energy. This equation set is:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}) + \nabla \cdot (\kappa \nabla \rho) \quad (1)$$

$$\frac{\partial (\rho \mathbf{v})}{\partial t} = -\nabla \cdot (\rho \mathbf{v} \mathbf{v}) + \nabla \cdot (\kappa \nabla \rho \mathbf{v}) - \nabla P' - (\rho - \rho_0) \mathbf{g} \hat{r} - 2\Omega \times \mathbf{v} \quad (2)$$

$$\frac{\partial (\rho \theta)}{\partial t} = -\nabla \cdot (\rho \theta \mathbf{v}) + \nabla \cdot (\kappa \nabla \rho \theta) + \frac{1}{c_p} \left(\frac{P_r}{P_0 + P'} \right)^a \sum_i L_i S_i + Q_{rad} \quad (3)$$

$$\frac{\partial (\rho q_i)}{\partial t} = -\nabla \cdot (\rho q_i \mathbf{v}) + \nabla \cdot (\kappa \nabla \rho q_i) + S \quad (4)$$

where $\rho_0(r)$ and $P_0(r)$ represent a one-dimensional hydrostatic base state, Q_{rad} represents the radiation transport terms, and S encapsulates the microphysical interactions for the hydrometeor fields. This equation set is solved by using a semi-implicit scheme in the vertical dimension and an explicit scheme in the horizontal dimension. This solution balances the horizontal and vertical time step limitations; typical time steps are a few seconds.

OMEGA physics include a bulk-water microphysics scheme (Lin *et al.*, 1983) that incorporates cloud formation, growth, and precipitation processes (Figure 1), a convective parameterization scheme (Kuo, 1965; Anthes, 1977) used in regions where the resolution is insufficient to resolve the convection explicitly, and a radiation scheme that approximates the effects of carbon dioxide and water vapor on the radiation budget. OMEGA also contains an extensive planetary boundary layer (PBL) package with first and 1.5 order $\kappa - \epsilon$ turbulence closure schemes. The PBL is treated separately as viscous sublayer (Deardroff, 1974), surface layer (Businger *et al.*, 1971), and transition layer.

Grid Elements and Coordinate System

OMEGA is based on an unstructured triangular prism computational mesh. This mesh is unstructured in the horizontal dimension and structured in the vertical dimension. The benefit of having a structured vertical dimension is a reduction of three orders of magnitude in the computational requirements of the model. An OMEGA grid element is shown in Figure 2. The scalar quantities are defined at the geometric center of each grid element, whereas the vector quantities are defined at the center of the top face. In each case, the scalar or vector quantities represent the average of the variable over the cell.

OMEGA uses a rotating Cartesian coordinate frame (Figure 3). The origin is fixed at the center of the earth and the frame oriented such that the z -axis passes through the North Pole, the x -axis passes through the intersection of the equator and the Prime Meridian, and the y -axis is orthogonal to both. In this coordinate frame, the equations of motion are in their simplest possible form. The OMEGA grid elements are stacked vertically such that all of the cells in a column have the same projection onto the surface of the earth (Figure 3). This common projected footprint considerably simplifies the grid generation.

ATDM MODEL DESCRIPTION

Embedded within OMEGA are both Eulerian and Lagrangian aerosol transport modules. The Eulerian dispersion algorithm is based on equation (4). The Lagrangian algorithm computes the trajectories of nonbuoyant, passive and massless particles, or Gaussian puffs, under the influence of highly resolved three-dimensional space- and time-varying wind fields. Particles or puff centroids can be released instantaneously or continuously and their positions computed by using grid volume averaged velocities. These velocities are computed by using resolvable scale wind components obtained directly from the OMEGA model.

Currently, the ATDM is being developed to more realistically simulate the release of a variety of effluents. This development includes the addition of a calculation for particle slip velocity, a scheme to model forced and buoyant plume rise, a calculation of subgrid scale turbulent velocity fluctuations evaluated from the OMEGA PBL formulation, and the incorporation of parameterizations of the vertical eddy diffusivities (Blackadar, 1979; Businger *et al.*, 1971; O'Brien, 1970;).

Once aerosols are initialized, their origin and subsequent locations on the unstructured grid are updated in the vertical direction by using a comparative search on aerosol and model layer altitudes. Horizontal locations are updated with a successive nearest-neighbor search routine that evaluates the cross product of vectors formed between relative particle and vertex locations (Lottati, 1993).

APPLICATIONS

The utility of the OMEGA unstructured adaptive grid has been demonstrated for many terrain and land/water scenarios. Examples include the geography and topography of the island of Taiwan, the Korean peninsula, and the Chesapeake Bay area. Recently, Bacon *et al.* (1993) presented an OMEGA grid that was adapted to both the underlying terrain and the land/water boundary information of the northeast U.S., with additional high resolution specified for the DCA-JFK-BOS air traffic corridor.

Figure 4 shows the variable resolution obtainable when the model is allowed to refine the grid in the vicinity of sulfur dioxide point source locations (EPA, 1993) and receptor network sites (Dennis, 1990). The advantages of this capability for improved subgrid representation of emissions and wet and dry removal mechanisms are readily apparent.

Figure 5 shows the results of an OMEGA/ATDM simulation applied to an idealized sea breeze over the Florida peninsula. For this simulation, a computational domain of roughly 600 km by 700 km by 6.5 km was defined with a grid consisting of 3,929 triangles (ranging from 4 km to 20 km in edge length) in each of 23 layers for a total of roughly 90,000 cells. The grid shown in Figure 5a has high resolution in the vicinity of coastlines, surface property boundaries, and areas with a high potential for convective initiation. Note that, for comparison, a rectangular grid with 4 km resolution would require 26,250 horizontal cells in each of the 23 layers for a total of nearly 600,000 cells.

A southwesterly uniform flow of 6.0 m/s was initialized over the OMEGA model domain to represent a typical summer day under the assumption that neither frontal nor tropical systems were present during the simulation. The ATDM was initialized with three near-surface continuous releases: one near the Kennedy Space Center, one just southwest of Lake Okeechobee, and one near Cedar Key on the west coast of Florida.

Over the 12 hours of model simulation, the continuous differential heating between the land and the water and the resulting thermal mixing in the PBL result in a classic sea breeze circulation over the peninsula. The resulting wind field is characterized by a well-defined stationary sea breeze convergence zone along the east coast, a weaker convergence zone along the west coast, and a mesoscale lake breeze circulation over Lake Okeechobee.

Figure 5b shows the centroid of the series of continuous Lagrangian tracer releases from the three sites after 12 hours of simulation. In addition to the Lagrangian transport, Figure 5b also shows the logarithmic contours for the Eulerian dispersion from the same release points (the concentration contours are separated by a factor of 10). The three plume configurations clearly show the influence of the enhanced circulation

CONCLUSIONS

OMEGA represents a departure from traditional methods used for atmospheric simulation. For the first time in recent years, advanced numerical methods developed by the computational fluid dynamics community have been applied to the problem. This has permitted the development of an extremely high resolution atmospheric simulation and aerosol dispersion tool.

ACKNOWLEDGMENTS

The authors wish to thank I. Lottati of SAIC for providing invaluable support in grid generation techniques, and our past and present Technical Monitors, C. Gallaway, M. Byers, J. Hodge, and R. Cox of the Defense Nuclear Agency for their collaboration and support, which has considerably improved the model. The authors also wish to thank C. Wayland of the U.S. EPA for providing the emission inventory data.

This work is supported by the Defense Nuclear Agency under contract DNA001-92-C0076.

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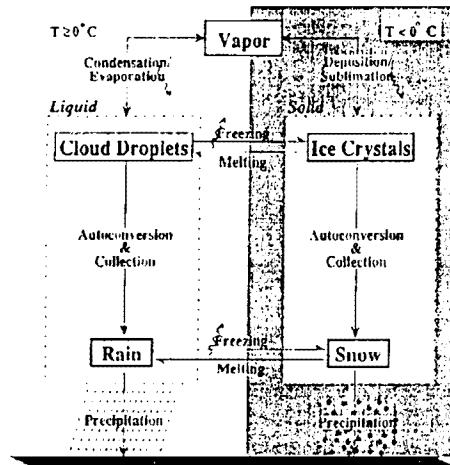


Figure 1. OMEGA microphysical processes.

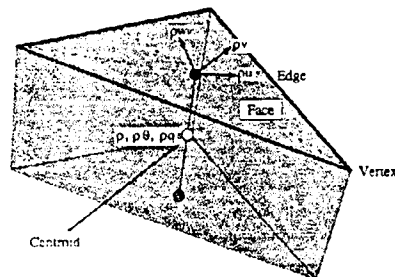


Figure 2. OMEGA grid element.

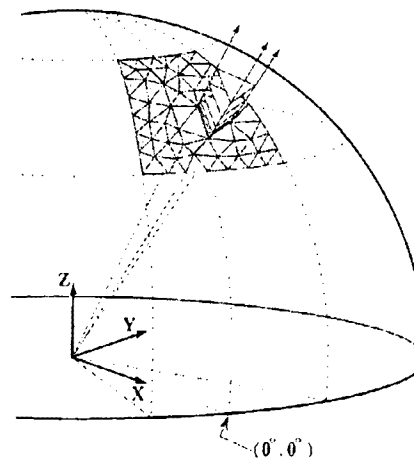


Figure 3. OMEGA coordinate system showing vertical alignment of the grid.

1990 REGIONAL INTERIM EMISSIONS INVENTORY
SUBSET OF SOURCES GREATER THAN 25,000 TPY SO₂

COMBINED RECEPTOR NETWORK SITE LOCATIONS
SUBSET OF A23, GEN, ME35, OME, OPT4, SUP SITES

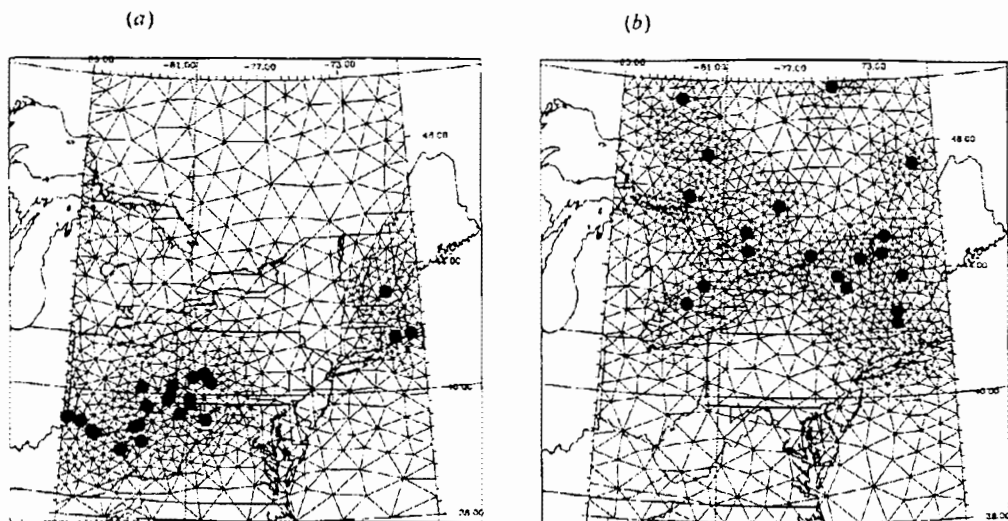


Figure 4. OMEGA grids in which the resolution was adapted to (a) source and (b) receptor locations.

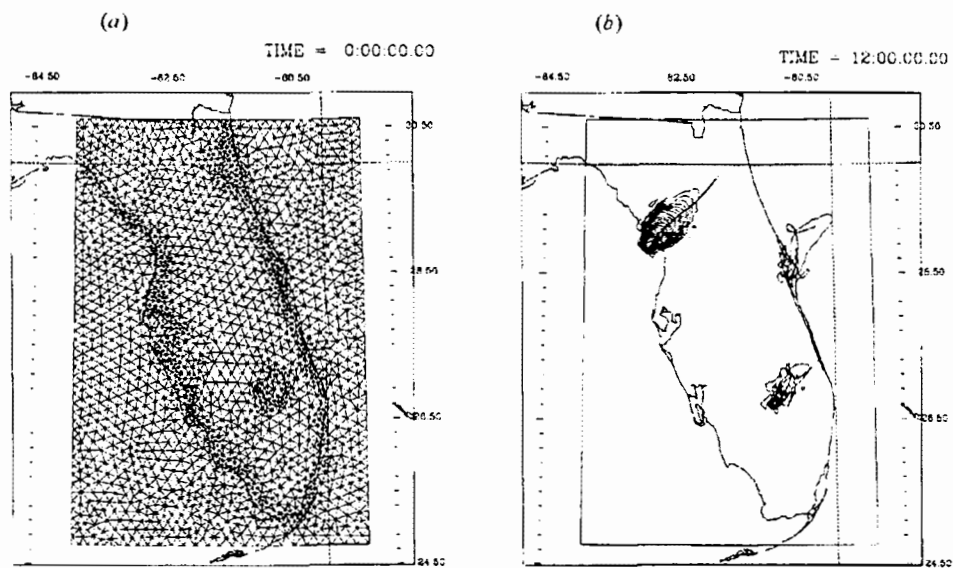


Figure 5. (a) OMEGA grid over Florida and (b) simulation of Lagrangian and Eulerian aerosol transport in a Florida sea breeze circulation using OMEGA.

SESSION 2:
VOC PORTABLE INSTRUMENTS/METHODS

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New Portable Micro Gas Chromatograph for Environmental Analysis

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Efforts directed at developing a truly portable method for the analysis of semivolatile compounds have led to the construction and testing of a new generation of micro-GC instrumentation. Building on the successful application of microbore GC columns for in-field analysis of volatile organic compounds, the instrument development group at the LSU-Institute for Environmental Studies has developed a hand portable GC capable of analyzing samples containing compounds with retention indices (100% dimethylpolysiloxane column) up to at least 2000 in less than 4 minutes, using less than 50 watts (peak) of electrical power. In addition to the ability to analyze semivolatile compounds, the chromatograph is capable of analyzing volatile organics competitively with the most sophisticated of the current commercial portable GCs. The presentation will evaluate chromatographic performance of the instrument at its latest stage of development and demonstrate some applications to environmental analysis using the prototype instrument.

**Triple Sorbent Thermal Desorption/Gas Chromatography/Mass Spectrometry
Determination of Vapor Phase Organic Contaminants**

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May, 1994

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** Managed by Martin Marietta Energy Systems, Inc., under contract DE-AC05-84OR21400
with the U.S. Department of Energy.

Triple Sorbent Thermal Desorption/Gas Chromatography/Mass Spectrometry Determination of Vapor Phase Organic Contaminants

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ABSTRACT

A thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS) method has been evaluated for the determination of volatile organic compounds (VOCs) in vapor phase samples using Carbosieve S-III/Carbotrap/Carbotrap C triple sorbent traps (TST), similar to those available from a commercial source. The analysis was carried out with a Hewlett-Packard 5985A or 5995 GC/MS system with a modified injector to adapt an in-house manufactured short-path desorber for transferring desorbate directly onto a cryofocusing loop for subsequent GC/MS analysis. Vapor phase standards generated from twenty six compounds were used for method validation, including alkanes, alkyl alcohols, alkyl ketones, and alkyl nitriles, a group of representative compounds that have previously been identified in a target airborne matrix. The method was validated based on the satisfactory results in terms of reproducibility, recovery rate, stability, and linearity. A relative standard deviation of 0.55 to 24.3% was obtained for the entire TD process (generation of gas phase standards, spiking the standards on and desorbing from TST) over a concentration range of 20 to 500 ng/trap. Linear correlation coefficients for the calibration curves as determined ranged from 0.81 to 0.99 and limits of detection ranged from 3 to 76 ng. For a majority of standards, recoveries of greater than 90% were observed. For three selected standards spiked on TSTs, minimal loss (10 to 22%) was observed after storing the spiked traps in a 4°C refrigerator for 29 days. The only chromatographable artifact observed was a 5% conversion of isopropanol to acetone. The validated method has been successfully applied to the determination of VOCs collected from various emission sources in a diversified concentration range.

INTRODUCTION

Recently, our laboratory has been involved in sampling and analyzing VOCs collected from various target airborne matrices. In order to evaluate the sampling adequacy and to assess any health-related impact based on the analysis results, a validated method must be employed. Therefore, the main objective of this study was to develop a methodology for TD/GC/MS determination of VOCs in the vapor phase samples collected on Carbotrap/Carbotrap C/Carbosieve S III triple sorbent traps. The validated method will eventually be used to monitor VOCs present in the headspace of potential emission sources. Techniques used for method validation included VOC standard generation, thermal desorption efficiency, reproducibility of spiking on and recovery from TST, internal standard selection, determination of detection limits, construction of calibration curves, and examination of possible artifact formation. As an example of applying the validated

methodology to a problem directed task, analytical results of VOCs present in the headspace in an underground waste storage tank at the Hanford site will be discussed. In the recent years, various TD/GC/MS methodologies have been reported in the literature (1-10). A majority of the thermal desorption interfaces used in the prototype or the commercially available thermal desorption devices employ one of the following pre-concentration techniques: (a) A short-path desorber uses solid sorbent traps of defined dimensions (1-5). The desorbed material is concentrated on an intermediate narrow sorbent trap, followed by transferring to the GC column via a second thermal desorption step. However, the existence of the second trap affords the opportunity for both sample loss and artifact formation. (b) A thermal desorption interface transfers VOCs directly onto a GC column (6-10), a packed or a cryogenically maintained capillary column. With this technique, unless a jet separator is installed on the transfer line (between GC outlet and MS source), the desorption flow will be limited by the carrier gas flow. Thus, the long desorption time will eventually cause band broadening of the analytes at the column inlet (7). However, with a jet separator, the instrument detection limit will be increased. In this study, a simple TD/GC/MS interface was constructed which enables us to change the injector port (HP 5985, or HP 5995) readily from injection mode to thermal desorption mode while maintaining the carrier gas at the optimal flow rate (less than 2 ml/min) and without installing a jet separator. The column was disconnected from the cyofocusing loop via a low dead volume union during the TD process, allowing the desorption gas purging through the TSTs at a flow rate of 40 ml/min. An in-house manufactured short-path desorber, capable of heating TSTs from ambient to 400°C in 2 min, was installed on a modified injector port to transfer the desorbed material directly through the glass liner in the injector port into the cryofocusing loop. This minimized any band-broadening of the analyte.

INSTRUMENTATION AND ANALYSIS

Triple Sorbent Traps Preparation

Triple sorbent traps (TST, 6 mm OD, 76 mm x 4 mm ID stainless steel tubing) were prepared in batches of 15 as the following: the traps were plugged at the upstream end of the sampling flow with approximate 15 mm of silanized glass wool and filled with a 14 mm length each of three carbonaceous adsorbents from Supelco (Bellefonte, PA). The least adsorptive one (20-40 mesh Carbotrap C) was packed first, tapping the side of the tube after adding the adsorbent to settle it in the tube. Carbotrap (20-40 mesh), was added next, again settling the adsorbent by tapping the tube. The most adsorptive material, Carbotsieve S-III (60-80 mesh), was added last with similar treatment. Another 15 mm plug of silanized glass wool was then inserted in the downstream end. Swagelok stainless steel caps and nuts and Vespel/Graphite ferrules (1/4" OD) were used to seal the traps. These traps are similar to Supelco Carbotrap 300, which was packed with a less proportion of Carbotsieve S-III and with glass wool partitions between sorbents. Each batch of TSTs was conditioned by thermal desorption on a manifold, which was placed in a gas chromatograph oven. The traps were heated at 400°C for 3 hours with helium (high purity, passed through an oxygen and molecular sieve trap) flowing opposite to the sampling direction at a flow rate of 60 ml/min. Two blank traps randomly selected from each batch were analyzed by TD/GC/MS prior to spiking and/or sample collection to ensure the cleanliness of the traps.

Gas Phase Standard Preparation and Spiking of TSTs

The gas generation methodology used in this study is similar to those described in the static dilution method and the EPA Methods TO-1 and TO-2 (9-11), except for the differences in analytes. The gas standard mixture of the neat liquid standards as listed in Table 1 and 2, was generated in a concentration range of 0.2 to 1.0 ug/ml. Briefly, 2 to 10 ul of neat liquid standard mixture was injected through a Mininert® valve into a 250 ml preheated (70°C) glass bottle. The mixture was stirred with a magnetic stirring bar and glass beads for 30 min to ensure complete vaporization of the liquid. Aliquots of this gas standard mixture were spiked onto TSTs via a preheated (70°C) injector to obtain a concentration of 20 to 1000 ng/trap. The injector was constructed with a 1/4" stainless steel Swagelok Tee with the trap attached to one end of the Tee, and helium gas pushed from the opposite end of the Tee at a rate of 200 ml/min. Gas standard was slowly injected into the stream of helium through a septum attached to the third end (90° to the trap) of the Tee. A total of 400 ml of helium was pushed through the trap after the injection to ensure even distribution of the standards on the trap.

TD/GC/MS Analysis of VOCs Collected on TSTs

Mass spectral analysis was performed either on a Hewlett-Packard 5985 GC/MS (equipped with an EI/CI dual ionization source), or on a Hewlett-Packard 5995 GC/MSD system. A modification was made on the capillary split/splitless inlet system (Figure) to introduce the desorbed gas sample onto the column. A male Swagelok 1/4" nut was welded on the septum retainer nut for direct connection of TST traps. A section of aluminum clad fused silica capillary tubing (0.53 mm ID, 5 cm in length) was inserted through the septum to serve as a transfer line to the glass liner in the injector port. A capillary inlet adaptor fitting (Restek, Port Matilda, PA, Cat. No. 20633) with a 1/16" Swagelok was installed at the base of the injector port. A cryogenic loop, constructed with 15 cm of stainless steel tubing (0.04" ID, 1/16" OD) was connected to the inlet adaptor with a 1/16" Vespel/graphite ferrule. A fused silica capillary column (Restek, Bellefonte, Rtx-5, 60 m, 0.32 mm ID, 1 um film thickness) was connected to the cryogenic loop via a 1/16" Valco zero-dead volume union. A flash heating tube furnace, capable of heating TSTs up to 400°C in 2 min, was constructed from a coiled resistor cable heater (Watlow Cable Heater Co., St. Louis, MO, 50 mm x 7 mm ID, 120 V, 240 W, 2 A). The heater was encased in a ceramic tube using high temperature cement.

In a typical analysis, the cryogenic loop was first immersed in a liquid nitrogen bath and the column was disconnected from the zero-dead volume union. A TST trap was then placed in the tube furnace and heated to 400°C. The trap was purged with helium at a flow rate of 40 ml/min for 7 min in the opposite direction of sampling flow. The column was connected back to the union to transfer the desorbed material from the cryogenic loop to the head of the column. The GC oven temperature program was initiated when the liquid nitrogen bath was removed from the cryogenic loop. The GC oven was held at 10°C for 10 min, then increased to 230°C at a rate of 3°C/min. The flow rate of carrier gas (helium) was held at 1.33 ml/min (16 psig head pressure). Both injector temperature and GC/MS transfer line temperature were held at 280°C. EI spectra were obtained with an electron energy of 70 eV, emission current of 300 uA, and a source temperature of 200°C. Mass spectral data were acquired at a scan rate of 266 amu/sec over a mass range of 35 to 300 amu. The integrated area of the total ions or of a selected ion was obtained for each

component for data manipulation.

RESULTS AND DISCUSSION

Thermal Desorption Efficiency

The gas standard was generated by evaporating a neat mixture of liquid standards in a heated gas bottle as described in the static dilution method (11). Aliquots of the gas standard were spiked onto triplicate TSTs at a concentration of 200 ng/trap for subsequent TD/GC/MS analysis. The air-based standard has several advantages over the standard method of spiking a liquid standard onto the trap. It represents more accurately the air sample matrix than liquid standards. By eliminating a large deposition of solvent (such as methanol) on the sorbent bed, not only all the active sites are available to trap small molecules, but also the capillary column performance improves, because evaporation of a large volume of solvent can cause flooding of the column. For each standard, the desorption efficiency was calculated based on the ratio of the integrated area for a selected ion generated from TD/GC/MS to that generated from direct injection of the same standard followed by GC/MS analysis. As indicated in Table 1, TD/GC/MS efficiency is greater than 91% for all the standards studied.

Recently, a number of investigations (12,13) have examined the issues of artifact formation from the VOCs that have been collected on TSTs. Because under the thermal desorption conditions, the large surface of TST carbonaceous media may act as a catalytic surface to facilitate thermal decomposition reaction for VOCs. In order to address this issue, we have compared the total ion chromatograms obtained from direct injection of a gas standard mixture with those obtained from TST that have been spiked with the same standard mixture. Results indicated that the two sets of total ion chromatograms were virtually identical, suggesting there is no chromatographable artifact formation produced from thermal desorption. The only indication that may suggest an artifact formation is a small frontal peak observed when isopropanol was in the standard mixture. Systematic further examination of the desorption of isopropanol from TST revealed that approximately 5% of isopropanol is converted to acetone during thermal desorption, probably through an oxidation process.

Internal Standards Selection

In order to monitor shipping, handling, sampling and recoveries, three surrogate standards were spiked on TSTs prior to sampling. A calibration internal standard was spiked on TSTs just prior to TD/GC/MS analysis to quantitate the analytes. The selection criteria included: (a) the selected compounds are thermally stable, and not likely to be present in the samples (deuterated analogs of the analyte are ideal), (b) their chemical structures and volatilities are similar to those of the analytes. Six compounds were initially selected and spiked on TSTs for TD/GC/MS analysis over a period of five days. They are d_8 -acetone, d -chloroform, hexafluorobenzene, d_8 -toluene, d_5 -bromobenzene, and d_6 -benzene. TD/GC/MS analysis results indicated that, with the exception of the first two compounds, the short term reproducibility was within 23% relative standard deviation (%RSD). Because of their high volatilities, the %RSD for d_8 -acetone and d -chloroform was greater than 33%. In order to minimize possible exposure to a potential carcinogen during shipping and sampling, d_6 -benzene was selected as a calibration internal standard, and hexafluorobenzene, d_8 -toluene, and d_5 -bromobenzene were selected as surrogate standards. A long term stability study was

carried out by spiking the three surrogate standards on TSTs and storing the traps in vials at 4°C. Duplicate or triplicate TSTs were analyzed on the 13th, 20th, 23rd, and 29th days of storage. The range of variation (10 to 24%) for the 29-day holding time experiments compares well with those obtained from the 5-day experiments (12 to 23%).

Reproducibility, Linearity, and Limit of Detection of TD/GC/MS

Triplicate TSTs were spiked with the gas standard at five concentrations, ranging from 20 to 500 ng/trap. Spiked TSTs were analyzed by GC/MS in random order over period of five days. The integrated area of a selected ion within an appropriate GC retention time window for each of the standards was used to calculate %RSD and the correlation coefficient (R^2). The ratio of the area for each standard to the area for the calibration internal standard (d_6 benzene) was also used in this calculation. Table 2 summarizes %RSD for 26 standards, calculated based on the area ratios. As indicated, once the instrument was tuned according to the manufacturer's specification, variation of the entire procedure (including gas standard generation, spiking onto and desorbing from TST) is less than 25%. As expected, reproducibility increases as the concentration of standard on TST increases. Linear regressions were performed using the same set of area ratios, and the results are summarized in Table 3. The correlation coefficients for all 24 standards ranged from 0.81 to 0.99, indicating the calibration curves remained linear over a concentration range of 20 to 500 ng/trap. This is a practical concentration for sampling, because 20 ng is generally near the instrument detection limit for most of the analytes, and 500 ng is within the breakthrough mass for TSTs. The instrument detection limits were estimated based on a signal to noise ratio of 3 (14,15). As shown in Table 3, except for 1-butanol, the detection limits for the remaining 23 standards are below 30 ng (or approximately 7 ppbv for a compound with a molecular weight of 100). The 1-butanol exhibits very poor chromatographic characteristics on the Rtx-5 (5% diphenyl 95% dimethylpolysiloxane) column because it is a polar compound. This may contribute to the high detection limit.

Application of the Validated Methodology

DOE's Hanford nuclear site is a 560 square miles installation in southeastern Washington State, at which are 177 large (0.5 to 1.1 million gallon) underground waste storage tanks (16). In order to determine the headspace components of these tanks, a number of TST were fabricated and shipped to the site for sampling. Prior to shipping the TSTs to the Hanford site, three surrogate standards were spiked on 50 TSTs at a concentration of 500 ng/trap from three batches of gas standard preparation. Every fifth spiked TST was retained for quality control usage. Five spiked TSTs were analyzed by TD/GC/MS to ensure the spiking reproducibility, and the remaining five were analyzed with the sample TSTs to evaluate the recovery rate. As indicated in Tables 4 and 5, the %RSD fell within 9% for the three surrogate standards, and the recovery rate from TST samples ranged from 45% to 117%, with hexafluorobenzene exhibiting the lowest recovery. VOCs identified in the headspace sample collected from a Hanford underground storage tank represent a wide range of chemical class and volatility (details of these findings will be reported elsewhere). Briefly, the VOCs found were alkanes and alkenes (C3-C16), alkanones (C3-C10), alkyl nitriles (C3-C9), aromatic hydrocarbons (one and two rings), and alkyl substituted (C1-C4) aromatic hydrocarbons, tributylphosphate, and dibutyl butylphosphonate. The concentrations for these compounds ranged from 0.15 to 60 mg/m³, with long chain hydrocarbons (C10 to

C15) being the most abundant components.

CONCLUSION

A thermal desorption/gas chromatography/mass spectrometry methodology has been developed for the determination of volatile organic compounds collected on the carbonaceous-based triple sorbent traps. An in house manufactured short-path desorber was adapted to a modified GC/MS injector for easy conversion of the injection port into a thermal desorption interface. A cryofocusing loop was installed at the injector base and can be disconnected from the GC column via a low dead volume union in order to accommodate the high flow during the thermal desorption process. The method was validated in terms of reproducibility, desorption efficiency, linearity, and detection limit. The validated method has been successfully applied to the characterization of VOC's collected from various emission sources including an underground storage tank at the Hanford site.

ACKNOWLEDGEMENT

Research was sponsored by the U.S. Department of Energy, Office of Technology Development, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. We wish to thank W. H. Griest of the Chemical and Analytical Sciences Division for the helpful comments which improved the manuscript, and R. R. Smith of the Chemical and Analytical Sciences Division for his assistance in obtaining the Hanford samples.

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Thermal Desorption/Gas Chromatography/Mass Spectrometry System

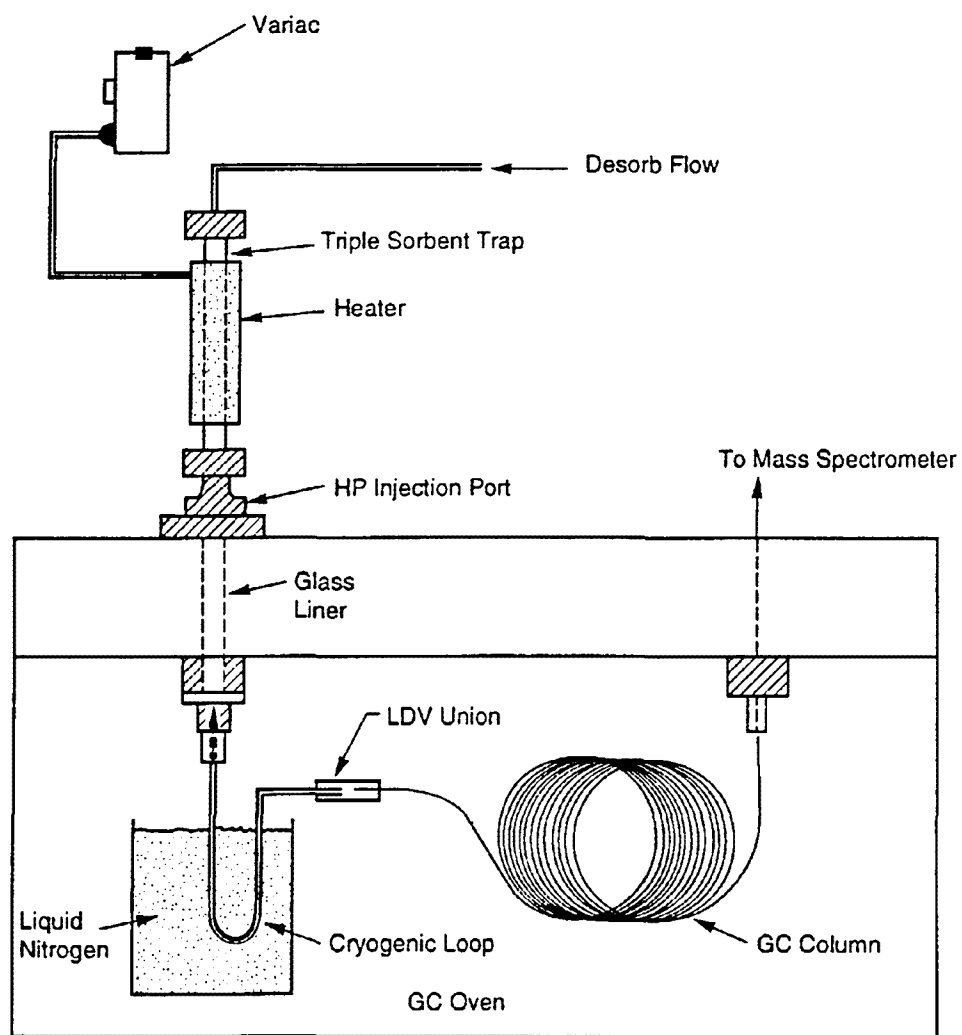


Table 1. Triple Sorbent Trap Desorption Efficiencies by Thermal Desorption/Gas Chromatography/Mass Spectrometry.

COMPOUNDS	% RECOVERY (HP 5985)	% RECOVERY (HP 5995)
Acetonitrile		111
Acetone	132	102
Hexane	96	98
1-Butanol	115	91
Benzene	102	97
Butane Nitrile	96	101
2-Pentanone	111	91
Heptane	99	104
Pentane Nitrile	102	106
Octane	99	110
Hexane Nitrile	102	104
2-Heptanone	97	109
Nonane	107	111
2-Octanone	119	112
Octane Nitrile	92	104

Table 2. Reproducibility of Thermal Desorption/Gas Chromatography/Mass Spectrometry.

COMPOUNDS	QUANTITIES SPIKED ON TST				
	20 ng	50 ng	90 ng	180 ng	500 ng
Acetonitrile	7.29*	5.76	7.34	6.32	8.34
Acetone	15.0	4.58	6.82	11.2	2.71
Methylene chloride	3.71	2.53	0.85	1.97	1.25
trans-1,2-Dichloroethylene	5.51	12.5	5.85	4.74	2.06
Propane Nitrile	1.49	4.13	8.80	19.7	3.71
Hexane	15.5	19.5	3.63	7.50	7.14
Hexafluorobenzene (SS)**	10.1	8.82	6.78	21.0	8.94
Benzene	2.95	2.30	4.22	0.57	1.65
1-Butanol	13.8	10.5	9.24	14.4	4.45
Butane Nitrile	5.57	5.28	4.49	10.2	5.19
2-Pentanone	8.32	4.91	9.75	7.57	3.11
d ₈ -Toluene (SS)**	1.73	4.67	1.02	1.71	1.36
Toluene	5.85	7.53	1.22	2.58	0.79
Pentane Nitrile	11.5	13.8	5.96	9.17	2.79
2-Hexanone	14.7	11.0	12.4	12.2	1.13
Octane	19.8	7.04	13.1	14.1	0.91
Hexane Nitrile	17.7	10.8	6.07	10.6	2.75
2-Heptanone	17.2	9.56	6.96	8.50	1.57
Nonane	24.3	7.44	9.23	9.06	1.30
d ₇ -Bromobenzene (SS)**	2.96	3.51	2.46	3.16	2.55
Heptane Nitrile	0.50	5.87	4.74	6.93	2.60
2-Octanone	20.7	5.54	6.14	9.27	1.50
Octane Nitrile	17.6	2.86	2.56	3.81	3.97
Nonane Nitrile	20.1	5.05	1.96	3.62	6.91
Dodecane	0.55	11.2	5.55	3.61	10.0
Tridecane	11.1	8.86	1.06	6.55	14.0

* Relative standard deviation

** Surrogate standards were spiked at a concentration of 500 ng/trap

Table 3. Linearity of Calibration Curves and Limit of Detection for Thermal Desorption/Gas Chromatography/Mass Spectrometry.

COMPOUNDS	HP 5995		HP 5985	
	Linearity (R^2)	Limit of Detection (ng)	Linearity (R^2)	Limit of Detection (ng)
Acetonitrile	0.9919	5		
Acetone	0.9991	4	0.9511	19
Methylene Chloride	0.9985	8		
trans-1,2-Dichloroethylene	0.9925	10	0.9181	27
Propane Nitrile	0.9940	8	0.9536	18
Hexane	0.9883	10		
Benzene	0.9931	6	0.9934	7
1-Butanol	0.9627	10	0.8122	76
Butane Nitrile	0.9984	4	0.9329	30
2-Pentanone	0.9821	3	0.9044	20
Heptane	0.9998	6		
Toluene	0.9899	5	0.9827	4
Pentane Nitrile	0.9911	11	0.9515	16
2-Hexanone	0.9919	3	0.9906	10
Octane	0.9915	5	0.9946	11
Hexane Nitrile	0.9992	8	0.9856	7
2-Heptanone	0.9996	10	0.9756	7
Nonane	0.9999	13	0.9869	7
Heptane Nitrile	0.9999	18	0.9672	7
2-Octanone	0.9999	9	0.9614	7
Octane Nitrile	0.9947	26		
Nonane Nitrile	0.8126	27		
Dodecane	0.8471	31	0.9756	5
Tridecane	0.8414	30	0.8756	7

Table 4. Results of Thermal Desorption/Gas Chromatography/Mass Spectrometry Analysis of Quality Control Triple Sorbent Traps for Sampling of Hanford Underground Storage Tank.

TST Spiked with Gas Standard	Hexafluorobenzene*	d ₈ -Toluene*	d ₅ -Bromobenzene*
Standard A	5778**	14387	5246
Standard B	5873	12815	4842
Standard B	6158	14991	4900
Standard C	6301	16424	5263
Standard C	6269	15281	5193
Average Response	6078	14780	5089
Standard Deviation	239	1324	202
% Relative Standard Deviation	3.93	8.96	3.96

* Surrogate standard spiked on TST's

** Selected ion response to approximate 500 ng surrogate IS

Table 5. Recovery of Surrogate Standards from Triple Sorbent Traps Sampled from a Hanford Underground Storage Tank*.

Hexafluorobenzene	d ₈ -Toluene	d ₅ -Bromobenzene
63	108	86
45	96	103
70	89	113
117	83	107
81	94	106
49	86	105
106**	117	103

* % Recovery analyzed with HP 5995 GC/MS

** % Recovery analyzed with HP 5985 GC/MS

**REMOTE MONITORING OF SUB PPB LEVELS OF VINYL CHLORIDE,
DICHLOROETHYLENE AND TRICHLOROETHYLENE VIA MODEM
OPERATED AUTOMATED GC**

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ABSTRACT

The need for remote monitoring of certain compounds in a sparsely populated area with limited user assistance led to the development and manufacture of a self contained, portable gas chromatograph with the appropriate software. Part per billion levels of Vinyl Chloride, Cis 1,2 Dichloroethylene and Trichloroethylene were detected in air using a trap for preconcentration of the compounds. The units were continuously calibrated with certified standards from Scott Specialty Gases, which in one case was 1 part per billion of the aforementioned compounds. The entire operation of the units, including monitoring instrument responses, changing operating parameters, data transfer, data review and data reporting was done entirely on a remote basis from approximately six hundred miles away using a remote computer with a modem and remote operating software. The entire system concept promises the availability of highly sensitive remote monitoring in sparsely populated areas for long periods of time.

KEYWORDS

Gas Chromatography, Environmental, Remote, Automation, Reproducibility

INTRODUCTION

The monitoring of Volatile Organic Compounds (VOCs) in air at remote locations typically involves either one of two approaches. The first is to send personnel into the field to periodically collect samples in Tedlar bags. The samples are then brought to a laboratory for analysis. There are several problems associated with this approach including the time delay between sample collection and analysis. This time delay can also lead to sample integrity problems. The other approach is to set up a laboratory gas chromatograph on site for continuous monitoring. There are several problems associated with this method including the need for a technician to continuously operate and maintain the instrument.

Sentex has developed a state of the art system which can be installed at a remote location, operate automatically without the need for personnel and can be contacted via modem for data transfer and other additional operations. The system is a self contained portable gas chromatograph (Figure 2) which in this case was set up to specifically monitor air for three particular compounds. The system, which is completely controlled by a lap top computer, samples automatically and periodically re-calibrates (re-standardizes) itself to ensure accuracy. Furthermore, the system does not have the same stringent environmental requirements as does a laboratory gas chromatograph.

Our client was involved with remediation of a site which required the need to perform air monitoring. In addition, there were two locations within the site which were to be monitored. Therefore, two gas chromatographs were installed and Figure 1 lists the compounds in question. Location I had a target detection limit of 1 part per billion. This location was a fence which bordered the site in a residential neighborhood. The second location was next to the building where the remediation was taking place. The site was located approximately 600 miles from the company's facility and the progress of the instruments was monitored via modem, to produce timely and accurate results. This project lasted approximately 4 months and the monitoring requirements were successfully met.

EXPERIMENTAL

The gas chromatograph worked in the following way. (Figure 3)

- (1) An internal pump pulled the air in and onto a trap for preconcentration. The trap consists of a quartz tube packed with 60/80 Carbosieve G (Supelco).
- (2) The VOC's were then thermally desorbed from the preconcentrator. This was accomplished by heating the platinum wire which was wrapped around the quartz tube.
- (3) The VOC's were swept into the column with carrier gas for separation and then into the detector (Figure 4).
- (4) All data was automatically stored to the hard drive of the computer.

The specific conditions for the gas chromatographs were as follows:

	Case I	Case II
Column:	4' 1% SP1000 on Carbopak B (Supelco)	Same
Carrier:	Argon	Same
Carrier Flow Rate:	25-30 cc/min	Same
Detector:	Argon Ionization Detector	Same
Oven Temperature:	100 degrees C	108 degrees C
Sample Time: (The time the pump runs to collect sample)	300 seconds	40 seconds
Run Time:	10 minutes	Same

In Case I, a column back flush was used so that at the end of every run the flow of carrier was reversed through the column to flush out any higher molecular weight material from the column. The reason for this was that since the unit was monitoring air at the fence bordering a residential neighborhood the possibility existed of picking up fumes discharged from naturally occurring activity such as heating, barbecuing or transportation. Both instruments analyzed two air samples per standard analysis. Figure 5 is a typical chromatogram for the standard in Case I. Figure 6 is a typical chromatogram for an air sample overlayed against the standard chromatogram. Figure 7 is a typical chromatogram for the standard in Case II. Figure 8 is a typical chromatogram for an air sample overlayed against the standard chromatogram. These chromatograms were downloaded via modem and printed at our facility in New Jersey.

RESULTS AND DISCUSSION

One of the biggest concerns about continuous, unattended analysis is the stability of the instrument. Since the instruments were continuously recalibrated, data for the calibration runs was reviewed to determine instrument reproducibility and stability. The information which needs to be scrutinized is peak retention time and peak area.

Figure 9 and 10 show the Analysis Summary. Essentially one can review the numerical results including sample number, date, time and so forth. Figure 9 and 10 represent Case I and Case II respectively. Upon reviewing the peak retention time and area one can see excellent reproducibility. The results for Case I are really quite good when considering the nature of the sample, i.e. calibrating at 1 part per billion level and drawing air from a residential area, and the fact that column back flush was activated after every run.

It should be noted that this Analysis Summary was downloaded via modem and printed in the company's facility on a weekly basis. The hard copies were then photocopied and sent to our client.

CONCLUSIONS

A rugged system for remote monitoring of volatile organic compounds in air via modem operated gas chromatography has been successfully developed and implemented. The system is fully automated and operates on an unattended basis. Furthermore, the system is capable of detecting volatile organic compounds at extremely low levels via preconcentration. The system uses standard, commercially available gas chromatographic columns.

The post run portion of the software allows review of the chromatograms and the numerical results. This is all accomplished via modem. Review of the data shows excellent reproducibility which indicates excellent instrument stability.

A request to monitor Vinyl Chloride at 0.1 part per billion in air on a continuous basis is presently being pursued. The challenge for the future will be to manufacture similar systems to continuously monitor volatile organic compounds at even lower concentrations and in even more complex environments.

FIGURE 1

CASE I

<u>COMPOUND</u>	<u>TARGET DETECTION LIMIT (1)</u>	<u>STD (2)</u>
Vinyl Chloride	1.00 ppb	1.15 ppb
Dichloroethylene	1.00 ppb	1.10 ppb
Trichloroethylene	1.00 ppb	1.09 ppb

CASE II

Vinyl Chloride	100.00 ppb	76.00 ppb
Dichloroethylene	500.00 ppb	502.00 ppb
Trichloroethylene	500.00 ppb	497.00 ppb

NOTES:

- (1) Detection in air
- (2) Standards prepared by Scott Specialty Gases

FIGURE 2.

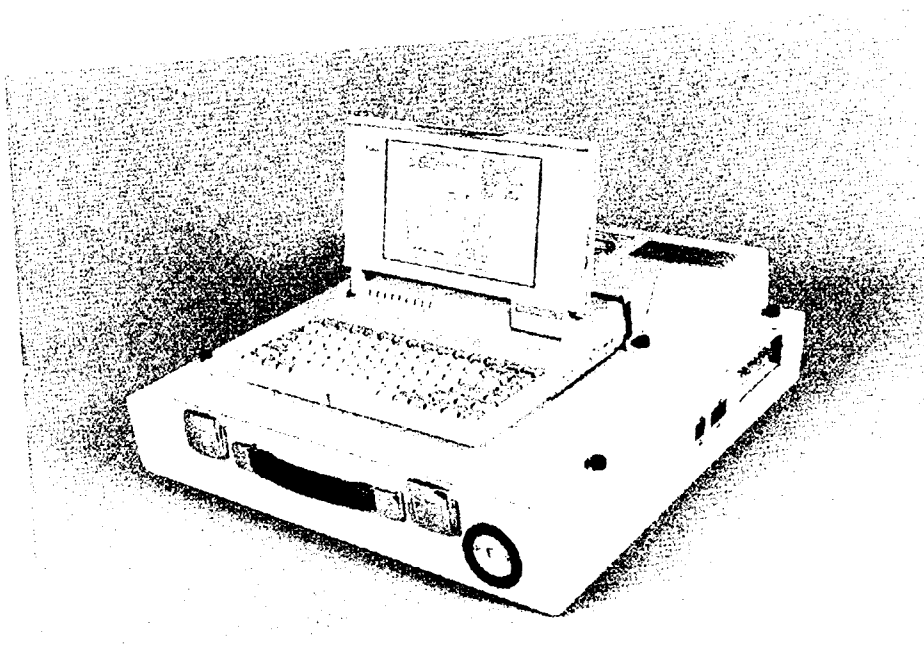


FIGURE 3.

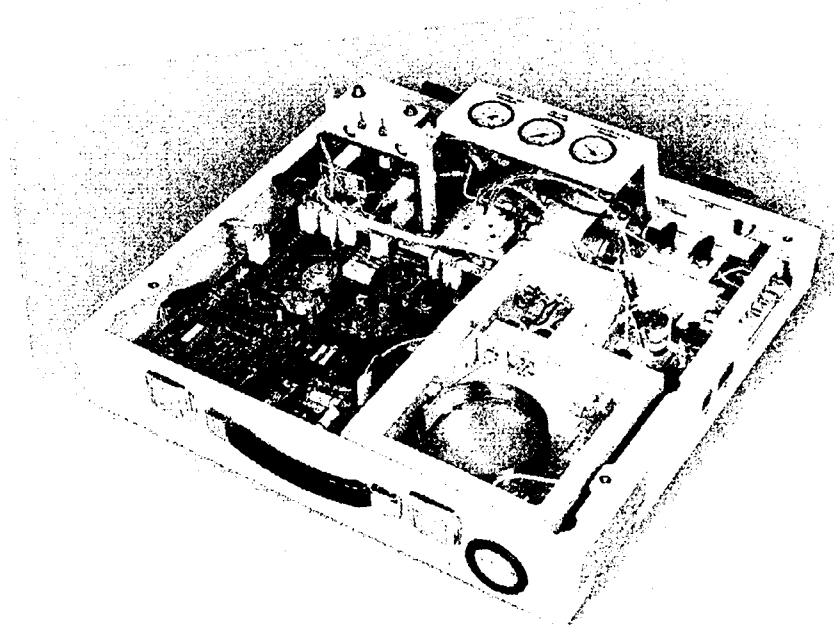


FIGURE 4.

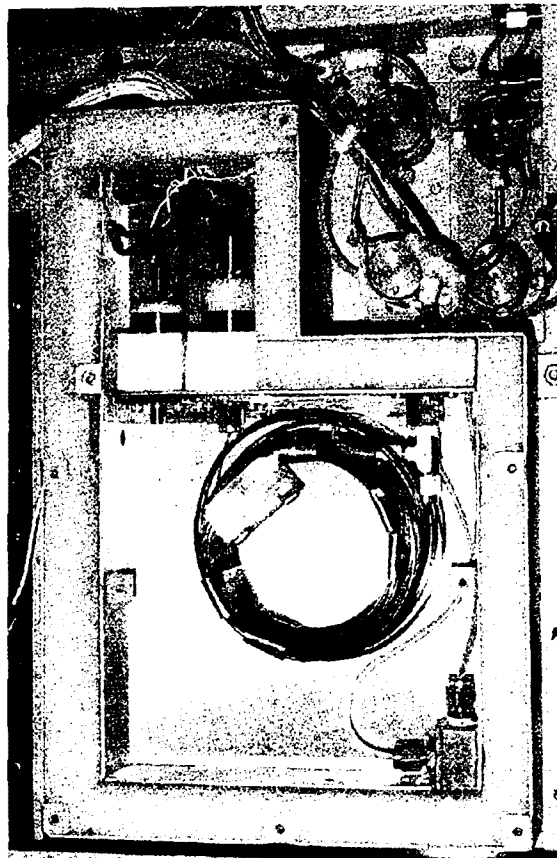


FIGURE 5

*** CHROMATOGRAPH REVIEW
 NAME:
 TRACE #556 Aug 13, 93 11:12

PRESS ? FOR HELP, <esc> TO EXIT (CONNECT)

PEAK#	NAME	RT	AREA
1	Impurity	14	5575 = 0.00 PPB
2	VinylChl	32	59009 = 1.15 PPB
3	DCE	120	130135 = 1.10 PPB
4	TCE	422	53226 = 1.09 PPB

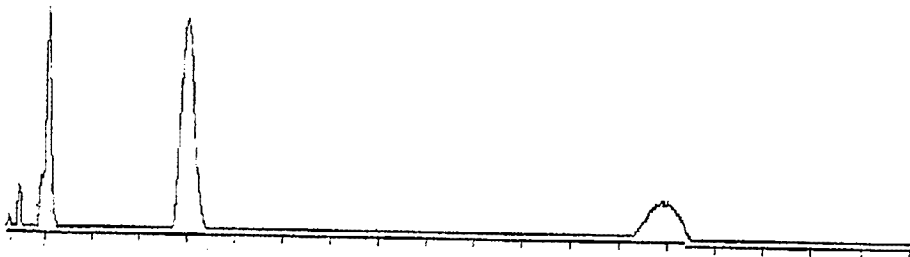


FIGURE 6

*** CHROMATOGRAPH REVIEW

PRESS ? FOR HELP, <esc> TO EXIT (CONNE

NAME:
 UPPER TRACE #555 492.00% Aug 13, 93 10:41
 LOWER TRACE #553 100.00%

COLUMN: 4'1%SP1000
 COLUMN PRESSURE: 26
 DETECTOR: AID
 TEMPERATURE: 100-100, 0 S
 SAMPLE TIME: 300
 GAIN: 10.000
 DURATION: 10 Minutes

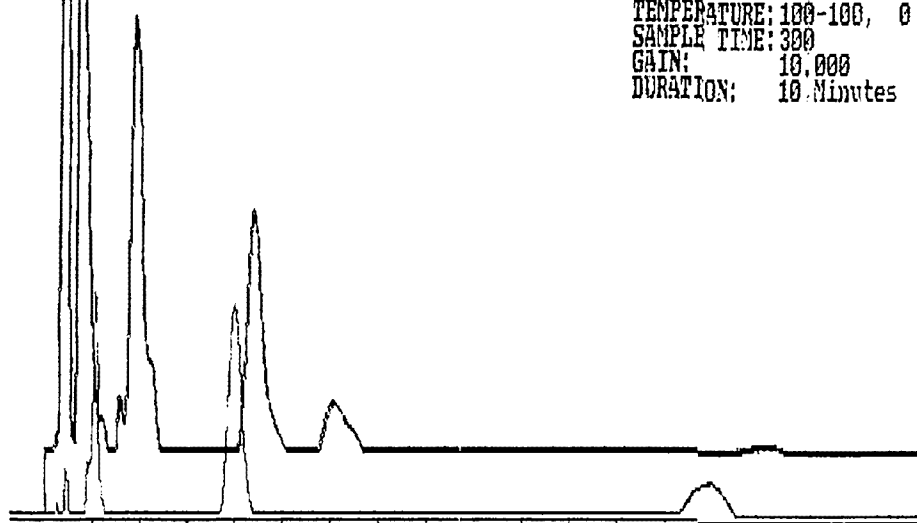


FIGURE 7

*** CHROMATOGRAPH REVIEW
 NAME:
 TRACE #1060 Sep 23, 93 15:59
 PRESS ? FOR HELP, <esc> TO EXIT (CONNECT)
 COLUMN: 4'1%SP1000
 COLUMN PRESSURE: 30
 DETECTOR: AID
 TEMPERATURE: 108-108, 0 Secs
 SAMPLE TIME: 40
 GAIN: 1.000
 DURATION: 10 Minutes

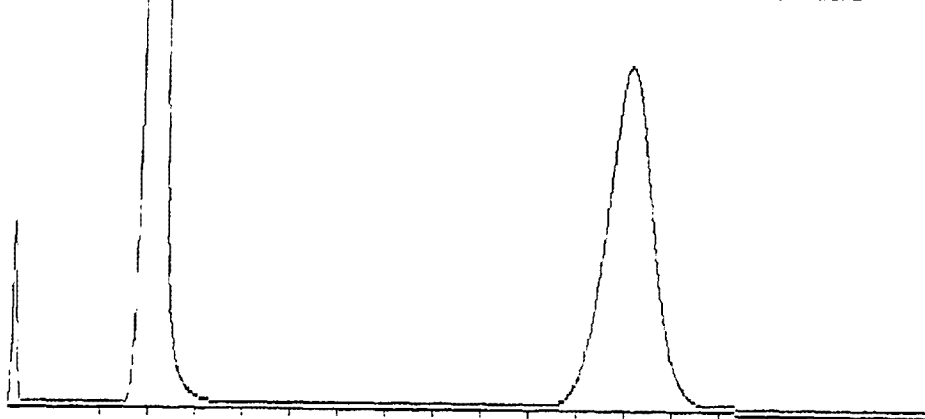


FIGURE 8

*** CHROMATOGRAPH REVIEW
 NAME:
 UPPER TRACE #1061 9.06% Sep 23, 93 16:30
 LOWER TRACE #1060 100.00%
 PRESS ? FOR HELP, <esc> TO EXIT (CONNECT)
 COLUMN: 4'1%SP1000
 COLUMN PRESSURE: 30
 DETECTOR: AID
 TEMPERATURE: 108-108, 0 Secs
 SAMPLE TIME: 40
 GAIN: 1.000
 DURATION: 10 Minutes

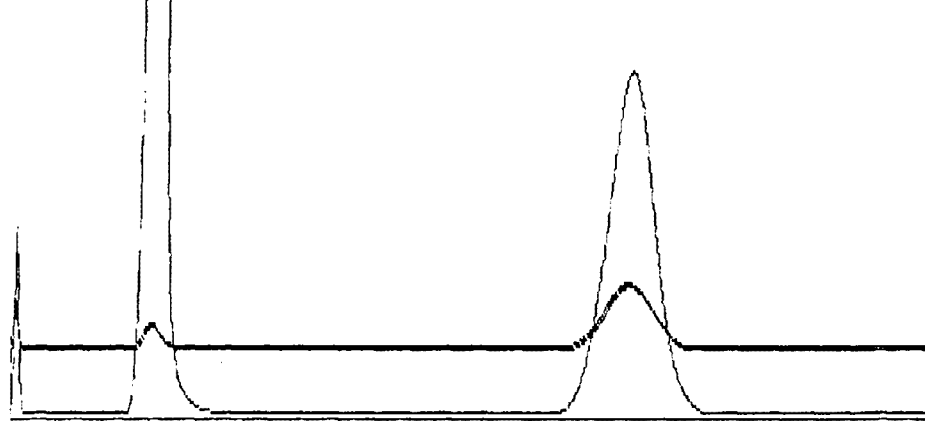


FIGURE 9

** ANALYSIS		*** PRESS <esc> TO STOP OR ANY OTHER KEY TO CONTINUE ***					
RACE	DATE	TIME	C/A	PEAK	CONCNT	RT	AREA
39	Aug 13,93	02:24	A	UNKNOWN	0.00 PPB	12	254918
39			A	UNKNOWN	0.00 PPB	23	186365
39			A	UNKNOWN	0.00 PPB	57	111393
39			A	UNKNOWN	0.00 PPB	133	26317
40	Aug 13,93	02:55	A	UNKNOWN	0.00 PPB	12	242915
40			A	UNKNOWN	0.00 PPB	23	166811
40			A	UNKNOWN	0.00 PPB	57	90012
40			A	UNKNOWN	0.00 PPB	133	13693
41	Aug 13,93	03:26	C	Impurity	0.00 PPB	14	3718
41			C	VinylChl	1.15 PPB	32	60579
41			C	DCE	1.10 PPB	120	129698
41			C	TCE	1.09 PPB	422	51454
42	Aug 13,93	03:57	A	UNKNOWN	0.00 PPB	12	229783
42			A	UNKNOWN	0.00 PPB	23	192872
42			A	UNKNOWN	0.00 PPB	57	93949
42			A	UNKNOWN	0.00 PPB	68	3779
42			A	UNKNOWN	0.00 PPB	132	9179
43	Aug 13,93	04:28	A	UNKNOWN	0.00 PPB	12	233762
43			A	UNKNOWN	0.00 PPB	23	207037
43			A	UNKNOWN	0.00 PPB	57	114105
43			A	UNKNOWN	0.00 PPB	133	42477

** ANALYSIS		*** PRESS <esc> TO STOP OR ANY OTHER KEY TO CONTINUE ***					
RACE	DATE	TIME	C/A	PEAK	CONCNT	RT	AREA
44	Aug 13,93	04:59	C	Impurity	0.00 PPB	14	3584
44			C	VinylChl	1.15 PPB	32	60790
44			C	DCE	1.10 PPB	120	130202
44			C	TCE	1.09 PPB	423	49783
45	Aug 13,93	05:30	A	UNKNOWN	0.00 PPB	12	229153
45			A	UNKNOWN	0.00 PPB	23	207919
45			A	UNKNOWN	0.00 PPB	57	114021
45			A	UNKNOWN	0.00 PPB	68	11485
45			A	UNKNOWN	0.00 PPB	133	40540
45			A	UNKNOWN	0.00 PPB	184	2479
46	Aug 13,93	06:01	A	UNKNOWN	0.00 PPB	12	226977
46			A	UNKNOWN	0.00 PPB	23	223493
46			A	UNKNOWN	0.00 PPB	48	2112
46			A	UNKNOWN	0.00 PPB	57	126002
46			A	UNKNOWN	0.00 PPB	68	7889
46			A	UNKNOWN	0.00 PPB	133	50139
46			A	UNKNOWN	0.00 PPB	183	3478
47	Aug 13,93	06:32	C	Impurity	0.00 PPB	14	5381
47			C	VinylChl	1.15 PPB	32	60489
47			C	DCE	1.10 PPB	120	131026
47			C	TCE	1.09 PPB	419	50152

FIGURE 10

```

** ANALYSIS          *** PRESS <esc> TO STOP OR ANY OTHER KEY TO CONTINUE ***
RACE DATE      TIME  C/A PEAK      CONCNT      RT      AREA      NAME
-----
73 Sep 20,93 05:18  A VINYL CL  19.90 PPB    28      60307
73              A DCE      7.25 PPB    114     155750
73              A TCE      91.07 PPB   408     1302292
74 Sep 20,93 05:50  A VINYL CL  26.78 PPB    28      81148
74              A DCE      2.30 PPB    114     49460
74              A TCE      40.95 PPB   406     585542
75 Sep 20,93 06:21  C VINYL CL  76.00 PPB    28      228413
75              C DCE     502.00 PPB   116    10684193
75              C TCE     497.00 PPB   406    7217404
76 Sep 20,93 06:52  A VINYL CL  28.88 PPB    28      86800
76              A DCE      7.48 PPB    114     159243
76              A TCE     91.51 PPB   407    1328963
77 Sep 20,93 07:24  A VINYL CL  29.17 PPB    28      87659
77              A DCE      2.05 PPB    113     43556
77              A TCE     38.50 PPB   407     559077
78 Sep 20,93 07:55  C VINYL CL  76.00 PPB    28      221974
78              C DCE     502.00 PPB   116    10757399
78              C TCE     497.00 PPB   407    7404651
79 Sep 20,93 08:27  A VINYL CL  32.33 PPB    28      94441
79              A DCE      5.99 PPB    114     128300
79              A TCE     89.91 PPB   407    1339603

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** ANALYSIS          *** PRESS <esc> TO STOP OR ANY OTHER KEY TO CONTINUE ***
RACE DATE      TIME  C/A PEAK      CONCNT      RT      AREA      NAME
-----
30 Sep 20,93 08:58  A VINYL CL  24.55 PPB    28      71724
30              A DCE      2.39 PPB    114     51242
30              A TCE     39.08 PPB   408     582290
31 Sep 20,93 09:30  C VINYL CL  76.00 PPB    28      225865
31              C DCE     502.00 PPB   116    10821523
31              C TCE     497.00 PPB   407    7301278
32 Sep 20,93 10:01  A DCE      12.15 PPB    114     261824
32              A TCE     90.05 PPB   407    1322917
33 Sep 20,93 10:33  A VINYL CL  23.09 PPB    28      68627
33              A DCE      2.14 PPB    113     46125
33              A TCE     36.90 PPB   407     542063
34 Sep 20,93 11:04  C VINYL CL  76.00 PPB    28      234194
34              C DCE     502.00 PPB   116    10893779
34              C TCE     497.00 PPB   406    7365398
35 Sep 20,93 11:35  A VINYL CL  26.21 PPB    28      80774
35              A DCE      7.63 PPB    114     165642
35              A TCE     93.13 PPB   407    1380140
35 Sep 20,93 12:07  A VINYL CL  27.39 PPB    28      84415
35              A DCE      2.12 PPB    114     46112
36              A TCE     39.44 PPB   407     584447
37 Sep 20,93 12:38  C VINYL CL  76.00 PPB    28      237199

```

FIGURE 11

SUMMARY

1. Remote monitoring of VOC's in air via modem operated GC.
2. Automated, unattended GC analysis
3. High sensitivity via preconcentration.
4. Use of standard GC columns.
5. Chromatogram review - post run comparison of curves.
6. Analysis summary - post run review of numerical results
7. Reproducibility.

Field Portable Environmental Sample Concentrator for VOCs in Air

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ABSTRACT

The demand for field portable analytical instrumentation is increasing as enforcement of environmental regulations and remediation efforts continues to increase worldwide. Such instrumentation must be rugged, reliable, easy and economical to use, yield rapid results and provide qualitative, as well as, quantitative, analyses in the field. In response to this demand, a low cost, microprocessor-controlled, high throughput, field portable environmental sample concentrator has been developed for on-site concentration of volatile organic compound (VOC) contamination in air. The instrument operates with a rechargeable, replaceable 12 V battery and houses a refillable internal supply of high purity purge gas providing 6 hours of field operation. Air samples are drawn through and concentrated on a three bed carbon-based adsorbent trap at ambient temperatures using an internal pump. The trap is then rapidly heated and the concentrated sample backflushed with helium into a syringe. The contents of the syringe can be introduced to a micro gas chromatograph (or any standard, portable GC) for rapid, on-site field analysis. Concentration enhancements of 1000-fold are achievable. Automated pre- and post-desorb purge events minimize sample carryover from run-to-run and improve the overall analytical accuracy of the instrument.

INTRODUCTION

Recent enactment and stricter enforcement of environmental regulations worldwide have not only forced many environmental analyses to be conducted in the field rather than the laboratory, but have also challenged the development of field portable analytical instrumentation which can compete with the performance capability of conventional laboratory instrumentation. Field techniques can provide several advantages over laboratory-based techniques such as more rapid return of information to the user from which critical decision can be made, larger reduction in sample handling and storage requirements, and lower overall direct costs [1]. The analytical demands of environmental analyses have also forced many portable instruments to operate at or near their detection limits, thus the need has developed for a means to enhance the sensitivity of these methods.

In response to this demand to operate analytical instrumentation at the cusp of their detection limit, a field portable environmental sample concentrator has been developed for the on-site analysis of VOCs in air. This paper will present the criteria for the development of a field portable sample concentrator, discuss how these criteria were achieved, and explain the operation and analytical performance of the sample concentrator.

Development Criteria for Field Portable Instrumentation

The criteria often present in the development of field portable instrumentation are not too dissimilar from those of other products; however, often analytical instruments have greater demands of performance and operation. Some of these design requirements include the following: (1) portability, (2) versatility, (3) high sample throughput, (4) precision and accuracy, (5) ease of use, and (6) economical operation. To satisfy these requirements, much attention and planning is given to the details of product development, although often one is limited to currently available technologies.

To address the requirement of **portability**, the weight and overall dimensions had to be such that the instrument could be carried to the field by an individual of average strength, that once in the field, the system could operate for an entire work day's analyses, and that the system was rugged and durable to withstand transport to and from the field and survive the demanding conditions often found in the field. To this end, the sample concentrator weighs only 16 kg and measures 18 cm high, 39 cm long, and 36 cm wide. The system houses a six hour supply of both high purity purge gas and electrical power, both rechargeable and field

serviceable. The cylinder houses 35 L of compressed gas, while the power is supplied by a standard 12 V, 6.5 Ah sealed lead acid battery which is available at most local hardware stores. The system is housed in a metal package for easy portability and has been designed to provide easy access to all critical parts of the instrument.

The system was also designed to be **versatile**. The system, when operated with the battery and the internal supply of purge gas, may be used on-site, in the field, or operated in the laboratory using 110/220 V line voltage. The system was initially designed for concentrating VOCs in air; however, a sparging unit will be developed which will allow the concentration of VOCs in water and soil samples. The concentrated analytes are desorbed into an ambient temperature gas tight syringe, allowing the sample to be transferred to any commercial gas chromatograph or other appropriate analytical technique for analysis. There is also an option to have two traps in the system, allowing for analytical redundancy by using the same adsorbent material in both traps or allowing for tailoring of trapping selectivity using two traps each packed with different adsorbent materials. Similarly, the adsorbent materials were initially selected to concentrate the entire list of compounds found in the EPA Method TO-14. These span in volatility from Freon 12 (b.p. = -29.8°C) to hexachlorobutadiene (b.p. = +215.0°C).

Several items were addressed in order to ensure **high sample throughput** capability. An option for the addition of a second trap was included such that one could be simultaneously adsorbing a sample while desorbing a second sample, therefore increasing productivity. The sample concentrator has a cycle time of about 15 minutes to achieve a 500-fold concentration enhancement, with the trap adsorption event dominating the cycle time (i.e., the volume loaded affects the duration of the loading event; 1 L of sample loaded at 100 ml/min will take 10 minutes). Similarly, it is possible to automate this instrument for multiple sample concentration and chromatographic analysis events by interfacing the unit with a stream switching valve and a gas chromatograph.

To ensure **precision and accuracy**, many different features were added to the sample concentrator. The system was built such that the sample contacts only inert electroformed nickel tubing, minimizing the possibility of carryover or analyte adsorption onto the walls of the transfer lines. Similarly, the entire flow path of the concentrated sample (i.e., the multi-port rotary valve and the Ni transfer lines) is heated to minimize sample loss due to condensation and adsorption. Designed into the microprocessor is on-board diagnostics, informing the user whenever a battery voltage is low, a heater is malfunctioning, or the rotary valve is in the wrong position for the particular event requested. Similarly, with the two trap option, analytical redundancy can be built into the instrument if the same adsorbent material is chosen for each trap. The system was designed with automated events which serve to ensure analytical reproducibility from run-to-run. Such events purge the system after desorption, while the system is still at the elevated desorption temperature, and after the initial start-up of the instrument, before the first adsorption/desorption cycle. These events assist in minimizing sample carryover, thus improving the reproducibility of the instrument. Lastly, with microprocessor control of the time and temperature parameters, one is ensured of reproducible experimental conditions from run to run.

The portable sample concentrator was also designed around **ease of use**. In the field, it is imperative that the instrument be user friendly and easy to operate. The microprocessor control guides the user through the operation of the instrument, displaying the event sequence and operational parameters to prompt the user. Similarly, it incorporates light emitting diodes (LEDs) and an audible beeper to prompt the user of events and inform the operator of the status of the run while this person is remote to the instrument. The menu-driven operation of the instrument allows the user to define experimental parameters such as times and temperatures, while user settable flow restrictors serve to control the adsorption and desorption flowrates. A bank of solenoid valves are triggered automatically by the firmware; the user need only change the position of the rotary valve and attach and detach the sample container and the syringe. All other instrumental events are controlled and executed automatically through the microprocessor. Lastly, should the traps or trap heaters need to be replaced in the field, they have been designed for easy removal and installation.

The use of portable analytical instrumentation in the field also holds the potential for the realization of substantial **economic** savings for the user and for more **efficient** use of the analyst's time. The ability to conduct on-site, real time analyses and receive immediate analytical feedback in the field provides the user with the capability to implement a more efficient response to remediation or emergency efforts. Similarly, on-site analyses eliminate the problems associated with the storage, handling, transportation, and integrity of environmental samples. Also, the portable sample concentrator provides a means by which to prescreen

environmental samples in the field prior to conducting more expensive laboratory analyses, eliminating the need to conduct more costly laboratory analyses on all samples. If the field results suggest that more detailed analyses are warranted, the sample can be shipped to the environmental laboratory for more extensive analyses. Likewise, when the portable sample concentrator is combined with a high speed, portable gas chromatograph, the combined package provides high sample throughput capability on-site, increasing the efficiency of the analyst.

Operation and Analytical Performance of a Portable Sample Concentrator

One might ask why one would even be interested in using a sample preconcentrator. The answer lies in the ability of the preconcentrator to selectively adsorb and enhance trace components from a homogenous sample, (e.g., air) and, subsequently, thermally desorb *all* of the trapped analytes (not just an aliquot, as in solvent desorption methods). As such, a preconcentrator can be used to enhance the sensitivity of any gas chromatographic detector by 100- to 1000-fold.

Operation

There are two basic methods used to concentrate a sample of low concentration to one of a higher, more easily detectable concentration [2]. The first method involves the use of cryogenics to "freeze out" the volatile components of interest from the background matrix of the sample. The advantage of cryogenics is that it traps everything with a boiling point greater than the temperature of the cryogen. However, it does not lend itself well to portability, as a cylinder of coolant (i.e., LN₂ or LCO₂) is required. Similarly, with samples of high humidity, water freezes in the cryogenic traps and eventually restricts the flow. Such interferences from H₂O and CO₂ are commonplace when using cryogenic sample concentration methods.

The other basic method of sample concentration involves the use of adsorbent materials, each offering unique degrees of analytical specificity. Adsorbent materials are characterized as highly inert, thermally stable chemical species and include high surface area carbon compounds such as graphitized carbon blacks and carbon molecular sieves, porous inorganics such as zeolite (i.e., aluminosilicates) molecular sieves (with large internal surface areas) and porous polymers such as Tenax (i.e., 2,6-diphenyl-*p*-phenyleneoxide). With the proper selection of adsorbent properties and mesh sizes, one can fine tune the trap's analyte selectivity, adsorption flowrate and adsorption/desorption efficiency such that sample concentration can be realized without the use of coolants and effectively allow the collection of a wide range of compounds (such as the Method TO-14 compounds). As such, these materials are ideal for mobile laboratories and field portable applications. They can suffer from limited breakthrough volumes (traps can be viewed as poor resolution, highly retentive chromatographic columns) and possible break down products during desorption of the concentrated analytes from the adsorbent surface. Analytes are typically adsorbed at ambient temperature ($\leq 50^{\circ}\text{C}$) and desorbed at elevated temperatures ($280\text{--}325^{\circ}\text{C}$), with temperature affecting the solubility or adsorption kinetics and thermodynamics for the trapped analytes.

With the use of multibed adsorbent traps, it is possible to tailor a trap that is capable of adsorbing a wide range of compounds of varying volatilities (such as the 41 compounds on the Method TO-14 list). Such traps are fabricated by using materials of increasing retention capability in the adsorption flow direction (typically achieved by increasing the effective surface area, porosity, or analyte solubility of the adsorbent materials in the flow direction) so that compounds of higher volatility pass through the first beds and adsorb on later beds farther downstream in the trap. Less volatile compounds tend to adsorb on the first bed and do not move to the later beds. Multibed traps that have been evaluated include Carbotrap C (surface area $\sim 10\text{ m}^2/\text{g}$), Carbotrap B ($\sim 100\text{ m}^2/\text{g}$), Carbosieve S-III ($\sim 820\text{ m}^2/\text{g}$), and Carbopack B ($\sim 100\text{ m}^2/\text{g}$). Carboxen-1000 ($\sim 1200\text{ m}^2/\text{g}$), Carboxen-1001 ($\sim 500\text{ m}^2/\text{g}$). Upon heating the adsorbent material, the analytes desorb from each bed under static flow conditions until the final desorption temperature is achieved. Once achieved, the desorbed, concentrated analytes are backflushed from the hot trap and into a syringe for chromatographic analysis.

The portable sample concentrator cycles through four basic events during each analysis. The first is the load event, which actuates a vacuum pump to pull sample through the ambient temperature adsorbent bed at a user selectable flowrate (typically 100-150 ml/min) for a user defined time period until a given volume of dilute sample has passed through the trap. After loading the trap, the system automatically purges the trap and

transfer lines with purge gas for several seconds, eliminating any excess moisture, air, and CO₂ and bathing the trap in an inert atmosphere prior to heating the adsorbent bed. This ensures that the adsorbent is heated in an oxygen-free environment, minimizing oxidation and degradation of the adsorbent material. After manually rotating the multiport valve to the desorb position, the trap heater begins to heat the trap to the user defined desorption temperature. It takes about 2 minutes to achieve the desorption temperature. After the trap has attained the preset temperature (typically about 325°C), a solenoid valve opens allowing purge gas to slowly (i.e., at a user set flowrate of usually 1-2 ml/min) pass through the hot adsorbent bed, backflushing the desorbed analytes from the trap and transferring them to the gas tight syringe for further analysis (typical desorption volume is 2-5 ml). Once the syringe has been removed, the system cycles through an automated post-desorb purge event, flushing the entire sample flowpath with copious amounts of purge gas while the system is still at the elevated desorption temperature. The system then automatically shuts down the trap heater and prompts the user to rotate the multiport valve to the load position, attach the next sample, and load this sample onto the trap. Fans assist in cooling the heated trap to the preset adsorption temperature.

Analytical Performance

The portable sample concentrator is capable of achieving 100- to 1000-fold concentration enhancement of most VOCs in air with 90% + recovery for most compounds. With an optimal desorption volume of 2 ml (at 90% + desorption efficiency, see Figure 1), a 500-fold concentration enhancement can be achieved by passing only 1000 ml of air through the trap. Thus a shorter cycle time is achieved (a cycle time can be as short as 8 minutes for a 100-fold concentration enhancement).

The system also exhibits nondetectable sample carryover if properly purged, implying tremendous analytical reproducibility (with variances $\leq 5\%$ for most compounds, see Table 1). The data of Table 1 also demonstrates the remarkable desorption efficiency of the multibed adsorbent traps, achieving 90% + recovery for most compounds over a wide volatility range. Similarly, the data of Table 2 demonstrates the tremendous retention capability of the multibed adsorbent traps. No detectable breakthrough has been observed when 5000 ml of 200 ppb Freon-12 (b.p. = -29.8°C) has been loaded onto the multibed adsorbent traps at ambient temperature; thus large concentration enhancements can be realized with the portable sample concentrator.

Typical chromatograms obtained with a high speed, micro gas chromatograph are shown in Figure 2. [3]. Note the amplification of the detector signal following concentration enhancement with the use of the sample concentrator. The first chromatogram (Figure 2.a.) displays the detector response for the micro thermal conductivity detector using a 20-40 ppm standard of each analyte. The second chromatogram (Figure 2.b.) displays the same detector response for a 200-fold dilution of the 20-40 ppm standard, without any concentration enhancement. The final chromatogram (Figure 2.c.) displays the analysis of the first 5 ml desorption of a 200-fold concentration of the diluted standard (adsorbed 1000 ml, desorbed into 5 ml, adsorbent materials: Carboxen-1000, Carboxen-1001). The equivalent peak areas and peak heights of the first and last chromatograms in Figure 2 (Figures 2.a and 2.c., respectively), implies the high adsorption/desorption efficiency and recovery of the multibed adsorbent trap and demonstrates the analytical power and utility of the portable sample concentrator in the field.

CONCLUSIONS

Portable instrumentation development is being fueled by the ever increasing demands of newly mandated and recently proposed environmental regulations and the more rigid enforcement of these regulations. As a result, analytical instrumentation intended for use in the field is being required to match many of the same capabilities and performance specifications as that of laboratory instrumentation. To assist portable analytical instrumentation in attaining this challenge, a portable environmental sample concentrator has been developed for VOCs in air. It functions to enhance the detection limit of analytical instrumentation used in environmental analyses, where often the viable detection threshold is challenged.

The portable sample concentrator described in this presentation allows 100- to 1000-fold concentration enhancement with greater than 90% recovery of analytes of widely differing volatilities with good analytical reproducibility. The instrument was specifically designed for ease-of-use in the field for an 8 hour workday and offers many of the same features and capabilities as laboratory instrumentation, only in a portable mode. Many of the limitations and challenges of designing and developing portable analytical instrumentation are

limited by presently available technologies. However, as available technologies advance, so to will the performance capabilities of portable analytical instrumentation.

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Table 1. Desorption efficiency and analytical reproducibility. Experimental conditions: adsorption: 2000 ml volume at 150 ml/min at 35°C; desorption: 2 ml volume at 2 ml/min at 325°C; adsorbents: Carbotrap C, Carbotrap B, Carbosieve S-III.

Compound	b.p. (°C)	Original Concentration (ng/L)	Desorption Efficiency (%)	Percent RSD (n = 4)
Freon 12	-29.8	500	92.4	4.32
Freon 11	23.7	500	90.6	4.30
Dichloromethane	39.8	65	91.0	6.77
Acetone	56.2	20	92.2	4.89
Chloroform	61.7	60	90.1	4.68
Carbon tetrachloride	76.5	53	94.3	6.97
Benzene	80.1	116	93.2	3.68
Trichloroethylene	87.0	74	94.5	3.75
Tetrachloroethylene	121.1	102	87.9	4.56
Toluene	130.0	110.6	91.0	4.58
Chlorobenzene	132.0	177	84.9	6.26
Ethylbenzene	136.2	118	87.0	6.62
<i>o</i> -Xylene	144.4	235	87.1	8.39

Table 2. Study of breakthrough volume for three-bed adsorbent trap. Experimental conditions: analyte: 100 ppb vinyl chloride; adsorption: 190 ml/min at 35°C; desorption: 2 ml/min at 300°C; adsorbents: Carbotrap C, Carbotrap B, Carbosieve S-III.

Adsorption volume (ml)	Desorption volume (ml)	Recovery (%)
54.5	5	100
535	5	94
3350	5	87

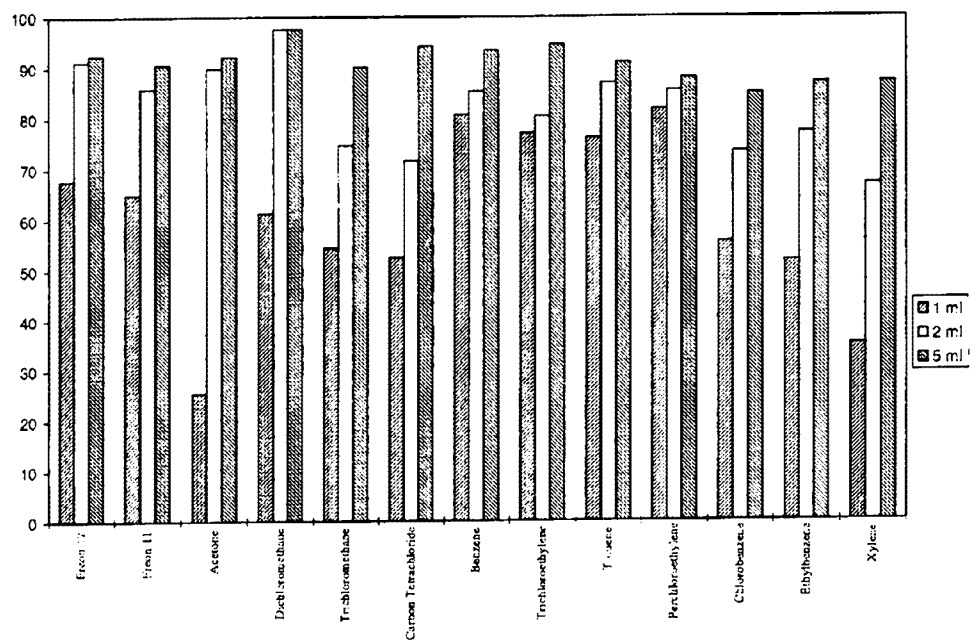


Figure 1. Desorption efficiency as a function of desorption volume. Experimental conditions: adsorption: 1000 ml volume at 150 ml/min at 35°C; desorption: 1 ml, 2 ml, 5 ml total successive volumes at 2 ml/min at 325°C. Adsorbent materials: Carbotrap C, Carbotrap B, Carbosieve S-III.

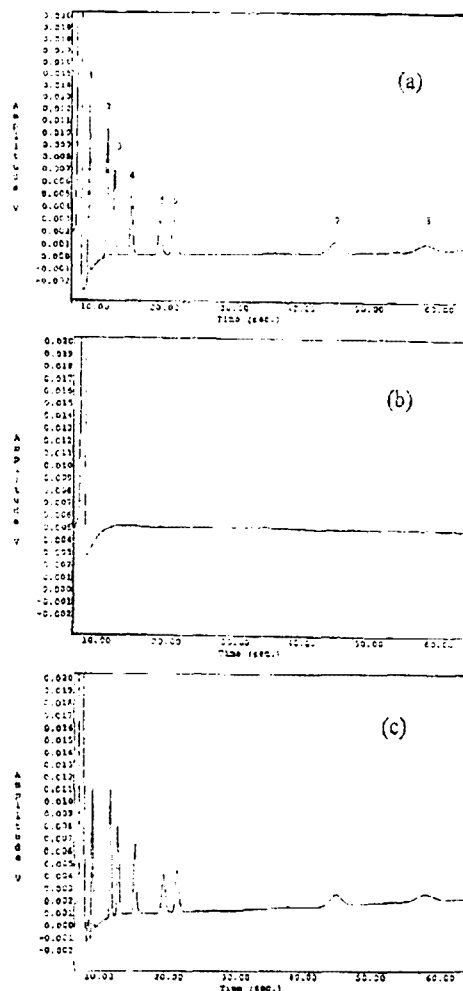


Figure 2. High speed chromatograms obtained on a MTI Analytical Instruments, M200 Micro Gas Chromatograph. Column: 4 m $\text{Al}_2\text{O}_3/\text{KCl}$, carrier gas: helium, column head pressure: 25.0 psi, column temperature: 170°C, sample time: 5 sec, inject time: 40 msec, detector: micro thermal conductivity detector, detector gain: medium. Peak identification: (1) Freon 11, (2) dichloromethane, (3) carbon tetrachloride, (4) trichloroethylene, (5) tetrachloroethylene, (6) benzene, (7) toluene, (8) chlorobenzene. Adsorption: 1000 ml at 90 ml/min at 35°C. Desorption: 5 ml at 2 ml/min at 330°C.

(a) Concentrated standard.

(b) 200-fold dilution of standard.

(c) First 5 ml desorption volume of 200-fold concentration of diluted standard.

SESSION 3:
ACID AEROSOLS

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Spatial Variation in Acidic Sulfate Concentrations within Metropolitan Philadelphia

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Acidic sulfate concentrations were measured in metropolitan Philadelphia during the summer of 1992, as part of a continuing effort to characterize acid aerosol and gas concentrations in urban environments. Sampling was performed simultaneously at six sites located within metropolitan Philadelphia, a site located in Camden, New Jersey, and at a rural site approximately 18 miles from the city center. Sites were selected based on their population density and on their relative locations within Philadelphia. Acid aerosol and gas sampling was performed on alternate days, with all samples collected for 12-hour periods beginning at 8AM. All samples were collected using modified Harvard-EPA Annular Denuder Systems (HEADS).

In this paper, we examine the spatial variation in acidic sulfate and ammonia concentrations within metropolitan Philadelphia. We also examine factors that may influence their variation. Outdoor sulfate concentrations were found to be uniform across metropolitan Philadelphia; however, considerable spatial variation in both aerosol strong acidity (H^+) and ammonia (NH_3) concentrations was observed. This variation was found to be independent of wind direction and other regional factors, but related to local factors, such as population density and distance from the center of the city. These results suggest that models must consider local factors in order to estimate outdoor H^+ concentrations accurately for urban environments.

The Effects of Meteorology on Concentrations of Acid Aerosols

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ABSTRACT

Ambient air samples of strong acid aerosol (H^+), sulfate (SO_4), ammonia (NH_3), and ammonium (NH_4) were collected in Pittsburgh and Uniontown, Pennsylvania during the summer of 1990. High correlations were found for both H^+ and SO_4 concentrations between Pittsburgh and the semi-rural site in Uniontown. One possible implication is that acid aerosols and their precursors are regionally transported.

To test this hypothesis, air samples from the Uniontown site were statistically analyzed for the meteorological relationships that resulted in episodic events of elevated ambient H^+ levels. Standard measures of atmospheric conditions in both Pittsburgh and Uniontown were used; they included temperature, pressure, relative humidity, wind speed and direction.

Results show that the episodic events of elevated H^+ occurred with the same general set of meteorological conditions. The major meteorological variables which correlated with the episodes were the mean wind speed in Pittsburgh and the mean westerly wind component (U) at Uniontown. These two variables accounted for one third of the variance.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

INTRODUCTION

Recent research into the effects of acid aerosols on humans indicates that exposure to atmospheric acid in the form of acidic sulfate particles adversely effects the respiratory system. Laboratory experiments have demonstrated that acidic sulfate particles produced observable changes in the respiratory tract of humans at concentrations as low as $40 \mu\text{gm}^{-3}$ (Lippmann¹, 1989). In order to better understand the effects that exposure to acid aerosols have on humans, epidemiologic air pollution studies have been conducted characterizing the spatial and temporal distribution of acid aerosols (Suh, *et al.*², 1992; Waldman, *et al.*³, 1992; Purdue, *et al.*⁴, 1992). To fully understand the processes responsible for the spatial and temporal distribution of acid aerosols requires a rigorous analysis of local and regional meteorology and its effect on H^+ concentrations. To date, few studies have included a comprehensive analysis of the effects of meteorology on acid aerosol concentrations. Therefore, this paper will examine the relationship between meteorological parameters and their effects on acid aerosol concentrations.

Ambient concentrations of H^+ that were collected in Uniontown, Pennsylvania during the summer of 1990 (Suh, *et al.*², 1992) were reevaluated to determine the relationships between meteorology and the magnitude of the H^+ concentrations. To accomplish this, an extensive database containing 21 meteorological parameters was compiled for the Uniontown/Pittsburgh region. The database included both surface and upper air meteorological parameters. The dates on which the meteorological measurements were observed coincided with the collection of the ambient H^+

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measurements. For the purposes of this paper, H^+ concentrations greater than or equal to one standard deviation from the arithmetic average of all H^+ measurements will be labeled an episode. H^+ concentrations greater than or equal to three standard deviations from the average will be called an extreme episode.

METHODS

Sampling Methods

Air quality and meteorological measurements were taken simultaneously in Pittsburgh (population $\approx 2,000,000$) and Uniontown (population $\approx 15,000$), Pennsylvania — located approximately 60 kilometers (km) southeast of Pittsburgh. Air quality measurements consisted of fine fraction aerosols (fine fraction in the 1990 study was defined by an aerodynamic diameter, $d_p \leq 2.1 \mu m$) and analyzed for total particulate strong acidity (H^+), sulfate (SO_4^{2-}), ammonia (NH_3), ammonium (NH_4^+), nitric acid (HNO_3), and nitrous acid (HNO_2). These samples were taken using the Harvard-EPA Annular Denuder System (HEADS) (Koutrakis, *et al.*⁵, 1988; Brauer, *et al.*⁶, 1989; Koutrakis, *et al.*⁷, 1989). The flow-rate for the HEADS was $10 L min^{-1}$. Twelve and 24-hour integrated HEADS samples were collected daily in Uniontown from 1 June 1990 through 30 August 1990. Six-hour samples were collected from 23 June 1990 through 18 August 1990. Six and 24-hour HEADS monitoring were conducted every second day in Pittsburgh from 2 July 1990 through 11 August 1990. All 6-hour samples were normally collected from 10:00 am to 4:00 pm (EDT). The 12- and 24-hour samples were normally collected from 8:00 am to 8:00 pm, then 8:00 pm to 8:00 am (EDT) for the 12-hour samples and 8:00 am to 8:00 am (EDT) for the 24-hour samples.

Meteorological data were collected at the Uniontown monitoring site from 4 June 1990 through 23 August 1990. The data included 10 minute vector average resultant wind speed and direction (collectively called the resultant wind vector). Wind speed and direction were measured using a Climatronics WM-III system, located 10 m above the ground. Ten minute integrated measurements of temperature and relative humidity were also made. Temperature and relative humidity were measured using Climatronics modular temperature (model 100093) and relative humidity (model 100098) sensors mounted inside a Climatronics WS-10 motor aspirated solar shield 4.5 m above the ground (Harvard⁸, 1993). Hourly means of temperature and humidity, and hourly vector averages for wind speed and direction were computed from the above data.

Meteorological data for Pittsburgh were measured by the National Weather Service at the Pittsburgh International Airport. Meteorological parameters were obtained for both the surface and 850 mb height. Surface parameters included: maximum daily temperature, daily mean wind speed, daily mean total cloud cover, and the 7:00 am barometric pressure. The 850 mb parameters included: temperature, dew-point temperature, wind speed, and the vectorized U and V wind direction components. Two values for each of the 850 mb parameters were obtained since measurements aloft are taken twice daily, at 00:00 GMT and at 12:00 GMT (8:00 pm (local time) and 8:00 am (local time), respectively). The 00:00 GMT measurement will be referred to as the p.m. measurement and the 12:00 GMT measurement will be called the a.m. measurement in this paper.

Analytical Methods

The daily meteorological data for Pittsburgh and Uniontown were combined into a single database and analyzed for the factors which were shared by groups of days having similar meteorological conditions. This provided a structure for the sampling period showing how each day compared to the rest of the days in regard to the meteorological conditions observed. Each day during the sampling period, having been grouped according to similar meteorological conditions, was then analyzed against the corresponding daily H^+ concentrations. Hence, it is possible to determine the meteorological factors associated with elevated levels of acid aerosol. A more detailed description of the approach is found below.

The 21 meteorological variables and 81 samples were analyzed using principal component analysis. Principal component analysis reduces the dimensionality of a matrix of observations and variables by reducing the number of dimensions which are needed to yield relatively stable results (Diewer *et al.*⁹, 1976). Each of the variables must be linearly related to some number of underlying factors so that the values of variables may be expressed as a set of n linear equations (Harman¹⁰, 1976). In order for a factor analysis to be effective, n needs to be less than the number of variables. Principal components reduces the original number of meteorological variables in the analysis while retaining a maximum amount of the variance in the observed data. The principal component analysis calculated components based on the correlation matrix. In this way, the proportion of the variance explained by each component is obtained by dividing the total number of variables into each corresponding eigenvalue. An eigenvalue is a measure of the variance explained by each component.

Next, cluster analyses were performed on the series of principal component scores to determine those days with similar meteorological conditions. Cluster analysis is similar to factor analysis in that it attempts to systematically group like variables (observations in this case). A two-stage clustering technique similar to that described in Eder *et al.*¹¹ (1994) was used. The first step uses *average linkage* cluster analysis, an unweighted pair-group method using arithmetic averages. The clusters are calculated from the factor scores from the above principal component analysis. The average linkage cluster analysis determines the initial number of clusters and the mean conditions within each cluster (Eder, *et al.*¹¹, 1994). The second step modifies the original clusters using the mean scores from the average linkage analysis in a *convergent k means* cluster analysis. Convergent k-means is an iterative method which selects points called cluster seeds as initial estimators of the cluster means. Each observation is assigned to the nearest seed to create an initial cluster solution. The cluster means of the initial solution replace the original cluster seeds and the process is repeated until a stable solution is achieved.

After the observations have been clustered according to homogeneous meteorological variables, regression analysis was performed to determine the meteorological variables that explained the most variance in the overall data and for each of the clusters. Utilizing a forward stepwise regression model, the meteorological variables that most influenced the ambient H^+ concentrations at Uniontown were determined.

Stepwise regression allows selection of independent variables to enter the regression model in the order of their ability to explain the residual variation in the dependent variable which has not been explained by the independent variables already included in the model. The first variable to enter the model is that independent variable with the highest F -value (this is the variable having the highest correlation with the dependent variable). The next variable to enter the model has the highest partial F among all the remaining variables. Inclusion of independent variables proceeds in this manner until addition of more independent variables does not significantly improve the prediction of the dependent variable; the significance being determined by the partial F tests (Kleinbaum and Kupper¹², 1978).

RESULTS AND DISCUSSION

Principal Components Analysis (PCA)

Examination (not shown) of the scree plot (Cattell¹³, 1966) indicates a 4 component solution. Component 1 has an eigenvalue equal to 6.3 and accounts for 30% of the variance in the model. It is indicative of wind parameters. This component has large (> 0.65) factor loadings for all of the non-vectorized wind speed variables as well as all of the U-component wind variables, indicating an important west/east component of the wind direction.

Component 2, explaining 23% of the variance in the model with an eigenvalue equal to 4.8, is a surrogate for temperature. This component has strong positive factor loadings for all of the air temperature variables as well as the mean dew point temperature for Uniontown (*MNDEWP U*).

The largest positive factor loading for the third component is for the p.m. mixing height

(*PMMXHT_P*) (loading = 0.63). This component has an eigenvalue of 2.7 and accounts for 13% of the variance in the data. Moderate negative loadings for the mean daily cloud cover at Pittsburgh (*MNCCOV_P*) (loading = -0.57) and the p.m. 850 mb dew-point temperature at Pittsburgh (*PM85DT_P*) (loading = -0.55) help indicate that this component is related to moisture parameters. The physical relationship between mixing height and cloud cover is shown statistically by this component. That is, the less cloud cover (associated in part with less moisture aloft), the greater the mixed layer tends to be, and vice versa.

The largest factor loadings for the fourth component are both negative; they are -0.60 for the a.m. 850 mb V-wind vector (*AM85VC_P*) and -0.45 for the p.m. 850 mb V-wind vector (*PM85VC_P*). The eigenvalue for this component is 1.7, accounting for 8% of the model's variance.

The four components explain 73% of the variance in the data. The variable with the largest communality (the sum of the squares of a variable's factor loadings across all of the factors) is the daily maximum temperature (*MXTEMP_P*) measured at Pittsburgh (communality = 0.94). The variable with the smallest communality is the p.m. 850 mb V-wind vector (*PM85VC_P*) (communality = 0.53). Having most of the variability for *MXTEMP_P* captured by the final solution while only capturing approximately 50% of the variability for the V-component of the wind at 850 mb (*PM85VC_P*) is a logical result since maximum daily temperature is less variable than wind.

Cluster Analyses

The number of clusters included in the final solution is determined using guidance from several statistical indices. The pseudo-F and pseudo- t^2 values exhibit a local maximum at the number of clusters to be found in the final cluster solution. Additionally, the cluster with the largest drop-off in the R^2 -value indicates the number of clusters to be used in the final solution (Eider *et al.*¹¹, 1994). Using these indicators, it was determined that 5 clusters correctly divided the data according to its unique meteorological regimes.

Individual Cluster Models

Cluster #1 (C1) was associated with all but one of the observed H^+ episodes. This cluster accounted for 25 (35%) observations. H^+ concentrations within this cluster averaged $160 \text{ nmol m}^{-3} \pm 126 \text{ nmol m}^{-3}$ (overall H^+ concentrations averaged $120 \text{ nmol m}^{-3} \pm 106 \text{ nmol m}^{-3}$). Nearly 20% of the variance in this cluster was accounted for by the daily mean wind speed (*MNWDSP_P*) at Pittsburgh. The mean U-component of the wind direction at Uniontown (*MNWDUC_U*) accounted for another 14% of the variance in the model. Both of these variables were significant at $\alpha = 0.05$.

All but one of the 25 values for *MNWDUC_U* in this cluster were positive indicative of a westerly wind direction. Examination of the actual data shows that 20 of the 25 observations in C1 had a positive V component to the mean wind direction at Uniontown (*MNWDVC_U*). A positive value for *MNWDVC_U* indicates a southerly component to the wind direction. Furthermore, all of the Uniontown observations which had "episodic" levels of H^+ also had a positive value for *MNWDUC_U* and all but one of those observations had a positive value for *MNWDVC_U*, indicating a generally southwesterly wind flow at the surface during episodes of elevated ambient acid aerosol.

Cluster #2 (C2) had 9 (13%) observations. The H^+ concentrations averaged $90 \text{ nmol m}^{-3} \pm 94 \text{ nmol m}^{-3}$. Most of the variance in this cluster (88%) was attributed to the daily mean cloud cover at Pittsburgh (*MNCCOV_P*). Another 10% of the variance was due to the p.m. wind speed at 850 mb at Pittsburgh (*PM85WS_P*).

Cluster #3 (C3) had 6 observations; 8% of the total number in the model. Unfortunately, 5 of the observations were missing the dependent variable H^+ , thus making a regression model for this cluster impossible. Cluster #4 (C4) had only 2 observations.

Cluster #5 (C5), with 8 observations (11% of the total), had an average H^+ of $50 \text{ nmol m}^{-3} \pm 35 \text{ nmol m}^{-3}$. The model for C5 had 70% of the variance accounted for by the a.m. 850 mb V

component of the wind (*AM85VC_P*). An additional 26% was accounted for by the mean wind speed at Uniontown (*MNWDSP_U*). Both of these variables were significant at $\alpha = 0.01$.

Overall Model

The overall regression model for the entire data set as a whole, that is, not separated into clusters, had three variables that were significant at the $\alpha \leq 0.05$ level. The first was the a.m. mixing height at Pittsburgh (*AMMXHT_P*) which accounted for 24% of the model variance ($\alpha = 0.0006$). Next, the mean U-component of the wind at Uniontown (*MNWDUC_U*) accounted for 16% ($\alpha = 0.001$). The mean daily wind speed at Pittsburgh (*MNWDSP_P*) accounted for another 7% of the model's variance ($\alpha = 0.05$). Together, these three variables accounted for just under 50% of the variance in H^+ concentrations in the overall model.

SUMMARY AND CONCLUSIONS

There were 5 episodes of elevated ambient H^+ concentrations ($\geq 226 \text{ nmol m}^{-3}$)[†] between 23 June 1990 and 23 August 1990. Each episode lasted between 24 and 48 hours with measured ambient H^+ concentrations reaching as high as 500 nmol m^{-3} . The episodes were associated with a unique set of meteorological conditions. One third of the variance in the H^+ concentrations during episodes were explained by two variables; the mean wind speed measured at Pittsburgh (*MNWDSP_P*) (19%) and the U-component of the mean wind direction measured at Uniontown (*MNWDUC_U*) (14%). Examination of the data shows that the episodes are concurrent with a southwesterly wind flow at the surface. The *MNWDSP_P* averaged $3.4 \pm 1.1 \text{ m s}^{-1}$ for C1 as a whole (i.e., during episodes and non episodes) and 2.4 m s^{-1} during H^+ episodes. The wind speed alone is probably not the important factor contributing to episodes of ambient H^+ as all but one (C4) of the clusters were within 1 standard deviation of the mean H^+ for C1, rather it is the direction of the wind which is likely the major contributing factor.

The conclusion drawn from this work is that strong acid aerosols and the precursors which produce them are regionally transported. The evidence suggests that the source of the acidic species is southwest of the Pittsburgh/Uniontown, PA vicinity. Additional work to more accurately pinpoint the source region of the acid species and their precursors is currently underway.

ACKNOWLEDGEMENTS

The field study aspect of this paper was funded by the Electric Power Research Institute (EPRI) under contracts RP1630-59 and RP-3009-04. The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under EPA Cooperative Agreement CR816740 to the Harvard School of Public Health.

The authors wish to thank William Wilson and Robert Burton of the U.S. EPA for their assistance. MZ thanks Gennaro Crescenti for supplying and supporting the programs to calculate the vector components of the wind used in this analysis; and George Allen for supplying the meteorological data collected in Uniontown, PA. HS thanks Sally Liu for her assistance during field sampling. The meteorological data for Pittsburgh was obtained from the National Oceanic and Atmospheric Administration's National Climatic Data Center, Asheville, North Carolina.

[†] 226 nmol m^{-3} is equal to the average 24-hour H^+ concentration for 23 June 1990 through 23 August 1990 plus one standard deviation.

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CASTNet Mountain Acid Deposition Monitoring Program

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ABSTRACT

Concern over the influence of air pollution on forest decline has led the U.S.E.P.A to establish the Mountain Acid Deposition Monitoring Program (MADMP) to quantify total deposition at high altitudes, i.e., above cloud base. Clouds can be a major source of atmospheric deposition to sensitive, mountain ecosystems. This program is a part of the Clean Air Status and Trends Network (CASTNet), a national assessment of the effects of the 1990 Clean Air Act. The objectives of MADMP are to estimate total deposition, measure cloud chemistry, and characterize spacial and temporal trends at four selected high altitude sites in the Eastern U.S.

An automated cloud collection system will be utilized in combination with continuous measurements of cloud liquid water content in order to estimate cloudwater deposition. Other relevant data will include continuous meteorological measurements, ozone and sulfur dioxide concentrations, wet deposition from rainfall analysis, and dry deposition from filter pack analysis. Quality assurance and quality control measures will be employed to maximize accuracy and precision.

INTRODUCTION

Forest decline at high altitudes has been extensively documented in Europe^{1,2} and the U.S.^{3,4,5} There is a consensus among researchers that, although a multiplicity of factors are involved in this decline, air pollutants are in some way playing a major role either directly through foliar damage or indirectly through modification of the soil.⁶ Mountain forests can experience very high rates of acid deposition due to high precipitation rates and exposure to clouds for long periods of time. Typically, much higher ion concentrations and higher acidities are deposited through cloud interception than through precipitation.^{7,8,9,10}

MOUNTAIN ACID DEPOSITION MONITORING PROGRAM (MADMP)

From 1986-1991 the U.S. Environmental Protection Agency funded the Mountain Cloud Chemistry Program (MCCP) as a principal source of atmospheric chemical and physical information. MCCP gathered the first significant data base on high altitude deposition in the eastern U.S. Now, within the Clean Air Status and Trends Network (CASTNet), EPA is authorizing the next phase of this investigation -- the Mountain Acid

Deposition Monitoring Program (MADMP). The objectives of the program will be to:

- Characterize total deposition of sulfur and nitrogen compounds to sensitive aquatic and terrestrial ecosystems at high elevation, i.e., above cloud base.
- Characterize spatial pattern of total deposition and quantify cloud deposition on a regional basis.
- Provide identification of trend in cloud water chemistry and total deposition by 1997 and quantify a trend, if any, by the year 2001.
- Evaluate the existing model for estimation of cloudwater deposition, and develop an improved model.

The immediate focus of the MADMP in the 1994 sampling season will be:

- The design and implementation of an automated cloud collection system in combination with the concurrent continuous measurement of cloud liquid water content (LWC), and meteorological parameters relevant to the cloud deposition process and trend analysis.
- The development of regional total deposition estimates to high elevation ecosystems in the Eastern United States.
- The development of a single database for cloud water chemical measurements, and relevant meteorological parameters by combining the EPA Mountain Cloud Chemistry project (MCCP) with the newly initiated MADMP measurements. This combined database will be subjected to statistical analysis for trend identification and assessment.

Four MADMP sites have been established for the 1994 field season: Clingman's Dome, Great Smoky Mountain Nat. Park, TN; Slide Mountain, Catskill State Park, NY; Whiteface Mountain, Adirondack State Park, NY; and Whitetop Mountain, Mt. Rogers Nat'l Recreational Area, VA. Sites under consideration for 1995 include: Mt. Washington, NH; Mt. Mansfield, VT; and Spruce Knob, WV. The selected sites have a history of atmospheric and ecological research records available. Furthermore, the sites selected for this long-term monitoring study represent a range of conditions, not only in terms of climate, air quality, soils and vegetation, but also in atmospheric input of acidifying substances.

Total deposition (consisting of dry, wet, and cloudwater deposition) will be estimated at all four sites. Wet deposition will be measured directly from analysis of rainwater samples, and dry and cloudwater deposition will be estimated using the NOAA multilayer model and the modified Lovett model, respectively. Calculation of dry deposition is derived from weekly filter pack concentrations of SO₂, HNO₃, SO₄, and NO₃, as well as continuous meteorological measurements. Cloudwater will be collected

automatically by a passive string collector when the following conditions are met: the liquid water content of the cloud is at least 0.05 g/m³, the wind speed is at least 2.5 m/sec, the temperature is above freezing. Only non-precipitating clouds will be sampled. The cloud liquid water content will be measured with a Particle Volume Monitor (PVM 100). Collection methods for the different parameters are summarized in Table 1.

Table 1. Summary of parameters measured and collection methods for MADMP

Parameter	Collection Method	Sampling Frequency	Resolution
Dry Deposition - SO ₂ , HNO ₃ , SO ₄ , NO ₃	Filter Pack	Weekly	7 Day Av.
Wet Deposition - Major Ions	Wet/Dry Collector	Weekly	7 Day Av.
Cloudwater Deposition - Major Ions	Mohrman Collector with Automated Cloud Sampler	Event	1 Hour Av.
Cloud - Liquid Water Content Particle Surface Area Droplet Effective Radius	Particle Volume Monitor	Event	5 Min. Av.
Ozone	UV Photometric	Continuous	1 Hour Av.
Sulfur Dioxide	Pulsed Fluorescence	Continuous	1 Hour Av.
Cloud Base	I.R. Scattering/ Operator Observ.	Continuous	1 Hour Av.
Meteorological- Wind Direction Wind Speed Temperature Relative Humidity Precipitation Solar Radiation Surface Wetness	Wind Vane Anemometer Thermistor Thin Film Capacitor Rain Gauge Pyranometer Conductive Grid	Continuous	1 Hour Av.

The quality assurance (QA) and quality control (QC) procedures for cloud collection/LWC measurement will not only ensure the comparability throughout the current CASTNet but will also allow incorporation of all earlier quality assured data of the MCCP into one single coherent data set. QC procedures include periodic comparisons of manual vs. automatic cloud collection, PVM vs. Valente filter methods of determining

liquid water content, and concurrent analysis of split samples by laboratories of ESE and the ASRC at Whiteface Mt. The MADMP QA plan has been developed for monitoring activities performed during the warm months of the year (approximately May through October) i.e., in the absence of supercooled cloud water. The collection of cloud water during winter months will be evaluated and may be initiated in the future.

ACKNOWLEDGEMENTS

This work is being funded wholly by the U.S. Environmental Protection Agency under contract no. 68-D2-0134.

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Gas-Particle Distribution, Neutralization and Size of Sulfate and Nitrate in the Southwestern Desert Aerosol

B.J. Turpin, P. Saxena, P.H. McMurry, and G. Allen

Observations made on 47 days during summer 1992 in Meadview, Arizona were used to characterize inorganic ionic and gaseous concentrations near the Grand Canyon. A sampler equipped with denuders to remove alkaline and acidic gases measured gaseous ammonia, sulfur dioxide and nitric acid and fine particulate ammonium, total extractable acidity (TEA), sulfate and nitrate. In addition, a set of impactors measured size-resolved sulfate, nitrate and ammonium.

The median 6-hr average fine particulate sulfate concentration was $1.6 \mu\text{g}/\text{m}^3$ with about two-thirds of the values below 2. Sulfur dioxide concentrations were comparable to sulfate concentrations. Two-thirds of the particulate-phase nitrate concentrations were less than $0.25 \mu\text{g}/\text{m}^3$, and the maximum value was 0.5. However, substantial nitric acid was present in the gas phase (median concentration of $2 \mu\text{g}/\text{m}^3$). In contrast to prior conclusions that sulfate in this region is generally completely neutralized by ammonia, the median ammonium to sulfate ratio in this study was 1.4. Furthermore, sulfate and ammonium concentrations were highly correlated. With one exception sulfate mass median diameters were $0.15\text{-}0.27 \mu\text{m}$. More than half of the TEA observations were less than 8 nanomoles/ m^3 , and the maximum value was 30.

The Influence of Transport on Aerosol Strong Acidity

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The degree of neutralization of the sulfuric acid portion of fine atmospheric aerosols (acid aerosols, H^+) varies considerably in time and space. This is due to variations in the amount of ammonia the acid aerosols come in contact with prior to collection. It is hypothesized that differences in the predominant transport direction and speed between collected samples will influence ammonia (NH_3) exposure and thus, the observed degree of neutralization. To study the influence of transport one year of every second day 24 hour acid aerosol measurements from four locations (collected by The Harvard School of Public Health and Health and Welfare Canada as part of the "24-Community Study") were combined with back-trajectories. Six different transport patterns were determined for each location by performing a cluster analysis on the trajectories associated with each aerosol measurement. The measured ratio of H^+ to SO_4^{2-} was also included in the clustering in an attempt to further distinguish how transport relates to aerosol neutralization. As expected, there were significant differences in the ratios between clusters. There were also differences, some of them significant, between the ambient levels of H^+ , SO_4^{2-} , NH_3 and SO_2 . The clusters associated with the higher H^+ and SO_4^{2-} concentrations were generally associated with transport from a southerly direction or slow transport (i.e., anticyclones). While there is overlap in the chemical characteristics of each cluster, the transport patterns associated with the clusters with higher ratios of H^+ to SO_4^{2-} appear to be different than the patterns associated with the other clusters. In multiple regression models relating H^+ to cluster, SO_2^{2-} and season, knowledge of cluster was found to explain, at a minimum, an additional 2-6% of the variance depending on location.

Clean Air Status and Trends Network Cloud Water Monitoring Program
J.J. Bowser, E.S. Edgerton, and V.A. Mohnen

The principal objectives of the cloud water sampling program within the Clean Air Status and Trends Network (CASTNET) are:

Characterize total deposition of sulfur and nitrogen compounds to sensitive aquatic and terrestrial ecosystems at high elevation, i.e., above cloud base;

Characterize spatial pattern of total deposition and quantify cloud deposition on a regional basis; and

Provide identification of trend in cloud water chemistry and total deposition by 1997 and quantify a trend, if any, by the year 2001.

High elevation ecosystems can experience increased deposition of sulfur and nitrogen compounds due to their frequent exposure to clouds, fog, dew or related deposition processes, and the higher wind speeds aloft causing higher collection efficiencies by the vegetation canopy.

The CASTNET cloud water deposition monitoring effort will focus on:

The design and implementation of an automated cloud collection system in combination with the concurrent continuous measurement of cloud liquid water content (LWC) and meteorological parameters relevant to the cloud deposition process and trend analysis

The development of regional cloud deposition estimates to high elevation ecosystems in the Eastern United States

The development of a single database for cloud water chemical measurements and relevant meteorological parameters by combining the EPA Mountain Cloud Chemistry Project (MCCP) with the newly initiated CASTNET measurements. This combined database will be subjected to statistical analysis for trend identification and assessment.

Four CASTNET high elevation monitoring sites have been selected for cloudwater collection. These are: Whiteface Mountain, NY; Belleayre Mountain, NY; Whitetop Mountain, VA; and Clingman's Dome, TN. Two or more additional sites will be evaluated for future measurements.

The selected sites have a history of atmospheric and ecological research records available. Furthermore, the sites selected for this long-term monitoring study represent a range of conditions not only in terms of climate, air quality, soils and vegetation, but also in atmospheric input of acidifying substances. Therefore, the efforts under this program either compliment or build on previous research at these sites and intensify their effort at these sites.

The quality assurance (QA) and quality control (QC) procedures for cloud collection/LWC measurement will not only ensure the comparability of data throughout the current CASTNET but will also allow incorporation of all earlier quality assured data of the MCCP into one single coherent data set. The CCMP QA plan has been developed for monitoring activities performed during the warm months of the year (approximately May through October) i.e., in the absence of supercooled cloud water. The collection of cloud water during winter months will be evaluated and may be initiated in the future.

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SESSION 4:
CARBONYL SAMPLING AND
ANALYSIS TECHNIQUES

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Investigation of Aldehyde Chemistry in Sampling Canisters

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During the summer of 1991, Battelle conducted analyses of air samples from surface and airborne platforms as part of the Lake Michigan Oxidant Study (LMOS). Formaldehyde (HCHO) was determined both by the routine analysis of DNPH cartridge samples, and by direct analysis of air collected in canisters for VOC measurement. The latter novel approach made use of Battelle's continuous HCHO monitor, and was motivated by the simplification of sampling that would result if both VOC and HCHO analyses could be done using canister samples. Comparison of HCHO results from the cartridge and canister analyses indicates that in most cases agreement is reasonable, but in about one-third of the results the canister HCHO data are considerably higher than the DNPH data. This difference has not been traced to any artifact from the canister analysis procedure for HCHO. Should the discrepancy be due to the formation of HCHO in the canisters under some conditions, presumably through reactive loss of ozone-precursor hydrocarbons, then these results would have implications for VOC measurements by canisters. The present paper reports on a review of the entire LMOS data set, intended to disclose any chemical causes for the discrepancy in HCHO results. The sample parameters reviewed for each DNPH/canister pair include: ozone content and total hydrocarbon content of the air at the time of sampling; residual content of individual reactive hydrocarbons (e.g., ethylene); location of sample (urban, rural, airborne); altitude of airborne samples; temperature and humidity of air sampled; and the absolute and relative HCHO levels indicated by the two analyses. The conclusions and recommendations drawn from this review will be discussed, in terms of both the LMOS data set, and the chemistry of air in canisters.

**AN ALTERNATIVE METHOD FOR MONITORING CARBONYLS, AND THE
DEVELOPMENT OF A 24-PORT FULLY AUTOMATED CARBONYL
SAMPLER FOR PAMS PROGRAM**

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ABSTRACT

We have investigated the possibility of collecting different aldehydes and ketones on different sorbents such as silica gel, molecular sieve and charcoal followed by solvent extraction, DNPH derivatization and HPLC/UV analysis. Carbonyl collection efficiencies for these sorbents were calculated relative to a DNPH coated C₁₈ sep-pak cartridge. From a limited number of laboratory experiments, at various concentrations, it appears that silica gel tubes can be used for sampling aldehydes (collection efficiencies ≈ 1), whereas charcoal tubes are suitable for collecting ketones. Molecular sieve was found to be unsuitable for collecting most of the carbonyl studied.

We also report the development of a fully automated 24 - port carbonyl sampler specially designed for EPA's PAMS program.

INTRODUCTION

One of the most pressing needs in atmospheric chemistry in recent years has been for a simple, sensitive method to measure low molecular weight oxygenated hydrocarbons, especially aldehydes and ketones (carbonyls). Carbonyls are actively investigated as pollutants emitted by indoor and outdoor sources and as products of hydrocarbon reactions in photochemical smog (1). It is important to measure these compounds because of their importance to atmospheric chemistry as products of the photochemical oxidation of hydrocarbons, precursors of ozone and other photochemical oxidants, and sources of free radicals and organic aerosols in the atmosphere. In addition to being produced as secondary pollutants, a number of carbonyls are emitted directly in auto exhaust, and from a variety of stationary sources, both anthropogenic and biogenic.

A correct understanding and assessment of the role of carbonyls in tropospheric chemistry requires accurate and precise measurement of these compounds along with their parent and product compounds. The concentration of carbonyls range from sub-ppbv in clean air to higher ppbv in urban and polluted air. Due to these trace amounts, determination of carbonyl compounds in ambient air, poses challenging problems. While conventional colorimetric methods are still in use, liquid chromatography analysis of carbonyls as their 2,4-dinitrophenylhydrazones, DNPH-LC, has gained acceptance in recent years (2-4). Thus, this method is now recommended by the intersociety committee and by the U.S.E.P.A. for the determination of formaldehyde and other carbonyls in air (5-6).

In spite of the numerous studies concerned with integrated air sampling, especially with the dinitrophenylhydrazine (DNPH) method, several questions regarding interferences and sampling artifacts have only been partly addressed or studied (7-8). The major concerns with air sampling of carbonyls which can effect the accuracy of the method are: (a) incomplete collection of carbonyls, (b) loss of carbonyls such as adsorption or chemical reaction with ambient air pollutants such as O_3 and SO_2 , (c) generation of carbonyls as artifacts, (d) formation of various interfering compounds, (e) variable blanks resulting from contamination of reagents and sampling equipment and (f) effect of ambient humidity on collection efficiency.

One of the main problems with the use of DNPH cartridges for the collection of carbonyls in ambient air is the high level of background carbonyl hydrazone contamination. DNPH cartridges get contaminated at different stages such as: (a) preparation, (b) storage and (c) handling and shipping. In fact for most ambient carbonyl measurements the detection limits are limited by the background contamination or blank levels of DNPH cartridges.

In this article we present results from an investigation into the possibility of collecting carbonyls on uncoated solid sorbents followed by solvent extraction, DNPH derivatization and HPLC/UV analysis. Collection efficiencies for six carbonyls (ie: formaldehyde, acetone, propionaldehyde, methyl ethyl ketone (MEK), benzaldehyde, and methyl isobutyl ketone (MIBK) at different concentrations were determined on three sorbents (silica gel, molec. sieve and charcoal) and compared to the corresponding collection efficiency by DNPH coated C_{18} cartridges. Sorbents tested in this investigation have been known to completely remove organic pollutants. Silica gel is very efficient in removing formaldehyde (9). Our effort was focused on the recovery of carbonyls followed by derivatization with DNPH and HPLC/UV analysis.

U.S.E.P.A. has recently launched an intensive carbonyl monitoring program in certain areas of the country where ozone

levels are high. This requires around the clock unattended monitoring of VOC's and carbonyls. To meet these monitoring requirements we designed a multiport (24-port) carbonyl sampler containing clean pump, mass-flow controller check valves, auto switching valves programmable timer, flow print-out device and related hardware and electronics.

EXPERIMENTAL

The carbonyl compounds used in this investigation were: formaldehyde and acetone (from Aldrich Chemicals), propionaldehyde, MEK, benzaldehyde and MIBK (from Poly Science Corp. Chemicals Division). All six compounds were mixed and diluted with methylene chloride and methanol (50:50) solution. Known amounts of this carbonyl mixture was introduced into a 25 liters Tedlar bag filled with purified ambient air. This carbonyl laden air was allowed to pass through one sorbent tube and one DNPH cartridge simultaneously at the rate of approximately 0.5 liters per minute. Sorbent tubes (charcoal and silica gel) were obtained from SKC Inc. Molecular sieve 5A (from Supelco, Inc.), packed as a cartridge in the laboratory, was also tested for collecting carbonyls. Small polyethylene cartridges (volume 0.5 ml) containing 0.4 grams of neutral, hydrophobic C_{18} sorbent packed by radial compression (Sep-Pak, Waters) were used in this work. Each cartridge is first cleaned and wetted by slowly pushing 2ml of HPLC-grade acetonitrile and is then loaded with 2 ml of a 0.6% DNPH solution in acetonitrile containing 1.0% H_3PO_4 and dried with UHP N_2 .

In one set of experiments sorbent tubes ie. silica gel, charcoal and molecular sieve were extracted by sonication with a 50:50 mixture of C_2H_5OH and CH_2Cl_2 . In the second set of experiments extraction was achieved using pure ethanol for silica and pure CH_2Cl_2 for charcoal sorbent tubes. In order to see which solvent is best for the extraction of carbonyls from charcoal tubes, extraction was carried out with different solvents (eg. H_2O , C_2H_5OH , CS_2 and CH_2Cl_2). All extracts from various sorbents were filtered with 0.2um nylon filters followed by DNPH derivatization by adding 1.0 ml of acidified 0.1% DNPH solution in acetonitrile. All mixtures containing CH_2Cl_2 or CS_2 , in the derivatized solution, were evaporated to dryness followed by the addition of 2.0 ml of pure carbonyl free acetonitrile. DNPH cartridges were extracted with 2.0 ml of pure acetonitrile.

The HPLC/UV system included Shimadzu-6 series UV detector, gradient LC pumps and a programmable autosampler. A 20 ul of the sample was injected each time on a C_{18} reversed phase analytical column (from Axxiom) having a C_{18} guard column. Acetonitrile and water used as eluents were filtered through 0.2 um filter and degassed. HPLC/UV system was calibrated using two independently prepared hydrazone standards, one obtained from Radian's Standards Division in Austin, Texas and the second prepared in

our laboratory. Good separation of various carbonyl hydrazones was achieved using the gradient elution system. Carbonyl identification involved matching retention times of unknowns with the standards. Carbonyls were quantified using response factors derived from standard hydrazones.

AAC and Northstar Instruments have designed a 24-port fully automated carbonyl sampler for EPA's PAMS program where short term (2-3 hrs.) samples collection is desired. Various components of this system are shown in Fig.1. This sampler automatically switches to the next sampling port at pre-selected times and the mass-flow meter prints out the sampling volume through that DNPH cartridge for that particular event. Various parts are electronically interfaced to carry out different operations. This unit can be operated from an external signal such as a telephone or any other pollution monitoring device. Check valves are used to prevent possible contamination of DNPH cartridges due to passive sampling of atmospheric carbonyls.

RESULTS AND DISCUSSION

Results from various tests are summarized in Tables 1-5. Carbonyls mixture used for these tests included: formaldehyde, propionaldehyde, benzaldehyde, acetone, methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK). Fifty microliters of each carbonyl was added to a solution containing 5 ml of CH_2Cl_2 and 1 ml of CH_3OH . Table 1 shows the collection of all six components on different sorbents including DNPH coated C_{18} cartridge when 4 ul of above carbonyl mixture solution was injected in 25 liter Tedlar bag. Sampling from the Tedlar bag was performed at 0.5 liter per minute. The above experiment was repeated at three other concentrations by introducing 8 ul, 10 ul and 15 ul of the carbonyl mixture in 25 liter Tedlar bag. Results from these tests show that silica gel is very efficient in trapping aldehydes but poor in retaining ketones. Charcoal, which is known to remove various pollutants with 100% efficiency (9) performed poorly ($\approx 20\%$ collection efficiency) for aldehydes but relatively good for ketones ($\approx 60\%$ collection efficiency). Molecular sieve did not collect most of the carbonyls tested except for benzaldehyde. In order to improve on the collection and recovery of carbonyls on charcoal a desorption recovery experiment was conducted. In this experiment three charcoal tubes and one DNPH coated C_{18} cartridge were collected from the same 25 liter Tedlar bag containing all the six carbonyls. Charcoal tubes were extracted individually with ethanol, CH_2Cl_2 , and CS_2 , respectively followed by: the addition of 1.0 ml of DNPH solution in acetonitrile (for derivatization), evaporation to dryness and addition of 2.0 ml of acetonitrile for HPLC/UV analysis. Results from this test shown in Table 4 clearly indicate CS_2 is a superior extracting solvent for charcoal and the net amount of ketones recovered using CS_2 as solvent is the same as collected on DNPH cartridge from the same bag. The lower carbonyl collection efficiency of charcoal in Tables 1-3 is due to the poor extraction efficiency of CH_2Cl_2 .

From the various tests performed in this investigation we conclude that air sampling for carbonyl compounds can be performed using silica gel and charcoal as sorbents followed by extraction, derivatization with DNPH and HPLC/UV analysis.

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Table 1. Collection of Aldehydes & Ketones on different Sorbents.
(4 ul of Standard Carbonyl Solution in 25 liter Tedlar bag)

Carbonyl	DNPH coated C18 (ug/ml)	Silica gel (ug/ml)	Mol. Sieve (ug/ml)	Charcoal (ug/ml)
Formaldehyde	7.95	6.78	2.64	2.90
Propionaldehyde	12.06	12.26	2.70	0.28
Benzaldehyde	15.47	15.50	18.10	0.70
Acetone	21.01	2.86	1.29	8.10
MEK	20.31	6.25	2.66	8.20
MIBK	14.70	4.27	2.78	7.80

Table 2. Collection of Aldehyde & Ketones on different Sorbents.
(8 ul of the Standard Carbonyl mixture in CH₂CL₂/CH₃OH
was added in 25 liter Tedlar bag)

Carbonyl	DNPH coated C18 (ug/ml)	Silica gel (ug/ml)	Mol. Sieve (ug/ml)	Charcoal (ug/ml)
Formaldehyde	12.95	12.88	7.49	4.54
Propionaldehyde	22.56	23.50	3.61	4.52
Benzaldehyde	31.23	34.05	36.10	2.10
Acetone	36.42	9.86	4.60	12.15
MEK	35.12	15.00	4.45	8.40
MIBK	30.36	7.96	7.56	10.50

Table 3. Collection of Aldehydes & Ketones on different Sorbents.
(a) 10 ul and (b) 15 ul of the Standard Carbonyl mixture
in CH₂CL₂/CH₃OH was added to 25 liter Tedlar bag.
Extraction of DNPH Cartridges was performed with 2.0 ml of CH₃CN;
Silica gel with 5.0 ml of Ethanol; Charcoal with 5.0 ml CH₂CL₂;
1.0 ml of derivatizing DNPH solution was added to Silica and Charcoal extract.

Carbonyl	DNPH coated C18 Cartridge		Silica gel		Charcoal	
	a	b	a	b	a	b
Formaldehyde	12.24	18.50	14.50	17.80	2.18	5.80
Propionaldehyde	38.82	60.00	30.70	53.50	1.88	1.88
Benzaldehyde	58.80	70.50	51.25	55.00	5.17	8.60
Acetone	46.46	65.60	10.05	12.13	24.37	38.24
MEK	56.63	72.10	10.17	16.70	32.42	48.80
MIBK	48.16	70.25	2.70	5.85	20.05	22.10

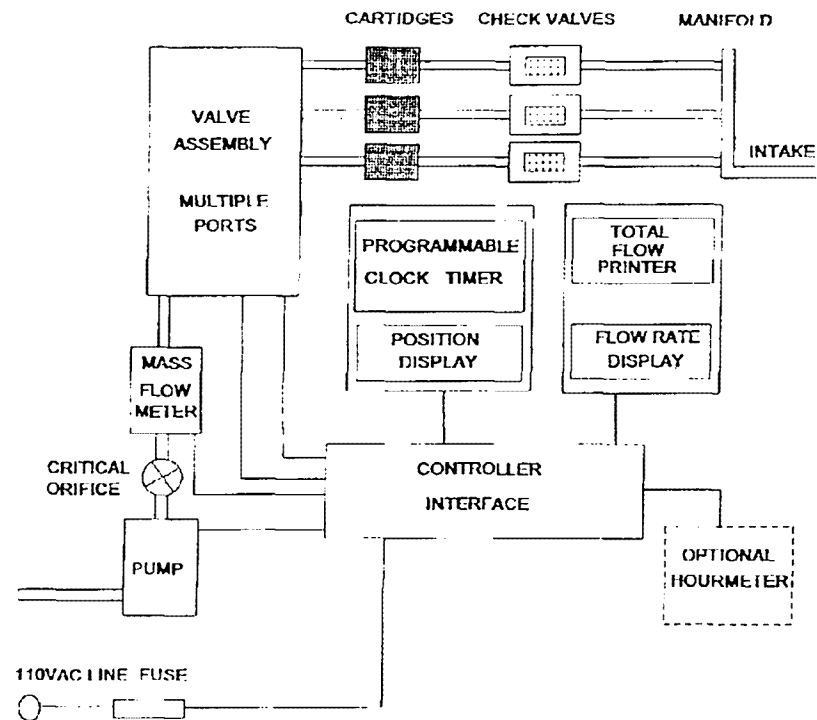
Table 4. A Study of desorption recovery of Carbonyls from Charcoal using different solvents and comparison with DNPH coated Cartridge. Charcoal tubes and DNPH cartridge were collected simultaneously from a 25 liter Tedlar bag containing carbonyl mixture.

Carbonyl (ug/ml)	Desorption Solvent used			DNPH coated C18 Cartridge
	Ethanol	CH ₂ Cl ₂	CS ₂	
Formaldehyde	1.80	0.45	1.40	8.05
Propionaldehyde	0.90	0.30	3.46	7.00
Benzaldehyde	0.10	0.85	4.60	7.52
Acetone	2.28	6.84	9.15	10.50
MEK	1.50	7.27	11.30	12.10
MIBK	0.30	3.25	10.55	10.45

Table 5. Average Collection efficiency of different Sorbents for Carbonyls relative to DNPH coated C18 Cartridge from five different sets of experiments.

Analyte	Silicagel (Extraction with C ₂ H ₅ OH)	Mol. Sieve (Extraction with C ₂ H ₅ OH)	Charcoal (Extraction with CS ₂)
Formaldehyde	0.99	0.45	0.30
Propionaldehyde	0.92	0.20	0.10
Benzaldehyde	0.90	0.95	0.10
Acetone	0.15	0.10	0.95
MEK	0.24	0.13	0.97
MIBK	0.17	0.22	0.94

Figure 1 Block Diagram of Multiport Ambient Air Sampler



Determination of Carbonyl Compounds by HPLC/UV Analysis in the CASTNet Air Toxics Monitoring Program (CATMP)

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The determination of carbonyl compounds in ambient air is one of the analytical requirements of the Environmental Protection Agency's (EPA's) Clean Air Status and Trends Network (CASTNet) Air Toxics Monitoring Program (CATMP). The CATMP was established in 1993 by EPA to reactivate and operate the Urban Air Toxics Monitoring Program (UATMP). The purpose of the program is to establish baseline toxics concentrations, develop air emission inventories, and to identify air toxic sources using chemical mass balance modeling techniques.

1993 results for the CATMP analysis of carbonyl compounds by method TO-11 are presented. Samples were collected using Waters' dinitrophenyl hydrazine (DNPH) impregnated cartridges and analyzed using high performance liquid chromatography (HPLC) with ultraviolet (UV) detection. A regulatory program approach to quality control was taken to insure that all aspects of shipping, sampling and analysis contained sufficient controls in order to produce data of acceptable and consistent precision and accuracy. Database presentations will include the overall quality assurance approach, quality control measurements, and sample results from eight sites. An examination of background interferences detected in the various control samples will also be discussed.

A Sequential Cartridge Sampler for Measuring Carbonyls and Toxic Organic Compounds

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A multi-channel sequential sampler has been developed to collect carbonyl compounds with silica gel or C-18 cartridges using EPA Method TO-11. The sampler automatically draws ambient air through the cartridges over a predetermined time sequence. The sample flow rate is continuously controlled and monitored using mass flow controllers. An additional channel is provided so that duplicate samples can be simultaneously obtained. The sampler can be interfaced with a micro-computer to provide custom timing sequences, acquire and store flow rate data, and perform quality assurance procedures. A field test was conducted in Claremont, California, using AmAA C-18 cartridges to sample formaldehyde. The results show good agreement with values obtained with a Tunable Diode Laser Absorption Spectrometer. Additional testing has also been performed to demonstrate long term reliability of the sampler.

Measurement of Carbonyl Compounds in an Industrialized Area

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ABSTRACT

There has been a history of health related complaints in the town of Wallingford, CT, especially from those people living in areas adjacent to the heavily industrialized Route 5 corridor. The Agency for Toxic Substances and Disease Registry of the Centers for Disease Control has been petitioned to assess the environmentally related health complaints and have concluded that there was insufficient air quality data from Wallingford to clarify and/or quantify the possible existence of a public health hazard. In order to address these complaints and needs, the DEP's Air Toxics Monitoring Group performed a year long study to monitor for selected VOC and carbonyl compounds. This paper reports on the measurements of selected carbonyl compounds, from several sites adjacent the Route 5 corridor, between October 1992 and October 1993. The analytical data show that there are likely correlations between wind direction and receptor locations and that there have been several instances where reported values of formaldehyde have exceeded Connecticut's Hazardous Limiting Values (HLVs) guidelines.

INTRODUCTION

Connecticut's Department of Environmental Protection (CT/DEP) has compiled a history of health related complaints from the town of Wallingford, CT. These complaints have focused on perceived poor air quality and odors, especially from those people living in areas adjacent to the industrialized Route 5 corridor. The Agency for Toxic Substances and Disease Registry (ATSDR) was petitioned to assess these environmentally related health complaints and summarily concluded that there was insufficient air quality data from Wallingford to clarify and/or quantify the existence of a possible public health hazard. A search of Connecticut's SARA Title III database suggested that there were several major sources of toxic air emissions in the area of concern. In order to address these complaints and needs, the CT/DEP's Air Toxics Monitoring Group performed a year long (and continuing) study to monitor for selected VOC and carbonyl compounds. This paper is a report on the measurements of selected carbonyl compounds, from several sites adjacent the complaint area, between October 1, 1992 and September 30, 1993.

SCOPE AND OBJECTIVE OF TESTING

Most of the previous air sampling in this vicinity had been long-term for specific criteria air pollutants, or short-term for VOCs. This previous short-term sampling was performed to assess the potential impact of certain air toxics at the fence line of a local chemical manufacturing facility. The CT/DEP Air Toxics Monitoring Group has attempted to characterize the air quality at several locations in the subject area, for a selection of carbonyl and other VOC compounds. Sampling was conducted at four sites, corresponding to the downwind directions from the cluster of industrialized sources, during seasonal prevailing winds. Samples were collected for 24-hour periods at six day intervals, following the USEPA's criteria air pollutant sampling schedule, regardless of predicted wind direction. Real time meteorological data were collected during the entire life of the sampling project, so that wind coupled sample values could be analyzed.

SAMPLING SITES

Samples were collected at four sites. These sites were selected by considering localized prevailing wind directions and potential emissions sources. The sampling sites were selected to maximize sample concentrations and have "upwind" and "downwind" sample pairs to compensate for variability in wind direction. The sites were also selected considering the normal practicalities of site accessibility and electric power availability.

Site #1 is located at Wallingford City Hall, an existing PM₁₀ monitoring site (Figure 1) about 1.25 miles north northeast of the industrial area. Site #2 is an 8 foot square monitoring shed erected on state land, by CT/DEP personnel, some 2000 feet to the south and east of a chemical manufacturing plant which is a TRI carbonyl source. Monitoring site #2 is climate controlled. Site #3 is located to the north northwest of the industrialized area, on property owned by the local electric utility. Site #3 went on line in the 1st quarter of 1993. Site #4 is located on the roof of a local fixture repair business, directly across the state highway and about 750 feet east of a chemical manufacturing plant. A fifth site was set up in October 1993, after the reporting period, at the Wallingford landfill, to assess potential emissions from that source.

SAMPLING METHODOLOGY

Carbonyl samples, VOC canister samples and relevant meteorological data were collected concurrently. Carbonyl samples were collected on dinitrophenylhydrazine (DNPH) coated silica cartridges, manufactured by Millipore/Waters, according to CT/DEP SOP T112. Samplers consisted of a 120 VAC pump, with flows controlled by micro-metering valves, capable of achieving flow rates of 300-1000 ml. per minute. The DNPH cartridges were mounted at the front end of the sampling train to minimize the chance of contamination from upstream sampling hardware.

To reduce the potential for carbonyl compounds being "scavenged" by ambient ozone, an ozone scrubber was installed upstream of the DNPH sampling cartridges. The ozone scrubber consisted of a coiled 3 meter length of 1/4 inch O.D. annealed copper tubing that had been soaked overnight in a saturated solution of potassium iodide (KI) and allowed to air dry. This scrubber coil was then cured at 80° C, wrapped with a heater strip and installed in an insulated sampling case. All of the outdoor carbonyl samplers were fabricated in weather-tight enclosures. The components of the two samplers at Site #2 were shelf-mounted in the temperature controlled shed. All carbonyl samplers were fabricated in-house, by Air Toxics personnel.

The samples were collected for 24-hours per day, on a six-day schedule, at several sites. The sampling sites were selected to maximize sample concentrations downwind of the industrial area, during periods of average localized prevailing winds. CT/DEP collected a minimum of 60 samples at each of 3 sites.

METEOROLOGY

During the Wallingford study, a portable meteorological monitoring station, equipped with sensors for wind speed and wind direction, ambient temperature and barometric pressure was installed at Site #4, on the roof of the DiMartino's Fixtures building. Wind direction data was collected to attempt to interpret whether high ambient concentrations of selected carbonyl compounds coincided with wind direction.

QUALITY ASSURANCE/QUALITY CONTROL

QA/QC samples were collected on a regular schedule during the study. A criterion of 1 QC sample per 10 field samples was followed. For each group of 10 field samples, a collocated sample, as well as a field blank, was collected at site #2. Laboratory "blanks" were analyzed along with each batch of field samples on a similar schedule. Each lot of DNPH sampling media was also "blank checked" prior to use in the field. The analyzed sampling media lot "blanks" were virtually all non-detects (ND) for the entire range of compounds of interest. Field blank concentrations were low enough to eliminate the need for background correction, i.e., subtract blank values from analytical field values.

SAMPLE ANALYSIS

The DNPH sample tubes were analyzed by high performance liquid chromatography (HPLC). An analytical protocol has been developed by CT/DEP's analytical support laboratory, the Environmental Research Institute (ERI), for analyzing up to 16 carbonyl compounds. This protocol, Method 1100, is based on EPA Method TO-11 and ASTM Method D5197-92 and modified for CT/DEP needs. Laboratory analyses showed excellent correlation between the collocated samples. A tabulation of analytical results with wind directions, by sample date, follows as Table 1.

DISCUSSION/CONCLUSIONS

The data from the year long study has been divided by quarters of the year. Our working hypothesis was that the concentrations of carbonyl compounds at any of our individual monitoring sites would be related to wind direction. The data was analyzed to correlate to the prevailing wind direction. The three compounds most prevalent at relatively high concentrations were formaldehyde, acetaldehyde and acetone and only data for these three compounds is presented here, with an emphasis on formaldehyde. The analytical data for formaldehyde was paired with wind direction data, for days when the wind prevailed from a particular sector at least 60% of the 24-hour sample period. This data was graphed to search out correlations among formaldehyde levels, site location and wind direction.

Significant prevailing wind directions were calculated, using data from our meteorological station at site #4. The analytical data were paired with this wind direction data for each sampling date for which the wind direction was significant for at least 60 percent of the time. The data set was then sorted by wind direction (in degrees) using a spreadsheet. The summarized data is depicted, by quarter, in Figures 2-5.

The data indicate that when the wind blows from the south, the formaldehyde concentration at site# 2 is greater than at site# 4, indicating a potential discrete source to the south. There are also some higher levels at site# 2 and site# 4 during winds from the NNE. There are no apparent industrial carbonyl sources upwind from these sites, suggesting that perhaps Interstate 91 to the east and the Wharton Brook connector/Route 5 interchange to the south, are potential line sources of both primary and secondary carbonyl emissions.

With the wind direction from the west to NNW, there are significantly higher concentrations of formaldehyde at site# 2 and to a lesser extent at site# 4. As site# 2 is directly downwind of a known TRI formaldehyde source under these conditions, these formaldehyde concentration values can be considered site specific. The presence of high formaldehyde concentrations at site# 3 (corresponding with lesser concentrations at sites# 2 and 4) when the wind is from the N and NW indicate a possible emissions source in that direction also.

Receptors at several of the monitoring sites received relatively high levels of formaldehyde. The analytical data show that there have been several instances where reported values of formaldehyde have exceeded Connecticut's Hazard Limiting Values (HLVs) guidelines². The variability of the data suggests the need for additional monitoring, in order to isolate and possibly remediate the formaldehyde emission sources. The VOC data that was collected in tandem with the carbonyl data will be analyzed as time permits. Perhaps a pattern of pollutants will emerge with various wind directions that will act as a source "fingerprint".

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Table 1. Formaldehyde Concentrations as Compared to Wind Direction at 4 Sites

<u>Wind Direction (Degrees)</u>	<u>Wind Direction</u>	<u>Site #1, Town Hall</u>	<u>Site #2, Route 5 Shed</u>	<u>Site #3, Wallingford Electric Co.</u>	<u>Site #4, Di- Martino's Fixtures</u>
4	N	2.20	5.10		1.50
7	N	2	14.6		2.9
7	N	0.4	2.50		2.10
12	NNE	1.10	17.20	1.200	2.30
14	NNE	0.80	10.60	1.000	1.10
17	NNE	1.50	4.30	1.800	2.00
19	NNE	1.50	4.20		1.60
23	NNE	2.5	3.7		2.5
28	NNE	1.8	13.00		0.50
30	NNE	2.70	2.70		2.40
30	NNE	0.5	5.80		1.70
31	NNE	0.6	3.00		1.00
37	NE	2.50	7.10	3.300	2.60
60	NE	1.3	3.9		2.9
66	ENE	3.00	7.50	2.900	3.60
133	SE	5.90	8.50	5.200	12.10
153	SE	4.00	4.00	5.20	3.40
153	SSE	2.20	13.00	3.300	3.50
161	S	0.70	4.80	5.80	1.80
165	SSE	1.80	5.20	3.200	2.40
174	S	1.50	8.20	3.30	6.10
175	S	2.40	3.80		2.80
177	S	1.9	10.80		5.30
180	S	0.7	2.20		1.80
185	S	2.70	5.20	5.200	5.70
187	S	4.30	5.50	8.500	4.80
188	S	1.7	4.2		5.9
196	SSW	1.1	6.2		3.6
200	SW	1.3	2.70		2.80
204	SSW	2.50	4.40	7.300	9.90
225	SW	3.7	18.3		3.1
233	WSW	1.20	4.70		1.20
238	WSW	2.20	4.00	4.400	10.00
274	W	1.8	2.3		8.4
289	WNW	1.30	5.10		2.20
309	NW	2.30	5.30		4.50
313	NW	1.8	6.2		1.7
325	NW	1.00	3.40	0.70	11.50
326	NW	2.80	13.20	2.100	6.80
327	NNW	3.50	6.10	6.60	0.50
328	NNW	1.5	25.6		1.7
335	NNW	3.1	3.8		3.9
348	N	1.2	17.80		3.20
351	N	1.1	6.5		0.8
359	N	0.50	7.50	6.30	1.50
360	N	3.1	2.2		1.7
360	N	1.5	5.3		2.9
360	N	0.2	14.30		1.30

Figure 1. Formaldehyde Concentration vs Wind Direction at 4 Sites (4th Quarter 1992)

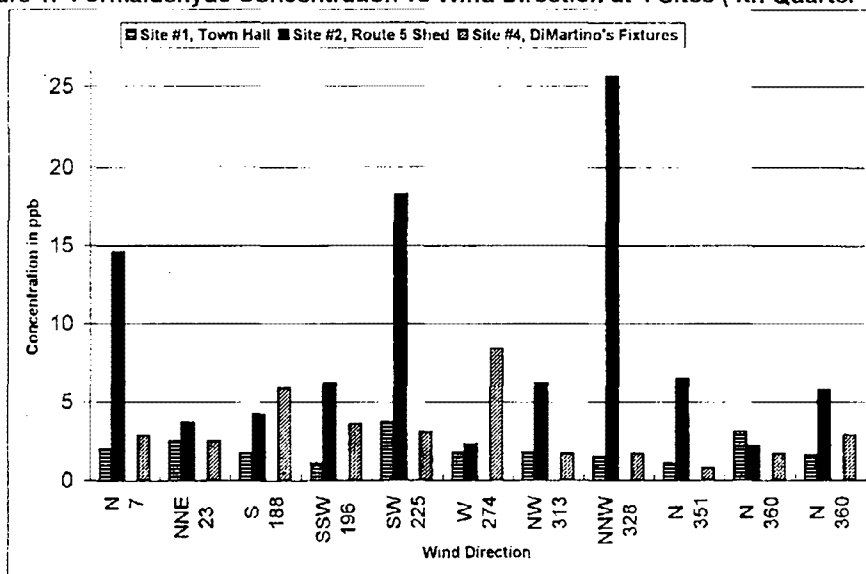


Figure 2. Formaldehyde Concentration vs Wind Direction at 4 Sites (1st Quarter 1993)

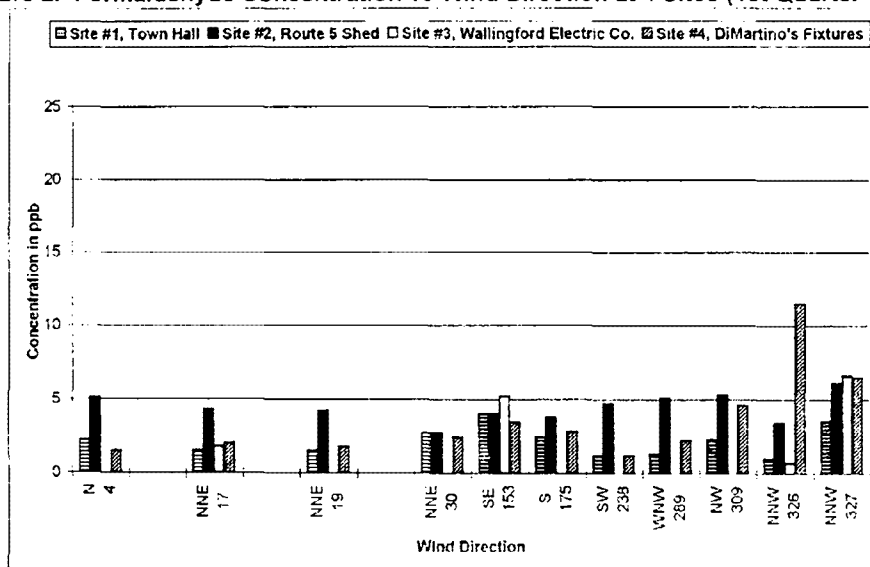


Figure 3. Formaldehyde Concentration vs Wind Direction at 4 Sites (2nd Quarter 1993)

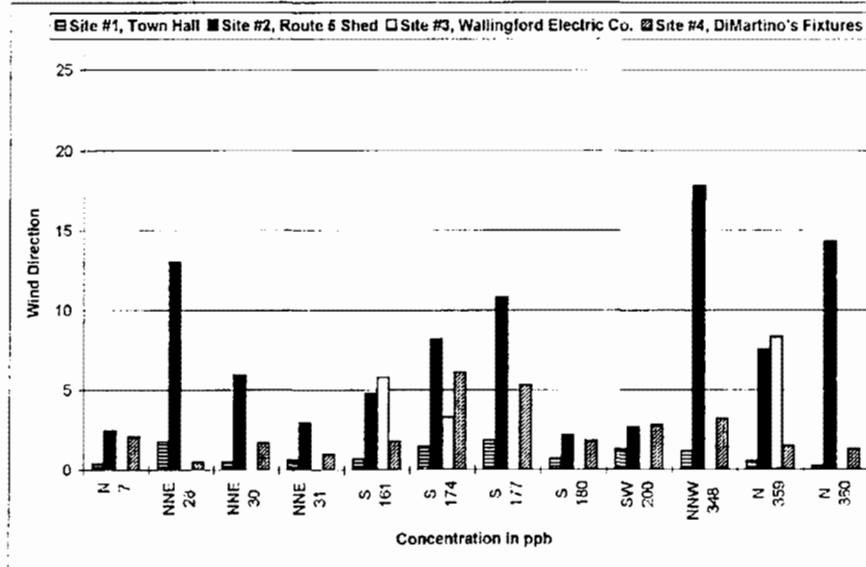
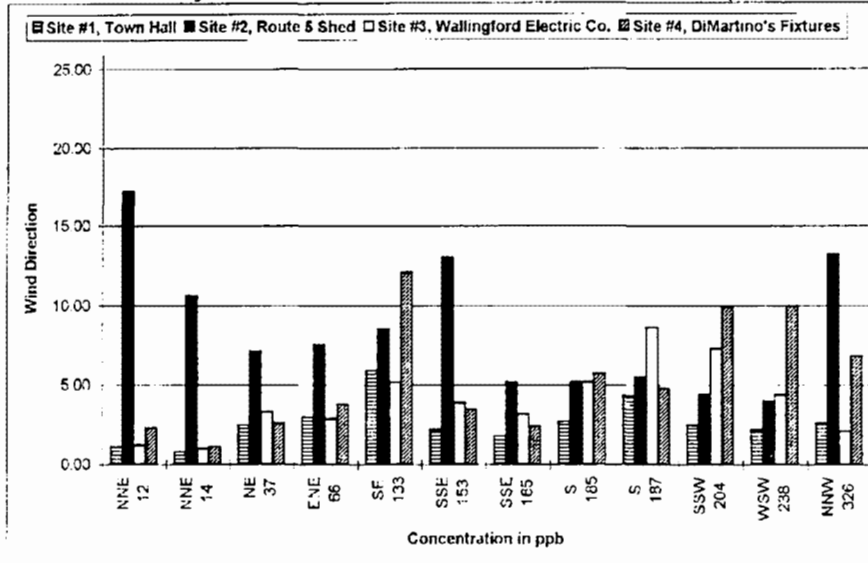
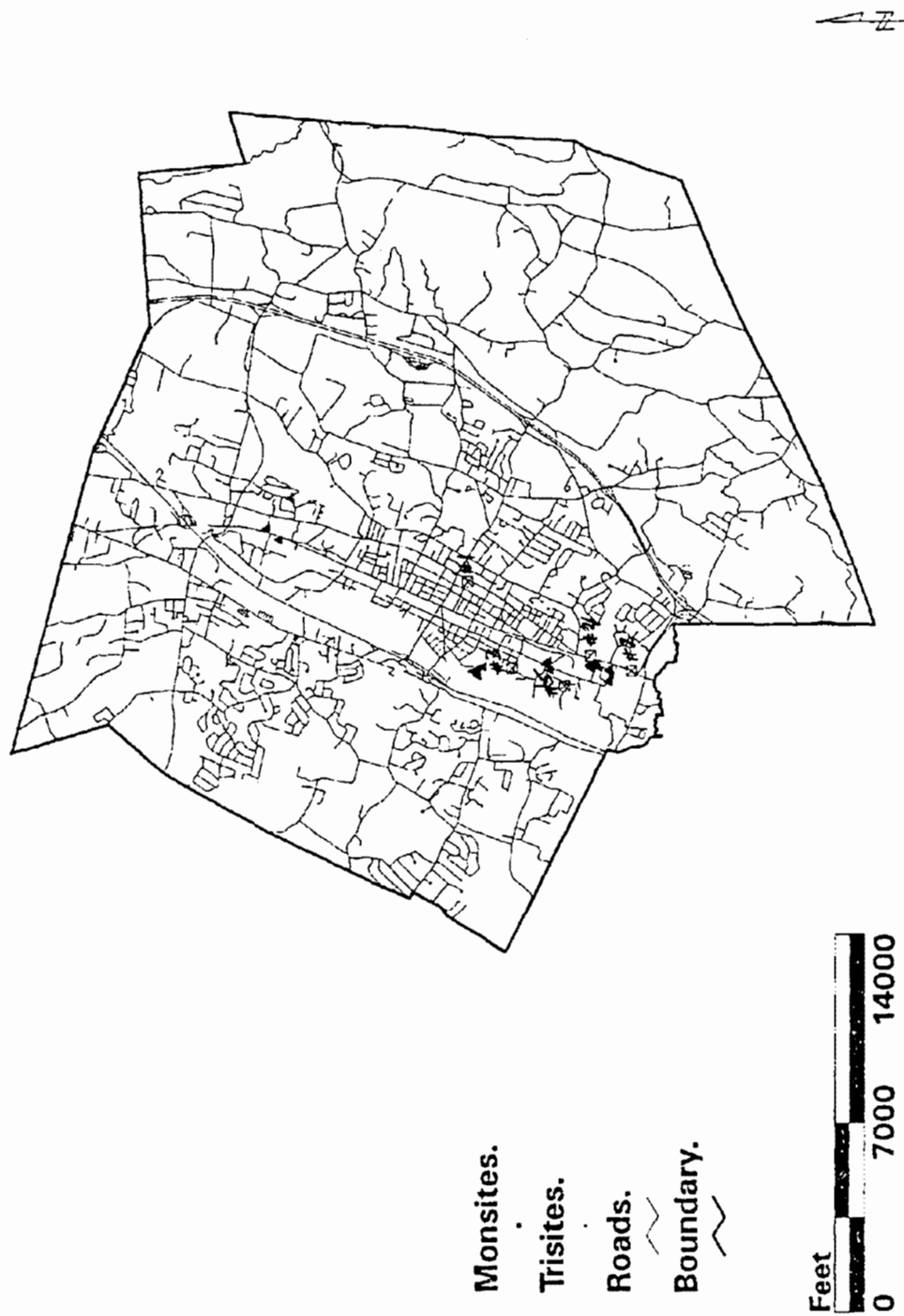


Figure 4. Formaldehyde Concentration vs Wind Direction at 4 Sites (3rd Quarter 1993)



Town of Wallingford, CT TRI & Air Monitoring Sites

Figure 5. Map of Target Area, TRI Facilities and Sampling Stations.



SESSION 5:

**ENHANCED OZONE MONITORING
STATUS AND DEVELOPMENT**

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Photochemical Assessment Monitoring: Overview and Current Status

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ABSTRACT

The Clean Air Act Amendments of 1990, established requirements for the Environmental Protection Agency (EPA) to develop rules for the establishment of enhanced ozone monitoring networks or Photochemical Assessment Monitoring Stations (PAMS) in ozone nonattainment areas designated as serious, severe, and extreme. The subsequent rules require these stations to collect ambient air measurements for a target list of volatile organic compounds including several carbonyls, oxides of nitrogen, ozone, and meteorological measurements, both surface and upper air.

Twenty-two areas in the United States are obligated to install and operate PAMS stations to aid in the identification, development, and implementation of effective ozone control strategies. This paper will examine the specific requirements of the PAMS rules and will provide information regarding the current status of the networks and overall implementation issues.

INTRODUCTION

Historically, despite comprehensive analyses which indicate that ozone in the United States has steadily declined over the past 10 years¹, many States continue to be plagued with an intractable and pervasive ozone nonattainment problem. Currently approximately 140 million persons reside in counties which are part of 94 designated ozone nonattainment areas²; of those areas, the 22 serious, severe, and extreme areas are particularly problematic. Heretofore, ozone control strategies employed by State and local air pollution control agencies focused on reductions in the emissions of volatile organic compounds (VOC) which are common photochemical precursors of ozone. Unfortunately, more recent data would lead these same agencies to believe that this strategy belied an overly simplistic view of a significantly complex problem where past successes have been a matter of fortune as much as effective strategy.

BACKGROUND

In its report, *Rethinking the Ozone Problem in Urban and Regional Air Pollution*³, the National Academy of Sciences, et al, noted that current ozone control programs:

- o did not adequately consider NO_x controls,
- o generally appeared to underestimate anthropogenic VOC emissions,
- o were inadequate to detect emissions trends, and
- o did not provide mechanisms for directly measuring the success of implemented controls.

The Academy clearly recognized the need to institute controlling functions such as routine ambient monitoring for ozone precursors. Additionally, they noted the need to re-invent ozone management strategies by documenting the emissions reductions which were predicted and what effect those reductions had on regional ozone levels.

On March 4, 1992, the Environmental Protection Agency proposed amendments to the ambient air quality surveillance rules (40 CFR Part 58) to provide for the enhanced monitoring of ozone and oxides of nitrogen and for the additional monitoring of volatile organic compounds (including carbonyls) to comply with the requirements of Title I, Section 182 of the Clean Air Act Amendments of 1990. These proposed modifications were proffered to obtain more comprehensive and representative data on ozone air pollution. Subsequently, following an extended public comment period, on February 12, 1993, the final rules were promulgated in the *Federal Register* (58 FR 8452). These regulations required the affected States to adopt and implement a program to improve ambient monitoring activities and the monitoring of emissions of oxides of nitrogen and volatile organic compounds and required States to establish Photochemical Assessment Monitoring Stations (PAMS) as part of their State Implementation Plan (SIP) monitoring networks in ozone nonattainment areas classified as serious, severe, or extreme. Additionally, each SIP for the affected areas must be amended to include provisions for such ambient monitoring. The principle reasons for requiring the collection of additional ambient air pollutant and meteorological data are, primarily, the historical challenges faced by the State and Local Government air pollution control agencies in attaining the National Ambient Air Quality Standards (NAAQS) for ozone nationwide, and secondly, the need for a more comprehensive air quality database for ozone and its precursors to explain the effects of ozone control strategies.

RULE REQUIREMENTS

Fundamentally, the PAMS requirements were designed to ensure the implementation of

ambient monitoring networks which provide information on the roles of ozone precursors, pollutant transport, and local meteorology in the photochemical process as well as to establish a feedback loop as a "reality check" on proposed ozone control strategies. Eventually, it was planned that the PAMS would provide a data base useful for evaluating the success of the control programs and developing mid-course SIP corrections. Specific provisions of the Rule require the establishment and operation of up to 5 PAMS stations in each affected Metropolitan Statistical Area or Consolidated Metropolitan Statistical Area (MSA/CMSA), depending on the population of the area (See Figure 1). Those stations are identified by number and defined as follows:

- o Site #1 - These sites will characterize upwind background and transported ozone/precursor concentrations entering the area and will identify those areas which are subjected to ozone transport. The #1 Sites are located in the predominant morning upwind direction from the local area of maximum precursor emissions and at a distance sufficient to obtain urban scale measurements.
- o Site #2 - These sites will monitor the magnitude and type of precursor emissions in the zone where maximum precursor emissions representative of the affected area are expected to impact and, of all the PAMS sites, are best suited for the monitoring of urban air toxic pollutants. The #2 Sites are generally located immediately downwind (using the same morning wind direction for locating Site #1) of the area of maximum precursor emissions and are typically placed near the downwind boundary of the central business district to obtain neighborhood scale measurements representative of the MSA/CMSA. Additionally, a second #2 Site in the second-most predominant morning wind direction may be required depending on the size of the area.
- o Site #3 - These sites are intended to monitor the maximum ozone concentrations which occur downwind from the area of maximum precursor emissions. Locations for #3 Sites should be chosen so that urban scale measurements are obtained. Typically, these sites are located 10 to 30 miles downwind from the fringe of the urban area.
- o Site #4 - These sites are established to quantify the extreme downwind levels of ozone and its precursor concentrations which exit the area and to identify those areas which are potentially contributing to ozone transport into other areas. The #4 Sites are located in the predominant afternoon downwind direction from the local area of maximum precursor emissions at a distance sufficient to obtain urban scale measurements.

Each PAMS station samples for speciated volatile organic compounds (VOC), often including several carbonyls, as well as ozone, oxides of nitrogen, and surface (10-meter) meteorological parameters; the network requirements vary somewhat with the size of the MSA/CMSA (See Tables I. and II.). Additionally, each area is required to install an upper air meteorological monitoring site at one location representative of the area. The Rule allows a 5 year transition or phase-in schedule for the program at a rate of at least one station per area per year. Further, the Rule provides for the submission and approval of alternative network designs and sampling schemes. Such alternative mechanisms for compliance with the rules are especially valuable to States which are currently engaged in some different form of ozone precursor monitoring which has proved adequate for their SIP needs.

Specific and often different monitoring objectives are associated with each individual PAMS monitoring location. These monitoring objectives can be summarized into categories to support the

following activities: control strategies, photochemical modeling, emissions inventories, trends, attainment/nonattainment decisions, and exposure analyses. EPA acknowledges, however, that in formulating the data requirements for the PAMS program, it was necessary to achieve some compromises, (i.e., some more crucial objectives would be better satisfied than other less important objectives). A monitoring network which adequately supports these six objectives will provide the initial stepping stones that constitute a pathway toward attainment of the National Ambient Air Quality Standard (NAAQS) for ozone.

NETWORK STATUS

For the 1994 PAMS monitoring season, EPA expects that approximately 49 sites out of a total of 94 planned sites will be operational in 20 networks located in the affected serious, severe, and extreme ozone nonattainment areas. Note that the Lake Michigan States and the South Coast/Southeast Desert areas of California have combined their networks and provided joint network plans. Table III. provides the status of each of the 20 resultant networks. Reported data observations to the Aerometric Information Retrieval System (AIRS) are expected to grow approximately 22% from approximately 36.1 million to 44 million observations by the end of the 1998 monitoring season.

Funding for the PAMS program has continued to grow commensurate to the needs of the program. Clean Air Act §105 Grant monies which are awarded to State and local air pollution control agencies, have increased from \$0.5 million in 1992 to \$8.5 million for 1995. Such funding will continue to be necessary to support the five-year implementation of PAMS which formally began with the 1994 season. In comparison, costs for 1994 are expected to be more than \$10 million and grow to \$18.7 million by 1995. Although these costs for the program incorporate numerous monitoring and support activities, the bulk of the monies will be spent for the monitoring of VOC/carbonyls (61%), for data processing/analysis (17%), and for the monitoring of meteorological parameters (11%).

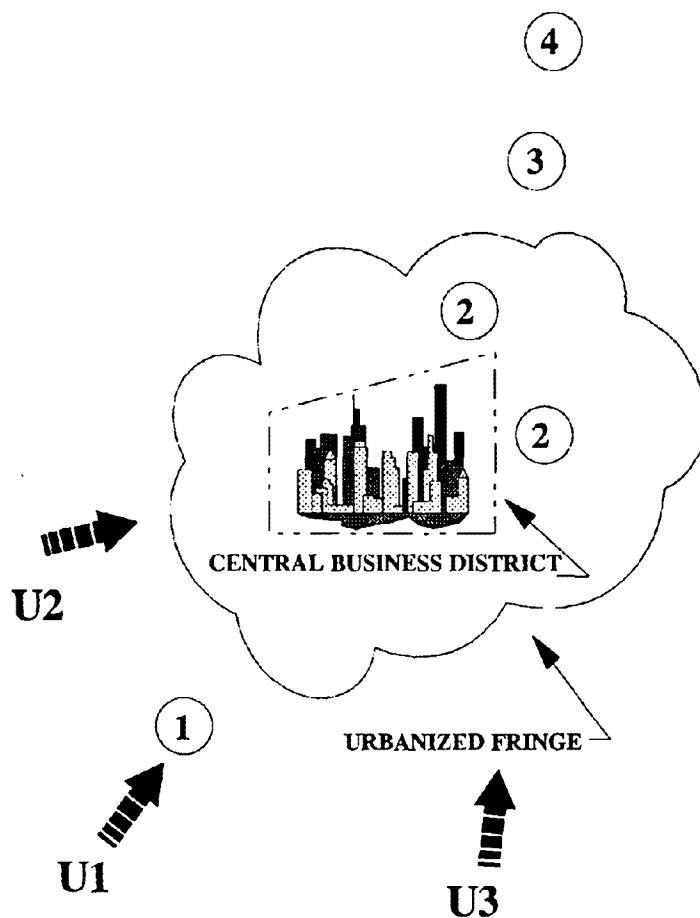
MONITORING GUIDANCE

In May 1994, the Environmental Protection Agency replaced its earlier network design and siting guidance with a more comprehensive *Photochemical Assessment Monitoring Stations Implementation Manual*⁶ (EPA-454/B-93-051). This new manual revises the material from the original siting criteria document and also includes new information on data quality objectives, screening techniques for siting, the network planning and approval process, the Aerometric Information Retrieval System (AIRS), the Technology Transfer Network (TTN), and other extensive guidance related to PAMS. Future chapters will contain such material as data analysis techniques, methods for tracking emissions inventory using PAMS data, and revisions to the *Technical Assistance Document for Sampling and Analysis of Ozone Precursors*⁷ or Technical Assistance Document (EPA 600/8-91-215). This manual will be issued in loose-leaf form to facilitate future revisions and additions.

CONCLUSIONS

With the completion of the PAMS network, projected for 1998, State and Federal agencies will for the first time have access to current local ozone, ozone precursor, and meteorological data. These data will provide the basis for re-focusing ozone control and precursor emissions management programs in those areas of the country most affected by high ozone concentrations.

**FIGURE 1. ISOLATED AREA
NETWORK DESIGN**



LEGEND:

① - PAMS SITES

U1 - HIGH OZONE DAY PREDOMINANT MORNING WIND DIRECTION

U2 - SECOND MOST PREDOMINANT HIGH OZONE DAY MORNING WIND DIRECTION

U3 - HIGH OZONE DAY PREDOMINANT AFTERNOON WIND DIRECTION

Table I.⁶ VOC Monitoring Requirements - Populations > 2,000,000

REQUIRED MONITORING SITE	POLLUTANT	MINIMUM MONITORING FREQUENCIES
SITE #1	VOC	Eight 3-hour samples every third day during the monitoring period and, One 24-hour sample every sixth day during the monitoring period (preferably year-round) OR if an agency chooses to monitor episodes, the following may be substituted: Eight 3-hour samples on the five peak ozone days plus each previous day and, Eight 3-hour samples every sixth day during the monitoring period and, One 24-hour sample every sixth day during the monitoring period (preferably year-round)
	Carbonyls	No regulatory requirement - Monitoring is preferred according to the schedule chosen for VOC
SITE #2	VOC	Eight 3-hour samples every day during the monitoring period and, One 24-hour sample every sixth day year-round and,
	Carbonyls	Eight 3-hour samples every day during the monitoring period and, One 24-hour sample every sixth day year-round
SITE #2 (Second)	VOC	Eight 3-hour samples every day during the monitoring period and, One 24-hour sample every sixth day year-round and,
	Carbonyls	Eight 3-hour samples every day during the monitoring period and, One 24-hour sample every sixth day year-round
SITE #3	VOC	Eight 3-hour samples every third day during the monitoring period and, One 24-hour sample every sixth day during the monitoring period (preferably year-round) OR if an agency chooses to monitor episodes, the following may be substituted: Eight 3-hour samples on the five peak ozone days plus each previous day and, Eight 3-hour samples every sixth day during the monitoring period and, One 24-hour sample every sixth day during the monitoring period (preferably year-round)
	Carbonyls	No regulatory requirement - Monitoring is preferred according to the schedule chosen for VOC
SITE 4	VOC	Eight 3-hour samples every third day during the monitoring period and, One 24-hour sample every sixth day during the monitoring period (preferably year-round) OR if an agency chooses to monitor episodes, the following may be substituted: Eight 3-hour samples on the five peak ozone days plus each previous day and, Eight 3-hour samples every sixth day during the monitoring period and, One 24-hour sample every sixth day during the monitoring period (preferably year-round)
	Carbonyls	No regulatory requirement - Monitoring is preferred according to the schedule chosen for VOC

Table II.⁶ Other Monitoring Requirements - Populations > 2,000,000

REQUIRED MONITORING SITE	POLLUTANT	MINIMUM MONITORING REQUIREMENTS
ALL SITES	Ozone	Continuous monitoring during the entire ozone season listed in Table 3-2
	Oxides of Nitrogen	Continuous monitoring during the PAMS monitoring period (preferably year-round)
	Meteorology	Surface (10-meter) continuous monitoring of wind speed/direction, ambient °T, barometric pressure, relative humidity, and solar radiation during the PAMS monitoring period (preferably year-round)
ONE REPRESENTATIVE SITE PER AREA	Upper Air Measurements	Monitoring of horizontal and vertical wind velocity profiles, air temperature, mixing layer height, stability class, and specific humidity are recommended during the PAMS monitoring period (preferably year-round)

Table III. Stations Proposed To Be Operational In 1994

Region	Area	Class	1994 Sites	Sites Proposed
I	Boston	Serious	3	5
I	Connecticut	Serious	2	5
I	Portsmouth	Serious	2	2
I	Providence	Serious	2	4
I	Springfield	Serious	2	3
II	New York	Severe	3	5
III	Baltimore	Severe	2	5
III	Philadelphia	Severe	3	5
III	Washington	Serious	3	5
IV	Atlanta	Serious	2	5
V	Lake Michigan	Severe	4	10
VI	Houston	Severe	2	5
VI	Baton Rouge	Serious	3	3
VI	Beaumont	Serious	1	2
VI	El Paso	Serious	1	3
IX	South Coast/ Southeast Desert	Extreme/ Severe	4	7
IX	San Diego	Severe	2	5
IX	Ventura Co	Severe	2	3
IX	Sacramento	Serious	1	4
IX	San Joaquin	Serious	5	6
TOT	20 Networks	...	49	94

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Enhanced Ozone Monitoring: A Regional Perspective

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The Enhanced Ozone Monitoring Regulation, commonly called Photochemical Assessment Monitoring Stations (PAMS), was promulgated on February 12, 1993. With PAMS, gas chromatographs (GCs) and meteorological instrumentation will be routinely operated in the field with expected data capture rates and quality assurance results similar to criteria pollutant network. PAMS data submittal will be difficult since more parameters are to be reported into the Aerometric Information Retrieval System (AIRS).

Efforts in the first year have focused on determining the location for the type II PAMS site, developing a network design, and developing quality assurance programs. The Regions and States look forward to developing a quality PAMS Program that will satisfy the data needs for modeling, emission reduction tracking, trends analysis, etc.

Introduction

By passage of the 1990 Clean Air Act, PAMS monitoring was required in ozone nonattainment areas designated extreme, serious, or severe. The regions and states are concentrating their efforts on implementing PAMS in these areas. In the future, additional areas could be included if the magnitude of the ozone design value falls into the serious, severe, or extreme category or if an area is bumped-up from a moderate ozone nonattainment area.

The first year of PAMS (1993) was a trial year for implementing the PAMS program. The Regions coordinated the PAMS Network Design Plans, selection of PAMS type II sites, and development of quality assurance measures and programs, where feasible with the States and the Office of Air Quality Planning and Standards (OAQPS).

For the ozone nonattainment areas requiring PAMS, the type II PAMS monitoring sites must become operational by June, 1994. Monitoring sites will be phased-in over a five-year period. Because some of these areas have populations less than 2,000,000, these urbanized areas will have their PAMS networks completed prior to the five years. In order to accelerate the implementation of PAMS, OAQPS is working with the Regions and States to have a second PAMS site operating in nine additional areas. Areas targeted for an additional PAMS site are New York City (site located in Connecticut), Philadelphia (site located in New Jersey), Baltimore, Chicago, Milwaukee, Houston, Los Angeles, S.E. Desert, San Diego, and Ventura County.

The following information examines the State and Regional activities used to implement the PAMS program nationwide.

Network Design

The basic network design plan requires a type I site (upwind site to be located approximately 10 to 30 miles upwind of the central business district), type II site (located downwind of the central business district in the predominant morning wind direction), type IIb site (located downwind of central business district in the second predominant morning wind direction), type III (located 10 to 30 miles downwind from the fringe of the urban area), and type IV sites (located near the downwind edge of the photochemical grid model domain).

Each serious, severe, or extreme ozone nonattainment area was required to submit to EPA its network design plan. Washington, Philadelphia, and Baltimore submitted traditional network design plans, while others areas submitted alternate PAMS network designs. In Region 6, each PAMS area will have some type of alternate plan. In Louisiana, prevailing meteorology and types of ozone precursors monitored will result in an alternate plan. For the PAMS areas in Texas, land-sea breeze effects in two of the areas and topographical effects in the other area will result in some deviations from the basic PAMS network design plan. Currently, the Texas Natural Resource Conservation Commission (TNRCC) is revising its PAMS network design plan. Other areas which submitted alternate network design plans are California and the Lake Michigan states.

For Region 9, the South Coast Air Quality Management District (SCAQMD) is the only district following the traditional network design plans for the Los Angeles and

the S.E. Desert air basins. Sacramento, San Diego, the San Joaquin Valley, and Ventura all submitted alternative PAMS plans. San Diego, the San Joaquin Valley, and Ventura have agreed to follow an alternative sampling schedule, California Alternative Plan (CAP II), which was negotiated between the California Air Resources Board, the Regional Office, and OAQPS.

All areas have submitted plans for approval, but reiterations of these plans are occurring due to further studies. The first pilot study developing a network design for PAMS was in Atlanta, Georgia. Also, the Louisiana Department of Environmental Quality (LDEQ) along with industry cooperation in Baton Rouge conducted a study modeling the expected ozone maximum concentration and used this information in selecting the three PAMS sites for Baton Rouge.

Additional studies have been conducted in Regions 1 and 3. These studies included canister sampling to determine the best location for the maximum ozone precursors (type II site). Region 1's study was conducted in five urbanized areas. Five canister sites were operated in each of the five urbanized areas; results were inconclusive due to problems in forecasting high ozone days. Region 3 conducted a saturation canister study to determine the location for the type II site; this study was conducted in Philadelphia.

Operation of PAMS Type II Sites

In 1993, PAMS type II sites were operational in several ozone nonattainment areas. These areas included Boston, East Hartford, Philadelphia, Baltimore, Houston, Beaumont-Pt. Arthur, Baton Rouge, San Diego, Los Angeles, S.E. Desert, Ventura, and Sacramento. The PAMS type II site for Boston and East Hartford received OAQPS approval and began operation in June, 1993. At the East Hartford site, two different vendors' continuous GCs were operated side by side for several weeks during 1993. Early results from this comparison indicate good agreement between the two instruments for many compounds. Since June, 1993, additional PAMS sites have been installed in Springfield, Massachusetts; Providence, Rhode Island; Portsmouth, New Hampshire; and Cape Elizabeth, Maine.

In Region 3, type II stations operated in Philadelphia and Baltimore. Also, type I stations operated in Delaware (upwind of Philadelphia) and in Virginia (upwind of Washington, D.C.).

Continuous GC sites operated in Houston and Baton Rouge during 1993, while canister sampling was conducted in Beaumont-Pt. Arthur. PAMS efforts in Houston and Beaumont-Pt. Arthur were part of a TNRCC study along the Texas Gulf Coast to: 1) fulfill trial year implementation of PAMS; and 2) develop a better data base of volatile organic compound information and meteorological data for modeling purposes.

In Region 9, PAMS type II sites operated in San Diego (El Cajon), Los Angeles (Pico Rivera), S.E. Desert (Upland), Ventura (El Rio), and Sacramento (Del Paso). The California Air Resources Board (CARB) was of great assistance to EPA by coordinating quarterly PAMS Technical Advisory Committee (PAMTAC) meetings and providing expertise in VOC sampling and analysis to the smaller California agencies.

1994 PAMS Operational Plans

In 1994, PAMS monitoring sites will again operate in East Hartford; Boston (Lynn, Massachusetts); Springfield, Massachusetts; and Providence, Rhode Island. Additional sites are expected in Portsmouth, New Hampshire; Stafford, Connecticut; Boston, Massachusetts (Newburyport); Springfield, Massachusetts; and Providence, Rhode Island (West Greenwich).

In Region 3, three additional stations will be operational, a type III in Baltimore, a type III in Washington, and in New Jersey, a type III station for Philadelphia.

In 1994, PAMS type II sites will operate in Chicago, Illinois and Milwaukee, Wisconsin. Four three-hour samples will be taken in a 24-hour period every three-days at these sites. Additionally, an automated continuous GC will be installed at the Chicago site and operated in parallel with the canister samples for comparison. If the continuous GC operation is successful, consideration will be given to installing automated GCs at the other type II sites.

In Region 6, PAMS type II monitoring sites will be operational in El Paso, Houston, Baton Rouge, and Beaumont (Pt. Arthur). A second PAMS site will also operate in Houston (Baytown).

The Region 9 PAMS type II sites operating in 1993 will continue to operate during 1994. Also, the severe and extreme nonattainment areas will attempt to establish an additional site accordingly: South Coast-an additional Type II and Type III, Ventura-Type III, San Diego-a second Type II, and Sacramento-Type III. In the San Joaquin Valley, additional type II and type III sites will operate. The CARB will augment the San Joaquin PAMS network with a dual purpose Type II/III site.

Meteorological Instrumentation Operation

During 1994, two upper air meteorological stations will be operating in Region 3; Rutgers University and the University of Maryland.

In Region 6, TNRCC contracted the operation in 1993 of one radar profiler and three acoustical sounders along the Gulf Coast. The radar profiler was located in Port Arthur and three acoustical sounders were located in Houston and Beaumont. Currently, this data are being processed. In 1994, these sites are planned for continuation with the addition of a site in El Paso.

In Region 9, two upper air meteorological stations will be operating in Southern California; one at Los Angeles International Airport and the other at Ontario Airport.

Quality Assurance

During 1993, Regions 1, 2, 3 conducted three round robin studies utilizing ambient samples. Split samples were exchanged between the Environmental Services Division (ESD) Laboratory of EPA Region 1, the ESD Laboratory of Region 2 and the Maryland Department of Environment Air Laboratory. The results of these intercomparisons showed that agreement between the laboratories was typically within 30%, and was within 0-20% approximately two-thirds of the time.

In addition, each type II PAMS site in Region 1 collected a collocated VOC

sample every sixth day which was sent to and analyzed by the Region's designated Regional Reference Laboratory (RRL); in Region 1, this laboratory is the EPA Environmental Services Division Laboratory. Region 1 had problems meeting the five business day turnaround target for getting results back to the state. Use of the dual column confirmation protocol and the duplicate analysis of each sample was very time consuming. Two options that are being considered by Region 1 to improve turnaround is to 1) eliminate routine duplicate analysis of each sample and conduct duplicate analysis of a portion of the samples (10-15%) for QA, and 2) routinely report results from the DB-1 column only and report the results from second confirmatory column when an obvious interference is suspected or as a spot check. All of Region 1's collocated results have been updated into AIRS for each PAMS site for each of the PAMS VOC parameters.

Also, Region 1 conducted a PAMS QA workshop in March, 1994. Subjects discussed were implementation of PAMS to quality assurance initiatives for PAMS.

During the summer of 1993, LDEQ and TNRCC used the EPA protocol gases to maintain the accuracy of the continuous GCs. Also, LDEQ conducted canister studies to compare these results with the continuous GCs. The TNRCC used a contractor for quality assurance of the continuous GCs.

Region 6 has been coordinating with LDEQ to develop a performance audit protocol for PAMS. In 1994, Region 6 is purchasing protocol gases at the 20 ppb concentration and will be developing a dilution device to dilute the gases to the appropriate concentration for conducting performance audits on the continuous GCs.

Districts in Region 9 are awaiting further guidance from EPA Headquarters with respect to acceptable PAMS quality assurance procedures. Addendum to the Air Monitoring Quality Assurance Manuals in Region 9 will be required through the FY95 105 Grant Program Objectives for air monitoring.

Data Handling

Some continuous GC data have been submitted for monitoring sites in Region 1. Massachusetts, Connecticut, and Maine expect to use Turbochrom 4.0 software to convert their 1993 data into AIRS format and submit into AIRS by June, 1994.

Region 3 was able to get PAMS data into AIRS for two of its sites. Currently, Region 3 is working with its states for submittal of additional PAMS data into AIRS.

In Region 6, Louisiana has completed submittal of the 1993 PAMS data into AIRS. The Region is continuing work with Texas on submittal of the data into AIRS.

Region 9 will be working with the State of California and affected districts to submit the PAMS data into AIRS.

Conclusions

EPA is continuing to work with the states to implement the Enhanced Ozone Monitoring regulation. Increased funding will enable more sites to become operational prior to the five-year implementation schedule.

EPA will be working with the states to analyze the PAMS data. It is essential to analyze the data from this program for emissions tracking, trends, and exposure

assessment. In FY95, EPA hopes to maintain a position in each of the Regions with PAMS areas for statistical analysis of data.

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VOC MEASUREMENTS

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Overview of VOC Measurement Technology in the PAMS Program

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ABSTRACT

The PAMS program began in early 1993 with an Implementation Teleconferencing Workshop for states and EPA regional offices to discuss the methodologies and programs available for assistance to support the enhanced monitoring regulations in the 1990 Clean Air Act Amendments. The teleconference was arranged by the Office of Air Quality Planning and Standards (OAQPS) with technical discussions from members of the Atmospheric Research and Exposure Assessment Laboratory (AREAL). Since then several states have commenced VOC measurement programs particularly by the operation of automated gas chromatograph (gc) systems. Quality assurance programs have been implemented to track performance of the measurement procedures. A number of issues were discussed at the Teleconference concerning operational components of the gc methodology. An overview of these issues is presented in this paper along with laboratory test results to support the conclusions.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

INTRODUCTION

In late April 1993 the Office of Air Quality Planning and Standards (OAQPS) sponsored a Photochemical Assessment Monitoring Stations (PAMS) Teleconference Workshop¹ for states and EPA regional offices to discuss the monitoring and methodology requirements for the Enhanced Ozone Monitoring Regulation in the 1990 Clean Air Act Amendments.² Before the workshop, the states and EPA regional offices received a Technical Assistance Document³ that described current state-of-the-art methodologies available for the PAMS program. The use of gas chromatographic (gc) techniques to measure speciated hydrocarbons is perhaps the most challenging analytical procedures required of the affected states in the PAMS program. The recommended approach consists of automated gc systems capable of obtaining hourly hydrocarbon measurements. The regulation², however, allows an alternate approach of collecting ambient air in canisters for various integrated time periods of 3, 6, and 24 hours followed by gc analysis. Regardless of the method of sample collection, the gc analysis systems have several similarities. All gc systems utilize some type of sample preconcentration to obtain measurable levels of the hydrocarbons. The preconcentrated sample is injected onto a gc column(s) to separate the hydrocarbons which are detected by a flame ionization detector (FID). The FID has a sensitive, linear response to organic compounds that contain carbon and hydrogen. The signal produced in the FID is amplified and integrated to produce peak area counts that are converted to parts-per-billion carbon (ppbC) concentration by a calibration factor. These and other operational aspects of the gc system are discussed in the Technical Assistance Document³ and were expanded upon during the Teleconference Workshop¹. Operational aspects of greatest concern were referred to as issues and included:

- ▶ Uniform Response of the FID
- ▶ Water Management System
- ▶ Canister Storage of Air Samples
- ▶ Quality Assurance Program
- ▶ Data Base Development Approaches

The purpose of this paper is to update and provide more recent information concerning these issues one year after the Teleconference Workshop¹.

EXPERIMENTAL

The C₂ to C₁₂ hydrocarbons were separated on a 60-m x 0.32-mm id DB-1 fused silica capillary column coated with a 1- μ m bonded liquid phase (J & W Scientific, Folsom, CA). Column temp conditions included a -50°C initial temp held for 2 min followed by temp programming at a rate of 8°C per min to a final temp of 200°C.⁴ Air samples for analyses were approximately 500 cm³ prepared by a manual preconcentration procedure. Details for the gc system, preconcentration procedure and calibration are provided elsewhere⁵. All samples were collected in 6-l stainless steel Summa canisters. In some tests air samples were dried using a Nafion dryer (Model MD 125-48F, Perma Pure Dryer, Toms River, NJ). The Nafion dryer consists of concentric tubes with the Nafion membrane inside a Teflon tube shell. Samples were taken at room temp (\approx 24°C) at a flowrate of 100 cm³ min⁻¹. During sample collection a counter-current flow of 200 cm³ min⁻¹ zero dry air was routed across the outside Nafion membrane to facilitate water removal.

RESULT AND DISCUSSION

Uniform Response of the Flame Ionization Detector

Since the development of the FID in 1958⁷, uniform response to hydrocarbons has been observed. The earliest documentation of FID response uniformity was reported by Steinberg⁷. He reported effective carbon response of unity for paraffinic and aromatic compounds and 0.95 for olefinic compounds. The only hydrocarbon type not near unity was acetylenic compounds with a 1.30 effective carbon response. Other later reports observed very similar FID response characteristics^{8,9}. Recently FID response characteristics were determined with a 16 compound gravimetric standard¹⁰ from the National Institute of Science and Technology (NIST). All compounds exhibited a per carbon response of $1.00 \pm 5\%$ with the exception of acetylene at 1.16.

Because all PAMS target compounds are hydrocarbons, FID calibration is simplified by the use of a single compound. The approach recommended in the Technical Assistance³ document is the use of a propane-in-air Standard Reference Material (SRM) available from NIST. Utilization of the 3 ppm concentration provides the capability of preparing diluted concentration levels in the range of typical ambient compounds. Some automated GC systems utilize two gc columns and dual FIDs requiring a two hydrocarbon calibration standard. A propane-benzene mixture is suggested for these systems although other similar boiling point compound mixtures could be utilized. A two compound mixture is currently not available from NIST. Such a mixture is available as a Certified Reference Material (CRM) from several gas manufacturers. NIST previously offered a benzene-in-nitrogen SRM, however, this single compound standard is no longer available.

Water Management Systems

Other than nitrogen and oxygen, water vapor is the most abundant component in ambient air. Its concentration is several orders of magnitude higher than the sum of nonmethane hydrocarbons. The presence of such large quantities of water is a problem to gc systems that utilize sub ambient temperatures for both the sample preconcentration and gc column components of an automated gc system. Water vapor forms ice under these conditions, resulting in trap and/or column plugging and subsequent carrier flowrate disruptions. Thus some type of water management approach is required. Several approaches to control water vapor injection onto the gc system are available. A hydrophobic absorbent material in the preconcentration step can selectively collect the hydrocarbons while passing water through the system. These absorbent materials however do not efficiently trap the C_2 - C_3 hydrocarbons. Another approach involves the controlled temp injection of the trapped ambient air components onto a second cryo-focusing trap prior to column injection to minimize the amount of water injected onto the gc column. With this approach, care must be taken to insure quantitative transfer of the heavier molecular weight C_8 - C_{12} compounds. The approach utilized on most of the automated gc systems, particularly at the time of the Teleconference Workshop¹, was a Nafion dryer in the system inlet to selectively remove water vapor prior to preconcentration of a sample. Nafion is a perfluorocarbon co polymer membrane that contains sulfonic acid side chain groups. Water vapor is attracted by the sulfonic acid groups and transported through the membrane where it is flushed away by a counter-current flow of dry hydrocarbon free air. While Nafion is commonly used in several automated gc systems, it has not been fully evaluated for the PAMS target compounds. Water soluble organic compounds such as the carbonyls and alcohols are expected to be at least partially removed by Nafion. For the PAMS target compounds only α - and β -pinene are expected to be affected by the Nafion dryer. Burns et. al.¹¹ have reported the transformation of C_{10} terpene compounds to other compounds by Nafion.

To test the adequacy of Nafion several types of sample mixtures were analyzed. The gc system utilized for these tests employs a controlled water vapor injection approach to analyze air samples that contain water vapor. Canister samples were analyzed with and without the Nafion dryer. Table I contains the results for the analysis of 7 different canister mixtures that contained PAMS hydrocarbons as well as other VOCs. Repeat analyses were performed on 2 of the 7 mixtures. Samples taken without Nafion are identified as **direct**. In Table I all VOC compounds, including the PAMS compounds, are included in the total nonmethane organic compounds (TNMOC). Three of the 7 mixtures evaluated demonstrated practically no effect from the use of the Nafion dryer. These were the PAMS proficiency mixtures 1 and 2 and the Naptha HC mixture. The proficiency mixtures consisted of only 18 PAMS hydrocarbons, none of which were α - and β -pinene in ultra pure nitrogen. Trace level concentrations of about 50 other compounds were also observed in the proficiency mixtures, however these levels were too insignificant to affect TNMOC. The Naptha mixture consisted of about 112 aliphatic hydrocarbons, 25 of which were PAMS target compounds.

Significant differences in TNMOC were observed for the remaining 4 mixtures. The PAMS hydrocarbon mixture contained n-decane and n-undecane in addition to all 55 PAMS hydrocarbons in humidified HC free air. The mixture also contained 257.2 and 160.4 ppbC α - and β -pinene respectively. For both sample analyses through Nafion α - and β -pinene were completely removed. The sum of other peaks (~ 157 ppbC) however could not account for the loss of α - and β -pinene. Nafion appears to effect 2 other PAMS compounds, 2-methyl-1-pentene and styrene. For the two PAMS sample analyses given in Table I, 15 and 73% 2-methyl-1-pentene respectively were removed by Nafion. GC/MS analysis suggests that Nafion converts 2-methyl-1-pentene quantitatively to another compound tentatively identified as 2-methyl-2-pentene. Styrene loss of 6 and 18% respectively were observed when the PAMS sample was twice taken through Nafion. No obvious product peaks were observed for styrene loss. The other 51 PAMS compounds were unaffected by Nafion as evidenced by typical 99% compound reproducibilities.

A Mexico City fuel vapor sample was also run and was interesting in that it contained 48 PAMS target compounds all of which excellently reproduced when re-analyzed through Nafion. The only major loss upon re-analysis through Nafion was methyl-*tert*-butylether (MTBE), an oxy-fuel additive. MTBE at 126.1 ppbC was completely removed by the Nafion dryer.

TNMOC for both the diluted auto exhaust and ambient air samples were significantly lowered when taken through the Nafion dryer. These complex mixtures consisted of more than 250 peaks, some of which were tailing peaks thought to be oxygenated hydrocarbons. These tailing peaks appeared to be most affected by Nafion. Chromatograms are compared in Figure 1 to demonstrate the Nafion drier's effect on peak reproducibility. Tailing peaks at 11.5 and 15.5 min are nearly completely removed when the sample was taken through Nafion. Other noticeable differences occur in peaks after 30.3 min. The peak at 30.1 min is n-undecane.

The effect that Nafion has on only the PAMS compounds is shown in Table II. Only the PAMS hydrocarbon mixture containing the 55 PAMS hydrocarbons was affected by Nafion. As explained earlier the difference in the two totals can be attributed to the complete conversion of α - and β -pinene to other compounds and the partial losses of 2-methyl-1-pentene and styrene. All other PAMS compounds appear not to be affected by Nafion. More tests are needed to confirm this conclusion.

Storage of PAMS Compounds in Canisters

For automated gc systems, canister storage is not generally an issue. Samples are directly introduced into the preconcentration trap over an integrated time period followed by injection onto the gc column. Some automated gc systems collect an integrated air sample into a canister from which an aliquot is then taken for analysis. Even with this approach canister storage is not a major concern. The regulation², however, does allow for the collection of canister samples over 3, 6, and 24 hour periods. In fact the regulation requires the collection of a 24-hour integrated sample every six days at PAMS sites. For these samples, canister storage is an issue since at least more than a day and in most cases several days storage occur prior to analysis. In previous years canisters have been routinely used to collect air samples in the field and returned to the laboratory for analysis. It is not uncommon to store canister samples for a week or more.

Although most storage results are not generally documented and reported, ambient air samples are found to be stable even though storage periods may be prolonged. To demonstrate the suitability of canister storage, Table III compares the sum of all peaks, TNMOC and the sum of only the PAMS peaks for a PAMS mixture stored in two, 6-l Summa canisters over a 7 month period. Both canisters showed excellent reproducibility for both TNMOC and PAMS compounds. Although the data are not presented, all of the 53 PAMS hydrocarbons in the mixtures demonstrated similar, excellent reproducibility. Figure 2 also demonstrates Summa canister storage stability by comparing the chromatograms of ambient air analyzed before and after 85 days of storage. The nearly 3 month storage period had very little effect on sample integrity. Largest differences occur with tailing peaks at retention times 11.5, 15.0, 25.5, and 30.7 min, none of which are PAMS compounds. The occurrence of change to any peak however suggests that storage periods are not unlimited. Thus even though air samples appear to store well in canisters, a minimized storage period prior to analysis is good laboratory practice.

Quality Assurance and Data Base Development

Operational components of the gc system that affect quality assurance were discussed at the Teleconference Workshop¹. These issues primarily focused on the operation of gc integrators and data processing systems such that accurate gc peak areas and correct peak identifications would result. GC systems, automated or manual, that preconcentrate 200 cm³ of ambient air are capable of detecting and resolving peaks below 1.0 ppbC. Typical ambient air chromatograms contain more than 130 peaks ranging in concentrations as much as two orders of magnitude above and one order below the 1.0 ppbC level. Several peaks are only partially resolved from neighboring peaks, and on occasion peaks co-elute on the tail of polar VOC peaks. Careful initial selection of integrator peak detection and integration parameters are well worth the effort for accurate peak area determinations. Forced baseline points and tangential skims are needed for tailing, coeluting and other peaks of a typical ambient air chromatogram. After initial setup, operators will need to routinely look at the baselines of all or a sub-set of the daily sample chromatograms to determine the adequacy of integration parameters. The purpose of this QA procedure is to refine the gc integration parameters to yield the best possible results.

Correct peak naming should be a companion part of this QA activity. Verification of each individual gc peak is desirable but perhaps too tedious particularly for gc operations generating 24 samples daily and 168 samples weekly. A more suitable approach would be the verification of correct reference peak selection. Peak naming software uses reference peaks to make retention time corrections before look-up of retention times in a calibration table of retention times and peak names. The reference peaks are prominent peak which are always present. If reference peaks are properly selected then most likely all other peaks will be properly named.

It is strongly recommended that both peak integration and reference peak naming verification procedures be implemented early in the setup of the PAMS gc systems. Likewise collected data should not be incorporated into a data base system such as AIRS until all data results are properly verified.

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Table I. Effect of Nafion on TNMOC.

Sample \ Analysis	Direct Analysis, ppbC	Analysis through Nafion, ppbC
PAMS HC mixture	8,753	8,344
PAMS HC mixture	8,766	8,313
Naphtha HC mixture	1,089	1,073
PAMS proficiency #1	259	259
PAMS proficiency #2	231	232
Mexico fuel vapor	1,161	1,033
Dilute auto exhaust	7,554	7,141
Dilute auto exhaust	7,414	7,079
Ambient air	430	367

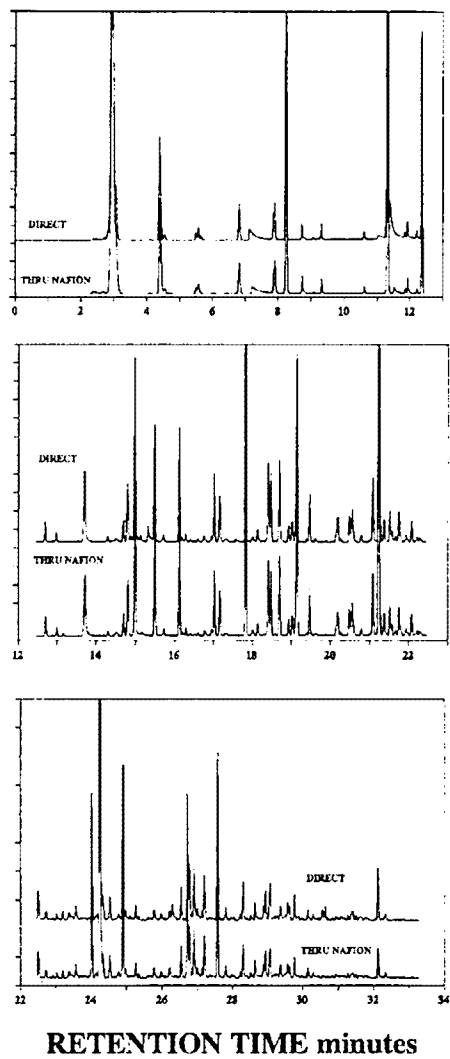
Table II. Effect of Nafion on PAMS compounds.

Sample \ Analysis	Direct Analysis, ppbC	Analysis through Nafion, ppbC
PAMS HC mixture	8,357	7,756
PAMS HC mixture	8,210	7,718
Naphtha HC mixture	690	680
PAMS proficiency #1	228	223
PAMS proficiency #2	219	221
Mexico fuel vapor	932	921
Dilute auto exhaust	6,046	6,007
Dilute auto exhaust	5,933	5,974
Ambient air	259	267

Table III. Storage of PAMS compounds in Summa canisters.

Canister ID	Measurement	Initial Conc, ppbC	Final Conc, ppbC
Canister A	TNMOC	1,035	1,155
	Σ PAMS cmpds	955	968
Canister B	TNMOC	1,103	1,018
	Σ PAMS cmpds	1,136	1,007

GC PEAK RESPONSE



**Figure 1. Analysis of a PAMS Compound Mixture
Direct and Through a Nafion Dryer**

GC PEAK RESPONSE

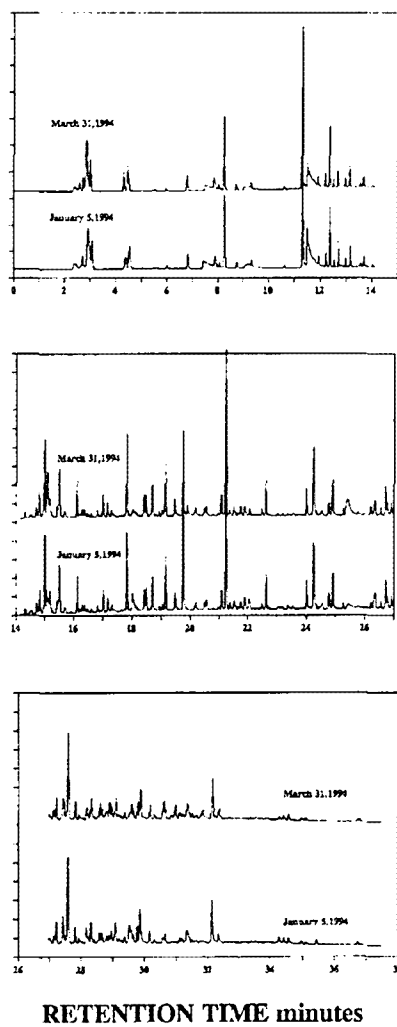


Figure 2. Storage of an RTP, NC Ambient Air Sample in a Summa Polished Canister

New Developments for the Monitoring of VOCs in PAMS

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New developments to improve existing PAMS instrumentation for ozone precursors include: (a) the use of solid adsorbents in a combined concentration and water management system; (b) the use of closed cycle coolers for refocusing of concentrated ozone precursors prior to analysis; and (c) the development of additional information on storage stability of ozone precursors. The use of solid adsorbents in a multisorbent packing to adsorb VOCs when sampling directly from the air manifold or when sampling from a canister, allows for an alternate water management system based on dry purging after sample collection. Water vapor is preferentially lost during the dry purge and the trapped ozone precursor hydrocarbons are then thermally desorbed, refocused, and then separated and detected. Commercial prototype closed cycle coolers have been tested for refocusing hydrocarbon precursors after desorption from multisorbent packings. The closed cycle coolers take the place of controller release of liquid nitrogen to refocus compounds in a small volume before release onto a GC column. For canister, information on additional storage stability work is now available for samples stored in SUMMA-polished canisters. The work consists of both model development for prediction of the storage stability in canisters and experimental tests using many of the ozone precursor compounds.

VALIDATING DATA FROM AUTOMATED PAMS GC SYSTEMS

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ABSTRACT

Automated, continuous gas chromatographic (GC) techniques are currently the most cost effective way to directly meet the rigorous speciated VOC sampling frequency required for Photochemical Assessment Monitoring Station (PAMS) ambient air quality surveillance monitoring networks. Validating data from these automated systems is the final and the most critical part of the chromatographic measurement process. The data is ultimately entered into the computer-based Aerometric Information and Retrieval System (AIRS)-Air Quality Subsystem (AQS) data base; therefore, the data must be consistent, reliable, and accurate. The EPA has defined data validation as a systematic process consisting of data editing, screening, checking, auditing, verification, certification, and review, for comparing a body of data to an established set of criteria to provide assurance that the data are adequate for their intended use. Prior to validating data, it is imperative that pre-measurement GC system setup and characterization, and Quality Assurance (QA) procedures for validating the GC data be performed to set the stage for successful validation of the generated data. The final data validation step, prior to AIRS-AQS entry, includes validating the chromatography result report, implementing a secondary processing/peak identification software, and qualitative or comparison review of a summary concentration ASCII report file. This paper discusses the procedures necessary to develop and implement an approach for validating speciated VOC data from automated, continuous GC PAMS systems.

INTRODUCTION

Automated gas chromatographic (GC) techniques are a viable and cost effective way to directly comply with the rigorous speciated volatile organic compound (VOC) sampling frequency required by the PAMS ambient air quality surveillance monitoring networks regulation. Measuring the numerous VOCs in the atmosphere on a daily and hourly basis using these automated GC systems produces extremely large and complex data sets. Managing and processing this data requires an intensive effort and good technical judgement to obtain reliable and consistent results for input of the data into any data base.

Validating data from automated GC systems is the final and most critical part of the chromatographic measurement process. There are four key aspects important in developing and implementing a complete data validation process: pre-measurement chromatographic system verification; quality assurance (QA) procedures and development of comprehensive data quality objectives (DQOs); and validation of the final data prior to AIRS-AQS data base entry. Although the data validation process is primarily embodied in the last of these aspects, all four are of critical importance to the overall process.

Pre-Measurement Chromatographic System Verification

Prior to making speciated VOC measurements using an automated GC system, the level of system operation must be thoroughly documented. Information collected during this process is important in characterizing the system operation and establishing a baseline for performance. The information from the pre-measurement system verification is used to determine system specific target analyte retention times, relative retention times, identification of co-eluting compounds and matrix effects, internal standard retention times and interferences, and detection limits.

The rigorous sampling frequency requirements and large data sets associated with the PAMS regulation requires the use of an automated GC system with an FID, and presumes the commercial availability of such systems. Although uncertainties exist, these systems must rely on the practical use of

retention times and relative retention times for peak identification. Commercial GC systems configured for this purpose should be suitably designed to provide for the stability of system parameters to ensure adequate peak identification based on retention time.

Calibration and retention time standards containing all of the target analytes and components of interest must be analyzed to determine specific retention time information and resolve chromatographic peak overlap and peak shape issues relative to the instrument conditions, analytical column(s), and chromatographic conditions used. Retention time is widely applied in chromatography and based on the information gathered from these standards. When verifying the retention times for a GC system it is important for the system to be operated for a period of 2 to 5 days to allow equilibration and retention time stabilization to occur. Several standards should be analyzed over a period of days to determine retention time variability. This variability is used to determine retention time windows for each component. It is very important that standards be prepared in humidified air, at a relative humidity similar to the samples being analyzed. When dealing with complex target analyte lists, as in the case for O₃ precursor measurements, preparing multiple standards that contain 10-15 target analytes that are of known retention order and well separated by retention time, will simplify peak identification and retention time assignment.

Relative Retention Time

The identification of sample components is determined by matching the retention times of the components in the standard with those in the sample. This procedure provides the chromatographer with a certain degree of confidence that the correct peak has been accurately identified. Peak identification by retention time is adequate for the PAMS network requirements. A compound's retention time is characteristic, though not unique, therefore it is possible for other compounds to have the same retention time. The presence of co-eluting compounds or missed peak identifications cannot be completely ruled out. Periodic confirmation of peak identification and quantification using more definitive techniques, such as GC/MS is encouraged. Although retention times are typically stable and reproducible, they are subject to system variability. To account for any retention time variations, relative retention time (RRT) can be used to aid in assigning peak identifications. Many commercial GC systems incorporate the use of relative retention times for peak identifications in their data acquisition and processing software. This makes the use of RRT for peak identification easy to implement. An adjusted or relative retention time can be determined by using both reference or internal standard peaks. Reference peaks are those components of the sample that are typically present in the sample matrix (reference peaks of opportunity). Internal standard peaks are components subsequently added to the sample that are uncommon to the sample matrix.

The relative retention time of a compound determined in this manner will vary with temperature and the analytical column stationary phase, but should otherwise be independent of other analytical conditions. The relative retention time method of peak identification works well when the target compound elutes relatively close to the reference peak used. The use of reference peaks in several retention time windows is recommended to compensate for retention time shifting that is not linear. This provides for reproducible relative retention time data for peak identification. A reference peak(s) should be chosen that is always or typically present in the sample matrix; is in the same general retention time area or carbon number range of the chromatogram; chromatographically behaves similar to target components (sharp peak shape); and is well separated from other components in the sample matrix. Suggested reference peaks include toluene, benzene and butane.

Internal Standards

When GC analysis is performed on a continuous basis at an often unattended or remote site, fluctuations in ambient temperature and other factors can cause variations in instrument performance and chromatographic retention times. Changes in ambient conditions can cause small changes or variations in carrier gas flow rate, column temperature, detector response, sample injection volumes, and sample

moisture content. Use of an internal standard(s) can help to minimize the influence of GC system variability. Internal standards are often used as reference peaks for determining relative retention times.

The internal standard should be added to the cryofocusing or adsorbent sample collection system, concurrent with sample collection, to minimize the effects of the sample matrix. The chief difficulty in using internal standards for VOC analysis is in finding an internal standard that does not interfere with the sample constituents. Characteristics that must be considered when choosing a suitable internal standard include components that are uncommon in ambient air; ease and reproducibility in handling and introducing into the GC system; similar in chemical and physical properties to those compounds being analyzed; moderate volatility and low vapor pressure comparable to the expected retention times and concentrations of the sample hydrocarbons; does not interfere with the measurement method; complete resolution from all other components present in the sample; stable under the conditions and method used; and does not react with components of the measurement system. Perfluorotoluene has been used as an internal standard.

Separation of the internal standard compound from other compounds normally found in the sample must be accomplished using the measurement system and methods implemented by the user to accomplish sample analyses. After choosing a suitable internal standard, it can be analyzed concurrently with the sample to adjust for variations in retention time and detector response.

Detection Limits

The development of methods to measure trace levels of organic compounds in ambient air and the need for the ability to measure extremely low concentration levels for risk assessment purposes, has warranted the need for the analytical system detection limits for the target compounds to be determined. The detection limit found should be sufficiently low enough to meet the program objectives. The detection limit is one of the most important performance characteristics of analytical system and must be viewed as a limitation to the methodology used. All results, even at concentrations below the estimated detection limit, should be reported. More information is gained when a result is reported even if the data are somewhat imprecise.

The GC system detection limit should not be determined until a complete, specific, and well defined analytical method has been developed. It is crucial that all sample processing steps used in the analytical method be included in the determination of the detection limit. There are numerous methods for determining an analyte method detection limit. The procedures and calculations used to determine detection limits must be consistent in order to make meaningful comparisons of the data for QA or other purposes. If the analytical method detection limit for most of the target hydrocarbon compounds is not approximately 1 ppb-Carbon, the sensitivity of the GC system and methodology used may not be adequate and should be re-evaluated and improved prior to use for O₃ precursor monitoring programs.

QUALITY ASSURANCE

It is important to develop and implement a QA program at the start of the monitoring program, prior to making field measurements. The QA program should include external and/or internal audit samples for determining accuracy; replicate analysis of selected samples, inter-laboratory sample exchange programs determining precision; and GC/MS corroboration for confirmation of qualitative results. Samples for QA analysis are prepared or collected, using an external preparation or sampling device, in SUMMA® canisters to permit repeated analyses by the automated GC system and sample exchange with other laboratories. An examination of the results from QA analyses is essential in developing comprehensive DQOs and confirming system performance and capabilities. If modifications are required for more accurate results, they can be made prior to the start of the measurement program. Implementing a pre-measurement QA program will assist the user in identifying inconsistencies and deficiencies so that overall data quality can be improved. Development of comprehensive DQOs from the QA program are used to assess the GC system performance and determine if the data meet the specified acceptance criteria.

Since automated GC systems employ "real-time" sample collection and measurement techniques, estimates of precision require repeat measurements of single or collocated SUMMA® canister samples that have been collected using an external sampling device. Objectives for precision should be

determined from the QA program, pre-measurement system verification, and historical information for the target compounds of interest.

An effective QA program consists of systematic procedures necessary to ensure consistency of the data with the needs of the monitoring program. QA samples for data quality assessments should be prepared at concentration levels indicative of typical network samples.

GC/MS Corroboration

The use of GC/MS for corroborative information focuses on the confirmation of the peak identification of components detected in the analysis performed by the GC/FID systems. An important utility of the GC/MS system lies in the ability of the MS to resolve questions concerning coeluting compounds and verify peak identifications obtained by GC/FID. If compound coelution occurs on a GC/FID system, a single peak which represents the sum of the coeluting compounds is observed, sometimes with no indication that coelution has occurred. If coelution occurs on the GC/MS system, the coeluting peaks can frequently be deconvoluted, especially if the mass spectra are dissimilar (i.e., benzene and 1,2-dichloroethane coelute on some chromatographic columns). In these cases, coeluting compounds are readily distinguished by MS. However, if the coeluting compounds are closely related (hydrocarbon isomers, for example) and have common ions in their mass spectra, the MS cannot deconvolute these compounds unless there is at least a small difference in retention times so that different signal maxima for the two compounds can be observed.

A direct comparison of the quantitative values obtained from GC/FID to the quantitative values obtained from GC/MS should not be made since GC/MS calibration is compound specific and automated GC/FID system calibration is based on one or two specific compounds.

DATA VALIDATION

In order to validate data from hydrocarbon O₃ precursor GC systems, systematic procedures for verifying the overall quality, consistency, and usability of the data generated must be developed. Although the data validation process is primarily embodied in this last step, prior to the development of systematic data validation procedures, pre-measurement system validation and QA measurements for establishing the DQOs must be completed.

The validation process is complex and may involve considerable operator interaction, review, and technical judgement. Several steps are required for data validation to ensure the quality of the data prior to entry into the AIRS-AQS data base. The data validation step consists of implementing the following principal elements of review:

- The chromatography result report file review; and
- The summary report file or "flat-file" qualitative comparison review.

Chromatography Result Report File Review

The chromatography result report file refers to two key pieces of information typically generated by PC-based GC data acquisition systems: the chromatogram and the external standard result or data report. This information is automatically stored to the computer hard disk and optionally printed out in hard copy form. The format for this information is a function of the GC data system acquisition method parameters as selected by the user. The chromatogram is a graphical representation of the detector response to the sample components as they elute from the analytical column and usually contains the retention time for peak elution. The result or data report is a summary of information about the chromatogram and typically includes header or sample identification information, peak retention times, peak names or peak identification, peak area counts, peak height, and resulting concentrations based on calibration information.

Due to the large volume of data generated as a result of the PAMS requirements, close scrutiny of all chromatograms and result data is not practical. However, all chromatograms as generated by the automated GC data acquisition system, should go through a cursory review by the station operator to determine if the quality of the chromatography (i.e., the peak shape, peak resolution, peak integration, retention times, and baseline) is acceptable. This level of review can be done quickly by an experienced

chromatographer and will aid in determining if the chromatographic system is performing properly. Comparison of the chromatogram to reference or historical information, such as calibration and typical sample chromatograms, can simplify this process. Chromatograms are also reviewed to determine if there are any gross errors present and whether chromatographic abnormalities, such as electronic spikes, contamination, or levels of target analytes above the electrometer or calibration ranges exist. If the chromatography is acceptable, it can then be further processed by the data reduction and/or peak identification software as chosen by the user.

The cursory review of chromatograms generated from instrument calibration and sample analyses may include the following: the signal from the FID or baseline is normal and the signal output is positive (on-scale); chromatographic peaks are present, integrated correctly, and the peak shape is sharp; the peak resolution or separation is acceptable based on historical instrument performance; all components have been eluted from the analytical column as indicated by a flat or normal baseline at the end of a run; and no chromatographic abnormalities exist, such as large contamination or non-target co-eluting compounds, and electronic spikes.

The relevant result reports must also go through a cursory review, in conjunction with the chromatogram, to ensure that the reference or internal standard compounds are identified correctly and the resulting retention times have not shifted.

Analytical instrument calibration is imperative to the ultimate quality and usefulness of the data generated. It is therefore, also important that the station operator review this information on a regular basis to ensure that DQOs are met and the system is operating properly during the measurement process. If the GC system calibration has gone awry and quality control sample results or internal standards do not agree within the bounds of the specified DQOs, the data should be appropriately qualified to indicate any impact on the analytical results. If "real-time" (same day) calibration review is implemented, quality issues can be identified and corrective actions, such as repeat analyses and instrument maintenance, can be performed prior to continuing data collection. If post analysis calibration information review is performed, the sample data should be flagged to clearly qualify any uncertainty in the results.

The results generated by the automated GC system can be subsequently reviewed and compared to the calibration or standard analyses information from the pre-measurement system validation. This secondary review of the results is used to ensure that correct peak assignments or identifications are made and that the resulting concentrations are correct. The information is also reviewed to determine whether the information used to make the peak identifications (i.e., retention times, relative retention times, retention indices, etc.) requires updating. The need for updating peak identification information is indicated by the frequency of missed or inaccurate peak identifications automatically made by the GC system. This subsequent secondary review of the data is labor intensive and manual, independent review of all data generated by the automated, GC system is not practical. The quality of this review will also be consistent with the amount of manpower that can be put towards it. If this manual, secondary data review is implemented for the monitoring network program, review of a sub set of the data should be considered. Typically, a minimum of 10 percent of the data are processed through a secondary data review. The secondary review involves reviewing the chromatograms, result reports, and concentration and peak identification results for consistency and accuracy. The minimum percentage of the chromatograms generated daily are selected by the station operator for secondary review. It is reasonable to choose chromatograms generated at the beginning and the end of an analysis day to bracket sample analyses. It can then be presumed that the data generated between acceptable secondary review is also correct.

Due to the generation of large, complex data sets and the fact that manual secondary data review is impractical, the user should consider implementing a commercially available secondary peak processing or identification software package as an alternative to manual review. Utilizing automated software peak identification and quantitation review will allow all of the chromatograms and result data to be processed. Software packages, such as MetaChrom™ (Meta Four Software, Inc.) have been designed to manage the processing of large and complex data sets.

Summary Report File or "Flat-File" Qualitative Comparison Review

Generating a data base or summary ASCII report file or "flat-file" of the concentration and peak identification results generated over time can assist the user in identifying system problems, target compound misidentifications, system contamination, outliers, or missed information. Qualitative comparison review of the final concentration results and peak identifications is valuable in checking for outliers or inconsistencies in peak identification, calculations, and results. The information can be globally reviewed for clear changes in trends. A typical ASCII file can contain a large number of measurements for the target O₃ precursor compounds of interest. For example, a system making continuous, hourly measurements of 56 target compounds can produce over 1,300 measurements per day. The summary files can be reduced into manageable segments for visual review. These files can be visually reviewed for potential outliers and other inconsistencies in the data (i.e., unusually high or unexpectedly low values, and missing data) to be identified for further verification or confirmation.

The ASCII summary data base file can be loaded or imported directly into spreadsheet software, such as Excel®, for further data processing or manipulation. Once loaded into the spreadsheet software, graphical representations of the continuous measurements can easily be generated. Generation of diurnal graphs of hourly site measurement information can be very useful in clearly identifying trends and determining if the potential for outliers exist in the data base. Trends in the data and the presence of potential outliers, or otherwise skewed information, can be easily identified. Whatever methodology used, the qualitative comparison review of summarized measurement data can be a useful tool in verifying the consistency and overall accuracy of the data generated from automated GC systems.

CONCLUSIONS

- Automated GC techniques are currently the most viable and cost-effective way to comply with the rigorous sampling frequency requirements of PAMS networks.
- Validating data from automated GC systems is the final and most critical part of the chromatographic measurement process.
- If practical, all chromatograms should go through a cursory review.
- Manual, secondary review considerations include reviewing a subset of data (10%) or implementing commercially available software.
- Qualitative comparison review should include ASCII or "flat-file" review of the data over time and/or graphical representations of continuous or hourly measurements.

DISCLAIMER

Although the information contained in this document has been funded wholly by the United States Environmental Protection Agency under Contract No. 68-D30033 to Radian Corporation, it does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

**A QA PROGRAM FOR THE PHOTOCHEMICAL
ASSESSMENT MONITORING NETWORK**

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ABSTRACT

The results obtained to date from a multi-purpose, cooperative effort between the US EPA and 22 state and local agencies operating photochemical assessment monitoring stations (PAMS) are presented. The purposes of this cooperative effort are: to provide training to the 22 agencies; to provide data on the precision and accuracy that can be expected from PAMS monitoring network measurement systems; to provide data on the performance that can be expected from a newly developed auditing system for PAMS compounds; and to lay the foundation for a nationwide audit program to be initiated in 1995.

INTRODUCTION

The U.S. EPA is conducting cooperative efforts with the 22 state and local agencies measuring oxidants and their precursors in the urban air as part of the PAMS network. These cooperative efforts have four main goals. First, to provide training to the 22 agencies who are measuring PAMS compounds as directed by the Clean Air Act Amendments of 1990. Second, to provide data on the precision and accuracy that can be expected from PAMS monitoring network measurement systems. Third, to provide data on the performance that can be expected from a newly developed auditing system for PAMS compounds. Fourth, to lay the foundation for a nationwide audit program for PAMS measurement systems which will be initiated in 1995.

EXPERIMENTAL

Volatile Organic Compounds

The effort began in the spring of 1993 when each of the organizations operating PAMS stations received a compressed gas cylinder containing the 55 PAMS target analytes. Each analyte was present at approximately 30 ppb carbon. Two compounds, which are not PAMS analytes (n-decane and n-undecane) and which elute later than any of the PAMS analytes, were added to the 55 component mixture to signal the analyst that the length of the sample chromatographic run was adequate. The vendor made up the retention time cylinders to be within 20% of 30 ppbC. The referee laboratory analyzed the cylinders to verify the compound identities. The propane and benzene concentrations, which serve as concentration standards as well as retention time standards, were certified by EPA's referee laboratory using primary standards from the National Institute for Standards and Technology (NIST).

These 55 component mixtures were provided to agencies operating PAMS sites primarily to ensure that all the agencies would be using accurately certified retention time standards.

The portion of the effort concerned with assessing and improving the proficiency of the organizations operating PAMS stations began in the summer of 1993, approximately 60 days after these organizations had received the retention time standards. In these proficiency studies, each organization receives a 1.5 L specially-treated aluminum cylinder which contained approximately 30 of the 55 target VOC analytes. This small cylinder was pressurized to approximately 500 psig to yield an effective gas volume of approximately 50L. The concentrations in the mixture ranged from 10 to 40 ppbv carbon.

Each organization introduces an aliquot of gas from the cylinder they receive into the sampling system they use for measuring PAMS VOC compounds and report the compounds and concentrations found to EPA. Since all participants in the proficiency study receive an identical mixture, EPA compiles the results and reports them for each analyte and for each

participant. The mean, median, variance and the difference from the reported and the expected value are also reported for each analyte. (The referee laboratory results serve as the expected value.)

Three stock or master gas mixtures are used to prepare the mixtures used in each proficiency study. These master mixtures contain from 20 to 34 target analytes in the concentration range of 10 to 250 ppbv carbon. The cylinder serial numbers and the concentrations in them are: AAL9817 (28 analytes at 45 ppbv), AAL001822 (34 analytes at 45 ppbv) and AAL029079 (20 analytes from 10 to 250 ppbv). Some of the PAMS analytes are contained in more than one of the mixtures. The mixtures used in the proficiency studies are obtained by transferring aliquots of the gas mixtures to the 1.5 L aluminum cylinders either with or without dilution air. A gas transfer system described elsewhere is used for these transfer operations.⁽¹⁾

Carbonyl Compounds

Glass tubes containing DNPH are spiked with solutions containing acetone, formaldehyde and acetaldehyde. The tubes, which contain 0.25 to 7 micrograms of each carbonyl are then sent to the PAMS organizations measuring aldehydes. These organizations analyze for the compounds, report the results to AREAL and receive a report similar to that sent to the organizations participating in the VOC proficiency studies. Two proficiency studies have been completed.

RESULTS AND DISCUSSION

Volatile Organic Compounds

The data obtained from the first two proficiency tests along with the medians, means, standard deviations and 95% confidence limits calculated for the percent differences, from the referee analyses, of each compound are listed in Table 1. The compounds are arranged in order of increasing retention times and generally show greater mean percent differences and 95% confidence limits for the later eluting components of the gas mixture than for earlier eluters. The results show a negative bias for the earlier eluting components and a positive bias for the late eluters.

The results from the second proficiency test are listed in Table 2. This is a similar gas mixture as used in the first test, but is not an identical one, as only seven components were common to both test mixtures. Concentrations ranges were similar in both cases. There was general improvement in both the means and standard deviations of the percent differences in the second test with a better balance between positive and negative biases. As in the first test, the accuracy and precision for the analyses of compounds with the longest retention times was poorer than for most of the other analytes. Of the more volatile compounds, acetylene showed the most variability.

The distribution of positive and negative percent differences of the medians for each compound are more evenly balanced when compared to the first test. The greatest variation was for compounds with relatively longer retention times such as n propylbenzene, styrene and 1,2,4-trimethylbenzene. The relatively large confidence limits for these compounds was caused by large lab-to-lab differences. Acetylene, an early eluter, was the only VOC that had predominant negative confidence limits. A direct comparison of the results from both tests is difficult because of the differences in the individual compounds but the VOCs in both tests spanned similar ranges of retention times and chemical type.

Carbonyl Compounds Results

Three of the PAMS carbonyl target compounds (formaldehyde, acetaldehyde and acetone) were spiked on DNPH cartridges and sent to six PAMS laboratories for analyses. Two sets of proficiency test samples have been analyzed for the above carbonyls and the data in Tables 3 and 4 list certain statistical parameters of the carbonyl results. It can be observed that the data from the second proficiency test are significantly improved over the first test.

Summary and Conclusions

The data presented on the results of the PAMS proficiency tests show that the majority of the participating laboratories are correctly identifying and analyzing most of the VOCs in the samples. Certain PAMS target compounds with the longest gas chromatographic retention times showed the greatest variation in both proficiency tests. Most of the data from both tests were within 20% of the referee analyses.

Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer review policies for scientific papers and approved for publication. The contents are not intended to represent Agency policy.

Reference

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Table 1. Percent differences of results from the first PAMS proficiency test

Compound	No. of Values	Referee	Median	Mean	Std.Dev.	95% Con. Limits	
		Analysis (ppb C)	(-----)	(-----)	(-----)	Lower	Upper
			% difference				
Ethylene	13	10.30	-9.71	-9.28	10.71	-16	-3
Ethane	13	10.20	-12.55	-18.54	21.28	-31	-6
Propane	14	14.70	-11.56	-10.93	10.89	-17	-5
1-Butene	15	18.90	-6.88	-7.47	15.57	-16	1
trans-2-Butene	15	18.00	-7.22	-12.14	27.82	-28	3
3-Methyl-1-Butene	13	22.60	-7.08	-2.36	14.16	-11	6
1-Pentene	14	20.70	-5.07	-5.27	8.19	-10	-1
Isoprene	15	16.50	-9.09	-9.45	35.31	-29	10
cis-2-Pentene	15	19.70	-8.63	-10.98	12.40	-18	-4
2,2-Dimethylbutane	14	30.40	7.73	7.88	7.94	12	3
4-Methyl-1-Pentene	13	26.40	-5.30	-5.30	10.85	-12	1
2,3-Dimethylbutane	14	28.60	-4.90	-4.91	10.08	-11	1
3-Methylpentane	12	29.00	-7.07	-14.96	27.38	-32	2
n-Hexane	15	28.20	-4.93	-8.93	29.48	-25	7
cis-2-Hexene	14	25.60	-4.47	-0.25	14.03	-8	8
2,4-Dimethylpentane	14	34.50	-4.00	0.13	15.53	-9	9
Cyclohexane	14	30.10	-4.53	-1.30	14.78	-10	7
2,3-Dimethylpentane	14	35.60	-3.29	0.77	15.48	-8	10
2,2,4-Trimethylpentane	15	41.70	-3.57	0.35	15.49	-8	9
Methylcyclohexane	14	35.60	-2.39	1.34	15.34	-8	10
2,3,4-Trimethylpentane	15	37.80	0.26	3.06	15.39	-5	12
2-Methylheptane	14	39.60	-0.43	2.74	15.94	-6	12
Ethylbenzene	15	28.20	13.48	7.47	37.32	-13	28
m/p-Xylene	14	27.80	15.83	16.87	25.58	2	32
o-Xylene	14	27.30	16.03	16.08	23.57	2	30
Isopropylbenzene	13	28.70	22.75	26.46	25.28	11	42
1,3,5-Trimethylbenzene	13	24.60	26.02	29.07	34.41	8	50

Table 2. Percent differences of results from the second PAMS proficiency test

Compound	No. of Values	Reference Value (ppb C)	Median (----- % difference -----)	Mean	Std.Dev.	95% Con. Limits Lower Upper
Acetylene	9	12.83	-18.16	-13.74	23.00	-31 4
Propylene	11	14.18	-1.27	4.17	23.96	-12 20
Isobutane	11	19.03	-0.68	-4.18	8.63	-10 2
n-Butane	11	19.20	-1.04	-6.78	16.63	-18 4
cis-2-Butene	11	18.35	-1.91	-3.66	7.42	-9 1
3-Methyl-1-Butene	11	22.25	1.12	2.90	23.48	-13 19
Isopentane	11	24.65	0.20	4.20	16.49	-7 15
n-Pentane	11	24.75	-0.61	0.98	11.49	-7 9
trans-2-Pentene	11	24.43	-1.76	-1.33	13.79	-11 8
2-Methyl-2-Butene	11	22.40	-1.34	-2.31	10.47	-9 5
Cyclopentene	11	23.58	-0.34	1.99	12.16	-6 10
Cyclopentane	11	24.83	-1.25	-2.49	14.23	-12 7
2-Methylpentane	11	30.15	0.83	1.42	15.91	-9 12
3-Methylpentane	10	29.60	-0.20	-2.74	11.23	-11 5
trans-2-Hexene	11	27.63	0.62	0.06	14.83	-10 10
cis-2-Hexene	11	28.88	0.42	1.27	14.06	-8 11
Methylcyclopentane	11	29.63	-0.10	1.26	16.56	-10 12
Benzene	11	29.28	0.00	-1.84	16.26	-13 9
Cyclohexane	11	30.38	1.05	-0.55	20.59	-14 13
2-Methylhexane	11	33.50	3.28	3.16	16.82	-8 14
3-Methylhexane	11	33.45	1.85	3.52	16.45	-8 15
2,2,4-Trimethylpentane	11	40.05	-1.87	-1.82	16.02	-13 9
n-Heptane	11	32.33	2.07	3.52	18.40	-9 16
Toluene	11	35.95	2.00	-1.64	11.00	-9 6
2-Methylheptane	11	37.90	0.26	0.85	16.28	-10 12
3-Methylheptane	11	36.73	1.01	0.78	14.43	-9 10
n-Octane	11	36.08	1.44	-0.93	19.52	-14 12
Ethylbenzene	11	33.18	-3.25	-5.93	18.18	-18 6
Styrene	11	19.50	-12.82	-8.36	40.56	-36 19
n-Nonane	10	38.68	-2.37	-1.57	6.45	-6 3
n-Propylbenzene	9	31.00	-3.87	-13.08	34.56	-40 13
1,2,4-Trimethylbenzene	9	33.58	-14.86	-13.65	30.80	-37 10

Table 3. Summary of results for first proficiency test for carbonyl compounds ($\mu\text{g}/\text{cartridge}$)

Compound	Sample No.	No. of Results	Amount Spiked	Median	Mean	Std. Dev.	95% Con. Limits	
							Lower	Upper
Formaldehyde	2	6	0.50	0.48	0.67	0.50	0.15	1.2
	3	6	5.00	4.17	11	17	-6.4	28
Acetaldehyde	2	6	1.02	1.04	1.71	1.64	-0.01	3.4
	3	6	3.92	3.16	5.01	4.57	0.22	9.8
Acetone	2	6	1.04	1.51	2.22	1.82	0.31	4.1
	3	6	3.99	3.99	5.98	5.19	0.53	11.4

Note: Results of the referee laboratory were not included in this data set.

Table 4. Summary of results for second proficiency test for carbonyl compounds ($\mu\text{g}/\text{cartridge}$)

Compound	Sample No.	No. of Results	Amount Spiked	Median	Mean	Std. Dev.	95% Con. Limits	
							Lower	Upper
Formaldehyde	2	6	0.60	0.72	0.76	0.22	0.53	0.99
	3	6	4.80	5.29	5.27	0.40	4.85	5.69
Acetaldehyde	2	6	1.20	1.49	1.52	0.20	1.31	1.73
	3	6	3.50	3.94	3.92	0.39	3.51	4.33
Acetone	2	6	1.20	1.34	1.39	0.21	1.17	1.61
	3	6	4.00	3.87	3.89	0.43	3.44	3.34

**Inter-Regional and Inter-State Quality Assurance for PAMS:
Regional Reference Laboratory Round Robin Comparisons**

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ABSTRACT

To ensure data comparability between the various State agencies conducting PAMS monitoring in EPA Regions I, II, and III, a Regional Reference Laboratory (RRL) was designated for each of these three EPA Regions. Three round robin samples were analyzed by each of the RRLs to determine the inter-laboratory variability.

Each of the round robin samples contained an ambient air sample, which was collected in passivated stainless steel canisters. Pollutant concentrations ranged from <1 ppbC to 30 ppbC. For compounds present in the sample at concentrations >5 ppbC, % percent differences between the three RRLs were <30% except for 2 instances. For compounds present in the sample at concentrations of 0-5 ppbC, % differences between RRLs were <30% approximately 3/4 of the time. Analysis of round robin samples conducted later in the monitoring season showed improved results relative to the earlier samples. Compound identification was consistent across all three laboratories with few false positives or false negatives evident.

INTRODUCTION

Air monitoring for the Photochemical Assessment Monitoring Stations (PAMS) program requires the measurement of volatile organic hydrocarbons and carbonyl compounds as well as ozone and oxides of nitrogen. Monitoring is required by Federal regulation in areas designated as non-attainment for the National Ambient Air Quality Standards for ozone. The PAMS network design regulations, as codified in 40CFR Part 58, typically requires 4 to 5 monitoring locations for each non-attainment area.

A critical concern at the EPA Regional and State level is the comparability of data between the various monitoring organizations collecting PAMS data. This concern is particularly acute for the Regions located in the Northeastern United States, because the density of ozone non-attainment areas there has resulted in PAMS monitoring networks with overlapping upwind and downwind sites that cut across State and EPA Regional borders. Previous monitoring experience for volatile organic hydrocarbons in ambient air, particularly in the Staten Island/New Jersey Urban Air Toxics Assessment Project (1987-1989), has shown that volatile organic hydrocarbon (VOC) analyses in ambient air are prone to variability on the order of 50 and 100% between any 2 monitoring organizations.

Since VOC monitoring is so critical for the PAMS program, EPA Regions I, II, and III have implemented a coordinated Quality Assurance Program for these compounds. A unique feature of this program is the designation of a Regional Reference Laboratory (RRL) within each of EPA Regions I, II, and III. The RRLs are responsible for analyzing VOC samples split and/or collocated with each of the organizations collecting PAMS data within its region. As a check for data consistency across Regional boundaries, round robin analyses of a single canister are conducted among each of the 3 RRLs. The results of 3 such round robin studies, conducted during the summer and fall of 1993, are discussed below.

MATERIALS AND METHODS

The first round robin was conducted using ambient air collected at a PAMS site in the field. The sample was actively collected in a canister to greater than atmospheric pressure. Round robin samples 2 and 3 were prepared by taking a 3-4 minute grab sample at a well travelled highway underpass. The canister was then pressurized to 22 psig by dilution with zero grade nitrogen. Each RRL performed its analysis using its laboratory, as opposed to field, instrument. The analytical equipment used by each laboratory varied. RRL A used GC/FID analysis with 2 column sample confirmation using DB-1 and DB-5 60 meter, 0.32 mm i.d., 1 μ m film thickness columns. RRL B and C used GC/MS systems with a 60 m, 0.32 mm i.d., 1 μ m film thickness columns. As a result of the use of a GC/MS systems, data for the C₂ hydrocarbons were not reported for these organizations. Sample concentration for all 3 laboratories was accomplished using the Entech 2000 sample concentrator, with LN₂ subambient GC cooling starting at -50 or -60C. All samples when analyzed were above atmospheric pressure with the exception of round robin sample 1, where the final analysis by laboratory B and C were carried out at near ambient or slightly subambient pressure.

RESULTS AND DISCUSSION

Data was considered valid for the round robin samples if any 2 of the 3 RRLs confirmed a particular observation. This approach was necessary, since the round robin canisters were ambient samples, and not prepared from standards. Thus, the "true" identities and concentrations of pollutants in the sample could not be known. A false negative identification was defined to occur when 2 RRLs confirmed the presence of a compound at a concentration > 1.0 ppbC, while the third RRL did not report it at all. Similarly, a false positive was defined as the identification of a pollutant at a concentration > 1 ppbC by one RRL that was not confirmed by the other 2 RRLs.

Table 1 shows the concentrations for 50 PAMS compounds for all 3 round robins, as reported by RRLs A, B, and C. Although there are 55 PAMS compounds, the C₂ compounds were not reported by RRL B and C because the analytical limitations of the GC/MS systems used by these organizations precluded their analysis. Alpha and beta pinene were also eliminated from the target list, because of sample instability in the reference standards used by all 3 RRLs. Examination of the data in Table 1 shows only 1 false positive existed. This was RRL A's cyclopentene data which was reported in round robin 1 at a concentration of 1.10 ppbC. False negatives were observed 3 times in round robin sample 1, twice with RRL C (2 methyl pentane and n-heptane) and once with RRL A (n-nonane). For round robin sample 2, false negatives were observed twice with RRL A (isobutane and trans-2-butene). No false negatives were found in round robin sample 3.

Tables 2-4 present an analysis of the round robin data by % difference relative to RRL B, across 3 classes of sample concentration; >5 ppbC, 1-5 ppbC, and <1 ppbC. Data for RRL A vs. B and RRL C vs. B were pooled because they showed the same trends. Direct comparisons relative to RRL A or showed similar results as comparisons made relative to RRL B.

As seen in Tables 2-4, compounds present at concentrations >5 ppbC showed the greatest agreement between RRLs. In round robin 1, only 1 out of 17 observations showed a % difference >30%. Similar results were observed in round robin 2. In round robin 3, no observations had % differences >30%, and in fact, % difference were <20% for all reported values.

Compounds present at 1-5 ppbC showed improved agreement between RRLs during the course of the study. In round robin 1, % differences >30% were found in 14 out of 40 reported values. In round robin 2, 8 out of 52 values were reported with % differences >30%, and by round robin 3 only 2 out of 58 values had % differences >30%.

Compounds present at concentrations <1 ppbC showed the same general improvement in agreement between RRLs during the progression from round robin 1 to round robin 3. In round robin 1, % differences were >30% for 7 out of 16 reported values. In round robin 2, 4 out of 22 values were present with % differences >30%, and in round robin 3, 4 out of 13 values had % differences that exceeded 30%.

CONCLUSION

The data show that PAMS analyses by the Regional Reference laboratories can be expected to be free from appreciable levels of false positives or false negatives. Also, close agreement between RRLs is demonstrated reality for compounds present at concentrations >5 ppbC. At pollutant concentrations of 1-5 ppbC, the agreement between RRLs was greater than was expected. However, further work is needed in order to have consistent agreement at <30% difference between RRLs. The fact that increasing agreement between RRLs was seen as the study progressed indicates that progress is being made in this effort. The results observed during these round robin studies indicates that the RRLs have the capability for analyzing an ambient air sample and achieving a strong consensus with respect to the identification and concentration of the compounds present. This capability can prove instrumental in minimizing the variability and inconsistency that has been the strongest Quality Assurance concern for the VOC analysis required for PAMS.

DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

REFERENCES

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Table 1. Pollutant concentrations of 50 PAMS as reported by the 3 Regional Reference Laboratories for 3 round robin comparisons (units are ppbC)

Compound	Round Robin 1			Round Robin 2			Round Robin 3		
	RRL A	RRL B	RRL C	RRL A	RRL B	RRL C	RRL A	RRL B	RRL C
Propylene	3.00	3.63	3.82	9.40	6.24	7.57	6.00	6.18	6.67
Propane	11.00	10.26	8.27	3.85	2.79	1.83	3.10	3.21	3.13
Isobutane	2.70	4.40	6.20		2.31	2.24	2.20	2.32	2.78
1-Butene	3.10	3.39	3.19	7.00	6.52	7.98	5.40	4.80	5.69
n-Butane	14.00	16.80	14.55	6.20	6.28	7.05	7.40	7.32	7.47
trans-2-Butene		0.93			1.57	1.45	1.10	1.45	1.07
cis-2-Butene		0.83	0.52	1.35	1.27	1.43	1.20	1.17	0.54
3-Methyl-1-butene		0.42	0.10	0.51	0.65	0.55	0.60	0.72	
Isopentane	19.00	26.40	25.13	19.50	21.00	23.80	23.00	24.20	24.99
1-Pentene	1.00	1.50	1.03	1.20	1.11	1.23	1.40	1.38	1.48
n-Pentane	7.80	8.75	8.38	7.05	7.75	8.93	9.80	9.70	10.89
Isoprene	8.10	8.60	7.97	2.90	3.12	3.03	2.00	1.99	2.07
Trans-2-Pentene		0.79	0.65	1.90	1.83	2.08	2.40	2.54	2.35
cis-2-Pentene		0.44	0.36	1.03	1.12	1.24	1.30	1.30	1.34
2-Methyl-2-butene		0.89	0.73	2.90	3.69	3.26	3.60	4.14	4.13
2,2-Dimethyl butane	0.95	0.83	0.31	1.30	1.20	1.37	1.40	1.74	1.77
Cyclopentene	1.10			0.53		0.35	0.60	0.62	0.65
4-Methyl-1-pentene					0.17	0.05			
Cyclopentane	1.20	1.50	1.13	0.71	0.68	0.76	0.90	0.79	0.64
2,3-Dimethyl butane	1.30	1.59	1.28	1.95	0.93	2.26	1.90	1.73	1.65
2-Methyl pentane	5.50	5.24		5.90	5.26	9.49	6.20	5.48	5.90
3-Methyl pentane	2.70	2.93	2.24	3.35	3.68	4.10	3.60	3.46	3.00
2-Methyl-1-pentene				0.83	1.00	0.94	0.90	0.80	0.44
n-Hexane	2.30	2.98	2.57	2.75	2.53	2.84	3.30	3.07	3.15
Trans-2-Hexene		0.27		0.82	0.72	0.71	0.80	0.76	0.71
cis-2-hexene					0.40	0.36	0.70	0.43	
Methyl cyclopentane	1.40	1.70	1.40	2.15	2.39	2.82	2.30	2.50	2.52
2,4-Dimethyl pentane	1.00	0.99	0.62	1.55	1.46	1.50	1.20	0.99	0.98
Benzene	4.60	5.09	4.33	11.00	11.04	10.96	9.90	11.22	10.02
Cyclohexane		0.71		0.48	0.35	0.33	7.20	7.55	8.04
2-Methyl hexane	1.80	6.75	7.36	2.05	2.57	3.32	2.10	2.13	2.68
2,3-Dimethyl pentane	1.30	2.12	1.53	2.10	2.28	2.59	1.30	1.33	1.35
3-Methyl hexane	1.80	3.75		2.80	2.69	2.28	2.30	2.45	2.63
2,2,4-Trimethyl pentane	3.20	4.54	3.34	5.00	5.60	5.67	3.70	3.54	3.54
n-Heptane	1.50	2.00		1.35	1.20	1.48	1.80	1.53	1.80
Methyl cyclohexane	1.10	1.27	0.67	1.03	0.97	0.86	1.20	1.04	0.98
2,3,4-Trimethyl pentane	1.00	1.58	0.74	2.00	2.37	1.79	1.40	1.18	1.14
Toluene	15.00	17.76	15.45	18.00	20.37	18.14	20.00	19.18	20.39
2-Methylheptane		1.34	0.44	0.94	1.30	0.61	1.10	1.08	1.12
3-Methyl heptane		0.83	0.58	0.84	1.01	1.19	1.10	1.45	1.05
n-Octane		1.34	0.74	0.74	0.94	0.75	1.20	1.26	0.99
Ethyl benzene	1.90	2.18	2.05	3.05	3.99	3.58	3.60	3.88	3.98
m/p-Xylene	5.70	6.28	6.26	11.00	14.32	11.36	12.00	13.20	13.10
Styrene	3.30	2.41	0.54	1.30	1.14	1.02	1.10	1.11	1.12
o-Xylene	2.60	2.41	2.40	4.45	5.44	4.14	4.70	5.50	5.01
n-Nonane		1.68	1.06	0.80		0.29	0.70	1.14	0.16
Isopropyl benzene		0.50	0.43	0.47	0.54	0.33		0.42	0.42
n-Propyl benzene	1.60	0.79	0.67	1.30	1.26	1.01	0.50	1.13	1.16
1,3,5-Trimethyl benzene	0.86	1.08	0.58	1.90	2.23	1.29	1.80	2.12	1.78
1,2,4-Trimethyl benzene	3.40	2.46	2.22	4.25	7.08	4.32	6.30	7.06	6.02

Table 2. Round robin 1: Combined % Differences of
RRL A vs. RRL B and RRL C vs. RRL B
for 50 Compounds in an Ambient Air Sample

Target Compound Concentration	Number of Compounds with % Differences of:			
	0-10%	10-20%	20-30%	> 30%
High (> 5 ppbC)	8	7	1	1
Medium (1-5 ppbC)	8	10	8	14
Low (< 1ppbC)	1	6	2	7

Table 3. Round robin 2: Combined % Differences of
RRL A vs. RRL B and RRL C vs. RRL B
for 50 Compounds in an Ambient Air Sample

Target Compound Concentration	Number of Compounds with % Differences of:			
	0-10%	10-20%	20-30%	> 30%
High (> 5 ppbC)	7	7	3	1
Medium (1-5 ppbC)	18	19	7	8
Low (< 1ppbC)	5	8	5	4

Table 4. Round robin 3: Combined % Differences of
RRL A vs. RRL B and RRL C vs. RRL B
for 50 Compounds in an Ambient Air Sample

Target Compound Concentration	Number of Compounds with % Differences of:			
	0-10%	10-20%	20-30%	> 30%
High (> 5 ppbC)	15	9	0	0
Medium (1-5 ppbC)	39	10	7	2
Low (< 1ppbC)	7	2	0	4

RTP Auto-GC Demonstration Experiment

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An Auto-GC demonstration was conducted at the AREAL test facility located in the ERC Annex at RTP, North Carolina throughout a four week period from August 31 to September 28, 1992. Five potential commercial vendors were invited to participate in this demonstration experiment.

The primary purpose of this experiment was to demonstrate the capabilities of the commercial automated gas chromatographic systems which had been developed up to that point, in measuring volatile hydrocarbon species in accordance with the provisions of the proposed requirements for monitoring ozone precursors. These proposed requirements and associated guideline documents were provided to each of the participant vendors.

Each of the five automated GC systems was set-up for hourly collection and analysis of the species targeted in the requirements and was operated from a common ambient air manifold under prescribed sampling schedules throughout the experiment. EPA Regional Offices, State and local air pollution agency representatives were invited to observe the operations of these systems, and technical information exchange was made between the EPA researchers and representatives of each of the participating manufacturers.

The experiment successfully demonstrated the operation of each of these emerging systems. Ninety-seven hours of operation provided sufficient data for inter-comparison of all five systems. The results of this comparison for 12 hydrocarbon species are summarized here.

Intercomparison of Two Automated Gas Chromatography Systems for the Analysis of Volatile Organic Gases in Ambient Air

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ABSTRACT

The relative performance of two commercial automated gas chromatography (Auto-GC) systems for ambient air monitoring is discussed. Both systems have proven their ability to quantify most of the C_2 - C_{10} compounds targeted in the U.S. EPA's enhanced monitoring program, at or below the requisite 1.0 part per billion carbon detection level. Neither cryogenic cooling of adsorption trap material nor low temperature (-180 °C) refocusing prior to sample injection were found to be necessary for satisfactory separation of these compounds. However, the permeation-style dryer utilized by both systems removes many polar and/or oxygenated species of interest. In addition to obtaining the technical expertise to operate Auto-GC systems, organizations involved in enhanced monitoring need to reevaluate their data handling resources. Raw data from these GC's must be backed-up, telemetered and quickly assessed in order to efficiently utilize resources and minimize lost data. Because existing data logging and telemetering systems are structured for relatively low data flows, the large quantity of raw data from a single GC (>1.5 Megabytes/day) can easily overwhelm such systems. Data management and assessment may well prove to be the most labor intensive activity associated with the enhanced monitoring program.

INTRODUCTION

Despite regulatory attempts spanning more than 20 years, a significant portion of the United States' population is still exposed to ozone levels deemed unhealthy by the U.S. EPA. In many areas of the U.S., the bulk of summertime ozone is anthropogenic in nature, resulting solely from photolysis of NO_2 molecules by ultraviolet radiation. The NO_2 arises from a complex series of reactions involving precursor compounds consisting of both volatile organic gases (VOGs) and oxides of nitrogen¹.

In order to more completely understand the genesis, transport, and fate of these ozone precursors the U.S. EPA has, as directed by the Clean Air Act Amendments of 1990, issued guidance for the creation of an "enhanced monitoring" network². In addition to increasing the spatial coverage of ozone and nitrogen oxide monitors, the guidance calls for the collection of data on speciated VOGs. Not only will this additional data aid in the understanding of ozone formation, it will provide both a missing metric against which emissions inventories can be compared and a baseline for evaluation of the efficacy of strategies involving VOG control.

Although Auto-GCs had been employed as early as 1990^{3,4} for intensive ambient analysis, they were still relatively unknown when, at the request of U.S. EPA Region I, the Air Monitoring and Radiation section of the Connecticut Department of Environmental Protection (CTDEP) began a performance evaluation. This study began in 1991 and was intended to: 1) determine the feasibility of using commercially available Auto-GCs to deliver continuous data on speciated VOGs; and 2) highlight problematical design or operational features in such systems that would preclude their use by "typical" State monitoring agencies.

We report here the results of our experiences to date with a CP 9000 (Chrompack, Inc., Raritan, NJ) Auto-GC, which was delivered in the summer of 1991, and with an "Ozone Precursor System" (OPS) obtained from the Perkin-Elmer Corporation (Norwalk, CT) in the spring of 1993. Our "on-line" experience thus far amounts to about 5000 hours. During approximately 800 of these hours the systems were operated simultaneously to gauge their comparability.

METHODOLOGY

Capillary column gas chromatography is a well established analytical method, and automated systems for laboratory analysis of air samples by both gas chromatography and liquid chromatography are not uncommon. However, adapting laboratory proven techniques and technologies for use in a continuous ambient air monitoring network has proven to be quite challenging.

The enhanced monitoring rules developed by the U.S. EPA call for continuous sampling of VOGs with a three hour minimum frequency (i.e. 8 samples/day) at photochemical assessment monitoring stations² (PAMS) during the months of June, July, and August. To be cost effective, any VOG analysis system installed at a field site must operate with no more than 2 manual interventions per week. Truly remote sites have even more stringent limits, and must operate on weekly, or even bi-weekly, visits. This minimal intervention requirement dictates that Auto-GC systems must have data telemetry capability, and although remote control of Auto-GC system functions may be desirable, it is not mandatory.

Siting/ Sample Introduction

After a brief familiarization period, the CP 9000 system was moved from the CTDEP Maintenance and Repair facility (then located in an urban, light-industrial section of Hartford, CT) to East Hartford, where the CTDEP established the first east coast "Type 2" PAMS. This suburban, light industrial site is described elsewhere³ in more detail. The instrument shelter housing the chromatography systems is maintained at 26 °C (1/- 3°) during the summer, with humidity (controlled by an air conditioner) typically ranging between 40% and 50%. Ambient air is drawn into the shelter from an elevation of approximately 3.75m via an 7.62cm I.D. Pyrex® glass manifold at 3000 lpm. Aliquot for analysis are drawn from near the central axis of the manifold by means of 3.18mm o.d. (2.108mm i.d.) pure nickel tubing. The sample line is equipped with a 2 micron sintered stainless steel particulate filter, located approximately 5cm downstream of the manifold. The inlet line and all fittings "wetted" by the sample were baked at 200 °C for 30 minutes prior to installation in order to drive off potential contaminants.

GC Hardware Description

The CP 9000 and OPS are functionally identical to the extent that each dries, captures, concentrates and analyzes ambient VOG's by utilizing Nafion® dryers, chilled adsorption traps, dual capillary columns and flame-ionization detectors (FIDs). However, significant differences exist in the methodologies employed for sample focusing and splitting. Each Auto-GC is discussed here, as appropriate, with further details regarding the CP 9000 available elsewhere⁴.

The OPS concentrates VOG's on a two-stage trap consisting of discrete Carbosieve III and Carbotrap C adsorbent beds. The adsorbents are housed in a narrow-bore glass tube held at -30 °C, by a Peltier cooling device, during sample collection. The 40 minute sample collection period (at 15 cc/min) is followed by flash-heating (40 °C/sec) of the trap to 180 °C. The concentrated VOG's are swept off of the adsorbent by a counter-flowing stream of ultra high purity helium and transported to the BP-1 column by a transfer line heated to 200 °C.

The OPS and CP 9000 systems have been similarly configured to provide consistency in operating procedures, data analysis, and maintenance. The differences between the two systems are evident in the sample trapping and sample splitting systems. The CP 9000 utilizes a primary two-stage trap held at -20 °C and a secondary trap (refocuser) cooled to -180 °C using liquid nitrogen (LN₂). The OPS utilizes a Peltier device both to cool the sample trap to -30 °C for sample focusing, and to generate the 325 °C temperature needed for trap desorb and purge cycles. At first glance, non-cryogen systems may seem preferable; however, the trap cooling system in the OPS is not without drawbacks. Peltier device icing has been encountered several times during regular operation due to elevated humidity in the ATD400 trap chamber. In the short-term, this ice formation reduces the systems' ability to quickly change temperature, causing delays in sample desorb and injection (See *Operating Conditions*). Long-term Peltier icing can cause corrosion, resulting in permanent damage to the device and premature replacement. Modifications made in the fall of 1993 to air flow patterns in the trap chamber may have solved the problem, but this phenomenon will be monitored closely during 1994.

The CP 9000 system is equipped with a sample splitter and delivers approximately equal sample volumes to each column, while the OPS utilizes a Deans switch which allows the effluent of the BP-1 column to initially flow to the PLOT column. Both systems utilize Al₂O₃ PLOT columns, however, Perkin Elmer specifies a Na₂SO₄ wash, while Chrompack specifies a KCl wash. This difference in washes results in altered PLOT column elution order between the two systems, while the BP-1 (OPS) and DB-1 (CP 9000) elution orders are identical for identified peaks.

The Deans switch on the OPS is pneumatically activated after 2-methyl-1-pentene has eluted from the BP-1 (approximately 12 minutes), and the sample is routed, via a short transfer column, to the second FID for analysis beginning with hexane. In theory, the use of a Deans switch should prolong the PLOT column lifetime since heavier (>C6) compounds are thought to de-stabilize PLOT-type columns. We have not noted specific PLOT column performance problems due to exposure to heavy compounds on the CP 9000, but should this occur, an optional Deans switch is now available for installation on that system.

A model 78-30 TOC zero-air generator (Balston, Haverhill, MA) is employed to generate dry, clean, hydrocarbon free air for use with the OPS since that system consumes significantly more compressed air than the CP 9000. This generator allows long periods of intervention-free operation, and has proven to be so efficient that it is now also used to supply the CP 9000.

Computer Hardware/Software Description

The Auto-GC control system used by the CTDEP employs IBM-PC compatible computer platforms, MS-DOS® and Windows® operating systems, and task-specific software applications. Data collection, processing, transfer, and storage comprise the bulk of the routine tasks. Data collection and processing is performed with Turbochrome® (PENelson, Cupertino, CA) software. This package collects data from a Perkin-Elmer 900 Series digital interface and performs peak identification, integration, and quantification. Data is initially stored in a "home" directory and copied to a "staging" directory for automated transfer to the Air Monitoring divisions computer, which provides a real-time view of system operation without requiring on-site presence.

Data transfer is performed by coordinating an event timer, Windows Cron (Chris Newbold, Rochester, NY), and a remote computer control package, PCAnywhere (PCA) for Windows® (Symantec, Cupertino, CA). In PCA terms, the HOST is polled by the REMOTE. PCA is run in host-mode at the monitoring site allowing a remote system to connect via phone line and assume remote control. The event timer (Cron) running on the remote system, launches PCA at predetermined times specifying a control script and operating parameters. PCA establishes a connection with the monitoring site computer, performs an unattended transfer of data from the host to the remote system, and then terminates the connection. Both raw data for chromatogram generation, and concentration data for analytical use, are transferred three times daily.

Auto-GC systems for ambient monitoring generate large quantities of data, on the order of 1.5 Megabytes (Mb) per day (when performing hourly analyses). This is based on a dual-column run with 20 Kilobytes (Kb) of raw data, 5Kb of result data, a 5Kb report, and possible log or additional report files per column, per run. The data must be archived, telemetered, and analyzed on a regular basis in order for decisions on GC system performance and air quality to be made. Data archiving is accomplished by the use of a post-processing script issued to MSDOS. This script creates a duplicate of both the completed raw and processed data on an archival storage device. The preferred device for data backup and off-line storage is the Bernoulli® (Omega, Roy, Utah) removable media drive. This device provides 90Mb or more of random access storage and is not only comparable to a traditional fixed disk system in performance and durability, but because it employs a removable disk medium, it also provides a handy method for manual transport of large quantities of data.

Reliable hardware and software integration is essential to data analysis, and several weak links in this area have become evident. Both GC packages have, at various times, experienced difficulty recognizing the hardware "key", a device installed on the workstation computer's parallel port, necessary for software operation. On the OPS, this failure was solved by the installation of a second parallel communications port, dedicated to the hardware key, but upcoming versions of Turbochrome (i.e. version 4.0) are reported to avoid this problem altogether. Software and hardware conflicts which result in PC "lockups" have been a constant problem at East Hartford. Installation of hardware-based "watchdog" reset cards (MVS, Merrimack, NH) which reset the system if no processor activity occurs for a set period of time (i.e. 2 minutes) has not only solved this problem but has greatly increased data capture and reduced the travel expense and time required to manually reset the system.

The appearance of large, randomly occurring "noise spikes" has plagued the PC associated with the OPS and has not been eliminated by power conditioning. Although initial relief was obtained by moving the IEEE 488 interface card (required for connection to the PE 900 Series interface) to a different expansion slot within the PC, the problem eventually returned and has persisted despite extensive efforts. These spikes must be identified prior to final data processing, as they may be mistaken for known compounds or become erroneous supplements to the total VOG values for the run. Occasional problems have arisen with unpaired hourly files on both systems where, for a variety of reasons, DB-1 column data is not available for a given PLOT column file, or vice versa. A decision stands to be made regarding the validity of these incomplete hourly files.

The large variety of, and interconnections between hardware and software required to operate an Auto-GC network dictate that technical expertise in computer systems operation, diagnosis and troubleshooting be readily available. Associated knowledge of data acquisition systems, chromatography systems and chemistry also prove useful in the accurate recognition, analysis and correction of data handling problems. To date, hardware/software integration problems with both the OPS and CP 9000 have absorbed more man-hours than any other category of activities.

Operating Conditions

Standard laboratory practice dictates both the use of oxygen traps on compressed carrier (helium) supplies to preserve column stationary phase integrity, and the use of desiccant-type dryers on combustion air supplies. These techniques are required on Auto-GCs which must operate reliably for long periods while unattended. An indicating desiccant installed downstream of the Balston air supply insures a dew point of less than -50 °C, which is required by the OPS to prevent Peltier/heater damage.

Many operating parameters and software options associated with Auto-GCs must be user selected or adjusted to optimize performance, while statutory considerations drive other choices. As noted earlier, VOG sampling at the East Hartford PAMS site is required during the months of June, July and August with a minimum frequency of 8 samples per day. In an attempt to correlate VOG data more closely with meteorological parameters and criteria pollutant data, CTDEP opted to sample on an hourly basis. In addition to improving the uniformity of data generated, this shorter sampling frequency simplifies quality assurance practices which dictate calibration under actual operating conditions. Calibration and blank analyses of three hour duration would not only require inordinate manpower, but would also result in the loss of much ambient data, therefore, hourly sampling was selected.

Trap/oven temperature considerations and analytical requirements are such that both Auto-GCs can draw ambient samples for only 40 minutes out of each hour. In order to insure hourly representativeness, sampling is begun at five minutes after the hour and continues until 15 minutes before the hour. This timing sequence was chosen not only for representativeness but also to allow for some "creep" due to timing shifts that may occur over time (See *GC Hardware*).

As noted, Turbochrome software provides the necessary data collection and processing control, and a "user-friendly" environment for the operator. Although Turbochrome provides limited functionality for post-run data analysis, it was found to be superior to Chrompack Mosaic® software used by the CP 9000 system. The CP 9000 data handling system was converted to Turbochrome in 1993, allowing complete data compatibility between platforms and providing a consistent user interface for both systems. The resulting system/report uniformity has significantly aided data analysis and personnel training.

Although both systems had been operated in tandem for over 600 hours before Turbochrome was adopted as the sole operating environment, a significant portion of the comparative data used in the preparation of this report was derived from a six day period in November of 1993. Intercomparisons of the two systems were greatly simplified once they began producing uniform reports and comparable chromatograms. For example, note the systems' similarity in their ability to resolve peaks in a 40 component calibration standard (Figure 1). Run to run variations occur but it appears that both systems resolve peaks equally well at ambient concentrations. This indicates that low temperature refocusing with cryogenic fluid is not absolutely necessary since the OPS can baseline-resolve most of the targeted compounds and separate the remainder at least as well as the CP 9000. Note however that β -pinene is thought to become fragmented in permeation-style dryers and that a preliminary analysis of ambient data from 1993 indicated that the diurnal pattern of both pinenes was identical to that of benzene, toluene, and isopentane, which are mobile source related, making it unlikely that the identified peaks were indeed, pinenes. As a result, we do not currently identify either α - or β -pinene on a routine basis.

Since the CP 9000 exposes both columns to the full range of C_2 - C_{10} compounds, it is not surprising that one or more targeted gases appear on both columns and, indeed, 14 such instances have been identified. Simultaneous operation of both systems (July, 1993) confirmed that the many of these "doubly" resolved compounds were being properly identified. An exception is 2-Methylpentane, for which Chrompack recommends using the PLOT column values for quantification. Although 2-Methylpentane, in the calibration standard, is well resolved on the CP 9000's PLOT column, it appears to co-elute with an unknown compound under ambient conditions. Figure 2 shows 2-Methylpentane PLOT column values from the OPS with results from both the PLOT column and DB-1 column of the CP 9000. Note the relatively constant agreement between the OPS PLOT column value for 2-Methylpentane and the DB-1 column output from the CP 9000. However, PLOT column values from the two systems show increasingly divergent values as the concentration increases, most probably due to co-elution. Therefore, 2-Methylpentane values from CP 9000 systems should be derived from the DB-1 column.

Although the Auto-GCs run continuously for extended periods of time without intervention, maintenance considerations such as compressed gas consumption, data storage limits, air generator maintenance, and chromatography workstation operation/maintenance, require on-site visits. Our experience has shown that semi-weekly site visits are the norm for the OPS, while the CP 9000 system requires more frequent intervention to maintain the LN₂ supply. Compressed gas supplies are closely monitored throughout the sampling season (June, July, August), as exhausted gas or LN₂ supplies have consistently been a leading cause of data loss. The CP 9000 consumes LN₂ at a rate of approximately 100 liters per day. 6200 liter tanks of hydrogen and helium are consumed slowly (approximately 60 to 90 days) by both systems, as is compressed nitrogen which is employed only by the CP 9000 system. Although the air generator can theoretically operate unattended for 14 days, surge-tank draining and inspection is performed on a weekly basis while inventorying gas supplies. Operating parameter values for both systems are shown in Table 1.

TABLE 1
Operating Parameter Comparison

PARAMETER	OPS	CP 9000
Sample Rate:	15cc/min. for 40 min.	20cc/min. for 40 min.
GC Oven Temp. Range:	46 - 200 °C	46 - 180 °C
FID Temp.:	250 °C	250 °C
Valve Temp.:	175 °C	175 °C
Desorb Temp.:	325 °C	250 °C
He Pressure	120 kPa (17.4 psig)	360 kPa (43.5 psig)
H ₂ Pressure	103 kPa (15.0 psig)	150 kPa (21.7 psig)
Air Pressure	159 kPa (23.0 psig)	150 kPa (21.7 psig)
Column A	PLOT 50m x 0.32mm ID Al ₂ O ₃ with Na ₂ SO ₄ Wash, 5u thickness Flow: 2.5 ml/min	PLOT 25m x 0.32mm ID Al ₂ O ₃ with KCl Wash, 5u thickness Flow: 2.9 ml/min
Column B	BP-1 50m x 0.23mm ID 1.0u Coating, Flow: 2.3 ml/min	DB-1 60m x 0.32mm ID 1.0u Coating, Flow: 1.5 ml/min

A final operating condition concerns the "minimum area reject" which is selected to prevent the integration of peaks below a threshold concentration. This factor may be determined by calculating the area equivalent to the required minimum detection level (MDL). For example, if a 1.0ppbc standard has an associated peak area of 15,000 mV/sec and a target MDL of 0.5ppbc is desired, the minimum area reject would be 7,500mV/sec. Peaks with an area (concentration) below the reject limit will not be integrated or identified. The area reject should be compared to baseline deviations as observed in "blank" runs or clean ambient runs in order to ensure that the reject area is sufficiently (2 to 5 times) above the observed baseline noise (Figure 3).

Quality Assurance

Quality Assurance (QA) activities to date have centered on problem prevention with emphasis also placed on ascertaining the accuracy and precision of collected data. Quality Control (QC) considerations begin with specific maintenance techniques such as leak checks, scrubber trap maintenance, and system cleanliness. QA progresses into areas such as performance audits, quantification standards, determination of MDLs and assessment of retention time stability.

Determination of part per billion concentrations with GC/FID technology is readily achieved but precautions to ensure system integrity must be taken. In addition to the previously mentioned particulate, oxygen, and moisture removing precautions, leak testing was performed on an "as needed" basis and "blank" samples were run immediately after most calibration standards. Both systems remained essentially leak-free during 1993 and blanks were acceptable, with the OPS showing only a few peaks in the single ppbc range (See Figure 4). No blank run data is available from the CP 9000 data collected under Turbochrome, but has previously been published⁵.

High quality calibration gas in sufficient quantity was not readily available until the summer of 1993. At that time ManTech Environmental Technologies (Research Triangle Park, NC) delivered a high pressure cylinder of calibration gas as part of the U.S. EPA's PAMS QA program. Although this 57-component gas was intended to serve only as a retention-time standard, the CTDEP had the cylinder independently quantified for 44 compounds as no other suitable quantification standard was then widely available. The independent quantification was made by GC/MS using standards traceable to the National Institute of Standards and Technology (NIST).

In the Fall of 1993 we participated in two national proficiency audits that required the assay of a 27-component and a 32-component gas, also provided by ManTech. Since no other quantification standard was available, the independently certified values from the retention-time standard were employed to generate response factors. Two audits were performed on the OPS as part of this proficiency test. Results were disappointing with the percent error for the first audit ranging from -47.2% to +36.6%, while the second audit indicated errors of -64.6% to +40.2%. Results for most compounds in each of these checks were in the +/- 30% range.

Subsequent to these proficiency audits, ManTech supplied quantitation data on each of the compounds in the high-pressure, retention-time standard. When response factors were calculated using this set of data, the results of the first audit improved, with 17 compounds within +/- 10% and 21 compounds within +/- 25%. The second audit improved with all 32 compounds falling within the +/- 25% range and 20 of those compounds within +/- 10%. Two observations can be drawn from this experience: 1) current Auto-GCs can be operated to meet the prescribed +/- 25% accuracy requirement⁷ set by the U.S. EPA, and 2) properly prepared, stable quantitation standards must be readily available if Auto-GCs are to be successfully employed. GC accuracy is totally dependant on calibration standard accuracy.

It has been noted that the ManTech retention standard demonstrated severe attenuation of the heaviest compounds, beginning with ethylbenzene (in 16 of 18 runs). This behavior was intermittent as one analysis of the standard would show attenuation while the analysis immediately following might not (Figure 5). Potential causes for this attenuation are transfer-line adsorption of the heavier compounds, or pressure-regulator/sample introduction system contamination. Since the ManTech quantitation cylinder did not display this same phenomenon, an in-house contamination or technique problem is suspected. This situation will be closely monitored in 1994.

The procedure for determining a system's MDL recommended by the US EPA calls for replicate analyses of a range of low concentration standards⁷. However, this approach is problematical since single ppbc level standards containing a significant number of the PAMS-targeted compounds are not only expensive but may themselves also lack the requisite accuracy. MDLs in GC systems are considered to be a function of the system's signal to noise ratio and can be approximated by determining the area of typical noise peaks on a blank sample or series of blank samples.

A baseline analysis routine is available in Turbochrome, allowing the chromatographer to select a representative section of baseline, and determine a Noise Threshold (NT) and an Area Threshold (AT). Sections of baseline from ambient, calibration, and blank runs return similar results for recommended NT and AT values. Figure 3 illustrates a section of baseline, its parent chromatogram, and the NT and AT values returned by Turbochrome. The AT of 68 mV/sec correlates to a concentration of 0.034 ppbc for a response factor of 2000. Initially, in order to minimize the inclusion of "noise" peaks, the AT was set at 1000mV/sec which effectively screened out peaks equivalent to approximately 0.5 ppbc. The AT used in actual data collection falls well below the 1.0 ppbc MDL set by the U.S. EPA for C2-C10 compounds. Further review of the MDL is ongoing, with the possible result of utilizing a lower MDL (i.e., 0.1 ppbc) in the future.

Currently available retention standards lack the range of concentrations needed to make them truly useful. Standards with uniform (10-30ppbc) concentrations may assure operators that their systems are properly quantifying compounds only if there is absolute confidence that no problems exist with elution order, but this has not been the case. Three or more discrete concentrations or ranges should be used in future retention standards (e.g., 5-10ppbc, 20-30ppbc, and 50-60ppbc) with compounds 1,4,7,10... having the lowest concentrations, compounds 2,5,8,11... having middle concentrations, and 3,6,12... having the highest concentrations. Problems with misidentifying closely eluting compounds would be greatly reduced if the compounds occurred in the standard at sufficiently varied concentrations or, alternatively, were available in three separate standards. Reliable elution order identification, necessary for long-term, controlled analytical consistency, is a PAMS program element that needs improvement.

Determination of total method performance in Auto-GC systems is complicated by the presence of a variety of target compounds, use of multiple columns, and potential for loss due to leaks or inefficiencies in sample trapping. The standard for system performance has been "audit cylinder" samples prepared by third-party sources. These mixtures typically contain 25 to 50 compounds, at levels from 25ppbc to 40ppbc. Initially, the concentrations are not known by the chromatographer, as is typical in an audit scenario. Once evaluated, the results of the audit are returned to the chromatographer with the actual concentration values. As is the case with retention standards, audit mixtures have several shortcomings for system performance analysis: 1) the concentrations are similar throughout the mixture and, 2) the number of compounds is high. Performance of FID-based GC systems is based on detector linearity with respect to concentration. A calibration mixture with the proper range of concentrations for several of the targeted compounds could be devised such that its replicate analyses could provide both an assessment of system performance and assurance that MDLs were being met for a group of compounds. Such a mixture has been suggested and is being refined in a cooperative effort between several New England states and U.S. EPA Region I. The proposed mixture is as follows:

Ethylene	5ppbc
Propane	10ppbc
Isobutane	1ppbc
n-butane	10ppbc
Isopentane	20ppbc
n-pentane	10ppbc
Isoprene	5ppbc
2-methylpentane	5ppbc

2-methyl-1-pentene	5ppbc
n-hexane	20ppbc
Benzene	5ppbc
Toluene	20ppbc
m,p-xylene	10ppbc
n-nonane	1ppbc
1,2,4-trimethylbenzene	10ppbc
Undecane	5ppbc

These compounds cover the C2-C3, C5-C6, and C8-C11 groups at 1, 5, and 20ppbc concentrations. On the OPS, the first nine compounds elute on the PLOT column, while the last seven elute on the DB-1 column. Compound selection was made based on carbon number, availability in standardized concentrations (i.e. NIST), and utility as a retention time marker for relative retention time calculation.

As the performance audit program matures, goals and procedures will undoubtedly evolve to improve the data quality from Auto-GC systems. Additionally, it is expected that calibration procedures and retention time standards will evolve to serve more than a single purpose. For example, calibration standards should assist in the verification of peak identification, determine detector linearity, assess long-term stability and assist in gauging overall system precision.

CONCLUSIONS

Both of the automated gas chromatographic systems described in this comparative report can meet the U.S. EPA's enhanced monitoring requirements. They both possess adequate sensitivity to detect single part per billion carbon levels of the targeted compounds within the specified $\pm 25\%$ accuracy limits. Although we have not been able to satisfactorily examine the repeatability (precision) of these systems, primarily because adequate QA standards have only recently become available, it appears probable that they both can meet the requisite 20% relative standard deviation target.

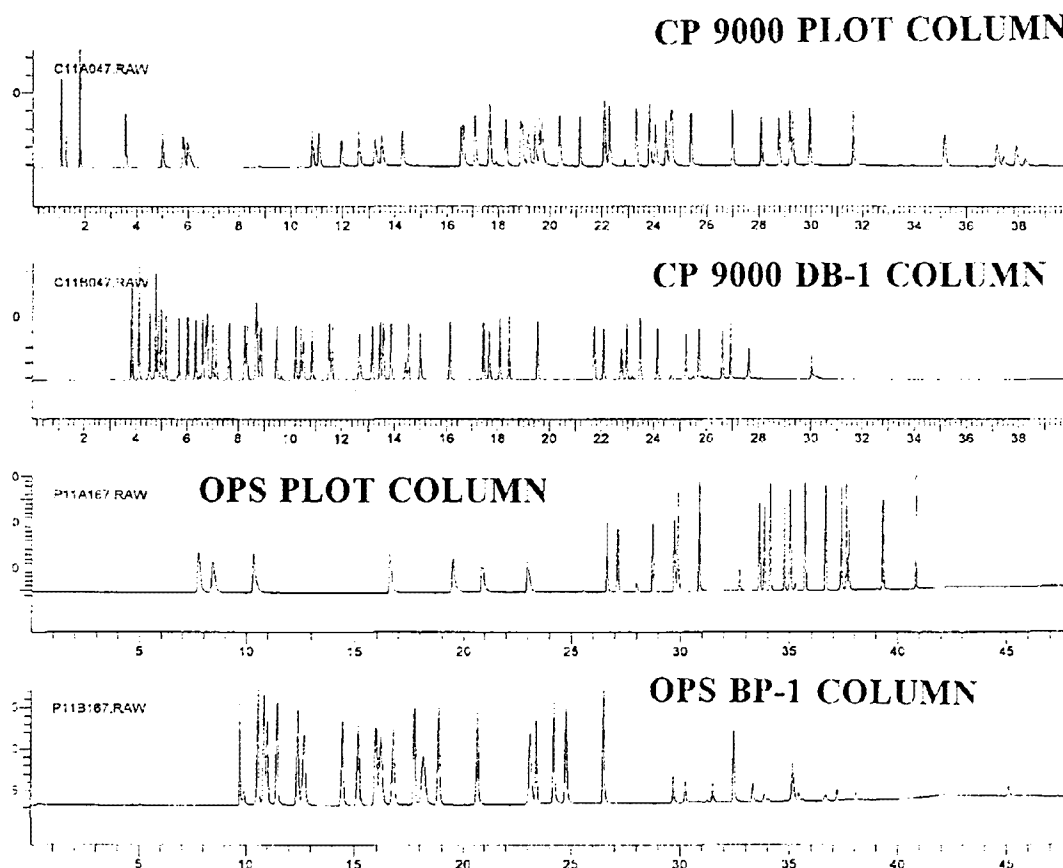
Hardware component reliability is sufficient to allow both systems to operate as continuous, near real-time monitors which can be successfully operated by state-level monitoring personnel. However, systems utilizing cryogenic fluids are more labor intensive and may be best suited for laboratory analysis of "canned" air samples. Non-cryogenic systems appear to be better suited for deployment at remote, unmanned stations.

Agencies endeavoring to construct Auto-GC networks should bear in mind the need to concurrently create reliable automated data telemetry systems of their own, since "turnkey" systems for this purpose do not currently exist. Note too, that labor and capital costs for telemetry and data analysis system development are not insignificant.

As Auto-GC technology matures, QA issues take on ever increasing importance. Hardware performance and system uniformity issues will be resolved in the very near future, but the quality of VOG data will be proportional to the quality of calibration standards available. It should be noted that since ozone is regional in nature, and precursor data will be required from a large network, operated by various agencies, the uniformity of QA standards will drive this network's data precision. It is incumbent upon the U.S. EPA to coordinate the supply of high quality, uniform QA standards for as long as the VOG network is operational. If this is not done, VOG data from various agencies in the enhanced monitoring program will not be comparable and, no matter what detection levels or accuracies are achieved individually, the data will have little regional validity/usefulness.

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**OPS and CP 9000 Chromatograms
From a 40-Component Calibration Standard**

FIGURE 1

2-Methylpentane CP9000 vs OPS - 7/93

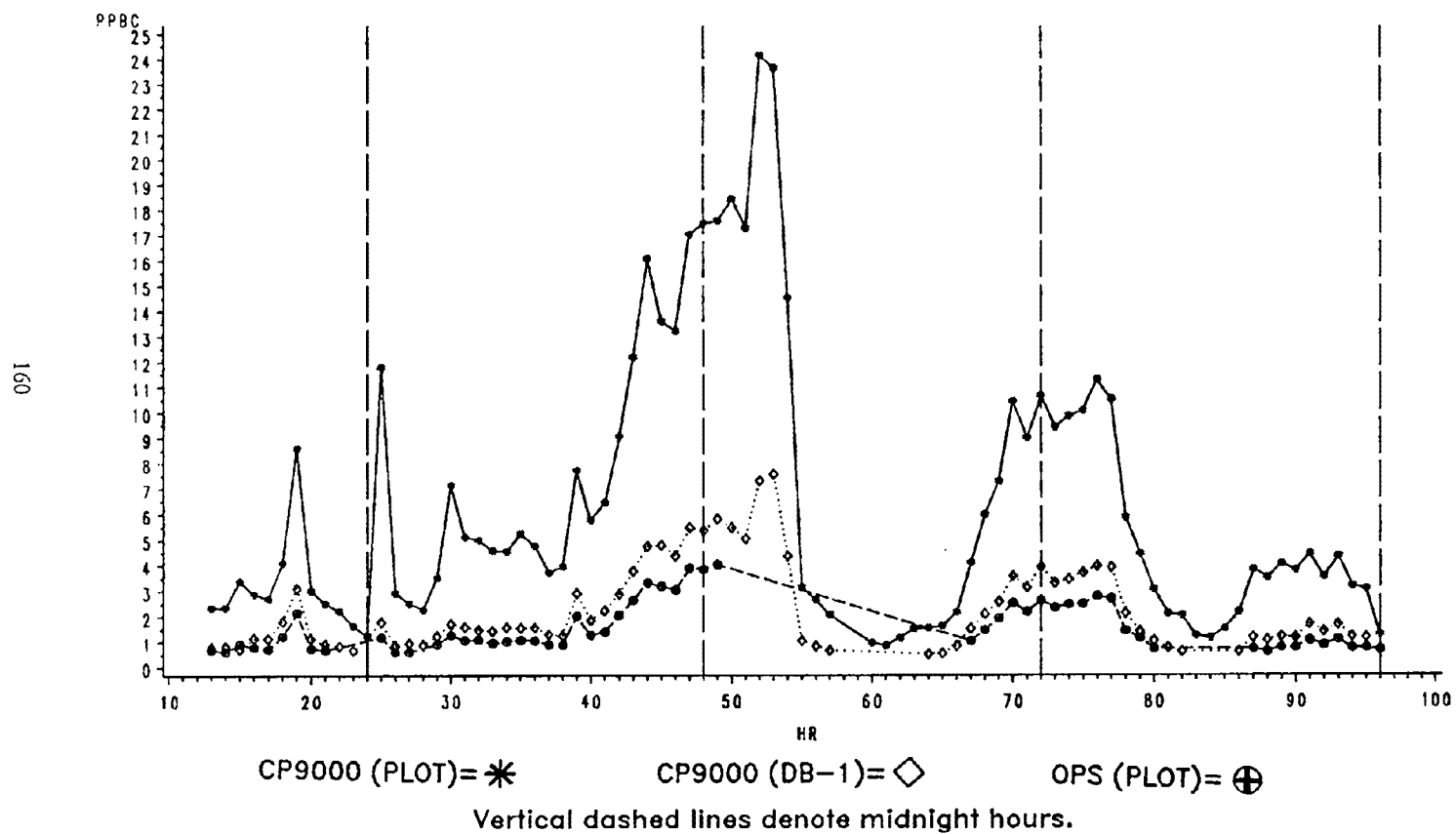
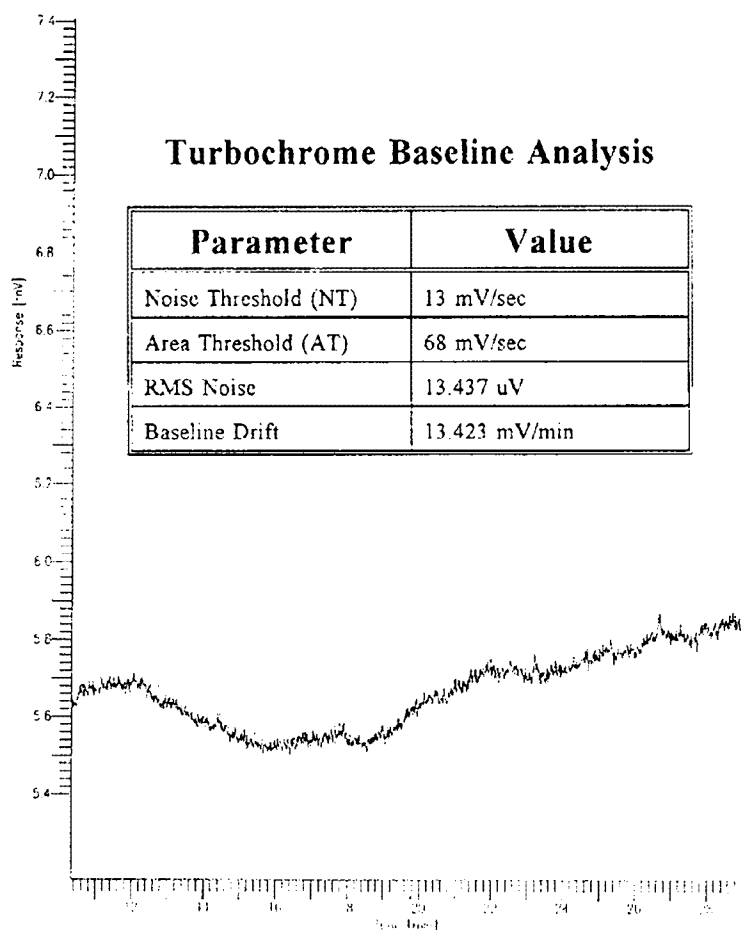
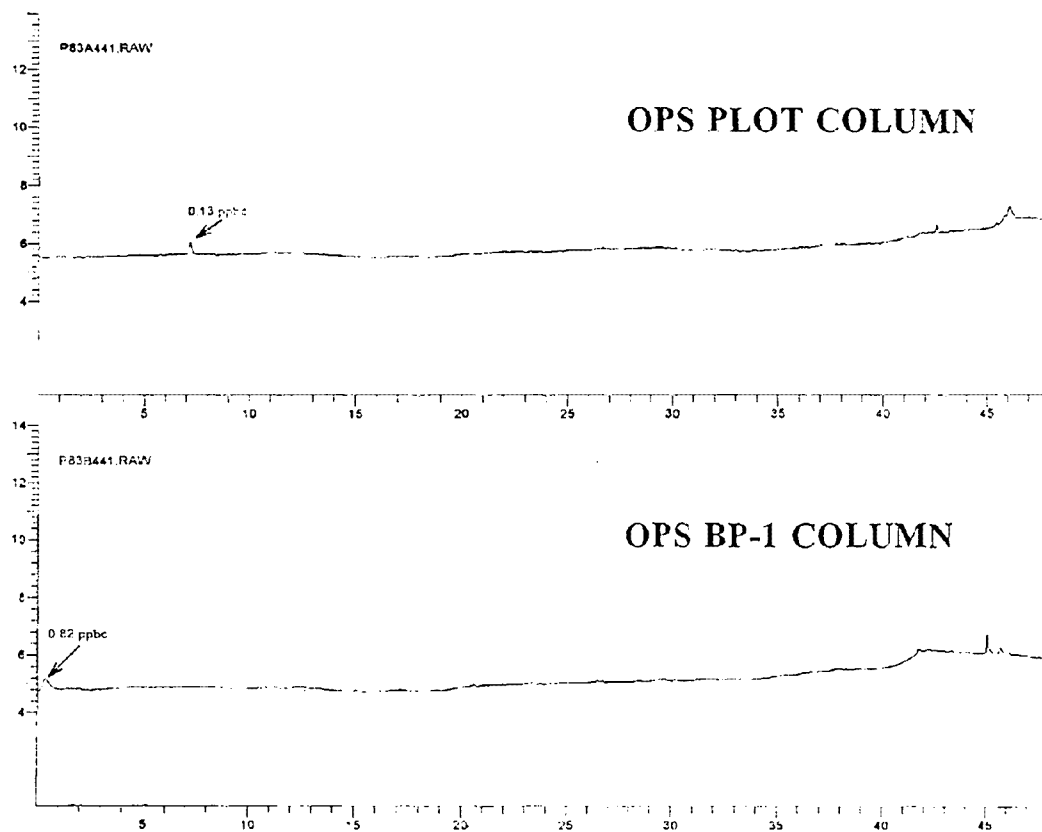


FIGURE 2



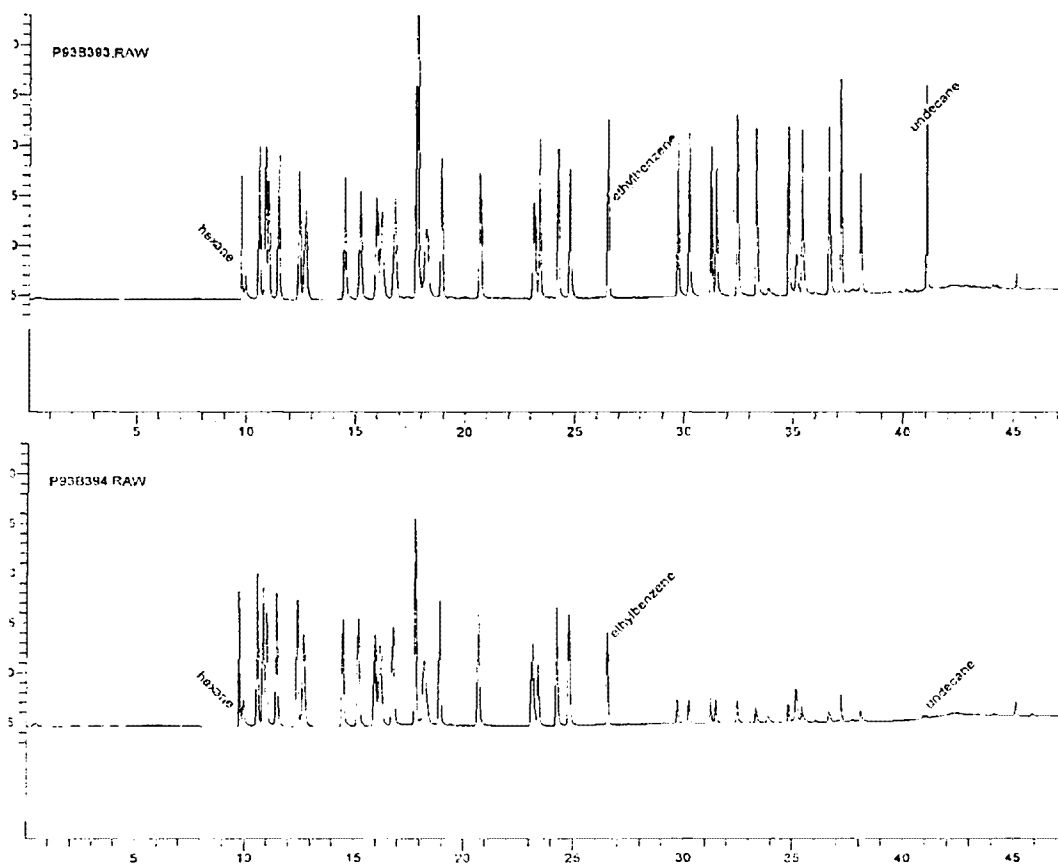
**Section of OPS PLOT Column Baseline
From a Blank Sample Analysis**

FIGURE 3



OPS Blank Run Chromatograms

FIGURE 4



**OPS DB-1 Column Peak Attenuation
Consecutive Calibration Runs**

FIGURE 5

Analysis Of Ozone Precursor Compounds In Houston, Texas Using Automated, Continuous Gas Chromatographs

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ABSTRACT

Over a period of nearly six months at two sites in Houston, Texas, automated continuous gas chromatographic (GC) systems collected one hour ambient air samples and analyzed them for the 55 U. S. Environmental Protection Agency (EPA) designated ozone precursor hydrocarbon compounds. A total of 6887 samples were collected and analyzed. During this study, rigorous quality assurance activities were instituted to maximize the quality of the data. Based on the results from these activities, preliminary estimates of combined accuracy for most of the 55 compounds fell within the 50-150 percent recovery or ± 50 percent difference range initially targeted. Precision for all but one of the compounds checked on a daily basis ranged from 8-21 percent relative standard deviation (%RSD). Data capture was 94-95 percent. An initial assessment was made on the ability of these GC systems to successfully analyze for the 55 ozone precursors.

INTRODUCTION

In the summer of 1993, the former Texas Air Control Board, now the Office of Air Quality of the Texas Natural Resource Conservation Commission (TNRCC) sponsored the Coastal Oxidant Assessment for Southeast Texas (COAST) study that had as its objective improvement of the technical basis for designing effective and cost-effective ozone control strategies for the upper gulf coast area of Texas. As plans for the COAST study began to develop, it was concluded that the acquisition of hourly speciated hydrocarbon measurements using automated, continuous GC systems could be an important component of the COAST study. Although observation of the EPA sponsored "shootout" involving five different automated continuous GC systems left the TNRCC staff with the impression that the participating systems needed further development before field deployment should be considered, the deadline for establishing Photochemical Assessment Monitoring Stations (PAMS) was fast approaching. PAMS type 2 sites (maximum ozone precursor emissions impact sites) require either the collection and analysis of eight 3-hour canister samples per day or the operation of continuous GC systems. Since the canister approach did not appear

to be feasible for TNRCC operations, automated continuous GC systems would have to be acquired for these sites.

The Perkin-Elmer (P/E) system was selected because it appeared to offer two distinct advantages for this work. First, the preconcentration (trapping) of the compounds of interest used a sorbent trap cooled by a Peltier device, thus eliminating the need for cryogenic liquids on-site. Second, a Dean's pressure switch permitted the utilization of two capillary columns for the more effective chromatographic separation of the C2 through C9 compounds. Therefore, as a part of COAST, two systems were subsequently contracted for purchase and deployment.

One system was sited in East Houston just north of the Houston ship channel downwind of fairly representative industrial and petrochemical emissions (designated Clinton Drive) and the other in the Galleria area of West Houston that is representative for heavy vehicular traffic emissions (designated Galleria). Sampling and analysis were performed for the 55 EPA designated ozone precursor compounds. For this project, the Radian Corporation in Austin purchased and deployed the systems. They also provided data and overall management for this project. Consolidated Sciences, Incorporated (CONSCI), located in Houston, handled all GC on-site activities.

INSTRUMENTAL

The P/E automated continuous GC system was composed of a modified P/E Model ATD 400 automatic thermal desorber, a P/E Model 8700 automatic GC equipped with dual flame ionization detectors (FID) and a PC-based chromatographic data handling system. The microprocessor-controlled ATD 400 trapped samples on an electrically cooled trap and thermal desorbed the samples directly onto the head of a GC column. The trap was composed of a 3 1/2"x 1/4" o.d. quartz tube packed with 60 mg of Carboxpack C and 44 mg of Carboxieve S3 solid adsorbent. A nafion® permeable membrane dryer upstream of the trap removed most of the moisture from the sample stream. Two capillary columns, a 50 m x .22 mm BP-1 (dimethylpolysiloxane) and a 50 m x .32 mm PLOT (Al₂O₃/Na₂SO₄) partitioned the sample components eluting to the FIDs. The columns acted in series until a Dean's pressure switch, inserted between the two columns to redirect the column carrier gas flows, was activated. At that point, column operation became parallel. The voltage output signals from the detectors were collected and processed by the 486 PC using P/E Nelson's Turbochrom 3, ver 3.2, chromatographic data handling software running under Microsoft's Windows environment. The entire system was integrated to provide a completely automatic sample collection cycle, gas chromatographic analysis and data collection and handling. A Balston Model 78-30 TOC air generator supplied hydrocarbon-free air for the FID, purge air for the Peltier cooler and a source of the daily control blanks. Several modifications were made to the original systems prior to their deployment. All sampling lines were heated. The zero air purge flow to the Peltier cooler was increased from 50 mL/min to 250 mL/min after sampling began to avoid frost buildup, which had been occurring on a regular basis.

OPERATION

Data collection at the two sites began June 18 and continued through November 30, 1993. Hourly ambient air sampling cycles, starting at the top of each hour, began with sample collection for 40 minutes on the sorbent tube held at -30°C. The sample flow rate was 15 mL/min. Helium (He) carrier gas was then directed through the tube in the reverse

direction and the tube ballistically heated to 325°C driving a portion of the sample onto the head of the BP-1 boiling point separation column (the remainder of the sample is discarded). As separation began on the BP-1 column, the sorbent tube was held at 325°C, purged with helium for 5 minutes and then cooled to -30°C to initiate the next sampling cycle.

During analysis the column oven temperature, initially held at 45°C for 15 minutes, was temperature-programmed at 5°C per minute to a temperature of 170°C then ramped at 15°C per min to 200°C and held for 6 minutes. At a predetermined time that would result in the elution of the low boiling point compounds through 1-hexene from the BP-1 column onto the PLOT column, the Dean's switch was activated to apply pressure to prevent the BP-1 carrier flow from entering the PLOT column instead diverting it to a second FID. An additional carrier gas flow was then provided for the PLOT column to complete the elution of the low boiling compounds to the first FID. Total analysis time for this scheme was approximate 48 minutes. Because the three units in the system were independently controlled by microprocessors and communicated only by indication of ready status signals, it became very important to closely monitor cycle timing in order to maintain sampling start times at the top of each hour.

The output signals from the FIDs were collected by the Turbochrom software which performed the initial analysis of the data based on parameters set by the operator. The processed data files were then stored along with the original raw chromatographic data files. Each system generated 96 data files and approximately 30 documentation files each day totaling nearly 3 megabytes of information. These files were electronically transferred to CONSCI's office in Houston where they were compressed for transfer to Radian in Austin. The compressed files were electronically transferred to a Radian computer on a nightly basis. At Radian, the files were decompressed and stored in a data base. The processed data files were manually reviewed based on "Quick Look" summary reports and, if necessary, reprocessed. A final review of the data for validation purposes completed the process. All of the contract operators and data managers involved in this project were both very knowledgeable and highly skilled in GC operations, VOC type analysis and data handling.

Detailed field operation, data transfer procedures and a description of the techniques and tools developed to process, verify, validate and transfer the collected data to the data base are provided in companion papers^{1,2,3}.

QUALITY ASSURANCE

Simultaneously with the data collection, a rigorous quality assurance/quality control (QA/QC) program based on the PAMS QA requirements promulgated in 40 CFR Part 58 on February 12, 1993, was implemented to ensure that the measurement data would be of the highest quality. Data quality objectives (DQO) for this operation were:

- Precision, ± 50 percent calculated as percent relative standard deviation
- Accuracy, 50-150 percent calculated as percent recovery or ± 50 percent calculated as percent difference
- Completeness, >80 percent (excluding daily calibration checks and blanks).

Routine QC efforts were used to continually evaluate system performance, as precision checks and to reduce the possibility of miss-identifying or not identifying target peaks. They also assisted in improving quantitation of these compounds. These efforts consisted of initial checkout and calibration of each system at the P/E Regional office followed by recalibration on-site. Initially, propane and toluene calibration response factors were used but a 12 component average response factor was developed in mid-July and used during the remainder of the study. A clean air blank and multicomponent (10-13 components) check standard were analyzed daily and a 55 component retention time standard was analyzed at least biweekly. In addition, cycle timing was closely monitored and adjusted for time slippage to keep the start of each sampling cycle at the top of the hour.

The QA activities included:

- 1) Generation of precision estimates using data from the multicomponent check standard analyses.
- 2) Conducting initial and final systems and performance audits
- 3) Participation in an interlaboratory comparison based on an EPA supplied 57 component standard.
- 4) Participation in an interlaboratory comparison based on collocated ambient canister samples.
- 5) Analysis of an EPA PAMS Proficiency Test sample.
- 6) Generation of accuracy estimates using data from the various QA activities.

The focus of the audits was a point-in-time assessment of the capabilities and potential limitation of the measurement systems in terms of 1) potential contribution of the measurement system to the measurement results, 2) quantitative performance at concentrations near the concentration for the target list compounds expected in the field operations, 3) qualitative and quantitative performance near the expected detection limits for the technology and, 4) quantitative performance for the target compounds in a potentially heavy interference situation (initial audit only).

The purpose of the 57 component and collocated interlaboratory comparisons, as well as the PAMS Proficiency Test, was to document systematic biases that may exist between laboratories and with the continuous GC systems so that such biases can be taken into account during the data analysis phase of the COAST Project. The main objective was to determine the consistency in the identification of hydrocarbon species, fraction of NMHC identified and concentrations for individual species and total NMHC.

RESULTS AND DISCUSSION

Precision estimates and percent mean recoveries for 10 of 11 standards in the QC mix (ethane, propane, butane, hexane, octane, 1-butene, benzene, toluene, ethylbenzene and n-propylbenzene), analyzed daily over the operating period are shown in Table 1. Precision appears to be relatively good for these compounds. For acetylene, both precision and percent mean recoveries are poor possibly due to instability of acetylene in the canisters.

For the initial performance audits conducted by Radian's QA staff, the GC systems were challenged with four humidified (67 percent relative humidity) samples consisting of an ultra high purity (UHP) air blank, a standard mixture of target compounds in UHP air, a previously well characterized ambient air sample and a spike of this sample. All of the audit samples were delivered at atmospheric pressure to the normal sampling port on the main system manifold.

The initial performance audit results at the Clinton Drive site indicated that the auto-identification of the respective compounds was very consistent, i. e., qualification averaged 85 percent. Recoveries generally ranged from 60-80 percent of theoretical. At the Galleria site, qualification averaged 93 percent while recoveries generally ranged from 90-150 percent of theoretical. Recoveries were low for β -pinene and the trimethylbenzenes (10-50 percent) at both sites. More current information suggests that both α - and β -pinene are converted to other compounds by the nafion® dryer and, therefore, have probably been miss-identified and miss-quantitated in this study. Beta-pinene, for example, is now reported to be converted to 1,2,4-trimethylbenzene, resulting in false or incorrect measurement of both compounds.

The final performance audits, conducted by TNRCC's QA staff, consisted of challenging the GC systems with two humidified samples similar to the first two in the initial audit (a well characterized ambient air sample was not available to the TNRCC for this audit). For the final performance audit, the Clinton Drive GC system correctly auto-identified 51 of 55 components and 51 had recoveries in the 50-150 percent range. At the Galleria site, all were correctly auto-identified and 51 had recoveries in the 50-150 percent range. Recoveries were low for acetylene (18 percent), isoprene (42 percent) and 1,2,4-trimethylbenzene (14-29 percent) at both sites, and for styrene (34 percent) at Clinton Drive and 2-methyl-1-pentene (14 percent) at Galleria. With these compounds, at issue may be the question of whether they are stable enough to reach the GC system or reach it chemically unchanged.

For the hydrocarbon interlaboratory comparison, the GC systems were challenged with an EPA supplied 57 component standard mixture, currently being used as a retention time calibration standard in the PAMS program. It contained the 55 compounds that are targeted for PAMS, plus decane and undecane, in 40 percent relative humidity air. This standard mixture was supplied to all the participating contractor laboratories. The standard mixture, initially analyzed by EPA, was also sent to Houston on August 18 where it was used to challenge the two continuous GC systems. Following its return to EPA, the standard mixture was analyzed a second time to determine its stability during the sample exchange.

Results of the analyses were in fairly good agreement with the mean of the EPA initial and final values. The relative mean differences for Clinton Drive and Galleria GCs were 8.7 percent and 2.2 percent respectively. However, the differences for individual species were highly variable and the standard deviation for Clinton Drive and Galleria were 22.4 percent and 14.9 percent respectively. The reason(s) for this will continue to be investigated. Both GCs measured substantially higher concentrations of isoprene and 2-methyl-2-butene and lower concentrations of 1,2,4-trimethylbenzene than reported by EPA. Both GCs reported concentrations of α -pinene and β -pinene while EPA found none present. At Clinton Drive, isopentane coeluted with cyclopentane while these compounds were separated at Galleria. The GCs did not analyze for decane and undecane since they are not ozone precursors.

For the collocated interlaboratory comparison, collocated ambient samples were simultaneously collected by each of three contractors at the Clinton site on August 18, 1993. Each contractor supplied their own sampler which was connected to a common manifold inside the sampling trailer. Three one-hour canister samples were collected by each participant beginning at 0700, 0900 and 1500 hours Central Daylight Time. After analysis by the individual laboratories, the samples were sent to EPA for analysis. After analysis the samples were returned to the four laboratories for reanalysis. These data were compared to data from the automated GC at the Clinton site for the same hourly periods.

Comparison of results for a number of representative compounds from EPA's analysis of the three sets of one-hour canister samples versus the Clinton Drive GC data for those hours are displayed in Table 2. The GC values were in reasonably good agreement with mean EPA values for these individual species from each canister sample collected for the given hour. The mean relative differences for all species with mean EPA values above 2 ppbC were -20.8 percent, -28.3 percent and -18.4 percent for the 0700, 0900 and 1500 hour samples respectively.

The GC systems were also challenged with an EPA PAMS Hydrocarbon Proficiency Test sample containing 27 components in dry air.

The summary data supplied by the EPA for the PAMS Proficiency Test sample contained the reference values and the mean of analyses from the participating laboratories. The percent differences between these results and those obtained from the two GC sites for eight of the 27 components in the test sample plus the average percent differences for all of the 27 components are presented in Table 3. The DQO for accuracy was met for all the compounds except for 3-methyl-1-butene (-93 percent and -95 percent) at both sites.

CONCLUSIONS

In general, both GC systems performed very well. While a number of significant problems were discovered during both the startup and the operation of these GC systems, most of these were eventually resolved satisfactorily. Data collection averaged above 90 percent for the entire period. The auto-identification component of the GC data analysis software appeared to function properly and the accuracy and precision DQOs for most of the 55 target compounds were met or exceeded. It is our judgment that these systems are capable of producing good quality data in the hands of knowledgeable and highly skilled personnel (however, will they when handled by less knowledgeable and skilled personnel?). Three of the 55 ozone precursor compounds (α -pinene, β -pinene and 1,2,4-trimethylbenzene) can not be accurately analyzed by this system when the nafion® dryer is employed. This problem must be resolved if the EPA requirement for the analysis of all 55 compounds is to be met with this system. The coelution of isopentane with cyclopentane from the GC system at the Clinton Drive site must also be addressed, possibly by replacing one or both capillary columns.

TNRCC oversight of contractor installation, optimization and operation of these systems has proved to be a valuable source of information for the future establishment of these systems at PAMS type 2 sites in Texas.

ACKNOWLEDGMENTS

I would like to acknowledge the support and assistance of Carol Meyer of CONSCI, Eric Fujita of Desert Research Institute, Ian Seeley of the Perkin-Elmer Corporation and especially Ken Rozacky, who was a part of the Radian QA staff during the initial portion of the COAST Study and is now a member of the TNRCC QA staff.

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Table 1
COLOCATED CANISTER VS CLINTON DRIVE CONT. GC RESULTS.

Percent Differences Based On EPA Mean Canister Values.			
	0700 Hrs	0900 Hrs	1500 Hrs
	% Diff	% Diff	% Diff
Ethane	23.4	18.6	6.7
Ethylene	-14.7	-15.9	26.9
Acetylene	-14.0	-33.9	-36.6
n-Pentane	17.6	20.5	19.0
i-Pentane	19.8	-2.3	16.2
Benzene	-30.3	-31.9	-24.4
Toluene	-13.6	-15.5	-5.4
m,p-Xylene	4.4	-2.0	7.5
Isoprene	-33.3	-18.9	1.6
1,2,4-Trimethylbenzene	-80.0	-95.2	-83.3
Mean (All cpds with EPA Values ≥ 2 ppbC)	-20.8	-28.3	-18.4

$$\% \text{ Diff} = (GC - EPA) / EPA * 100$$

Table 2
DAILY CHECK STANDARDS.

Mean Recoveries (MR) and Relative Standard Deviations (RSD).

	Clinton Drive		Galleria	
	% MR	% RSD	% MR	% RSD
Ethane	108.8	12.7	88.4	12.3
Propane	118.8	14.9	109.0	13.7
Butane	116.3	11.9	107.1	10.0
Hexane	108.1	11.9	103.0	7.9
Octane	104.5	13.1	104.0	12.2
Acetylene	44.9	79.6	35.1	93.1
1-Butene	82.3	14.4	84.9	14.4
Benzene	100.8	11.7	96.4	12.1
Toluene	94.8	12.9	93.1	9.9
Ethylbenzene	88.3	15.8	95.5	12.2
n-Propylbenzene	70.9	21.5	83.2	12.7

Table 3
PAMS PROFICIENCY TEST PF930701.

	Clinton Drive		Galleria	
	%Diff vs Referee	%Diff vs Mean of Labs	%Diff vs Referee	%Diff vs Mean of Labs
Ethylene	9.7	19.8	-26.2	-19.4
Propane	4.8	17.6	-12.2	-1.5
1-Butene	-26.5	-20.5	-30.2	-24.5
1-Pentene	24.2	31.1	10.6	-5.7
Isoprene	-12.1	-2.9	-20.6	-12.3
Ethylbenzene	-4.3	-10.9	12.4	4.6
m+p-Xylene	-6.1	-19.7	13.7	-2.7
o-Xylene	1.5	-12.6	16.1	0.0
Average (27 components)	-2.3	0.0	-9.6	-8.8

**Interlaboratory Comparison for Analysis of Hydrocarbons
During the Coastal Oxidant Assessment for Southeast Texas (COAST) Project**

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ABSTRACT

An interlaboratory comparison study was conducted during the Coastal Oxidant Assessment for Southeast Texas (COAST) project for measurement of ambient hydrocarbons in order to document potential systematic biases among participating laboratories. The study consisted of two reference samples, an EPA standard mixture and an archived ambient sample from Atlanta, and three ambient samples collected during the field study by each of the three contractors at the same location and periods. The collocated ambient samples were analyzed by the contracting laboratory and by the Environmental Protection Agency Atmospheric Research and Exposure Assessment Laboratory, which served as the referee laboratory. This paper describes the study protocol, and reports differences among laboratories in compound identification, fraction identified, and concentrations for individual and total hydrocarbons.

INTRODUCTION

In the summer of 1993, a field measurement program was carried out in the Houston-Port Arthur area as part of the Coastal Oxidant Assessment for Southeast Texas (COAST) project. The purpose of the COAST project is to develop a comprehensive air quality and meteorological database for the Southeast Texas which can be used to enhance the understanding of the relationship between emissions and spatial and temporal distributions of pollutants so that air quality simulation models, and ultimately, air quality management strategies can be improved.

An important part of the COAST Project is the acquisition of high quality, ground level and aloft speciated hydrocarbon data. Up to six one-hour ground-level canisters samples were collected on intensive study days at five sites in Houston and one site in Port Arthur, and analyzed for C_2 to C_{12} hydrocarbon compounds by Laboratory C. Canister samples were collected aloft, and analyzed for C_2 to C_{10} hydrocarbons by Laboratory B. Hourly speciated hydrocarbon measurements were also made at the Clinton and Galleria sampling sites using automated gas chromatographs. Because hydrocarbon speciation measurements were made by three separate contractors, an interlaboratory comparison was conducted as part of the quality assurance program for the COAST Project to document significant systematic biases that may exist among participating laboratories. Besides measurements made specifically for the COAST study, the intercomparison study also included sampling and analytical methods that are currently used by Laboratory D and Laboratory A to routinely monitor ozone precursors and toxic air pollutants. The specific objectives of the interlaboratory comparison study were to determine the consistency among laboratories in the identification of hydrocarbon species, fraction of nonmethane hydrocarbons (NMHC) identified, and concentrations for individual species and total NMHC. Additionally, sample stability and potential for sampling artifacts were examined.

EXPERIMENTAL

The laboratory intercomparison consisted of two reference samples: a standard mixture supplied by the Environmental Protection Agency and an ambient sample from Atlanta which was collected by the U. S. Environmental Protection Agency (EPA) and archived by Oregon Graduate Institute of Science and Technology (OGI); and three one-hour ambient samples collected simultaneously by each of the three contractors at the same time and location. The comparison samples were analyzed by the respective contracting laboratory and by the EPA's Atmospheric Research and Exposure Assessment Laboratory (AREAL), which served as the reference laboratory.

The EPA standard mixture is currently being used as a retention time calibration standard in the Photochemical Assessment Monitoring Station (PAMS) program. It contains the 55 compounds that are targeted for PAMS, plus decane and undecane, in approximately the same concentration for each compound. Four aliquots of the PAMS mixture were transferred from the main storage cylinder into four separate 6-liter stainless steel canisters, first by filling the canisters with zero humidified air up to 10 psi, then by adding the PAMS mixture up to a final pressure of 25 psi. Total hydrocarbon concentration did not vary among the four samples by more than 5 percent. The four calibration samples were analyzed by EPA, then distributed simultaneously to each of the four participating laboratories. The PAMS sample

labeled COAST4 was also analyzed by the automated gas chromatograph at both the Clinton (Auto-GC1) and Galleria sites (Auto-GC2). Upon their return, the calibration samples were analyzed a second time by EPA to determine the stability of the mixture during the sample exchange.

The archived ambient sample from Atlanta was originally collected in seven 32-L tanks by EPA in September 1992. The samples were composited into one master tank (350 psig) by OGI and divided into three 15-L tanks. One 15-L tank (SPO-6) at 65 psig was sent to AREAL for analysis and distribution to the other participants in the interlaboratory comparison. The sample was then sent to each participating laboratory in round-robin fashion in the following order: B, EPA, C, A, D, and EPA (second analysis).

The collocated ambient samples were collected simultaneously by each of the three contractors at the Clinton site on August 18, 1993. Each contractor supplied their own sampler which was connected to a common manifold inside the sampling trailer. Under the supervision of the quality assurance contractor (AcroVironment), three one-hour canister samples were collected by each participant beginning at 0700, 0900 and 1500 (EDT). The samples were first sent to the respective analytical laboratories. After analysis by the individual laboratories, the samples were sent to EPA for analysis. After analysis by EPA, the samples were returned to the four laboratories for reanalysis. Data from the automated gas chromatograph at the Clinton site were also submitted for the same hourly period as during collocated sampling.

All data were submitted to the Desert Research Institute for compilation and analysis. Each laboratory was requested to submit copies of chromatograms and data report (species identification, retention times, individual species concentrations in ppbC, total identified and total unidentified). The total concentration of identified and unidentified hydrocarbons that is reported by different laboratories for the same sample depends on the particular requirements of the sponsor which determine how the chromatographic data are obtained and processed. Rather than specifying a list of compounds to be reported, each laboratory was requested to report those hydrocarbon species and total concentrations that are required by their respective contracts. The following are the project-specific measurement objectives for each laboratory.

EPA (Ref. Lab)	Speciation of C ₂ to C ₁₂ hydrocarbons, total NMHC and total unidentified.
Laboratory A:	Nineteen toxic air pollutants, of which six are hydrocarbons.
Laboratory B:	Speciation of C ₂ to C ₁₂ hydrocarbons, total NMHC and total unidentified.
Laboratory C:	Speciation of C ₂ to C ₁₂ hydrocarbons, total NMHC and total unidentified.
Laboratory D:	55 PAMS compounds and total NMOC up to 1,2,4-trimethylbenzene.
Automated GC	55 PAMS compounds and total NMOC up to 1,2,4-trimethylbenzene.

Analytical Methods

Several similarities exist in the analytical systems and procedures used by the five laboratories. All groups, except laboratory A, employed commercial gas chromatographic systems equipped with flame ionization detectors (GC-FID), a cryogenic concentration step, and computerized data acquisition systems. Table 1 summarizes the gas chromatographic methods and conditions employed by the five study participants. EPA, laboratory B and laboratory D used essentially the same chromatographic methods. The light-end (C₂ and C₃) hydrocarbons were analyzed separately using a packed column, and hydrocarbons larger than C₃ were resolved on a 60-meter by 0.25 or 0.32 mm ID DB-1 capillary column. The three laboratories also use similar temperature programs. Laboratory C used a 100-m by 0.25 mm ID Petrocol DH capillary column for the entire range of C₂-C₁₂ hydrocarbons. The use of a narrow bore column reduces the column capacity, and appropriate precautions were taken by Laboratory C to avoid introducing excess water which can affect peak resolution in the light hydrocarbon region of the chromatogram. Otherwise, the gas chromatographic methods employed by laboratory C are comparable to the other three laboratories. Laboratory A used an ENTECH M-2000 cryogenic sampler for sample concentration and delivery, a DB-624 capillary column for chromatographic separation and an ion trap detector for quantitation.

Automated, semi-continuous hydrocarbon speciation was performed using a Perkin Elmer ATD 400 concentrator coupled to a Perkin Elmer 5700 gas chromatograph. In this arrangement, ambient samples are collected each hour over a 40-minute period on a sorbent trap of Carbotrap C and Carbosieve S III. The desorbed sample first goes onto a narrow bore BP-1 methyl silicone column. Lighter compounds are allowed to migrate through the BP-1 column onto an aluminum oxide and sodium sulfate PLOT column for separation. The BP-1 column effluent is switched from the PLOT column to a restrictor and a second FID detector immediately before the elution of hexane. Both columns are then eluted into separate FID to detect the compound of interest.

Procedures used for instrument calibration varied among the groups. For calibration of the FID, EPA used propane and laboratory C used propane for C_2 to C_4 hydrocarbons and hexane for greater than C_4 , while laboratory D used specific response factors for 63 compounds. The automated gas chromatograph was calibrated against the average response of ethane, propane, butane and 1-butene for hydrocarbons eluting before hexane and against the average response of hexane, benzene, toluene, ethylbenzene and octane for all other targeted hydrocarbons. The systematic biases resulting from variations in FID response among different calibration gases are typically less than 5 percent. The groups mentioned above calibrated their chromatographs in volume concentration units (area response/ppbC). In contrast, the calibration by laboratory B is in terms of mass (area response/ng) of neohexane, which is used as an internal standard in each sample. For comparative purposes, Laboratory B converted their hydrocarbon concentrations from $\mu\text{g}/\text{m}^3$ units to ppbC. A problem exists in selecting the most suitable conversion factor(s). For a fixed volume concentration (ppbC) the mass concentration $\mu\text{g}/\text{m}^3$ will vary from hydrocarbon to hydrocarbon because the molecular weight/number of carbon atoms ratio is not constant for all hydrocarbons. At 1 atm pressure and 25 °C, the ($\mu\text{g}/\text{m}^3$) to ppbC conversion factor for methane is 1.5 and 1.88 for benzene. The conversion factor for propane (1.67) was selected by Laboratory B. If conversion factors specific to each hydrocarbon are employed instead, the corresponding concentrations will be up to 5 percent higher for alkane, 5 to 10 percent higher for alkenes and cycloalkane, and 10 to 15 percent higher for aromatic hydrocarbons.

Besides selection of the endpoint of the gas chromatographic run, the primary factors that can affect total measured concentrations include selection of threshold levels for peak integration and losses during cryogenic concentration/desorption and surface adsorption within the inlet system.

RESULTS

EPA PAMS Retention Time Calibration Standard. The PAMS retention time calibration standard contains the 57 hydrocarbon species listed in Table 2. The table also lists several other compounds that were reported by one or more of the laboratories (labeled Xn). Before comparing each laboratory's results with those of EPA, EPA's initial and final analyses of the four PAMS calibration standards (COAST 2, 3 and 4) were compared to determined variations among the PAMS samples and storage stability. The composition of COAST 2 and 3 were very similar. In both samples, concentrations of 2-methyl-1-pentene, α -pinene and β -pinene were at or near zero. Instead of 2-methyl-1-pentene, 2-methyl-2-pentene (identified by EPA by mass spectra and retention time estimates) appeared in both COAST 2 and 3 in concentrations nearly equivalent to the amount of 2-methyl-1-pentene originally in the PAMS sample. Surface-assisted rearrangement is the most reasonable explanation according to EPA. Additionally, the concentrations of isoprene, 2-methyl-2-butene and styrene were lower than other PAMS compounds which may indicate some loss of these compounds as well. Besides the apparent loss of 2-methyl-1-pentene, α -pinene and β -pinene, COAST 4 shows nearly complete loss of isoprene, 2-methyl-2-butene and 2-methyl-2-pentene (much greater than in COAST 2 and 3). Repeat analysis of the COAST 3 and COAST 4 PAMS samples over a two to three month period shows that the samples remained essentially unchanged. Therefore, the differences between the COAST samples probably occurred during or soon after the samples were transferred from the main storage tank.

Results for analysis of PAMS standard by each of the laboratories (normalized to the average concentration of the four PAMS samples) are summarized in Tables 1. Compounds that exhibited loss over time or were inconsistently identified by one or more of the laboratories were excluded for the purposes of establishing mean biases. The 43 compounds included in calculating the mean bias are indicated by asterisks in Table 2. For the four stable compounds reported by Laboratory A, the relative differences, $(\text{Lab } x - \text{EPA})/\text{EPA}$, between EPA and Laboratory A range from -16 to +18 percent, with a mean relative difference of $0 \pm 12\%$. The concentrations for COAST2 reported by laboratory B are consistently lower than EPA's values with a mean relative difference of $-17 \pm 2.8\%$. The low standard deviation indicates that the differences between Laboratory B and EPA are probably due to a systematic calibration bias. The magnitudes of the differences are still marginally within the overall measurement uncertainty of $\pm 20\%$. Each laboratory reported two compounds not reported by the other (2-methyl-2-pentene and cis-2-hexene for EPA and trans-4-methyl-2-pentene and cis-3-hexene for Laboratory B). Peak identifications need to be confirmed for these compounds since all four compounds elute within the same region of the chromatogram. The analysis of COAST3 by laboratory C also yielded consistently lower values than EPA's with a mean relative difference of $-15 \pm 6.9\%$. The consistent bias between Laboratory C and EPA is nearly identical to the bias observed between laboratory B and EPA. Therefore analysis by Laboratory B and C should, for the most part, agree well. The differences for three of the compounds, ethylene (-72%), acetylene (-39.7%) and undecane (-58.6%), exceeded 3 times the standard deviation. Laboratory C did not report 4-methyl-1-pentene, and reported two additional compounds, p-ethyltoluene and 1,2,3-trimethylbenzene. On average, the analysis of COAST4 by Laboratory D is in good agreement with values reported by EPA. The mean difference is $-5 \pm 8.4\%$. Because laboratory D used individual species-specific FID response factors rather than an average factor, there is greater variability in the bias for individual species than the previous two comparisons. A small peak of about 2 ppbC was identified by EPA as 2-methyl-2-pentene, while Laboratory D identified the peak as 2-methyl-1-pentene. Laboratory D also reported α -pinene (1.6 ppbC), β -pinene (1.1 ppbC) and 1,2,3-trimethylbenzene (3.9 ppbC), while EPA did not report the presence of these compounds in the sample.

Analyses of the COAST 4 samples by the automated gas chromatograph at the Galleria site (Auto-GC2) were in good agreement with EPA (mean relative differences of $0 \pm 11\%$). Measurements by the automated gas chromatograph at the Clinton site were, on average, 9 percent higher than EPA with a larger standard deviation of 18.5 percent. Much of the discrepancy is confined to a section of the chromatogram from 3-methyl-1-butene to 3-methylpentane. Concentrations for the ten compounds that elute within these two peaks average about 40 percent higher than EPA's values. Excluding these ten compounds, the mean bias is $0 \pm 10\%$. In addition, isopentane coelutes with cyclopentane within this region of the chromatogram for Auto-GC1. Both auto-GCs reported α -pinene and β -pinene while EPA reported none.

Archived Ambient Sample from Atlanta. Like the PAMS sample, the purpose of this sample is to evaluate the comparability of analytical systems used by each of the laboratories. The greater number of compounds in the ambient sample and wider range of concentrations, especially near the detection limit, provides more detailed evaluation of instrument sensitivity. Table 3 shows the individual and total concentrations measured by each laboratory for the fifteen most abundant species and ratios of the total to EPA's value. The means of the ratios for each species and standard deviations are also shown. Totals are also shown for the 55 PAMS species, other identified C_2 - C_{12} hydrocarbons, total unidentified, total C_2 - C_{12} hydrocarbons, identified $>\text{C}_{12}$ - C_{12} hydrocarbons, and total C_2 - C_{12} hydrocarbons. EPA's data also include peaks that are identified by carbon number and compound type (i.e., paraffin, olefin, or aromatic). EPA's "generic" identifications are based upon the chemical scrubber technique developed by Klosterman and Sigshy (ES&T, Vol. I, p. 309, 1967) and some confirmation by gas chromatography/mass spectrometry.

The results for Laboratory A, B and D are generally consistent with the analysis of the PAMS sample. Mean ratios to EPA for the fifteen most abundant compounds are 0.84 ± 0.08 for Laboratory A (3 species), 0.88 ± 0.13 for laboratory B, and 0.87 ± 0.26 for Laboratory D. Similar ratios were also obtained by Laboratory B and D for totals of the PAMS and C_2 - C_{10} hydrocarbons. While Laboratory C showed a negative bias relative to EPA for the PAMS sample, the concentrations reported for the Atlanta sample was, on average, 34 percent higher than the corresponding values obtained by EPA. Laboratory C's bias was less for total of the 55 PAMS compounds (+ 21.5%), considerably less for total C_2 - C_{10} hydrocarbons (+ 3.7%), and negative for total C_2 - C_{12} hydrocarbons (- 6.8%). This trend indicates that Laboratory C underreported the concentrations for larger hydrocarbons relative to EPA by 28 percent. Differences were also large for the light hydrocarbons as well due to poor peak resolution at the C_2 portion of the chromatogram. Laboratory C reported that 400 ml of sample was loaded instead of the normal volume of 100 to 200ml, resulting in excess water in the column that affected peak resolution for the C_2 compounds.

Collocated Samples from the Clinton Site. The analysis of collocated ambient samples by each of the laboratories and the corresponding analysis by EPA is summarized for the 0700 CDT sample in Table 4. The summary statistics in Table 3 are also shown in Table 4. Comparisons are appropriate to the project-specific measurement objectives of each laboratory. The biases that were observed for the analysis of the PAMS retention time calibration samples are also evident in the analysis of the collocated ambient samples. The mean ratios of each laboratory's values to that of EPA's for the nineteen most abundant species are 1.02 ± 0.22 , 0.90 ± 0.11 , 0.86 ± 0.14 , and 0.79 ± 0.17 for laboratory A, B, C and D, respectively and 0.88 ± 0.26 for the auto-GC. These ratios are similar to those based on a broader comparison of the total concentration of the 55 PAMS species.

For laboratory B and C, comparisons based on the total concentration of all identified C_2 - C_{10} (up to n-decane) hydrocarbons (including EPA's generically identified hydrocarbons) produced more variable results. The corresponding ratios are 0.71 and 0.56 for laboratory B and C, respectively. Allowing for consistent biases in the measurements, the distributions obtained by each laboratory for total concentrations of identified hydrocarbon by carbon number are similar to EPA's distribution up to 8 carbon atoms. Beyond C_8 , there is a significant drop in the concentrations of identified compounds reported by all laboratories. While the discrepancy between Laboratory B and EPA can be explained by the greater unidentified fraction reported by Laboratory B (41%), Laboratory C reported only 8% unidentified, which was a smaller fraction than reported by EPA. The original chromatographic data were subsequently reprocessed by Laboratory C using a different peak integration threshold value (-2 instead of 0 on the HP ChemStation). As a result, the number of measurable peaks increased from 63 to 188. The total concentration of unidentified hydrocarbons increased from 19 to 172 ppbC, and total NMHC increase from 251 to 426 ppbC (bias relative to EPA for the reintegrated data is 0.76).

Evaluation of Sampling Artifacts. The cleanliness of canisters and sampling systems is essential for accurate hydrocarbon measurements. Though the cleanliness of canisters and samplers is not specifically addressed in this intercomparison, examination of collocated ambient samples provides some indication of the potential for sampling artifacts. Since collocated samples were collected by each group through a common manifold, compositional differences among collocated samples (based upon EPA's analysis of the samples) are probably due to the sampling system. EPA's analysis of the collocated ambient samples for the 0700 sampling periods is presented in Tables 4. The table also includes mean concentrations for each species and coefficients of variation among the collocated samples. Uniformly low CVs indicate that the samples were not significantly affected by the sampling system for the more abundant species.

The coefficient of variations for identified species with concentration above 5 ppbC are generally less than 10% for 0700 samples. While sums of the concentrations of all identified peaks are in good agreement for the four collocated 0700 samples (CV of less than 3 percent), sums of the generically identified peaks are more variable (251, 116, 178 and 126 ppbC for laboratory A, B, C and D,

respectively). Most of these compounds are higher molecular weight hydrocarbons in the range of C_9 to C_{12} . These compounds are more likely to adsorb onto the internal surfaces of the canisters. Release of adsorbed material in subsequent samples depends upon a number of factors, including level of past exposure, canister cleaning procedure, moisture content, and canister pressure. Relative to the sample from Laboratory B (lowest total C_2 - C_{12} hydrocarbons), samples from Laboratory A, C and D were 52, 33 and 14 percent higher, respectively. These data suggest that the canister and/or sampling system employed by laboratory A and C were not as clean as those used by Laboratory B and D.

CONCLUSIONS

Because of wide variations in analytical methods and operating conditions, the normal accuracy determination procedures cannot be applied to measurement of ambient hydrocarbon levels. Therefore an interlaboratory comparison is an essential component of quality assurance for field studies involving ambient hydrocarbon measurements.

While all of the laboratories had little difficulty identifying the major peaks that are commonly found in urban air samples, discrepancies exist for isomers such as 2-methyl-1-pentene and 2-methyl-2-pentene, cis-2-hexene and cis-3-hexene, and many of the higher molecular-weight species (C_8 and higher) such as α and β -pinene. Four laboratories using the same analytical method, but with differing procedures, and two automated gas chromatographs showed an average coefficient of variation of 12 percent (based on analysis of the PAMS sample). The coefficient of variation for concentrations less than 5 ppbC are substantially higher, particularly for greater than C_8 hydrocarbons. Results of the interlaboratory comparison showed that these compounds are significant contributors to total hydrocarbon concentrations in the Houston area. Cleanliness of the sampling system and selection of the peak integration threshold are important factors in the total measured concentration of hydrocarbons. Losses during cryogenic concentration/desorption and surface adsorption within the inlet system are other important factors that were not assessed in this interlaboratory comparison.

Table 1
Summary of Gas Chromatographic Methods and Conditions Utilized by Study Participants

Parameter	EPA (Reference Lab)	Laboratory A	Laboratory B	Laboratory C	Laboratory D	Automated GC
Canister Cleaning	Not applicable for this intercomparison	Evacuate to <29.5 psig, filled with nitrogen to <15 psig, and analyzed.	Evacuate to <0.1 torr vacuum at 125 C for 3 hours. Accept if <0.2 ppbC per hydrocarbon peak.	Evacuate to 0.01 torr vacuum at 120 C for 4 hours. Analyze 10% by T0-T2. Accept if <20 ppbC.	Series of humid and dry pressurizations and evacuations in heated oven, over 4-hour period. Analyze by T0-T2. Accept if <0 ppbC.	Not applicable
Separate C2-C3 Analysis	J&W Scientific GSQ, 30m x 0.53 mm ID. Initial 40 C held for 4 min, ramp up at 10 C/min to 200 C (5 min. hold).		HP 5790/FID, isothermal 45 C sample freeport 150-100cmL, packed column or phenylsilyonate/Parasil C.	No	J&W Scientific GSQ, 30m x 0.53 mm ID. Initial 50 C held for 2 min, ramp up at 4 C/min to 85C then 25 C/min to 220 C.	No
Target Species	Individual and "generic" C4-C13 hydrocarbons, total NMHC & unidentified HC	six hydrocarbon TACs	Individual C4-C10 hydrocarbons, total NMHC & unidentified HC	Individual C2-C10 hydrocarbons, total NMHC & unidentified HC	C4-C10 (55 compounds plus total NMHC & unidentified)	PAMS species + total
Gas Chromatograph	HP 5890A	Varian 3400	HP 5890A	HP 5890	HP 5890	Perkin Elmer 5700
Detector	HP 5890 FID	Saturn II MS ion trap	HP 5890 FID	HP 5890 FID	HP 5890 FID	Dual FID
Nelson Dryer	No	No	No	No	No	Yes
Column	J&W Scientific DB 1, 50m x 0.32 mm ID x 1 um	DB 624 capillary column	J&W Scientific DB 1, 50m x 0.25 mm ID x 1 um	Supelco Petrocol DH 100m x 0.25 mm ID x 0.5 um	J&W Scientific DB 1, 60m x 0.32 mm ID x 1 um	Dual column: BP 1 methyl silicone and aluminum oxide and sodium sulfate PLOT column.
Sample loading	500 ml cryo trap, 6" x 1/8" stainless steel with glass beads at liquid oxygen or argon temperature.	1 liter in ENTECH M 2000 cryogenic sampler at liquid nitrogen temperature.	500 ml cryo trap, 6" x 1/8" stainless steel with glass beads at liquid oxygen temperature.	100 to 200 ml cryo trap, 8" x 1/8" stainless steel with glass beads at liquid oxygen temperature.	500 ml cryo trap, 6" x 1/8" stainless steel with glass beads at liquid nitrogen temperature.	Ambient sample concentrated on Carbotrap C and Carboxieve 5 III at -30 C for 40 min each hour.
Injection/desorption	Hot water bath.	Transferred at 120 C onto head of column at 35 C.	@ 90 C with hot water and injected onto head of column at -60 C for cryo focusing.	@ 90 C with hot water and injected onto head of column at -20 C for cryo-focusing.	Transferred at 200 C onto head of column at -50 C.	PE ATD 400 is used for concentration and desorption. Sample is thermally desorbed at 360 C.
GC temperature program	Initially at -30 C (2 min. hold); ramp up at 3 C/min. to +200 C (11.75 min. hold).	Initially at 35 C (2 min. hold); ramp up at 10 C/min. to +200 C.	Initially at 60 C (5 min. hold); ramp up at 4C/min. to +200C.	Initially at -20 C (5 min. hold); ramp up at 4 C/min. to +200 C.	Initially at -50 C (2 min. hold); ramp up at 6 C/min. to 175 C, then 15 C/min. to 225 C.	Sample first goes through BP 1 at 46 C. Lights are transferred to PLOT column and both columns are eluted into separate FID.
Reference standards	NBS SRM propane	Relative intensity of ion for a 5 ppbv standards of specific sample.	Neohexane internal standard (0.22 ppmv) traced to NIST (NBS) benzene SRM 0.254 ppmv	Average response factor for NIST propane and hexane	Individual response factor for 63 analytes (al. NBS traceable).	Average response for ethane, propane, butane and 1-butene on the PLOT and average response of hexene, benzene, toluene, ethylbenzene and octane for BP.
Data Processing	ChromPerfect for integration and custom software for peak identification	Saturn II data reduction software	HP 3396A integrator	HP Chromstation	Perkin Elmer Nelson Turbochrome data package	Processed on-site using PE Nelson Turbochrome data package. Data stored to Bernoulli disk.
Identifier/confirmation	Multi-component retention time standard. GC/MS confirmation.	GC/MS spectra	Retention time of standard chromatogram. GC/MS Full Scan spectra	55 component retention time standard	63 component retention time standard daily. 35 component standard quarterly.	PAMS retention time calibration standard.

Table 2. Analysis of PAMS retention time calibration standard (concentration in ppbC).

		EPA	A	B	C	D	Auto-GC1	Auto-GC2
		Average	COAST-1	COAST-2	COAST-3	COAST-4	COAST-4	COAST-4
1	Ethylene	16.1		12.4	4.0	18.6	15.7	14.4
2 *	Acetylene	24.9		20.7	15.3	17.9	20.3	16.1
3 *	Ethane	17.7		14.1	18.8	21.5	20.0	18.4
4 *	Propane	16.0		12.7	12.6	15.4	18.4	17.5
5 *	Propane	17.0		13.6	15.0	15.7	19.9	17.4
6 *	Isobutane	16.8		14.1	14.2	15.4	15.4	16.3
7 *	1-Butene/Isobutene	16.2		14.9	14.6	17.9	13.2	13.9
8 *	n-Butane	16.6		13.6	14.6	14.3	17.5	17.2
9 *	trans-2-Butene	15.3		13.2	15.0	15.8	16.4	17.3
10 *	cis-2-Butene	15.0		12.9	14.3	14.2	13.7	15.6
11 *	3-Methyl-1-Butene	15.7		12.9	13.7	14.6	18.9	11.1
12 *	Isopentane	17.7		14.4	15.0	16.7	45.0	19.4
13 *	1-Pentene	17.2		14.3	14.7	16.1	24.2	17.0
14 *	n-Pentane	17.7		14.6	15.0	17.2	25.0	19.5
15 *	Isoprene	10.7		12.5	13.4	12.3	8.1	11.2
16 *	trans-2-Pentene	16.6		14.2	15.3	15.7	24.6	17.6
17 *	cis-2-Pentene	16.0		13.9	14.8	14.8	24.1	16.7
18 *	2-Methyl-2-Butene	10.1		12.0	12.8	12.1	23.9	16.0
19 *	2,2-Dimethylbutane	18.3		15.2	15.0	16.7	25.6	20.2
20 *	Cyclopentane	14.6		13.6	14.5	14.6	21.0	15.3
21 *	4-Methyl-1-Pentene	17.0		13.7	0.0	14.3	11.6	18.2
22 *	Cyclopentane	17.8		14.5	14.8	16.2	0.0	18.0
23 *	2,3-Dimethylbutane	17.8		14.4	15.0	17.0	22.9	18.7
24 *	2-Methylpentane	18.3		14.4	15.2	18.0	22.8	18.0
25 *	3-Methylpentane	18.1		14.9	15.2	16.7	23.7	18.6
26 *	2-Methyl-1-Pentene	2.4				1.8		
X1	2-Methyl-2-Pentene	10.9			12.9			
27 *	n-Hexane	17.7		14.6	14.9	17.0	18.7	17.2
28 *	trans-2-Hexene	16.3		13.8	14.5	13.8	14.0	13.4
X2	4-4-Methyl-2-Pentene			14.1				
29 *	cis-2-Hexene	16.7			14.8	14.3	17.3	23.6
X3	cis-3-Hexene			14.1				
30 *	Methylcyclopentane	17.6		14.5	15.1	15.5	19.2	13.7
31 *	2,4-Dimethylpentane	17.3		14.3	14.6	15.6	17.8	23.2
32 *	Benzene	17.8	15.0	14.3	14.3	16.4	16.8	17.5
33 *	Cyclohexane	17.6		14.6	14.7	15.8	18.7	18.5
34 *	2-Methylhexane	17.5		14.9	14.7	15.6	18.8	16.2
35 *	2,3-Dimethylpentane	17.9		14.7	15.0	18.2	19.3	20.2
36 *	3-Methylhexane	18.2		15.5	15.5	16.6	19.9	18.4
37 *	2,2,4-Trimethylpentane	18.2		14.3	15.1	16.2	19.2	19.2
38 *	n-Heptane	17.6		14.6	14.8	17.1	18.8	17.9
39 *	Methylcyclohexane	17.7		14.8	14.9	15.7	19.5	18.3
40 *	2,3,4-Trimethylpentane	17.7		14.8	14.9	16.3	19.5	19.0
41 *	Toluene	18.0	15.9	14.7	14.5	16.2	17.0	17.2
42 *	2-Methylheptane	17.8		14.7	14.9	16.3	18.7	18.0
43 *	3-Methylheptane	17.9		14.9	15.1	17.2	19.3	18.6
44 *	n-Octane	17.8		14.8	14.8	15.8	17.9	17.9
45 *	Ethylbenzene	17.8	18.5	14.8	14.7	20.3	17.1	17.4
46 *	m&p-Xylene	17.3	20.3	14.3	14.3	15.0	15.5	16.0
47 *	Styrene	13.8	13.3	11.3	10.2	23.3	9.5	8.6
48 *	o-Xylene	17.6		14.4	14.2	15.8	16.3	16.6
49 *	n-Nonane	17.7		14.9	14.7	16.0	16.0	18.3
50 *	Isopropylbenzene	17.2		14.2	14.0	15.3	16.2	16.9
51 *	n-Propylbenzene	17.2		14.2	13.4	17.9	14.5	16.1
X4	p-Ethyltoluene				6.5			
52 *	α-Pinene					1.6	7.0	4.3
53 *	1,3,5-Trimethylbenzene	17.4		13.9	12.8	19.6	14.7	15.9
54 *	β-Pinene	0.7				1.1	17.4	19.7
55 *	1,2,4-Trimethylbenzene	23.3		19.3	17.7	20.1	5.0	4.8
56 *	n-Decane	17.4		14.4	13.2	15.9		
X5	1,2,3-Trimethylbenzene				3.7	4.0		
57 *	n-Undecane	16.5			8.7	14.2		
* Mean ratio to EPA			1.001	0.830	0.850	0.945	1.087	1.002
Standard deviation of ratio			0.127	0.028	0.069	0.084	0.185	0.113

Xn: Compounds not included in preparing PAMS mixture.

* Included in calculation of mean bias.

Table 3. Comparison of Most Abundant Species and Totals - Atlanta Ambient Sample

LABORATORY	A	B	C	D	EPA
ANALYSIS DATE	10/06/93	07/22/93	9/1/93	10/18/93	11/23/93
CANISTER #	SP06	SP06	SP06	SP06	SP06
Concentration (ppbC)					
i-Pentane		12.1	18.9	11.7	13.3
Toluene	11.2	10.3	16.2	18.7	12.5
Ethylene		6.6	7.8	8.4	7.5
Acetylene		7.0	0.3	5.6	7.1
m/p-Xylene	6.3	6.0	8.8	4.9	7.0
Isoprene		6.0	10.0	4.5	6.7
n-Pentane		5.1	8.3	4.8	5.8
n-Butane		4.8	6.9	3.9	5.5
2, 2, 4 TriMePentane		4.1	6.1	3.6	5.1
Benzene	3.7	4.0	6.2	4.6	5.0
Propane		4.2	4.8	4.5	4.8
Ethane		4.6	16.3	6.2	4.6
3Me Pentane		2.3	4.8	2.1	4.4
2Me Pentane		4.7	6.0	3.5	4.0
1, 2, 4 TriMeBenzene		3.6	5.0	2.3	3.9
Summary					
Total of Abundant Species		85.4	126.3	89.0	97.3
Ratio of total to EPA		0.88	1.30	0.92	1.05
Mean ratio to EPA	0.82	0.88	1.34	0.87	
Standard Deviation of ratio	0.08	0.13	0.67	0.26	
Total 55 PAMS species					
Other C2-C10 identified		14	14	45	11
C2-C10 generic ID					41
Total C2-C10 identified		134	192	165	199
Unidentified		48	27	8	13
Total C2-C10		181	220	173	212
all >C10-C12 identified			1		25
Total C2-C12			221		237

Table 4. Comparison of Most Abundant Species and Totals (Concentrations in ppbC) - Ambient Collocated Sample (Clinton Site, 8/18/93, 0700 CDT)

Sample Collected by	A	A	B	B	C	C	D	D	Auto-GC		
Sample Analyzed by	A	EPA	B	EPA	C	EPA	D	EPA		EPA	EPA
Sample ID	#00220	#00220	TXB-A1	TXB-A1	S131	S131	1812	1812	Cont. GC	Average	CV
Analysis Date	08/26/93	10/18/93	08/18/93	11/16/93	09/01/93	10/26/93	08/24/93	10/17/93	08/18/93		
Concentration (ppbC)											
i-Pentane		21.7	21.8	24.0	23.8	33.4	22.1	23.5	30.8	25.7	17.8%
Toluene	19.1	21.3	20.1	22.2	22.2	21.9	19.2	23.1	19.1	22.1	3.0%
Ethylene		13.3	11.8	13.5	6.3	15.9	16.4	16.0	12.2	14.2	7.4%
m/p-Xylene	16.5	13.6	12.8	13.6	14.0	13.7	9.9	13.3	14.2	13.6	1.2%
Ethane		10.4	9.8	10.5	9.4	10.9	14.2	12.4	13.7	11.1	7.3%
1, 2, 4 TriMeBenzene		11.0	7.3	9.7	9.8	10.8	5.3	8.7	2.0	10.0	9.4%
Benzene	6.8	10.2	8.3	9.6	7.6	9.5	8.7	10.2	6.9	9.9	3.5%
Acetylene		8.8	11.9	9.3	9.1	8.8	8.1	10.5	8.0	9.3	7.5%
2Me Pentane		8.7	7.6	8.7	8.0	8.2	6.8	8.6	5.6	8.5	2.6%
n-Pentane		8.4	7.5	8.5	8.1	8.7	6.9	8.4	10.0	8.5	1.7%
2, 2, 4 TriMePentane		7.3	6.7	7.9	6.8	7.9	5.7	7.8	6.9	7.7	3.0%
n-Butane		7.4	6.7	7.0	6.4	6.9	4.4	6.9	6.0	7.0	3.0%
Propane		5.8	6.0	7.3	5.9	7.5	6.5	7.4	6.8	7.0	9.7%
Propene		7.9	5.2	6.4	5.9	6.4	5.9	6.4	6.6	6.8	9.4%
3Me Pentane		6.5	4.5	5.9	5.9	6.2	3.9	6.6	2.0	6.3	4.3%
o-Xylene	6.9	5.5	5.0	5.4	5.1	5.6	3.2	5.3	4.4	5.5	2.5%
3Me Hexane		5.1	3.1	3.8	3.4	5.9	1.7	4.3	2.9	4.8	17.0%
n-Hexane		5.0	4.0	4.2	4.0	4.6	3.7	4.6	2.9	4.6	6.2%
EthBenzene	5.2	4.7	4.2	4.7	3.7	4.3	3.6	4.4	3.4	4.5	4.2%
Summary											
Total of Abundant Species		183	164	182	163	195	156	188	164	187	2.8%
Ratio of total to EPA			0.90		0.84		0.83		0.88		
Mean Ratio to EPA	1.02		0.90		0.86		0.79		0.82		
Standard Deviation of Ra	0.22		0.11		0.14		0.17		0.26		
Total 55 PAMS species		250	215	243	201	263	202	261	218	254	3.3%
Other C2-C10 identified		30	27	30	20	30	37	28	0	29	3.8%
C2-C10 generic ID		138		70		106		69		96	30.1%
Total C2-C10 identified		418	242	343	224	399	239	358	218	379	
Unidentified		91	169	21	19	71	31	54	132	59	43.0%
Total C2-C10		509	411	364	243	470	269	412	350	439	12.6%
All C11-C12 identified		124		52	7	82		61		80	34.6%
Total C2-C12		633		416	251	552		473		518	15.8%

A Comparison of the Results of a Total Non-Methane Organic Compound Analyzer with Those from a Canister-Based Monitoring Program

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The need for frequent measurements of total non-methane organic compounds (TNMOC) in ambient air has been emphasized by data analysis of both the Southern California Air Quality Study (1987) and the Atlanta 1990 Ozone and Ozone Precursor Study. Although the TNMOC concentrations may vary considerably both temporally and spatially within a given area, it has been shown that, in California at least, the NMOC composition does not vary appreciably within that area. As a result, the staff of the California Air Resources Board have worked closely with a commercial instrument manufacturer to produce a prototype TNMOC analyzer. This instrument was field tested during the 1993 ozone season in parallel with a canister collection program for PDFID and speciated hydrocarbons. A comparison of the results from the TNMOC analyzer, a specially modified Combustion Engineering Model 8202a CH₄/THC analyzer, and the canister-based program will be presented.

A Fully Remote Control Cryogenless Ozone Precursor System with Improved Sensitivity

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In compliance with Title I of the 1990 Clean Air Act Amendment (1990 CAAA), hydrocarbons in the C2-C10 molecular weight range will be monitored to assess their contribution to ozone formation in approximately 35 cities which exceed current ozone standards during summer months. Speciation of these compounds in urban air requires preconcentration of a 300 cc sample size in order to reach the required 0.1-0.2 ppbc detection limits by GC/FID. Analyzing the C2-C10 hydrocarbon fraction can either be performed real time by placing the analytical instrumentation at the sampling site, or by collecting the ambient air in separate SUMMA passivated canisters every 3 hours. In addition, sample analysis can be performed either by using cryogen to preconcentrate the sample and cool the GC for single column GC/FID, or by using sorbent traps and two columns in the GC which eliminates the need for liquid cryogen. Once implemented, on-site analysis using cryogenless operation requires the least amount of manpower to operate providing from weeks to months of uninterrupted data generation.

A cryogenless C2-C10 "AUTOGC" system is presented that exceeds the monitoring requirements specified in the technical assistance document for ozone precursor monitoring. Samples can be analyzed hourly or once every 3, 8, or 24 hours to provide as much resolution as necessary. Sampling frequency can be changed via modem to accommodate periods of high and low ozone concentrations. A benchtop 16-position manifold makes it possible to analyze other gas streams at programmed intervals, such as propane and hexane standards, retention time standards, and system blanks. Integration of the ambient air sample first into a canister allows standards and blanks to be run while continuing to analyze ambient air 24 hours per day. Access to the GC/FID and preconcentrator are possible via modem using a Windows™ interface for data retrieval, verification of proper operation, and adjustment of method parameters. Data will be presented showing performance in determining ozone precursor concentrations in Los Angeles, California.

The Determination of Ozone Precursors with a Built-in Preconcentrator and Capillary GC/Dual FID

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Title I of the Clean Air Act Amendments of 1990 requires cities or air quality districts that are non-compliant with the Ozone National Ambient Air Quality Standard of 120 ppbv to make continuous measurements of targeted ozone precursors. Air samples must be obtained on a one to three hour basis with the requirement that a high percentage of the time interval will be spent in the sample collection process. The preconcentration of the target analytes from these samples by adsorbent trapping rather than the traditional use of cryogenic preconcentration on glass beads with liquid nitrogen has been utilized over the past few years for this application.

An Ozone Precursor GC system has been configured with a new built-in sample preconcentration trap (SPT) and associated valving capable of preconcentrating a 200 mL air sample. The sample which may be drawn either from a canister or directly from the ambient air first passes through a stripper column for moisture removal and then through an adsorbent trap. The adsorbent trap is cooled to initial conditions with a very small amount of liquid carbon dioxide providing many runs from one cylinder. Following trapping, the precursors are quickly desorbed with the fast heating (40°C/sec) SPT to parallel columns of Alumina Plot and DB-1 for chromatographic separation and quantitation of the trapped analytes. Dual FIDs provide detection.

Optimization of the trapping and chromatographic parameters has been performed using a 60 component EPA precursor standard. The results of these studies and a description of the integrated system will be presented.

AUTO GC SYSTEM FOR ENHANCED OZONE MONITORING NETWORK

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1. Abstract

A Perkin-Elmer Model ATD-400 Thermal Desorption System was specially adapted for the collection of whole-air samples. The C_2 to $n-C_{10}$ hydrocarbons were trapped using Peltier cooling on Carbotrap/Carbosieve adsorbents at -30°C . A Deans switch allowed the C_2 to C_6 fraction to be separated using a porous layer open tubular column while a methyl silicone column separated the C_6 to C_{10} fraction. No cryogen was used in the collection or analysis. Ozone precursor concentrations were detected at the 0.1 ppbV level. Area repeatability was less than 10%, with retention time precision over 100 hours of approximately 1% RSD for most compounds. Remote communications allowed chromatography to be monitored and files to be downloaded to a central office. Data in .CSV format was directly assimilated by spreadsheet software for diurnal inspection and customized reporting. Data were archived using external Bernoulli disks.

1. Introduction

Since early 1993 systems have been established [1,2] that allow ambient air to be monitored for certain VOCs which aid in the formation of ozone in the presence of oxides of nitrogen and sunlight [3,4]. These compounds are defined in the Clean Air Act Amendments of 1990. The system that has been designed [4] (and field operated during 1993) allows these VOC species to be sampled from the ambient air on a regular basis to provide a continuous record.

2. Instrument Design

A schematic of the system is shown in Figure 1. A 600mL sample of air (typically, but not limited to, ambient air) is drawn by means of a small sampling pump through the cold trap of

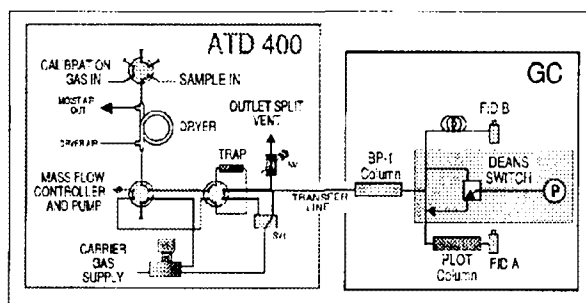


Figure 1. Sample Collection

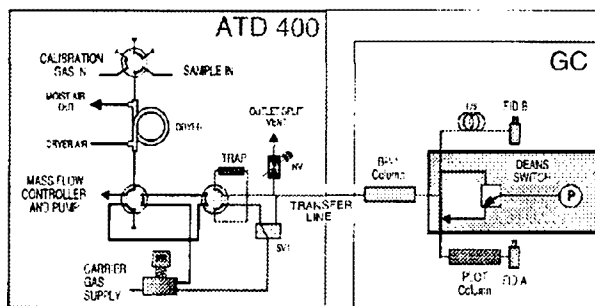


Figure 2 Cold Trap Desorption

The trap lower temperature is set to -30°C by peltier effect (electric) cooling while the air sample is obtained. Improvements have been made in the last year to the physical shape of the trap tube and the manner in which the sorbents are retained. The previous design proved robust for 5000 to 10000 hours, but the new arrangement is expected to provide unlimited service (Figure 3). This design offers the additional advantage of allowing lower flow rates to be used during desorb since the dead volume at the outlet end of the trap is eliminated.

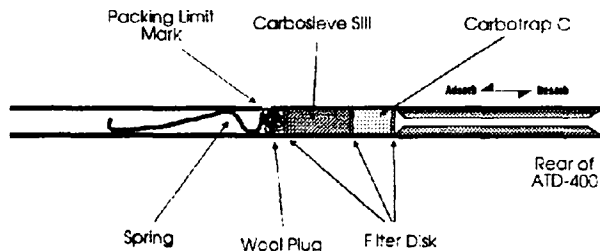


Figure 3 New Design of Cold Trap

Once the sample is collected the trap is heated at 2400degC/min. to 325°C to ensure that the VOCs are desorbed rapidly from the cold trap in a fast, focussed band consistent with the requirements of the capillary column. (Figure 2). During this process the desorbed gas flow through the trap is reversed to prevent the more volatile components from contacting the stronger adsorbent. Trap flow is approximately 5mL/min. with approximately 2.5mL/min being passed to the column.

4 Sample Analysis

The first GC column is a 50m x 0.22mm ID, x 1.0µm methyl silicone (BP-1®). The first (approx. 14 minutes) of compounds eluting from the BP-1 are switched by a pressure-balanced Deans' switch to a 50m x 0.32mm ID, Al₂O₃-Na₂SO₄ porous layer open tubular (PLOT) column and detected by an FID. Later eluting components from the BP-1 (approx. 14 minutes to 48 minutes) are detected directly by a second FID connected via a transfer line. The chromatograms obtained from a 600cc sample of a nominal 5ppbv, 75% RH retention standard canister are shown in Figure 4.

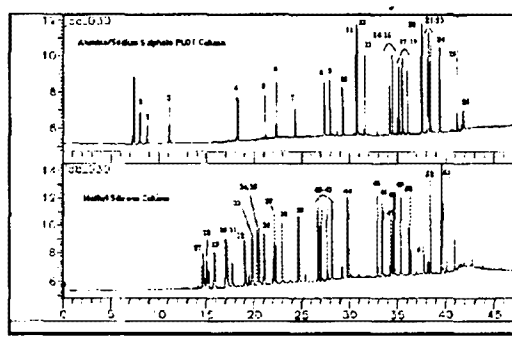


Figure 4. The Ozone Precursor Chromatogram

Initially a BP-5® (methyl 5% phenyl silicone) column was used for this work[6] to resolve the C₆ to n-C₁₀ hydrocarbons. However some important coelutions occurred resulting in the final selection of a non-polar methyl silicone column. In this chromatogram all components are resolved; the component identifications are listed below.

1	Ethane	19	cis-2-Pentene	37	2,2,4-Trimethylpentane
2	Ethylene	20	2,2-Dimethylbutane	38	n-Heptane
3	Propane	21	3-Methylpentane	39	Methylcyclohexane
4	Propene	22	2-Methylpentane	40	2,3,4-Trimethylpentane
5	Isobutane	23	2,3-Dimethylbutane	41	Toluene
6	n-Butane	24	Isoprene	42	2-Methylheptane
7	Acetylene	25	4-Methyl-1-pentene	43	3-Methylheptane
8	trans-2-Butene	26	2-Methyl-1-pentene	44	n-Octane
9	1-Butene	27	n-Hexane	45	Ethylbenzene
10	cis-2-Butene	28	trans-2-Hexene	46	p-Xylene
11	Cyclopentane	29	cis-2-Hexene	47	Styrene
12	Isopentane	30	Methylcyclopentane	48	o-Xylene
13	n-Pentane	31	2,4-Dimethylpentane	49	n-Nonane
14	2-Methyl-2-butene	32	Benzene	50	Isopropylbenzene
15	Cyclopentene	33	Cyclohexane	51	n-Propylbenzene
16	trans-2-Pentene	34	2-Methylhexane	52	1,3,5-Trimethylbenzene
17	3-Methyl-1-butene	35	2,3-Dimethylpentane	53	1,2,4-Trimethylbenzene
18	1-Pentene	36	3-Methylhexane		

Isobutene, a-pinene and b-pinene are not quantitative in this analysis since they are modified or removed by the dryer. Decane and undecane have recently been proposed in addition to the eluents shown[8]. Separation of the 53 hydrocarbons is achieved using the multidimensional column set utilizing a Deans' pressure balanced switch. At the low flow rates used, performance of the switch is superior to that obtained with a rotary valve. By ensuring that no compounds more volatile than hexene (in the elution order) are presented to the PLOT column this system, when operated continuously, provides optimum stability. (Note that in this system no component elutes on both columns.)

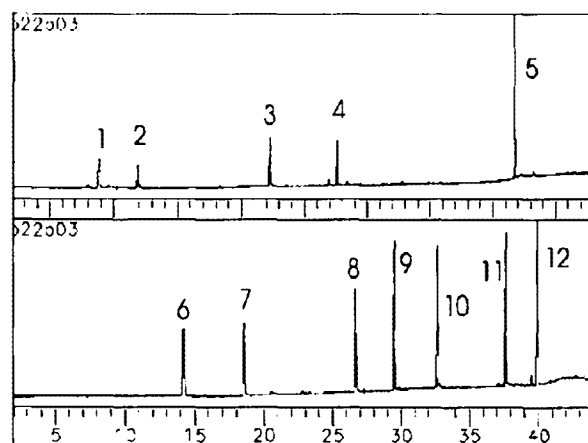
The chromatographic conditions used for this analysis were:

GC:	Initial Oven Temp.	46°C	ATD:	Column Head Pressure	48psi
	Initial Oven Time.	15min		Collection Time	40min.
	Ramp Rate	5degC/min.		Sample Collection Flow	15cc/min.
	Oven Temp.	170°C		Cold Trap Low Temp.	-30°C
	Ramp Rate	15degC/min.		Cold Trap High Temp.	325°C
	Final Oven Temp.	200°C		Trap Hold at High Temp.	10min.
	Final Oven Time	6min.		Cycle Time	60min.
	Mid-point Pressure	21.5psi			

Trap Packing: 44mg Carboxpack® C/60mg Carboxieve® SIII

Moisture management is by means of a semi-permeable membrane dryer, the performance of which has been described [7]. It is interesting to note that without this dryer so many compounds are detected in ambient air that the analysis would require a mass spectrometer, which would negate the possibility of an unattended field unit. The dryer actually performs a useful service as a selective filter for the hydrocarbons only, which allows a FID/FID autonomous analysis.

Calibrations are performed using a multi-component traceable standard such as that shown below. Since the analysis uses a single response factor for both the target analytes and the unknowns on each column, the user may select the component to be used as the calibration standard from this mixture. Typically butane or pentane is used for the PLOT column and toluene for the methyl silicone column. The concentrations of components are shown. Note that the standard must be humidified to approximately 75%RH



Stated Concentrations:

1	Ethane	0.47ppbC
2	Propane	3.04
3	Butane	8.7
4	1-Butene	12.8
5	1-Hexene	20.3
6	Hexane	23.9
7	Benzene	24.7
8	Toluene	28.1
9	Octane	32.9
10	Ethylbenzene	32.5
11	Propylbenzene	39.9
12	Decane	29.4

Figure 5. Chromatogram of a 12 Component Standard

Peak area repeatability for successive samples of calibrant is shown in Table 1. Retention time stability data from 105 hours of sequential sampling is shown in Table 2

Table 1: Area Repeatability				
Name	Replicates	Mean	SD	%RSD
Ethane	8	76236	3574	4.69
Ethylene	8	69492	3378	4.86
Acetylene	8	47997	2779	5.79
1-Butene	8	118966	5743	4.83
Cyclopentane	8	150602	5071	3.37
1-Pentene	8	128217	3446	2.67
Benzene	8	298474	10300	3.45
Toluene	8	122969	4643	3.78
n-Octane	8	130084	2946	2.26
Ethylbenzene	8	54167	3309	6.11
p-Xylene	8	110158	4882	4.43
Styrene	8	106367	4069	3.83
Isopropylbenzene	8	121744	9252	7.60
1,3,5-Trimelbenzene	8	140447	4586	3.27

Table 2: Retention Time Stability		
Name	Average RT	%RSD
Ethane	8.75	0.27
Ethylene	9.47	0.37
Acetylene	23.52	0.82
Butane	22.25	0.45
Isopentane	30.61	0.25
n-Pentane	31.44	0.24
1-Hexene	41.66	0.23
n-Hexane	14.07	0.23
Benzene	18.45	0.16
Toluene	26.63	0.10
n-Octane	29.48	0.07
Ethylbenzene	32.68	0.07
o-Xylene	34.47	0.06
1,3,5-trimebenzene	38.85	0.07

The following chromatogram shows the actual performance of this system under field conditions. This chromatogram was obtained by modem from a field site operating in California at 11pm in December 1993.

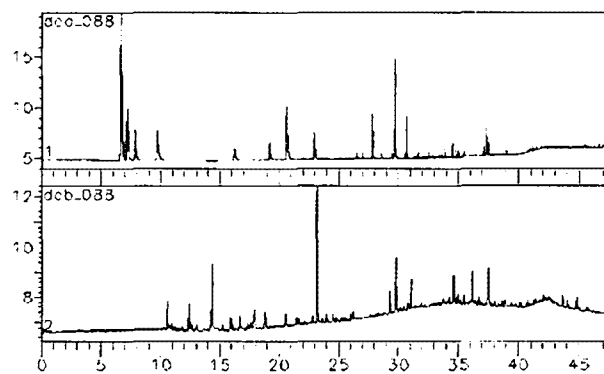


Figure 6. Actual chromatogram from a field station, acquired by modem

5. Conclusions

A system has been designed to detect the Ozone Precursor compounds stipulated under the Clean Air Act. Since Peltier cooling is used to trap the VOC species no liquid cryogen is required. Operation for a two week unattended period is possible by configuring gas supplies for continuous operation. Optimum stability, coupled with enhanced resolution of the C_2 compounds is achieved by multidimensional chromatography. The system may be accessed and files transferred using high speed data communications. Automatic recovery in the event of a power failure ensures the maximum data capture rate even for remote installations.

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ACKNOWLEDGEMENT

The ATD-400 On-Line Air Monitoring Capability and Ozone Precursor Application was developed by the Perkin-Elmer Corporation in collaboration with the US EPA Exposure and Assessment Laboratory under an FTTA agreement.

Enhanced Monitoring of Ozone Precursors – Speciated and Total NMOC

Sharon Reiss and Richard Jesser
Graseby/Nutech

For the past two years, Graseby/Nutech has supported an automated cryogenic system for the concentration and subsequent speciation of NMOC's that contribute to the formation of ozone in ambient air. This system consists of a cryogenic concentrator interfaced with a GC/FID with pressure programming capabilities. The appeal of this approach is twofold:

- a. high quality data associated with cryotrapping;
- b. single column/single detector for a simple hardware scheme generating no more than one data file for each sample.

Although this cryogenic application may be the best choice in a stationary laboratory, the use of liquid nitrogen in a remote or temporary location is not always practical. For this reason, Graseby/Nutech is developing a non-cryo continuous monitoring system that is simple in design without being complicated in operation or maintenance.

CARBONYL MEASUREMENTS

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Parameters Influencing the Precision and Accuracy of Carbonyl Measurements Using DNPH Cartridges

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While DNPH cartridges have been used by the author to measure ambient air carbonyl compounds in all major air quality studies throughout California and other parts of the United States over the past ten years, there are still remaining issues with the method that need to be addressed in order to produce unbiased results. At typical ambient levels, the method precision is in the range of 10 to 25%. Automated sequential samplers were employed in these studies. They have been very reliable and produced data with good precision when memory-protected timers and flow controllers were used. Samplers account for up to approximately 30% of the error. The precision of the HPLC analytical technique with an autosampler or using an internal standard has a precision of $\pm 2\%$ or less. DNPH cartridge blank variability is the largest factor that controls the method's lower quantifiable limit, which is approximately 0.5 ppbv for 60 liters of air sampled. The cartridge substrate (C18 vs silica) used for DNPH impregnation appeared to have varying extent of ozone interference. While it was thought that DNPH cartridges made with C18 bonded silica have less problems with ozone than plain silica, more recent experimental data showed that when both types were impregnated under identical conditions, silica cartridges performed equally or better, suggesting that the composition of DNPH reagent was also important in determining the extent of the ozone artifact seen.

The Design and Use of DNPH-Coated Silica Cartridges for the Analysis of Carbonyls in Outdoor Air

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The determination of formaldehyde, acetaldehyde and acetone concentrations in ambient air is a required specification of the PAMS regulation. Section 5.0 of the Technical Assistance Document defines the testing methodology for measuring carbonyls in ambient air. This testing methodology is based on the use of DNPH coated silica cartridges. The user is given the choice of either preparing their own cartridges or purchasing them from a commercial source.

Waters introduced the DNPH Silica Sep-Pak Cartridge into the marketplace in 1991. This cartridge is now in widespread use throughout the world in numerous carbonyl air monitoring applications. A key component of our success has been the transferal of our product and application expertise to our customers.

This presentation will focus the keys for the successful utilization of the precoated DNPH cartridges for carbonyl monitoring in ambient air. Product design and product performance issues such as lot-to-lot consistency, shelflife, sample stability and potential analyte interferences will be addressed. Examples of actual analysis problems, their symptoms and solutions will also be presented.

**Measuring Ambient Carbonyls Using DNPH-Coated Substrates:
Comparison of C18 and Silica Gel with and without Ozone Scrubbers**

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Carbonyls in ambient air play a critical role in atmospheric chemistry, including ozone formation on urban and regional scales. Recently mandated requirements to report ambient levels of formaldehyde and other carbonyls as part of the nationwide PAMS monitoring program underline the importance of obtaining reliable, interference-free data when measuring ppb levels of carbonyls in urban air. The DNPH-liquid chromatography method, initially described by Kuwata et al. in Japan and by Grosjean and Fung in the U.S., has since been endorsed by ASTM, EPA (e.g., TO 11) and other agencies; this method has been suggested by EPA as the method of choice for PAMS monitoring of ambient levels of carbonyls measured using co-located C18 and silica gel substrates with and without scrubbers to remove ambient ozone. As part of this study, the performance of several types of ozone scrubbers has been evaluated. The results will be discussed with special emphasis on PAMS requirements for monitoring of ambient carbonyls by state and local air pollution control agencies.

An Evaluation of Commercial Devices for Automated Sequential Sampling of Carbonyl Compounds in Air

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ABSTRACT

This paper reports an evaluation of four prototype commercial devices for automated sequential sampling of carbonyl compounds in air. The purpose of this study was to evaluate how well the four samplers met the requirements for automated sequential sampling stated in the EPA guidance document.¹ The four samplers tested were prototype instruments obtained on loan from the respective manufacturers, and represented widely differing approaches to the carbonyl sampling issue. The four manufacturers who participated in this study were Xontech, Inc.; Graseby-Andersen; Supelco-Xitech; and Scientific Instrumentation Specialists. A questionnaire and weighting system were devised, which resulted in a numerical ranking of the samplers on several key requirements and characteristics. The Xontech sampler received the highest overall rating, and met most of the requirements stated in the EPA guidance document except the ability to sample commercially available precoated DNPH cartridges. The Supelco Xitech sampler received the second highest rating. The main limitation of this sampler was the open tube arrangement from the sampling manifold to the sampling cartridges, which could possibly lead to contamination. The SIS sampler received the third highest rating. Modifications to accept carbonyl cartridges instead of sorbent tubes, and to allow simultaneous parallel sampling, are needed to make this sampler a viable system for automated carbonyl sampling. The Graseby Andersen sampler received the lowest rating, largely due to the fact that the sampler has no automated sampling capability.

INTRODUCTION

Recently, the U.S. EPA issued a guidance document for measurement of ozone precursor compounds in ambient air¹. Included in that document were the target characteristics of a sequential sampling device for carbonyl compounds in air. The sampler must accommodate two different types of 2,4-dinitrophenylhydrazine (DNPH) cartridges, i.e., DNPH precoated SepPak silica gel cartridges as well as the SepPak C18 cartridges that are uncoated. The sampler must be capable of collecting at least eight (8) cartridges at intervals of three (3) hours from an ambient air manifold inside a monitoring station, and must also collect a 24 hour sample and a colocated sample. The sampler must be capable of accurately and precisely sampling 100-1500 ml/min of ambient air. The sampler must have a flexible timing option for sequential operation, and must allow for operator input of start and stop times as well as sample collection time. The sampler must have an appropriate inlet design to minimize sample loss and avoid contamination, and must incorporate a scrubber to remove ozone (O₃) from the sample air upstream of the DNPH cartridges. The sampler must also have provisions for sealing each cartridge before and after each sampling period to ensure sample integrity.

Commercially available DNPH cartridges include the silica gel cartridge pre-coated with DNPH, the uncoated silica gel cartridge, and the uncoated C-18 cartridge. The coated and uncoated silica gel cartridges have different shapes and connecting tubes. This difference in cartridge configuration presents a problem for the design of carbonyl samplers. The pre-coated silica gel cartridges present a potential advantage to the user, in the savings of time and effort needed to coat the cartridges in

the laboratory. This factor may be important in large sampling efforts, such as may be implemented by various states in response to the ozone precursor monitoring requirements. The C-18 cartridge is commercially available only uncoated. Thus users selecting the C-18 cartridge for carbonyl sampling must perform DNPH coating in the laboratory. The C-18 cartridges are reported to have somewhat lower capacity and higher background contamination than the silica gel cartridges¹. However, a reported advantage of the C-18 cartridges is a lower sensitivity to ozone interference, relative to the silica gel cartridges¹.

In the present study, four commercial carbonyl samplers intended to meet the requirements of the EPA guidance document¹ were evaluated relative to those requirements. The four samplers tested were prototype instruments obtained on loan from the respective manufacturers: Xontech, Inc. (XI); Grasehy-Andersen (GA); Supelco-Xitech (SX); and Scientific Instrumentation Specialists (SIS). In this study the four samplers were set up and operated in a laboratory setting, and evaluated by several staff familiar with carbonyl sampling and field measurements. The review included sampler operation, review of manufacturers' literature, and direct consultation with the manufacturers. A questionnaire and score weighting system were devised, to provide a quantitative ranking of the samplers on several key requirements and characteristics. This evaluation was confined to the laboratory, i.e., no ambient air sampling or direct intercomparison of the samplers was conducted. It must be stressed that the samplers tested were prototypes, and consequently were still in development.

EXPERIMENTAL PROCEDURE

Descriptions of the Samplers

Xontech, Inc. (XI). The Xontech Model 925 Aldehyde Sampler consists of two aluminum rack type modules, positioned one on top of the other, with an external vacuum pump. The top rack unit houses most of the electronics such as the timers, mass flow controllers and readout devices as well as the ozone scrubber. The scrubber is located in a separate compartment where the temperature can be maintained at a constant level. The top unit consists of three mass flow controllers and three sample duration clocks (in HRS/MIN), one of each for the 24 hour cartridge sample, the colocated sample cartridge and the sequential cartridge samples. Each mass flow controller is independently adjusted and has its own readout unit on the front panel. The main timer unit is used to program start and stop times for the 24 hour sample as well as the sequential samples. The top unit also includes a selector switch to select which of the eight sequential cartridges will be simultaneous with the colocated sample. The bottom rack unit of the XI sampler houses the two multiport valves that divert the sample flow to the appropriate cartridges and seal the inlet and outlet of each cartridge before and after sampling. Mounted to the front of the lower rack unit are the sampling cartridge holders. Each holder consists of a black cylindrical metal tube threaded on one end, and equipped with a quick connect fitting on the other. The cartridge holder uses a soft plastic washer which fits over one end of an uncoated silica gel or C-18 cartridge. The threaded end of the holder screws into a pipe-to-Swagelok connector, compressing the rubber washer to make a seal. The Swagelok connector is attached to a bulkhead union which runs through the front of the case and into the module to connect to one of the multiport valves. The vacuum pump is separate from the two rack units and connects to the bottom unit with a vacuum line.

Scientific Instrumentation Specialists (SIS). The Scientific Instrumentation Specialists (SIS) sampler is presently not configured for aldehyde cartridges but for adsorbent tubes. The components of the SIS sampler are housed in a single aluminum box with a removable lid. The bottom section of the box contains the electronic components, pump, mass flow controller and solenoid valves, and is covered with an aluminum plate. The sample inlet and outlet lines run through this plate to allow access for connection of sampling tubes on the top of the instrument. The sample control keypad, LED output and flow adjustment is also accessed from this top panel.

A 12 volt DC receptacle is available for battery operation. The sampler is designed for sequential sampling using 12 adsorbent sampling tubes, mounted in groups of 6 to two flow manifolds on the top of the device. The existing flow manifolds of the SIS sampler are too large to allow installation of any of the commercial DNPH cartridge designs.

All operations of the SIS sampler are programmed using the micro-processor based keypad and LED readout. This programmability allows for setting different flow rates, purge times, and sampling times for each separate sampling tube as well as daily start and stop times. The SIS unit presently has the capability to sample 12 tubes sequentially but does not allow the collection of a colocated sample or a 24 hour sample. One of the 12 tubes not programmed to be sampled could be used as a blank. This sampler presently does not have an ozone scrubber, and since the sampler is currently designed for use with adsorbent tubes requiring low flows, it cannot provide flows of up to 1.5 liters/min.

Supelco-Xitech (SX). The Supelco-Xitech sampler is built into a molded plastic suitcase, which has a hinged lid for access to components. The sampler is compact, but weighs nearly 50 pounds, which strains the capacity of the case and handle. Contained in the top lid of the case are the air sampling manifold and inlet lines, the heated enclosure that holds the ozone scrubber, three manual timers (sample time, sample interval time, and sample delay time), the solenoid valves, and associated electronics. Located in the bottom of the case are the two mass flow controllers and two pumps (one each for the sequential sample and for the continuous 24 hour sample), the mass flow control unit, two temperature controllers (one for heating the ozone scrubber and one for heating the case), an optional data logger, and associated electronics. The tubing connecting the cartridges to the manifold and solenoid valves is made of silicone rubber, which allows easy attachment of both silica gel and C-18 sampling cartridges. A fitting is provided on the outside of the case to attach a heated sample line. A backup battery is provided to maintain the timers during a short power outage. In a power outage the pumps, heaters, etc. will stop but the cartridges will remain intact. Once power is restored, operation will resume on the proper cartridge. However, the manifold end of the cartridges is not sealed by a valve, i.e., the cartridges are open to the manifold at all times. As currently configured, the SX sampler incorporates 9 cartridges. These are used for eight 3-hour sequential samples, and for one 24-hour simultaneous sample. At present the SX sampler has no capability for collecting a colocated 3-hour sample. Blank cartridges may be taken using two additional ports on the sampling manifold.

Graseby-Andersen (GA). The GA sampler was built into a Graseby-Andersen sampling "doghouse", as might be used for high-volume filter sampling. The GA sampler uses a simple pump and on/off timer arrangement, essentially as used in a standard filter sampler. The sampler incorporates no mass flow control, heated lines, or ozone scrubber, and is equipped for four sampling channels. Sampling cartridges are mounted beneath the roof of the enclosure, by connection to four nylon Swagelok fittings. Cartridges mounted to these fittings are always open to the atmosphere at the inlet end. Flow is drawn through the cartridges by a large pump, more than sufficient to achieve sampling rates of up to 1.5 L/min. Flow control is accomplished by stainless steel needle valves, located under the top panel of the sampler. Each of the four sample flows is controlled by a separate needle valve. The GA sampler is not automated, and requires manual flow adjustment. The sampler can be set up manually to collect colocated samples, but any sequencing of samples must be done manually.

Operator Evaluation Forms

In order to make evaluation of the carbonyl samplers as quantitative as possible, a questionnaire was developed to allow ranking of the samplers in several key areas. The form lists 11 characteristics of the samplers, and requests a numerical rating of the sampler on each characteristic, on a scale of 1 to 5 points. An overall rating is also called for. The various characteristics were weighted differently by applying a multiplier of 3, 5, or 10 to the numerical rating on each

characteristic. A perfect score on the form is 405 points. The form also includes space for comments by the evaluator, to include additional information or observations not readily included in the numerical ratings. Each sampler was evaluated independently on its own characteristics, i.e., side-by-side comparison with other samplers was not conducted. A separate form was used for each sampler, and the evaluators did not see the results or comments from previous evaluators. The quantitative ratings from the forms were compiled and compared for each of the characteristics on the form. A final ranking of the samplers on the basis of the total score was also determined.

RESULTS

Xontech, Inc. (XI). The XI sampler was the most complete of the four samplers in terms of features. The design seemed to be well thought out as evidenced by the easily accessible compartment for changing the ozone scrubber and the multivalve approach to sealing the inlet and outlet of each cartridge. The system was compact enough to work in confined spaces within a mobile lab and yet provided flexible sampling capabilities including blanks, 24 hour samples, and colocated short-term samples. Although operation of the control timer was tedious to learn at first, once an operator became familiar with the programming the timer operation was fairly straightforward. The XI sampler was not able to accommodate the precoated Waters cartridges (the flange on those cartridges is too large to fit within the holder), which would be a disadvantage to those users who would prefer not to prepare their own sample cartridges. Also, the installation of the C-18 and uncoated silica gel cartridges in the system is made using a flat, soft plastic washer, which is not properly compressed by the existing cartridge holder design. As a result, the washer failed to properly seal the cartridges. The sampler is contained in two separate aluminum boxes one on top of the other. This design would not lend itself to easy access to the components in the bottom section for maintenance without disconnecting all of the sampling lines between each section. The XI sampler had no battery backup capability, which could lead to loss of samples during a power outage.

Scientific Instrumentation Specialists (SIS). The SIS sampler was not configured for use with carbonyl cartridges. However, the system had a number of nice features. All operations were programmed using a microprocessor based keypad and LED readout. This microprocessor capability allows for wide flexibility in choosing sampling times, purge times and flows for each sampling cartridge. In its present configuration, the SIS unit does not have an ozone scrubber or heated sample line, and cannot sample carbonyl cartridges at flow rates up to 1.5 L/min. Although the sampler is configured with 12 sampling channels, collection of a 24-hour or a colocated short-term sample is not possible. The unit is fairly compact and light weight although to assure a flow of 1.5 L/min, a much larger pump would be necessary, which would probably increase the size and weight. The SIS sampler does have a battery backup feature which would allow for continued use during a short power outage using an external 12 volt battery.

Supelco-Xitech (SX). The SX sampler is well conceived and provides easy access to all components. However, the packaging of this sampler is not as well engineered as that of the XI or SIS samplers, due to its nature as a prototype. The setup of the sampler is fairly simple and straightforward. The SX sampler is presently not capable of sealing the inlet of each cartridge, which could result in contamination before and after sampling by diffusion of carbonyls within the sampling manifold. The SX sampler is not capable of collecting a colocated short-term sample. The system is equipped with a heated sample line and battery backup for short power outages. The SX sampler is configured for use with an optional data logger, to monitor fluctuations in sample flow from cartridge to cartridge, and to record when power outages have occurred.

Graseby-Andersen (GA). The GA sampler was rugged and easy to use but was not capable of automated sequential carbonyl sampling. This unit would be useful for sampling up to four cartridges simultaneously, as long as an operator was present to start and stop sampling. No electronic timing or mass flow control capabilities exist in this sampler.

Quantitative Evaluation of Samplers

The numerical ratings of the samplers are summarized in Table 1, which shows the score obtained by each sampler for each item on the review form, along with the total score for each sampler.

The Xontech (XI) sampler received the highest overall rating, and the Graseby-Andersen (GA) the lowest. These results are consistent with the general degree of sophistication and state of development of these samplers. The Supelco-Xitech (SX) and SIS samplers received intermediate ratings. However, all of the samplers scored well in some categories and poorly in others. None of the samplers fully meets the requirements, as shown by the fact that none received more than about three-fourths of the total possible score in the ratings. The Graseby-Andersen sampler scored particularly poorly in sequencing capabilities, cartridge sealing, number of sampling channels, provision for an ozone scrubber and a heated sample line, and in overall reviewer opinion. Since these are all very important characteristics, it is clear that sampler does not yet approach the requirements set out in the guidance document¹. The other three samplers showed limitations in various areas. The Xontech and SIS samplers were judged to be difficult to service in the field. The Supelco-Xitech sampler was downgraded for its cartridge sealing capabilities. The SIS sampler was deficient in having no provision for an ozone scrubber, and both Xontech and SIS had no heated sample line. The SIS sampler was highly rated in the area of sequencing capabilities, despite its inability to sample 24-hour or short term colocated samples in parallel with the sequenced samples. This result probably indicates that the reviewers interpreted this item to mean solely the capabilities for successive 3-hour sample sequencing. In that regard, the SIS sampler is highly capable.

Interestingly, the order of the ratings on the issue of estimated cost was exactly opposite to the overall ratings, i.e., the samplers which best met the sampling requirements were judged to be most expensive. The reason for this judgment is that these samplers are intended for operation at multiple field sites in sampling networks. It may be economically impossible for state or other agencies to equip multiple sites with a relatively expensive sampler design. The challenge for instrument manufacturers clearly is to build the needed capabilities into a readily affordable package.

Discussions with the manufacturers revealed that modifications are planned by all four to address at least some of the limitations found in this study.

CONCLUSIONS

The tested samplers differ widely in complexity and capabilities, but none of the four specifically meet all of the criteria stated in the EPA guidance document. Three of the samplers have features that would be valuable when combined together. Such features include the multiport valve feature and multiple sampling capabilities of the Xontech system; the data logger, battery backup feature, and ability to accept various cartridge designs of the Supelco Xitech system; and the microprocessor control of the SIS sampler. The Graseby-Andersen sampler fell far short of the capabilities required by the guidance document. The estimated cost of the samplers paralleled the overall ratings of the samplers, i.e., the samplers which best met the sampling requirements were judged to be most expensive. This would be a factor in efforts to implement multi-site automated measurement capabilities.

Further evaluation of the automated carbonyl samplers should be conducted under field sampling conditions, as well as in controlled laboratory conditions. Further evaluations should include actual ambient sampling with various cartridge designs with each of the carbonyl samplers, and intercomparison of ambient results among the various samplers.

ACKNOWLEDGEMENT

Although this work was supported by the U.S. Environmental Protection Agency under Contract No. 68-D0-0007 to Battelle, this paper has not undergone Agency review, and no official

endorsement should be inferred. We thank William McClenny of EPA for initiating this evaluation. We also thank the four vendors for the loan of their samplers for this evaluation.

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Table 1. Results of quantitative ratings of automated carbonyl samplers.

Characteristics	Max. Possible Score	Ratings ^(a)			
		XI	SX	SIS	GA
Setup and Operation	25	20	20	25	18
Durability	25	18	18	23	23
Field Serviceability	15	9	12	7	14
Replacement Parts	15	10	11	9	14
Sequencing Capabilities	25	19	17	23	5
Sealing of Cartridges	50	38	20	37	10
Sampling Rate	50	38	40	40	45
Sampling Channels	50	50	40	37	10
Ozone Scrubber	50	45	47	10	10
Heated Sample Line	25	8	23	7	5
Low Cost	25	10	13	18	20
Overall Opinion	50	43	33	30	10
Total	405	308	294	266	184

(a) Values shown are the average of from 2 to 4 weighted ratings scores provided by individual reviewers
 XI - Xontech, Inc.; SX - Supelco-Xitech; SIS - Scientific Instrumentation Specialists; GA - Graseby-Andersen.

**Performance Measurements of C₁-C₃ Carbonyl Compounds
Using DNPH-Coated Silica Gel and C₁₈ Cartridges**

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Measurements have been conducted to examine the performance of formaldehyde, acetaldehyde, and acetone using silica and C₁₈ cartridges coated with 2,4-dinitrophenylhydrazine. Laboratory measurements for formaldehyde were conducted using a paraformaldehyde generator to produce reproducible and constant concentrations of the compound. For acetaldehyde and acetone, known concentrations were generated in Teflon chambers. The compounds were routed into a sampling manifold where simultaneous measurements could be made with multiple cartridges. Typical concentrations employed in the study were as follows. HCHO: 0.5-25 ppbv; CH₃CHO; 0.5-10 ppbv; CH₃C(O)CH₃; 0.5-10 ppbv. Additional measurements were conducted for these compounds in the presence of potentially interfering compounds such as ozone and water vapor. Serial cartridge collections were periodically used to investigate breakthrough the carbonyl compounds.

EVALUATION OF AN INTELLIGENT MULTI-CANISTER / MULTI-CARTRIDGE SAMPLER FOR THE COLLECTION OF OZONE PRECURSORS

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ABSTRACT

Air monitoring requirements for Enhanced Ozone Monitoring (EOM) set down in the 40 CFR Part 58 require the collection of 8 three hour Volatile Organic Compound (VOC)/carbonyl samples each sampling day. To meet EOM monitoring requirements for Southeastern Wisconsin, we have designed and built a sampler capable of collecting multiple canisters (for VOCs) and multiple cartridges (for carbonyls). The sampler is comprised of three modular units, the canister collection system, the cartridge collection system, and a personal computer which acts as an intelligent controller. The intelligent controller will track all samples from the sampler setup, through sampling, to sampler take down. Relevant sampling data such as initial canister vacuum, final canister pressure, and sampling flow rates are all recorded by the sampler. At the completion of the sampling episode, all sampling data are down loaded to the project database. We will report on the design of the sampler and the sampler performance during an initial season of sampling.

INTRODUCTION

Ozone is the most pervasive air pollution problem in Wisconsin affecting the eastern shoreline from the Illinois border to the Door County peninsula¹. With the enactment of the Clean Air Act Amendments (CAAA) of 1990 and the non attainment designation of "severe" for 6 counties in southeast Wisconsin², the Wisconsin Department of Natural Resources (WDNR) began to develop plans for Enhanced Ozone Monitoring (as required by Title I, CAAA) including plans to establish a Photochemical Assessment Monitoring Station (PAMS) network.

The WDNR has conducted ozone monitoring for over 25 years and has been monitoring ozone precursors since the early total Nonmethane Organic Compound (NMOC) studies began in 1987. Since 1987, the Air Monitoring section of the WDNR has developed an expertise in all areas of monitoring ozone precursors, at ground stations and from aircraft platforms³. When these studies began, there were few commercial systems for the collection and analysis of ozone precursor sampling. Using USEPA guidance⁴, we fabricated all sampling systems (canister and cartridge), canister cleaning systems, and analytical systems (PDFID). While these simple systems were adequate for the collection of daily 6 to 9 am samples for programs such as the NMOC program, they were inadequate for the more rigorous sampling demands of the PAMS network which can include daily sampling for up to 8 samples. With experience building both canister and cartridge samplers (and a lack of commercially available instrumentation), we chose to design and build new samplers for both of these parameters that would be capable of meeting the most rigorous sampling schedule planned for the PAMS network. In planning the new sampler, we began by developing a list of key elements for the new sampling system that included the following:

- 1.) the sampling system must collect valid canister and carbonyl samples;
- 2.) the sampling system must be capable of collecting samples around the clock for multiple days;

- 3.) turn key operation of the sampling system;
- 4.) the sampling system must perform quality control tasks (collect duplicate samples; perform the pre- and post sampling checks of vacuum, pressure, and flow);
- 5.) the sampling system must track samples and collect relevant sampling data; and
- 6.) the sampling system should transmit sampling data to the monitoring database.

From these objectives, we developed a comprehensive design for a multiple canister/multiple cartridge sampler capable of collecting 8 three hour samples each sampling day. This paper will report on the design and initial testing of the Wisconsin multiple cartridge/multiple canister sampler, hereafter referred to as the PAMS sampler. The PAMS sampler consists of a VOC sampler unit, a carbonyl sampler unit, and a computer acting as an intelligent controller.

SAMPLING EQUIPMENT

Design considerations for the VOC sampler unit require a method of sampling that automatically captures a volume of ambient air which can be analyzed for a host of parameters at a later time. The sample is collected in specially treated stainless steel canisters. Eight canisters and one duplicate canister are to be collected daily.

Design considerations for the carbonyl sampler unit require a method of sampling that draws ambient air through a pre-packed silica gel cartridge coated with acidified 2,4 dinitro phenylhydrazine (DNPH) which can later be analyzed for the desired parameters. Air is drawn through the cartridge at a predetermined sample flow rate for a defined period of time. Eight cartridges and one duplicate cartridge are to be collected daily.

Each canister and cartridge has to be representative of the three hour sample period. This requires precise control of the sample flow throughout the three hour sampling interval. Canister pressures have to be known before, during, and after sampling. The sampling system flow paths have to be purged prior to collection of samples. All parameters related to sample collection need to be stored in a file for later sample processing and data validation. Consideration was given to using and/or adapting commercially available components in the design wherever possible. Panels, enclosures, and cartridge holders required a certain amount of machining and are unique to the overall instruments.

VOC Sampler Hardware. The VOC sampler is designed to automatically collect eight canister samples and one duplicate under the control of an intelligent process control and data acquisition system. The VOC sample system consists of a sampling pump that has stainless steel internal flow stream components and an equipment rack to hold all nine canisters along with the VOC sampler. The sampler has six main elements: a multi-position valve (11 port, dead end flow path), mass flow controller, digital input/output, analog to digital measurement, digital to analog control, and communications interface to the computer control and acquisition system.

Carbonyl Sampler Hardware. The carbonyl sampler is designed to automatically collect eight cartridge samples and one duplicate under the control of an intelligent process control and data acquisition system. The carbonyl sample system consists of the carbonyl sampler, a heated ozone scrubber, and a sample pump. The sampler has seven main elements: cartridge holders, a multi-position valve (22 port, trapping flow path), a mass flow controller, digital input/output, analog to digital measurement, digital to analog control, and communications interface to the computer control and acquisition system.

PAMS COMPUTER CONTROL SYSTEM

The program to control the automatic sampling instrumentation was loaded on a 386DX-33 personal computer (PC) with 4 MB RAM, 100 MB hard disk. The program was written as an autoloading, MS - Windows 3.1 application under MS Visual Basic for Windows Rev. 2.0. It was felt that a Windows application would have a lower learning curve over a DOS based application. To reduce transcription errors when entering sample information, a bar code reader was incorporated into the system. Using the bar code reader, the operator scanned sample identifications and sample port locations into the operating data base. When all of the sampling information was entered, the operator was asked to perform a system wide leak check as part of a QC procedure. Finally, the operator pushed a start button (Windows control button), at which time, the system made a final completeness check and started the sampling process.

Automatic Sampling. The system stayed in a holding pattern until 15 minutes before the first sample was to be taken. At this time, the sample pumps were started to purge the sample lines. Next, at sample time (00:00 hours), the multi-position valves were moved to the proper sample port, the mass flow controller's set points were established and sampling begun. During sampling, the computer tracked the sample flow rates and sample pressures. The VOC sample pressure changed from near 0 mm Hg absolute to about 2200 mm Hg absolute. The sample pressure transducer for the carbonyl sampler monitored the vacuum draw of the sample pump. The data logging process tracked and recorded the minimum, maximum, and average sample flow rates as well as the beginning and ending pressure readings throughout the three hour sample period. At the end of the sample period, the logged data was sent to the hard disk and the cycle repeated until all eight samples were taken. After the last sample, the collected data was transferred to a spreadsheet ready data file where the operator copied the information to a floppy disk. Before removing the completed samples, the operator was asked to perform another QC leak check. Finally, the computer program would reset itself for the next run.

SAMPLER EVALUATION

The sampler was evaluated at an urban Milwaukee site over the course of the 1993 Ozone Precursor Monitoring Program/Intensive Sampling Period. This period encompassed the months of June, July and August (and was extended to early September). During this period of intensive sampling, 8 three hour samples (both canister and cartridge) were collected every third day. Samples were analyzed for PAMS target compounds⁷ and additional compounds requested by the WDNR. The PAMS sampler was evaluated on two criteria: the first is the ability of the sampler to carry out the complex task of collecting multiple samples; and the second is the ability of the sampler to collect valid samples. The first criteria is defined by how well the sampler carried out assigned tasks and the overall data completeness. The second criteria is defined by sampler blank, the duplicate samples, and collocated samples (against an independent sampler).

Completeness and Sampler Operations

The PAMS sampler was designed to complete intensive sampling conducted during the summer months and to collect a total of 264 samples (240 samples plus 24 duplicates). A total of 242 canister samples (91.6% completeness) and 260 carbonyl samples (98.5% completeness) were actually collected during this period. A problem with condensed water plugging the mass flow controllers of the VOC sampler caused the largest loss of samples (5.7%). The problem was remedied by the installation of a sample line moisture trap.

Sampler Blank (Certification)

The sampling units of the PAMS sampler were constructed with inert material (chromatographic grade stainless steel) wherever possible and care was taken to reduce the use of synthetic materials. Prior to the start of sampling, the sampler was purged with humidified zero air. After this purge, a sampler blank test was conducted to determine if the sampler had a significant background that might contaminate samples. The test was conducted by challenging the VOC sampler with humidified zero air and collecting canister samples for analysis. The carbonyl sampler was challenged with carbonyl free ambient air.

Canister sampler. Analysis of a single canister sample from channel #4 (randomly selected) showed a background of 53 ppbC. The gas chromatographic (GC) analysis detected only trace amounts of 3 target compounds (toluene, xylene, and 1,2,3-trimethylbenzene). No other target compounds were detected and the measured background was made up of unidentified compounds. Additional investigation of the detected peaks found that 10.5% was made up of an early poorly chromatographed peak (possibly an oxygenated compound); 38.1% was from two chloroflorocarbons, chlorodifluoromethane (Freon 22) and trichlorotrifluoroethane (Freon 113); and the remaining 46.5% was unidentified compounds all eluting after toluene.

The post sampling blank was substantially cleaner than the pre-sampling blank. Total NMOC concentrations were less than 5 ppbC with only trace quantities of benzene and toluene detected. The sampler background was acceptable for the collection of target PAMS compounds. The remaining background is of some concern, but its absence in the post sampler check suggests that the background is not permanent. In future sampling years, we will reduce the use of cleaning spray (containing fluorocarbons) and increase the purging of the sampler prior to the sampling program.

Cartridge sampler. Analysis of three cartridges used to test the 9 channels showed carbonyl concentrations 2 times the concentrations found in the blank cartridge. The results would calculate to average concentrations of 0.2 ppbv for formaldehyde, 0.1 ppbv for acetaldehyde, and 0.7 ppbv for acetone. These levels were acceptable for sampling. Acetone does show a high background, but this is likely associated with a high cartridge blank.

Duplicate Samples

The sampling unit was constructed with 8 sampling channels. The eighth channel of both the canister and the carbonyl sampler is split to allow for the collection of duplicate samples. The sampling channels are sampled in numerical order. The starting channel is varied so the duplicate samples are collected for different time periods (and conditions) over the course of the study. Summary results from the duplicate samples are shown in Table 1. Analysis of the hydrocarbon data showed a 9% Relative Percent Difference (RPD) for the total nonmethane hydrocarbons values. Overall the speciated data from the 22 samples sets contained 1650 data pairs. Of these pairs, 437 (26%) were below the detectable level on both the channels and were deemed "acceptable". For 99 pairs (6%), the hydrocarbon species was detected in only one of the two channels. This was concentration related as this number dropped to less than 1% for concentration greater than twice the detection limit. The average RPD for the remaining 1213 data pairs was 24%. The species RPD was affected by concentration and the average RPD dropped to 16% for mean concentrations greater than 0.4 ppbC (twice the MDL).

The carbonyl sampling unit collected a total of 25 duplicate sample sets analyzed for a total of 75 species data pairs. The average concentration measured was 2.4 ppbv. The average RPD was calculated to be 23% (ranging from 0 to 154.7%) and the median RPD to be 9.5%.

Two thirds of the data pairs had RPDs less than 15%. There was no apparent difference in the duplicates collected for the three carbonyl species. In two of the sample pairs (3%) carbonyls were detected in only one sample of the set. Duplicate sampling also picked up two anomalous data points (RPD > 100%) that are being investigated for a possible acetone interference.

Collocated samples

As part of the WDNR quality assurance plan, three collocated samples were collected periodically throughout the summer. Collocated samples were collected on an independent WDNR sampler for the identical time period as the primary sample collected on the PAMS sampler. Results for collocated samples are shown in Table 2. The overall comparison of samplers were good and improved throughout the sampling period. The initial comparison of total NMOC indicated a large percent difference (-130.3) due to a large difference in late eluting unidentified compounds. The collocated carbonyl sampler lacked an ozone scrubber. This may account for the higher percent differences seen in the formaldehyde pairs.

CONCLUSIONS

We feel the Wisconsin PAMS sampler was an overall success. The sampler successfully performed required sampling, including duplicate sampling and quality control functions. The data completeness was good and can be expected to improve as the sampler operation becomes more routine. The operation of the system was simple and site operators trained to use more elementary canister and cartridge samplers were able to quickly adapt to the more advanced PAMS sampler. The sampler successfully tracked samples and collected relevant sampling data. The transmission of the sampling data from the sampler to the Department's database was smooth and seamless. The reconciliation of the sampling records and the results database was an easier process with far fewer problems than occurred with the hand keyed information. Sample validity tests indicate that the majority of the monitoring data are acceptable and meet WDNR quality assurance objectives.

The Wisconsin PAMS network will include four stations and will be part of a Lake Michigan regional monitoring plan⁶. In 1994, the WDNR will establish its second PAMS monitoring station at Harrington Beach and deploy a second PAMS sampler at this site. The only physical modification expected to be made in new samplers is to increase the valve bore on the trapping multi-position valve from 0.050 to 0.067 inches. The present bore size was found to limit flow through the DNPH cartridges. Software changes are expected to be more extensive and are the result of changes in the monitoring plan to include forecasted sampling days. Plans for the program include a change from a preset sampling schedule with a maximum of eight sample periods to continuous sampling using a spreadsheet style input screen. Sampling times and dates will be changeable from a remote computer via modem communications. Future plans include data logging and control of other monitored parameters such as O₃ and NO_x. In anticipation of these software changes, a new computer platform will be used. This computer will be a 486DX2-66 with 16 MB RAM and a 340 MB hard disk and will use a multi-tasking operating system.

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Table 1. Duplicate Sample Analysis, Summary of Relative Percent Difference

Parameter	# Pairs	Average RPD	Median RPD	Range
Total alkanes	22	6.0%	5.6%	0.2 to 19.0%
Total alkenes	22	14.3%	9.3%	0.8 to 42.9%
Total aromatics	22	6.0%	5.3%	0.0 to 21.1%
Total NMOC	22	9.5%	6.7%	1.2 to 31.4%
Total unidentified	22	25.9%	17.9%	1.3 to 85.1%
VOC Target Species (taken as a whole)	1213	23.8%	11.8%	0.0 to 142.9%
Acetone	25	27.4%	9.2%	0.8 to 154.7%
Acetaldehyde	25	22.4%	9.2%	0.0 to 100%
Formaldehyde	25	19%	10.1%	0.0 to 100%

Table 2: Collocated Samples Percent Difference

Parameters	06-Jul	27-Jul	02-Aug	26-Aug
Total alkanes	-26.8%	no sample	35.9%	-12.27%
Total alkenes	-31.7%	no sample	36.1%	-11.2%
Total aromatics	-26.7%	no sample	24.6%	-11.6%
Total NMOC	-130.3%	no sample	31.1%	-16.4%
Total unidentified	-502.9%	no sample	27.0%	-32.8%
VOC Target Species	-34.6%	no sample	27.4%	-16.8
Acetone	-35.4%	8.9%	20.7%	-3.9%
Acetaldehyde	-31.3%	17.7%	14.5%	-13.1%
Formaldehyde	27.4	50.1%	48.7%	38.2%

THE DEVELOPMENT OF A CARBONYL SAMPLER FOR ENOM/PAM SITES

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ABSTRACT

In accordance with the Clean Air Act Amendments of 1990, rules were developed for the establishment of the Enhanced Ozone Monitoring Network and Photochemical Assessment Monitoring Stations (PAMS) in ozone nonattainment areas. These rules require the stations to collect ambient air measurements for a target list of meteorological measurements of surface and upper air. Included in the VOCs are several aldehydes. In the past, canister sampling and analysis for C_2 - C_{10} hydrocarbons have been the subject of much discussion and implementation. Presently carbonyl compounds, especially low molecular weight aldehyde and ketones are receiving increased attention as toxic air pollutants or as intermediates in many photochemical reactions. Because these compounds occur in trace concentrations ranging from sub-parts per billion to higher parts per billion in the atmosphere, sampling for carbonyl compounds poses some challenging problems. XonTech, Inc. has designed a carbonyl sampler suitable for Ozone Precursors Monitoring Program or the PAMS requirement of short time monitoring around the clock. The design, features, and operation of this sampler will be presented.

INTRODUCTION

The focus of attention at this symposium for the last few years has been the sampling and analysis strategy for the volatile organic compounds. The target list for VOCs has been the C_2 - C_{10} hydrocarbons. Two sampling methods for the collection of VOCs are provided by the USEPA Technical Assistance Document. The first method is the Canister Collection. This involves using a sample pump, pressurizing the sample air into a stainless steel canister whose interior surfaces have been conditioned by the 'Summa' processes. While canister sampling has been used to collect some carbonyl compounds, it is not suitable for low molecular weight carbonyls, especially the highly water soluble formaldehyde. The second method is the on-site automated GC system, or commonly known as the Continuous GC Method. This method is based on emerging technology and as such is subject to continuing evaluation and improvements in the future.

CARBONYL COMPOUNDS

Recently, increased attention has been given to the carbonyl compounds. The low molecular weight aldehydes and ketones such as formaldehyde, acetaldehyde and acetone are required specifications for the proposed enhanced ozone precursors air

monitoring. Some of these carbonyls are major promoters in the formation of photochemical ozone, and short term exposure to these compounds is known to cause irritation of the eyes, skin and mucous membranes of the upper respiratory tract. The major emission sources of the carbonyls appear to be vehicle exhaust, incineration of waste, and burning of fuels. In addition, significant amounts of atmospheric carbonyls can result from photochemical reactions between ROC & NO_x. The proposed sampling methodology for carbonyl compounds is the USEPA Method T0-11 which utilizes DNPH-coated silica gel cartridges. Because of the trace concentrations of these compounds, typically in the range of low 1 ppb - 20 ppb, sampling for carbonyls poses some challenging problems.

PROBLEMS IN CARBONYL SAMPLING

Interferences

- 1) Formaldehyde contamination of DNPH reagent used in coating the solid adsorbent is a frequently encountered problem.
- 2) Ozone has been shown to interfere negatively¹ and positively by reacting with both DNPH and its hydrazone derivatives in the cartridge.
- 3) Exposure of DNPH coated sampling cartridges to direct sunlight may produce artifacts and should be avoided.²
- 4) Sampling rate restriction.

Solutions to minimize interferences

- 1) Recrystallization and purification of DNPH reagent.
- 2) The most direct solution to the ozone interference is to remove ozone before the sample stream reaches the cartridge. This process entails constructing an ozone denuder or scrubber and placing it in front of the cartridge. The denuder can be constructed in two ways.
 - a) A 3-ft. ¼" O.D. copper tubing that is filled with a saturated solution of KI, and allowed to stand for about 5 minutes, drained and dried with a stream of zero air or nitrogen for about 1 hour. (The capacity of ozone in such a denuder is about 10 ppm - hour of ozone.³)
 - b) Filter denuder - a 47mm glass fiber or cellulose filter impregnated with a saturated solution of KI and dried under N₂ or clean air. This kind of denuder has been calculated to last for ~ 1 - 2 weeks of sampling.

- 3) Provide cartridge holder to prevent direct exposure to sunlight.
- 4) The flow rate limitation is principally due to the pressure drop across the DNPH-coated cartridges. We have tested a large number of cartridges, compliments of Dr. Crowley of Waters Associates, and our results indicated that the maximum flow rate is limited to about 1.25 liters/min. This limitation allows us to select a mass flow controller with the appropriate flow range and a suitable pump.

CARBONYL SAMPLER

In the past, XTI has collaborated with CARB in designing a microprocessor controlled Model 920 sampler for CARB's formaldehyde studies. This consists of a sampling unit, a control unit and a pump unit. The sampling unit has 8 channels, and each channel has its own mass flow controller. The sliding valve exposes the cartridge at the sampling start time and seals the cartridge at the end time. A print out giving the total flow, power fail time if any, start time, end time, sampling date, sampling station, etc. is provided for each channel.

Based on this experience, XonTech has developed a new carbonyl sampler to meet the present requirement of ENOM/PAM sites. A prototype carbonyl sampler was developed for EPA evaluation. This evaluation was reported by Tom Kelly of Battelle in a paper presented earlier this morning. Since then, the prototype sampler has evolved into a microprocessor controlled/PC interface unit to meet the requirements of variances obtained by different State agencies.

SPECIFICATIONS OF MODEL 925 CARBONYL SAMPLER

- 1.0 The Model 925 is a microprocessor controlled carbonyl sampler. The instrument consists of a control unit and a tube unit. The control unit can operate up to 4 tube units.

2.0 SAMPLE CHANNELS

- 2.1 One 24 hour channel.

Programmable start time, date and duration.

- 2.2 One collocated/24 hour channel.

Programmable start time, date and duration.

- 2.3 Eight "X" hour channels (typically set to 3 hours).

Programmable start time, date and duration for all 8 channels.

2.4 One field blank tube holder.

3.0 CLOCK

3.1 Battery-backed clock and microprocessor memory retains time, date and sampling program during periods of power failure.

3.2 The sampling valve used to select the 8 "X" hour sample channels will advance to the proper channel when power is restored.

4.0 ELECTRONIC MASS FLOW CONTROLLERS (3)

4.1 24 hour channel - adjustable from 0 to 1.50 liter/min. full scale. (Practical range is .15 to 1.35 liter/min.)

4.2 Collocational/24 hour channel - adjustable from 0 to 1.5 liters/min. full scale. (Practical range is .15 to 1.35 liter/min.)

4.3 8 "X" hour channels - adjustable from 0 to 1.5 liters/min. full scale. (Practical range is .15 to 1.35 liter/min.)

5.0 DENUDER OVEN

5.1 A denuder oven with programmable temperature controller is provided in each tube chassis, the temperature is adjustable from ambient to +80°C. The rotary valves, the solenoid valves, and all sampling tubes are likewise heated.

5.2 Filter type denuder holder optional.

6.0 ELAPSED TIME DISPLAY

6.1 Elapsed time can be displayed for the 24 hour, collocated/24 hour and 8 "X" hour channels to show total sampling time.

7.0 POWER FAILURE DISPLAY

7.1 The default display screen indicates if a power failure has occurred. The duration of the power failure can then be displayed for all channels.

7.2 A power failure is defined as a loss of AC power for more than 1 minute.

8.0 FLOW DISPLAY

8.1 The default display screen indicates if a flow error has occurred. The duration of the flow error can then be displayed for all channels.

8.2 A flow error is defined as a flow that varies by more than $\pm 10\%$ of the set flow within the practical range of .15 to 1.35 liters/min.

8.3 The elapsed time counter for the affected channel will stop accumulating time during conditions of low flow.

9.0 TEMPERATURE CONTROL

9.1 Control box temperature is sensed and used to control an internal heater or fan to keep the flow controllers within their operating temperature range.

10.0 REMOTE CONTROL

10.1 A RS-232 modem port is provided on the control unit. An optional modem allows communications to be established between the 925 control unit and a remote personal computer. The remote computer has access to all 925 operator inputs and displays. This allows the 925 to be programmed remotely and re-programmed for episode sampling.

11.0 SAMPLE INTEGRITY

11.1 All sample tubes are sealed on both ends when not sampling.

11.2 All tubing and fittings upstream of the sample tubes are stainless steel. Solenoid valves are stainless steel with viton o-rings.

12.0 AVAILABLE TUBE HOLDERS

12.1 Sep-pak.

12.2 2 X Sep-pak.

12.3 New Sep-pak (Walters).

12.4 2 X New Sep-pak.

12.5 NIOSH type tubes.

13.0 SAMPLE PUMP

13.1 Oil-free system vacuum pump rated 5 liters/minute at -25"Hg.

14.0 PACKAGING

14.1 Control chassis.

Contains the microprocessor, display, keyboard and mass flow controllers.

7" High X 19" Wide X 13" Depth, 25 Lbs.

19" rack mountable.

14.2 Tube chassis.

Contains the 8 position rotary valve and position indicator, solenoids, denuder oven, temperature controller and tube/filter holders with quick-connect fittings.

14" High X 19" Wide X 13" Depth (tube fittings extend an additional 2.5" from rear panel), 35 Lbs.

19" rack mountable.

15.0 EXPANSION

15.1 One control chassis will control up to 4 tube chassis (40 sample tubes total).

16.0 OPTIONS

16.1 Weather-resistant chassis enclosure.

16.2 Fan aspirated sample manifold.

16.3 Additional tube chassis.

16.4 Modem.

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**The Supelco™ Carbonyl Ambient Air Sampler
for
EPA - 600-4-84-041², Method TO-11**

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Abstract

Supelco is proud to announce the introduction of new sequential air samplers for **PAMS**. This new technology satisfies all requirements of **Section 182** of the **1990 Clean Air Act**, **EPA 40 CFR Part 58** and **ASTM Standard D 5197-92¹** for sampling of formaldehyde and other carbonyl compounds. Due to the vigorous demand of nonstop sampling for several months, Supelco has developed a totally independent (redundant) modular sampling concept to insure no sampling time is lost due to maintenance. These instruments are capable of operating unattended for up to four complete days. This paper will address the different types of samplers and their operating features and specifications.

During the research and development of the Supelco carbonyl sampler technology, Supelco identified four major areas of concern by individuals required to implement the new PAMS¹ monitoring program. These areas were: I. manpower vs automation, II. sequential sample collection, III. sample protection, and IV. sampling integrity.

I. Manpower vs Automation

The PAMS¹ program requires 24 hour continuous sampling from June to September. This rigorous schedule creates an uneasy choice between additional personnel or automation to cover weekends and holidays. There are three possible operation choices one can make using the different Supelco samplers.

The first choice requires daily attendance, i.e. the most manpower with the lowest capital equipment cost. This choice will require a minimum of two Model 2010 (Figure 1) samplers or one Model 2052 (Figure 2) sampler. The Model 2010 sampler can be placed outside under a protective covering, whereas the Model 2052 sampler has to be operated indoors. The Model 2052 sampler is less costly because it has two sequential modules sharing a single air flow source.

The second choice requires weekday attendance with 2-day weekends, i.e. manpower only during the work week with no provision for holidays or a four day work week. This choice will require four Model 2010 samplers or one Model 2054 (Figure 3) sampler. There is a major equipment cost reduction by choosing the Model 2054 because it has four sequential modules sharing one flow source and takes up a lot less space. Here is how the four sequential modules are used to cover a 2-day weekend:

Friday 12:00 noon preparation for unattended operation for a 2-day weekend :

#1 module is sampling and will finish 12:00PM Friday night

#2 module is waiting and will sample Friday night 12:00PM to Saturday night 12:00PM

#3 module is waiting and will sample Saturday night 12:00PM to Sunday night 12:00PM

#4 module is waiting and will sample Sunday night 12:00PM to Monday night 12:00PM

The third choice requires weekday attendance with 3-day weekends, i.e. manpower only during a work week which could have a three day weekend or i.e. four day work week. This choice will require five Model 2010 samplers or one Model 2055 (Figure 4) sampler. There is a major equipment cost reduction by choosing the Model 2055 because it has five sequential modules sharing one flow source and takes up a lot less space. Here is how the five sequential modules are used to cover a 3-day weekend or 4-day work week.

Thursday 12:00 noon preparation for unattended operation for a 3-day weekend :

#1 module is sampling and will finish 12:00PM Thursday night

#2 module is waiting and will sample Thursday night 12:00PM to Friday night 12:00PM

#3 module is waiting and will sample Friday night 12:00PM to Saturday night 12:00PM

#4 module is waiting and will sample Saturday night 12:00PM to Sunday night 12:00PM

#5 module is waiting and will sample Sunday night 12:00PM to Monday night 12:00PM

Model 2010

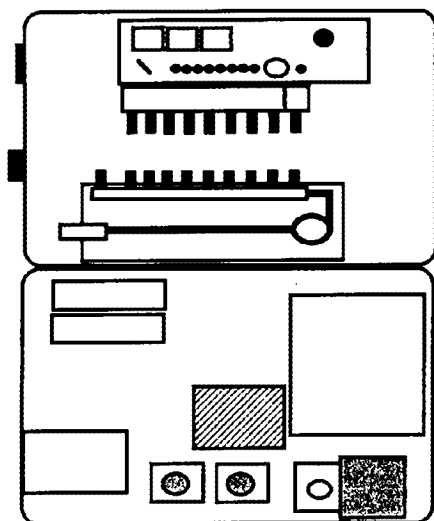


Figure 1

MODEL 2052

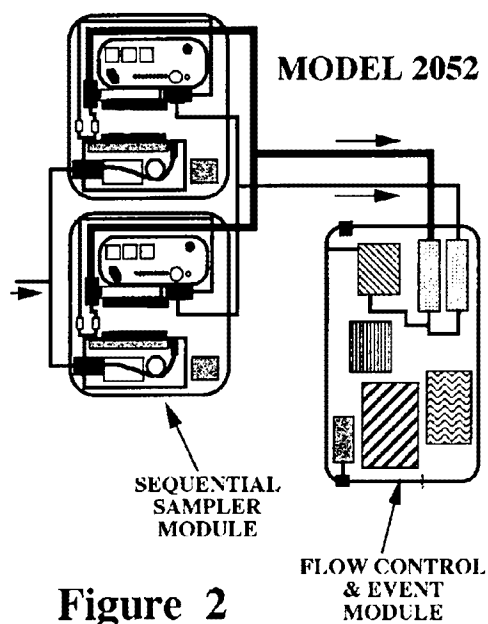


Figure 2

MODEL 2054

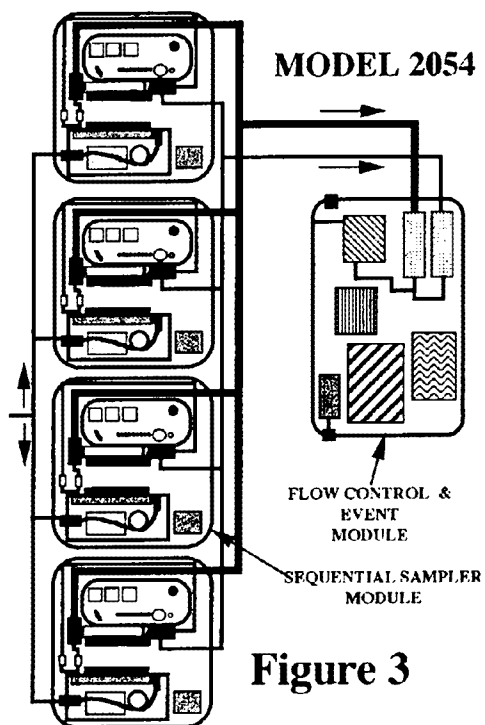


Figure 3

MODEL 2055

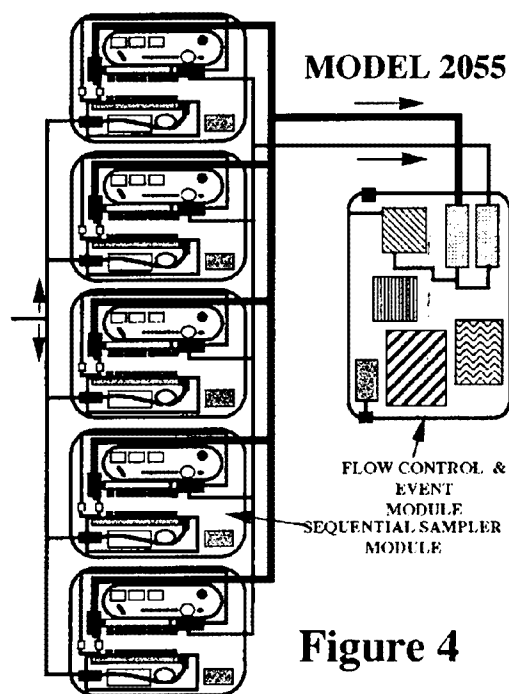


Figure 4

II. Sequential Sample Collection

The PAMS¹ method of collecting samples had two basic requirements. The sampling technology must be able to collect eight 3-hour samples in a sequential manner starting at midnight. Also, the sampling technology must be able to collect a 24-hour sample simultaneously with the sequenced samples. Our field research also revealed two additional sampling requirements: ability to sequence two cartridges in series (for a breakthrough confirmation) and ability to use the ninth sample to co-locate with any of the sequenced samples or as a 24-hour reality check. The Supelco sequential module was designed to address all of the above requirements.

The three timers (Figures 5 & 6) in the sequential module provide: a system delay (0-10 hours) so the user can set up the sequencers during working hours and have the sequencers begin sampling at midnight; a delay between samples (0-10 hours) which is normally set to zero for PAMS sampling; and a sample time (0-10 hours) for each of the sequenced samples.

The 9 position co-location switch is used to control the ninth sample. PAMS¹ requires that a 24-hour reality check be taken every sixth day at certain times. Switch positions 1-8 are used to co-locate the ninth sample with one of the sequenced samples and the 9th position is used for the 24-hour reality check. We have also added green indicator lights for all of the nine samples to give a visual indication of which samples are active.

Two design features were incorporated into our samplers to accommodate two cartridges in-line for breakthrough confirmation. We provided enough space between the control valves and the inlet manifold to attach two sample cartridges, and we sized the vacuum pump to provide up to 1 liter per minute flow rate through both cartridges. There is only one limitation when performing a breakthrough check: the vacuum pump does not have enough flow capacity to accommodate two cartridges in-line plus a co-located sample. Therefore, breakthrough studies should be performed when the 24-hour reality check is not required.

III. Sample Protection

PAMS¹ has identified three interferences which can affect the silica gel-based DNPH cartridges. moisture (water), ozone, and sunlight will cause contamination of the sample. There is one additional concern we discovered in our field research which is passive air exposure to the sample cartridges during the 24 hour sampling period.

Moisture in the inlet sample train is of concern when the ambient air temperature goes below 15°C. The solution we have provided to remedy this situation is an optional 3 meter long heated external sample line and a heated inlet manifold oven (the housing includes a 1-meter long denuder and a sample manifold). Each of these heated zones is independently controlled.

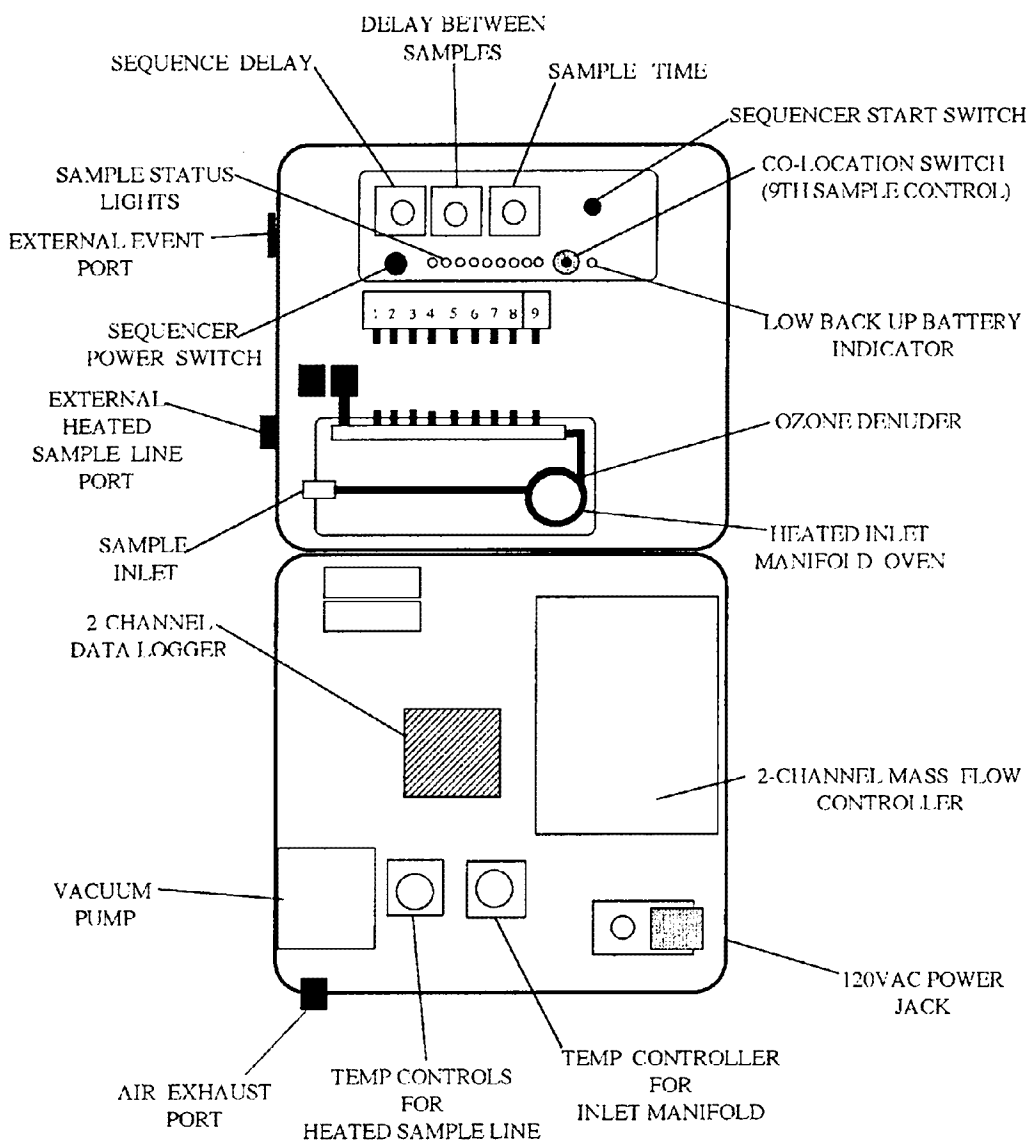
Ozone is always present in any air sample taken. Therefore, we have designed an easily removable 1 meter X 1/4" dia. copper denuder ozone scrubber (10,000 ppb-hour capacity) for removing light concentrations of ozone in the air.

To protect the samples from direct sunlight during the 24-hour sample period, we have designed an easily removable cover plate which surrounds all of the samples.

The final interference to the DNPH cartridges is from passive air exposure while the cartridge is connected to the manifold. We have incorporated an in-line stainless steel check valve upstream of every sample.

MODEL 2010 SEQUENTIAL SAMPLER

Figure 5



SEQUENTIAL SAMPLER MODULE

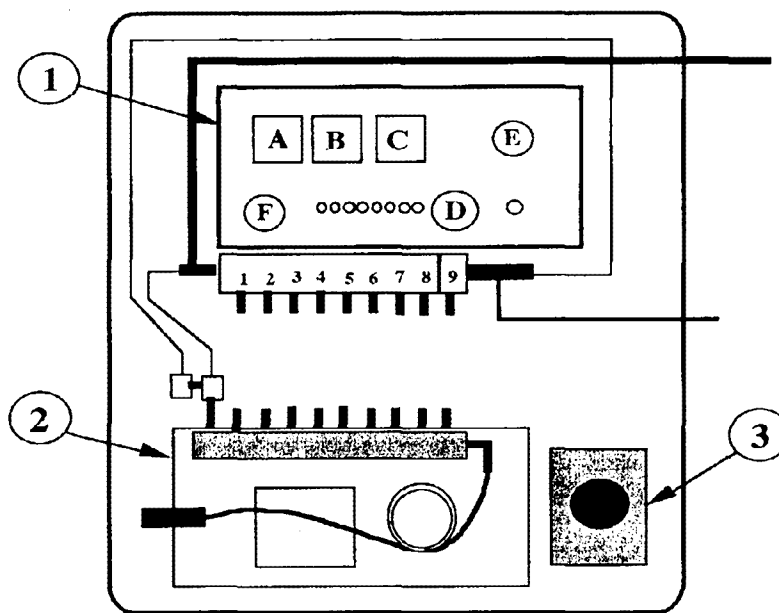


Figure 6

Item 1 is the sequential timer module that performs the following functions:

Timer (A) delays the sequence start time, from 0 to 10 hours.

Timer (B) creates a delay between each sample, from 0 to 10 hours.

Timer (C) sets the sampling time for the eight sequenced samples, from 0 to 10 hours.

The nine small green lights to the left of knob (D) indicate which sample(s) are active.

The red light to the right of knob (D) indicates when the back-up battery is low.

When this light is on, there is not enough battery power to protect the sequencer if AC power is lost.

Knob (D) is a 9 position switch which is used to select when the ninth sample valve will be active. It can be active at the same time as any one of the eight sequenced samples (positions 1-8), or during all eight sequenced samples (position 9).

Button (F) is the manual start switch that activates the sequencer.

Toggle switch (F) is to apply power to the sequencer.

Item 2 is the inlet manifold module which includes the following hardware:

Copper denuder 1/4" dia., 1 meter long.

Stainless steel inlet manifold, nine barbed sample ports, each with built-in check valve.

100-watt heater with built-in thermal couple.

Insulated aluminum housing with lid that covers module and samples.

Item 3 is the heater controller for the inlet manifold module. The temperature range is 0-150° F.

FLOW CONTROL & EVENT MODULE

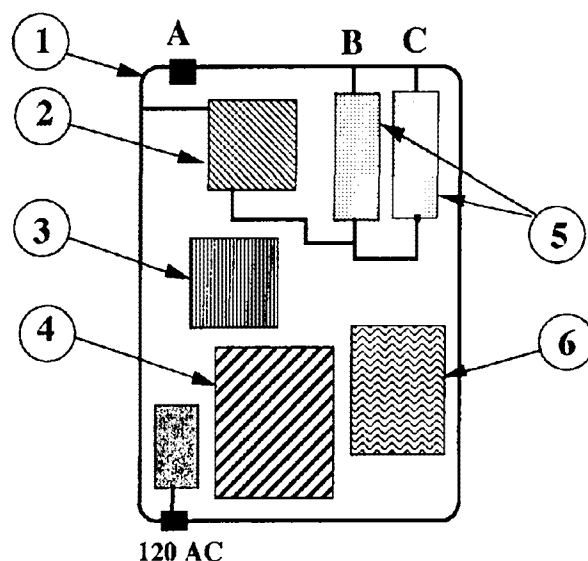


Figure 7

Item 1 is the flow control & event module housing, a plastic, lockable case with a fused 120VAC power jack. "A" is an external event port. "B" is the vacuum air supply to the ninth sample valve. "C" is the vacuum air supply for sample valves 1-8.

Item 2 is the main air supply pump for sampling. It is capable of maintaining up to 2 liters per minute flow rates to each electronic mass flow controller "5", providing there is only one sample cartridge on each flow stream.

Item 3 is an OPTIONAL two-channel data logger for recording the actual flow history for both sequenced samples 1-8 and the ninth sample. The flow data is stored on a memory card which is later downloaded into an IBM compatible computer.

Item 4 is a two-channel electronic mass flow controller module. Its functions include: controlling Items 5; displaying (1/2" high digital readout) the set flow rate and actual flow rate of each flow controller; user controls for setting the desired flow rate for each flow channel; and two output signals for recording actual flow rate histories.

Items 5 are electronic mass flow controllers with a flow range of 0-2 liters per minute.

Item 6 is the external events program module. This module has a 4 digit, 7 segment digital display, 1/2" high. This module is capable of programming multiple events for preselecting the sample run day and time, and the duration of each run for up to 7 days in advance. This module includes a battery back up feature to maintain the correct time for at least 8 hours in the event of a power failure.

IV. Sampling Integrity

There are two requirements for maintaining a stable sampling environment. The air flow through the sample cartridges must be maintained using an electronically controlled mass flow meter, and there must be some type of external method of confirming that the air flow was not interrupted for more than 5 minutes. We have one additional issue, which is having battery back-up maintain the electronic sequencer when there is a momentary loss of AC power.

There are two independent electronic mass flow controllers (Figure 5&7), one for the sequenced samples and one for the 24-hour sample. This independence allows the user to select a flow rate for the sequenced samples that is different from that of the 24-hour sample.

We have incorporated two methods for flow rate confirmation. The first is an in-board two channel electronic flow data logger (Figure 5&7) with memory card storage (used to transfer flow data to an IBM compatible PC). The second method for collecting flow data is through our external event port. This port (DB-25 connector) allows an external data system to monitor both mass flow controllers and receive a remote start signal for the sequencer.

The sequencer control panel (Figure 5&6) has a red indicator light, to the right of the 9-position switch, which will come on when the back-up battery is too low to sustain the sequencer during a short AC power loss. The back-up battery (rechargeable sealed lead acid) is constantly being charged when the sampler is plugged into AC power.

Conclusion

We feel our sampling technology satisfies all of the PAMS¹ sampling requirements (according to Battelle's evaluation in August 1993), is very easy for field technicians to operate (no software programming required to set the sequencer), and has a cost effective design with the highest quality components available.

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OXIDES OF NITROGEN - NO_y

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Measurement of Total Reactive Odd-Nitrogen (NO_y) in the Rural and Non-Rural Troposphere

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Measurements of total reactive odd-nitrogen (NO_y) have become increasingly important to the understanding of the atmospheric transport and transformation processes affecting the burden of reactive oxides of nitrogen (in particular $\text{NO}_x = \text{NO} + \text{NO}_2$) and their influence on controlling atmospheric oxidant levels (specially O_3 and OH) in many rural and non-urban environments. NO_y measurements have become useful indicators of the total abundance of the various reservoir forms of NO_x as urban air parcels become progressively processed in the lower atmosphere. The accurate measurement of NO_y under these varying conditions represent a unique set of measurement challenges, as NO_y goes from tens of ppbv levels in predominately NO_x -rich mixtures of odd-nitrogen to ppbv and sub-ppbv levels in NO_x -poor mixtures. The instrument issues affecting measurements of NO_y using an Au-catalytic convertor system will be addressed for conditions relevant to sampling in the rural and non-urban atmosphere.

Recent Advances in the Design of NO₂ Photolytic Convertors

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Several photolytic convertor designs have evolved from the quantitative conversions of NO₂ into the more readily and conveniently measurable species NO (via $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$). To date the most popular of these designs utilizes the high spectral brightness of a well collimated short-arc lamp to produce a relatively compact and efficient (i.e., 40-80%) system for converting ambient NO₂ into NO. Although reasonably reliable, these convertors can be prone to subtle nuances that can lead to measurement artifacts under differing sampling conditions. To circumvent these potential problems, as well as the problem of short lamp lifetime, several new photolytic convertor designs have been evaluated. This paper will discuss the design criteria and test results for these new convertor designs.

Development of NO/NO_x/NO_y Monitors for Urban Air Sampling

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ABSTRACT

The ideal methodology for NO, NO_x, and NO_y would have the following attributes: compatibility with existing monitoring network facilities and procedures; equipment cost in the range of current network "NO_x" monitors; capability for specific monitoring of NO, NO₂, and NO_y; detection limit of 0.1 ppb or lower. This report describes an evaluation of two approaches to meet these monitoring network needs. Both approaches make use of commercially available instruments for detection, with continuous pretreatment of the sample for selectivity. System A makes use of two commercial chemiluminescence instruments to monitor NO, NO_y, and NO₂. System B utilizes the luminol chemiluminescence reaction to detect NO₂, and employs multiple catalysts to obtain measurements of NO_x and NO_y. This report describes these two approaches and evaluates them in terms of linearity, converter efficiency, interferences, and detection limits.

INTRODUCTION

The Clean Air Act Amendments of 1990 (Title I, Section 182) mandated enhanced monitoring of ozone precursors, including nitric oxide (NO), nitrogen dioxide (NO₂) and oxides of nitrogen (NO_x, where NO_x = NO + NO₂). The primary purpose of these nitrogen oxides measurements is to track progress toward achieving the National Ambient Air Quality Standard for ozone. Many air quality specialists believe there is also great value in measuring total oxidized nitrogen (NO_y), where NO_y includes NO and its gaseous phase oxidation products (NO_y = NO + NO₂ + HONO + HNO₃ + 2xN₂O₅ + HO₂NO₂ + PAN + organic nitrates + etc.). NO_y measurements are useful in a number of ways, including urban photochemical grid model diagnostics and emissions inventory verification.

Currently, the instrumentation used to monitor nitrogen oxides in urban monitoring networks measures NO and "NO_x", where "NO_x" includes NO, NO₂, and some not well characterized fraction of other NO_y constituents^{1,2}. NO₂ is determined as the difference between "NO_x" and NO, and is therefore subject to positive bias from other NO_y constituents. The ideal methodology for urban air nitrogen oxides monitoring would have the following attributes: compatibility with existing monitoring network facilities and procedures; equipment cost in the range of current network "NO_x" monitors; capability for specific monitoring of NO, NO₂, and NO_y; detection limit of 0.1 ppb or lower.

This report describes an evaluation of two approaches to meet these monitoring network needs. System A makes use of two commercial chemiluminescence instruments to monitor NO, NO_y, and NO₂. One of the instruments detects NO by its chemiluminescent reaction with O₃, while the other detects NO₂ by its chemiluminescent reaction with luminol. A heated molybdenum catalytic converter is used to reduce NO_y constituents to NO for detection. System B utilizes the luminol chemiluminescence reaction to detect NO₂, and employs multiple catalysts to obtain measurements of NO_x and NO_y. Nitric oxide is determined as the difference between NO_x and NO₂. This paper describes these two approaches and compares them in terms of linearity, converter efficiency, interferences, and detection limits.

DESCRIPTION OF APPROACHES

Schematic diagrams of the two systems evaluated for urban nitrogen oxides monitoring are shown in Figures 1 and 2. These figures show the final concepts that evolved during our evaluation of the two approaches. Not all components were included in all evaluation experiments. Figure 1 shows a diagram of System A, which relies on dual detectors with minimal sample pretreatment. It consists of the Scintrex Model LMA-3 analyzer for NO_2 and the Thermo Environmental Model 42S for NO and NO_y . The Model 42S contains a 375°C molybdenum catalytic converter which is used in the NO_y measurement. The NO and NO_y are measured sequentially by the Model 42S, whereas NO_2 is measured continuously in parallel by the LMA-3. System B is shown in Figure 2. This approach requires only one analyzer, the LMA-3, to make sequential measurements of NO_2 , NO_x , and NO_y , using multiple pretreatment approaches. In an automated system, the data acquisition computer or a timer switches three valves to direct the sample flow as follows: 1) through a Na_2CO_3 impregnated filter for removal of HONO and direct to the analyzer to measure NO_2 ; 2) through a Na_2CO_3 -impregnated filter, Nafion drier and CrO_3 oxidizer to measure NO_x ; 3) through a 375°C molybdenum converter, Nafion drier and CrO_3 oxidizer to measure NO_y . In all three modes of System B, the final measurement is in the form of NO_2 by the LMA-3 instrument. A Nafion drier is shown upstream of the CrO_3 oxidizer. The CrO_3 quantitatively oxidizes NO to NO_2 at relative humidities between 35 and 80 percent.³ The Nafion drier is sized according to flow rate, to reduce the humidity to about 80 percent of its ambient value, to ensure that the oxidizer is always exposed to humidities lower than 80 percent. At locations where the relative humidity is often lower than 35 percent, the drier should not be used, or it should be used in a reverse configuration to humidify the air stream.

Both Figures 1 and 2 show an ozone scrubber (Scintrex) preceding the LMA-3 analyzer. The purpose of this scrubber is to eliminate the positive bias to NO_2 caused by atmospheric ozone. In a previous study⁴ we found that the scrubber removed O_3 , but also removed a portion of the NO_2 . The ozone interference is normally expected to be small at urban levels of NO_2 , so the ozone scrubber may not be required in all applications.

RESULTS

Linearity

Nitric oxide is the fundamental species measured by the Model 42S analyzer, and NO_2 is the fundamental species measured by the LMA-3 analyzer. We examined the linearity of the two analyzers for their respective analytes using dynamic dilution for NO, and dynamic dilution combined with gas phase titration for NO_2 . Excellent linearity was exhibited by the Model 42S up to at least 175 ppbv, as expected based on numerous other studies.^{5,6} The linear range of the luminol chemiluminescence technique is limited, and depends on the formulation of the luminol solution, among other things.^{2,4,7-9} At low concentrations, the response may be nonlinear somewhere below 6 ppm.^{4,7,8} In this study, tests on two different days showed good linearity up to at least 80 ppb. Use of the luminol method at higher concentrations may require a correction for nonlinearity.^{2,9}

Converter Efficiency

Both approaches employ a heated molybdenum converter in the NO_y mode, and System B also requires a CrO_3 oxidizer in the NO_x and NO_y modes. The efficiencies of the two molybdenum converters were evaluated using NO_2 generated by gas phase titration, using a primary NO in N_2 standard (NIST) to prepare the initial dilute NO samples. The NO_2 reduction efficiency of the two converters was 100 percent, with an uncertainty of 1 percent.

The efficiency of the CrO_3 oxidizer was examined in a number of experiments. In one experiment, the analyzer was presented with five levels of NO generated by dynamic dilution of a primary standard with ultrahigh purity air. The results indicate an oxidation efficiency of 100

percent for the CrO_3 converter, with an uncertainty of 5 percent. In another test, the LMA 3 was presented with five levels of NO_2 and five similar levels of NO in separate tests. The NO was monitored as NO_2 downstream of the CrO_3 oxidizer. The results indicate high conversion efficiency. However, a slight deviation from the 1:1 response line was noted at concentrations ≥ 80 ppbv. This is consistent with the nonlinear response of the LMA-3 at higher NO_2 levels, and is not indicative of inefficient NO oxidation.

A separate gas phase titration experiment combined the molybdenum converter and the CrO_3 oxidizer, and employed all three measurement modes of System B, i.e., the molybdenum and CrO_3 converters in series to monitor NO_y , the CrO_3 converter to monitor NO_x , and analysis without a converter to monitor NO_2 . The initial NO mixing ratio of 80 ppbv was reduced to 18 ppbv in four steps by oxidation with O_3 . During the titration, the measured NO_x and NO_y remained nearly constant at 80 ppb, confirming that the CrO_3 and molybdenum converter efficiencies are near 100 percent.

For the two systems to measure NO_y , the molybdenum converters must also reduce other NO_y constituents to NO. Both systems were challenged with six different oxidized nitrogen species (peroxyacetyl nitrate, nitric acid, nitrous acid, acetonitrile, isopropyl nitrate, nitrobenzene). The response in NO_y mode to each chemical was determined at three levels between 0 and 50 ppbv in high purity air at 50 percent humidity. PAN, HNO_3 , and HONO were quantitatively reduced to NO and detected in the NO_y mode by both systems. An initial experiment with nitric acid showed only partial response for System A. This was found to be due to incomplete transmission of the adsorptive HNO_3 to the instrument through the inlet plumbing and filter provided with the Model 42S. Monitoring NO_y with this instrument may require heating the filter and internal plumbing, to assure that nitric acid in the sample stream is transferred to the internal molybdenum converter. Isopropyl nitrate was converted to NO by both moly converters, but acetonitrile and nitrobenzene were not. Acetonitrile is not generally considered a component of NO_y , and it is not measured as such by these systems. Nitro-organic chemicals fall into the generally accepted NO_y definition, but our results show that nitrobenzene is not measured by these systems. Thus the measured NO_y reported from both Systems A and B does not include some nitro-organic compounds.

Interferences

No interferences were found with the NO measurement in System A. However, NO and PAN interfere with measurement of NO_x . Nitric oxide yields a slight negative interference, as previously reported.² This interference is only significant at high NO/ NO_2 ratios. PAN also interferes with NO_2 monitoring by luminol chemiluminescence in System A. Previous studies have reported a 20-25 percent interference; i.e. 1 ppb of PAN is measured as 0.2 ppb of NO_2 .^{4,9} In the present work, we observed an even greater interference of 38 ± 3 percent.

The interferences in NO_2 measurement in System B are the same as for System A. These interferences were discussed above. Two interferences were observed in the NO_x mode. PAN was found to interfere to the same degree as it does in the NO_2 mode. This suggests that PAN is not influenced by the Nafion drier or the CrO_3 oxidizer. The other NO_x interference is nitrous acid, which is oxidized to NO_2 by the CrO_3 oxidizer. However, the HONO interference to NO_x can be eliminated by the insertion of an acid scrubbing filter in the sample flow path for the NO_x mode (see Figure 2).

Detection Limits

The Model 42S was operated on its most sensitive range (20 ppbv f.s.) with a time constant of 150 seconds, and sampled ultra-high purity air, or air from the prereactor in the 42S, for five minutes each. The detection limit was calculated as the standard deviation multiplied by three. For the two separate experiments, the detection limits of the Model 42S were 46 pptv and 14 pptv, the lower value obtained using the prereactor. Both values are entirely satisfactory for the urban

monitoring needs noted in the Introduction. The detection limit of the LMA-3 for NO_2 has been determined in previous studies as 10–15 pptv.^{4,8} The LMA-3 achieves these detection limits while retaining rapid response times, i.e., using an electronic time constant of 5 seconds or less.

DISCUSSION

The limited linear range of the luminol NO_2 instrument could be troublesome for System B, where high NO_x and NO_y mixing ratios (detected by conversion to NO_2) could exceed the linear range of the detector, even if ambient NO_2 were within the linear range. The nonlinear response can be corrected during data processing.^{2,9}

Ozone is known to interfere with the luminol NO_2 measurement, but was not included in this study because it has been evaluated by others.^{2,4,8-10} Drummond et al.⁹ have reported a positive O_3 response of 1.0 percent relative to NO_2 , and Kelly et al.⁴ report a response of 0.33 percent. If the relative response ratio is 1 percent (0.01), then a 10 percent bias in the NO_2 measurement will result for ambient O_3/NO_2 of 10 (e.g., 100 ppb O_3 and 10 ppb NO_2). This interference can be significant for urban areas when O_3/NO_2 ratios exceed about 10. In contrast, Drummond et al.¹⁰ have recently reported that the O_3 interference is slightly negative for $\text{NO}_2 > 5$ ppb, and that this interference can usually be neglected. A commercial O_3 scrubber is available, but it also removes a small portion of the NO_2 in the sample.^{4,10} Because the interference due to O_3 appears to vary from one study to the next, it seems prudent for users of the luminol technology to evaluate whether the ozone scrubber is needed in their application.

Suppression of the luminol NO_2 signal by NO may be important in some urban areas, especially at night and early morning, when relatively high NO/NO_2 ratios are observed. At $\text{NO}/\text{NO}_2 = 10$, the observed NO interference will cause a 12 percent error in NO_2 . Corrections for this interference can be made during data processing. The interference due to NO can affect NO_2 calibrations performed by gas phase titration of NO with ozone. At the lowest NO_2 concentrations, the NO/NO_2 ratio can be high enough to cause a significant suppression of the NO_2 signal. Users can adjust their calibration conditions to minimize this effect or can correct the luminol calibration data for this effect.

The positive interference in NO_2 measurement due to PAN can be significant during periods of photochemical activity, and the bias caused by PAN cannot be corrected a priori from System A or System B data. Because of PAN's thermal instability, we investigated the use of a low temperature converter to decompose PAN without affecting NO_2 , but our efforts were unsuccessful. Drummond et al.¹⁰ recently reported use of a scrubber that removes NO_2 while passing nearly 100 percent of PAN. If this scrubber were used to zero the luminol monitor, the PAN interference would be eliminated during subtraction of the "zero air" signal. Unfortunately, we were not aware of this report during our experimental study, so we have not evaluated this new scrubber.

Acetonitrile does not respond with either system. Nitrobenzene, which could be considered a constituent of NO_y , also does not respond on either system. This is not considered to be a serious deficiency of these two approaches, because the nitro-organic content of urban atmospheres is expected to be extremely small.

The detection limits of both systems represent improvement over those of the existing instruments used for urban monitoring. With System A, the lowest detection limit involves using a time constant of 150 seconds for the NO and NO_y measurements. On the other hand, System B provides excellent detection limits together with exceptional response time (time constant of 5 seconds) in all three measurement modes, but the measurements of NO_2 , NO_x , and NO_y must be made sequentially. Consequently, the sampling time in each mode needs to be kept short. This requirement can be accommodated by System B because of the rapid response of the luminol detector.

CONCLUSIONS

Both approaches have much lower detection limits than the instruments currently used for routine monitoring, and both systems provide a measure of NO_x that is better characterized than that from current network monitors. However, both systems are more complex than the instruments currently in use. The advantages of System B depend on the efficiencies of the two converters, and these efficiencies should be checked frequently. System B also measures the NO_2 , NO_x , and NO_y components sequentially, so true simultaneous results are not available and hysteresis errors can occur during periods of rapid concentration fluctuation. For System A, the lowest detection limits for NO and NO_y are achieved at response times of several minutes, so very short term fluctuations cannot be assessed. In addition, the initial cost of System A is greater than either System B or current network instruments used to monitor nitrogen oxides.

ACKNOWLEDGMENT

Although this work was supported by the U.S. EPA under Contract No. 68-D0-0007, this paper has not undergone Agency review, and no official endorsement should be inferred.

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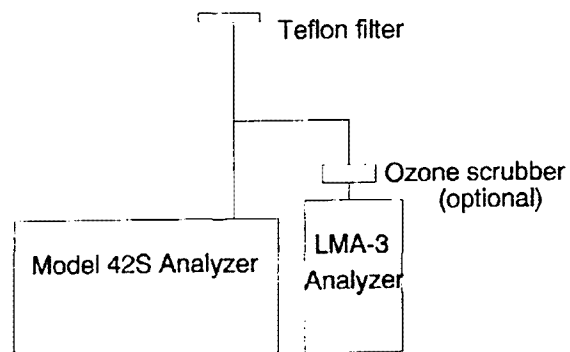


Figure 1. Schematic diagram of components for system A, dual monitor approach.

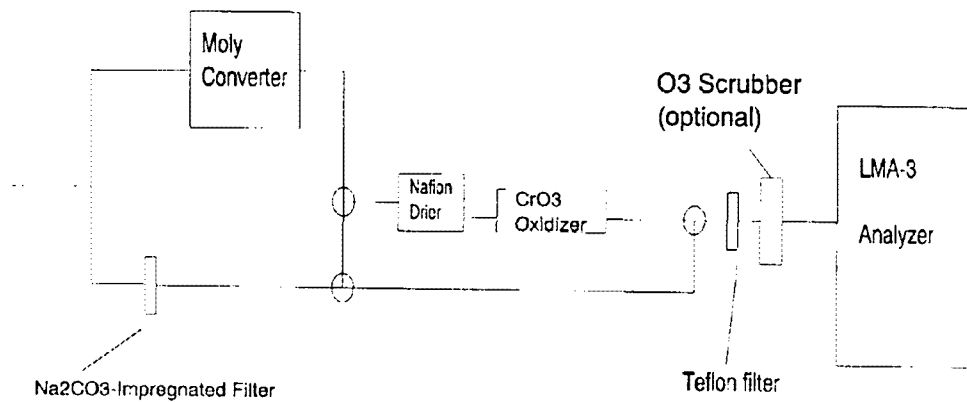


Figure 2. Schematic diagram of components for system B, multiple pretreatment approach.

A Commercial Approach to NO_x Measurement

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The accurate measurement of total reactive nitrogen compounds, commonly termed NO_x, is considered vital to a better understanding of tropospheric oxidation chemistry, acid transport and deposition modeling, and as critical component of overall atmospheric stability and chemistry. Virtually all measurements have relied upon the exclusive use and operation of instrumentation developed for NO_x sensitivity and selectivity by the research community. This paper describes the potential for commercial instrumentation to provide, either directly or with minimal modification, accurate NO_x concentration data.

First, a description of high sensitivity NO chemiluminescence instrumentation is given. This includes plumbing configuration, modifications made to standard compliance monitoring analyzers for improved sensitivity, selectivity, and stability, and both general and specific calibration and operation procedures.

Second, the selection of commercially available NO_x converters is presented. Individual advantages and disadvantages are discussed.

Third, modifications to the currently available high sensitivity commercial instrumentation in order to obtain more reliable NO and NO_x data are suggested. The modifications emphasize cost effectiveness, simplicity, and user operation.

Finally, a discussion of field measurements taken with suitably modified commercial instrumentation is given. Difficulties in operation, instrument reliability, and data interpretation are discussed.

Temporal Variation of Nitrogen Oxide Fluxes From Agricultural Soils In the Upper Coastal Plain of North Carolina

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ABSTRACT

Measurements of soil flux of NO show that in some cases these emission rates are comparable to anthropogenic emissions in urban areas, contributing to rural O₃ formation. Soil NO flux measurements were made from 18 Aug 1993 to 1 Sep 1993 and from 7 Feb 1994 to 23 Mar 1994 in the Upper Coastal Plain of North Carolina in an effort to determine the magnitude of the fluxes and the relationship of natural NO emissions to typical agricultural management practices. The overall average NO emission rates (using a dynamic chamber technique) during the summer varied in proportion to the amount of applied fertilizer N to each crop. For the winter period, the measured emissions followed the carbon-nitrogen ratio of the plant residue plowed back into the soil after the fall harvest. The NO flux rates were negatively correlated to soil temperature.

INTRODUCTION

Measurements of soil flux of NO show that in some cases, comparable emission rates exist between anthropogenic emissions in urban areas and agricultural areas (Williams et al., 1988). Understanding and quantifying soil emissions of NO is of importance in understanding the formation of tropospheric ozone. This is particularly true in rural areas where man-made sources of NO are minimal since ozone production will be dependent upon biogenic sources of NO (Valente and Thornton, 1993).

In this paper we present preliminary soil NO measurements made in two seasons (late Summer, Aug-Sep 1993 and late Winter/early Spring, Feb-Mar 1994, herein referred to as summer and winter) in the Upper Coastal Plain of North Carolina, and also some preliminary observations concerning process-based mechanisms controlling NO emission. The objectives are to assess the impact of crop type and fertilizer application rates on soil NO emissions by making measurements on two different phases of agricultural management.

MEASUREMENT TECHNIQUE

Chamber Design and Operation

The soil NO measurements were performed using a dynamic chamber technique as described in Kim et al., 1994. One chamber, using ambient air as the carrier gas, was used during the summer period. For the winter measurements, simultaneous measurements were taken from two identical chambers placed within ≈ 20 cm of each other. The first chamber was operated as indicated above. Purified nitrogen was utilized as the carrier gas in the second chamber, with all other conditions and sampling techniques remaining constant. This second chamber was added to assess the effects of ongoing reactions in the chamber/bag, as well as to discern the changes in NO emission in aerobic and anaerobic conditions.

Sampling Site

Flux measurements in both the summer and winter experiments were made in the same three general crop (non-irrigated) fields at the Central Crops Research Station (105 m MSL) operated by North Carolina State University. The Field Laboratory is located ~ 10 km east-southeast of Raleigh, in the Upper Coastal Plain region of NC. The dominant soil type in each of the fields sampled is Norfolk sandy loam (Fine-Loamy, Siliceous, Thermic Typic Paleudult; Daniels et al., 1984). Each field sampled during the summer experiments contained a different row crop (soybean, cotton, or corn) grown using fertilizer rates and management techniques representative of those commonly used throughout the Coastal Plains region of the southeastern United States. These same fields were sampled again during the winter, while covered with a sparse cover of winter wheat.

RESULTS AND DISCUSSION

Late Summer 1993 Measurement Period

Figure 1 shows the composite hourly NO flux by crop type. During mid-morning the time-averaged NO flux reached a peak, with the maximum values for each crop varying proportionally to the level of applied fertilizer nitrogen in that field. Table 1 summarizes the NO emissions, soil and air temperatures, and soil parameters for the summer measurements period. This measurement period saw essentially no rainfall, and the three fields were not irrigated. The soil water content in the top 15 cm of the soil subsequently remained at or below the estimated permanent wilting point for this soil type.

Late Winter/Early Spring 1994 Measurement Period

Ambient air as the carrier gas. Figure 2 shows the composite hourly NO flux by crop for the winter measurement period. Again we see the early morning peak, with a drop to near zero in the afternoon. The evening peaks in the soybean field flux values came during the diurnal profile measurements, and represent only one data point. However, we don't believe these values are anomalous, since the adjacent points reflect the trend. We currently have no explanation for these increased values.

Table 2 summarizes the NO emissions, soil and air temperatures, and soil parameters measured in the winter experiments. Soil water contents were much higher for the winter measurements, with the percent water-filled pore space (%WFPS) in the optimum range for NO production (Davidson, 1991).

Nitrogen as the carrier gas. To assess the influence of ongoing reactions in the chamber when using ambient air as the carrier gas, we used nitrogen as the carrier gas in a second chamber adjacent to the ambient air chamber during the winter experiment. The composite hourly NO flux by crop location measured using this nitrogen carrier is shown in Figure 3. As before, we see an early morning peak in NO emission and subsequent decline to a relatively constant value, approaching zero, in the corn location data. In contrast, in the other two crop fields the time-averaged flux signature departs from the previous pattern. The soybean NO flux signature shows a steady increase until mid-afternoon, declining to a mean of approximately $10 \text{ ng N m}^{-2} \text{ s}^{-1}$. The cotton NO emissions also depart from the earlier pattern, with a morning increase, leveling to roughly $5 \text{ ng N m}^{-2} \text{ s}^{-1}$ during the afternoon and evening hours. These nitrogen carrier temporal signatures suggest the effect of available nitrogen and soil temperature on microbial biomass. During this fallow agricultural-management phase, all the original nitrogen from the Spring fertilizer application is leached out; the main source of available nitrogen for the soil microbes is that associated with the crop residue plowed back into the soil. Table 2 shows the soil total extractable nitrogen for the winter measurement period was larger than the summer period, with the exception of the corn location. The soybean residue has a carbon-to-nitrogen (C/N) ratio of $\approx 15:1$, so ample nitrogen is available for production of NO by nitrification/denitrification after mineralization. The cotton and corn residue has a C/N ratio approximately twice that of the soybean residue, therefore there's relatively little nitrogen available to the microbes, and this is utilized in mineralization, with little excess for NO production. The soybean (and cotton to a lesser degree) time-averaged flux levels mimic the diurnal soil temperature pattern. We currently have no explanation for the corn flux signature.

Interaction of Soil Temperature and Soil Water Content

The previous figures show NO flux as a function of time of day and available nitrogen. Certainly temperature and soil moisture are equally important to NO emission. As in the atmosphere, soil moisture and soil temperature are often inversely correlated, allowing one factor to possibly offset or dominate the other. When the soil is moist and the soil temperature is moderate, flux of NO often exhibits the exponential relationship with soil temperature described by Williams et al. (1987). However, when the soil temperature and/or soil moisture content is not optimal for biogenic processes, the relationship between these two parameters is less well-defined.

During the summer measurement period, soil moisture was extremely low (Table 1). Therefore, as soil temperature increased, the subsequent moisture stress increased on the soil microbes responsible for NO production. Figure 4 reveals an inverse relationship between soil temperature and NO flux for the summer measurements with an R^2 of 0.76 for both soybean and cotton.

The relationship between composite soil temperature and NO flux for the winter measurements is less clear. In the ambient air carrier experiments (Figure 5) the trend is roughly exponentially decreasing soil NO flux with increasing soil temperature for both soybean ($R^2=0.74$) and cotton ($R^2=0.74$). The corn data exhibits a more complex relationship, with an increasing exponential relationship suggested up to roughly 10-12 °C, and then a decreasing exponential relationship at higher temperatures. Fitting an exponential curve to the overall corn trend returns an R^2 of only 0.03, while fitting individual exponential curves to the lower half and upper half of the composite temperature groups returns R^2 values of 0.94 and 0.72 respectively. This suggests the onset of moisture stress on the soil microbes at the upper temperatures, since the corn field soil had the lowest average soil moisture, coupled with the highest average soil temperature.

A look at the composite soil temperature versus NO flux when nitrogen was used as the carrier gas (Figure 6) again suggests an interaction with soil moisture content. Here the soybean data reveals an exponentially increasing NO flux with increasing soil temperature ($R^2=0.76$) while the cotton data shows no clear trend ($R^2=0.05$). Fitting the exponential model to the overall corn data returns an R^2 of 0.25. If we again separate the composite corn data into lower and upper temperature groups, the resulting R^2 values are 0.37 for the lower temperature band and 0.88 for the upper band. These results suggest an interaction of soil temperature and soil moisture on the subsequent NO flux produced, possibly confounded by the available nitrogen in the soil.

SUMMARY AND CONCLUSIONS

In the summer experiments, NO flux magnitudes by crop varied according to the amount of fertilizer nitrogen applied on the crop location. Both average NO flux and fertilizer nitrogen applied follow the ranking soybean<cotton<corn. In the winter measurements the average NO flux levels varied with the C/N ratio, i.e. soybean>cotton>corn for the ambient air carrier measurements, and soybean>corn>cotton for the nitrogen carrier measurements.

The winter nitrogen carrier measurements suggest that significant fluxes are generated during fallow periods when the plant residue is mixed back into the soil, a common agricultural practice.

These results demonstrate that emission of NO from soils can be an important source of atmospheric NO concentration in the rural Southeastern US. We are currently developing a comprehensive characterization of NO flux from soils in the southeast US over several different soil types and agricultural management practices. Regardless, these preliminary results suggest agricultural management practiced must be accounted for when assessing the factors affecting ambient air quality.

ACKNOWLEDGMENTS

This research has been funded through a cooperative agreement with the United States Environmental Protection Agency (CR 822-58-01-0) as part of the Characterization of Emissions of Nitrogen Oxides from the Soils of Southeast U.S. Project. The contents of this document do not necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial or non-commercial products constitute endorsement or recommendation for use.

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Crop		Soil Temp (C)	Air Temp (C)	Total Extractable Nitrogen #	% WFPS ^	Air Carrier NO Flux *
Soybean	Average	25.6	29.7	0.74	3.49	1.79
	Std Dev	1.4	3.4	0.19	2.44	1.92
	Min	23.3	22.2	0.55	1.8	-1.01
	Max	27.4	33.5	0.97	7.8	6.86
Cotton	Average	27.5	28.2	1.53	2.63	3.77
	Std Dev	2.5	6.4	0.8	0.74	5.89
	Min	23.6	17.5	0.79	1.78	-0.07
	Max	32.5	39	2.89	3.29	36.02
Corn	Average	n/a	36	9.59	1.1	8.05
	Std Dev	-	3.8	8.55	0.6	12.94
	Min	-	24	3.92	0.58	-0.54
	Max	-	40	19.43	1.75	52.79

Units are mg-N/kg

^ Percent Water-Filled Pore Space

* Units are ng N m⁻² s⁻¹.

Table 1. Data summary for the 18 Aug - 1 Sep 1993 measurement period.

Crop		Soil Temp (C)	Air Temp (C)	Total Extractable Nitrogen #	% WFPS ^	Air Carrier NO Flux *	N2 Carrier NO Flux *
Soybean	Average	8.41	12.01	4.13	47.18	10.23	9.18
	Std Dev	3.55	5.56	0.92	3.19	20.15	12.03
	Min	0.90	0.00	3.08	43.10	-10.77	0.00
	Max	14.20	23.80	5.25	51.50	133.06	52.23
Cotton	Average	10.00	13.22	6.49	54.85	5.07	6.22
	Std Dev	5.25	9.02	3.42	6.09	12.56	8.93
	Min	3.30	1.70	3.23	48.00	-11.71	0.34
	Max	21.00	31.50	10.28	62.20	109.55	42.43
Corn	Average	12.45	16.99	4.54	34.10	3.68	8.31
	Std Dev	4.70	9.21	0.41	7.21	5.96	17.12
	Min	3.30	-1.50	4.20	26.00	-17.51	0.00
	Max	20.70	32.20	5.16	43.40	40.39	96.90

Units are mg-N/kg

^ Percent Water-Filled Pore Space

* Units are ng N m⁻² s⁻¹.

Table 2. Data summary for the 7 Feb - 18 Mar 1994 measurement period

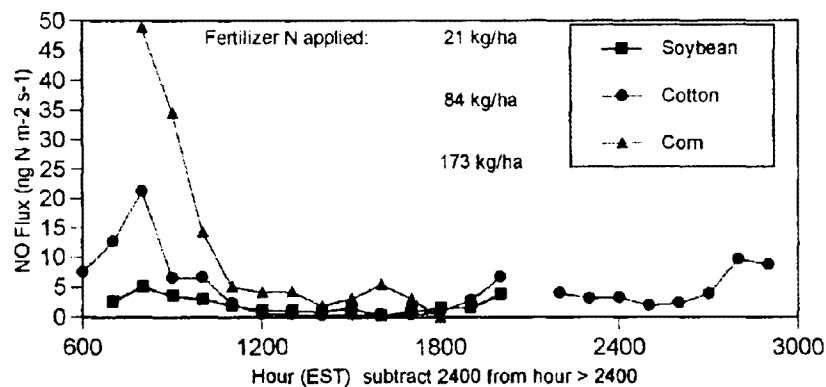


Figure 1. Composite Hourly NO Flux, Summer 93, Ambient Air as the Carrier

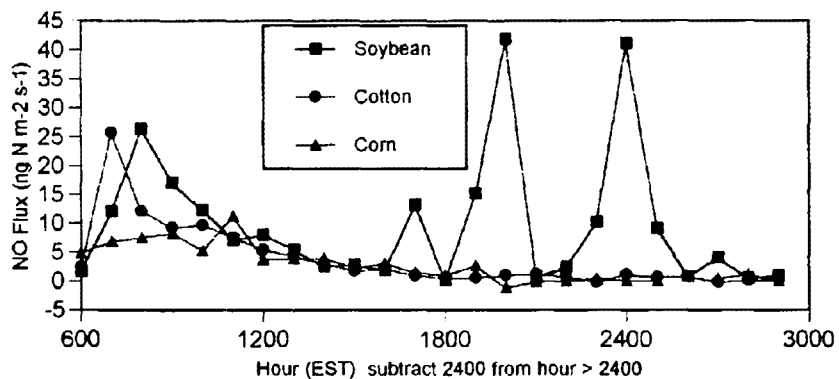


Figure 2. Composite Hourly NO Flux, Winter/Spring 94, Ambient Air as the Carrier

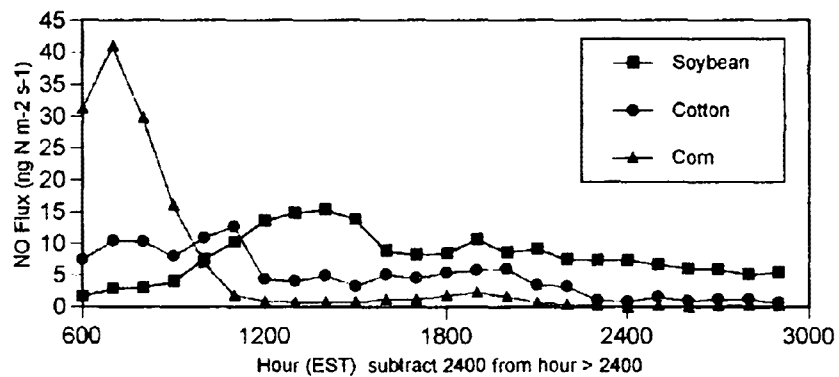


Figure 3. Composite Hourly NO Flux, Winter/Spring 94, Nitrogen as the Carrier

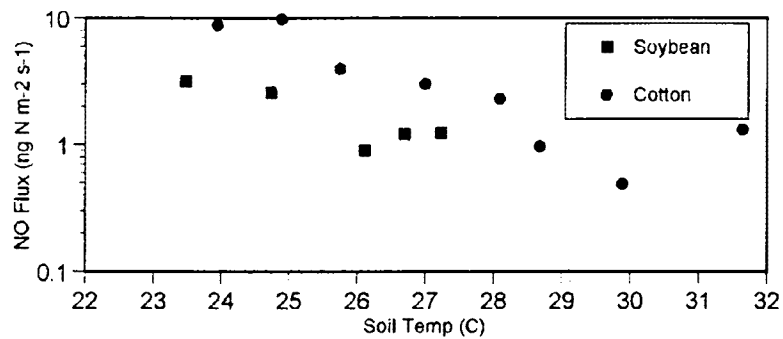


Figure 4. Composite Soil Temperature vs NO Flux, Summer 93, Ambient Air as the Carrier

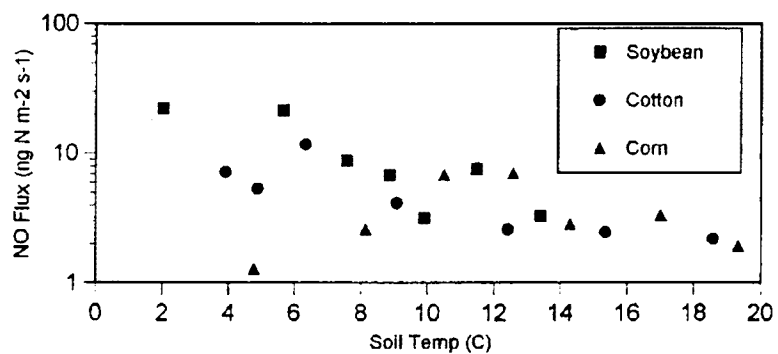


Figure 5. Composite Soil Temperature vs NO Flux, Winter/Spring 94, Ambient Air as the Carrier

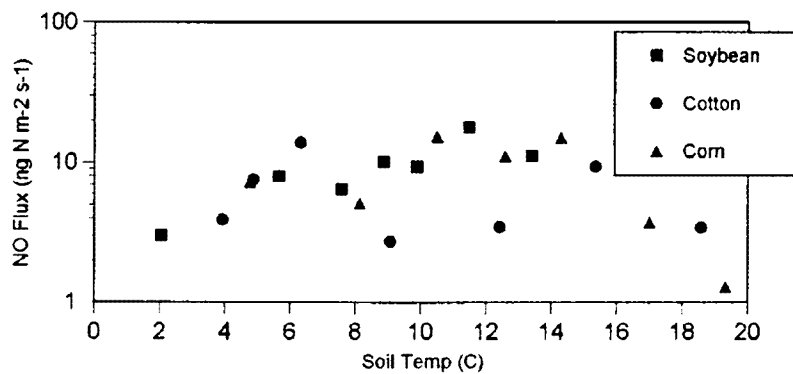


Figure 6. Composite Soil Temperature vs NO Flux, Winter/Spring 94, Nitrogen as the Carrier

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METEOROLOGY

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Overview of PAMS Meteorological Monitoring Requirements

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ABSTRACT

The Photochemical Assessment Monitoring Station (PAMS) requires the incorporation of surface and upper air meteorological instrumentation. The platform for the surface instrumentation is a 10 m tower. The variables to be collected include horizontal wind speed, horizontal wind direction, air temperature, relative humidity, solar radiation, and barometric pressure. Upper air data may be acquired using a variety of platforms which include aircraft, tall towers, tethered and expendable radiosondes, and ground-based remote profilers. The variables to be collected include profiles of horizontal wind speed and direction, vertical wind speed, and air temperature. In addition, the mixing layer height should be determined from the upper air data. This paper summarizes the meteorological sensor requirements for PAMS which are not specifically addressed in the Code of Federal Regulations (40 CFR Part 58).

INTRODUCTION

The United States Environmental Protection Agency (EPA) has revised the ambient air quality surveillance regulations in Title 40 Part 58 of the Code of Federal Regulations (EPA, 1993). 40 CFR Part 58 requires the States to establish a network of Photochemical Assessment Monitoring Stations (PAMS) in ozone nonattainment areas which are classified as serious, severe, or extreme. Each PAMS must include provisions for enhanced monitoring of ozone and its precursors such as nitrogen oxides and volatile organic compounds. In addition, surface and upper air meteorological data must be acquired. EPA's authority for the enhanced monitoring regulations is provided for in Title I, Section 182 of the Clean Air Act Amendments of 1990.

The importance of a high quality meteorological data base for these nonattainment areas can not be overstated. These data are necessary to assist in the development and evaluation of new ozone control strategies, emissions tracking, trend analysis, exposure assessment, and numerical modeling (EPA, 1991). However, guidance is not provided in 40 CFR Part 58 on the specification of meteorological instrumentation that is to be used for PAMS. The regulation references two documents which are supposed to specify instrument type, characteristics, siting, and other quality assurance and quality control issues. The first is the *Technical Assistance Document for Sampling and Analysis of Ozone Precursors* (EPA, 1991). This document (TAD) was written to provide direction on sampling and analysis methodology for Regional, State, and local EPA personnel involved in enhanced ozone monitoring activities. The second is the *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV: Meteorological Measurements* (EPA, 1989). Unfortunately, the current version of the TAD lacks the specifics needed to establish a meteorological monitoring system for PAMS. The Quality Assurance Handbook, however, contains a great deal on instrument specifications, but no detail on how to apply it to PAMS.

This paper will attempt to consolidate the available EPA guidance on meteorological monitoring and apply it to PAMS. Where guidance is absent, this paper will try to make recommendations on instrument types and procedures.

¹ On assignment to the Atmospheric Research and Exposure Assessment Laboratory, U. S. Environmental Protection Agency

SURFACE METEOROLOGICAL INSTRUMENTATION

Guidance for making surface meteorological measurements is provided in several EPA documents and is summarized in this paper. They include: *On-Site Meteorological Instrumentation Requirements to Characterize Diffusion from Point Sources* (EPA, 1981), *Ambient Monitoring Guidelines for Prevention of Significant Deterioration* (EPA, 1987a), *On-Site Meteorological Program Guidance for Regulatory Modeling Applications* (EPA, 1987b), and *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV: Meteorological Measurements* (EPA, 1989). Additional information is provided in the *Instructor's Handbook on Meteorological Instrumentation* (NCAR, 1985). The guidance found in all of these references has its roots in the *Guide to Meteorological Instruments and Methods of Observation* (WMO, 1983).

The surface meteorological variables which are required to be measured at each PAMS site include horizontal wind speed and wind direction, ambient air temperature, relative humidity, solar radiation, and barometric pressure. Since these variables need to be measured at different heights, a tower is usually the most advantageous measurement platform. For PAMS, a 10 m tower is required.

The most preferable type of tower is the open lattice or open grid variety since it creates the least amount of turbulence. The tower must be rugged enough so that it can be climbed safely to install and service the instruments. Folding or collapsible towers are desirable since they allow the instruments to be serviced at the ground. The tower should be sufficiently rigid to hold the instruments in proper orientation at all times. Solid structures such as stacks, water storage tanks, grain elevators, and cooling towers should be avoided since they can create significant wind flow distortions.

The primary objective of instrument siting (horizontal and vertical probe placement) and exposure (spacing from obstructions) is to place the sensor in a location where it can make precise measurements that are representative of the general state of the atmosphere in that region under study. The choice of a site must be made with a complete understanding of the regional geography, the sources being investigated, and the potential uses of the data being collected. Ideally, the tower should be located in an open level area. If the terrain has significant topographic features, different levels of the tower may be under the influence of different meteorological regimes at the same time. If this is the case, such conditions should be well documented. Secondary considerations such as accessibility and security must be taken into account, but should not be allowed to compromise data quality.

These basic meteorological variables should be sampled at least once every 10 seconds and recorded digitally by a data logger as one hour averages. The observation time should correspond to the time at the end of the averaging period (i.e., 0200, 0300, etc.) and be recorded as local standard time. The clock for the data acquisition system should have an accuracy of ± 1 minute per week.

Wind Speed and Direction

Horizontal wind speed (m s^{-1}) and wind direction (degrees clockwise from geographical north) are the most important meteorological variables needed to understand transport and dispersion processes. These two variables help determine the initial dilution experienced by a plume, transport direction, and atmospheric stability parameters such as the standard deviation of the wind direction (σ_θ).

The most commonly used instruments for measuring wind speed and direction in air quality studies are: Cup anemometer and wind vane, propeller anemometer mounted on the front of a wind vane, and two horizontal propellers mounted at right angles to each other.

The standard exposure of a wind sensor over level, open terrain is 10 m above the ground. Open terrain is defined as an area where the horizontal distance between the instrument and any obstruction is at least ten times the height of that obstruction. An obstruction may be man-made (e.g., building) or natural (e.g., trees). Where a standard exposure is unobtainable, the anemometer should be installed at a height that its indications are reasonably unaffected by local obstructions and represents, as far as possible, what the wind at 10 m would be if there were no obstructions in the vicinity.

The wind sensor should be mounted on a mast at a distance of at least one tower width projected vertically from the top of the tower. If the tower is greater than 10 m, then the wind sensor should be

mounted on a boom projecting horizontally out from the tower. Precautions must be taken to ensure that the wind measurements are not unduly influenced by the tower. Turbulence in the immediate wake of the tower (even a lattice type) can be severe. Therefore, the sensor should be located at a horizontal distance of at least twice the maximum width of the tower away from the nearest point on the tower. The boom should project into the direction which provides the least distortion for the most important wind direction. For example, the boom should be aligned in a northwesterly or southeasterly direction if the predominant wind is from the southwest.

A sensor with high accuracy at low wind speeds is desirable since air pollution concentrations are inversely proportional to wind speed. A low starting threshold speed is required for PAMS applications. Light weight molded plastic or polystyrene foam should be employed for cups, propeller blades, and tail fins to achieve a starting speed of $\leq 0.5 \text{ m s}^{-1}$. Wind speed for a cup or propeller anemometer should be accurate to $\pm 0.2 \text{ m s}^{-1} + 5\%$ of observed speed from 0.5 to 5 m s^{-1} . At wind speeds greater than 5 m s^{-1} , the accuracy should be 5% of the observed speed, never to exceed $\pm 2.5 \text{ m s}^{-1}$. Resolution should be $\leq 0.1 \text{ m s}^{-1}$. The distance constant (the distance of passage through the cup or propeller required for sensor to indicate a 63% step change in the wind speed) should be $\leq 5 \text{ m}$. The wind direction should be accurate to $\pm 5^\circ$ with a resolution of $\leq 1^\circ$. The starting speed should be $\leq 0.5 \text{ m s}^{-1}$ from a 10° deflection. The delay distance (50% recovery from a 10° deflection) should be $\leq 5 \text{ m}$ and the damping ratio should lie between 0.4 and 0.7 .

Air Temperature

Ambient air temperature ($^\circ\text{C}$) measurements are used for estimating buoyancy flux in plume rise computations and for converting pollutant concentrations. The most common type of sensor used is the platinum temperature probe (RTD). This type of sensor provides an accurate measurement with a stable calibration over a wide temperature range.

The temperature probe should be mounted on the tower 2 m above the ground and away from the tower at a distance of at least one tower width from the closest point on the tower. This height is consistent with WMO (1983) standard monitoring procedures. The measurement should be made over a plot of open, level ground at least 9 m in diameter. The ground surface should be covered with non-irrigated or unwatered short grass or, in areas which lack a vegetation cover, natural earth. The surface must not be concrete, asphalt, or oil-soaked. If there is a large paved area nearby, the sensor should be at least 30 m away from it. Areas to avoid also include large industrial heat sources, roof tops, steep slopes, hollows, high vegetation, swamps, snow drifts, standing water, and air exhausts (e.g., tunnels and subway entrances). The probe should be located at a distance from any obstructions of at least four times their height.

The air temperature probe should have an accuracy of $\pm 0.5 \text{ }^\circ\text{C}$ over a range of -20 to $+40 \text{ }^\circ\text{C}$ with a resolution of $\leq 0.1 \text{ }^\circ\text{C}$. The time constant (63%) should be ≤ 60 seconds. Solar radiation is the largest source of error for ambient air temperature measurements. Adequate shielding is needed to provide a representative measurement of the atmosphere. The best type of shield is one which provides forced aspiration at a rate of $\geq 3 \text{ m s}^{-1}$. Ideally, the radiation shield should block the sensor from view of the sun, sky, ground, and surrounding objects. The shield should reflect all incident radiation and not reradiate any of that energy towards the sensor. The probe must also be protected from precipitation and condensation, otherwise evaporative effects will lead to a depressed temperature measurement (i.e., wet bulb temperature).

Relative Humidity

Atmospheric humidity is expressed in various ways. It may be represented as vapor pressure (hPa), dew point temperature ($^\circ\text{C}$), specific humidity (g kg^{-1}), mixing ratio (g kg^{-1}), absolute humidity (g m^{-3}), or relative humidity (%RH). All variables except the relative humidity provide a complete specification of the amount of water vapor in the atmosphere. However, any of these variables can easily be derived from the relative humidity given the ambient air temperature and barometric pressure.

There are various methods of measuring atmospheric humidity. However, the emergence of thin-film technology has produced relative humidity sensors which are fairly accurate, compact, and inexpensive. They are also becoming increasingly common as they lend themselves to easy installation for automatic recording

stations.

The relative humidity sensor should be installed with the same siting considerations given to the air temperature sensor. The probe should be housed in the same aspirated radiation shield at 2 m above the ground. The accuracy should be at least ± 3 %RH over a temperature range of -20 to $+40$ °C with a resolution of ≤ 0.5 %RH or better. The time constant (63%) should be ≤ 60 seconds.

The thin-film elements of the humidity probe must be protected from contaminants such as salt, hydrocarbons, and other particulates. These pollutants can easily corrupt the sensing element and lead to failure of the probe. The best protection is the use of a porous membrane filter which allows the passage of ambient air and water vapor while keeping out particulate matter.

Solar Radiation

Solar (sometimes call shortwave) radiation is the electromagnetic radiation of the sun which is represented as an energy flux (W m^{-2}). Solar radiation measurements are useful for heat flux calculations estimating atmospheric stability and understanding photochemical reactions (i.e., ozone generation). 97% of the solar radiation incident at the top of the earth's atmosphere lies between 0.29 and 3.0 μm . The solar spectrum is comprised of ultraviolet radiation (0.29 to 0.40 μm), visible light (0.40 to 0.73 μm), and near-infrared (0.73 to 4.0 μm) radiation. A portion of this energy penetrates through the atmosphere and is received at the earth's surface. The rest is scattered and/or absorbed by gas molecules, aerosols, cloud droplets, and cloud crystals. The instrument needed for measuring this variable covering the range of the solar spectrum is a pyranometer. This sensor measures global (direct and diffuse) radiation when installed facing upwards in a horizontal plane tangent to the earth's surface.

Solar radiation measurements should be taken in a location with an unrestricted view of the sky which is free from any obstructions. There should be no object above the horizontal plane of the sensor that could possibly cast a shadow or reflect light on it (including the tower). In addition, the pyranometer should not be placed near light colored walls or artificial sources of radiation. In practice, the horizon should not exceed 5°, especially from the east-northeast through the south to the west-northwest. A 5° horizon will obstruct only about 1% of the global radiation and thus can be considered negligible.

There is no height requirement for a pyranometer. A tall platform or a rooftop usually make ideal locations for sensor placement. If such facilities are not readily available, then the best strategy is to place the instrument directly south of the tower and its guy wires. Regardless of where the pyranometer is installed, it is important that the instrument be level with the horizontal plane to better than 1°. Any tilt from the horizontal plane may introduce significant errors (see Katsaros and DeVault, 1986). Most pyranometers usually have a circular spirit level attached so that proper leveling may be achieved.

EPA accuracy requirement for a solar radiation measurements is $\pm 5\%$ with a resolution of $\leq 10 \text{ W m}^{-2}$. It is desirable to obtain a sensor which meets the WMO criteria of a Secondary Standard or First Class pyranometer (Table 1) if reliable heat flux and stability parameters are to be calculated.

Barometric Pressure

Very little EPA guidance is available for acquiring barometric pressure (hPa) because it is not generally required in many air pollution applications. However, time series of these data are quite useful in examining trends in the weather on the order of several days or more. It is also an important variable which is used in the calculation of thermodynamic quantities such as air density, absolute humidity and potential temperature. Note that standard sea level pressure is 1013.25 hPa.

There are numerous commercially available pressure transducers which range widely both in price and performance. Most of these sensors are capable of delivering barometric pressure with an overall accuracy of ± 1.0 hPa with a resolution of ≤ 0.1 hPa as required by EPA guidance. While no guidance is available for response time, it should be ≤ 60 seconds.

The barometric pressure does not have to be obtained at 10 m as suggested in the TAD. The sensor can be placed at the base of the tower or inside a shelter. Ideally, the sensor should be placed at 2 m above the ground. If a value for the pressure at 10 m (p_{10}) is desired, then a simple correction to the 2 m pressure

(p_2) may be applied by using the hypsometric equation

$$p_{10} = p_2 e^{\frac{g(z_2 - z_{10})}{R_v T_v}}$$

where z_2 and z_{10} are 2 and 10 m, respectively, g is the acceleration due to gravity (9.81 m s^{-2}), R_v is the universal gas constant for dry air ($287.05 \text{ J kg}^{-1} \text{ K}^{-1}$), and T_v is mean virtual air temperature (K) in the layer between z_2 and z_{10} which is computed by using

$$T_v = T(1 + 0.61w)$$

where T is the mean ambient air temperature (K) between z_2 and z_{10} , and w is the mixing ratio (g g^{-1}). The decrease in pressure between the 2 and 10 m is on the order of 1 hPa for a typical ambient air temperature of 20°C and mixing ratio of 15 g kg^{-1} . Altitude of the station above mean sea level and the height of the pressure sensor above ground level should be documented in the event that sea level pressure needs to be computed using the hypsometric equation.

If the pressure sensor is placed indoors, accommodations should be made to vent the pressure port to the outside environment. One end of a tube should be attached to the sensor's pressure port and the other ended vented to the outside of the trailer or shelter so that pressurization due to the air conditioning or heating system is avoided. The wind can often cause dynamical changes of pressure in a room where a sensor is placed. These fluctuations may be on the order of 2 to 3 hPa when strong or gusty winds prevail.

UPPER AIR METEOROLOGICAL INSTRUMENTATION

40 CFR Part 58 requires the measurement of upper air meteorology. However, the regulation does not contain specific details on which variables need to be measured. The TAD, however, does suggest that profiles of horizontal wind velocity, vertical wind velocity, and air temperature be acquired. Also needed is an estimate of the mixing layer height and stability class of the atmospheric boundary layer. There is a special emphasis on knowing the depth of the atmospheric boundary layer. The mixing height is an important variable in many EPA regulatory models since it determines the vertical extent of turbulent mixing of pollutants during neutral and unstable atmospheric conditions.

There are a variety of measurement platforms which can be used to acquire these data. They include aircraft, towers, tethered and expendable balloon systems, and ground-based remote profilers. As with any measurement system, each has many advantages and disadvantages.

Unfortunately, the temporal and spatial density of these variables have not been clearly defined. In addition, the number of upper air stations needed for each nonattainment area is also uncertain. The TAD infers that there should be at least one upper air station for each area. Many of the EPA documents cited in this paper lack the necessary guidance for acquiring upper air information. Until further guidance is established by EPA, sampling of upper air meteorology is left to the discretion of the States. The information presented below provides recommendations for sampling platforms; each approach is briefly discussed.

Aircraft

Aircraft are the ultimate mobile observation station. They are capable of traversing large horizontal and vertical areas in a relatively short period of time. This platform can be equipped with meteorological instrumentation and an assortment of chemical sensors. Traditionally, aircraft are used for intense episodic field studies which often focus on model evaluation. Lenschow (1986) provides an excellent overview of aircraft measurements in boundary layer applications. While an aircraft can provide detailed atmospheric observations over large areas, the total sampling time is relatively short because of fuel considerations. Aircraft may also be subject to Federal Aviation Administration (FAA) restrictions on flight paths over urban

areas. In addition, the operating cost for this type of platform is extremely expensive. Therefore, aircraft are not considered feasible for routine PAMS applications.

Tall Towers

Tall towers, usually in excess of 100 m, sometimes are used in the assessment of local meteorological conditions, diffusion studies, and micro-meteorological research projects. In many instances, it is best to take advantage of existing towers since installation of new platforms incur large costs. The main disadvantage of a tall tower is that it can not determine the mixing layer height under most daytime convective conditions since the atmospheric boundary layer commonly exceeds 1000 m. Maintenance costs can also be high since access to the instrumentation is sometimes difficult. The logistics of siting a tower in an urban setting can also be quite formidable. While an instrumented tall tower may be able to resolve the lowest part of the atmospheric boundary layer, it is not the most ideally suited upper air platform for PAMS.

Balloon Systems

Balloon based measurement systems offer a relatively inexpensive means of measuring upper air meteorology. There are two types: Radiosonde (sometimes called rawinsonde) and tethered sonde.

The radiosonde was designed to be reliable, robust, light weight, and small in bulk. Because this package is expendable, it is mass produced at low cost. The radiosonde is comprised of sensors, a tracking device, and a radio transmitter. This sensor package is suspended from a hydrogen or helium balloon which is released from the surface. Air temperature is measured with a bimetallic strip, ceramic semi-conductor, or a wire resistor. The relative humidity is acquired with the use of a carbon hygistor or a thin-film capacitive chip. The barometric pressure is obtained with the use of aneroid capsules. Ground-based radar is used to determine horizontal wind speed and direction. The radiosonde is capable of easily traversing the depth of the troposphere and reaching well into the stratosphere.

A tethered sonde system is comprised of a tethered balloon with several sonde packages attached to the line. Variables measured include horizontal wind speed and direction, air temperature, relative humidity, and barometric pressure. These data are telemetered to the ground by radio or conductors incorporated within the tethering cable. The tethered sonde system is capable of achieving altitudes up to 1000 m. However, this system can only operate in light to moderate wind conditions (5 m s^{-1} at the surface, 15 m s^{-1} aloft). A tethered balloon may also pose as an aviation hazard and is subject to FAA regulations. A permit must be obtained for permission to operate such a system. The main disadvantage for these balloon systems is that they can be very labor intensive, especially if data are needed on an hourly basis.

Remote Profilers

In recent years, remote sensing has played an increasingly important role in atmospheric boundary layer studies. Ground-based remote profilers have gained a reputation as effective tools for acquiring upper air information. However, while these profiling systems have been approved and used to develop meteorological databases required as input for dispersion models, there is a distinct void in terms of guidance needed to help potential users and the regulatory community. Because of their unique nature and constant evolution, the EPA guidance for profilers is more generic than that which already exists for many well established in-situ meteorological sensors. However, efforts are underway to provide more clearly defined guidance and standard operating procedures and will appear in the next edition of the *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV: Meteorological Measurements*.

There are two basic types of wind profiling systems. The first type is a radar which transmits a 915 MHz electromagnetic signal and has a range of approximately 90 to 3000 m with a vertical resolution of 75 to 150 m. The second type is a sodar (sound detection and ranging) which transmits a 2 to 5 KHz acoustic signal and has a range of about 60 to 600 m with a resolution of about 50 m. Both systems transmit their respective signals in pulses. Each pulse is both reflected and absorbed by the atmosphere as it moves upwards. The vertical range of each pulse is determined by how high it can go before the signal becomes so weak that the energy reflected back to the antenna can no longer be detected. That is, as long as the reflected

pulses can be discerned from background noise, meaningful wind velocities can be obtained by comparing the Doppler shift of the output signal to that of the return signal. The attenuation of the pulses are functions of signal type, signal power, and atmospheric conditions. A radio acoustic sounding system (RASS) utilizes a combination of electromagnetic and acoustic pulses to derive an air temperature profile in the range of about 90 to 1200 meters.

Siting of these profilers is sometimes a difficult task. Artificial and natural objects located near the sensors can potentially interfere with the transmission and return signals, thereby contaminating the wind velocity data. The acoustic pulses emitted by a sodar and a RASS are quite audible and could become a nuisance to residents who live near the installation site. However, the main advantage to these systems is that they can operate remotely for extended periods of times with no or very little supervision.

SUMMARY

The Photochemical Assessment Monitoring Station will require the incorporation of surface and upper air meteorological instrumentation. The surface variables include horizontal wind speed and direction, air temperature, relative humidity, solar radiation, and barometric pressure. Sensor specifications are summarized in Table 2. Upper air variables should include profiles of horizontal and vertical wind velocity, air temperature, and mixing height. Ranges and accuracies (based on surface sensor requirements) are given in Table 3. Personnel from State, Regional and local EPA agencies are strongly encouraged to comment on and recommend any improvements to these requirements so that high quality meteorological data may be obtained in these ozone nonattainment areas.

DISCLAIMER

This document has been reviewed in accordance with U. S. Environmental Protection Agency policy and approval for publication. Mention of trade names or commercial products does not constitute EPA endorsement or recommendation for use.

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Table 1
WMO (1983) Classification of Pyranometers

Characteristic	Units	Secondary Standard	First Class	Second Class
Resolution	W m ⁻²	±1	±5	±10
Stability	%FS year ⁻¹	±1	±2	±5
Cosine Response	%	±3	±7	±15
Azimuth Response	%	±3	±5	±10
Temperature Response	%	±1	±2	±5
Nonlinearity	%FS	±0.5	±2	±5
Spectral Sensitivity	%	±2	±5	±10
Response Time (99%)	seconds	25	60	240

Table 2
Summary of sensor requirements for surface meteorological variables based on available EPA and WMO guidance.

Variable	Height (m)	Range	Accuracy	Resolution	Time / Distance Constants
Wind Speed	10	0.5 to 50 m s ⁻¹	±5%	0.1 m s ⁻¹	5 m (63% response)
Wind Direction	10	0 to 360°	±5°	1°	5 m (50% recovery)
Air Temperature	2	-20 to 40 °C	±0.5 °C	0.1 °C	60 s (63% response)
Relative Humidity	2	0 to 100 %RH	±3 %RH	0.5 %RH	60 s (63% response)
Solar Radiation	any	0 to 1200 W m ⁻²	±5%	10 W m ⁻²	60 s (99% response)
Barometric Pressure	2	800 to 1100 hPa	±1 hPa	0.1 hPa	60 s (63% response)

Table 3
Summary of sensor requirements for upper air meteorological variables based on available EPA and WMO guidance.

Variable	Range	Accuracy
Wind Speed	0 to 50 m s ⁻¹	±1 m s ⁻¹
Wind Direction	0 to 360°	±10°
Air Temperature	-20 to 40 °C	±0.5 °C
Relative Humidity ¹	0 to 100 %RH	±5 %RH
Barometric Pressure ¹	650 to 1050 hPa	±1 hPa
Altitude	0 to 3000 m	±1%

¹While upper air relative humidity and barometric pressure data are not required for PAMS, they are desired measurements, especially for thermodynamic computations.

SODAR, RADAR Profiler and RASS Operating Principles and PAMS Applications

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ABSTRACT

Meteorological remote sensing is most commonly thought of as weather satellites taking the cloud pictures we see on television. Less widely known, but equally well developed and routinely fielded in recent years, are ground-based systems that look upward into the lower atmosphere to provide wind and temperature measurements in vertical profile. All such "profilers" operate on the interaction of their transmitted pulse with the atmosphere and provide measurements based upon interpretation of the signal reflected back to the system's antenna. Such systems include the "sodar," using strictly acoustic signals, the "radar profiler," using electromagnetic transmissions, and the "RASS," incorporating acoustic and electromagnetic interactions.

This paper provides an overview of sodar, radar profiler, and RASS technology, with emphasis on operating principles and potential Photochemical Assessment Monitoring Station (PAMS) applications. A description of the capabilities and limitations of each system is included, based upon experience in its operational use supporting ozone-related field measurement programs in recent years. The combined use of the three types of systems for upper air meteorological monitoring at the first PAMS site in New Jersey is highlighted.

INTRODUCTION

Sound Detection And Ranging (SODAR) systems have been increasingly used in meteorological field measurement programs over the past decade. During the past several years, boundary layer radar profilers and the Radio Acoustic Sounding System (RASS) have similarly become commercially available and used in data collection programs. Following common usage, "sodar" and "radar" appear in lower case in the body of this paper, while "RASS" appears in upper case.

OPERATING PRINCIPLES

Sodars and radar profilers measure atmospheric turbulence and wind profiles using similar principles but with two different kinds of waves, acoustic and electromagnetic. The techniques are based on transmitting a high-power localized pulse into the atmosphere, and analyzing the amplitude and frequency of the portion of the transmitted signal that is reflected back to the antenna by atmospheric scattering. More detail about these remote sensing methods can be found in three recent collections of papers.^{1,2,3}

The scattering is produced by small fluctuations in the wave propagation speed through the medium. For a sodar, the scattering strength is proportional to the temperature structure parameter (C_T^2) which is a measure of the root mean square variation in the temperature between two points. For a radar profiler, the scattering is proportional to the refractive index structure parameter (C_n^2). Small-scale turbulent eddies (with scale near the transmitted

wavelength) produce the atmospheric fluctuations. Hence the strength of the echo signal is a direct measure of the turbulence in the atmosphere.

The echo signal is Doppler-shifted in frequency due to the motion of the scattering air mass. For example, if the wind component along the beam axis is toward the antenna, the echo frequency is shifted upward by the amount $2(v)(f_t)/(c)$, where f_t is the transmit frequency, c is the propagation speed of the wave (acoustic or electromagnetic), and v is the radial velocity component. Hence by analyzing the frequency of the echo return as a function of delay (travel time), a profile of the radial wind velocity component is obtained. The full three-dimensional wind vector profile is obtained by measuring the radial winds along three (or more) independent beam directions near the vertical. Typically a vertical beam and two to four oblique beams, tilted 15 to 20 degrees down from the vertical in different directions, are used. Separate antennas may be used for each beam, or a single phased array may be steered to the different beam directions in sequence. Trigonometric relationships are used to transform the radial wind profiles to the customary horizontal wind speed and direction and vertical wind speed (or to any other desired coordinate system).

The wavelengths used are selected based on the dominant eddy scale in the region of the atmosphere being studied. In the boundary layer, considerations based on the inner scale turbulence¹ indicate that the optimum wavelengths are between 0.1 and 0.4 meters. In the U.S., excellent results have been obtained with the 0.33 meter (915 MHz) boundary layer profilers. Sodar systems are typically operated with wavelengths between 0.1 meters (3,400 Hz) and 0.34 meters (1,000 Hz). At higher altitudes, the inner scale becomes larger and longer wavelength (lower frequency) remote sensing systems should therefore be used. For example, 0.75 meter (404 MHz) and 6 meter (50 MHz) profilers routinely operate to altitudes of 12 km and 20 km, respectively. Similarly, higher frequency, shorter wavelength sodars ("minisodars") will produce higher resolution data at the cost of less altitude coverage.

Vertical profiles are produced by relating the turbulence or wind values to the height of the corresponding scattering volume. This calculation is based on the travel time from the antenna to the scattering volume and back. For sodar, since the speed of sound is about 340 meters per second, the round-trip travel time to the maximum ranges attainable (about 1,000 meters) is about 6 seconds. Hence the repetition rate for typical sodar systems is about 6 to 10 pulses per minute. Electromagnetic waves travel at the speed of light, and a typical maximum range for a boundary layer radar profiler is 5,000 meters. In this case the pulse repetition frequency would be about 20,000 pulses per second. Because of the large difference in data flow rates, the low level signal processing is handled differently for the two types of systems.

Sodar (Acoustic Sounder)

The components of a typical sodar system include the acoustic antennas, signal generator and power amplifier, receiver, analog-to-digital converter, signal processing software, and archive and display software. The acoustic antennas form directional beams about 8 to 10 degrees wide (between half-power points), with acoustic absorption cuffs to reduce the antenna response along the ground. Historically, separate antennas have been used for each beam, although steered phased array antennas, which have become available recently, can provide a more compact and portable system. Signal processing functions include bandpass filtering (to reject broadband background noise), calculation of the amplitude and frequency of the return signal, and algorithms to selectively reject contributions from interferences (such as background noise, transient acoustic sources, and reflections from fixed objects).

Radar Profiler

Commercial boundary layer radar profilers use microstrip panel antenna modules, about 1 meter square and several inches thick, mounted in a four-panel array low to the ground. The panels are installed inside a clutter screen, which performs a function similar to the acoustic

absorption cuff, to reduce ground clutter. As in the sodar case, either separate antennas for each beam, or multiple beams formed in sequence by a single phased array antenna, may be used.

Because of the high frequency and high data rates involved, special purpose analog and digital electronics components are required to generate pulses and to sample and process the return signal. For transmitting, custom pulse generator and RF power amplifier circuits must be used to satisfy the bandwidth and power requirements. Similar stringent requirements are placed on the receiver circuitry which filters and bandshifts the signal prior to sampling. Signal processing boards specially designed for the radar profiler application and commercially available DSP (Digital Signal Processing) coprocessor boards are used for the high data rate signal averaging and spectral analysis tasks.

Radio Acoustic Sounding System (RASS)

RASS is a method for combining acoustic and electromagnetic profiles to measure temperature profiles in the boundary layer. The acoustic wave modulates the density, and hence the refractive index, when it propagates through the atmosphere. When the radar and acoustic beams are co-axial, and the acoustic wavelength is half the radar wavelength, the radar wave is scattered strongly from the propagating sound waves. The Doppler shift of the scattered radar wave is proportional to the propagation speed of the acoustic wave, which in turn is related to the virtual temperature.

For the boundary layer profiler (915 MHz radar frequency), the matching acoustic frequency is near 2,000 Hz. The acoustic frequency is swept over a band about 100 Hz wide, to cover the matching acoustic wavelengths for the expected range of virtual temperatures in the profile.

The vertical wind affects the acoustic wave velocity, particularly under convective conditions. To account for this, the vertical wind velocity component is measured at the same time as the acoustic wave velocity and the correction is applied.

EMPLOYMENT CONSIDERATIONS

Employment of sodar, boundary layer radar profiler, and RASS systems involves a three step process of system selection, siting, and routine operations. The first step is to choose the system(s) appropriate to the need. The second step relates to installation, requiring proper placement of the outdoor antenna component, provision for environmentally controlled sheltering of the controlling PC and associated electronics, and supply of an electric power source. This step may also include considerations of power conditioning, fencing or other security measures, and providing telephone service to the site if remote control and data retrieval is desired. Once operational, the third step involves changing operator-selectable parameters as may be desired, data retrieval and quality assurance procedures, periodic preventive maintenance, and as-required corrective maintenance. Important to each of these three employment steps are capability and limitation considerations, as highlighted below.

System Selection

The decision to employ a sodar, radar or RASS meteorological remote sensing system commonly results from need for vertical profiling well above tower height and/or need for time-continuous data measurements not possible with balloon-borne systems. Of these three remote sensing options, however, the decision to employ a particular system, or particular combination of systems, normally results from a comparison of data measurement needs versus the data capabilities of the respective systems, in concert with budgets.

Cost considerations favor the sodar, while data height capability favors the radar profiler. RASS is limited to a single data type, virtual temperature profiling, and is therefore commonly selected in combination with either a radar profiler or a sodar. The addition of RASS

capability to a radar profiler adds a relatively small cost compared with adding RASS to a sodar.

While data measurement heights of all three systems vary with atmospheric conditions, system configuration and any siting limitations, sodars generally provide measurements in the range starting at 20 to 50 meters above ground level and extending up to 500 to 1000 meters above ground level. In addition to wind profiling, sodar measurements of echo signal strength provide a means of estimating boundary layer mixing height, as a function of time, up through that portion of the boundary layer within the height range of the sodar.

As implied by the name, boundary layer radar profilers provide measurements, under most conditions, throughout the depth of the boundary layer. Radar profiler measurements generally extend over a range starting at about 100 meters above ground level up through 3 to 5 kilometers above the ground. Like sodars, radar profilers provide both wind measurements throughout their vertical range and echo signal strength measurements that can be used to estimate boundary layer depth as a function of time.

Vertical resolution of wind data is commonly 25 meter increments for sodars and 100 meter increments for radar profilers. For RASS, virtual temperature measurements commonly start at 100 meters above ground level and extend to about 1 to 1.5 kilometers above ground level, with 60 to 100 meter vertical resolution.

Atmospheric conditions influence the performance of all three systems. Rain is a significant limiting factor. Also notable are strong winds that deflect the acoustic beams and thus reduce the maximum height capability of sodar and RASS systems. Radar profilers equipped with RASS operate either in the wind or virtual temperature profiling mode, alternating between modes on a schedule established by the user. Where RASS is used in conjunction with a sodar, alternating mode sequencing is similarly necessary unless separate acoustic antennas are provided for each system. Simultaneous operation of a RASS and a sodar also requires sufficient acoustic frequency or physical distance separation between the two systems to preclude RASS transmission interference with sodar signal-echo reception.

System Siting

Trailer mounting of sodar, radar profiler and RASS systems is an available option, but generally selected only when frequent moves to different siting locations are anticipated. Whether mounted on a trailer or on the ground, each system must be provided a power source and a small environmentally-controlled shelter. Positioning inside security fencing and providing a telephone circuit link to the system are also generally recommended provisions.

Choice of site location, as well as antenna beam-pointing directions, should consider the interaction of sodar, radar profiler and RASS systems with their surroundings. For sodar and RASS systems, a key siting consideration is potential noise nuisance impact. Acoustic transmissions each few seconds from a sodar, or continuously from a RASS during its designated operating cycle, can be irritating to people living or working in the vicinity. As a general rule, positioning of sodar and RASS systems at least 500 meters, and preferably 1,000 meters, from residences and offices is recommended. This minimum recommended distance may need to be considerably greater if the sodar or RASS system does not include a protective acoustic absorption cuff around the transmitting antenna, particularly if the antenna is specially configured with high power transmit capability.

Siting of sodars also needs to consider active and passive sources of interference in the vicinity that could degrade their performance. For example, since sodar operation relies on return atmospheric signal echo strength being detectable above the background noise level, an average broadband noise level above about 50 dB at a site could degrade sodar measurement height capability. Transient noise sources may also have a negative data impact if their frequency is near that of the sodar, and particularly when a data time-averaging parameter setting of five minutes or less is used. Passive noise sources degrading sodar performance are

stationary objects that reflect the sodar acoustic transmission back to the antenna as a strong signal with a zero (or near-zero) doppler shift. Structures such as buildings and towers in the vicinity are potential reflection sources and should generally be avoided. As with the nuisance factor caused by sodars, the susceptibility of sodars to degradation by nearby active and passive noise sources is reduced if the system includes an acoustic absorption cuff(s) around the antenna(s). Additional techniques for mitigating stationary object reflections are to rotate the antenna(s) until the reflections are minimized or eliminated, and to include software algorithms to detect and eliminate stationary object reflection signals.

Radar profilers require site approval licenses from the FCC and, while not subject to acoustic nuisance or acoustic interference problems, need to be sited with potential radar ground clutter sources in mind. Most significant is to minimize direct radar view of moving targets like tall trees or power lines that sway in the wind or busy roadways. A side-lobe clutter screen helps minimize the adverse impact of ground clutter sources, as does rotating the antenna orientation relative to a source. Software detection and elimination of non-atmospheric clutter sources has also been developed and helps minimize data contamination.

System Operations

Sodar, radar profiler, and RASS systems require minimal manpower resource to operate because they are capable of continuous, unattended data collection. However, provisions must be made for periodic interaction with these systems and their data as part of a quality assurance program.

The most basic need is to make periodic site checks; either by telephone modem or in person, to assure neither power nor system failures have interrupted data measurements. While the systems have no moving parts and failure rates are generally low, a check of some sort on at least a weekly or bi-weekly basis is advisable. On a scheduled monthly or quarterly basis, brief site visits are also recommended to make visual inspections, to perform any prescribed system audit procedures such as checking antenna level and alignment, and to download data if not done remotely by telephone.

Data reviews need to be sufficiently frequent to detect any degradation of data quality so that unscheduled maintenance action can be initiated, when required, in a timely manner. Data processing needs to include screening procedures to check for any data inconsistencies that the system failed to detect and invalidate. This data validation portion of the quality assurance program needs to also detect any trends indicating need to change user-selectable parameter settings in the system's software. Examples of key user-selectable parameter settings impacting data measurements include transmit pulse length, data time-averaging interval, and data acceptance threshold level.

DATA EXAMPLES SUPPORTING AIR QUALITY MEASUREMENT PROGRAMS

Sodar

Figure 1 shows 10 hours of sodar wind data recorded in northern Thailand during system installation in support of an air quality study. In this example, the sodar software is configured to average the wind data over 15 minute sampling periods, in vertical increments of 25m, using a pulse length of 25m. In addition to the automatic checks made by the software, the depicted wind data have been validated to level 1.0 by user interaction (invalidating two sodar-reported wind values and marking as suspect four others).

Radar Profiler

Figure 2 shows 24 hours of 915 MHz radar profiler wind data recorded at Jefferson County Airport in southeast Texas. This profiler was installed by the Texas Natural Resources Conservation Commission in support of their ozone non-attainment field measurements

program. In this data example, the radar profiler software is configured to average the wind data over 49 minute sampling periods, in vertical increments of 202m, using a pulse length of 405m. A strong cold front moved through the area around noon and the radar profiler measurements clearly show the abrupt shift in the winds associated with the front. Also available simultaneously from the radar profiler are 101m pulse length data (not shown) that provide even greater resolution in the lower 1 to 2 kilometers.

Radio Acoustic Sounding System (RASS)

Figure 3 shows six hours of 915 MHz radar profiler RASS virtual temperature data recorded at Los Angeles International Airport. This profiler was installed by the South Coast Air Quality Management District to evaluate its usefulness in support of air quality studies in the Los Angeles Basin. In this data example, the progressive development of the marine inversion caused by the daytime strengthening of the sea breeze is evident. In this case the RASS software was configured to average the virtual temperature data over 8 minute sampling periods, in vertical increments of 105 meters, using a pulse length of 105 meters. The RASS provides the means to acquire data depicting boundary layer temperature structure detail up to about 1500 meters (atmospheric dependent).

POTENTIAL PAMS APPLICATIONS (THE NEW JERSEY EXAMPLE)

The 1993 revision of federal regulations on air quality (40 CFR Part 58) established enhanced monitoring requirements to satisfy the Clean Air Act amendments of 1990. This revision requires States to establish photochemical assessment monitoring stations (PAMS) as part of their State Implementation Plan (SIP) for ozone nonattainment areas classified as serious, severe, or extreme. Twenty-two areas with 90 PAMS requirements were initially identified nation-wide. All 90 sites require meteorological measurements using a 10 meter tower while each of the 22 areas requires at least one upper air measuring system.

In addressing State of New Jersey PAMS upper air measurement needs, remote sensing was chosen as the most attractive alternative because it provides time-continuous data throughout the boundary layer. Specifically, a sodar, radar profiler and RASS combination was selected, along with a 20 meter tower, for installation at an urban site near New Brunswick on the campus of Cook College, Rutgers-The State University of New Jersey. This is being undertaken as a cooperative venture of the State, the University, and private industry.

Figure 4 depicts the complimentary capabilities of the sodar, radar profiler and RASS, as will be employed at the New Jersey PAMS site. The sodar and radar profiler both provide winds aloft and boundary layer height information, with the radar profiler able to measure up through the top of the boundary layer and the sodar providing enhanced vertical resolution in the critical lower 1,000 meters. The overlapping portions of the sodar and radar profiler vertical measurements also provide valuable data redundancy for quality assurance crosscheck purposes. Completing the picture is the RASS addition to the radar profiler, which adds quantitative temperature profile measurements to the data base.

CONCLUSIONS

This paper provides information on sodar, radar profiler, and RASS operating principles and employment considerations, shows a few data examples, and highlights the combined use of these meteorological remote sensing systems in the New Jersey PAMS application.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the contributions of the Government of Thailand, Texas Natural Resources Conservation Commission, and California South Coast Air Quality Management District for the data used in this paper. The authors also appreciate the New Jersey PAMS information provided by Dr. Reiss, Cook College, Rutgers-The State University of New Jersey.

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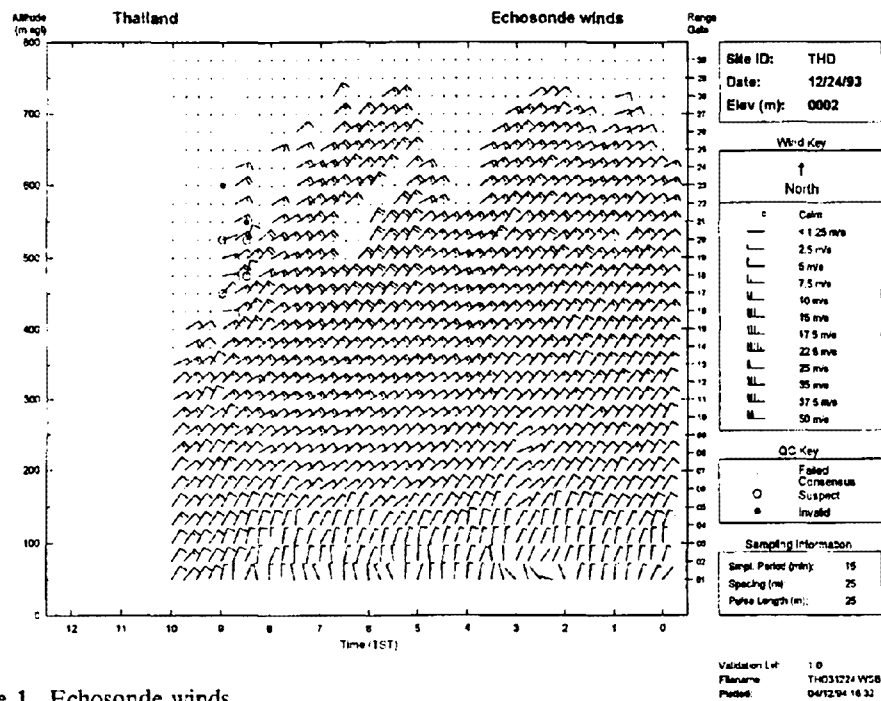


Figure 1. Echosonde winds.

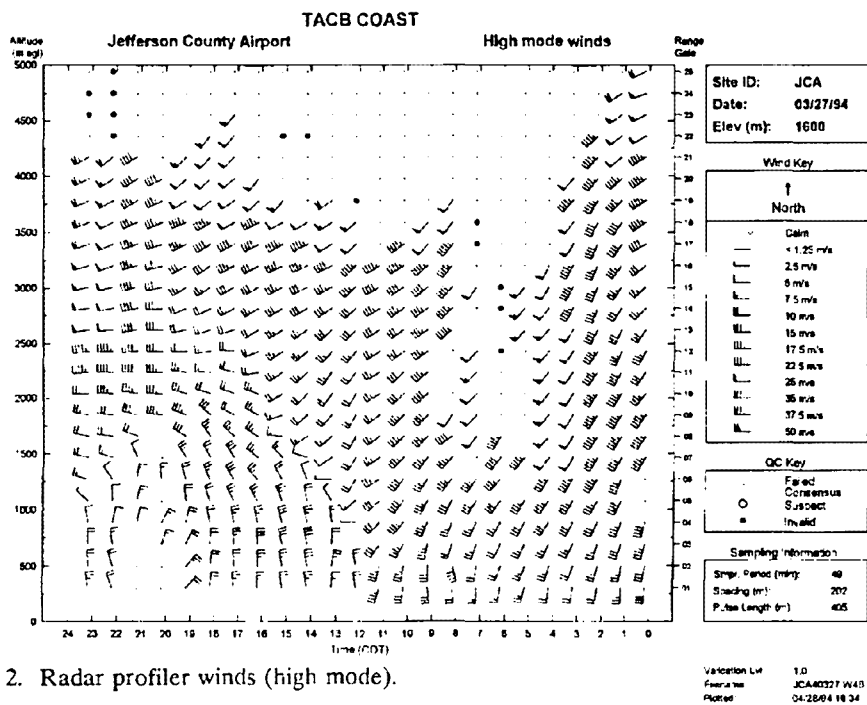


Figure 2. Radar profiler winds (high mode).

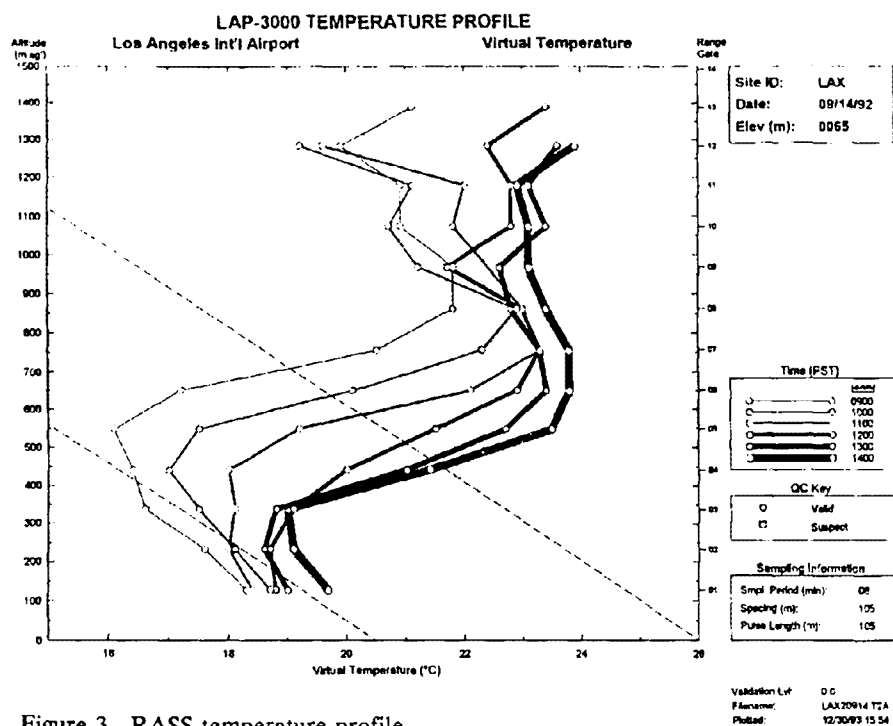


Figure 3. RASS temperature profile.

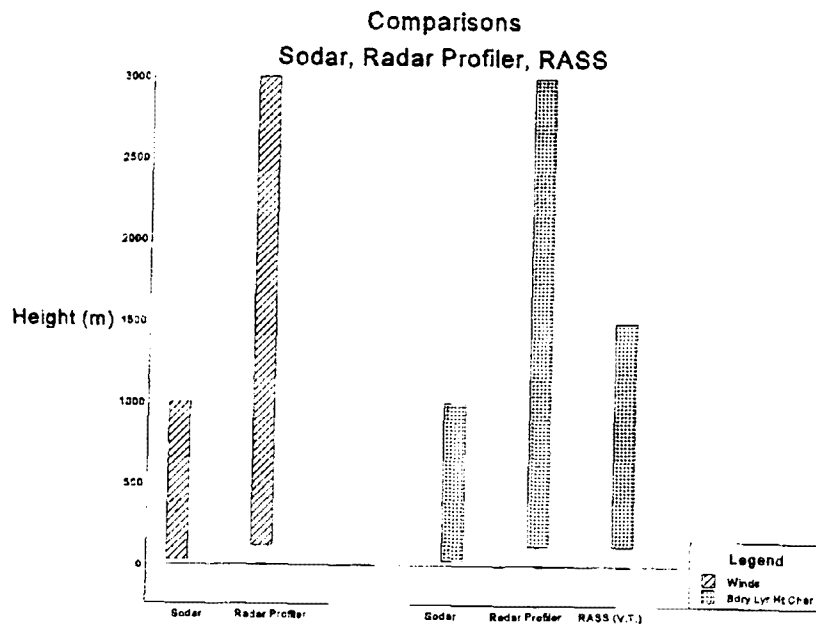


Figure 4. Wind profiles and boundary layer height characterization.

Siting Guidance for Boundary-Layer Meteorological Profilers

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ABSTRACT

The increased operational use of 915-MHz radar wind profilers and radio acoustic sounding systems (RASS) reveals potential problems with their siting and necessitates an evaluation of siting criteria for these instruments. Siting involves two scales, local and regional. The local area is defined within 1 km of the instrument site, and a region may be as large as an entire state. After a brief discussion of the site preparation, ground clutter problems are discussed. The wind profilers should not be placed with clutter sources (e.g., trees, telephone or power cables, hills with vegetation) that rise greater than 20° above the horizon, and preferably greater than 5° above the horizon. More recently discovered is the problem of contamination from migrating birds, so consideration must be given to those periods or situations that influence bird migration, e.g., season, time of day, and weather conditions. Finally, brief mention is made of regional siting considerations, particularly in areas of complex terrain in which nearby terrain features may affect the measured wind or temperature profiles and result in spatially unrepresentative measurements. For this, it is recommended that results of a boundary-layer meteorological model be evaluated in urban regions located in complex terrain. Spatial correlations of wind fields derived from the model can be used to determine spatially representative locations.

INTRODUCTION

The boundary layer wind profilers, operating at 915-MHz,¹ often with accompanying radio acoustic sounding systems² (RASS), have, in recent years, been temporarily deployed, usually in arrays for regional air quality studies.³ Some studies in the United States are beginning to deploy or are considering deployment of permanent wind profiler/RASS installation for either local or regional pollution transport monitoring. With the increased use of these versatile instruments, consideration of optimum siting of wind profiler/RASS instruments becomes increasingly important. Yet, no such guidance exists in open literature.

The discussions to follow describe guidance and criteria for siting of 915-MHz wind profilers with RASS. The information is not meant to be comprehensive or quantitative in all cases. Lack of space prevents a totally comprehensive discussion, and some siting considerations are not conducive to quantitative treatment. In the next sections, we cover site preparation (e.g., shelter, power, antenna area), ground clutter problems, recently discovered problems with bird contamination, and regional siting considerations in complex terrain regions for the purpose of spatial representativeness.

SITE PREPARATION

The very basic electronics for the wind profiler/RASS consists of a receiver/transmitter, an audio amplifier, and a specially configured PC. Space requirements are quite small, but a recommended building or trailer size is 8'x12' to allow working space. As with most electronics, environmental control is required, preferably in the 65°-80°F range. The entire radar/RASS central electronics unit can operate on a 110 V, 15 A circuit, but, with the air conditioning required in many areas, a 30 A circuit or more may be required. Because the radar is computer keyboard controlled, proper interior lighting is required and a telephone may be needed if radar/RASS data are to be transmitted over a phone line. Often, in more remote areas, or areas with very temporary installation, cellular phones can be used.

Because of the noise generated from the RASS/acoustic antennas, it is recommended to locate the installation at least 0.5 km from the nearest home. However, factories or offices usually generate their own noise or are environmentally enclosed. Therefore, those working inside or on factory grounds are usually not annoyed by RASS.

The radar antenna must be within 100' (the length of the cables to the antenna), but not less than 20' from the electronics enclosure. The cables must be protected from vehicular or foot traffic. They can be buried in conduit or "blocked" with wood in a shallow trench.

The radar antenna and four RASS acoustic source antennas require a cleared, fairly level area of about 10x10 m. We are assuming an installation with a standard phased-array radar antenna with RF-absorbing screens (clutter screens). It is strongly recommended that the radar antenna, at least, be placed on a cement slab for permanent installations. This will stabilize the antenna level. The leveling of the acoustic antennas is not critical, but the radar antenna should be leveled to within 0.1°-0.2° to insure that accurate vertical wind corrections are used with minimal contamination from the horizontal wind. An electronic leveling device with a digital display is recommended for precise leveling. The radar antenna clutter screens should be guyed to the ground. Each of the four acoustic source antennas should be placed as close as possible to the corners of the clutter fences on the radar antenna. For security reasons, it is preferable to surround the radar antennas, guy wires, and acoustic antennas with a 6' chain-link fence. This is imperative in rural fields in which large animals, particularly cattle, roam.

Figure 1 diagrams a typical radar wind profiler/RASS installation.

CLUTTER CONSIDERATIONS

Figure 2 presents a three-dimensional beam-pattern diagram from a test of a phased-array, 924-MHz radar antenna with a 4'-high clutter screen with a curved edge similar to the commercial version. The test was conducted from actual measurements in the atmosphere at the Army's Fort Huachuca facility in Arizona. The 924-MHz frequency was used rather than 915 MHz because 915 MHz is not authorized at many Army installations. The measurements are in decibels scaled to the maximum transmitted intensity at the centroid of the beam (0 db) and the pattern is from the vertical beam using a prolonged receiver.

If one uses the criteria that the beam width is defined at the -3 db points, Fig. 2 shows that the beam is about 12° wide at its widest point. Because this width is only slightly larger than that for sodars (~9°), one may initially assume that reflections from objects near the ground would not be a problem, but because of the weak, natural atmospheric scattering at 915 MHz, the side lobes present a particular problem. Because the radar receiver is very sensitive (down to as low as around -20 db below the beam centroid), one can see from Fig. 2 that reflections from side lobes could present a problem. Compounding this is that plants and leaves can present strong reflections because of their moisture content to which this frequency is particularly sensitive. Strong reflections can also occur from metal objects. When objects are vibrating with the wind, they can appear strongly in the Doppler spectrum with nearly zero Doppler shift. An automated algorithm is used to eliminate ground clutter interference with the Doppler returns by searching for abrupt biases in Doppler shifts from upper gates to lower gates, and the technique is usually successful except with light winds or strong wind shears. Nearly continuously moving objects like vehicles, numerous aircraft, and even people or animals can present serious contamination. Locations where these can occur should be avoided, if possible. Occasional moving objects usually do not present a problem because of the consistency tests with radar software.

A general rule is to avoid clutter greater than 5° above the horizon, and certainly avoid clutter greater than 20° above the horizon.⁴ With a four-beam system, one beam can be turned off in a particularly bad clutter direction. Also, the antenna can be oriented so that the orthogonal beams point in directions of minimum clutter. A beam pattern with azimuthal information like the one presented in Fig. 2 is useful for such orientation information.

MIGRATING BIRD CONTAMINATION

Although it has been long known that birds present a strong reflective cross section for 915-MHz radars, it was not accepted that they significantly contaminated the derived winds from the Doppler return because of their random flying patterns. It has been assumed until recently that the consensus algorithms used with radar wind processing would eliminate the contamination in the mean. However, it is now clear that migrating groups of birds, in non-random flight patterns, can significantly contaminate the radar-derived winds.⁵

Merritt⁶ present new methods that appear to be mostly successful in eliminating, in real time, the bird contamination and they will be used with new commercial systems. However, there can be enough ambiguity in the bird contamination that it is not always clear that the contamination is removed. This problem is not really a siting consideration, but more of a timing consideration. Migrations can occur most months of the year over North America, except for December and January, perhaps part of February, and for a brief period in late June and early July when the birds are nesting. The migrations nearly always occur during the dark hours. However, there is a regional difference in the exact timing of the migrations and weather events do change the patterns. There are continental locations at which bird contamination would never be a problem, adjacent to or within major mountain ranges.

REGIONAL SITING CONSIDERATIONS AND SPATIAL REPRESENTATIVENESS

A final consideration for wind profiler/RASS siting is with the regional or mesoscale, from several kilometers to up to 500 km from the instrument site. When instruments that measure atmospheric parameters are deployed, one would prefer that these parameters are representative of an area surrounding the measurement location. Gaynor et al.⁷ have documented the importance of this, particularly in complex terrain, and also explained how representativeness can be qualitatively determined. Figure 3 presents an example from this work of a gridded complex wind pattern measured in northern California at three levels using an array of light wind profilers indicated by the dots. These winds are very much influenced by the terrain features.

Figure 4 shows contours of spatial correlations from the site designated "TRN" for the east-west wind components (u) and the north-south wind component (v) and for a morning and afternoon case (the first and second columns, respectively, of graphs in Fig. 3). Although this example uses gridded data from actual measurements, one could envision using spatial wind correlations from results from complex terrain meteorological models to assist in optimum siting of wind profilers. Gaynor et al.⁷ have shown that the spatial correlation patterns can be effected by time of day (atmospheric stability), height above ground, and the synoptic weather situations. Therefore, one must be careful that all important effects are included before siting decisions are made.

SUMMARY

Although presenting a somewhat comprehensive account of siting guidelines for wind profiler/RASS instrumentation, limited space precluded a detailed discussion. Not mentioned here are nonquantifiable siting concerns like access to phone or other communication for data links, frequency clearance, property access considerations, and for convenience of personnel to the site for visits and maintenance. It is hoped, however, that the discussions concerning site preparation, the very important ground clutter minimization, the bird problem (not purely a siting consideration), and, finally, regional or mesoscale siting optimizations are helpful, particularly in that such guidelines do not yet exist in the published literature.

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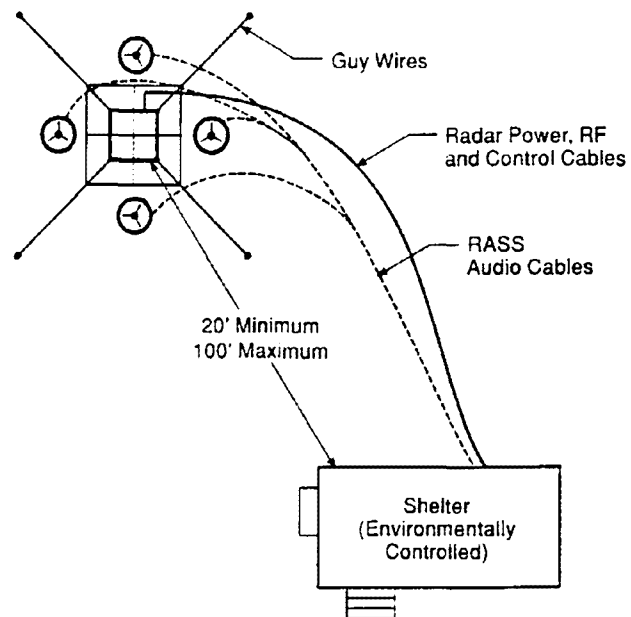


Figure 1. Diagram of a typical radar wind profiler/RASS installation.

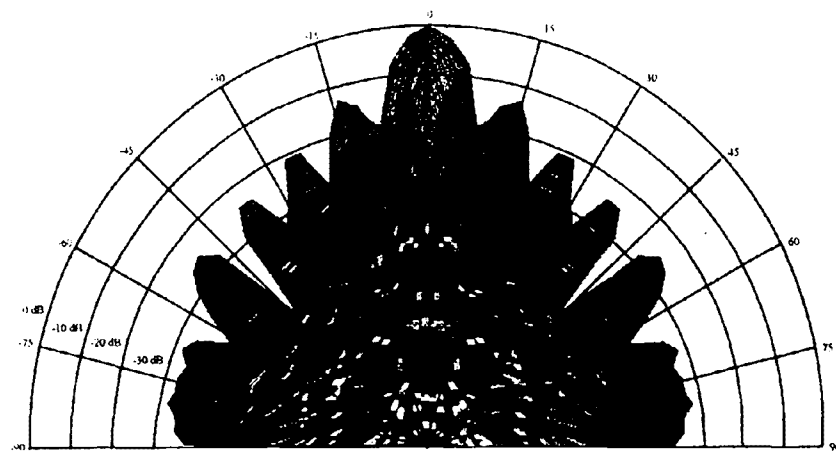


Figure 2. Three-dimensional beam-pattern diagram of a typical 924-MHz wind profiler phased-array antenna; vertical beam from a polarized receiver.

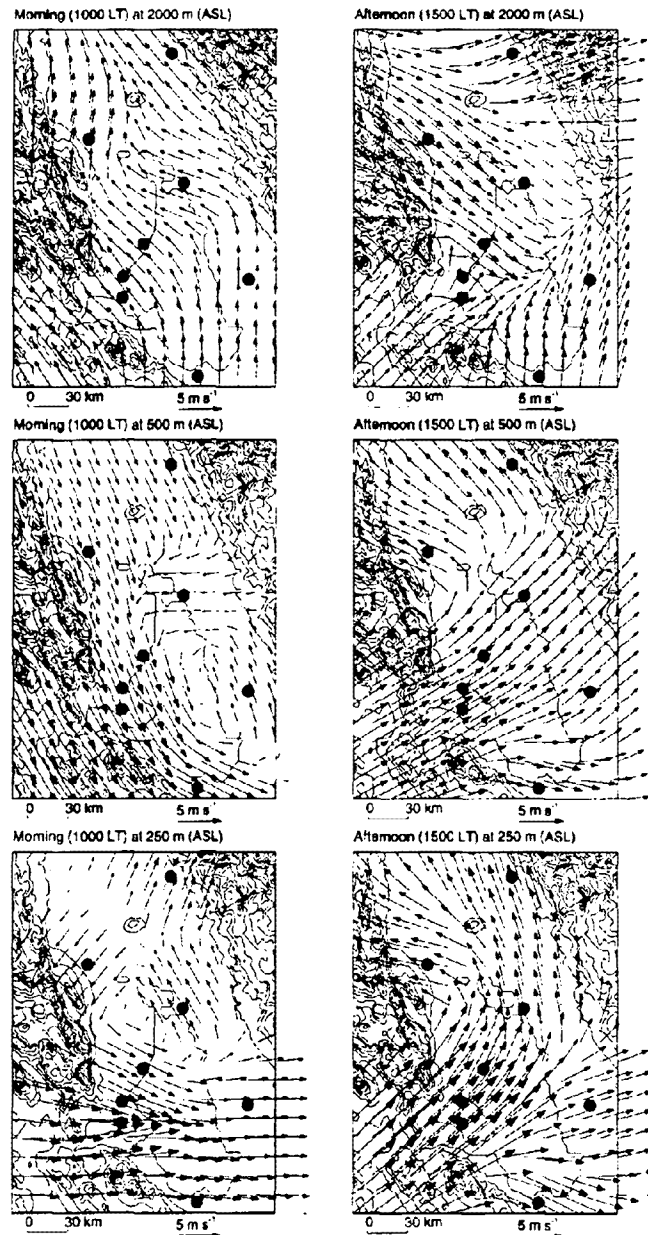


Figure 3. Wind speed and direction arrows for morning (1000 LT), left panels, and afternoon (1500 LT), right panels, at three levels ASL. The dots indicate the location of the wind profilers (from Gaynor et al.⁷). The location is centered around Sacramento Valley in California, and the terrain contours begin at 10 m and are in 100-m intervals.

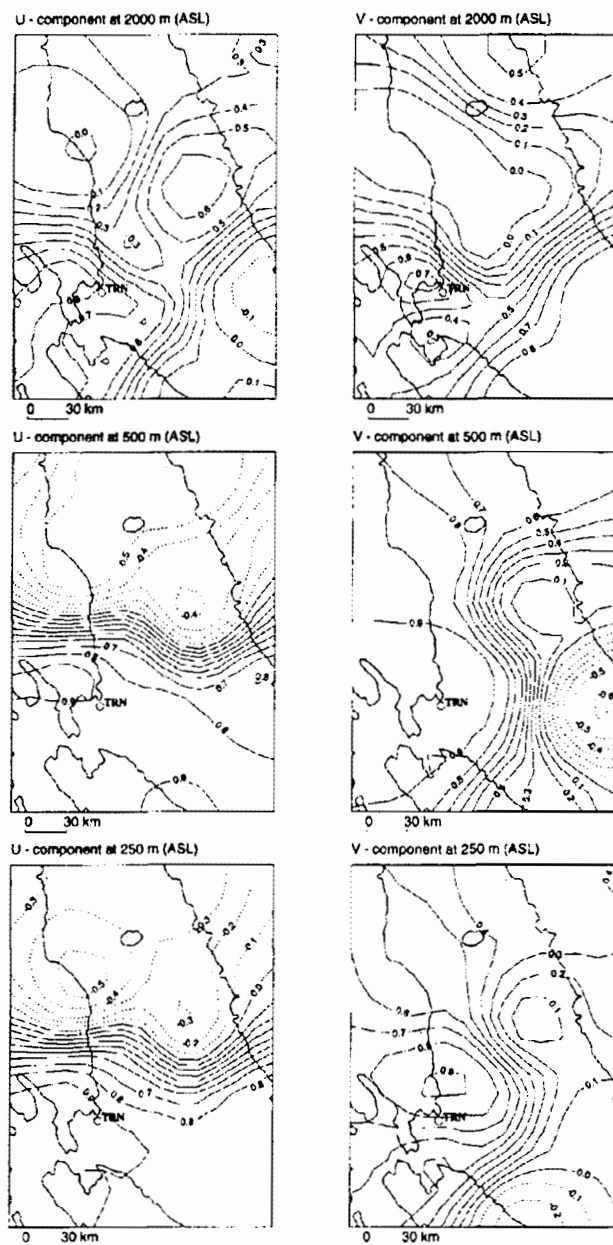


Figure 4. Spatial correlations between the site (TRN) and other grid points for u (left panels) and v (right panels) wind components. The correlations are for the morning (left panel of Fig. 3) at three levels. The dots show the wind profiler sites (from Gaynor et al.⁷). The location is the same as Fig. 3, and the single-terrain contour is 100 m ASL for reference.

Quality Assurance For PAMS Upper Air Monitoring Sites

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ABSTRACT

Quality assurance procedures are outlined for ground-based remote sensors used to acquire upper air meteorological data. Acceptance testing, calibration procedures, performance audits, operation, maintenance, and quality control are briefly discussed.

INTRODUCTION

Surface and upper air meteorology play a vital role in the formation and transport of O_3 . Consequently, meteorology has an impact on population exposure to O_3 . In order to support monitoring objectives associated with model inputs and performance evaluations, meteorological monitoring is required for each Photochemical Assessment Monitoring Station (PAMS). Surface meteorological measurements should begin within the first year of network operation. Upper air meteorological data (up to 3 km) for determining mixing heights should be collected corresponding to specific model input requirements.

Ground level meteorological variables to be measured as part of enhanced O_3 network monitoring include wind speed, wind direction, ambient air temperature, relative humidity, solar radiation, and barometric pressure. Specific guidance on siting and quality assurance may be found in the *On-Site Meteorological Program Guidance for Regulatory Modeling Applications* (EPA-450/4-87-013), and the *Quality Assurance Handbook for Air Pollution Measurement Systems: Volume IV - Meteorological Measurements* (EPA-600/4-90-003).

The mixing height is the maximum depth of the atmosphere from the surface up to a vertical height below which thorough mixing of pollutants can occur. Mixing height estimates are required for PAMS. There are numerous strategies for measuring mixing heights, which are outlined in the *Technical Assistance Document for Sampling and Analysis of Ozone Precursors* (EPA-600/8-91-215). During this presentation we will discuss quality assurance and control requirements for upper air monitoring systems.

The SODAR uses acoustic waves to measure vertical profiles of wind. This device provides a method for estimating winds and mixing height. SODARs are usually configured to obtain the most reliable data set possible for a given field site. Configuration of a profiler may include modification of the profiler output signal frequency, output signal power, averaging intervals and averaging techniques. The overall accuracy of an acquired data base is dependent, in part, on the surrounding terrain, nearby buildings, atmospheric stability, noise sources, and insect and bird activity. Therefore, when compiling a set of specifications for the purchase of a remote sensing device, it is important to determine site specific information that will aid the manufacturer in configuring the device to fit the user's needs. The following sections describe basic quality assurance required for the meteorological remote monitoring component of PAMS.

ACCEPTANCE TESTING

Acceptance testing is designed to determine if a newly installed device is performing according to the manufacturer's specifications. The acceptance test is crucial for a profiler since data produced by such an instrument can not be easily verified by simple tests. The following acceptance test is valid for the SODAR,

¹On Assignment to the Atmospheric Research and Exposure Assessment Laboratory, U. S. Environmental Protection Agency.

radar and RASS.

A valid acceptance test consists of an intercomparison between the system to be tested and either a tall tower, tethersonde, or a mini-sodar. Although these sensors do not qualify as transfer standards, they do possess the required sensitivity to determine if the remote sensing device is operating normally (within some broad limits). The test consists of the comparison of data at a minimum of two heights and must compare all output generated by the remote sensing device (e.g., wind speed, wind direction, virtual air temperature). Figure 1 is a work sheet that may be used for performing an acceptance test on a SODAR using a tethersonde as the standard. The work sheet may be easily modified for use with other types of systems.

Determination of atmospheric stability at the measurement heights is the first step for an acceptance test of a profiling system. Stability is an important factor for an acceptance test because turbulence is required to be present in order to provide a mechanism to reflect the output signal back to the receiver. Pasquill-Gifford stability categories of B or C are probably the most desirable turbulent conditions for performing this test. These two classes typically provide a reasonable amount of turbulence to reflect output signals back to the surface. In addition, the turbulence is such that it will not significantly "bounce" the tetherballoon, thereby avoiding unnecessary accelerations (which can introduce measurement errors) on the instrumentation attached to the tetherline. Ideally, wind speeds should be between 2 and 5 m s⁻¹. Wind speeds of less than 2 m s⁻¹ may be too variable for a reliable comparison, while wind speeds greater than 5 m s⁻¹ will cause problems for the tethersonde as it is dragged out in more of a horizontal fashion rather than in a vertical profile.

The tetherballoon should be situated downwind and far enough away from the SODAR so that it will not interfere (i.e., reflect) with the acoustic signal. A facsimile chart should be printed during the test to determine if the tethersonde is interfering with the SODAR. If the tethersonde is interfering, it will show up on the facsimile chart as a solid line. The tetherballoon should be launched to the first sampling height and data should be collected for at least 15 to 20 minutes. The time series information obtained from the tethersonde should match the same time period over which the SODAR is averaging its data. Average wind speeds and directions from both systems, along with their corresponding sample height, should then be entered into the work sheet. This procedure should be repeated to obtain similar information for at least one other height. Additional levels may be necessary if the data from the two systems do not fall within the desired limits.

The next step is to subtract the time averaged wind speed obtained from the tethersonde from that obtained from the SODAR and record this information under the column titled "Bias Wind Speed." Repeat this procedure for the wind direction information. Determine the average bias for each section. If the absolute value of the average bias is less than the reported accuracy of the SODAR system, then the profiler passes the acceptance test. If the test fails, it may be due to unsuitable atmospheric conditions at the measurement heights. The test should then be repeated during conditions more favorable for SODAR operation, i.e., mid-to-late morning with clear skies and 10 m wind speeds between 2 and 5 m s⁻¹.

CALIBRATION AND PERFORMANCE AUDITS

Calibration of ground-based remote meteorological sensing devices has been difficult to accomplish since the development of such instrumentation. Direct comparisons with rawinsondes, tetherballoons, or instrumented towers are not always adequate because of the difficulty in comparing point estimates with large volume estimates, as well as the problem of separation distance between the two platforms. The difficulty of performing calibrations on profiling systems has hindered their acceptance by the regulatory community. Recent advances in QA/QC of SODARs have led to the development of a transponder (responder) unit which simulates returned echoes to a SODAR. This device allows the user to calibrate the instrument, much like using a constant speed motor to calibrate a cup anemometer. A similar device has been developed for radars. This device is capable of analyzing the frequency and power output of the transducers.

OPERATION, MAINTENANCE AND QC

SODARs, radars and RASS have automated operating systems that require very little input from the user. Variables such as height ranges, averaging times, and frequency and power output may be adjusted as needed, but most of the system operations are performed automatically. The wind data should be stored in its vector components (u, v, w). This provides the user with useful information, especially in instances where the wind direction may be in question. Daily or weekly operations should include checking the computer hard drive to insure there is enough room to store data. This will avoid the potential for data loss due to insufficient disk space.

For the first few weeks after installation, the data should be checked on a daily basis to determine if the system is working properly. Time series plots of all variables should be produced and analyzed by a meteorologist to determine if there are any problems. This step is important for detecting any bias or anomalies in the data set. It is usually at this point that false echoes are detected. All inspections and maintenance procedures should be entered into a site log book for documentation.

Maintenance should include weekly checks on the antenna array, cables, and all other connections. The antenna and antenna shelter should be checked and cleared of any debris. All cables should be systematically checked for any breaks due to weathering, animal bites or cuts due to human activities. If damage is detected, the cable should be immediately replaced. All other connections should be checked to insure proper operation. If diagnostic routines are not automatically initiated, then they should be performed manually on a weekly basis.

Unlike in-situ instruments, data quality from SODARs, radars and RASS is strongly dependent on atmospheric conditions. Data from a remote sensing device should be plotted and analyzed on a weekly basis to determine system performance. Analysis of percent data capture versus height will help determine what meteorological conditions create missing values. This information is useful to aid in the evaluation of the system. For instance, data at certain heights are not recorded during particular meteorological conditions but are fine at others. This information can then be used as an aid in determining system performance when the system appears to be malfunctioning.

Systematic routines used to inspect these data provide a level of quality control (QC). These QC checks should be performed by a meteorologist who is familiar with the physical nature of profiler data sets. Such a person will more than likely spot and correct any problems. Without a qualified inspector, the potential exists for data to be corrupted and to go unnoticed.

When a problem is found by the QC inspector, a discrepancy report should be issued which brings the users into the data QC loop. Their inspection and corrective action is reported back to the QC inspector closing the loop. Because of this QC loop, the measurement system can be operated "in control" and valid data produced.

DISCLAIMER

This document has been reviewed in accordance with U. S. Environmental Protection Agency policy and approval for publication. Mention of trade names or commercial products does not constitute EPA endorsement or recommendation for use.

Instrument Type _____ Date: _____

Instrument Serial No. _____ Time: _____

Acceptance Test Report By _____

Specified Accuracy: Wind Speed _____ (m/s); Wind Direction _____ (Deg)

Tethersonde Serial No. _____

Atmospheric Stability During Test (A, B, C, D, E, F, G)

Number of Minutes in Average _____

Height (m)	Average Sodar Wind Speed(m/s)	Average Tethersonde Wind Speed (m/s)	Bias Wind Speed (m/s)
---------------	----------------------------------	---	--------------------------

_____	_____	- _____	= _____
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_____	_____	- _____	= _____
-------	-------	---------	---------

_____	_____	- _____	= _____
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Average Bias _____

If Absolute Value of Average Bias is $\leq 0.5 \text{ m s}^{-1}$ then System Passes Test _____
(Initial)

If Absolute Value of Average Bias is $> 0.5 \text{ m s}^{-1}$ then System Fails Test _____
(Initial)

Height (m)	Average Sodar Wind Dir. (Deg)	Average Tethersonde Wind Dir. (Deg)	Bias Wind Dir. (Deg)
---------------	----------------------------------	--	-------------------------

_____	_____	- _____	= _____
-------	-------	---------	---------

_____	_____	- _____	= _____
-------	-------	---------	---------

_____	_____	- _____	= _____
-------	-------	---------	---------

Average Bias _____

If Absolute Value of Average Bias is $\leq 6^\circ$ then System Passes Test _____
(Initial)

If Absolute Value of Average Bias is $> 6^\circ$ then System Fails Test _____
(Initial)

Figure 1 Work sheet for computing SODAR Bias

Collecting and Interpreting Upper Air Meteorological Data for the PAMS Network Using Radar Profilers and RASS

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Remote sensors like radar wind profilers equipped with Radio Acoustic Sounding Systems (RASS) are likely candidates for collecting the upper air meteorological data required for the PAMS network. Upper air winds and temperatures collected for PAMS will be used to analyze and model meteorological processes that accompany periods of high ozone concentrations; to initialize and evaluate the performance of air quality models; and to support analyses of emission control strategies. Profilers offer several advantages for collecting continuously and unmanned, providing improved temporal resolution at lower cost; data are available in near-real time, simplifying quality control (QC) activities; and profilers measure vertical velocity (w), which is an important parameter for diagnosing and accurately modeling many meteorological processes.

Wind profilers measure wind speed, wind direction, and vertical velocity from approximately 100 m agl to altitudes as high as 3-5 km with a vertical resolutions of 60-100 m; RASS measures temperature to altitudes of 1-2 km with the same vertical resolution. Profilers also produce lower-level information that is proving extremely useful for identifying and analyzing key atmospheric processes and features that accompany periods of poor air quality, such as mixing depth and turbulence information. Using a number of examples of the types of data provided by profilers, we describe uses of profiler data in recent air quality studies and discuss issues related to data management, quality control, and data interpretation.

DATA ASSESSMENT AND INTERPRETATION

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Photochemical Assessment Monitoring: Program Objectives And Data Uses

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ABSTRACT

In order to design the Photochemical Assessment Monitoring Stations (PAMS) program requirements, EPA considered a wealth of program objectives; additionally, the Agency recognized the vast potential for a myriad of uses for the data. The Agency anticipates that the measurements will be valuable for verifying emission inventories and corroborating area wide emissions reductions. The data is expected to be used to evaluate, adjust, and provide input to the photochemical grid models utilized by the States to develop and demonstrate the success of their control strategies. The PAMS will provide constructive information for the evaluation of population exposure and the development of ambient ozone and ozone precursor trends.

This paper will examine the development of the PAMS program objectives and the potential role of the extensive PAMS data base for resolving ozone nonattainment.

INTRODUCTION

In accordance with the Clean Air Act Amendments of 1990, the Environmental Protection Agency (EPA) developed rules for the establishment of enhanced ozone monitoring networks, termed Photochemical Assessment Monitoring Stations (PAMS), in ozone nonattainment areas designated as serious, severe, and extreme. These rules were promulgated on March 4, 1992, amending the air quality surveillance regulations (40 CFR Part 58). The resultant monitoring networks will provide for the monitoring of a target list of volatile organic compounds (VOC) including several carbonyls, and oxides of nitrogen (NO , NO_2 , and NO_x), ozone, and both surface and upper air meteorological measurements.

These PAMS data will improve the ability of the State and Local air pollution control agencies to identify and respond to ozone nonattainment situations by developing and implementing cost-effective ozone control strategies. Further, the Agency believes that the measurements will be beneficial in verifying precursor emission inventories and corroborating area-wide emissions reductions. The data will be used to evaluate, adjust, and provide input to the photochemical grid models utilized by the States to develop and demonstrate the success of their control strategies. The PAMS will provide constructive information for the evaluation of population exposure and the development of ambient ozone and ozone precursor trends.

PROGRAM OBJECTIVES AND DATA USES

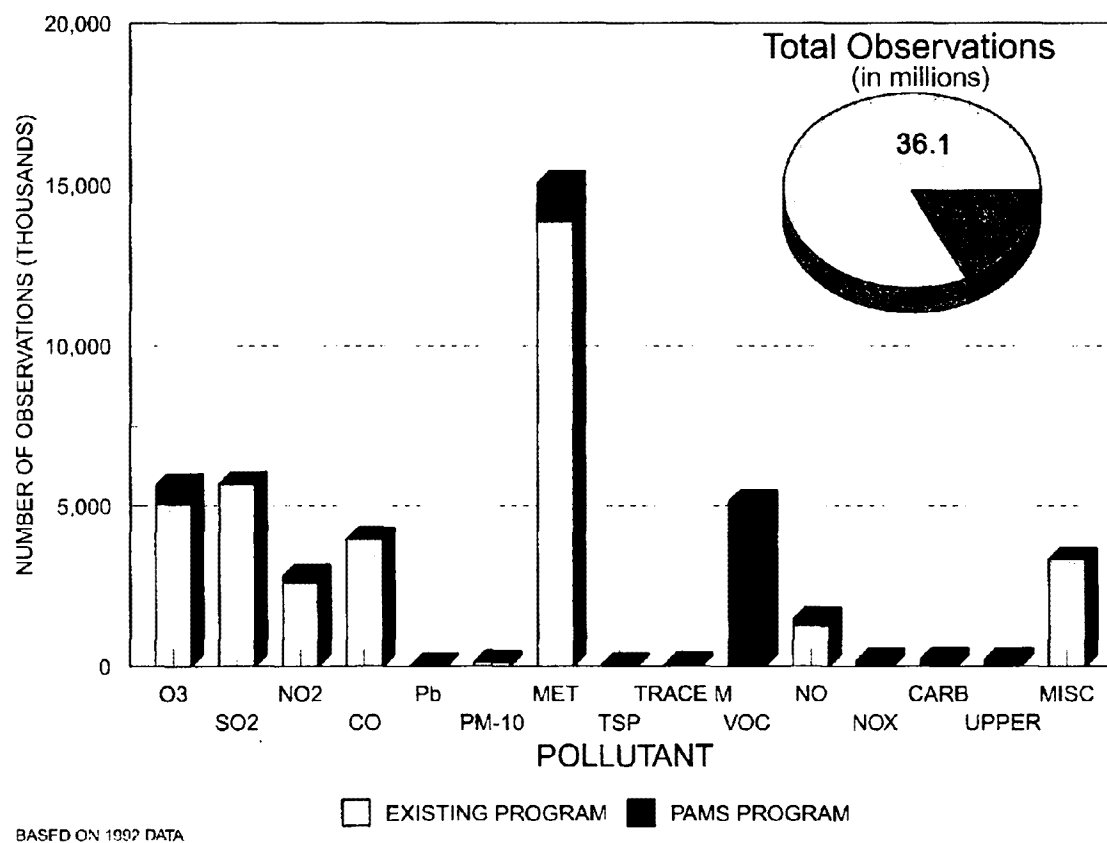
In the early days of the design phase for PAMS, EPA recognized that the program should attempt to realize a number of ambitious goals or objectives; those objectives formed the cornerstone for the development of the PAMS rules. Key to the development of the specific requirements was the acknowledgment by the Agency that it would be unlikely that all objectives could be satisfied to the same degree, i.e., the important objectives would take precedence over the less important ones. With that premise in mind, EPA promoted the development of minimal PAMS networks with the exhortation to the State and local agencies to provide a more comprehensive monitoring system as time and resources allowed. A brief discussion of each of those primary PAMS objectives and companion data uses follows in the order of their importance:

- The first objective of the PAMS program was to provide an ambient air data base which could supply representative ambient VOC profiles and concentrations for certain targeted VOC species. Measuring these parameters would allow State and local air pollution control agencies to conduct evaluations of current State Implementation Plan (SIP) ozone control strategies and initiate future mid course corrections. With a local ozone and ozone precursor data base in hand, the agencies could refocus their control and enforcement strategies to provide a more expeditious path to attainment of the National Ambient Air Quality Standard (NAAQS) for ozone. This focus will additionally provide a forum for comparing the cost-effectiveness of alternate control strategies and precursor emissions reduction techniques.
- Secondly, the PAMS requirements were fashioned to yield data which could serve as initial and boundary condition information for photochemical grid models. By providing local, current meteorological and ambient air quality measurements, modelers can refine available estimates of initial and boundary conditions, evaluate the predictive capability of the models, and, at the same time, minimize the any adjustment of model inputs. These data will, in effect, reduce the uncertainties associated with estimating computer model inputs and increase the probability that the model is adapting to local photochemical phenomena.

- As a third objective, PAMS provides speciated ambient ozone precursor measurements which can be utilized to compare to the emissions from sources in an affected area. Local emissions inventories constitute integral components of the SIP development process and additionally serve as the primary inputs to the photochemical models. PAMS, for the first time, will provide States with the limited ability to independently verify those inventories and optimize their accuracy. Given that the tracking of trends in reported inventories is a critical measure of the effectiveness of any emissions reduction strategy, an independent comparison is vital to ensure the meeting of reduction and attainment goals. Specialized computer modeling techniques can often be used to identify particularly large sources of precursors which significantly impact the ozone nonattainment problem.
- As a fourth objective, these networks are intended to supply ambient data which could be used to prepare pollutant trends assessments. Over time, PAMS data can be used to develop ambient trends for targeted VOC, several nitrogen species, and conceivably for some toxic air pollutants. As more PAMS are established in each affected area, the trends analyses will obviously become more meaningful. Utilizing information from similar PAMS sites and the newly gathered meteorological data will increase the utility of the various trends analyses.
- Additionally, the Rule requires measurements of selected criteria pollutants including ozone and several commonly-measured oxides of nitrogen at PAMS stations; these data can therefore be utilized for observing ozone exceedances and providing the basis for attainment/nonattainment decisions. If the NO₂ data are gathered with the Federal Reference Method (FRM) and are taken on a year-round basis, they can be utilized to augment monitoring for compliance with the NO₂ NAAQS. By expanding the spatial coverage of NAAQS-related monitoring, PAMS will allow States to better appraise their jurisdiction's compliance with the NAAQSs and develop/track maintenance plans.
- Finally, PAMS stations can provide additional measurements of selected criteria and non-criteria pollutants to better characterize ozone and toxic air pollutant exposure to the inhabitants of serious, severe, or extreme areas. By employing the year-round measurements for VOC at #2 Sites, analysts can calculate average annual exposure rates for those measured VOC which are considered toxic. Although compliance with Title I, Section 182 of the Clean Air Act Amendments does not require the measurement and analysis of additional toxic air pollutants, the Agency believes that the PAMS stations can serve as cost-effective platforms for a future enhanced air toxics monitoring program and allow the consideration of air toxics impacts in the development of future ozone control strategies.

With the full implementation of the PAMS program, reported data observations reported to the Aerometric Information Retrieval System (AIRS) are expected to grow approximately 22% from approximately 36.1 million to 44 million observations by the end of the 1998 monitoring season. Figure 1. shows the most significant growth in number of measurements occurring for volatile organic compounds (VOC including carbonyls) and for surface/upper air meteorology. Processing and analyzing these data will be a notable challenge to EPA and the State/Local air pollution control agencies.

Figure 1. Increases in Ambient Monitoring Observations Due to PAMS



CONCLUSIONS

Currently, data from the 1993 monitoring season are being processed into AIRS. With the inclusion of appropriate quality assurance techniques, these measurements should provide the foundation for a continuing program which supports the six primary PAMS objectives. As a result, scientists from varied disciplines such as SIP development, photochemical modeling, emissions inventories, data analysis and air toxics evaluations can utilize a common data base to integrate their planning and research.

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Receptor Modeling of VOC Data

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Receptor modeling refers to a set of procedures for identifying and quantifying the sources of ambient air pollution impacting a monitoring site (receptor) primarily on the basis of chemical species concentration measurements at the receptor. In its purest form receptor modeling requires neither emissions inventory information nor meteorological data for its implementation. The very large quantities of volatile organic compound (VOC) ambient data that are beginning to be generated in the Photochemical Assessment Monitoring Stations (PAMS) network offer an unusual opportunity for receptor modeling applications. We will discuss primarily the Chemical Mass Balance (CMB) method of receptor modeling, illustrating it with recent results from analysis of the EPA 1990 Atlanta Ozone Precursor Study. The design of that study has many similarities (species measured, number of stations, etc.) to what is being implemented in PAMS, and thus provides a first assessment of the receptor modeling possibilities with PAMS data.

Motor Vehicle Volatile Hydrocarbon Source Profiles for Chemical Mass Balance Receptor Modeling

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ABSTRACT

The Chemical Mass Balance (CMB) receptor model can be used to estimate source contributions of volatile hydrocarbons. The model requires chemical profiles of sources as well as ambient data as input. Researchers often rely on "off-the-shelf" profiles which are not necessarily representative of the airshed they are studying. A method for obtaining hydrocarbon profiles of motor vehicle and related emissions for the airshed of interest is described. This work was conducted as part of the 1990 "Atlanta Ozone Precursor Monitoring Study". Motor vehicle emissions were sampled in canisters beside a roadway in a tunnel-like underpass during the morning rush-hour. Three octane grades of gasoline were purchased from 6 major vendors in Atlanta. Canister samples were prepared using these fuels to approximate the whole gasoline and gasoline vapor composition of the fuels in use during the study. All samples were analyzed by GC/FID for their hydrocarbon content. Profiles were developed from these samples to represent the hydrocarbon composition of emissions from a roadway, composite headspace gasoline and composite whole gasoline. The roadway profile is compared with similar profiles in the literature and recommendations are made regarding its use in the CMB model. The roadway and fuel profiles are discussed in the context of the MOBILE5 model outputs. The measured headspace gasoline vapor profile is compared with a headspace gasoline vapor profile calculated from the measured whole gasoline profile by means of Raoult's Law.

INTRODUCTION

During the summer of 1990, the U.S. Environmental Protection Agency (EPA) conducted a 2-month, 6-site air quality monitoring study in the Atlanta metropolitan area, known as the "Atlanta Ozone Precursor Monitoring Study".^{1,2} The study produced a large body of hydrocarbon data similar to that measured in the PAMS network. Transportation-related sources contribute a significant portion of the volatile hydrocarbon emissions. Many of these compounds serve as precursors to the formation of ozone in the troposphere, and some are toxic or even carcinogenic.

Chemical Mass Balance (CMB) analysis is a procedure which is used to estimate source contribution estimates by expressing the ambient concentration of selected species as a linear combination of contributions from different sources (or source categories).³ The species contribution from each source is expressed as the total mass coming from the source times the fraction of the species in the total mass emissions of that source. The fraction of each species of the total is also known as the species "abundance" in the source emissions, and the set of species abundances for a source is known as the "source profile" or "source fingerprint". Source profiles can be calculated from the ambient data⁴ by an appropriately skilled individual, but are most often measured in the field or in the laboratory. Ideally, profiles to be used in CMB calculations are measured in the same airshed and during the same time period as the ambient measurements to which they will be applied, as opposed to selecting "off-the-shelf" profiles.

A method for obtaining hydrocarbon profiles of motor vehicle and related emissions for the airshed of interest is described. The profiles reported were measured during the 1990 Atlanta Ozone Precursor Monitoring Study and can be used in the Chemical Mass Balance (CMB) model to estimate the relative contribution of these sources to the total ambient hydrocarbon concentration.

The CMB model source estimates can be used to reconcile ambient data with emissions inventories and to estimate the relative importance of the hydrocarbon source to ozone formation.

EXPERIMENTAL

Sample Collection and Preparation

Roadway samples were pumped into evacuated (initial pressure < 0.1 torr) SUMMA®-polished stainless steel canisters using a 12-volt battery-operated pump (Model 158, Metal Bellows Corporation, Sharonville, MA) and a throttle valve to maintain a sample flowrate of approximately 1.2 L min⁻¹. Sampling continued for 12-15 min to achieve a final pressure of approximately 25 psig. Samples were collected on the shoulder of the I-75/I-85 roadway northbound below the I-20 overpass. This location was chosen for its high traffic volume and for the extended, almost tunnel-like overpass covering the roadway. Samples were collected on 3 separate occasions between 8/23/90 and 8/27/90 (on weekdays only) during the 7 am to 8 am hour when traffic density reached a maximum. On each of 3 sampling days, 3 samples were collected - 2 concurrently followed by one additional sample - for a total of 9 roadway samples. Light-duty gasoline vehicles dominated the approximately 1000 or more vehicles passing by the samplers during each sampling interval. Vehicles traveled at steady-state speeds ranging between approximately 30 to 60 mph. Profiles measured at the side of a roadway, while representative of a large number and population of vehicles, cannot represent the entire vehicle population under all driving conditions. This will be discussed further in a later section.

Samples of 3 octane grades of gasoline were purchased from 6 major commercial vendors (Texaco, Gulf, Exxon, Amoco, Shell, and Chevron) in the Atlanta area on August 28, 1990 to approximate the fuel mix that existed during the study. The samples were stored in tightly sealed one-gallon steel containers and returned to the Atmospheric Research and Exposure Assessment Laboratory in Research Triangle Park, North Carolina for analysis. All samples were prepared in canisters and analyzed within 1 month of collection. Time elapsed between sample preparation and analysis never exceeded 2 weeks. Prepared canister samples were analyzed for both total and headspace composition to approximate the range of possible gasoline evaporation mechanisms.

To prepare samples for headspace analysis, the one gallon cans of gasoline were immersed in an ice bath at approximately 4°C. The cooled gasoline was transferred to graduated 125 mL Erlenmeyer flasks to the 100 mL mark and closed with a neoprene rubber stopper penetrated with a 50 cm x 0.25 cm pyrex glass tube. The glass tube extended through the rubber stopper to about 35-40 mm above the liquid layer and was closed at the end extending from the flask with a septum assembly. The stoppered flasks containing gasoline were immersed in constant temperature baths maintained at 24 ± 1°C and 32 ± 2°C. These temperatures were selected to approximate the range of ambient temperatures in Atlanta during August. The highest test temperature was limited to 32°C because of pressure build-up in the apparatus at higher temperatures. After a 15 min equilibrium period, 500 µL headspace samples were taken and injected into evacuated (< 0.1 torr) 6 L SUMMA®-polished canisters. The canisters were filled with humidified zero-hydrocarbon air to about 30 psig. The relative humidity in the prepared canister samples was approximately 50%.

Whole gasoline samples were prepared by injecting 0.01 µL liquid gasoline at 23 ± 1°C directly into evacuated (< 0.1 torr) canisters. Canisters were then pressurized with humidified zero hydrocarbon air to about 30 psig.

Sample Analysis

The C₂ - C₁₂ non-methane hydrocarbons were measured with two gas chromatographic columns. Most compounds were separated on a 60 m x 0.32 mm ID DB-1 fused silica column with a 1 µm liquid phase film thickness (J&W Scientific, Folsom, CA). The column temperature conditions consisted of a -50°C initial temperature held for 2 min followed by an 8°C per min temperature program rate to a final temperature of 200°C held for 11.75 min. This procedure reliably separates all but the C₂ hydrocarbons, which were analyzed on a 30 m x 0.53 mm ID GSQ

gas-solid fused silica column (J&W Scientific) to improve separation. Column temperature conditions for separating the C_2 hydrocarbons consisted of a 40°C initial temperature held for 4 min followed by a 10°C per min temperature program rate to a final temperature of 200°C held for 5 min. Both GC systems used similar preconcentration approaches which conditioned approximately 500 mL samples for analysis. Details of the preconcentration system and analytical procedure can be found in Reference 5.

RESULTS

Source profiles are reported in Table 1 as a percent of total NMOC (TNMOC) on a ppbC basis. TNMOC is defined here as the integrated FID response of all GC peaks eluting from the column. In these samples the last GC peak eluted at 39.597 minutes, which corresponds to a Retention Index of 1488. Thirty-two compounds are reported reported here. A more detailed speciation is presented in Reference 6.

For each of 3 sets of roadway samples (i.e., 3 sampling days), 2 of the samples were collected concurrently followed by one additional sample. To determine if there is a statistically significant difference in median values among the 3 profiles of each sample set, a Friedman repeated measures analysis of variance was applied to each set of 3 profiles. In each case, there is a difference among the 3 profiles greater than would be expected by chance ($p < 0.03$). To determine which profiles are different, a Student-Newman-Keuls multiple comparison test was subsequently applied to each set of profiles. The results indicated that for each sample set there is a significant difference ($p < 0.05$) between profiles not collected concurrently, but no significant difference between the 2 concurrently obtained profiles. Based on this statistical evaluation, it was determined that each set of concurrent samples would be averaged together and the result treated as an individual sample, for a total of 6 rather than 9 individual roadway profiles. These 6 profiles were averaged to produce the roadway profile presented on Table 1. No suitable background samples were collected concurrent with the roadway samples, so no background corrections were applied. An average TNMOC of 1950 ppbC was measured at the roadway sampling site on 08/24/90. This is considerably higher than the TNMOC concentrations of 610 ppbC and 690 ppbC measured at 2 urban monitoring sites (part of the 6-site network) on 08/24/90 at approximately the same time period as the roadway sampling. Furthermore, it is expected that automotive emissions contribute the largest fraction of TNMOC at these monitoring sites. It follows that the non-mobile source background in the roadway samples is probably fairly small for most NMOC's. Two obvious exceptions are propane and ethane, which have fugitive natural gas and propane fuel as their principal sources.

The whole gasoline and gasoline headspace vapor profiles were calculated from a combination of weighted and unweighted averages. Profiles were first calculated for each octane by averaging the results from each of the 6 vendors, giving equal weight to each vendor. Next, the vendor averages for each octane were averaged together, weighted according to 1989 national sales figures for the 3 standard fuel grades.⁷ Local gasoline sales data were unavailable. According to the national figures, 87-octane fuels accounted for 58% of sales, 89-octane fuels accounted for 5% of sales, and 92/93-octane (premium grade) fuels accounted for 24% of sales. (Some vendors sell 92-octane fuel while others sell 93-octane fuel. For simplicity, these are considered together.) Leaded gasoline accounts for the remaining 13% of the sales. As there was no leaded gasoline for sale in Atlanta during the study, weighted averages were calculated from the national sales figures renormalized to exclude leaded fuel. The weighted standard deviations are also reported.

DISCUSSION

General

Profiles presented in Table 1 are based on TNMOC defined as the total integrated FID response obtained from the GC analysis. For CMB receptor modeling applications, we recommend a more narrow definition of "total" NMOC tailored to the particular application. For instance, a

TNMOC consistent with emissions inventories would be appropriate for emissions inventory validation work. Some have suggested that "total" be defined as the sum of selected alkanes, alkenes, and aromatics.^{8,9} This method avoids inclusion of unapportionable compounds, such as reaction products or biogenic species and species below quantifiable levels. Users of the profiles presented here can renormalize the profiles to whatever definition of "total" they choose.

The roadway profile is distinguished by > 1% abundances of the lightest hydrocarbons, especially ethene and acetylene, which are characteristic products of combustion. Beyond n-butane, however, species abundances in the roadway profile are similar to abundances in the whole gasoline profile. This observation is consistent with the results of recent studies attributing about 50% of tailpipe hydrocarbon emissions to unburned fuel rather than combustion products.^{10,11} Comparison of the roadway and whole gasoline profiles by compound class reveals that they have equivalent alkane contributions of 40% each and comparable aromatic contributions of 25% and 35% for roadway and whole gas, respectively. This roadway-to-fuel ratio for aromatics is consistent with the tailpipe-to-fuel ratio for aromatics of 0.68 ± 0.07 found in a study of 1989 model year vehicles.¹¹ Alkenes plus acetylene constitute 19% of the roadway profile compared with only 7% of the whole gas profile, reflecting the importance of those combustion products in the roadway profiles. The roadway profile is higher in benzene but lower in hydrocarbon-substituted benzenes compared with whole gasoline, most likely due to de-alkylation which occurs during combustion. Evidence of this process was demonstrated by Kaiser et al.¹² by burning pure toluene in a spark-ignited engine and finding benzene to represent 6% of the combustion product.

Headspace profiles, which reflect the composition of the gasoline vapor above the liquid, are heavily weighted toward the lighter (lower boiling point) alkanes, especially i-pentane, n-butane, n-pentane, and i-butane. The partial pressures of compounds diminish as molecular weights increase beyond the C₆ compounds (boiling points higher than 32°C test temperatures); thus, components beyond C₆ constitute lesser fractions of the headspace vapor compared with the whole gasoline. Alkanes constitute the bulk of the headspace profiles (77% on average) followed by alkenes (16%) and aromatics (3.5%).

Comparisons with Other U.S. Studies

There are a number of U.S. studies which report the composition of tailpipe emissions from light-duty gasoline automobiles. These include both roadway^{13,15} and dynamometer^{16,17,20} tests, each of which has advantages and disadvantages. Emissions from a large number of vehicles using a variety of fuels can be sampled during a roadside test, but driving conditions are typically limited to warmed-up vehicles operating at steady-state speeds. Conversely, dynamometer tests sample an array of driving conditions or "cycles", including cold start, but the number of vehicles and types of fuels that can be tested is quite limited. Furthermore, conditions such as high-speed driving and high acceleration and deceleration rates may not be adequately represented in either test situation.

Eight of the more abundant compounds commonly reported in automobile exhaust profiles are presented in Figure 1 as ratios to acetylene. Ratios are reported for the roadway profile presented in this work, plus two additional roadway studies^{13,14} and one laboratory dynamometer study¹³. The results of that dynamometer study, known as the 46-car study, are frequently cited and used to represent automobile exhaust in CMB analyses.^{21,24} The work of Doskey et al.¹⁵ is not included because of reported analytical problems. Ratios rather than absolute abundances are shown to avoid inconsistencies in the TNMOC definitions from each of the studies.

The error bars in Figure 2 represent the car-to-car or sample-to-sample variability for each ratio. The species abundance ratios calculated from the 46-car dynamometer study results are much more variable than those calculated from the results of the 3 roadway studies. The roadway studies effectively sample exhaust from hundreds or even thousands of cars, thereby averaging out the rather large car-to-car variability indicated by the large error bars on the 46-car results. Furthermore, the 46-car study used just 2 fuel types in their test program, while roadway studies represent an average of all grades and brands of in-use fuels.

These intercomparisons serve to illustrate the choices and compromises that must be made in selecting a profile to represent vehicle emissions in a CMB calculation. In order to get profiles with smaller variability, roadway profiles such as those presented here are the better choice because vehicle and fuel variability are integrated over a large number of vehicles. However, in choosing roadway profiles, there is the risk of underrepresenting cold-start, idle, and high acceleration or deceleration modes. Dynamometer profiles may also underrepresent high acceleration/deceleration.

Source Profiles and the MOBILE5 Model Outputs

Source profiles are being used in CMB analyses with ambient NMOC concentrations to reconcile ambient measurements with NMOC emissions inventories.^{8,21-24} Estimates of NMOC emissions from gasoline-powered vehicles used in emissions inventory development are obtained by using the Mobile Source Emission Factor Model, MOBILE5²⁵. Model outputs include emission factors for exhaust and for hot soak, diurnal, refueling and running loss evaporative emissions. The MOBILE5 model distinguishes emissions by mechanism, while the CMB model distinguishes emissions by NMOC composition. Thus, individual profiles reported in Table 1 are not uniquely associated with any one emission factor output of MOBILE5, and application of these profiles to CMB source contribution estimates will lead to a composite of the emissions produced by MOBILE5.

The roadway profile represents a composite of tailpipe exhaust and running losses produced by warmed-up engines during steady-state driving conditions. The whole gasoline profile is chemically similar to hot soak emissions and gasoline spillage or leakage. The headspace vapor profile represents the composite of diurnal evaporative emissions and vapor displacement that occurs as a result of vehicle refueling. Vapor displacement and spillage/leakage events associated with refilling underground storage tanks and similar activities should produce emissions chemically similar to the whole gasoline and headspace vapor profiles, but since they are not directly vehicle related, they are not included in MOBILE5 emission factor estimates.

The MOBILE5 model includes options for a variety of composition totals (not speciation) for exhaust hydrocarbons to accommodate various end-uses of the model output. For producing baseline emissions inventories, volatile organic compounds (VOC's) should be used to represent hydrocarbons. The U.S. EPA has defined VOC as any organic compound that participates in atmospheric photochemical reactions and produces ozone faster than ethane. Among those compounds considered non-reactive, and therefore excluded from the VOC definition, are methane and ethane, compounds which do appear in motor vehicle exhaust emissions. Ethane is included in the roadway profile presented in Table 1. In addition, the VOC option includes formaldehyde and acetaldehyde, compounds which are not measured or only partially measured by flame ionization detection and which are not represented in the roadway profile.

COMPARISON OF CALCULATED GASOLINE HEADSPACE PROFILES WITH MEASURED COMPOSITIONS

Headspace compositions are reported for a composite of the 3 octane grades of 6 major brands of gasoline at temperatures of $24 \pm 1^\circ\text{C}$ and $32 \pm 2^\circ\text{C}$. For application of profiles to modeling of mobile source activities, it is desirable to know headspace compositions at even more temperatures. One study²⁶ indicates temperatures much higher than ambient may be important for headspace vapor emissions, suggesting that fuel tank temperatures may rise as much as 25°C above ambient, depending on driving time/trip length. It is impractical, however, to measure headspace profiles at more than a small number of discrete temperatures, especially when gasoline samples of several vendors at several octanes are being considered. Furthermore, the maximum headspace temperature produced for this work was limited by pressure build-up in the apparatus.

Nelson et al.²⁷ calculated gasoline vapor compositions from their average gasoline composition by means of Raoult's Law. They report that this procedure accurately reflects the equilibrium vapor composition obtained by measurements of the vapor over individual gasoline

samples. Since both liquid and headspace compositions were determined for the Atlanta gasolines, headspace compositions were calculated and compared with observed compositions. Results for the 24°C are presented here. Similar results were obtained with the 32°C data:

Raoult's Law states that the mole fraction of component i (X_i) in an ideal solution is equal to the ratio of the partial pressure of i above the solution (P_i^{part}) to the vapor pressure of pure component i (P_i^{pure}), provided the vapor behaves as an ideal gas:

$$P_i^{\text{part}} \div P_i^{\text{pure}} = X_i.$$

If the mole fraction of each component i in gasoline is known, and the vapor pressure of the pure component is known or can be calculated for the temperature of interest, the above equation can be solved for the partial pressure of each component i above the gasoline. The partial pressures are proportional to the composition of the vapor above the gasoline.

Raoult's Law was applied to the Atlanta average gasoline composition discussed earlier. The vapor pressures of pure components were calculated for 24°C using the Antoine equation,²³ which relates vapor pressure (P , in Torr) and temperature (t , in degrees C) as follows:

$$\log P = A - B \div (t + C),$$

where A , B , and C are constants characteristic of each species. While other procedures are available for calculating vapor pressure, Antoine equation constants are available for the widest range of compounds found in gasoline.

Vapor pressures of 33 species could be reliably calculated by this method. The other hydrocarbon components of the Atlanta gasoline were out of the range of temperatures over which the Antoine equation is valid (i.e., their boiling points are too high or too low) or Antoine constants were unavailable. Headspace vapor composition calculated from Raoult's Law for 24°C is compared with the measured 24°C headspace vapor composition in Figure 2 for the 33 species. Profile abundances have been normalized to the sum of the 33 species. This normalization makes it possible to calculate headspace vapor abundances for the species partial pressures calculated using Raoult's Law as described above. Agreement between calculated and measured headspace composition is excellent. Equations for the regression lines shown in Figure 2 are as follows: $(0.038 \pm 0.059) + (0.987 \pm 0.007) \times \text{MEAS} = \text{CALC}$, $R^2 = 0.999$ for all data points, and $(-0.043 \pm 0.062) + (1.032 \pm 0.033) \times \text{MEAS} = \text{CALC}$, $R^2 = 0.971$ for data excluding the 2 highest data points (inset graph). The difference between the calculated and measured values for each species, as well as the difference between the calculated and regression-derived values, is 1 ppb% or less for this example.

If the gasoline vapor composition can be reliably constructed entirely from a measured gasoline composition and Raoult's Law calculations, the need for doing separate chemical analyses of the gasoline vapor could be eliminated. In theory, vapor composition could be calculated at any ambient temperature, within the vapor pressure calculation restrictions. This would represent a considerable savings in both samples required and analyses performed. Another use for model-derived vapor profiles is found in the application of the SAFER model,²⁹ which extracts source profiles from ambient data. The cornerstone of this model is the application of physical constraints to the data to prevent unrealistic profiles from being produced. Application of Raoult's Law to measured or model-derived whole gasoline composition can be used to produce physical constraints for headspace vapor composition for use in the SAFER model.

CONCLUSIONS

An emissions profile of motor vehicles in operation was produced from samples collected alongside a roadway in a tunnel-like underpass. This roadway profile is distinguished by >1% abundances of the lightest hydrocarbons, especially ethene and acetylene, which are characteristic

products of combustion. Beyond n-butane, however, species abundances in the roadway profile are similar to abundances in the whole gasoline profile, supporting previous observations which estimate a substantial portion of tailpipe hydrocarbon emissions to be unburned fuel rather than combustion products.

Roadway sampling captures both the exhaust (tailpipe) and evaporative (running loss) emissions of motor vehicles. Emission rates of the exhaust and evaporative emissions processes are both sensitive to operating conditions (e.g., temperature, vehicle speed), but in different ways. Hence, certain operating conditions will influence the mix of exhaust and evaporative emissions and thus the overall roadway profile. Furthermore, the exhaust profile is influenced by air/fuel ratio, acceleration mode and condition of the catalyst, especially for important combustion marker compounds such as acetylene and olefinic hydrocarbons.

The roadway samples collected in this study, while representative of a large number and population of vehicles, do not represent the entire vehicle population under all driving conditions, so profiles presented here should be applied with this fact in mind. Future efforts to obtain vehicle exhaust source profiles should strive to incorporate samples which represent a variety of locations and driving conditions, to the extent possible. The authors recognize that this approach is not always practical when one considers the need to minimize the mixing of background air with roadway emissions. Given that about half of the hydrocarbon species in vehicle exhaust may represent unburned fuel, a change in locale to sample different driving conditions may have little effect on many species in the roadway profile. However, as indicated above, the species most likely to be influential in the apportionment of roadway emissions are affected by changes in operating conditions. The choice of currently available roadway profiles for CMB calculations involves compromising the range of driving conditions represented in dynamometer tests to obtain data for a large and representative set of vehicles and fuels. Neither test may adequately represent high acceleration or deceleration modes.

Calculations were performed using Raoult's Law to compare headspace vapor compositions calculated from gasoline composition with those measured directly. The agreement for the 33 compounds tested was excellent, suggesting that such an approach could be used to generate headspace profiles, provided that the fuel approximates an ideal solution. Alcohol-fuel blends may deviate significantly from ideal solution characteristics. The calculation approach would permit headspace composition determinations for a range of temperatures, but would be limited somewhat by compound volatility and availability of vapor pressure data. Headspace profiles could be calculated for a range of temperatures to assess the sensitivity of the profiles to the rise in fuel tank temperature during vehicle operation.

ACKNOWLEDGEMENTS

The authors thank Vinson Thompson for preparing the canister sampling equipment and participating in the sample collection, and Frank Black, Roy Zweidinger and Larry Cupitt for their insightful comments.

DISCLAIMER

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendations for use.

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Table 1. Source profiles (averages and standard deviations) in ppbC%.

Species name	Roadway	Whole gas weighted avg	Headspace, 24°C weighted avg	Headspace, 32°C weighted avg
Ethylene	4.34 ± 0.47	0.00631 ± 0.00027	0.0066 ± 0.0010	0.0102 ± 0.0052
Acetylene	3.80 ± 0.64	0.00269 ± 0.00078	0.0047 ± 0.0040	0 ± 0
Ethane	1.55 ± 0.19	0.0209 ± 0.0031	0.143 ± 0.039	0.19 ± 0.11
Propene	1.96 ± 0.18	0.0424 ± 0.0052	0.133 ± 0.011	0.114 ± 0.012
Propane	1.05 ± 0.18	0.080 ± 0.016	0.97 ± 0.28	0.85 ± 0.30
i-Butane	1.12 ± 0.25	0.599 ± 0.078	5.13 ± 0.84	4.63 ± 0.41
1-Butene	1.181 ± 0.090	0.128 ± 0.023	0.88 ± 0.46	0.86 ± 0.46
n-Butane	4.11 ± 0.71	3.23 ± 0.34	21.8 ± 4.6	20.0 ± 2.9
i-Pentane	8.64 ± 0.84	7.37 ± 0.52	27.9 ± 1.5	26.89 ± 0.70
n-Pentane	2.66 ± 0.27	2.76 ± 0.74	7.4 ± 2.1	7.2 ± 2.2
2,3-Dimethylbutane	0.863 ± 0.025	0.88 ± 0.14	1.49 ± 0.45	1.55 ± 0.56
2-Methylpentane	2.434 ± 0.099	2.88 ± 0.95	3.53 ± 0.87	3.65 ± 0.74
3-Methylpentane	1.418 ± 0.062	1.79 ± 0.60	1.93 ± 0.46	2.01 ± 0.38
n-Hexane	1.088 ± 0.058	1.50 ± 0.49	1.20 ± 0.32	1.25 ± 0.26
Methylcyclopentane	0.783 ± 0.038	1.10 ± 0.38	0.81 ± 0.24	0.86 ± 0.19
2,4-Dimethylpentane	0.704 ± 0.058	0.754 ± 0.027	0.52 ± 0.16	0.63 ± 0.31
Benzene	2.73 ± 0.19	1.53 ± 0.28	0.856 ± 0.048	0.929 ± 0.056
Cyclohexane	0.166 ± 0.011	0.249 ± 0.075	0.122 ± 0.043	0.122 ± 0.044
2-Methylhexane	0.874 ± 0.053	1.28 ± 0.40	0.46 ± 0.11	0.550 ± 0.058
2,3-Dimethylpentane	0.901 ± 0.060	1.020 ± 0.039	0.46 ± 0.15	0.62 ± 0.36
2,2,4-Trimethylpentane	2.51 ± 0.23	2.82 ± 0.87	0.99 ± 0.60	1.5 ± 1.4
n-Heptane	0.540 ± 0.038	0.85 ± 0.18	0.208 ± 0.041	0.267 ± 0.010
2,3,4-Trimethylpentane	0.95 ± 0.11	1.33 ± 0.34	0.23 ± 0.10	0.40 ± 0.33
Toluene	6.59 ± 0.36	8.11 ± 0.80	1.26 ± 0.24	1.85 ± 0.96
n-Octane	0.286 ± 0.012	0.451 ± 0.031	0.0335 ± 0.0067	0.0619 ± 0.034
Ethylbenzene	1.280 ± 0.033	1.80 ± 0.38	0.105 ± 0.016	0.188 ± 0.084
m/p-Xylene	4.35 ± 0.14	6.3 ± 1.4	0.323 ± 0.052	0.59 ± 0.26
o-Xylene	1.662 ± 0.080	2.60 ± 0.62	0.117 ± 0.021	0.214 ± 0.091
n-Nonane	0.214 ± 0.025	0.215 ± 0.013	0.0077 ± 0.0020	0.0156 ± 0.0031
n-Propylbenzene	0.353 ± 0.032	0.71 ± 0.13	0.0210 ± 0.0024	0.037 ± 0.011
1,3,5-Trimethylbenzene	0.749 ± 0.060	1.42 ± 0.26	0.0381 ± 0.0033	0.061 ± 0.011
1,2,4-Trimethylbenzene	2.16 ± 0.22	4.18 ± 0.73	0.107 ± 0.011	0.169 ± 0.029

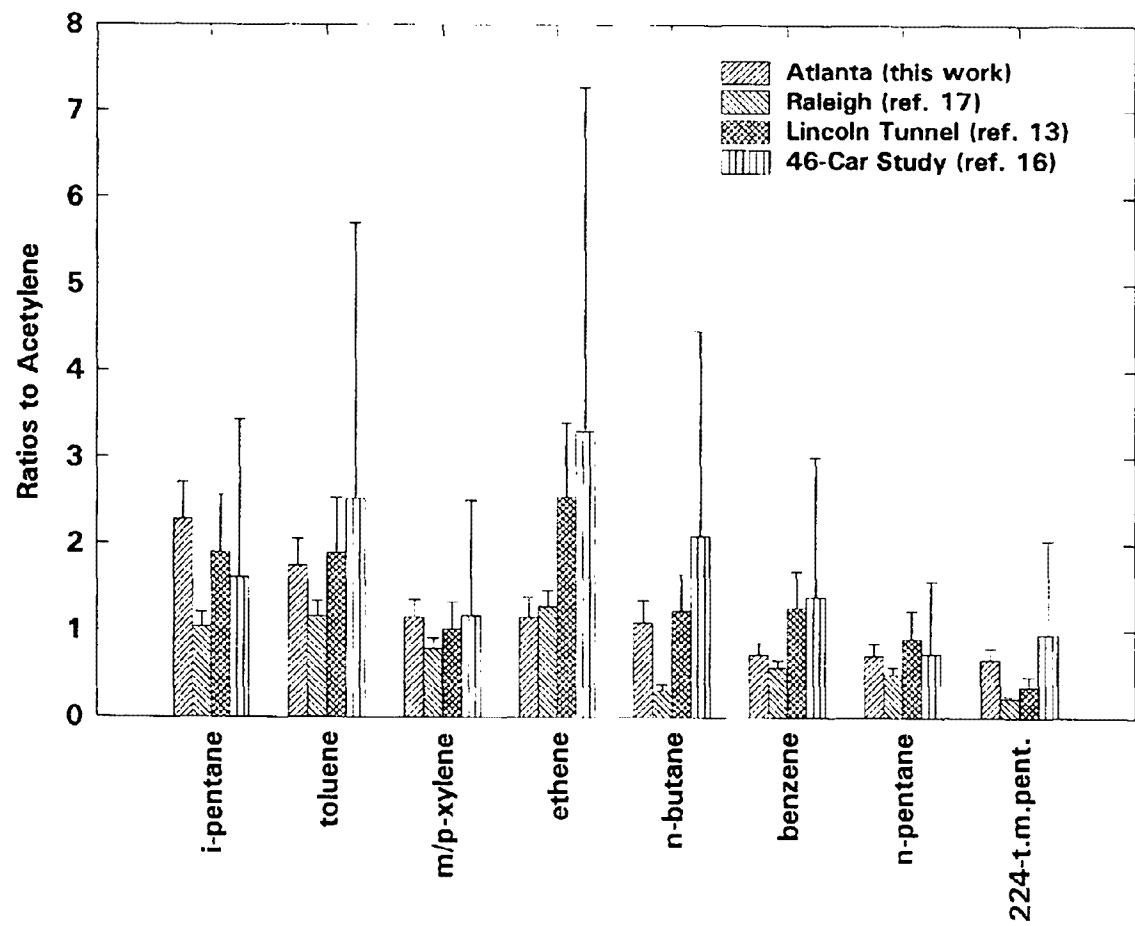


Figure 1. Ratios of selected compounds to acetylene in roadway or automotive emissions for three roadway studies (including this work) and one laboratory study.

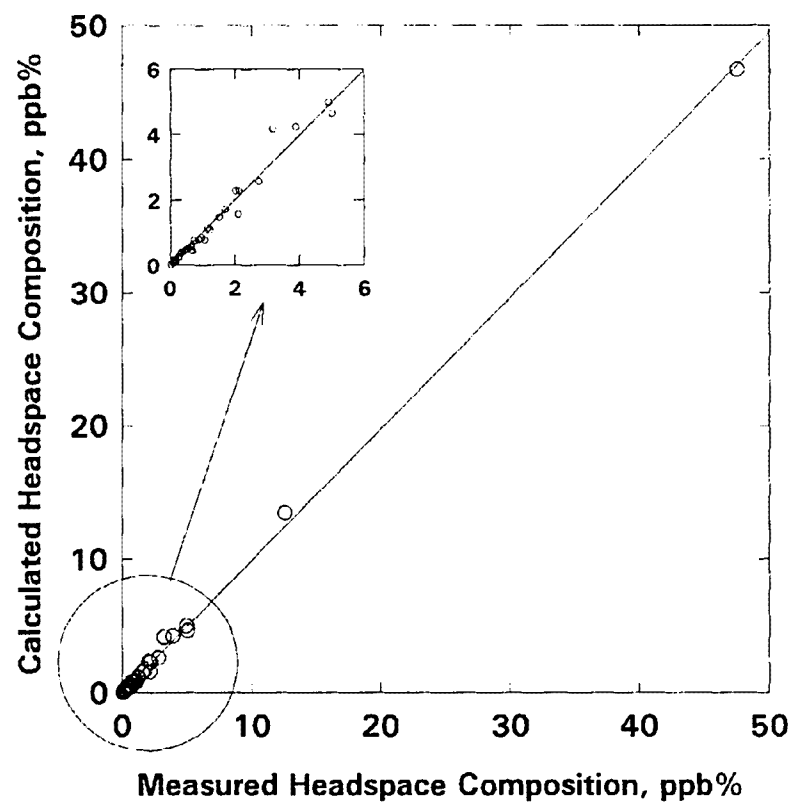


Figure 2. Gasoline headspace vapor composition calculated from Raoult's Law for 24C headspace composition. Regression line is shown.

PAMS Data Uses for Modeling and Control Strategy Development/Assessment

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Data from the Photochemical Assessment Measurement Stations (PAMS) are intended to serve multiple objectives, including photochemical modeling support, developing and assessing success of control programs, and tracking air quality and emission trends. This paper discusses various aspects of potential uses of PAMS data in developing ozone precursor control strategies.

PAMS data will support model applications by providing boundary conditions to drive the applications and an observational base to diagnose model behavior and evaluate performance. Within this context, the PAMS data are utilized implicitly, via model support, in the control strategy development process. PAMS data will be interpreted more explicitly given the current emphasis on the use of observational data as an independent means for developing directionally accurate precursor control strategies.

This paper will discuss the relative strengths and gaps in the PAMS program toward supporting development of sound precursor control strategies.

Diurnal Non-Methane Hydrocarbon Species Patterns in California

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INTRODUCTION

The California Air Resources Board (CARB) has been conducting Non-Methane Hydrocarbon (NMHC) monitoring at various locations throughout the state since the summer of 1988. Samples were initially collected from 0600 - 0900 hrs. (PDT) each third day (0600 - 0900 and 1300 - 1600 hrs. in 1992) during the summer ozone season (June through October). The program started with very limited capacities, with only total NMHC (PDFID, U.S. EPA TO-12)¹ being measured in 1988. In addition to PDFID measurements, limited speciation measurements of the hydrocarbons were made in 1989. In an attempt to define the hydrocarbon speciation patterns in California, the speciation measurements were normalized to the total NMHC concentrations, and the results were presented at the Tropospheric Ozone and the Environment Conference in Los Angeles in March of 1990². The conclusion of this work was that, although total NMHC concentrations varied considerably from location to location, the speciated hydrocarbon pattern was remarkably similar at all sites. The data collected during the 1990 and 1991 summer program, using speciation techniques similar to those recommended by the U.S. EPA³, continued to support that conclusion⁴. The data represented samples taken from 0600 - 0900 every third day from a total of thirteen separate urban areas throughout California.

In the winter of 1991-92, a special Sacramento Area Winter Hydrocarbon Study was undertaken to determine the specific hydrocarbon speciation patterns within a complex, extended urban/suburban metropolitan area⁵. The study was designed to identify changes in the patterns due to known stationary sources, with sampling at four fixed locations and fifty samples taken near sources with a mobile monitoring station. Samples were taken at 0600 - 0900 and 1300 - 1600 hours every third day. The four fixed sites represented a central business district, two sites immediately downwind of maximum ozone precursor emissions, and a downwind receptor site. The conclusions of this study were that the hydrocarbon speciation profiles in Sacramento were very similar at all sites and during all sampling periods. In addition, the ambient NMHC profiles between the summer and winter in the Sacramento area were also very similar.

The analyses of the Southern California Air Quality Study (SCAQS)⁶ and the Atlanta 1990 Ozone and Ozone Precursor Study⁷ supported the conclusions of CARB staff for ambient NMHC speciation profiles in both California and in one other major urbanized area. In these data reviews, the conclusions were that, although total NMHC concentrations vary considerably from location to location and from time to time, the measured NMHC speciation pattern varied little. The implications were that, to better define NMHC ozone precursor behavior, frequent total NMHC measurements were required, but speciated NMHC measurements need only be made on a periodic basis.

The limitation of the above studies was that sampling only occurred during the daylight hours, and the diurnal stability of the NMHC speciation pattern could only be inferred. In an effort to better define the behavior of NMHC

speciation patterns on a 24-hour basis, the recent Photochemical Assessment Monitoring Stations (PAMS) regulation⁸ requires an around-the-clock NMHC speciation component at the Type 2 site scheduled for implementation in 1994. The regulation does specify, however, that, if adequate supporting data are available, an alternative monitoring plan would be acceptable.

In order to determine the diurnal stability of the NMHC speciation patterns in California, CARB established a diurnal monitoring program at its Fresno-First Avenue monitoring site as part of the 1993 ozone season program. The Fresno site was selected for several reasons. This site is a candidate for a PAMS Type 2 site in the Fresno area and is fully instrumented. The site has been operational for many years and is one where speciated NMHC measurements have been made in 1991 (0600 - 0900 hrs) and 1992 (0600 - 0900 and 1300 - 1600 hrs). The Fresno urbanized area is one that represents a variety of possible ozone precursor sources. The area surrounding Fresno is highly agricultural (biogenic emissions), yet the urban population (over 600,000) is large enough to represent a typical urban environment. In addition, Fresno may be impacted by precursor transport from other parts of the state. All of these factors make the Fresno site an ideal location for a demonstration study.

EXPERIMENTAL

Samples were collected in 6-liter Summa-polished stainless steel canisters starting on June 15, 1993. The sampling frequency was 0000 - 0300 hrs, 0500 - 0800 hrs, 1200 - 1500 hrs, and 1700 - 2000 hrs, Pacific Standard Time, until October 1, then the sampling schedule was increased to include full 24-hour coverage (8 each 3-hr samples per day) through October 31, 1993. The samples were collected using a Xontech Model 910a automated air sampling system, including a Xontech Model 912 multiple-port sampling accessory. This system can be pre-programmed to sample up to 16 samples per day, or can be programmed for multiple sampling periods on multiple days. After collection, the samples were shipped to the CARB Sacramento laboratory for analysis.

All samples were analyzed for total NMHC (PDFID) and speciated NMHC. The PDFID instrumentation and technique have been reported previously (2). The NMHC speciation instrumentation included a Nutech 3550 automated cryogenic preconcentration system, a dual FID, dual column Perkin-Elmer Model 8500 gas chromatographic system, and a PC-based Perkin-Elmer/Nelson 2600 data collection system. A schematic of the system is shown in Figure 1. The dual column system included a 60m, 0.32 mm id., 1 micron film DB-1 capillary column and a 50m, 0.32 mm id. AI203/Na2SO4 PLOT column in tandem. The C2 - C4 hydrocarbons are sent to the PLOT column after desorption. These hydrocarbons are separated and detected on one of the FIDs. The remainder of the hydrocarbons are separated by the DB-1 column and detected on the second FID. Both signals are collected by the data system, and the files are later merged to form the final report.

The speciation instrumentation is calibrated using a NIST Reference Material standard containing ethane, propane, propene, hexane, benzene, o-xylene, and 1,2,4 trimethyl benzene. The PLOT column FID is calibrated with the propane component of the standard, and the DB-1 FID is calibrated with hexane component. Both systems are calibrated for response to hydrocarbons on a per-carbon basis. Since the other compounds represent the full spectrum of hydrocarbons analyzed by the program, and the concentrations are certified by NIST, the remainder of the components are used to make sure that the instrumentation is operating properly and that there are no losses. Individual compounds in the samples are identified by retention time. Retention times have been assigned using the PAMS 56-compound mix available from the U.S. EPA (Radian Corp.) and a 67 compound mix purchased from Scott-Marlin, Inc. All calibration standards, retention time mixes, and blanks are sub-sampled from high pressure gas cylinders into humidified stainless steel canisters prior to use.

In addition to the quality control procedures described above, the laboratory is a participant in the U.S. EPA PAMS audit program (managed by MANTECH) and the National Center for Atmospheric Research International Hydrocarbon Intercomparison Study. The results received so far from these programs indicate that the laboratory program produces measurements generally comparable to those of the reference laboratories.

RESULTS AND DISCUSSION

Figure 2 is a graphical representation of all PDFID measurements made at the Fresno-First St. site. Several observations can be made. The first is that, with the exception of the month of October, almost all of the measurements were below 40 part per hundred-million Carbon (pphmC, or, 400 ppbC), and the majority of the concentrations were less than 20 pphmC. This is a common feature for measurements made in other locations in California during the 1993 ozone season. Meteorological conditions during the summer of 1993 were conducive to lower than usual ambient concentrations. Note that both PDFID and speciation measurements made at these concentrations will be less precise than at higher concentrations, and the measurement precision will affect the normalized speciation data to a greater degree. The other observation is that the total NMHC concentrations are extremely variable, and that no obvious diurnal pattern is present. In general, the midnight (0000 - 0300) sample concentrations are higher than those of the rest of the sampling periods, but there are obvious exceptions. All sampling periods show at least one high total NMHC concentration for the sampling day in question. During the June through September monitoring period, the average concentration of the 0000-0300 time period was 26.7 pphmC, the average concentration of the 0500-0800 period was 23.9 pphmC, the average concentration of the 1200-1500 period was 21.5 pphmC, and the average concentration of the 1700-2000 hr. period was 18.5 pphmC. This midnight maximum is often noted in carbon monoxide diurnal measurements.

Figure 3 represents the seasonal average normalized values (individual hydrocarbon concentration divided by PDFID-total NMHC concentration times 100%) for eight selected hydrocarbon species. Seven of these species were chosen because they represent major contributors to ambient hydrocarbon concentrations, while isoprene was chosen as a biogenic emission tracer. The normalized value for each species is plotted as a function of sampling time. In contrast to the total NMHC concentrations, the normalized values for each hydrocarbon species are consistent for all sampling periods. Where minor variations exist, they might have been predicted. All paraffins show a constant normalized value throughout the day, whereas the more reactive aromatics show a dip in value during the afternoon periods. This would be due to photooxidation in the afternoon. Note, however, that the normalized values for toluene and m/p-xylene return to morning levels in the evening sampling period. Isoprene values, though very low, do show a marked increase in the afternoon and evening periods, consistent with biogenic activity.

Figures 4, 5, 6, and 7 represent the average normalized value and standard deviation of all measurements for the selected hydrocarbon species. Note that the relative standard deviation for most of the measurements is 25% or less. This figure includes not only the actual variation in concentration of the hydrocarbon in the atmosphere, but also the precision inherent in the PDFID and the speciation measurement process. Given that the measurement process variability is insignificant (it isn't, especially given the low concentrations encountered in 1993), the data indicate that the maximum variability of each hydrocarbon contribution to the total NMHC concentrations in the atmosphere is approximately 25 - 30%.

CONCLUSION

The diurnal measurements made at the Fresno-First Avenue monitoring site further support the consistent nature of the NMHC species patterns found in past studies. In addition, this work demonstrates that the hydrocarbon species patterns extend throughout the 24-hour period, even in a complex demographic area. The data generated supports CARB's position that frequent, high-quality total NMHC measurements are necessary, but only infrequent NMHC speciation is necessary to determine the characteristics of ambient hydrocarbon concentrations. Further, it has been shown that diurnal sampling and analysis may not be necessary, or, at least, diurnal measurements need only be taken periodically. From a data analysis or modeling perspective, the data further supports early morning and afternoon sampling as showing the greatest differences in species profiles.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the invaluable support of the CARB Air Quality Surveillance Branch. It is through their efforts that sampling equipment is set up, maintained, and that samples are properly obtained in the field. We would also like to acknowledge the staff of the CARB Quality

Management and Operations Support Branch who have, for several years, worked closely with NIST in the development of ambient-level calibration standards for use by our laboratory.

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8. Federal Register, Vol. 58, No. 28, February 12, 1993, pg. 8452

PE 8500 GAS CHROMATOGRAPH

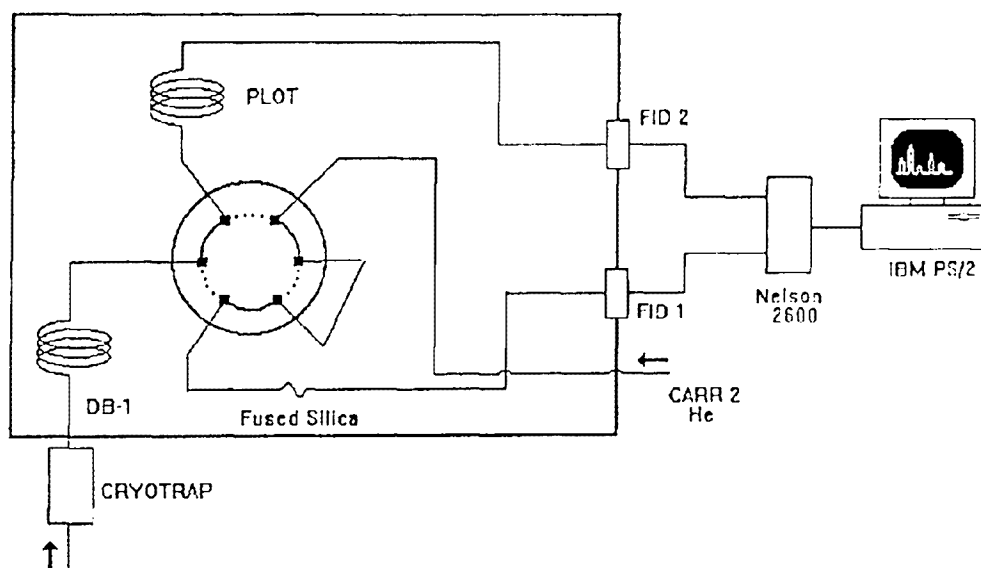


Figure 1. Schematic of GC used in NMHC speciation.

1993 Speciated NHMC Fresno-First - PDFID

Note: 06:00 & 18:00 included for 05:00
& 17:00 Samples, 10/1 to 10/31

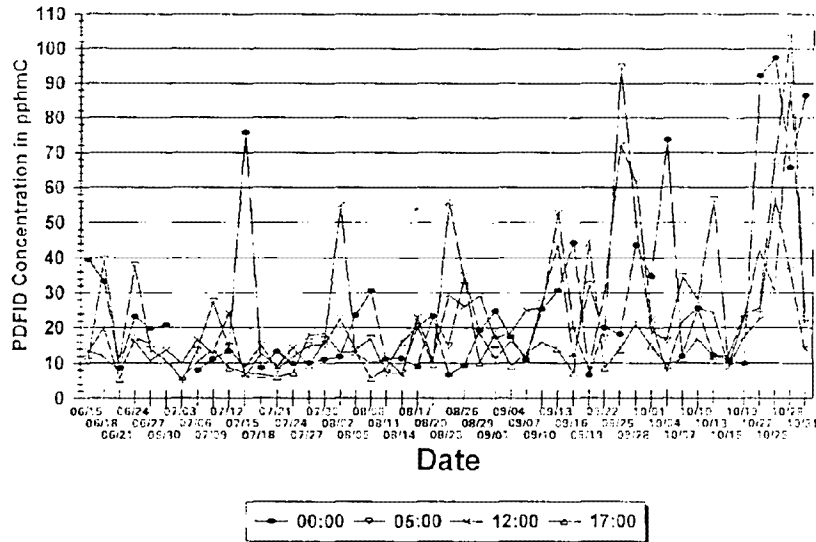


Figure 2. Total NMHC concentrations for each sampling period

1993 Speciated NHMC 6/15/93 to 10/31/93

Note: 06:00 & 18:00 included for 05:00
& 17:00 Samples, 10/1 to 10/31

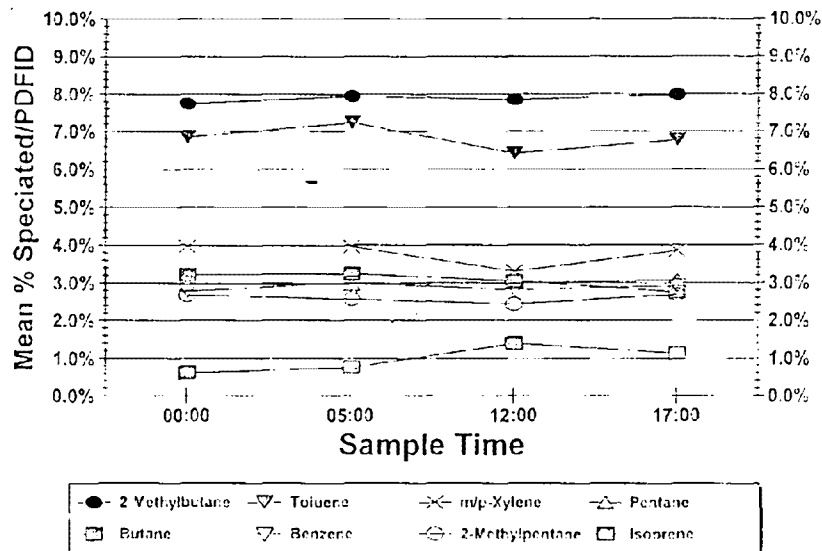


Figure 3. Seasonal average normalized concentrations for species

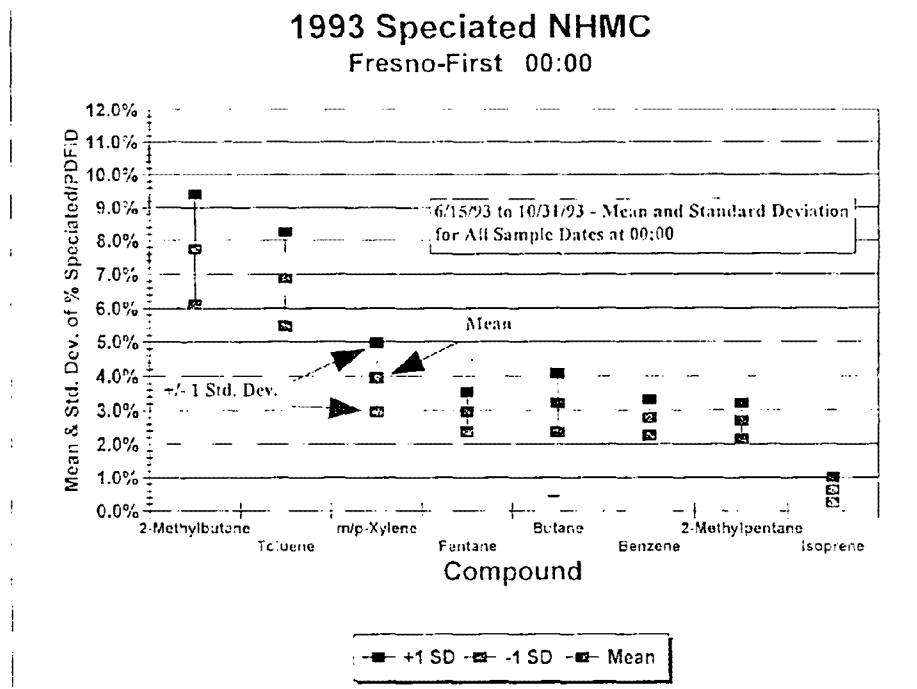


Figure 4. Variability of normalized concentrations for 00:00-0300

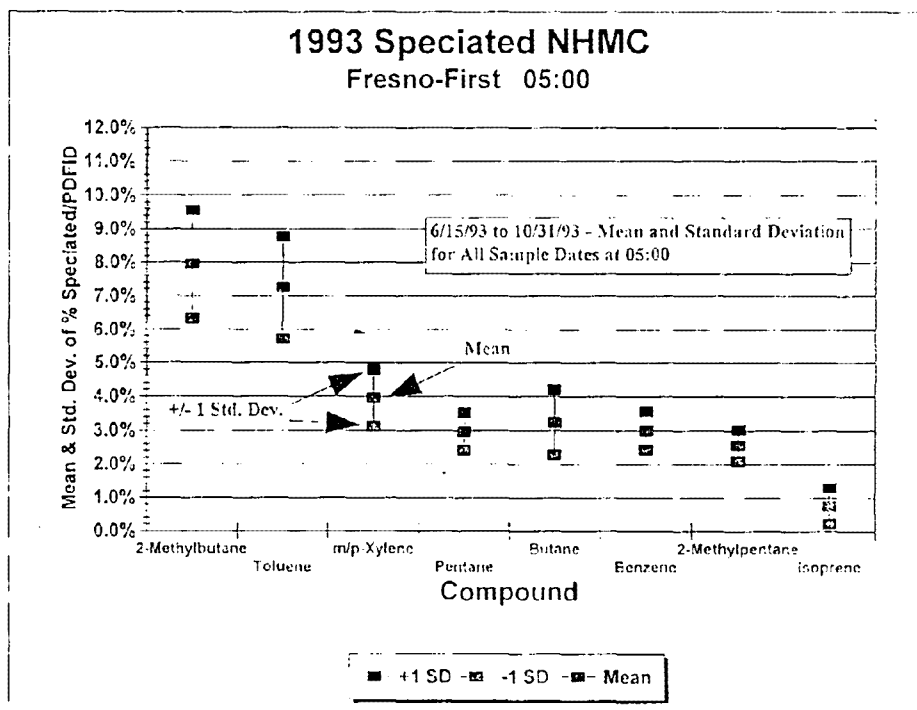


Figure 5. Variability of normalized concentrations for 500-0800

1993 Speciated NHMC Fresno-First 12:00

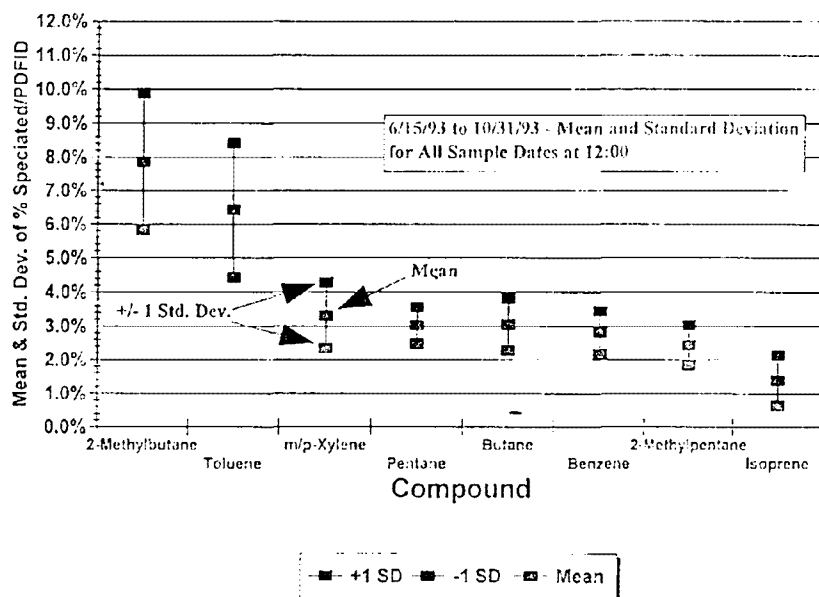


Figure 6. Variability of normalized concentrations for 1200-1500

1993 Speciated NHMC Fresno-First 17:00

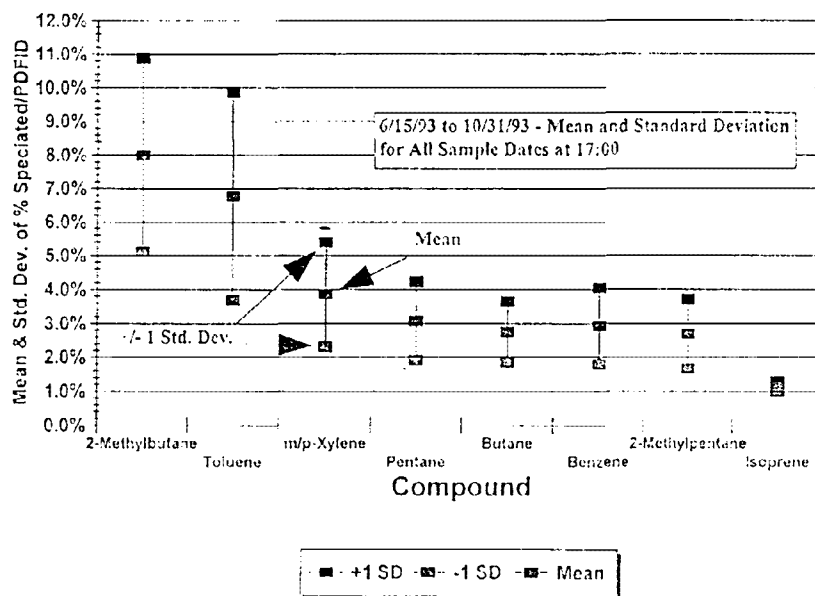


Figure 7. Variability of normalized concentrations for 1700-2000

Preliminary PAMS Data Analyses

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ABSTRACT

The Photochemical Assessment Monitoring Stations (PAMS) program is designed to provide enhanced monitoring of ozone and its precursors in twenty-two areas throughout the United States (serious, severe, and extreme ozone non-attainment areas). The PAMS program will generate a vast data set valuable to air quality modelers, developers of emissions inventories, regulators, and policy makers. The monitoring objectives of the PAMS program include: determination of National Ambient Air Quality Standard (NAAQS) attainment status, control strategy development, SIP control and strategy evaluation, emissions tracking, and ambient trends. This paper reviews the PAMS monitoring objectives and data uses, and presents example exploratory data analysis techniques (univariate and multivariate) which can be used to evaluate and interpret this data.

INTRODUCTION

The PAMS program will generate a significant volume of data at a substantial cost. The effort to extract information from these data should ideally be commensurate with the effort to generate the data. Thoughtful evaluation of the PAMS data demands a clear exposition of goals of the analysis, an understanding of the applicable analytic techniques, and an ability to interpret the results of any analysis. The Environmental Protection Agency (EPA) has developed a series of recommendations for the analysis of the PAMS data¹. This conceptual description of assessment approaches will be included in the PAMS Implementation Manual. The plan provides suggested analytic approaches to each of the PAMS monitoring objectives summarized below. Activity is currently underway to develop illustrations of analyses of PAMS data to supplement this plan. Some of these initial efforts are presented in this paper.

PAMS MONITORING OBJECTIVES/DATA USES

The following outline summarizes the monitoring objectives and data uses of the PAMS program.

- **NAAQS Attainment and Control Strategy Development**

PAMS data can be used in the assessment of ozone and precursor transport as well as in episode selection, domain definition, and initial and boundary condition estimation for photochemical grid modeling. The data can also be employed in evaluating model performance.

- **SIP Control Strategy Evaluation**

By providing a data set of ambient measurements of VOC profiles and trends, PAMS will be invaluable in evaluating the effectiveness of emission control measures as well as the identification of the most efficient future control strategies.

- **Emissions Tracking**

The speciated ambient VOC measurements from PAMS can be used to corroborate the local emission inventories. In addition, PAMS data may, over time, be useful in tracking emission reductions from specific control strategies and compliance with overall emission reduction requirements.

- **Ambient Trends**

PAMS data will allow the identification and assessment of ambient air quality trends for ozone, ozone precursors and air toxics.

- **Exposure Assessment**

The ambient monitoring data generated by PAMS will serve as important inputs in estimating potential exposure to ozone, nitrogen dioxide and air toxics.

PAMS Data Availability

While the PAMS regulations require the initial site to be operated during the 1994 ozone season, varying degrees of sampling were performed at nineteen of the twenty-two PAMS areas in 1993². Although twenty-two PAMS sites were operating in 1993, only limited data is currently available via EPA's Aerometric Information Retrieval System. Given both the early stage of the PAMS program (i.e., networks will not be completely established until 1998) and the limited availability of PAMS data (i.e., only a few states have reported), this paper can not address all the monitoring objectives summarized previously. Instead, the analyses focus on exploratory analyses applicable to PAMS data.

Data Checking/Exploratory Data Analysis

Prior to any analyses, the data should be checked for anomalous values, large gaps of in the time series of the data, and any other anomalous features. One screening technique is the use of univariate statistical procedures. For example, Figure 1, which is the output of the univariate procedure from the Statistical Analysis System (SAS) package, provides diagnostic information such as moments, quantiles, extremes, counts, and distributional graphics. In this example, the number of zero values is more than half the number of observations. This results in a degenerate distribution as can be seen in the histogram and box plot.

Another useful tool is a simple time series plot of a variable. Large gaps are very noticeable and large excursions or spikes are easily seen. These situations call for further investigation of the quality of these particular data. Figure 2 displaying a time series plot of carbon monoxide data using the VOYAGER exploratory data package illustrates this concept.

The final technique illustrated is a scatter plot matrix (Figure 3). The scatter plot matrix is an arrangement of many scatter plots of different variables. This type of display allows the analyst to see how "outliers" fit in with more than one variable and most important, how different variables might be related. Another way to accomplish the latter is to examine a correlation matrix for "high" correlations in the data. The scatter plot is superior to the correlation matrix since it is easier to see relationships and is not bound by linear relationships quantified by the correlation matrix.

VOC/NO_x Ratios

As mentioned previously, the PAMS data can be valuable to the development and

evaluation of SIP control strategies. First, the data can be used to provide a check of emission inventory data. Although this corroboration will have limitations, it will be an independent check that was unavailable before PAMS. Initially, characteristic ratios such as VOC/NO_x, VOC/CO, or individual VOC/TNMOC ratios can be used as points of comparison with the emission inventory. As the program progresses, the data can also be used to specific emission reduction program effectiveness by comparing the trends of ambient VOC measurements with VOC emission inventories. In addition, VOC/NO_x ratios estimated from PAMS data can be used to determine the relative influence of VOC and NO_x emissions reductions and therefore inform the development of control strategies. More specifically, Chang et al. determined that a ratio of less than 8.5 implies a VOC control strategy is the best approach while a larger ratio implies that a NO_x control strategy is more effective⁷.

Multivariate Techniques

The PAMS data include measurements of fifty-nine organic compounds, six meteorological variables, and four gaseous pollutant parameters. The dimensionality of the data is intimidating at best. Several classical multivariate statistical techniques reduce the dimensionality of the problem by forming new variables as linear combinations of the original variables. In other words if we let $X_i, i=1,2,3,\dots,n$ be the original variables, then $Y_j=\sum a_{ij}X_i$ is a linear combination of the X_i . It is hoped in all these exercises that the number of j 's needed is much smaller than the number of i 's. The usual starting point in all these techniques is a matrix of the correlations between all possible pairs of variables. The first of these techniques is factor analysis, which decomposes the matrix with the aim of finding unknown factors that cause different linear combinations of the variables to track each other. The factors could be considered unknown sources of precursors in different combinations. The second technique is principal component analysis. This technique decomposes the matrix with the aim of preserving the most variation expressed in the original set of variables in the fewest set of linear combinations possible. The third procedure, canonical correlation, decomposes the matrix with the aim of discovering the linear combination of a set of independent variables that has the maximum correlation with the corresponding linear combination of all the dependent variables (just one in this case, ozone). The last technique we suggest is the standard statistical multivariate linear model. The earlier techniques can be used to identify potential model terms and how they should be included in such a model. The guiding purpose behind all these analyses is to try to see what variables in the data are useful in predicting ozone levels. Once these have been discovered, the ozone control strategy could be guided by the findings of these analyses.

CONCLUSIONS

The wealth and complexity of PAMS data has the potential to pose such a range of possible analytic approaches that existing data analysis capabilities could be overwhelmed resulting in untimely, ill conceived, and/or poorly focused evaluations. At the same time, this data should be considered invaluable to the formulation of ozone control strategies. The data base which will result from the PAMS program is a very rich one deserving much scrutiny. The examples presented in this paper and even those outlined in the PAMS data analysis plan barely scratch the surface. Every illustration generated has opened another pathway that would take weeks to fully explore. Those who are tasked with analyzing data from the PAMS program should use all guidance as a starting point and recognize that an array of existing statistical procedures can be used in the analysis of these data.

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3Chang, T.Y.; S.J. Rudy; G. Kuntasal; Gorse, R.A. Atmos. Environ., **1989** 23, 1629-1644.

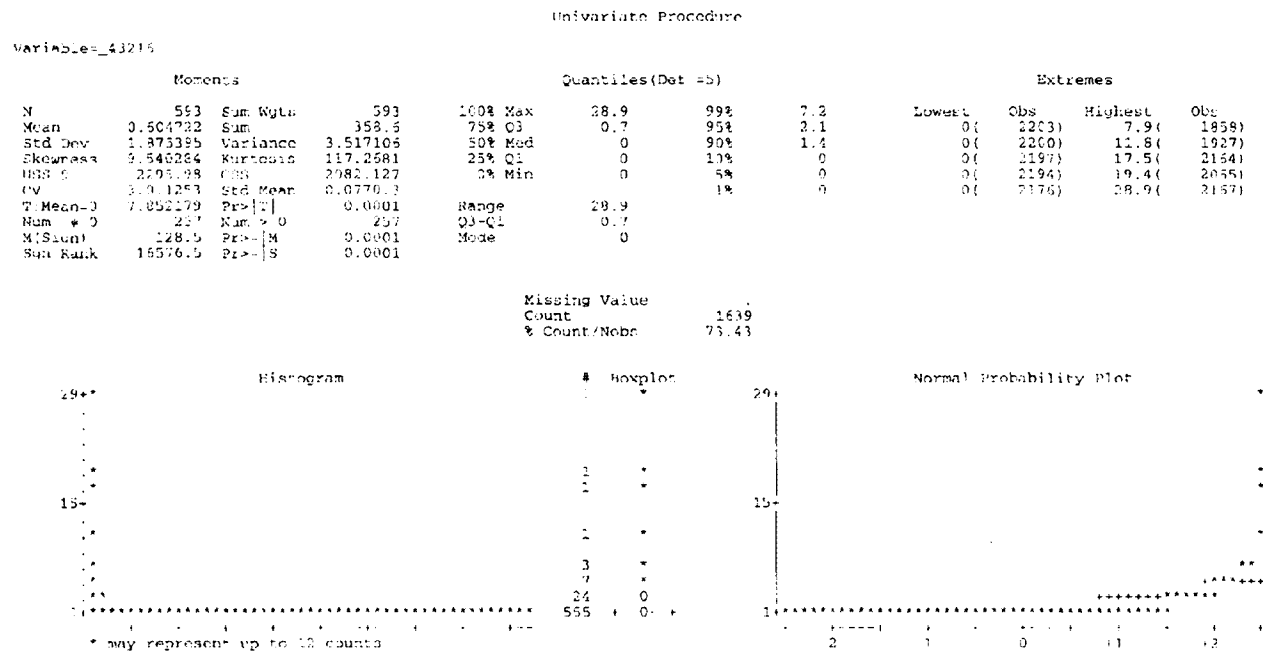
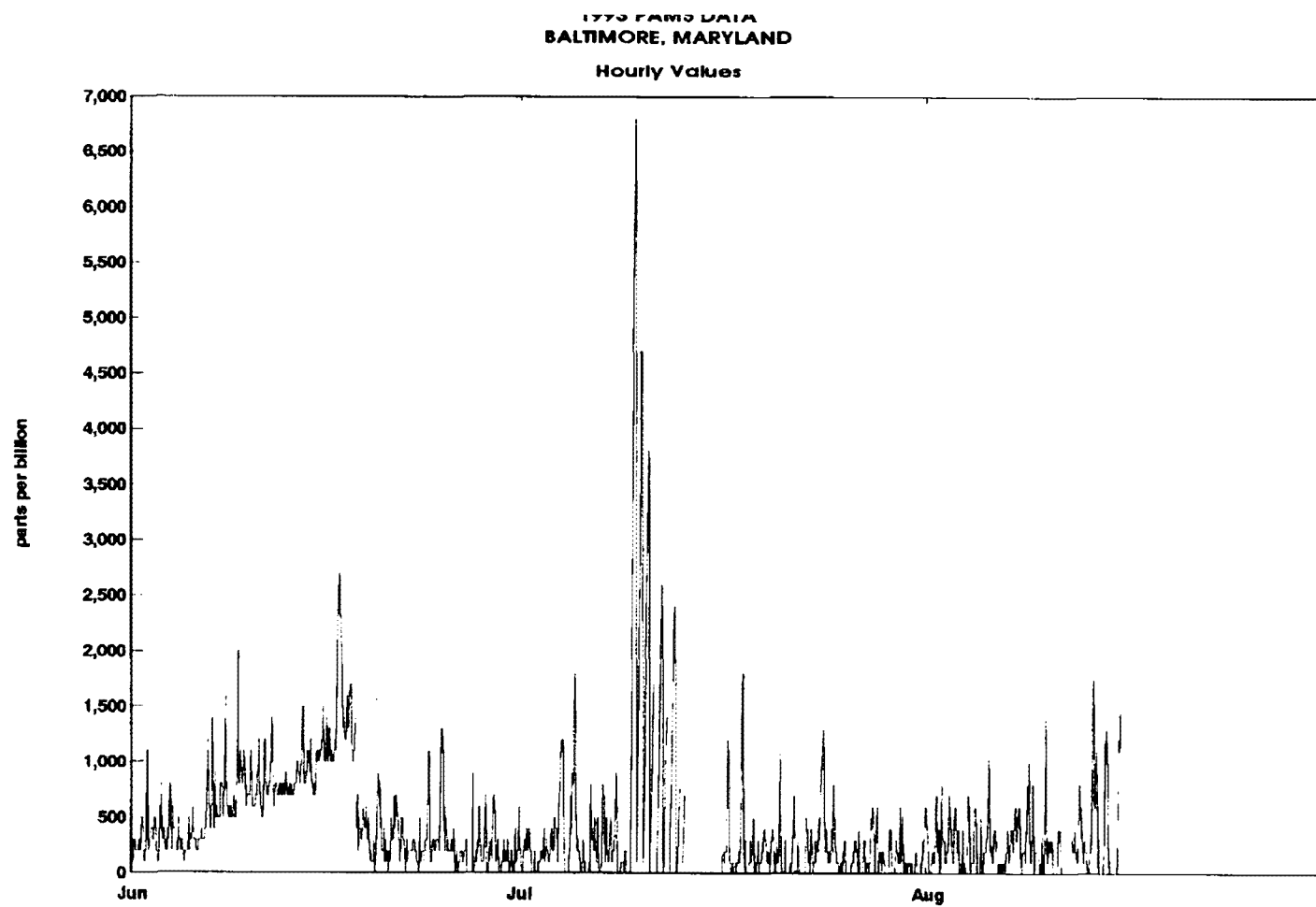


Figure 1. Example output from SAS Univariate Procedure



CARBON MONOXIDE
Figure 2. Hourly PAMS CO Data from Baltimore

BALTIMORE PAMS DATA 1993
SPECIES AND PERCENT OF TNMOC

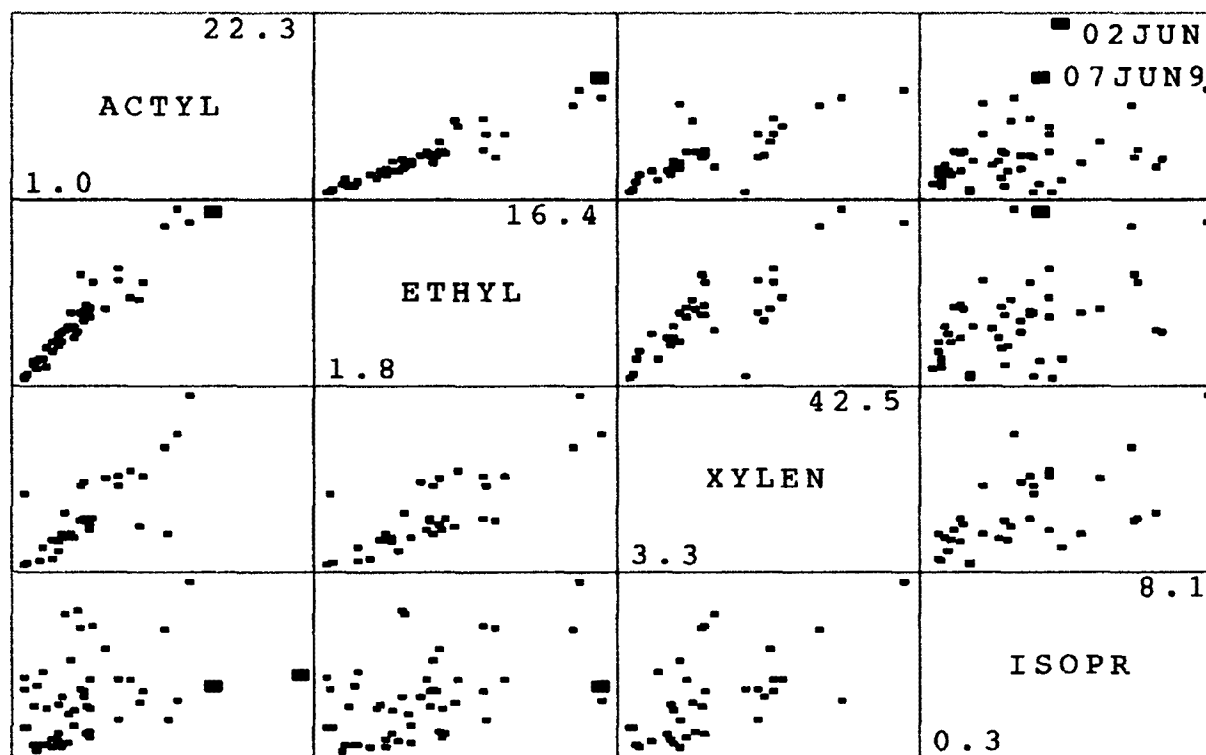


Figure 3. Scatter-plot Matrix - Baltimore PAMS Data

SESSION 6:
SOURCE SAMPLING

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SAMPLING AND ANALYSIS INFORMATION AIDS FOR STATIONARY SOURCE PERSONNEL

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ABSTRACT

The Environmental Protection Agency, in developing and evaluating sampling and analysis methodology for stationary sources, has compiled information on availability and applicability of sampling and analytical methods. Information has also been summarized on the applicability of the gas chromatography/mass spectrometry as the analytical method. All of this information is accessible in three documents: "Stationary Source Sampling and Analysis Directory, Version 2" (SSSADIR), "Handbook of GC/MS Data and Information for Selected Clean Air Act Amendments Compounds" (Handbook), and "Literature Review of CAAA Compounds" (LitRev). The SSSADIR has information on which sampling and analytical methods to use for organic compounds listed in Title III of the Clean Air Act Amendments (CAAA) of 1990, as well as Appendices VIII and IX of RCRA compounds, and the status of method evaluation for these analytes. The Handbook provides information on the mass spectra of selected CAAA analytes, primary quantitation ions, relative retention times and compatibility of the organic compounds in solution. The LitRev provides information on CAAA compounds for which EPA has no potential methods available but provides suggestions on ways to develop methods.

INTRODUCTION

The Source Methods Research Branch, Atmospheric Research and Exposure Assessment Laboratory, US Environmental Protection Agency, while evaluating stationary source sampling and analytical methodology for use in conjunction with the hazardous waste incineration regulations (Appendices VIII and IX, RCRA) and the Clean Air Act Amendments, Title III, 1990¹, has assembled information on all the compounds listed. Some compounds have validated methods available, some have methods that might work, and others have no method available at this time. This base of information has been gathered into three EPA reports. These reports are:

1. Stationary Source Sampling and Analysis Directory, Version 2² (SSSADIR)
2. Handbook of GC/MS Data and Information for Selected Clean Air Act Amendments Compounds³ (Handbook)
3. Literature Review of CAAA Compounds⁴ (LitRev)

The contents of each of these information aids are discussed below.

SSSADIR

Most databases of sampling and analytical methods are analyte-based. If a method has a specific list of analytes to which that method is applicable, the database can readily locate all

methods which are applicable for that analyte. However, many sampling and analytical methods for stationary sources do not incorporate a specific list of applicable analytes. These methods (such as Method 0030)⁵ include only some general guidance (e.g., a boiling point range) on the analytes which should be amenable to the method. In an analyte-based database, it is impossible to find out that Method 0030 is the method of choice for sampling and analysis of carbon tetrachloride in stationary sources. The Stationary Source Sampling and Analysis Directory (SSSADIR), a database stand alone program that can be run on any personal computer, provides a solution to the problem of locating appropriate stationary source sampling and analytical methods for specific analytes. This version of SSSADIR replaces the "POHCs Directory, Version 1"⁶. The original POHCs Directory contained only the compounds listed in Appendix VIII⁷. The SSSADIR has retained all these compounds, edited and upgraded to incorporate recent information, and has added all the compounds from Appendix IX⁸ and the compounds listed in Title III Amendments to the Clean Air Act of 1990. The present directory contains information on properties (e.g., boiling point, melting point, flammability) for each individual compound listed. If a validated method is available for the compound, this validated method is listed with the pertinent reference. However, if no method validation information is available, either a proposed method is listed or the method is left blank which says that no method is known at this time. Problems with the sampling or analytical methodology are listed with suggestions for solutions, if known. Physical properties are provided to permit comparison of one compound to another compound of known properties (such as incinerability). The database may be searched by several parameters such as name, CAS number, boiling point, incinerability index, and problems in sampling or analysis.

The database provides a snapshot of available information at one point in time. Since method evaluation and method development is an ongoing effort within the Environmental Protection Agency, new information is constantly becoming available. Future updates to the database will focus on making information on method evaluation available to provide guidance on selection of methods. No matter what information is available to suggest that a given compound "should work" using a specified sampling and analytical methodology, the ultimate test is always provided by an actual field evaluation of that methodology and compound at a stationary source. Even a successful method evaluation at a particular stationary source does not guarantee universal success for the methodology and analyte at any or every stationary source. However, the guidance available through SSSADIR can provide a starting point for determining applicable methodology.

HANDBOOK

The "Handbook of GC/MS Data and Information for Selected Clean Air Act Amendments Compounds" contains information on all of the Clean Air Act organic compounds that are chromatographable. The total ion chromatograms are included along with the chromatographic and mass spectrometric conditions. A reference mass spectrum is provided and the primary quantitation ions are identified. Response factors relative to the appropriate Internal Standards (Method 8270 or Method 5041)⁵ are provided. The compatibility of compounds in solution is discussed and proposed compatible mixtures are suggested for standards.

The information contained in the Handbook is useful in the development of analytical methods. For several of the analytical methods for volatile and semivolatile organic compounds (especially Methods 0010 and 0030)⁵, gas chromatography/mass spectrometry is the required analytical method. In developing a sampling and analytical methodology for a given analyte, the analytical methodology must be developed first. If the analyte cannot be analyzed successfully, the applicability of the sampling methodology cannot be evaluated. It should not be necessary for several laboratories to demonstrate, individually, that a given analyte is not amenable to the analytical conditions of Method 8270, if this information can be supplied in a Handbook. Also, the Handbook

can be useful in evaluating the applicability of GC/MS methodology. It is a time-consuming process to generate a GC/MS calibration curve for all of the semivolatile organic compounds listed in Title III of the CAAA, so there is a tendency to use a standard calibration curve that is already available in most laboratories (i.e., Method 8270) and identify other semivolatile organic CAAA analytes as additional peaks. This procedure is valid only if a given CAAA analyte is amenable to the analytical methodology, and this information is available from the Handbook. It is very important to know with confidence if a given analyte is not observed because: 1. it is not present at the stationary source sampled or 2. the compound could not be analyzed by GC/MS.

LITREV

The "Literature Review of CAAA Compounds" deals with the compounds in the Clean Air Act Amendments where no known methods are presently available and none of the existing methods are expected to provide an acceptable level of performance. The LitRev incorporates the opinions of several experts in the field of stationary source sampling and analysis relative to possible approaches in providing new or revised methodology. Many physical properties are listed for each candidate compound. Chemical structures are provided for approximately 100 compounds.

The LitRev provides physical and chemical properties of the analytes in suggesting appropriate sampling and analytical methodologies. Considering the VOST, for example, Method 0030 provides only a single guideline for application of the methodology: the analyte must have a boiling point $\leq 100^{\circ}\text{C}$. Approximately 40-50 of the organic analytes on the Clean Air Act list meet this requirement, but the 0030 methodology is not successful for all of these analytes. A careful consideration of the physical and chemical properties of triethylamine, for example, shows a very high water solubility for this compound. Since the Method 0030 analytical methodology requires the analytes to be purged from the sorbent tubes through a purge flask containing water, consideration of the water solubility of triethylamine dictates that analytical system response to this analyte will be poor, at best, because the analyte will not be purged from the water. In fact, no analytical system response is obtained. The LitRev incorporates information that may save experimentation in various laboratories to demonstrate that a given methodology does not work.

CONCLUSIONS

Three sources of information have been prepared by the Source Methods Research Branch, Atmospheric Research and Exposure Assessment Laboratory, US Environmental Protection Agency to assist the personnel who perform the stationary source sampling and analysis for compliance with the Clean Air Act Amendments of 1990, Title III and with the hazardous waste incineration regulations. The information included in these three sources provides the current knowledge of hazardous waste incineration for each of the compounds listed under Appendices VIII and IX of RCRA and in the 1990 Amendments to the Clean Air Act, Title III.

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DISCLAIMER

The compilation of the information in this document has been partially funded by the United States Environmental Protection Agency under contract 68-D1-0010 to Radian Corporation and contract 68-02-4442 to Southern Research Institute. It has been subjected to Agency review and approved for publication.
Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Hexavalent Chromium Emissions From Aerospace Operations-A Case Study

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ABSTRACT

Northrop Aircraft Division (NAD) is subject to several air toxic regulations such as EPA SARA Title III, California Assembly Bill 2588 (AB2588), and Proposition 65 and is a voluntary participant in air toxic emissions reduction programs such as the EPA 33/50 and MERIT Program. To quantify emissions, NAD initially followed regulatory guidelines which recommend that emission inventories of air toxics be based on engineering assumptions and conservative emission factors in absence of specific source test data. NAD was concerned that Chromium VI emissions from NAD's spray coating and chemical tank line operations were not representative due to these techniques. More recently, NAD has relied upon information from its ongoing source testing program to determine emission rates of Chromium VI. Based on these source test results, NAD revised emission calculations for use in Chromium VI inventories, impact assessments and control strategies. NAD has been successful in demonstrating a significant difference between emissions calculated utilizing the source test results and emissions based on the traditional mass balance using agency suggested methods.

INTRODUCTION

This paper discusses reportable Chromium VI emission reductions at NAD based on improved emission information and the application of control technologies on various sources.

During 1989 and 1990, among other facilities in California, NAD was required to prepare Air Toxics Inventory Plans (ATIPs)^{1,2} and Air Toxics Inventory Reports (ATIRs)^{3,4} in accordance with AB2588. At the time, there were not sufficient scientific data or methods available to accurately quantify Chromium VI emissions from spray coating operations. NAD prioritized spray coating and chromium conversion coating operations at two facilities for conducting a source test program to establish more representative emission factors.

Since the emissions of Chromium VI depend on a variety of factors such as configuration of the source, type of coating, applicator, filter media, and Chromium VI content in the coating; the emission factors established for NAD sources should only be utilized by similar sources after comparison of the referenced factors.

SOURCES

NAD utilizes various spray booths and chemical process tanks to apply chromated coatings to aerospace components. The sources outlined in Table 1 were prime candidates for testing based on emission rates and the type of operation. The emission factors obtained from source test results for these candidate sources were extrapolated to similar sources at NAD. The tested sources are indicated in Table 1.

Y12 Facility

Electrostatic Spray Booths No. 3 & 4 utilize a three-part mixture coating (AKZO 463-0600078, X515, and TL 164; mix ratio 2:2:1). The mixture contains 1.1% of Chromium VI by weight. The coating is applied by automated electrostatic spray guns with high transfer efficiency (i.e. 92%). One booth coats the front side of the component and the second booth coats the back side. These booths contained conventional dry filters with 97% (agency suggested) control efficiency at the time of source testing. Shortly after the source test, High Efficiency Particulate Air (HEPA) Filters with 99.97%⁵ control efficiency were retrofitted downstream of the conventional dry filters.

A deoxidizing tank which contains a chromated solution (AMCHEM 7) is used in the tank line at the Y12 facility. This process is similar to a "carwash" type of operation through which aerospace parts are conveyed. The solution is sprayed on the aerospace parts inside the enclosure from both sides with the excess solution recycled back into the tank.

East Complex

Spray Booth No. 31W is open from two sides. A conveyor passes large Boeing 747 skins through this booth where a mixture of AKZO 463-0600078 and X515 (mix ratio 1:1) is manually applied with HVLP spray guns. This spray booth has wet scrubber controls in a down draft configuration. The agency suggested control efficiency of such a system is 90%.

Spray Booth No. 2 is equipped with conventional dry filters bank with an agency suggested control efficiency 97%. The HVLP gun is used to manually apply the coating to aircraft components. Since NAD is changing the coating from a solvent based coating (DeSoto 515X385D) to a water reducible coating (Deft 44GN011), separate source tests were conducted during each coating operation.

EMISSION CALCULATION METHODS

Mass Balance

When coatings are applied to a substrate inside a spray booth, the majority of the particles/solids are transferred to the substrate surface. However, some particles are transmitted as overspray of which 1) some drop out onto the floor, and 2) some are captured by the filter media controls with some remaining fraction emitted through the stack into the atmosphere. In the mass balance emission calculation method, regulatory agencies did not allow credit for dropout rates in the absence of test data. As a part of the source test program, NAD conducted an experiment at its Y12 facility in the electrostatic booth to determine the dropout percentage of the Chromium VI particles. The results indicate 22% of the oversprayed Chromium VI particles dropped out in the booth.

In 1990, NAD conservatively utilized and overestimated the Chromium VI emissions in its emission inventory based upon the following method:

Spray Booths. Chromium VI emissions² (lb/year) = Usage X Density X wt% X (1-TE) X (1-CE)

Where:

Usage	=	usage of chromated coating, gallons/year
Density	=	density of chromated coating, lb/gallon
wt%	=	weight percent of Chromium VI in the chromated coating
TE	=	transfer efficiency of the spray gun
		Electrostatic = 0.92 (92%), HVLP = 0.65 (65%)
CE	=	control efficiency of the filter media
		Conventional dry filters = 0.97 (97%), Water scrubber = 0.9 (90%)

Y12 Tank Line. Chromium VI emissions² (lb/year) = Usage X Density X wt% X (1-TE)

Where:

Usage	=	usage of chromated solution, gallons/year
Density	=	density of chromated solution, lb/gallon
wt%	=	weight percent of Chromium VI in the chromated solution
TE	=	transfer efficiency of the spray heads 0.98 (98%)

Note: Transfer efficiency is assumed to be 98% since the solution is sprayed through the sprinkler heads which do not atomize Chromium VI particles and the excess solution is recycled back into the tank. This assumption was approved by the South Coast Air Quality Management District's (SCAQMD's) staff.

Source Test

Spray Booths. As discussed above, various factors affect the particulate emissions. In order to simplify the emission estimation, NAD conducted source tests on candidate sources at the stack. In the

case of spray booths, the total amount of coating sprayed was measured. Grab samples of the coating were analyzed for Chromium VI content. Triplicate samples of stack exhaust gases were collected during the spray coating operation. The amount of total Chromium was analyzed for each sample. The total Chromium was considered as Chromium VI per the SCAQMD staff's suggestion.

The emission factor established from the source test results, indirectly included all efficiencies such as transfer efficiency, dropout rate, and control efficiency of the filter media. A summary of these source test results is presented in Table 2. The following algorithms were utilized to calculate Chromium VI emissions based on the source test results:

- 1) Chromium VI emissions from Y12 Electrostatic Spray Booths No. 3 & 4, East Complex Spray Booth No. 31W, and East Complex Spray Booth No. 2 with water based coating, lb/year = (Emission Factor^{6, 7, 8, 11}, pounds of Chromium VI emission/gallon of mixed coating sprayed, Table 2) X (gallons of mixed coating sprayed/year)
- 2) Chromium VI emissions from East Complex Spray Booth No. 2 with solvent based coating, lb/year = (Emission Factor⁹, pounds of Chromium VI emission/pounds of Chromium VI sprayed, Table 2) X [(Usage, gallons of coating with Chromium VI/year) X (Density of the coating with Chromium VI, lb/gallon) X (wt% of Chromium VI in the coating)]. This algorithm is utilized to calculate Chromium VI emissions from most of the East Complex and West Complex spray booths with the conventional dry filters and HVLP spray gun.

None of the above algorithms were useful for Spray Booths No. 22 & 23 at East Complex and area sources of Chromium VI at East Complex and West Complex, because of the different applicator, configuration, and Chromium VI content in the coating. The dropout rate⁶ of 22% was used in the mass balance algorithm to estimate Chromium VI emission:

- 1) Spray Booths No. 22 & 23:

Chromium VI emissions⁴ (lb/year) = Usage X Density X wt% X (1-TE) X (1-CE) X (1-Dropout)

Where:

- Usage = usage of chromated coating, gallons/year
- Density = density of chromated coating, lb/gallon
- wt% = weight percent of Chromium VI in the chromated coating
- TE = transfer efficiency of the spray gun
Electrostatic = 0.57 (57%) measured for Booth No. 22 while permitting,
HVLP = 0.65 (65%)
- CE = control efficiency of the filter media
Water scrubber = 0.9 (90%)
- Dropout = Percentage of overspray dropout on the floor = 0.22 (22%)

- 2) Area Source at East Complex and West Complex:

Chromium VI emissions⁴ (lb/year) = Usage X Density X wt% X (1-TE) X (1-Dropout)

Where:

- Usage = usage of chromated coating, gallons/year
- Density = density of chromated coating, lb/gallon
- wt% = weight percent of Chromium VI in the chromated coating
- TE = transfer efficiency of the spray gun, HVLP = 0.65 (65%),
Conventional gun = 0.5 (50%)
- Dropout = Percentage of overspray dropout on the floor = 0.22 (22%)

Chromium VI emissions were calculated using 1991 throughput data and a strategy was developed for comparison between mass balance and source test method. Also, the same strategy was utilized to prioritize the installation of retrofit controls on spray booths. Figure 1 shows the comparison of Chromium VI emissions for East Complex sources and Figure 2 shows the comparison of Chromium VI emissions for Y12 facility spray booths.

Y12 Tank Line. Since the tank line at Y12 facility maintains a constant concentration of Chromium VI in the solution and the emission factor established for this process could not be

extrapolated to any other process at NAD, an emission factor was developed which depends on the number of operating hours (i.e. pounds of Chromium VI emission/hour). Therefore, in order to calculate Chromium VI emissions, the only variable needed is number of operating hours per year.

$$\text{Chromium VI emissions (lb/year)} = \text{Number of operating hours/year} \times (\text{Emission Factor}^{16}, \text{pounds of Chromium VI emission/hour})$$

Based on mass balance, Chromium VI emission from the tank line was calculated to be 2.12 lb/year. After source test, the emission was calculated to be 0.38 lb/year. NAD was able to demonstrate 82% reduction based upon utilization of source test results.

CONCLUSION

As demonstrated in Figure 1 and Figure 2, due to source test results, NAD has documented approximately a 90% reduction in Chromium VI emissions from spray booth operations where HVLP guns are used and conventional dry filters are installed for particulate control. For booth No. 22, 23, and area source, emission factors derived from the source test could not be extrapolated because of dissimilarities with the tested sources; only the 22% dropout rate measured at Y12 facility was used in the mass balance emission estimation method to calculate Chromium VI emissions. Figure 2 shows that emissions from electrostatic booths at Y12 are reduced by 96% because of the source test. Spray booth operations at West Complex have also realized approximately a 90% reduction in Chromium VI emissions because of the source test on booth No. 2 at East Complex. Figure 1 shows the comparison of Chromium VI emissions from spray coating operations at East Complex. Figure 2 shows the comparison of Chromium VI emissions from Y12 electrostatic booths and HVLP booths. It also shows the comparison after HEPA filters installation. After HEPA filters, Chromium VI emissions are practically negligible.

The significant emission reductions may be the result of higher transfer efficiency of the applicator, dropout rate, and control efficiency of the filter system. Further study is required to determine the specific cause of the significant difference between mass balance calculations and source test results, since the transfer efficiency of the applicator and the control efficiency of the filter media were not measured while conducting source tests.

Other similar sources may benefit from this method if the emission factors are applied after careful comparison of the source configuration, Chromium VI content in coating, type of applicator, and type of control. The 22% dropout rate may also be used by other sources depending on the above referenced comparison.

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Table 1. Candidate sources for source testing.

Facility	Source	Description
Y12	Electrostatic spray booths no. 3 & 4	Automated, robotic electrostatic spray gun, conventional dry filters
Y12	Tank line no. 14	Liquid spray similar to "car wash", no controls
East Complex	Spray booth no. 31W	High Volume Low Pressure (HVLP) gun, manual operation, water scrubber filter/control
East Complex	Spray booth no. 2	HVLP gun, manual operation, dry filter/control, solvent based coating
East Complex	Spray booth no. 2	HVLP gun, manual operation, dry filter/control, water reducible coating

Table 2. Summary of source test results

Source	Emission Factor	Source Test Method
Y12 electrostatic spray booth no. 3 & 4	4.075E-05 pounds of Chromium VI emission/gallon of mixed coating sprayed	SCAQMD Method 205.1
Y12 tank line no. 14	6.63E-04 pounds of Chromium VI emission/hour	SCAQMD Method 205.1
East Complex spray booth no. 31W	6.75E-04 pounds of Chromium VI emission/gallon of mixed coating sprayed	California Air Resources Board (CARB) Method 425
East Complex spray booth no. 2 with water reducible coating	2.62E-04 pounds of Chromium VI emission/gallon of mixed coating sprayed	California Air Resources Board (CARB) Method 425
East Complex spray booth no. 2 with solvent based coating	1.09E-03 pounds of Chromium VI emission/pounds of Chromium VI sprayed	California Air Resources Board (CARB) Method 425

Figure 1. East Complex-Chromium VI emission comparison

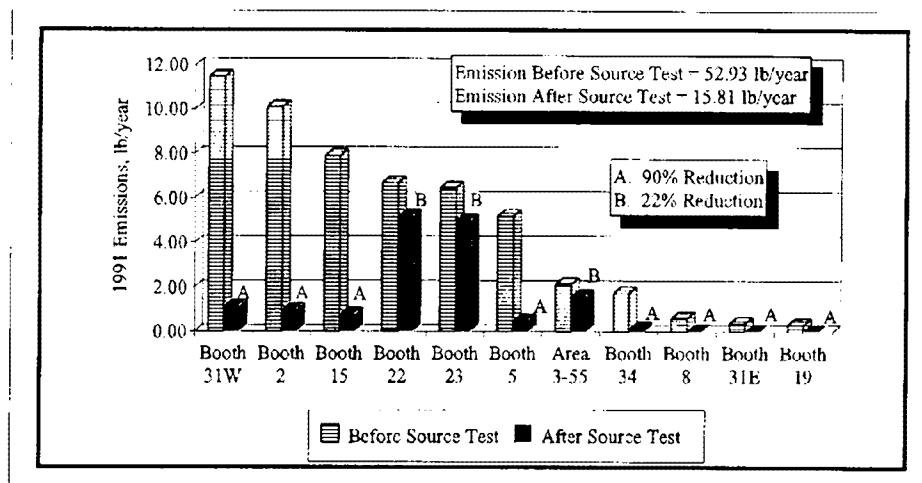
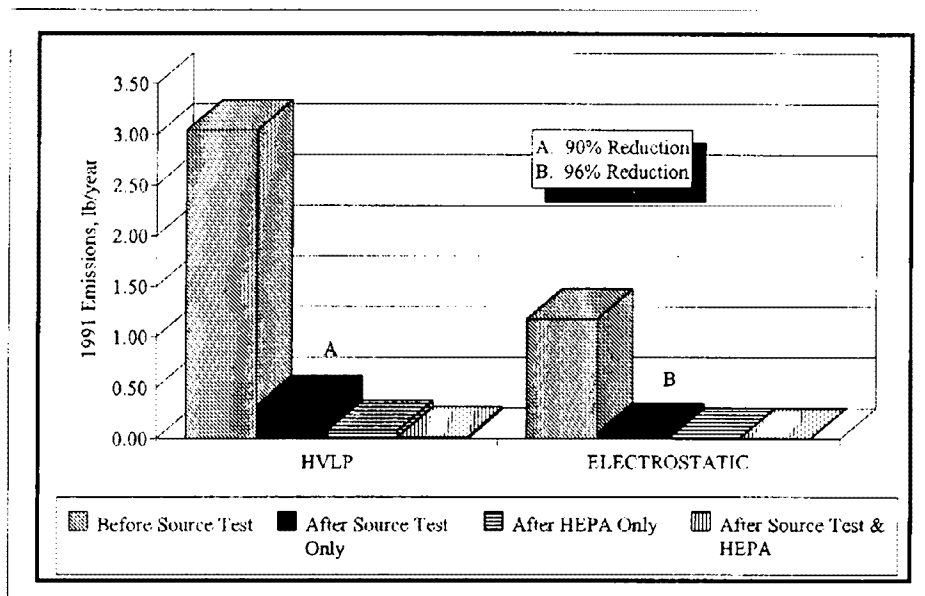


Figure 2. Y12 Facility-Chromium VI emission comparison



The Use of Canisters/GC-MS and a Portable Gas Chromatograph to Characterize Emissions from an Air Stripper

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Abstract

Demonstrating and maintaining removal efficiencies for various volatile organic compounds (VOCs) in an air stripper/carbon adsorption system would ideally be done through continuous real-time monitoring. However, especially for state funded cleanup operations, cost considerations and timeliness of decisions become the overriding factors. Method TO-14, consisting of whole air samples obtained in stainless steel canisters shipped for GC-MS analysis, is the conventional method to speciate and quantitate VOCs at the sub-parts per billion levels found in the carbon adsorption system outlet. Unfortunately, method TO-14 does not provide real time information, and can be expensive. This paper summarizes the results obtained from using both method TO-14 and a portable gas chromatograph with a photoionization detector to characterize emissions from an air-stripper/carbon adsorption system. Field experience indicates that a combination of both methods can achieve the desired results at a reasonable cost.

Introduction

The Washington State Department of Ecology, Toxic Cleanup Program is conducting one of its largest cleanup operations consisting of chromium-contaminated groundwater that threatens the City of Vancouver's drinking water aquifer. Water analysis revealed VOCs, presumably originating at a neighboring specialty gas facility, at levels which the city's wastewater treatment plant would not accept. An air stripper was installed to remove the VOCs present in the chromium-treated stream.

An air permit was needed to operate the air stripper. A carbon adsorption system was determined to be the best available control technology. The Toxics Cleanup Program requested assistance from the Air Quality Program in gathering process air data from the air stripper and carbon adsorption system to obtain that permit.

Trichloroethylene (TCE) was present in water samples at the highest concentration (160 ppb-4.1 ppm). TCE, a carcinogen, has one of the lowest acceptable source impact levels (ASIL) in air (130 parts per trillion), therefore it was flagged as the main VOC of concern from this site. The ASIL is an incremental fence line number used to screen proposed releases of toxic air pollutants.

The Air Quality Program gathered TCE and VOC data through GC-MS analysis of whole air samples obtained in evacuated passivated canisters, and with a portable gas chromatograph (PGC). Berkley et. al. (1) have conducted a comparison of both methods under ambient applications only. Their work suggests that the PGC can produce valid estimates of ambient background concentrations. The work conducted here subjected the PGC to field performance as a source test instrument, at levels varying from parts per trillion to parts per million.

Methods

Near real-time analysis of trichloroethylene was conducted using a portable gas chromatograph (Photovac 10S70). Instrument operating parameters were as follows: the carrier gas was ultra zero air (<0.1 ppm hydrocarbon) with a flow rate of 10 ml/min at 40 PSIG. The column is a dimethyl polysiloxane (CPSil5-Chromapak) capillary, wall-coated type 2 μ df (0.53 mm ID X 10 m) operated at 50 C. The instrument is equipped with a single chamber photoionization detector consisting of an electrodeless discharge tube excited with a radio frequency source producing 10.6 electron volts as described by Barker and Leveson (2). Sample volume was 500 μ L (0.5 ml) and was introduced to the GC by direct syringe injection. The window for retention time peak identification was set at plus or minus 5% initially, and at

plus or minus 10% for the last set of data collected. The minimum peak area was set to 5 mV-seconds.

Calibration standards for the PGC were prepared ranging from 0.26 ppb to 7.4 ppm. Standard preparation was conducted through dilution of saturated headspace vapor above pure reagent-grade TCE liquid injected into Tedlar bags containing one liter of ultra zero air. This method is used in hazardous waste site surveying (3) and published in a technical bulletin (4). The PGC was also challenged with a certified, independent standard (Scott Specialty Gases) at 1.21 ppm TCE level.

Initially only PGC measurements were conducted. Subsequently, six-liter passivated canisters (SIS) were used to obtain grab samples from the ducts in and out of the carbon adsorption system. PGC measurements were conducted before and after the canister grab samples were collected to compare the values obtained through both methods. All canisters were analyzed for 41 compounds by GC-MS (Performance Analytical Laboratory) in accordance with EPA Method TO-14 (5). USEPA/Department of Ecology Environmental Investigations Laboratory at Manchester performed quality assurance review of blanks, calibration curves, surrogate recoveries, mass ratios and quantitation submitted by the contractor.

Air Stripper/Carbon Adsorption System Description and Sampling

An air stripping column (0.76 m ID X 6.7 m high) removes VOCs from the effluent of the chromium treatment system. The off-gas from the air stripper is blown through a manifold into five granular activated carbon units arranged in parallel. A sixth carbon unit is connected in series to the manifold outlet of the other five units. The gas exits into the atmosphere after passing through the sixth unit.

The trichloroethylene concentration into the carbon adsorption tanks varies widely depending primarily on the wells being pumped for treatment. Concentrations in water vary from 160 ppb to 4.1 ppm. This results in calculated carbon adsorption tank inlet trichloroethylene concentrations ranging from 250 ppb to 6.3 ppm.

Samples from the carbon adsorption inlet and outlet were collected at three sampling points. One of the sampling points is located in the air stripper outlet duct that feeds the activated carbon tanks. The other sampling points are at the stack and at the manifold outlet of the five carbon tanks. Stack and duct velocities and volumetric flowrates were determined using USEPA Method 2 (6).

The data gathered provided adequate information to secure the air permit. Further canister sampling to ensure compliance with the permit was accomplished through a contract (SAIC).

Results and Discussion

Out of the forty-one TO-14 compounds analyzed, six were present in the inlet at concentrations above 50 ppb. These six compounds were also identified previously in water analysis of the inlet stream to the air stripper. Table 1 contains the data gathered on these six compounds, and the removal efficiency achieved by the system.

The TCE outlet concentrations were found to be below the detection limit for the GC-MS, and in the part per trillion level for the PGC. Table 2 contains a comparison of the results obtained through both methods. Note that the samples were not obtained simultaneously. The detection limits for the GC-MS analysis were calculated to be 0.5 and 0.1 ppb, both are within the range measured by the PGC. It appears that the PGC/PID exhibited more sensitivity to TCE than GC-MS. If the PGC measured concentrations are true, the GC-MS analysis should have revealed at least trace levels. If the reported detection limits for the GC-MS analysis are correct, the PGC could be reporting false positives. Another question that arises is the suitability of the calibration standards used for the PGC in the parts per trillion level. Certified calibrations in the parts per trillion level are not yet readily commercially available. It is possible that the calibration gas used for the PGC was off by a few hundred parts per trillion.

The above discussion highlights the need for the sampling team to determine what degree of accuracy is necessary for the task at hand. In this case, the measured values were needed to calculate removal efficiencies, and plus or minus one part per

billion is probably an adequate uncertainty limit. At high inlet concentrations that translates to the difference between 99.97% and 99.98%, at the lowest inlet concentrations it is the difference between 99.2% and 99.6% removal efficiencies.

The percent difference between the PGC and TO-14 was 75% for the inlet sample. This difference is large, but expected because the appropriate range of PGC standard was not available in the field that day. As shown in table 2, the calibration concentration used for the PGC for the inlet samples was 260 ppb, but the chromatograms resulting after injection of the inlet sample were full scale, and slightly "topped off".

No interfering peaks were noticed in the PGC chromatograms. Retention time stability was good during each individual sampling set (the coefficient of variation ranged from 0.5% - 1.99%); however as seen in table 3, the mean retention time did shift between sets. The shift could be due to unexplained changes in oven temperature. Unfortunately, the PGC model used for this study does not measure oven temperature.

An apparent false positive was obtained in the September 1993 canister sampling for compliance testing. PGC measurements were not taken that day. Methylene chloride and trichlorofluoromethane were found in higher concentrations in the outlet than the inlet, indicating either external sample contamination or evolution from the carbon tanks of these compounds. The water analysis did not show methylene chloride coming into the air stripper at all. These data lead to an exceedance of the permit conditions. Could this mean improperly regenerated carbon? Although the laboratory blanks did not indicate contamination, without canister field blanks or field duplicates it is hard to determine the source of the levels encountered. Weeks later, when the results arrived, the carbon had already been changed so carbon samples were not available to analyze for the above compounds. This experience points out that it is very useful to have two different analytical tools to double check each other, especially when field blanks or field duplicates were not taken due to cost considerations.

The cost per sample for method TO-14 is \$500, including analysis, canister rental, and quality assurance review. The cost per each PGC run to the Air Quality Program was approximately \$100. The PGC cost per sample was calculated by summing up the capital cost incurred in equipment purchasing, personnel training, and dividing by the total amount of samples analyzed with it to date.

Conclusions

This project served to highlight the strengths and weaknesses associated with both a field PGC and method TO-14. The portable gas chromatograph was capable of quantitating trichloroethylene, for the purpose of determining removal efficiencies, within an adequate uncertainty interval. Laboratory preparation is essential before the trip. Transporting to the field duplicate standards at each expected range is recommended to ensure appropriate quantitation. Standard preparation in the parts per trillion level is the task with the lowest degree of confidence that needs to be accomplished for use of the PGC. Certified standards at those levels are not yet commercially available. The advantage of near real time response of the PGC can not be underestimated. In this case, the ability to obtain data right away served to assure the permitting agency of the control technology effectiveness, and helped to expedite the permit.

Method TO-14 is the method of choice to obtain multi-parameter VOC information with reliable precision and accuracy. However, it is extremely important to ensure that the sampling budget allows for canister field duplicates and field blanks during every sampling exercise. The lack of such leads to incomplete data which renders the data gathered less useful, and, as in this case, may lead to a perceived exceedance of permit conditions.

The cost of method TO-14 is approximately five times higher per sample than the use of PGC. Once the PGC has proven adequate, when compared to method TO-14, at the levels and parameters it is challenged with, its use in combination with occasional canister samples, can result in useful data at less cost. Both methods can be subject to positive (and negative) interferences; therefore, utilizing both methods provides more clues to ascertain the accuracy of the data obtained.

Acknowledgements

The authors would like to acknowledge Mary Beth Hayes, Kimberly Hayden and Joyce Austin who peer reviewed this paper, and Mohsen Kourehdar who participated in this project.

Disclaimer: Mention of trade names, commercial products, contract laboratories or consulting firms does not constitute endorsement or recommendation for use.

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Table 1. Canister/GC-MS Data and Calculated Removal Efficiencies

Compound	Inlet (ppb)	Stack (ppb)	Before final carbon tank (ppb)	Percent Removal Efficiency
acetone	53 J	nd	nd	100
trichlorofluoromethane	1500	180	290 J	88.2
cis-1,2 dichloroethylene	57 J	nd	nd	100
1,1,1 trichloroethane	25 J	17	0.11 J	63.6
trichloroethylene	5500 J	nd	nd	99.99
tetrachloroethylene	300 J	0.19 J	nd	99.96

The J qualifier signifies that the compound was detected at a concentration below the calibration curve range.

Table 2. Trichloroethylene Concentrations Measured with the PGC and TO-14

Sample	Date	Calibration Concentration (PPB)	Mean of PGC Measured Concentration (PPB)	Mean of TO-14 Measured Concentration (PPB)
Stack	4-12-93	0.74	0.23	
Before final carbon tank	4-12-93	0.74	0.25	
Inlet	4-12-93	7400	360	
Stack	5-13-93	0.250	0.45	Not Detected (Detection limit was 0.5 ppb)
Before final carbon tank	5-13-93	0.250	0.30	Not Detected (Detection limit was 0.5 ppb)
Inlet	5-13-93	250	1400	5500

Table 3. PGC Retention Time Stability for Trichloroethylene

Outlet and Inlet Samples			Calibration Runs		
Number of runs	Retention time mean (seconds)	Coefficient of variation	Number of runs	Retention time mean (seconds)	Coefficient of variation
8	100.48	1.02%	4	98.8	1.99%
3	150.6	1.07%	1	144.7	-
6	146.9	0.72%	1	140	-
3	133	0.52%	1	136	-

Improvements in Preparation of Samples Generated by SW-846 Method 0010

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A field evaluation study for SW-846 Method 0010 was conducted at a stationary source emission site with a high moisture content. The recovery of the dynamically spiked analytes and the spikes added before the laboratory preparation of the XAD-2® resin were low. The sampling train media had been prepared according to Method 0010 protocol, so the laboratory procedures were examined in detail for sources of error. The XAD-2®, wet because of the source matrix, was difficult to fully remove from the glass trap using only methylene chloride. Because Method 0010 does not specify the solvent to use for trap rinsing, and since the probe was washed in the field with a 50:50 mixture of methylene chloride and methanol, this mixture was used to transfer the XAD-2® from the trap to the Soxhlet extractor. The low recoveries were attributed to the presence of the methanol in the final extract. (The methanol is removed from the probe rinses during the laboratory sample preparation process.) A proposed method will be presented that permits the physical removal of wet XAD-2® from the sampling trap without the use of methanol and an alternate procedure is provided for removal of methanol from the trap rinse before sample extract concentration.

INTRODUCTION

A field study was performed using dynamic spiking techniques to evaluate the performance of SW-846 Method 0010 (Modified Method 5 Train) for sampling and Method 8270 (GC/MS with capillary column) for the analysis of semivolatile halogenated organic compounds listed in the Clean Air Act Amendments of 1990, Title III. Using the guidelines of EPA Method 301¹, quadruple Method 0010 sampling trains with four collocated probes were used. Dynamic spiking equipment and procedures had been developed and evaluated to allow dynamic spiking of a methylene chloride solution of the compounds of interest for the duration of each Method 0010 sampling run.² Two trains were spiked and two trains were unspiked during each run.

EXPERIMENTAL

The field evaluation study was conducted at a facility where waste chemicals were incinerated in a coal-fired boiler. A "biosludge" consisting of 10 percent organic matter and 90 percent water was fed continually to the incinerator. A site presurvey showed that none of the proposed analytes was present and there was approximately 10 percent moisture in the background emissions. Method 0010 sampling trains were recovered in the field, and components were shipped to the laboratory for preparation and analysis. Methylene chloride extracts were generated of the following train components: 1. Filter/front half rinse, 2. XAD-2® sampling module and Condensate/condensate rinse. The final volume for these sampling train components was 5 mL, rather than the 1 mL final volume specified by Method 8270.

RESULTS AND DISCUSSION

Results for the GC/MS analysis are summarized in Table I. Eight sampling runs using quadruple trains had been performed in the field; acceptable results were obtained for only four runs (1,2,3,6). For those four runs, most compounds results were generally comparable to laboratory and field results.^{2,3} However, results from other sampling runs showed very low recoveries for the surrogate compounds and many of the spiked compounds were not detected.

Table I
Summary of Results for All Eight Runs and All Sampling Trains,
Using Surrogate-Corrected Data

Run	Train A Spiked			Train B Spiked			Train C Unspiked			Train D Unspiked		
	X	C	F	X	C	F	X	C	F	X	C	F
1	y	y	y	y	y	y	y	y	y	y	y	y
2	y	y	y	y	y	y	y	y	y	n	y	y
3	y	y	y	y	y	y	y	y	y	y	y	y
4	n	y	n	n	y	n	y	y	n	y	y	y
5	Z	y	y	Z	y	n	y	y	y	y	y	y
6	y	y	n	y	n	n	Z	y	y	Z	y	y
7	n	n	n	y	y	y	Z	y	Z	y	y	Z
8	n	y	Z	y	y	y	Z	y	y	y	y	Z

Note: Recoveries for C and D Trains refer to recoveries of surrogate compounds and isotopically-labeled analogs. X - XAD-2® module; C - Condensate fraction; F - Filter fraction; Z - Partial success; some but not all analytes detected; y - All analytes detected; n - No analytes detected.

Careful examination of the data for all of the sampling runs showed that, in general:

1. Recoveries of the surrogate compounds spiked in the laboratory were low for the XAD-2® where most of the organic compounds were expected to be retained,
2. Isotopically-labeled compounds spiked in the laboratory to track recovery were frequently not observed at all,
3. The majority of the analytes spiked in the field were not observed, and
4. Recoveries for field-spiked analytes that were observed ranged from 4 percent to 63 percent.

Since the surrogate compounds and isotopically-labeled compounds are spiked in the laboratory after return of the sampling train components, problems were in the laboratory preparation rather than in the field spiking.

The important parameter is recovery of spiked organic compounds from XAD-2® since this is where they are located. Recovery results for these field samples were sufficiently different from previous recovery results observed from laboratory² and field studies³ that an explanation for the low recoveries was pursued. Quality control results from method blanks (filters, water, solvents, XAD-2®) were examined. Recoveries from method blanks were acceptable to high, indicating that general laboratory sample preparation and analysis procedures were done properly.

Method spike (train components spiked with analytes and surrogate compounds in the laboratory) recovery data were also examined. The method spikes are extracted and analyzed with the field samples. The results obtained for the XAD-2® method spikes (Table II) are typical; acceptable to high recoveries indicated that surrogate and sample spiking, preparation, and analysis procedures were in control.

Table II

Spiked Compounds and Surrogates Recovered
from Dry Method 0010 XAD-2® Traps

Compound	Theoretical Amount	% Recovery			
Surrogate	(µg)	MS-A	MS-B	MS-C	MS-D
2-Fluorophenol	991	107	99	108	102
Phenol-d ₅	1010	112	106	113	108
Nitrobenzene-d ₅	509	112	95	104	98
2-Fluorobiphenyl	490	119	115	122	111
2,4,6-Tribromophenol	997	67	74	73	66
Terphenyl-d ₁₄	501	135	112	115	108
Epichlorohydrin-d ₃	250	99	68	76	71
Chlorobenzene-d ₅	350	94	91	106	93
1,1,2,2-Tetrachloroethane-d ₂	254	114	93	99	91
Bis(chloroethyl)ether-d ₈	333	104	91	95	87
Benzyl chloride-d ₅	244	103	122	130	117
2,4,5-Trichlorophenol-d ₂	129	ND	ND	106	ND
Targets	(µg)	% Recovery			
Epichlorohydrin	199	991	68	72	74
cis-1,3-Dichloropropene	159	87	67	71	76
trans-1,3-Dichloropropene	34	365	77	80	86
1,1,2-Trichloroethane	195	98	77	84	86
1,2-Dibromoethane	196	95	84	94	95
Tetrachloroethene	195	86	82	92	92
Chlorobenzene	200	99	92	96	100
Bromoform	202	101	101	120	127
1,1,2,2-Tetrachloroethane	200	101	84	91	92
Bis(chloromethyl)ether	252	80	70	72	74
1,4-Dichlorobenzene	226	96	119	125	131
Benzyl chloride	202	102	95	105	104
Hexachloroethane	185	107	103	112	114
1,2-Dibromo-3-chloropropane	272	103	109	118	121
1,2,4-Trichlorobenzene	198	104	120	132	135
Hexachlorobutadiene	200	107	126	139	148
Benzotrichloride	199	106	126	141	142
2-Chloroacetophenone	229	112	108	116	120
Hexachlorocyclopentadiene	204	135	133	133	133
2,4,6-Trichlorophenol	237	109	121	129	129
2,4,5-Trichlorophenol	194	101	127	130	139
Hexachlorobenzene	222	102	110	124	121
Pentachlorophenol	202	83	100	87	54
Pentachloronitrobenzene	216	101	106	113	114
Chlorobenzilate	200	116	110	123	130
3,3'-Dichlorobenzidine	190	142	140	171	158

An examination of the quality control samples, indicated that a systematic error in sample spiking, sample preparation, or analytical procedures did not appear to be the cause of the low recoveries. Method blanks and method spikes were prepared and analyzed with the field samples,

using the same spiking solutions and the same procedures. The original extracts, which had been archived after mass spectral analysis, were next examined visually to determine if the appearance of these extracts was qualitatively or quantitatively different from the appearance of the quality control samples. Several key differences were observed:

Method blanks and method spikes were light yellow in color and had the appearance of several mL of clear organic solvent. The color of field sample extracts ranged from clear to nearly brown. Some of the field extracts were clearly completely aqueous, with only small pools of organic liquid floating on top, two phases were clearly visible in some of the field extracts; and many of the field samples were not methylene chloride extracts, since only a slight odor of methylene chloride was detected when vials were opened.

Laboratory sample preparation procedures and observations were carefully reviewed with laboratory staff. The observation was reported that many of the field samples required far longer (3-4 hours) than the usual amount of time (20-30 minutes) to achieve concentration to 5 mL using Kuderna-Danish concentration procedures.

The obvious difference between the quality control samples and the field samples was that the laboratory-generated sampling train media were dry, while the field XAD-2® samples were wet because of the moisture content of the source. Dry XAD-2® can simply be poured from the sampling module to the Soxhlet extraction apparatus. Wet XAD-2® does not pour, but sticks to the glass walls of the sampling module and is not readily moved from the sampling module with methylene chloride rinses. Typical procedures used for the removal of wet XAD-2® from the sampling module include repeated rinses with methylene chloride, which frequently leaves significant amounts of the wet XAD-2® in the sampling module, or tapping the sampling module against the laboratory bench top, which often results in breakage of the sampling module. Laboratory staff had tapped the XAD-2® from the modules to remove as much as possible, rinsed the walls of the module with methylene chloride, and performed a final rinse of the sampling module with methanol. If a sufficiently large amount of methanol is present when sample concentration is performed, methylene chloride will be driven off rather than methanol, and the final extract will consist of a methanol solution with significant losses of surrogate compounds and analytes.

The rinses used in the field recovery of Method 0010 train components consist of 50:50 methylene chloride: methanol, which form a homogeneous solution. The methanol can be separated from the methylene chloride only if sufficient water is added to create two distinct phases. However 100 mL of methylene chloride can hold up to 15 mL of water without separating into two distinct phases. According to the method, sample extracts are dried by filtering through a bed of dry sodium sulfate. If sufficient water is present, the sodium sulfate will cake and will not dry the extract efficiently. Thus, after drying, if the sodium sulfate cakes, an extract may consist of methylene chloride, water, and methanol, all in one phase. If a solution of this composition is concentrated, methylene chloride will be lost before the water and methanol are lost, resulting not only in a water/methanol solution if sufficient quantities of water and methanol are present in the original extract but also in loss of target compounds due to higher concentration temperatures. However, if sufficient water (50-100 mL) to effect separation of phases is added prior to extraction, the methanol will be driven into the aqueous phase and excellent recoveries of spiked surrogate compounds and analytes can be obtained.

Laboratory experiments were conducted to reproduce the conditions under which the field samples had been extracted. Replicate samples of dry XAD-2® were spiked with surrogate compounds and analytes to provide a baseline for recovery. Excellent recoveries and good reproducibility were obtained. Next, wet XAD-2® was prepared and spiked with surrogate compounds and analytes. The 40 g quantity of XAD-2® which is contained in the sampling module of the Method 0010 train retains approximately 50 mL of water when water is poured through the resin bed. This 50 mL of retained water does not produce a distinct water layer when the spiked wet XAD-2® is extracted and analyzed. When the extracts from the wet XAD-2® were concentrated and analyzed, recoveries were slightly lower than the recoveries obtained with dry XAD-2® and

reproducibility was slightly poorer, but both recovery and reproducibility were acceptable. The wet XAD-2® was prepared and spiked in the Soxhlet extractor, so no transfer of wet XAD-2® was required. Wet XAD-2® alone does not depress recoveries significantly.

The major problem appeared to occur in the transfer of the wet XAD-2®. A procedure was therefore developed to transfer the wet XAD-2® without the use of methanol, using the apparatus shown in Figure 1. The glass wool is removed from the end of the sampling module and placed in the Soxhlet extractor to ensure extraction. A small piece of pre-cleaned glass wool is placed in the arm of the Soxhlet extractor to ensure that no XAD-2® enters the side-arm. The sampling module is inverted (glass frit up) over the Soxhlet extractor, approximately 5-10 mL of methylene chloride is added above the glass frit, and air pressure created by squeezing the rubber bulb shown in Figure 1 is used to gently but firmly push the methylene chloride through the frit, forcing the resin out of the sampling module. This process is repeated 3 to 5 times, and a Teflon® wash bottle containing methylene chloride is used to rinse the walls of the sampling module to transfer resin which adheres to the walls of the sampling module. After 3-5 methylene chloride rinses, no more than a monolayer of XAD-2® usually remains in the sampling module. The glass wool plug is removed from the side arm of the Soxhlet and added to the Soxhlet. A flowchart for the overall method is shown in Figure 2. This transfer procedure has been used successfully to transfer XAD-2® from sampling modules used in sampling a source with 55 percent moisture: excellent recoveries of both surrogate compounds and spiked analytes were obtained. In addition, this procedure is far more efficient than the procedure of tapping the resin out of the sampling module. Three transfers using the rubber bulb can be performed in one or two minutes.

The investigation with subsequent laboratory study illustrates the value of sufficient quality control data in determining the cause of a problem with data quality. A new procedure for the preparation of Method 0010 train components for analysis by SW-846 Method 8270 has been written. In this procedure, the use of methanol in the laboratory is directly and specifically prohibited to ensure that the final extracts consist of methylene chloride, not a mixture of methylene chloride and methanol. Also, addition of sufficient water to ensure that two distinct phases are produced when both water and methanol are components of the solution (for example, in the sampling train rinses of the front half and the condensate) is a required part of the procedure. This procedure is currently being subjected to EPA review.

DISCLAIMER

The information in this document has been funded wholly by the United States Environmental Protection Agency under contract 68-D1-0010 to Radian Corporation. It has been subjected to the Agency's peer review and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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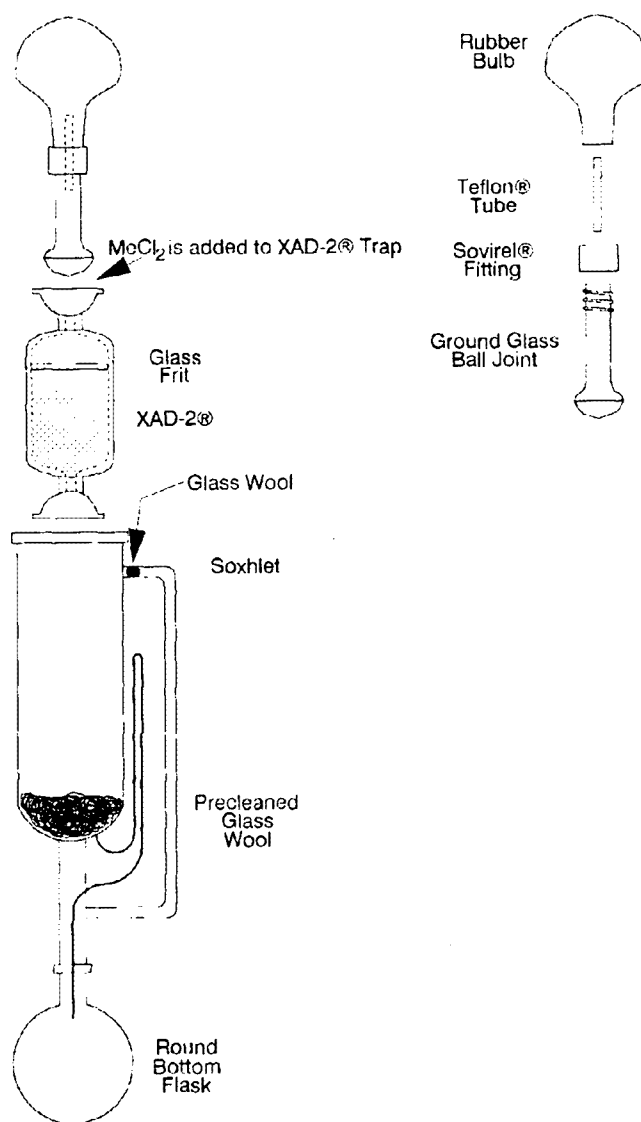


Figure 1. Transfer of Wet XAD-2®

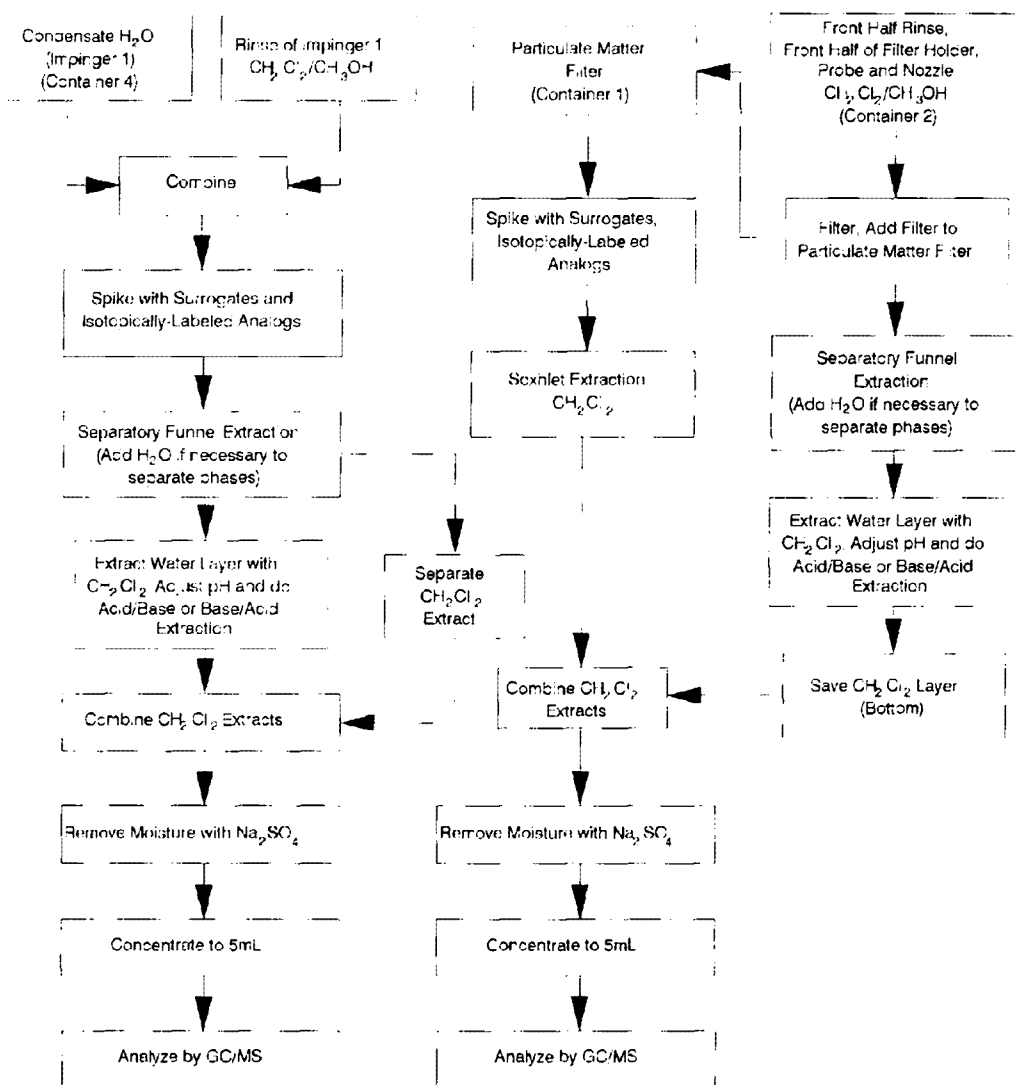


Figure 2. Sample Preparation Scheme for Method 0010 Train Components

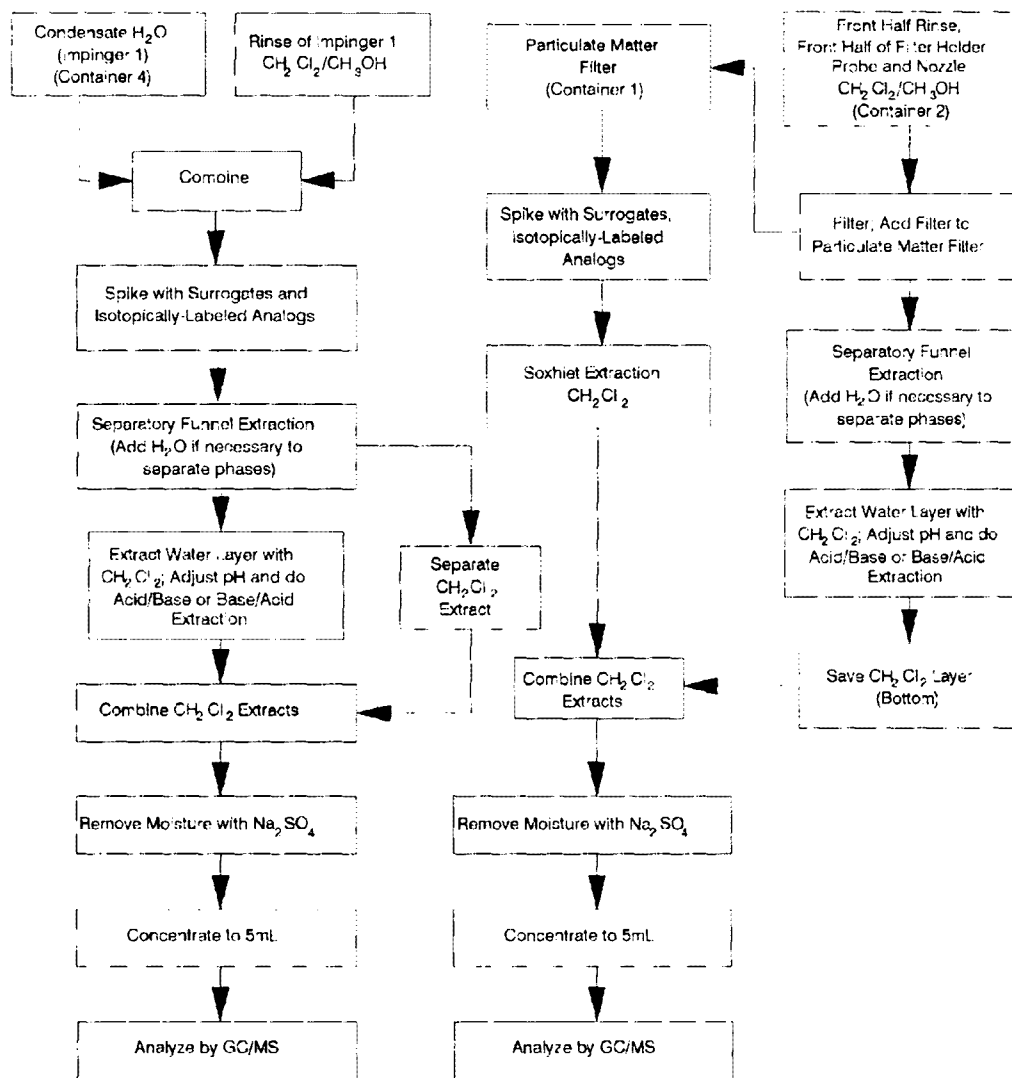


Figure 2. (Continued)

EVALUATION OF GAS CHROMATOGRAPHY DETECTION SYSTEMS FOR TOTAL GASEOUS NONMETHANE ORGANIC COMPOUNDS

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ABSTRACT

The development of an emissions monitoring prototype instrument to provide continuous or semi-continuous quantitative measurement of total gaseous nonmethane organic carbon (TGNMOC) emissions from stationary sources will allow for better characterization and control of compounds under the Clean Air Act Amendments of 1990, Title III. To meet this development goal a search has been initiated to identify detection systems for TGNMOC that are both simple to use and accurate. The measurement of oxygenated compounds are of particular interest since many emission sources may have a large proportion of them. Detection system identification has been accomplished by conducting a search of detector manufacturers' literature, and talking with manufacturers' technical personnel. Several detector systems, marketed as appropriate for TGNMOC measurement, have been identified and evaluated in the laboratory. The detection systems evaluated include a Catalyzed Flame Ionization Detector and a Thermionic Ionization Detector, both produced by DETector and Engineering Technology, Inc., and an Oxygen-Flame Ionization Detector and an Elemental Analyzer, both produced by Fisons Corporation. The primary performance goal for the detection systems required that those systems yield equal response for all organic compounds in a mixture, including oxygenated compounds, based on carbon number. None of the detection systems evaluated met the primary performance goal of uniformly measuring organic carbon, regardless of the chemical structure of compounds in the sample. While some success was realized for many classes of organic compounds, oxygenated compounds presented a challenge that none of the detection systems could master.

INTRODUCTION

The primary objective of this effort was to identify an appropriate detection system for incorporation into a prototype total gaseous nonmethane organic carbon (TGNMOC) emissions monitoring instrument. The accurate measurement of TGNMOC is critical to the characterization of many industrial processes.

Although the flame ionization detector (FID) has been used as a universal detector for complex mixtures of organic compounds, compounds containing heteroatoms have been shown to yield lower response than straight chain aliphatic hydrocarbons,¹ giving an underestimate of organic carbon. The Catalyzed Flame Ionization Detector (CFID) produced by DETector Engineering and Technology, Inc. (Walnut Creek, CA) is marketed as a detection system that provides enhanced responses for heteroatom compounds. The CFID is a combination ignitor, polarizer, and catalytic source made of nickel/aluminum oxide-coated ceramic. Ionization is achieved with a hydrogen/air flame and all organic compounds are ionized to some extent. The sensitivity of the CFID is

controlled by varying the heating current applied to the catalytic source. The higher the current applied, the greater the source temperature and the greater the sensitivity. The current setting, thermal conductivity, and flow rates of the carrier gases influence the temperature of the source to some extent.

The Thermionic Flame Ionization Detector (TID), also produced by DETector Engineering and Technology, is marketed as an oxygen-selective detector when operated in a nitrogen (N_2) environment. The TID is a heated, alkali-coated ceramic source. Ionization is achieved by the extraction of an electrical charge from the heated thermionic source, controlled by the surface work function, the surface temperature and the gas composition surrounding the source surface. The manufacturer has reported very high specificity and sensitivity to compounds containing electronegative functional groups from a low work function source operated at temperatures around 300°C in a N_2 environment.₂

The Oxygen-Flame Ionization Detector (O-FID) produced by Fisons Instruments (Danvers, MA) is marketed as the recommended detection system of the European Economic Community and the U.S. Environmental Protection Agency (U.S. EPA) for analysis of oxygenated compounds in gasoline. The O-FID is comprised of a cracking reactor, an activated nickel methanizer, and a standard FID. The cracking reactor is a platinum-rhodium catalyst tube that is heated to about 1200°C . All compounds eluting from a chromatographic column flow through the cracking reactor and are disintegrated into their individual elements. After disintegration, carbon monoxide (CO) is formed from elemental carbon and oxygen (O_2). Any unreacted carbon is deposited on the inside of the reactor tube. Hydrogen (H_2) passes undetected through the methanizer and FID assembly. The methanizer converts the CO into methane for detection by the FID. The signal produced is proportional to the O_2 contents in the sample. With a split rate of 1:80, the O-FID has a detection limit of 5-10 ppmC with a linear range of three orders of magnitude. The range is limited by the cracking capacity of the reactor. The cracking capacity depends upon the cracking temperature of the reactor and the individual type of molecule to be disintegrated, therefore, the cracking temperature only has to exceed a molecule's reaction temperature threshold to obtain complete cracking.

Fisons also produces an Elemental Analyzer (EA) marketed as a detection system for simultaneous carbon, H_2 , N_2 , and O_2 determinations from solid, liquid or gas samples. The sample to be analyzed is injected into a sealed combustion chamber, that is packed with catalytic materials (i.e., nickel coated carbon) and is maintained at a temperature of around 1060°C . As the sample enters the combustion chamber, O_2 is injected into the helium (He) carrier gas that is flowing through the chamber. The resulting catalytic oxidation will theoretically assure complete oxidation of the sample. The combustion gases and N_2 are swept through the reduction reactor and into a chromatographic column by the He carrier gas. The measured concentration of each compound is determined by a Thermal Conductivity Detector (TCD) as they elute from the column. High detection limits and detection of methane (CH_4) and CO_2 interfere with this detection systems application to TGNMOC.

EXPERIMENTAL PROCEDURES

The FID, CFID and TID were evaluated with liquid standards containing oxygenated and non-oxygenated compounds as listed in Table 1.

The CFID assembly was installed on the existing FID tower of a Varian 3400 Gas Chromatograph (GC). Operating conditions of the GC/CFID system are listed in Table 2. The parameters listed in this table were kept constant throughout the evaluation of the CFID. The current applied to the CFID source was varied to evaluate the oxygenated compounds responses and to choose the current setting at which the CFID responded linearly to number of carbons, with the sensitivity required to meet the project's stationary source sampling goals. An example chromatogram with identified peaks from the CFID evaluation is shown in Figure 1.

Table 1
Response Factors in Area Counts/nmolC for Data Using the
Flame Ionization Detector and the Thermionic Ionization Detector

Analyte	CFID Response Factor	FID Response Factor	TID Response Factor
Acetaldehyde	7324	8696	9415
Methanol	4388	12657	41098
Acetone	6769	20176	7132
2-Butanone	6997	15420	7283
Benzene	12967	20092	9
Butyl Cellosolve®	7647	15548	130705
Benzaldehyde	8008	17800	395
Hexane	*	18316	4134
Heptane	*	13866	34520
iso-Octane	*	23113	8097
Nonane	*	18502	23918
Methylene Chloride	*	15404	127274
Triethylamine	*	12308	454899

* -- Not Analyzed

The TID was installed on the existing FID tower of a Varian 3400 GC. Operating conditions for the optimization and evaluation experiments are listed in Table 2. The TID was optimized and evaluated for oxygenated compounds by analysis of a liquid standard containing oxygenated compounds. Liquid standards containing aliphatics, a chlorinated compound, and a substituted amine were also analyzed under the same operating conditions as the oxygenated compounds.

For comparison, all compounds analyzed by the GC/TID system were also analyzed by a conventional GC/FID system.

RESULTS

The results from the evaluation studies of the CFID, the FID, and the TID are presented graphically in Figures 2, 3, and 4, respectively. For comparability, the response factors are stated in units of area counts per nanomole of carbon. Nanomoles of carbon are the moles of analyte injected onto the GC column multiplied by the number of carbons associated with a molecule of the analyte. The response factors are plotted against the number of carbons in each compound analyzed. Table 3 lists each compound analyzed and the number of carbons in each compound. The average response factor for the detection system represented in each graph was also plotted. In an ideal situation, the response factor from each specific detector should be the same for each compound, regardless of the number of carbons. The horizontal line shown in each graph represents the ideal response.

CONCLUSIONS

Five detectors were evaluated for their ability to provide a linear response to organic carbon contents in oxygenated and non-oxygenated organic compounds. The FID and CFID did provide a linear response to organic carbon content in volatile oxygenated compounds, and

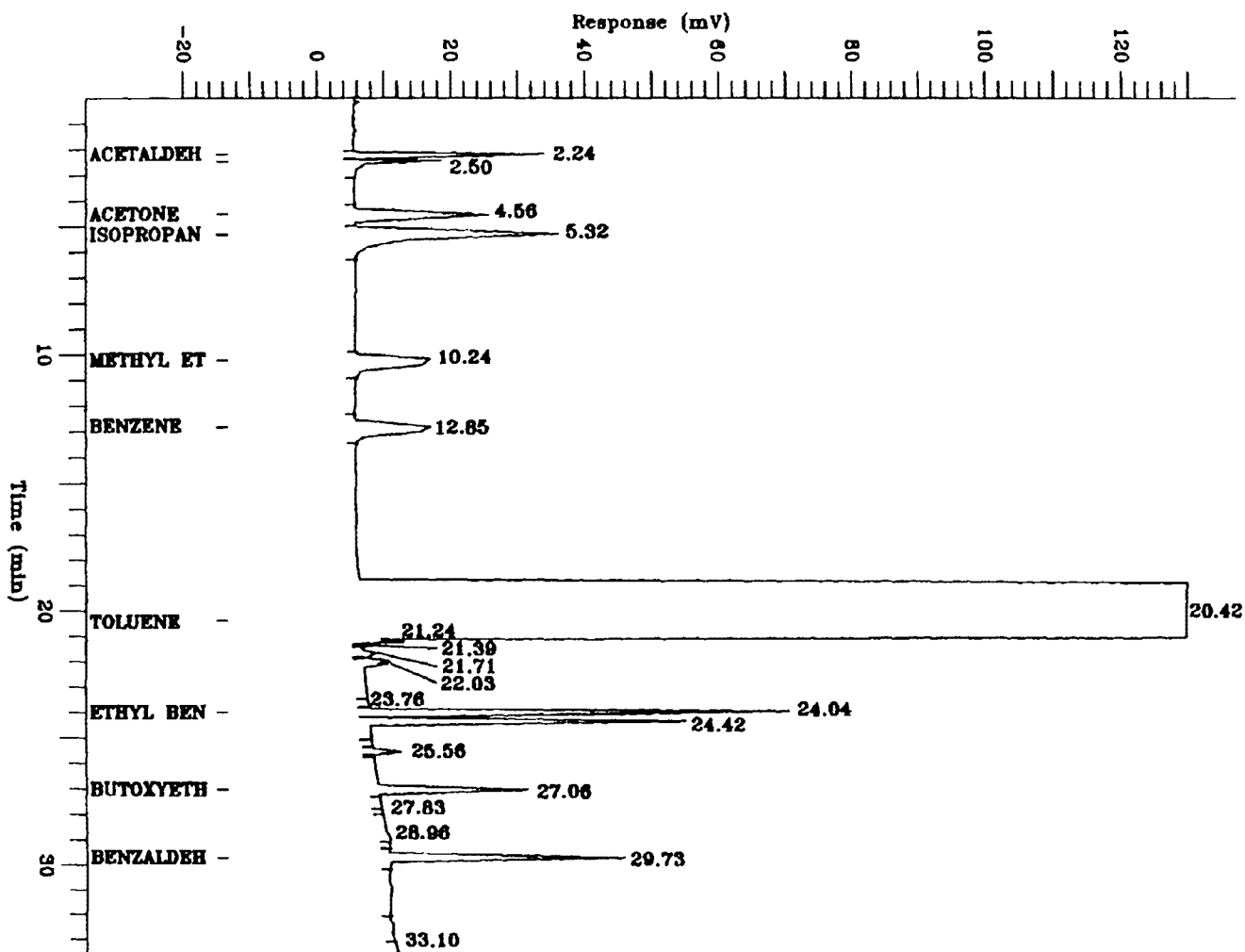


Figure 1. Example GC/CFD Chromatogram

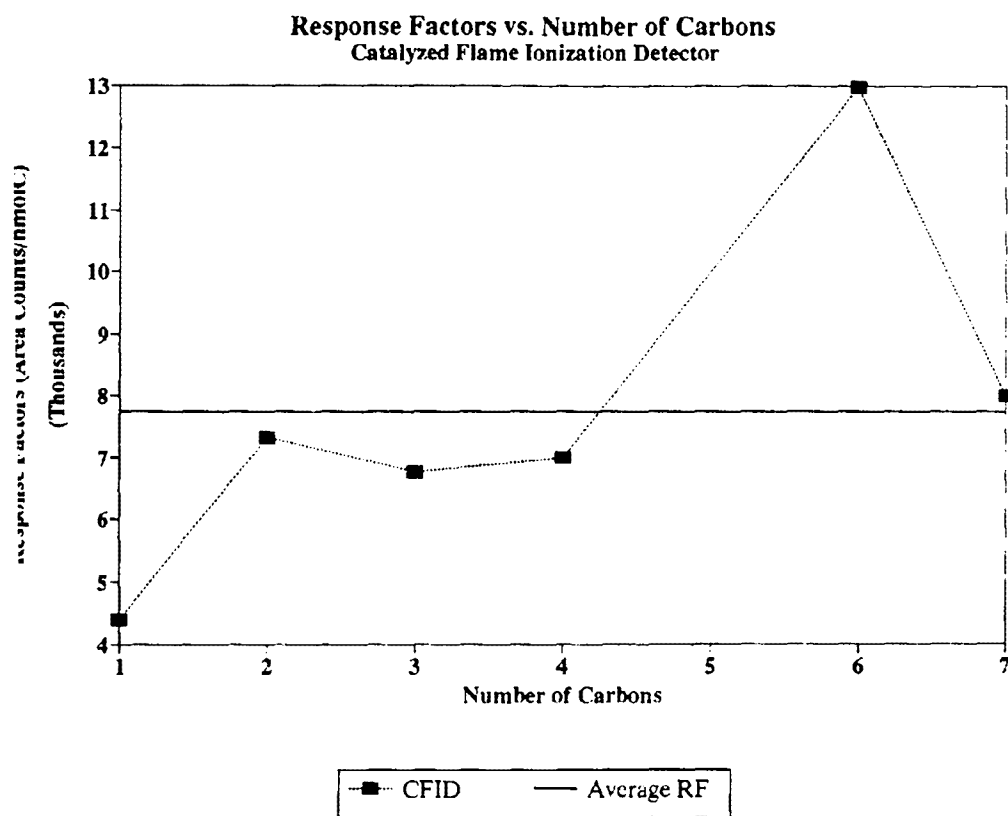


Figure 2. Comparison of Measured Response Factors and the Average Response Factor for the CFID

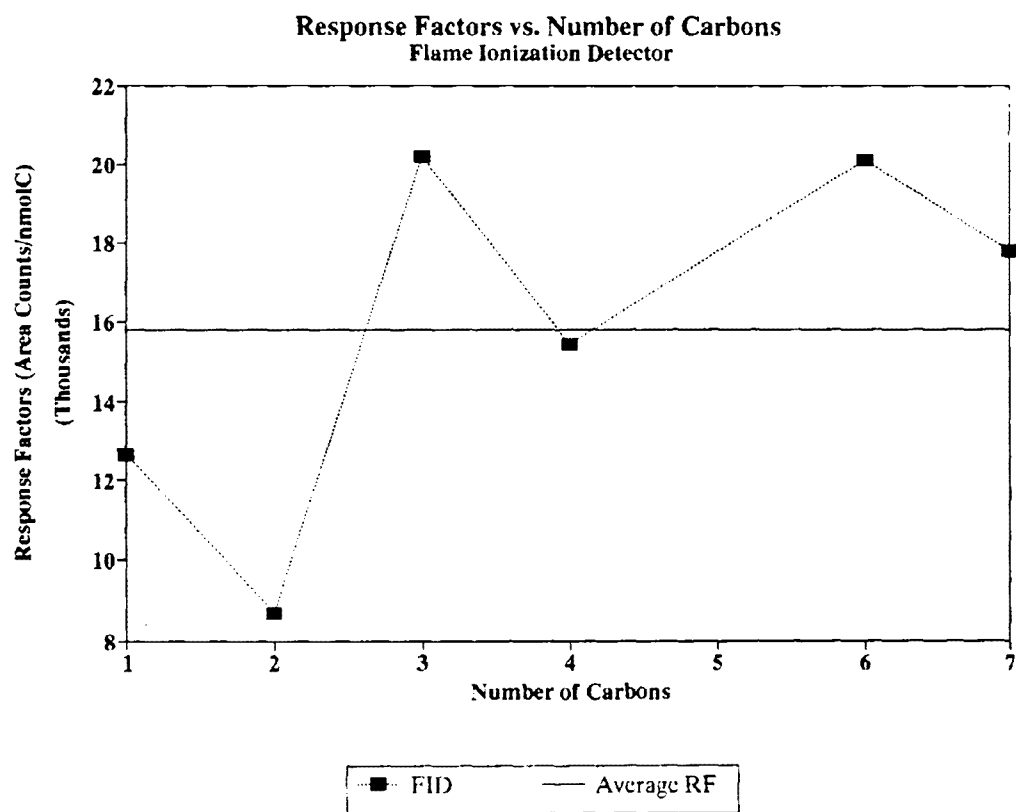


Figure 3. Comparison of Measured Response Factors and the Average Response Factor for the FID

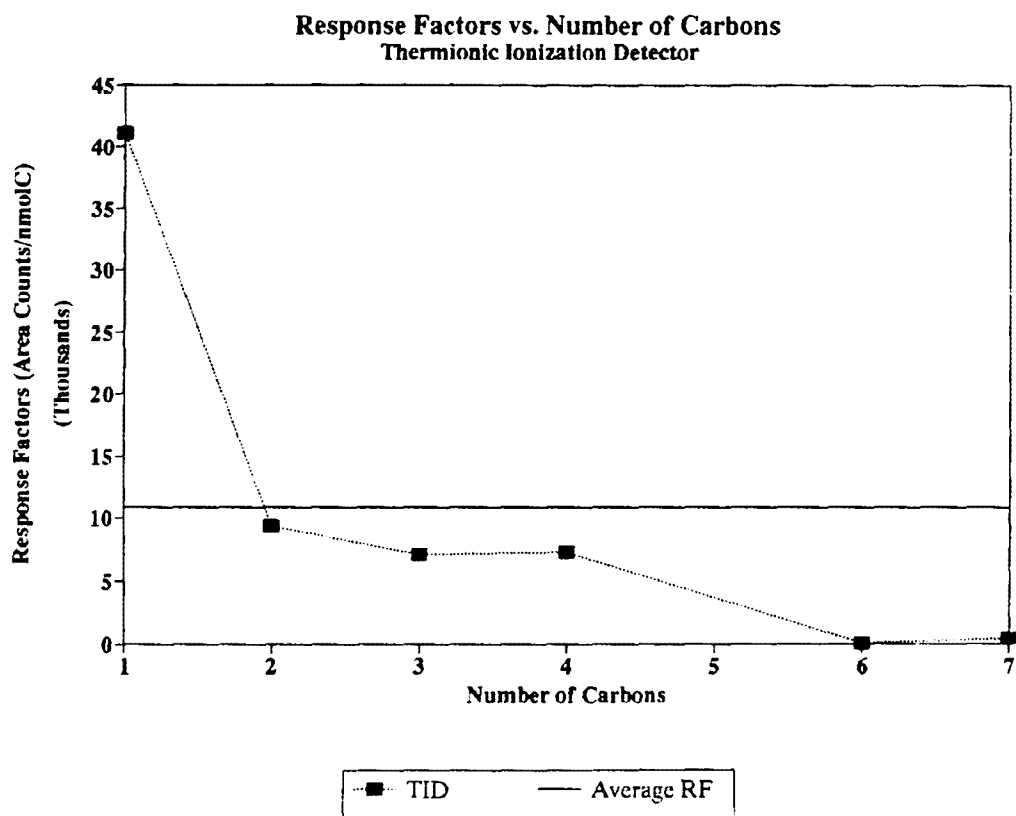


Figure 4. Comparison of Measured Response Factors and the Average Response Factor for the TID

Table 2
Operating Parameters for Detection Systems Evaluated

Instrument	Varian 3400 GC with FID tower and cryogen capability	
Column	J&W DB-624 30 m x 0.53mm Serial #S9516312	
Carrier Gas	5.8 mL/min (He) for FID, CFID 4.2 mL/min (He) for TID	
Detector: Gases (FID, CFID)	Gas 1 (Air): 304 mL/min Makeup (He): 30 mL/min	Gas 2 (H ₂): 30 mL/min
Detector Gases (TID)	Gas 1 (N ₂): 19.5 mL/min (subtract carrier gas flow rate)	Gas 2 (N ₂): 76.9 mL/min
Temperature Set-points (FID, CFID)	Injector: 200°C Detector: 205°C Oven: 25°C for 8 min, then ramp @ 4°C/min to 110°C	
Temperature Set-points (TID)	Injector: 200 °C Detector: 320°C (Condition 3) Oven: 25°C for 8 min, then ramp @ 4°C/min to 110°C	
Current Applied to Source (CFID, TID)	CFID: 3.0 amps.	TID: 3.2 amps.
Injection Volume	2 µL by autosampler	
Analysis Time	40 min. for separation of compounds in each standard	
Data Acquisition System	Turbochrom (Perkin-Elmer)	

Table 3
Compounds Analyzed and Associated Number of Carbons

Compound	Number of Carbons
Methanol	1
Acetaldehyde	2
Acetone	3
Methyl Ethyl Ketone (2-Butanone)	4
Benzene	6
Benzaldehyde	7

other non-oxygenated organic compounds, such as benzene. However, they did not yield a 1:1 carbon response relationship between these two groups.

The TID provided enhanced responses specific for alcohols (methanol, Butyl Cellosolve®), chlorinated compounds (methylene chloride) and amines (trimethylamine). The detector did not respond well (i.e., low sensitivity) to aromatics such as benzene, or aldehydes and ketones such as benzaldehyde, acetone, or acetaldehyde. The detector did not provide a linear response factor for organic carbon in unsubstituted aliphatic compounds. The TID also did not yield a 1:1 carbon response relationship, for any of the compounds considered. However, it should be noted that a comparison of TID responses to heptanone as a representative ketone, octanal as a representative aldehyde, and 1-decanol as a representative alcohol, was performed by the manufacturer.² Their

comparison showed that the response factors for the ketone and the aldehyde were similar to the response factor for the alcohol.

The O-FID and EA detection systems were not able to analyze gaseous samples containing oxygenated compounds and were, therefore, not applicable to the measurement of gaseous TGNMOC. The technical support manager for Fisons stated that the O-FID was only suitable for analysis of matrices that did not contain a predominant volume of oxygenated species. The detector was built for analysis of gasoline, consisting of many components with no one predominant oxygenated organic compound. An air sample, containing percentage levels of N₂, O₂, and CO₂, and ppm levels of oxygenated and non-oxygenated organic compounds, would saturate the methanizer, and cause the detection system to malfunction. As a result, no evaluation samples were analyzed on this detection system. A gas standard containing oxygenated organic compounds and benzene was sent to the Fison lab for evaluation of the EA detection system but were not analyzed because Fisons could not develop an appropriate method for analysis of the gaseous sample.

None of the detectors evaluated met the primary performance goal of universal, linear, organic carbon response. While some success was realized for many classes of organic compounds, oxygenated compounds presented the strongest challenge to the detection systems evaluated. Within an individual chemical class, a 1:1 linear carbon response relationship was achieved, but a linear carbon response relationship was not achieved when comparing one chemical class to another. These detections are useful for selective applications, but they do not meet the needs of an universal detector for total carbon in a sample containing a mixture of compounds from various chemical classes.

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Sampling of Volatile Organic Compounds From Combustion Sources Using Tedlar® Bags with Analysis by GC/MS

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ABSTRACT

A Tedlar® bag method (Draft SW-846 Method 0040) provides a detailed procedure for sampling volatile organic compounds from gaseous effluent sources such as hazardous waste incinerators. This method may be applied in situations where SW-846 Method 0030 (VOST) is not applicable such as highly concentrated (> 1 ppm) or very low boiling ($< 30^{\circ}\text{C}$) compounds. Method 0040 may also be applied to compounds at high concentration (> 1 ppm) with boiling points $\leq 121^{\circ}\text{C}$. Appropriate analytes must exhibit a loss in a Tedlar® bag of less than 20% over a 72-hour storage time. Either constant or proportional sampling may be used depending upon the variability in the emission flow rate. Gas chromatography/mass spectrometry (GC/MS) is the analytical method of choice. To develop an accurate and reproducible analytical method, a fixed loop interface to the GC/MS was designed. Calibration and instrument detection limits were determined for selected analytes. Instrument detection limits for vinyl chloride and benzene were 0.5 and 1.2 ppm, respectively. Accurate and reproducible preparation of gaseous standards in Tedlar® bags and dynamic spiking into the sampling train were demonstrated.

INTRODUCTION

Draft Method 0040 establishes standardized test conditions and sample handling procedures for the collection of volatile organic compounds from gaseous effluent sources such as hazardous waste incinerators by time integrated evacuated Tedlar® bags. Specific guidelines governing the use of Tedlar® bags for sample collection and storage are also provided in the draft method. The draft Method 0040 sampling train incorporates a heated particulate filter and a cooled condensate collector and is thus able to handle complex source streams such as those with high moisture and particulate loading.

The primary application of draft Method 0040 is with highly concentrated (> 1 ppm) or with very low boiling ($< 30^{\circ}\text{C}$) compounds, where Method 0030 is not applicable. Compounds with boiling points of $\leq 121^{\circ}\text{C}$, present at a concentration below the respective condensation point are also candidate analytes. Applicable compounds must exhibit a loss in a Tedlar® bag of less than 20% over a 72-hour storage time. Gas chromatography/mass spectrometry (GC/MS) is the analytical method of choice because of its unique ability to provide positive identification of compounds in complex mixtures like stack gas. Draft Method 0040 is not applicable to the collection of samples in areas where there is an explosion hazard. Isokinetic sampling is not used and therefore the method is not applicable to the collection of highly water soluble volatile organic compounds contained in an aerosol of water. Either constant or proportional rate sampling may be used, depending upon the extent of the variability of the emission flow rate. Available stability data suggest that draft Method 0040 may not perform well in sampling streams containing polar and reactive compounds.¹ The use of a Tedlar® bag to sample polar, reactive compounds needs to be evaluated before sampling.

EXPERIMENTAL PROCEDURE

Method 0040 Sampling Train: A detailed schematic of the principal components of the sampling train is shown in Figure 1. A representative sample is drawn by vacuum from a stationary source through a heated sample probe and filter. The sample then passes into a condenser where the moisture and condensable components are removed. Gaseous emissions are then collected in a Tedlar® bag held in a rigid, opaque container which is connected to a control console. The console controls the system vacuum, sample flow rate, and source, probe, filter and condenser temperatures. The source velocity and temperature are monitored during sampling and the sampling rate is adjusted proportionally if the emission flow rate varies by more than 20% over the sampling period. Otherwise, constant rate sampling is used.

The dry gas sample and the corresponding condensate are transported to a GC/MS. The dry gas is analyzed by direct injection. The condensate is analyzed by purge and trap GC/MS, according to the SW-846 Method 8240.² The total amount of analyte in the sample is determined by summing the individual amounts from the bag and the condensate.

The number of sampling runs to be performed must be determined by the regulatory personnel. Field and method blanks, field spiked samples, contamination checks and performance audits are required. At least one field spike sample is taken per 10 field samples. Spiking is performed by either gaseous or liquid injection into the bag, or by dynamic spiking into the train. Method performance criteria have been tentatively set according to the SW-846 Method 0030 guidelines. Accuracy (percent recovery) must be greater than 50% and less than 150%. Precision must be less than 50%.

Teflon® must be used for all sample lines and connections. All Tedlar® bags must be flushed with nitrogen and checked for background contamination prior to usage. The bags must be protected from sharp objects, direct sunlight and low ambient temperatures (below 0°C) that could cause condensation of any of the analytes. The bag samples must be analyzed within 72 hours of sample collection unless it can be shown that significant (>20%) sample degradation does not occur over a longer period of sample storage. The bags must be stored in rigid, opaque containers during all sampling, storage and transport procedures. Bags may only be shipped by ground transportation. The condensate collected during sampling must be recovered separately in 40 mL vials for each individual bag sample collected using headspace-free conditions.

Analytical conditions: Analytical conditions are shown in Table 1. To develop an accurate and reproducible analytical method, a sample introduction interface³ to the GC/MS was designed. Sample and internal standard (d_3 -toluene) are prepared in separate bags. The bags are then attached to separate ports and the respective loops are loaded by squeezing the bags. The sample and internal standard are simultaneously injected by means of pneumatically controlled valves and subsequently combined in the transfer line. Internal standardization and pneumatic sample introduction are both features that lend greater accuracy to this method by minimizing the effects of operator error.

Analytical quality assurance procedures consist of ensuring the accuracy of mass spectrometric mass assignment, tuning and calibration, according to the procedures outlined in SW-846 Method 8240.² Calibration was based on at least three concentration levels using a Tedlar® bag for each level. The calibration range spanned 50ng to 500ng on column (10 µg/L to 100 µg/L). Quantitation was performed against the response of an internal standard, d_3 -toluene, introduced simultaneously with each sample introduction. An average response factor was obtained from the three levels. A valid calibration curve showed a relative standard deviation of the individual response factors at each level of $\leq 30\%$. A daily calibration check was performed by analyzing a mid-level calibration standard. The check was considered valid if, as above, calculated response factors did not vary by more than 30% from the mean response factors from the calibration curve. All samples (including detection limit standards) were quantitated using the response factors generated from the daily calibration check.

Six analytes were selected for the evaluation of the sampling and analytical protocols. These compounds were selected on the basis of existing stability data,¹ to test the boiling point range of Method 0040. The compounds are vinyl chloride, trichlorofluoromethane, methylene chloride, benzene, toluene and tetrachloroethene with a boiling point range of -19°C to 121°C. The compound d_3 -toluene was selected as an internal standard for all six analytes.

RESULTS AND DISCUSSION

Several parameters were evaluated. The analytical interface was evaluated for reproducibility of injection. Two standard procedures for preparing GC/MS standards in Tedlar® bags were evaluated and the more reproducible procedure of the two was used to generate standards to calibrate the GC/MS. An instrument detection limit study was subsequently performed. Finally, the sampling train was evaluated by replicate dynamic spiking. All sample lines and fittings from the stock cylinders to the bag were constructed with Teflon®. All Tedlar® bag samples and standards were stored at room temperature in sealed styrofoam containers placed in cardboard boxes. Only new bags were used, and one bag per batch was checked for background contamination. One method blank was generated for each level during dynamic spiking. To ensure proper mixing of analyte gases with the diluent nitrogen, Tedlar® bag standards were allowed to sit overnight prior to analysis.

Reproducibility of Injection: Reproducibility of injection was evaluated by performing repeat injections through the sample inlet of the fixed loop interface using a standard prepared in a SUMMA® polished canister as well as a Tedlar® bag standard. A mean and percent relative standard deviation (%RSD) of the area counts from extracted ion profiles for each of the six analytes were then calculated. Similarly, d_8 -toluene was repeatedly injected using the internal standard inlet. The %RSDs for six injections were less than 4% in all cases. The fixed loop interface was shown to be effective in introducing sample and internal standard reproducibly into the GC/MS system. In addition, there was comparable reproducibility in sample introduction between bag and canister standards.

Preparation of Tedlar® Bag Standards: Tedlar® bag standards were prepared from a stock cylinder containing the six analytes at a concentration of 500 $\mu\text{g/L}$. Nitrogen from an additional cylinder was used as a diluent. Standards were prepared either by allowing the gaseous standards from a stock cylinder to flow into a bag simultaneously with the nitrogen for a length of time, or in a step-wise fashion, by introducing the spiking compounds into a bag already partially filled with nitrogen, and then allowing nitrogen flow again for a specified time. Standards at four concentration levels were prepared using each method. The levels ranged from approximately 10 $\mu\text{g/L}$ to 100 $\mu\text{g/L}$. The internal standard was prepared by injecting 5 μL of a methanol solution of d_8 -toluene through a heated injection port into a Tedlar® bag containing 1 L of nitrogen.

The standards were analyzed and the results quantitated against the response of d_8 -toluene. Three of the four standards were used to establish instrument calibration and reproducibility. The fourth standard (in the middle of the calibration range) was then analyzed and the analyte amounts were quantitated to evaluate accuracy. Results showed a notable difference between the two methods of preparation. The step-wise method showed greater accuracy (for all compounds except for tetrachloroethene), higher precision and higher compound response than the simultaneous method.

Instrument Detection Limit: The instrument detection limit study was performed by preparing a standard at 2.2 $\mu\text{g/L}$ and injecting it nine times. The quantitated amounts in each of the nine replicate analyses were then subjected to a student's T test and evaluated according to the criteria outlined in 40CFR Part 136B¹ for the determination of the method detection limit. The instrument detection limits are as follows:

vinyl chloride	0.5 $\mu\text{g/L}$	benzene	1.2 $\mu\text{g/L}$
trichlorofluoromethane	0.5 $\mu\text{g/L}$	toluene	2.0 $\mu\text{g/L}$
methylene chloride	0.7 $\mu\text{g/L}$	tetrachloroethene	4.7 $\mu\text{g/L}$

Dynamic Spiking: Dynamic spiking was performed into a sampling train assembled as shown in Figure 1. Boiling water was used to generate an atmosphere with 100% moisture in a fume hood. Experiments were performed in triplicate at two concentration levels: 20 $\mu\text{g/L}$ and 80 $\mu\text{g/L}$. Sampling time was 20 minutes at a rate of 1 L/min.

The results (Tables 2 and 3) show excellent precision and a positive bias (mean % difference) at both levels. The bias appears higher for all compounds at the 20 $\mu\text{g/L}$ level. There also appears to be an increase in bias with boiling point at the 80 $\mu\text{g/L}$ level. Tetrachloroethene in both cases appears to show the greatest inaccuracy. The bias may have been caused by volume discrepancies between measured and actual volumes during dynamic spiking experiments. Experiments performed to evaluate

this discrepancy showed a 10%-30% difference. However, lack of sufficient data prevents a better definition of this difference. The problem may have been caused by inefficient operation of the check valve at the bag inlet in the sampling train assembly, and may therefore be mitigated by its removal.

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Table 1. Analytical Conditions

Instrument	Sample Introduction Interface ³ (SI) Varian 3400 Gas Chromatograph (GC) Finnigan 4500 Mass Spectrometer (MS)
SI Conditions	Carrier Gas: Helium Sample Loop Size: 5 mL
GC Conditions	DB-624 capillary column, 30 m, 0.53 mm I.D., 3 μ film Temperature Program: -60°C to 200°C @ 20°C/min Carrier Gas: Helium Interface Oven Temperature: 200°C
MS Conditions	Mode: Electron Ionization, Full Scan Electron Energy: 70 eV Mass Range: 35-260 amu Scan Rate: 1 scan/sec

Table 2. Accuracy and Precision of Dynamically Spiked Samples – Level 1

Sample Label Analyte	Accuracy Percent Difference Between Theoretical and Quantitated Values						Precision
	Run 1	Run 2	Run 3	Run 4	Run 5	Mean	%RSD
Vinyl chloride	3.33	6.40	4.27	8.63	8.12	6.15	4.59
Trichlorofluoromethane	8.86	7.40	8.29	11.63	13.41	9.92	3.70
Methylene chloride	7.82	5.93	10.62	9.90	16.24	10.10	5.03
Benzene	9.81	12.89	13.88	16.77	23.91	15.45	5.59
Toluene	16.71	22.08	21.62	23.36	33.47	23.45	6.07
Tetrachloroethene	19.23	27.22	26.28	32.74	43.41	29.77	7.26

Table 3. Accuracy and Precision of Dynamically Spiked Samples – Level II

Sample Label Analyte	Accuracy Percent Difference Between Theoretical and Quantitated Values						Precision
	Run 6	Run 7	Run 8	Run 9	Run 10	Mean	%RSD
Vinyl chloride	35.41	59.02	37.13	36.86	29.41	39.57	8.15
Trichlorofluoromethane	35.10	52.73	32.76	30.73	26.15	35.29	7.90
Methylene chloride	28.23	37.64	28.36	25.70	24.39	28.86	4.59
Benzene	31.75	54.17	39.86	40.00	35.99	40.35	5.61
Toluene	31.43	56.52	40.25	37.43	38.37	40.80	6.47
Tetrachloroethene	50.14	94.28	71.60	71.56	70.08	71.53	8.46

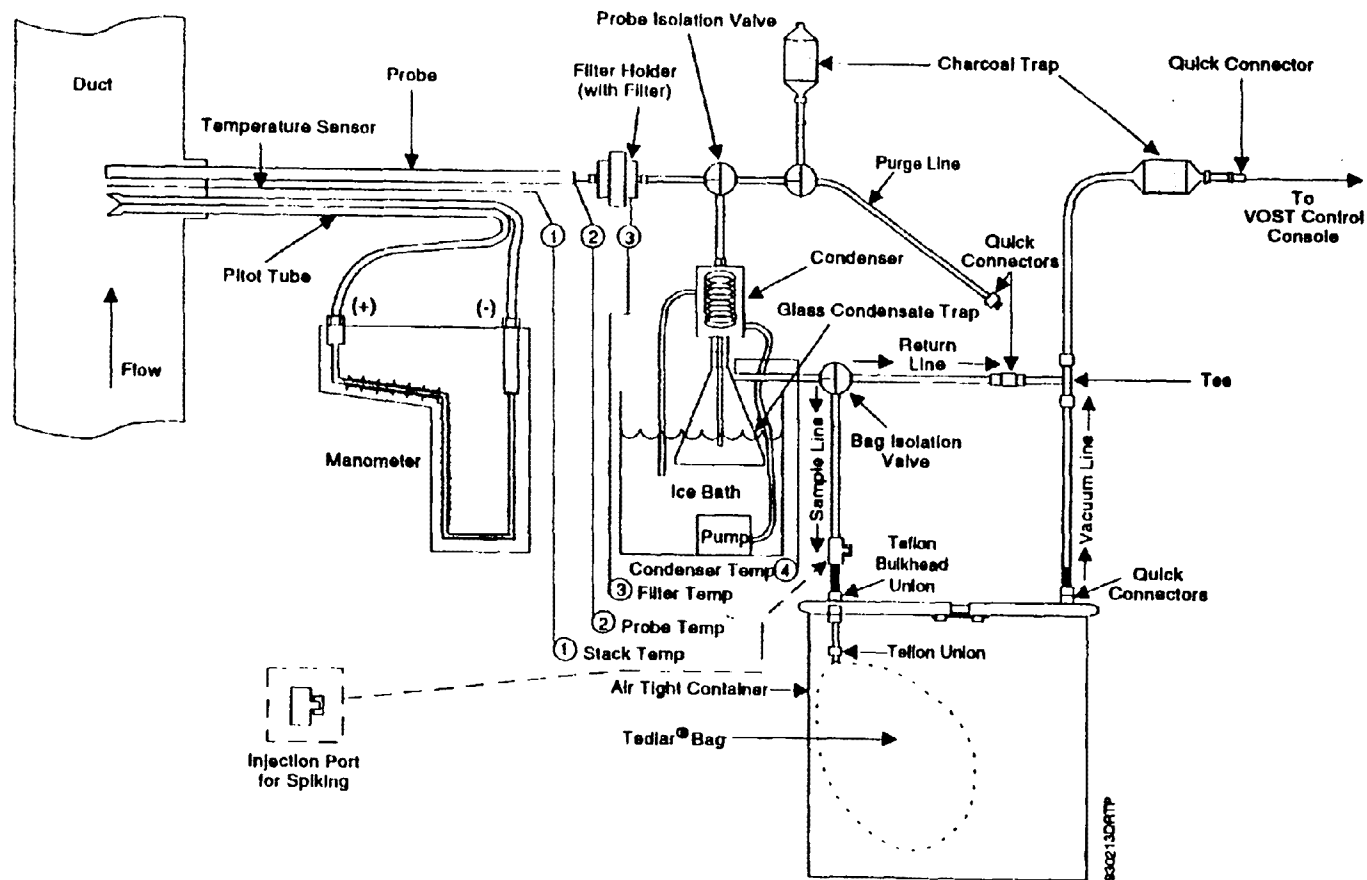


Figure 1. Schematic of the Method 0040 Sampling Train

Field Evaluation of a Modified VOST Sampling Method

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ABSTRACT

The VOST (SW-846 Method 0030) specifies the use of Tenax® and a particular petroleum-based charcoal (SKC Lot 104, or its equivalent), that is no longer commercially available. In field evaluation studies of VOST methodology, a replacement petroleum-based charcoal has been used. Candidate replacement sorbents for charcoal were studied, and Anasorb® 747, a carbon-based sorbent, was selected for field testing. The sampling train was modified to use only Anasorb® in the back tube and Tenax® in the two front tubes to avoid analytical difficulties associated with the analysis of the sequential bed back tube used in the standard VOST train.

The standard (SW-846 Method 0030) and the modified VOST methods were evaluated at a chemical manufacturing facility using a quadruple probe system with quadruple trains. In this field test, known concentrations of the halogenated volatile organic compounds, that are listed in the Clean Air Act Amendments of 1990, Title III, were introduced into the VOST train and the modified VOST train, using the same certified gas cylinder as a source of test compounds. Statistical tests of the comparability of methods were performed on a compound-by-compound basis. For most compounds, the VOST and modified VOST methods were found to be statistically equivalent.

INTRODUCTION

The Volatile Organic Sampling Train (VOST, Method 0030¹) has been used for nearly ten years to collect volatile organic compounds from stationary sources.² The Method 0030 sampling train incorporates two tubes of sorbent: Tenax-GC® (a phenylene oxide polymer), with a second tube containing sequential beds of Tenax-GC® and SKC Lot 104 petroleum-based charcoal or equivalent. Lot 104 petroleum-based charcoal has been commercially unavailable for several years, and Method 0030 contains no procedures for determining equivalency of other lots or other types of charcoal. At present, there is no uniformity among users of the VOST method in selecting an alternative to SKC Lot 104. One of the substitute charcoals frequently used is coconut charcoal, a product not thoroughly evaluated for VOST applications and one that retains water more than petroleum-based charcoal.

A previous study³ selected Anasorb® 747 as a substitute for SKC Lot 104 petroleum-based charcoal, to obtain better consistency of performance and guarantee availability of an abundant supply.

In addition to replacing the charcoal sorbent, the decision was made to eliminate the sequential bed second tube of the VOST train. This would allow optimum analytical conditions to be developed for thermal desorption of each sorbent. A laboratory study³ established that when a full tube of carbon-based sorbent is used, two Tenax® tubes prior to the Anasorb® tube are required to avoid breakthrough of compounds that are difficult to recover from carbon-based sorbents. For

analytes tested other than methyl chloride, ethyl chloride, vinyl chloride, and methyl bromide. recovery from carbon-based sorbents tended to be low, even at desorption temperatures of 350°C. Since Tenax® retains these compounds poorly, a carbon-based sorbent is required to trap these gases. The modified VOST train is shown in Figure 1: the two Tenax® tubes are placed after the first condenser, with the Anasorb® tube after the second condenser. Analytical procedures of Method 5041¹ were also modified to deal with the additional tube without increasing the total number of analyses. In the field evaluation study, the three tubes were analyzed individually in order to examine the distribution of analytes, but in routine application, the two Tenax® tubes may be combined for desorption and analysis, with a separate analysis performed for the Anasorb® tube. A calibration curve with analytes and internal standards purged from water was demonstrated to be superior to other methods tested for initial calibrations and daily calibration check samples; surrogate compounds were spiked on the sorbent tubes, as in the standard procedure¹.

The dynamic spiking system previously described^{2,3} allowed the modified VOST methodology to be evaluated by using a certified cylinder of gaseous standards during dynamic spiking in the field. The modified VOST procedure was evaluated using VOST (Method 0030) as a reference method. According to the guidelines of EPA Method 301⁴, field validation may be performed by side-by-side comparison of a candidate method to a validated method to establish statistically comparable performance for the same analytes in the same matrix (i.e., same source category). The test site selected for the field evaluation was a coal-fired boiler that burned chemical waste at a chemical manufacturing facility.

Bias, any systematic positive or negative difference between the measured value and the true value of a sample, may result from analytical interferences, errors in calibration, or inefficiencies in the collection or recovery of an analyte. When the bias of the method is determined for a given analyte, a correction for the bias may be made. The EPA Method 301 allows for this bias correction within a range of 90 percent to 110 percent when a candidate method is being compared to a reference method. Bias correction factors outside this range may be grounds for rejecting the candidate method.

Precision is the variability in the data from the entire measurement system (both sampling and analysis) as determined from multiple or collocated sampling trains. Following the EPA Method 301 procedures, multiple samples using at least two paired sampling trains determine the precision of the entire system. Use of quadruple (Quad) trains with four collocated sampling probes and four similar sampling trains allows simultaneous operation of two spiked trains and two unspiked trains. A total of twenty runs (10 for each method) using quadruple collocated sampling trains were collected using both VOST and modified VOST to provide adequate samples for statistical (bias and precision) comparison of the two methods and to allow backup samples in the event that any sample became invalid due to breakage or loss of data during analysis.

In the field, spiking gas was allowed to flow through the dynamic spiking apparatus for two hours each day before directing the flow to the sampling trains to minimize any adsorptive losses during actual Quad sampling runs. Prior to the field test, the spiking gas flow rate delivered to each of two trains was set to a nominal 3.0 ml/min (250 ng over a 20-minute sampling period). The actual amount delivered was calculated from the measured spiking gas flow rate, the measured period of time during which spiking occurred, and the measured concentration of the individual components in the cylinder gas mixture. Following collection all modified VOST sampling tubes were transported and stored at 4°C and were analyzed within 30 days after collection. Analytical results for the first complete six paired sampling runs (as per Method 301) of both VOST and modified VOST are shown in Table I. Using the criteria for acceptable VOST method performance shown in the EPA Quality Assurance Handbook for Hazardous Waste Incineration⁵, the compounds shown in the shaded area of Table II meet the criteria for acceptable performance.

Using the criteria outlined for comparability of method performance in the EPA Method 301 to compare modified VOST to VOST as a reference method, the following compounds are comparable: chlorobenzene, methyl chloride (chloromethane), vinyl chloride, chloroform, methyl

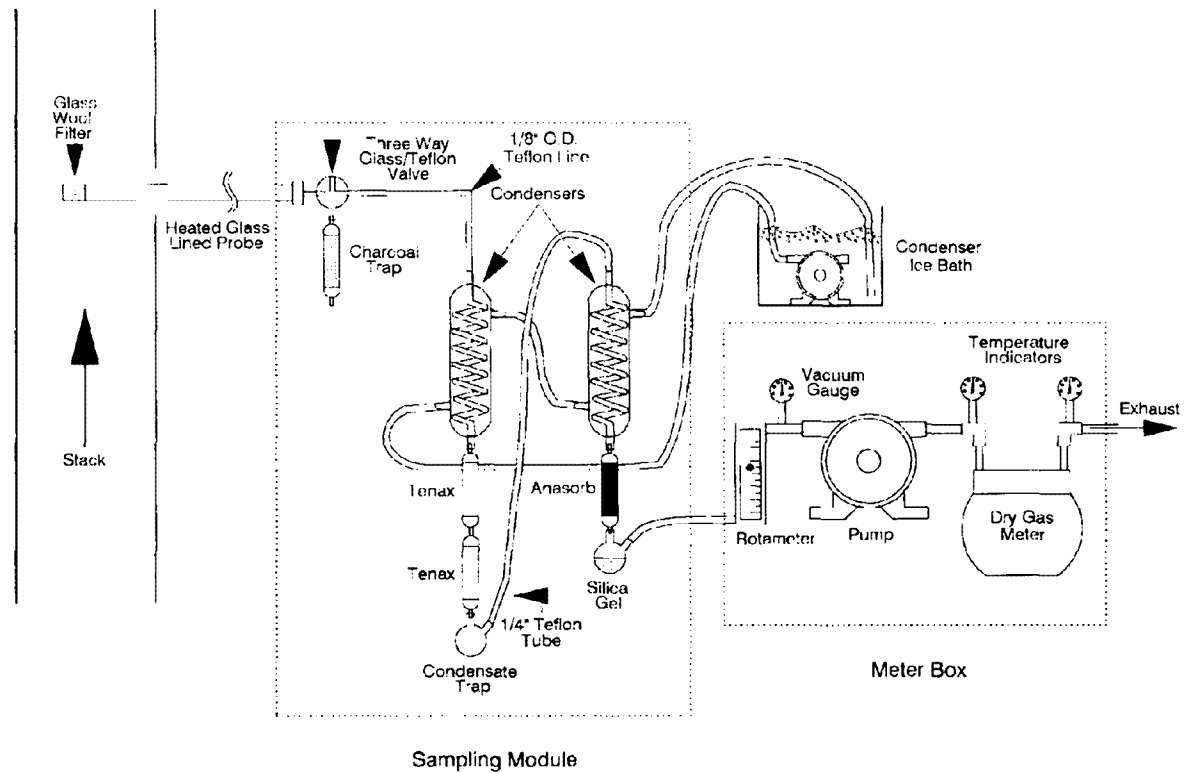


Figure 1. Modified VOST Sampling Train

Table I
Results of VOST and Modified VOST

Compound	Modified VOST		VOST	
	Mean Percent Recovery ¹	Percent RSD	Mean Percent Recovery ¹	Percent RSD
Methyl Chloride (Chloromethane)	167.5	56.4	255.3	58.1
Ethylidene Dichloride (1,1-Dichloroethane)	96.2*	12.6	86.0*	13.2
Chlorobenzene	91.6*	13.0	84.8*	27.9
Vinyl chloride	44.2	24.2	37.3	39.5
Vinylidene Chloride (1,1-Dichloroethene)	96.8*	17.2	77.8*	25.1
Chloroform	98.4*	20.4	95.3*	14.3
Propylene Dichloride (1,2-Dichloropropane)	149.4*	14.0	117.7*	30.0
Methyl Bromide (Bromomethane)	45.7	46.7	52.8*	27.8
Ethyl Chloride (Chloroethane)	45.3	30.0	31.4	37.6
Methylene chloride	120.7*	10.9	90.8*	11.7
Methyl Chloroform (1,1,1-Trichloroethane)	87.1*	12.1	96.8*	19.4
Carbon tetrachloride	89.3*	12.5	85.7*	13.8
Ethylene Dichloride (1,2-Dichloroethane)	83.2*	25.1	78.6*	27.7
Trichloroethene	148.7*	3.4	124.0*	16.8
cis-1,3-Dichloropropene	118.4*	21.0	83.5*	16.1
trans-1,3-Dichloropropene	75.2*	32.6	47.9*	35.0
1,1,2-Trichloroethane	117.3*	20.5	81.4*	14.4
Tetrachloroethene	61.8*	8.0	57.5*	12.5

Table I
(Continued)

Compound	Modified VOST		VOST	
	Mean Percent Recovery ¹	Percent RSD	Mean Percent Recovery ¹	Percent RSD
Methyl iodide (Iodomethane)	89.0*	11.9	77.8*	20.4
Allyl Chloride (3-Chloropropene)	26.0	21.1	36.4	29.6
Ethylene Dibromide (1,2-Dibromoethane)	108.5*	23.2	81.6*	31.0
Chloroprene	85.8*	15.3	76.4*	12.3
Vinyl Bromide	38.0	22.5	28.4	30.9

¹ Mean of 6 runs (12 sets of dynamically-spiked tubes).

* Recoveries marked with asterisk (*) indicate acceptable performance, using the criteria of recovery from 50 to 150 percent, with percent relative standard deviation of 50 or less.⁷

bromide (bromomethane), methyl chloroform (1,1,1-trichloroethane), carbon tetrachloride, ethylene dichloride (1,2-dichloroethane), tetrachloroethene, methyl iodide (iodomethane), and allyl chloride (3-chloropropene). When recoveries are compared for VOST and modified VOST, the modified VOST usually shows better recovery. When precision is compared between VOST and modified VOST, the modified VOST shows better precision. The statistical comparison is performed on a compound-by-compound basis to determine the equivalence of the two sets of results. The statistical comparison does not determine which method is better, only whether the two methods are comparable within a specified range. On the basis of a compound-by-compound comparison, the two methods are comparable for the compounds listed above and, where they differ, the modified VOST method usually demonstrates better performance in both recovery and precision. For the compounds which did not meet the Method 301 criteria for acceptable performance of the method, the VOST or modified VOST could still be used as a screening method to establish the presence or absence of these compounds.

Methyl chloride (chloromethane) exhibited recoveries far above the acceptable range, consistent with results in previous studies.^{4,5} The compound appears to be formed during the time that the halogenated analytes are on the sorbent tubes. Since this analyte may be formed on the sorbent tubes, methyl chloride is not an appropriate analyte for the VOST or modified VOST method. Methyl chloride (chloromethane), ethyl chloride (chloroethane), methyl bromide (bromomethane), vinyl bromide, and vinyl chloride were observed exclusively or primarily on the back (Anasorb®) tube, as expected. Compounds with 30 percent or more sorption on the second Tenax® tube were methylene chloride and methyl iodide (iodomethane). Compounds with a significant component (>20% but <30%) on the second Tenax® tube included: vinylidene chloride (1,1-dichloroethene), methyl chloroform (1,1,1-trichloroethane), carbon tetrachloride, allyl chloride

Table II
Mean Recoveries and Precision of Analytes,
Using the Modified VOST Method

Compound	Mean Recovery, % ¹	% RSD
methyl chloride (chloromethane)	167.5	56.4
propylene chloride (1,2-dichloropropane)	149.4	14.0
trichloroethene	148.7	3.4
methylene chloride	120.7	10.9
cis-1,3-dichloropropene	118.4	21.0
1,1,2-trichloroethane	117.3	20.5
ethylene dibromide (1,2-dibromoethane)	108.5	23.2
chloroform	98.4	20.4
vinylidene chloride (1,1-dichloroethene)	96.8	17.2
ethylidene chloride (1,1-dichloroethane)	96.2	12.6
chlorobenzene	91.6	13.0
carbon tetrachloride	89.3	12.5
methyl iodide (iodomethane)	89.0	11.9
methyl chloroform (1,1,1-trichloroethane)	87.1	12.1
chloroprene	85.8	15.3
ethylene dichloride (1,2-dichloroethane)	83.2	25.1
trans-1,3-dichloropropene	75.2	32.6
tetrachloroethene	61.8	8.9
bromomethane	45.7	46.7
ethyl chloride (chloroethane)	45.3	30.0
vinyl chloride	44.2	24.2
vinyl bromide	38.0	22.5
allyl chloride (3-chloropropene)	26.0	21.1

¹The shaded area indicates recoveries from 50 to 150 percent with %RSD of 50 or less.²(3-chloropropene), and vinyl bromide. Compounds recovered at acceptable levels (50-150% for RCRA, 70-130% for NSPS), with acceptable precision (percent relative standard deviation less than or equal to 50) are valid candidates for VOST or modified VOST.

DISCLAIMER

This material has been funded wholly or in part by the Environmental Protection Agency under contract 68-D1-0010 to Radian Corporation. It has been subjected to the Agency's review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Comparison of Sampling and Analytical Methods for the Collection and Determination of Methylene Diphenyl Diisocyanate (MDI) from Oriented Strand Board (OSB) Sources

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The ICI Polyurethanes Group conducted a multi-variant study of sampling and analytical methods for the collection and determination of MDI from 3 different OSB sources. The study evaluated 3 different sampling trains and derivatizing reagents at 2 probe temperatures as follows:

1. A 4-Nitro-N-propylbenzylamine (Nitro reagent) filter alone at ambient probe temperature,
2. A 1-(2-Methoxyphenyl) piperazine (12MP) filter followed by two impingers containing the same reagent in Toluene at ambient probe temperature,
3. A dual 12MP impinger train followed by a 12MP treated filter also at ambient probe temperatures,
4. A dual 12MP impinger train followed by a 12MP treated filter also at a probe temperature of 250 °F,
5. A dual 1-(2-pyridyl)piperazine (12PP) impinger train also at a probe temperature of 250 °F.

The analytical portion of the study compared results using Normal and Reversed Phase HPLC determination of the Nitro reagent samples and Reversed Phase HPLC determination of the 12MP and 12PP samples. Additional LC-MS studies were conducted to confirm and identify the cause of a positive bias in the Normal Phase Nitro reagent analytical results.

The analytical and sampling results will be presented.

Pen-Based Computer System for Performing Source Test Calculations

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The Emission Measurement Branch has developed open-based computer system for Methods 1 through 5 (40 CFR 60, appendix A) which is designed to perform on-site emission source test calculations and for data reduction after the test effort has concluded. The system uses EXCEL for Windows and is suitable for use by anyone who performs emission tests, observes emission tests, or who needs to reduce or verify emission testing data. The system is designed for people who have minimal computer skills, and data can be handwritten upon a computer screen using an electronic stylus or "pen"; keyboard and "spin button" data entry options are also available. When sufficient data have been entered, the system performs the calculations and displays the results. Future plans are to adapt the pen-based system to as many Environmental Protection Agency methods as applicable; and the programs will be available on the Emission Measurement Technical Information Center Computer Bulletin Board as well as upon request.

ODOR INCIDENT SAMPLER For FENCELINE EVALUATION OF AIR TOXICS

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ABSTRACT

Governmental air toxic regulatory agencies receive numerous daily complaints from the public regarding air pollution related odor incidents. Historically, due to the sporadic frequency of occurrence of such incidents, it has been difficult if not impossible for a regulatory group to capture the "Odor Incident/Maximum Concentration" type sample, without the use of expensive continuous air monitoring devices. In an effort to overcome this Suffolk County designed an "Odor Incident Sampler" which can be activated simply by the general public. The device performs all air sampling functions when a complainant plugs the unit into an electrical line. Upon activation of the Odor Sampler the individual records the start time, and then notifies the appropriate regulatory agency that an odor incident is occurring. Within an appropriate time period air quality agency personnel collect the sample(s) and recharge the sampler for subsequent run-offs.

Various types of air sampling equipment can be placed inside the locked tamper proof shelter (for example, Sorbent Tubes, Summa Cannisters, Impingers, etc.).

Project examples are presented, including details of sample collection, and laboratory analysis.

INTRODUCTION

Under the 1990 Clean Air Act Amendments (CAAA) and subsequent additions governmental agencies are required to monitor and regulate 189 Hazardous Air Pollutants¹. The CAAA requires special controls called National Emissions Standards for Hazardous Air Pollutants (NESHAPS) for pollutants that cause serious or irreversible health effects.

To aid in the implementation of the CAAA, the U.S. Environmental Protection Agency (EPA) encourages state and local agencies to develop their own air toxics programs to monitor and control high-risk "point" sources, and address multi-pollutant, multi-source urban toxics problems². In addition NYS has published short term (1 hour) Guideline Concentrations (SGC's) and Annual Guideline Concentrations (AGC's) for which no state or federal ambient air quality standards exist³.

To help address the above concerns Suffolk County has developed the "Odor Incident Sampler."

EXPERIMENTAL

The Odor Incident Sampler (OIS) diagrammed in Figure 1, was originally designed in late 1989, constructed and tested in the early spring of 1990 and initially field deployed in May 1990. The OIS was designed with the following features:

- (1) Sample Media Integrity - A General Valve Corporation, Fairfield, New Jersey model 9-89-900 stainless steel valve (with model 90-29-100 valve driver) was placed in line with sample media between inlet probe and media contact point. The two-way solenoid valve which is normally closed prevents air from diffusing into the sample media. Since back diffusion through the other

end of the sampling train (the vacuum pump end) does not occur, one solenoid valve is adequate in preventing air diffusion for at least two (2) months.

- (2) Ease of Activation - By plugging the unit into an electrical outlet, the OIS automatically performs all necessary air sampling functions.
- (3) Inlet Probe Integrity - Only stainless steel tubing and fittings are used.
- (4) Documentation of Critical Parameters - An inline timer allows the selection of the targeted sample duration period (normally one (1) hour). An elapsed timer keeps track of the actual time sampled. Flow rates are checked before and after sampling.
- (5) Citizen/Complainant Documentation - The complainant who activates the OIS is asked to fill out an Odor Incident Report Form which documents the date and time of activation, temperature, estimated wind speed and direction, and odor intensity rating. Upon activation the complainant telephones an air quality official to report OIS start up, and to arrange sample pick up and recharging of the media. Once activation time is established, resident reported meteorological measurements are compared to official meteorological station readings, in order to best determine the origin of the source of pollution.
- (6) Multiple Sample Collection - Although the design as shown is for the collection of a single sample, changeover to a multiple sample collection may be easily accomplished by using a branched inlet into the existing manifold port (see Figure 1.)
- (7) Shelter - Protection of sampling equipment from rain and snow.
- (8) Security - Unit is constructed with a locking mechanism for protection against vandalism. In addition it is recommended that the unit be placed in a secure area.
- (9) Stabilizing Platform - The placing of cinder blocks on the stabilizing supports proves to be adequate in preventing the unit from toppling over during high wind conditions.
- (10) Utilities - adequate outlets are needed for incorporating additional samplers. Fluorescent lighting to provide visibility for the interior of the OIS is required to allow possible recharge during evening hours.

Desirable additional features for a commercially manufactured⁽⁴⁾ OIS unit should include any or all of the following:

- (1) Modem Activation - This feature enables a network of samplers to be activated simultaneously.
- (2) Microprocessor/Data logger Based System - With battery back-up and real time clock to electronically document critical air sampling parameters.
- (3) Ground Fault Interruption
- (4) Shelter Heating and Cooling - This enables an agency to utilize temperature sensitive media (i.e., impinger: liquids freezing) to be sampled throughout the year.
- (5) Wind Sensor - Although desirable this feature is not necessary if meteorological information is available locally.

LABORATORY ANALYSIS

Samples are analyzed according to sample type. For example, the majority of samples collected to date, involves the analysis of toxic VOC's as listed in the Clean Air Act, utilizing an automated non cryogenic multi-layer

Sorbent tube, GC/MS technology⁴. (see Table 1.)

Additional methodologies used for the project examples cited below, are NIOSH Method 3500 for formaldehyde using an impinger collection, and EPA Method 8270B utilizing a Hi-Volume filter collection.

RESULTS and DISCUSSION

After four (4) years of air sample collection, the original OIS and subsequent newer versions, continue to function as designed, with no major mechanical or pneumatic problems encountered.

The public has been very appreciative of the employment of the OIS. People prefer to have their odor episode occurrences addressed with actual monitoring, thereby proving or disproving the existence of a health concern.

Two OIS project examples are listed below. Both projects were initiated because people in a residential area complained about odorous emissions from a nearby industrial source.

(1) Circuit Board Manufacturer - Formaldehyde concentrations on a homeowners property exceeded both the state and federal (1 hour) standards. (see Table 2.) Methylene Chloride was also found to be above background levels, however, no existing standard was exceeded. (see Table 4.)

(2) Plastics Remanufacturing Corporation - Bis(2-Ethyl Hexyl) Phthalate was detected in particulate matter at concentrations which far exceeded ambient levels. (see Table 3.) Additional air contaminants which exceeded background levels included 1,1-Dichloroethylene and 1,1,1-Trichloroethane. (See Table 4.)

CONCLUSION

The use of the OIS demonstrates the ability to collect Odor Incident/Maximum Concentration air samples which can be used for compliance purposes. Although Continuous Air Monitoring (CAM) is often necessary, use of the OIS can be a cost effective alternative, which reduces the volume of CAM required.

Fence-line air monitoring of fugitive emissions from point sources to evaluate acute population exposure, is a proven application for the Odor Incident Sampler.

ACKNOWLEDGMENTS

We gratefully acknowledge Suffolk County Health Commissioner, Mary E. Hibberd, M.D., M.P.H., Chief Medical Examiner Sigmund M. Merchel, M.D., and Robert Capp, Sideris Caramintzos, Mary Carpentieri and Arthur Lussos from the NYS Department of Environmental Conservation for their project support and leadership.

The authors especially appreciate the co-operation and contributions of Ida Puntunieri, Jo Ann Laager, and Barry Passin in the production of the manuscript and visual aids.

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TABLE 1. CLEAN AIR ACT AMENDMENT - VOC's
(28 nL Standard)

Time	Compound	Time	Compound	Time	Compound
6.65	Freon 12	30.67	1,2-Epoxybutane	45.35	Ethylbenzene
8.01	Freon 114	31.21	Methyl ethyl Ketone	45.54	m-Xylene
8.56	Chloromethane	32.65	Chloroform	46.53	o-Xylene
9.73	Vinyl Chloride	34.40	1,1,1-Trichloroethane	46.58	Styrene
10.14	1,3-Butadiene	35.31	2,2,4-Trimethylpentane	47.28	Bromoform
10.78	Ethylene Oxide	35.41	Carbon Tetrachloride	47.32	Isopropyl Benzene
10.98	Methanol	35.77	1,2-Dichloroethane	47.55	1,1,1,2-Tetrachloroethane
13.32	Bromomethane	35.95	Benzene	47.61	Int. Std./Bromofluorobenzene
14.27	Chloroethane	37.59	Trichloroethylene	47.86	1,2,3-Trichloropropane
15.98	Bromoethane	38.13	Ethyl Acrylate	48.50	1,3,5-Trimethylbenzene
16.69	Freon 11	38.42	1,2-Dichloropropane	49.32	1,2,4-Trimethylbenzene
19.59	2-Propenal	38.82	Methyl Methacrylate	49.47	Dichloroethylether
30.44	Propylene Oxide	39.25	1,4-Dioxane	50.13	m-Dichlorobenzene
20.57	Freon 113	39.26	2-Nitropropane	50.32	p-Dichlorobenzene
20.94	1,1-Dichloroethylene	40.19	Methyl Isobutyl Ketone	50.51	o-Chlorotoluene
21.91	Acetonitrile	40.22	Epichlorohydrin	50.57	p-Diethylbenzene
22.34	Todolmethane	40.66	cis-1,3-Dichloropropene	51.06	o-Dichlorobenzene
23.53	1-Chloro-1-Propene	41.60	Toluene	53.00	1,3,5-Trichlorobenzene
24.10	Methylene Chloride	41.93	trans-1,3-Dichloropropene	53.04	Nitrobenzene
25.35	2-Propenenitrile	42.32	1,1,2-Trichloroethane	54.19	1,2,4-Trichlorobenzene
25.95	Methyl tert-Butyl Ether	43.28	Tetrachloroethylene	54.49	Hexachlorobutadiene
27.60	Hexane	44.10	1,2-Dibromoethane	54.77	Naphthalene
28.67	1,1-Dichloroethane	45.20	Chlorobenzene		
29.26	Vinyl Acetate	45.26	1,1,1,2-Tetrachloroethane		

Table 2. Circuit Board Manufacturer -- Impinger - OIS Collection

OIS Formaldehyde Results		
Residence	Date (1993)	Conc. ppb(v)
RM	6/30	717
RM	7/8	>1513
RM	7/14	562
RM	7/26	213
ML	8/6	< 22
RM	8/10	29
ML	8/10	< 25
RM	8/10	409
ML	8/11	< 29

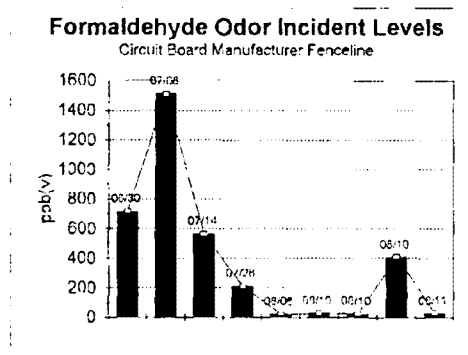


Table 3. Plastics Remanufacturing Particulate OIS Collection

OIS - Bis (2-Ethyl Hexyl) Phthalate Results*	
Date (1993)	Conc. ug/m ³
7/16	0.067
7/21	0.105
7/23	0.092
8/4	0.193
9/30	0.108
10/18	0.580
11/1	0.279
12/7	0.305

* Background Subtle County Particulate Conc of Bis (2-Ethyl Hexyl) Phthalate = <0.001 ug/m³

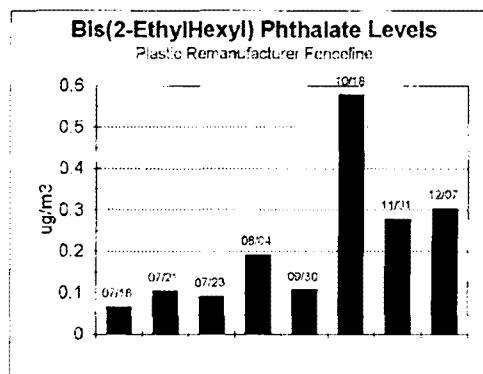


Table 4. VOC Project Results
Sorbent Tube - OIS Collection

Industrial Source of Emissions	OIS-VOC Maximum Results / Comparisons				
	1,1,1-Dichloroethylene	Methylene Chloride	1,1,1-Trichloroethane	Benzene	1,2,4-Trimethylbenzene
Plastics Remfg.	>15.1	0.7	>20.6	3.5	0.8
Circuit Bd.Mfg	2.1	8.3	1.8	4.6	1.0

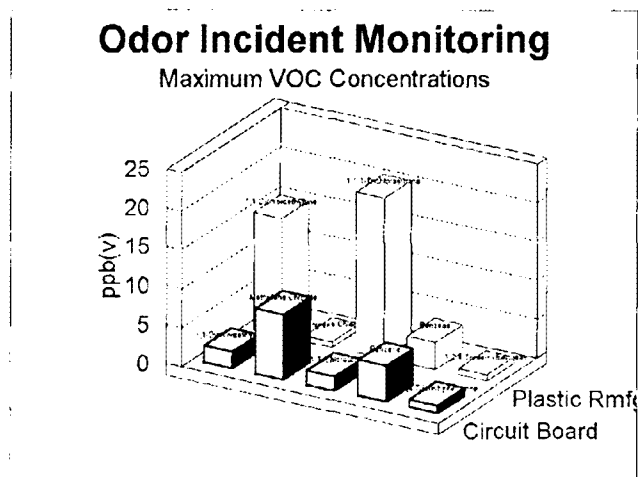
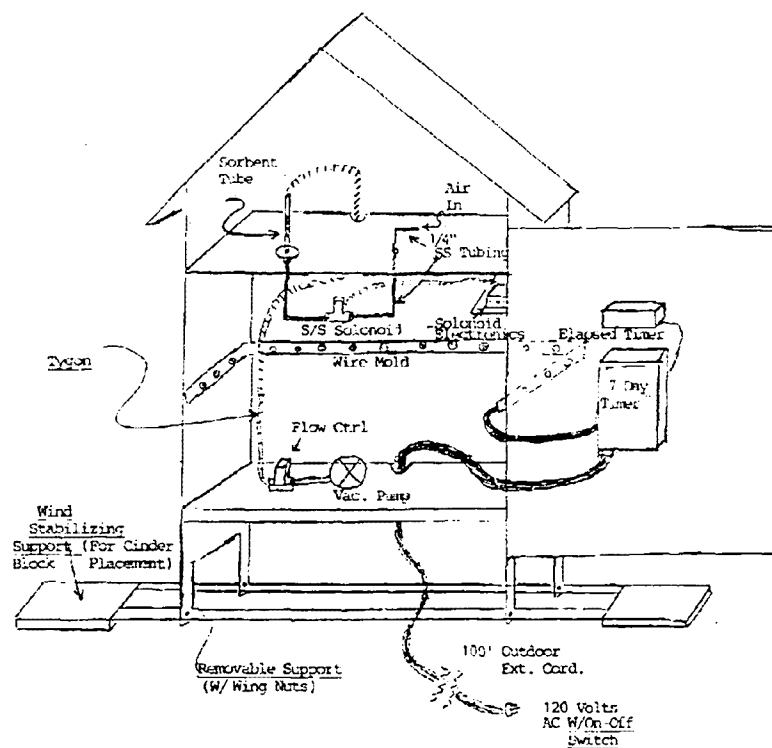


Figure 1. Odor Incident Sampler



SESSION 7:
GLOBAL CLIMATE CHANGE,
MOUNT MITCHELL

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**Monitoring of Regional Chemical Climate Change
at Mount Mitchell, North Carolina**

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One of the objectives of the National Global Change Program is to seek plausible answers to the following question: What is the radiative forcing from greenhouse gases, aerosols, and clouds on the Earth's climate system, and what are the feedbacks and processes that regulate the net radiative balance of the earth's atmosphere? A critical survey of the existing evidence reveals that the trends in the average global temperature of the Earth-Troposphere system and in global precipitation patterns are mitigated by several natural and anthropogenic differences between the northern versus southern hemisphere. In contrast, climatic changes on a regional scale have been more convincing during the last two decades. A case in point is the frequency of droughts experienced in the Southeast. The objectives of our study are addressed to understand the cloud-climate feedback mechanisms on a regional scale, with particular emphasis on the climate of the Southeastern U.S. We aim to study the impact of the natural and anthropogenic aerosols on the regional cloud albedo. This is done by observing the microphysico-chemical characteristics of clouds that form at Mt. Mitchell, NC (highest peak, 6,684 ft or 2,017 m MSI. in the eastern U.S.; Mt. Mitchell State Park is a designated United Nations Biosphere Reserve). The cloud reflectivity is simultaneously monitored by the satellite-based Advanced Very High Resolution Radiometer (AVHRR). Clouds with contrasting microphysical and radiative characteristics are formed at the site when air masses of marine, continental, or highly polluted origins arrive. Analysis of the First Year Data Base suggests that our project offers some very promising insights into the cloud-climate feedback mechanisms. Clouds formed by polluted air masses had pH as low as 2.4 and by marine air masses as high as 4.75. The latter were found least reflective.

Air Mass History versus Cloud Water Acidity: Observations and Model Results from a Remote Rural Site

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ABSTRACT

Cloud water acidity, as measured at a remote rural observing site, is related to the pathway, or trajectory, taken by air parcels passing over areas with varying levels of pollutant emissions. Areas of the country that are high emitters of pollutants, such as SO_x and NO_x , affect the cloud water acidity of the ensuing clouds. Field studies at Mount Mitchell State Park (2,038 meters MSL) during June and August of 1993 have resulted in observations of cloud water acidity for 37 cloud events of varying durations. The measurements were taken with a passive cloud water collector mounted atop a 16.5 meter meteorological tower. Calculations of the backward trajectories for these cloud events are accomplished by utilizing a hybrid Eulerian-Lagrangian computer model called Hybrid Single-Particle Lagrangian Integrated Trajectories, or HY-SPLIT. In this study, comparisons of selected cloud events from the 1993 field season with similar cloud events observed during the 1986-1988 field seasons are investigated. Of the six cases investigated here, four events contained cloud water acidity averages which fell within the range of historical data from 1986-1988, for the air masses determined from model back trajectories. Two other cases, both marine in origin, had average acidities slightly below those based on historical ranges.

INTRODUCTION

Interest in the potential effects that increases in the levels of airborne pollutants could have on the atmosphere has steadily accelerated in recent times. It has been postulated (Ghan, et al., 1990)¹ that greenhouse warming of the earth's troposphere due to a doubling of CO_2 could be counteracted by a small 2% increase in the shortwave albedo of low level clouds. The determination of albedo of clouds forming over certain areas can be done by assessing the air mass origin of the clouds via back trajectory analysis. In this paper, we will attempt to show a potentially useful method for performing the required back trajectory analysis. For the purposes of this particular study, the scope will be reduced to a comparison of certain data-sampling instances, from here on referred to as cloud events, with similar cases from a previous study spanning over the years 1986-1988. There are two reasons for performing this comparison. The first is to elucidate a method for monitoring long-term changes in cloud chemistry characteristics. The second reason is to evaluate the effectiveness of the modeling technique used to generate the air mass histories in this study.

Categorization of air masses traversing the Mount Mitchell observation site can be done by utilizing emissions data provided by the Environmental Protection Agency (EPA, 1993)². The Regional Emission Inventories for the 48 contiguous United States allow categorization by state of various forms of anthropogenic pollutants such as SO_x and NO_x . By using these emissions data, the statewide graphical representations of the country's heaviest pollution sources can be formulated, as shown in Figures 1a and 1b. For both cases, it can be seen where the largest pollutant emitters are located, relative to Mount Mitchell. Thus, a categorization of air masses by geometric proximity to Mount Mitchell has been devised (Lin and Saxena, 1991)³. The air masses are called "polluted" if they are transported from a region bounded by 290° to 65° (Sector 1) azimuth relative to Mount Mitchell, "marine" (i.e., "clean") if transported from a region bounded by 210° to 65° (Sector 2), and "continental" if transported from a region bounded by 210° to 290° (Sector 3). Obviously, considerable cross-over between the three

sectors is possible and expected. However, some air masses which move primarily within one sector are expected to exhibit cloud acidity characteristics which reflect the level of pollution within that sector.

Experimental Methods

Cloud water samples were taken at Mount Mitchell during two month-long campaigns in June and August of 1993. The main observational platform was a 16.5 meter walk-up tower instrumented at the top with an R. M. Young wind speed and direction windbird, a temperature/humidity probe, and a barometric pressure transducer. A detailed review of the experimental procedures employed during the field season for the receipt and analysis of cloud water will be given elsewhere in these proceedings (Saxena, 1994)⁴.

Results and Discussion

Of all the events monitored during the 1993 field season, six events were chosen for this study to be investigated further. These six events were chosen based on the following criteria (see Table 1):

- 1) The desire for a variation of the air mass sectors (i.e., a representative sampling of sectors)
- 2) Wide range of cloud acidity averages (average pH's) of the study volume.
- 3) The desire for cloud events essentially free of liquid precipitation (See Table 1 footnotes for events where some liquid precipitation was encountered).
- 4) The desire for a representative mixture of events of varying length (i.e., long: greater than or equal to 8 hours, and short: less than 8 hours).
- 5) The desire for a roughly equivalent number of events from each of the 1993 field season months, June and August, so as to reduce any potential climatological bias.

The computer model which was used to produce the back trajectories for the above cases is known as Hybrid Single-Particle Lagrangian Integrated Trajectories, or HY-SPLIT (Draxler, 1992)⁵. This model is a Multiple-Layer Lagrangian program which uses pre-formatted meteorological data as the basis for the trajectory calculations. A number of gridded data formats can be used in this program, but for the purposes of this study, the Nested Grid Model (NGM), version 06, was employed, primarily because it is easily archived and routinely maintained at the Air Resources Laboratory in Silver Spring, Maryland. Air mass trajectories from the 1986-1988 field seasons, which will be the comparison base for this study, were generated via hand analysis of consecutive 850 millibar charts. Thus, it is a key purpose of this document to demonstrate a much more advanced method for the production of the trajectories.

Case 1--June 19, 1993: 0500Z-0700Z. The back trajectory generated by HY-SPLIT is given in Figure 2. The trajectory in Figure 2 is for 0600Z and had a corresponding pH value of 3.22. This cloud episode is categorized as being short in duration, about 2 hours, and having a fairly low average pH of 3.19 ± 0.04 . Thus based on our air mass sectors, we would expect this trajectory to have at least passed through fairly polluted regions of the United States (Sector 1). Interestingly, Figure 2 clearly shows an anticyclonic 48-hour trajectory with its starting point near the South Carolina coast. This should indicate that since the air mass is of marine sector origin, the cloud water acidity for this event should probably be somewhat higher than is observed. How much higher is somewhat subjective, but historically for Mount Mitchell, marine air masses would be expected to result in pH values in excess of 3.44 (on average) (Lin and Saxena, 1991)³. That this was not observed is of some interest, because in assessing the cloud water acidity of the majority of "marine" events for the entire 1993 field season, including those events that contained samples with rain, this phenomenon was a repeated occurrence. Reasons for the perceived low values are not obvious, but one possibility is the existence of individually high pollutant emitters in Sector 2, probably fairly close to Mount Mitchell. Comparison with the short marine trajectory as derived for May 16, 1987 indicates the obvious discrepancy. This event trajectory is matched in Table 1 with an average pH of 3.63 ± 0.13 , (see Figure 6 for the trajectory) which is much easier to understand given the air mass origin. Thus, we could suspect that there may perhaps be a flaw or other problem with the model or model calculation routine. This seems unlikely, however, as one very obvious characteristic of

the model trajectories for all the 1993 events (which were run every hour of each event) is that the results are all very consistent with each other. Wildly changing trajectory directions over the course of a very short period of time during a particular event would certainly indicate a design flaw, or other problem, but this was almost never the case.

Case 2--June 16, 1993: 1100Z-1300Z. This event (Figure 2 shows the representative trajectory, for which the corresponding pH at 1200Z was 3.45) had an average pH of 3.44 ± 0.01 and was again short in duration, approximately 2 hours. The nature of this event, as indicated by the trajectory, is clearly continental (Sector 3) and thus should reflect a moderate pH level, which it seems to do. Moderate here would most likely consist of pH levels from a low (very roughly) of 3.04 to a high of 3.94 (Lin and Saxena, 1991)³ based upon historical averages from the 1986-1988 field seasons. The average for this event falls well within that range. For the corresponding case during the 1986 field season (August 4, 1986), which was a long event, the average pH was 3.05 ± 0.32 , which is right at the lower boundary for that which might be expected unless the upper end of the standard deviation is considered. This is probably due to the fact that not all of this trajectory was contained entirely within the continental sector (Sector 3). As shown in Figure 5, this trajectory passed near the termination point at Mount Mitchell through Sector 1 (the polluted sector), and thus undoubtedly picked up some of the more polluted characteristics. Unfortunately, due to the relative lack of events from the 1993 field season which closely conformed to the requirements enumerated at the beginning of this section (e.g., little or no cloud with rain, desire for varying event lengths, air mass sectors, etc.) it was necessary to compare this event with an event from the 1986-1988 dataset which did not necessarily match the pathway exactly. However, if the fact that the August 4, 1986 example did pass at least partially pass through a polluted sector is accepted as true, then the corresponding reduction in pH is somewhat more acceptable.

Case 3--August 8, 1993: 0200Z-0600Z. Figure 3 shows a representative trajectory for the short (≈ 4 hour) cloud event of August 8, 1993. Again, a continental trajectory is in evidence, with a corresponding cloud water acidity average of 3.64 ± 0.13 , and an individual value at 0400Z of 3.61. Here, the average acidity fits in very well with historical averages for this type of air mass trajectory, as explained for the previous case. Again, though not all of the trajectory runs for this event are shown, a noticeable consistency was observed in that all examples run essentially due west through Tennessee and into either northern Arkansas or southern Missouri. The corresponding case from the 1986 field study (July 1, 1986) does not actually carry along the same path line as does the August 8th example, but in this case does still pass entirely within one sector (Sector 3). As can be seen from Figure 5, the 1986 example displays more curvature at the start point in south-central Missouri but more or less covers a similar region of Sector 3. The resulting cloud water acidity average for the July 1, 1986 trajectory was 3.22 ± 0.17 , and this also was a short event, as given in Table 1. Thus, we can see that both events contain pH averages which reside within the accepted regime for an event with a suspected continental air mass history.

Case 4--August 19, 1993: 0800Z-1400Z. The fourth example to be briefly investigated in this study is that of the short (≈ 6 hour) cloud event of August 19, 1993, which, from Table 1, had an average pH of 2.96 ± 0.08 . This acidity level is fairly low and was one of the lowest average pH events for the entire 1993 field season (tied for fourth lowest overall and second lowest in August). The trajectory in this case, as given in Figure 3 (pH 2.86 at 1100Z), passes mainly through northern North Carolina, southwestern West Virginia, and Ohio, which means that a clearly polluted influence (Sector 1) is indicated to be dominant in this example. As seen in Figures 1a and 1b, West Virginia and Ohio, are, on average, very heavy emitters of SO_x , and thus reduction of overall cloud water acidity would certainly be expected. This case was also fairly rare for the 1993 field season in that it was almost exclusively the only event over which the entire time period of the event resulted in trajectories emanating from the polluted sector (all other events which indicated polluted influence also contained at least some trajectory components within the other two sectors). The chosen case of correspondence from the 1987 field season (August 12, 1987, shown in Figure 6) was very similar in overall track and length and resulted in

an average acidity of 3.27 ± 0.29 , which though somewhat higher, falls well within the prescribed historical range (from the 1986-1988 field seasons) for the polluted sector of approximately pH 2.94 to 3.82.

Case 5--June 24 to 25, 1993: 24/2200Z-25/1500Z. The fifth case to be discussed here is an example of a long event with trajectories largely observed in the marine sector, as in Figure 4. The actual value of the pH for the trajectory in Figure 4 was 3.47 on June 25th, at 0700Z. From Table 1, it is shown that the event itself had an average pH of 3.27 ± 0.21 , which is below the lower end of accepted "climatological" norms for this region. As mentioned in Case 1, it is unknown as to what may be suppressing the acidity for trajectories emanating from this region, however, in this case, two possibilities may exist. First, depending upon the actual path of the trajectory close to Mount Mitchell, there may be local heavy pollutant emissions which may "artificially" reduce the pH even though the majority of the air mass traverses relatively "clean" regions. The second possibility is that the average may be a statistical anomaly. Even though the average is quite low for this event, the range of pH's observed for this event spanned from a low of 2.86 to a high reading of 3.51. The 2.86 and other pH's below 3.00 were observed at the beginning and the end of this event. This is common for many cloud events and is usually a result of a low liquid water content (LWC) which occurs at the beginning and end of most cloud events due to the evaporation of cloud droplets in the forming and dissipating stages, respectively (Lin and Saxena, 1991)². The only event from the 1986-1988 field studies which at least crosses similar areas as compared to this trajectory is a trajectory computed for the short event of August 19, 1986. This trajectory, though not similar in path, crossed a large percentage of North Carolina from the east as did this example. The 1986 event had average pH of 4.55 ± 0.09 and thus clearly exhibits expected marine acidity levels. See Figure 5 for the actual path of this trajectory.

Case 6--August 5, 1993: 0100Z-1600Z. The last of the cases to be investigated in this paper involves the long (≈ 15 hour) event on August 5, 1993. The average pH for this case was given in Table 1 as 3.48 ± 0.28 . The trajectory for 0900Z given in Figure 4 clearly shows a zonal (east-west) continental trajectory with a corresponding observed pH of 3.59. This example almost perfectly gives a representative pH value for suspected trajectories emerging from the continental sector. In fact, all trajectories for this event were very similar to the example in Figure 4, and all observed pH values with the exception of the last three or four in the time period were in the region of 3.50 (again, at the dissipation stage of the event, pH's dropped likely due to evaporative effects). The example chosen from 1987 (June 29, see Figure 5) turns out to be very similar in the pH average (pH 3.56 ± 0.30 , see Table 1) for the event and it also runs essentially east-west (with a small amount of north-south meander near the origin) and thus compares with the 1993 example very well for both criteria. The comparison between these two events therefore appears to be qualitatively the best of the six comparisons presented here and thus may indicate that, at least for the continental sector, very little overall change in pollutant emissions for that sector has occurred in the time span between the two study campaigns.

CONCLUSIONS

One of the objectives from the work at Mount Mitchell was to quantify the origin of air masses traversing the observing site. In this paper, we have experimented with a model which will do this. From the above case studies, it is clear that all of the cloud events from the 1993 field season can be investigated in the same manner. All that was attempted in this paper was a demonstration of a methodology that could be used to perform such a task. Additionally, we sought to determine if the model is, in fact, an accurate measurement tool for the stated purpose. The majority of the results presented here indicate that the model is of sufficient accuracy to ensure use on a much wider scale for the same purpose, although the data also shows that in some cases, there may be small-scale influences which affect expected results. Thirdly, we can conclude that in order to assess long-term changes in the acidity of cloud water impacting Mount Mitchell, much more on-site data sampling is needed, over many years. Based on the results of this necessarily limited study, is it unclear whether or not increasing or

decreasing levels of pollutant emissions are having a noticeable effect on cloud water acidity. Many more field seasons will be required to quantify the net effect conclusively.

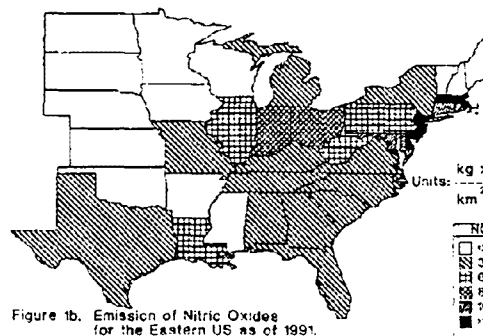
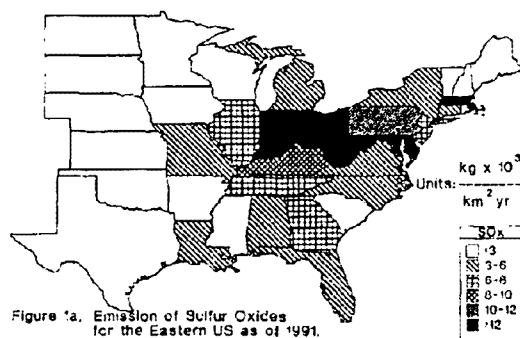
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Table 1. Cloud event type, length, average cloud water acidity values, and dominant air mass sectors for selected 1993 field season events and corresponding events from the 1986-1988 field study.

Event	Event Length	Hours (Approx.)	Avg. pH	Dev.	Air Mass Sector	Event	Event Length	Hours (Approx.)	Avg. pH	Dev.	Air Mass Sector
6/19/93	Short	2	3.19	0.04	2	5/16/87	Short	3	3.63	0.13	2
6/16/93	Short	2	3.44	0.01	3	8/4/86	Long	11	3.05	0.32	1 and 3
8/6/93	Short	4	3.64	0.13	3	7/1/86	Short	4	3.22	0.17	3
8/19/93	Short	6	2.66	0.08	1	8/12/87	Short	6	3.27	0.29	1
6/24-25/93*	Long	17	3.27	0.21	2	8/15/86	Short	4	4.55	0.09	2
8/5/93**	Long	15	3.48	0.23	3	6/29/86	Long	10	3.56	0.30	3

Notes: * - Cloud and Rain @ 3/24/2300Z; ** - Cloud and Rain @ 8/5/0100-0200Z.



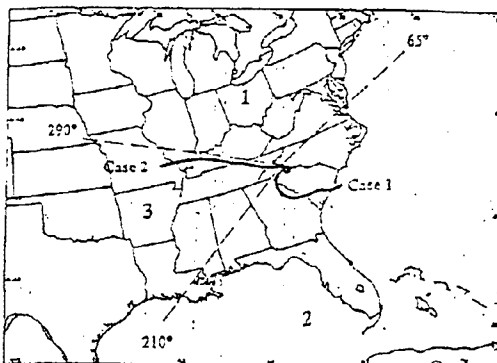


Figure 2. Model back trajectories for Case 1 (period ending on June 19, 1993/0600Z; p11 3.22) and Case 2 (period ending on June 16, 1993/1200Z; p11 3.44).

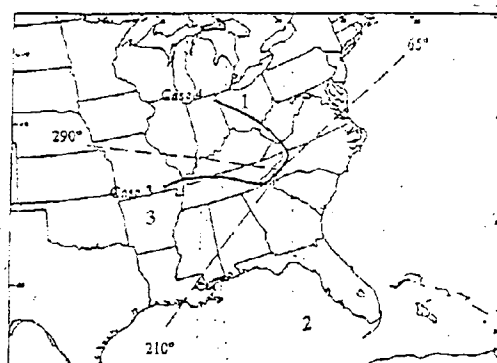


Figure 3. Model back trajectories for Case 3 (period ending on August 3, 1993/0400Z; p11 3.61) and Case 4 (period ending on August 19, 1993/1200Z; p11 3.56).

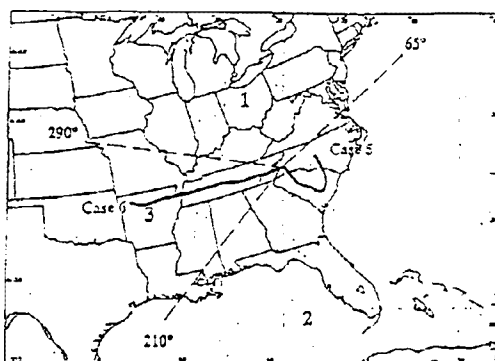


Figure 4. Model back trajectories for Case 5 (period ending on June 25/0700Z; p11 3.47) and Case 6 (period ending on August 5, 1993/0900Z; p11 3.59).

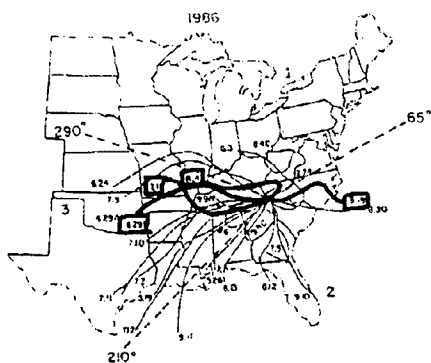


Figure 5. Hand-analyzed back trajectories for the 1986 field season. Highlighted trajectories are those for which comparisons were made in the text (Yeh, 1988)⁵.

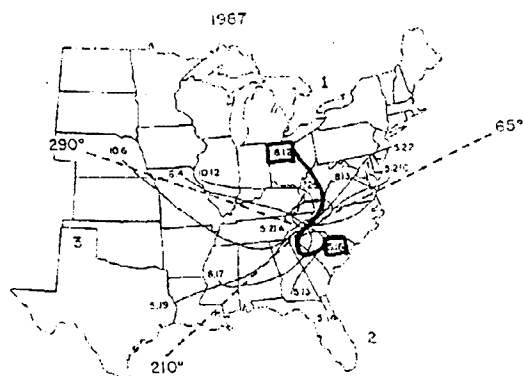


Figure 6. Hand-analyzed back trajectories for the 1987 field season. Highlighted trajectories are those for which comparisons were made in the text (Yeh, 1988)⁵.

The Effect Of Anthropogenic Pollution On Cloud Microstructure, pH and Albedo: Case Studies and Climatic Implications

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ABSTRACT

In situ cloud measurements were taken during 39 individual cloud events between June and October 1993 in Mount Mitchell State Park, North Carolina. Cloud droplet spectra were obtained using a Forward Scattering Spectrometer Probe (FSSP) and used to determine total droplet concentrations, average droplet radii and cloud liquid water content. The cloud water samples were collected and analyzed for pH and chemical composition. Meteorological data were recorded and used to verify air mass history through back trajectory analysis. A total of 119 hourly cases were available with simultaneous FSSP spectra, pH measurements, chemical analysis and meteorological data.

A strong positive correlation (coefficient = +0.608) was detected between pH and average droplet radius. Also, there was a strong negative correlation (coefficient = -0.609) between pH and total droplet concentration. The data were then sorted into three populations based on pH: $\text{pH} < 3.0$ ($n = 20$), $3.0 \leq \text{pH} < 3.7$ ($n = 75$), and $\text{pH} \geq 3.7$ ($n = 24$). It was observed that low pH values were associated, on average, with higher number concentrations and lower average radii, and *vice versa*. Cloud albedos were calculated for four cases and these compared favorably with the ones retrieved from Advanced Very High Resolution Radiometer (AVHRR). Thus, higher pollution content of clouds is shown to produce higher cloud albedos, which has a cooling effect on the regional climate.

INTRODUCTION

There is currently a significant amount of interest in understanding the effect of anthropogenic pollution present in cloud forming air masses on the resulting cloud droplet sizes and number concentrations. The desire to quantify the relationship between pollution and cloud microstructure is fueled by the debate over global change due to the greenhouse effect. Given the recent concern over climate change it is important that our fundamental theoretical understanding be supported by a wealth of field data which will quantitatively describe the relevant processes.

It is well understood theoretically that low level clouds produce an indirect cooling effect by increasing the shortwave albedo of the earth¹. Increasing anthropogenic emissions can potentially enhance this cooling effect by changing the cloud droplet distribution, which largely determines the cloud optical depth and albedo. Through gas-to-particle conversion urban pollution, particularly sulfates and nitrates, form efficient cloud condensation nuclei (CCN). In a cloud forming air mass, elevated CCN should produce greater droplet concentration and reduced droplet size. This in turn increases the cloud optical depth through the following relationship².

$$\tau = h \left(\frac{9\pi w^2 N}{2\rho^2} \right)^{\frac{1}{3}} \quad (1)$$

where

- h = cloud thickness in m
- N = cloud droplet number concentration in m^{-3}
- w = cloud liquid water content in g m^{-3}
- ρ = density of liquid water (10^6 g m^{-3})

After calculating τ , the cloud albedo can be evaluated as³

$$A = \frac{\tau}{\tau + 7.7} \quad (2)$$

For constant cloud liquid water content, larger N implies larger optical thickness and thus larger cloud albedo. By increasing the average cloud optical depth, elevated CCN concentrations lead to an overall increase in the planetary albedo and hence produce a cooling effect.

It has been estimated⁴ that the greenhouse warming of the earth-troposphere system caused by a doubling of carbon dioxide could be counteracted by a meager 2% increase in the shortwave albedo of global low level cloud cover. Charlson et al.⁵ have estimated the current climate forcing due to anthropogenic sulfate alone to be comparable in magnitude but opposite in sign to the current forcings due to greenhouse gasses. Wigley⁶ and more recently Saxena and Grovenstein⁷ have shown that climate is more sensitive to changes in SO_2 emissions than to changes in CO_2 emissions.

It is clearly central to our understanding of anthropogenically driven climate change to quantitatively show differences in microstructure and reflectivity between clouds formed in air masses with a variety of pollution contents. By comparing these various types of clouds, we can better determine the present anthropogenic climate perturbation, as well as make more scientific predictions of future impacts. Although these differences are described theoretically, there is no currently available field observational data base to provide detailed validation of the theory. Several important field studies have been conducted that provide strong verification of many aspects of the proposed mechanisms for pollution induced increases in cloud albedo.

During project METROMEX (Metropolitan Meteorological Experiment), Braham⁸ has shown that anthropogenic effluents cause an increase in the number concentration of droplets and precipitation in clouds formed downwind of urban-industrial regions. Alkezweeny, et al.⁹ have found that clouds formed in urban plumes from metropolitan areas can increase droplet concentrations and decrease the median volume diameter with regard to clouds formed in nearby unpolluted air masses.

Studies of the influence of anthropogenic pollution on albedo using actual measurements of cloud reflectivity have been few and often lead to contradictory conclusions. For example, Kondrat'yev et al.¹⁰ have found that city pollution lowered cloud albedo. In contrast, Radke et al.¹¹ have shown that anthropogenic effluents can significantly enhance cloud reflectivity. During project FIRE [First ISCCP (International Satellite Cloud Climatology Project) Regional Experiment] airborne measurements were taken across ship tracks while using the Advanced Very High Resolution Radiometer (AVHRR) aboard the NOAA-10 polar orbiting satellite to retrieve cloud reflectivities. Their results show an increase in total droplet concentration, liquid water content and total condensable nuclei concentration within the ship tracks compared to surrounding noncontaminated clouds. The AVHRR data showed higher cloud reflectivity ($68.3 \pm 1.4\%$) for the ship track clouds compared with that ($60.9 \pm 4.5\%$) for the surrounding clouds at $0.63 \mu\text{m}$ and $3.7 \mu\text{m}$ wavelengths. If the ship exhaust is considered as a surrogate for anthropogenic pollution, the change in cloud reflectivity produced as a result of land-based emissions could cause considerable regional and perhaps global climate perturbations.

METHOD

In situ cloud measurements were taken on Gibbs Peak (2006 msl) in the Mount Mitchell State Park, in rural western North Carolina. This site has several important advantages for the study of cloud microstructure and chemistry. The site, which extends into the free troposphere, is far from local pollution sources, allowing for the study of long range transport of both natural and anthropogenic aerosol. The site experiences cloudiness on 71% of the days during the summer¹². Thus sufficient data is obtainable in a single season to allow for stable statistics. Due to its position in mid-latitude, eastern North America, the clouds passing over the site vary in origin from heavily polluted to cleaner continental and marine air masses. Recently the site has been designated a United Nations Biosphere Reserve so that our measurements and others can be used over a very long time span to accurately gauge regional climate change.

Cloud droplet spectra were obtained using a Particle Measuring Systems Forward Scattering Spectrometer Probe (FSSP). The FSSP can accurately count and size particles from 0.5 to $47.0 \mu\text{m}$. A description of the operation of the FSSP is given by Knollenberg¹³. Spectra were taken every 3 seconds during cloud events and later averaged over 5 minute and 1 hour intervals. From each 15 bin histogram spectrum, total droplet concentration (N , m^{-3}), average droplet radius (r_{ave} , μm), and cloud liquid water content (w , g m^{-3}) are easily computed.

Cloud water samples were collected coincident with the FSSP spectra using an ASRC type passive string impaction collector. Samples were collected continuously and retrieved hourly. On site pH measurements were made for each sample immediately after retrieval. Samples were stored at 4°C and later analyzed for chemical composition using a Dionex 2010i ion chromatograph.

Meteorological data (wind speed and direction, pressure, and temperature) was recorded and used for back trajectory analysis using HY-SPLIT model. Forty-eight hour 3-D back trajectory graphs were generated using 2 hour integration intervals. The model also produces skew-T diagrams for selected times during the events. These skew-T diagrams were used to determine cloud heights for reflectance calculations.

Measurements were made during 39 individual cloud events between June and October 1993. Out of this data, 119 cases were available with simultaneous FSSP spectra, pH measurements, chemical composition and meteorological data.

RESULTS

When a cloud forms in a polluted air mass, the concentration of cloud droplets will be high, due to elevated concentrations of CCN. Then, limited available liquid water guarantees that r_{ave} will remain small. To investigate the relationships between pH and N and between pH and r_{ave} , we calculated correlation coefficients and produced scatter plots using the corresponding data pairs for all 136 available cases. Figure 1 shows pH versus droplet number concentration and Figure 2 shows pH versus average droplet radius. As can be seen, there is a strong positive correlation (coefficient = +0.608) between pH and average droplet radius. It can also be seen that there is a strong negative correlation (coefficient = -0.609) between pH and droplet concentration. The coefficient of correlation between pH and lwc was small (0.202), therefore pH is independent of cloud liquid water content. Thus cloud water pH is strongly influenced by both droplet size and concentration.

To investigate the dependence of pH on cloud microstructure more closely, the 119 cases with coincident pH and FSSP data were sorted into three populations: $pH < 3.0$ ($n = 20$), $3.0 \leq pH < 3.7$ ($n = 75$), and $pH \geq 3.7$ ($n = 24$). The average values for N, r_{ave} , lwc, and pH are shown for each population in Table 1. The \pm values represent standard errors ($s/\sqrt{n-1}$). It is seen that low pH values are associated, on average, with higher number concentrations and lower average radii; high pH values are associated, on average, with lower number concentrations and higher average radii; intermediate pH values are associated, on average, with intermediate values of both number concentration and average radii; while liquid water contents are reasonably consistent across populations.

Four cases were selected for analysis of cloud albedo and its effect on pH. The four cases, which are all short orographic events, cover a large range of pH values and thus represent clouds formed in air masses with a variety of pollution contents. Each of the three pH populations given above is represented by one or more cases. These events occurred on June 7, 1993 ($pH = 3.07$), June 14, 1993 ($pH = 2.84$), June 18, 1993 ($pH = 3.77$) and August 4, 1993 ($pH = 3.65$). For each of these cases, AVHRR data was used to determine the cloud albedo. Using in situ measurements of cloud microstructure, a second value of the cloud albedo was calculated from equation (1). Since the clouds were all orographic in nature, the clouds were all relatively thin and the heights varied by less than 15% of each other. This fact allows us to de-convolve the effect of cloud height, through equation (1), on the calculated cloud albedos. Thus, the microstructural parameters, which are closely linked to pH, produce the greatest variation in the calculated albedo values. Table 2 summarizes the cloud pH, microstructure and reflectivity for the four cases. There is generally good agreement between the satellite derived albedos and those calculated. Figures 3 and 4 show, respectively, the dependence of Albedo upon N and r_{ave} for these events. The AVHRR data set represents the satellite retrieved values while the in situ data set represents the albedo calculated from equation (1) and (2). In figure 3 there is an obvious positive trend with albedo increasing as cloud droplet concentration increases. In figure 4 there is an obvious negative trend with albedo decreasing as average droplet radius increases. Figure 5 shows the relationship between pH and albedo. Here the close agreement between the two albedo values is evident. The albedo is shown to decrease with increasing pH, giving strong evidence that heavily polluted air masses develop higher albedo clouds which produce a regional cooling effect.

CONCLUSIONS

Cloud pH, microstructure and albedo are closely related. For a given CCN composition, cloud pH is largely controlled by droplet concentration and size, which are each controlled by the amount of CCN present in the cloud-forming air mass. Since anthropogenic pollution produces efficient CCN, the amount of pollution present in the cloud-forming air mass will effect the droplet distributions. Greater levels of CCN will lead to increased droplet concentrations and smaller droplets. Because anthropoge-

effluents produce primarily acidic sulfates and nitrates, more pollution means lower pH. Cloud albedo can be calculated from in situ microphysical measurements and is shown to vary inversely with pH. Satellite measured cloud albedos closely match those calculated values. This research supports the proposition that pollution content has a positive effect on cloud albedo. Thus, pollution is responsible for producing regional climatic cooling by limiting the incoming solar radiation that reaches the surface.

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Table 1. Population mean microphysical and chemical composition parameters for three pH intervals. The \pm values represent standard errors. The average pH for each population was calculated by taking the minus log of the average $[H^+]$.

	pH < 3.0	3.0 \leq pH < 3.7	3.7 \leq pH
Number of cases	20	75	24
pH min-max	2.51-2.99	3.01-3.69	3.74-4.69
N (cm ⁻³)	717 \pm 63	553 \pm 25	281 \pm 20
r _{ave} (μ m)	3.12 \pm 0.20	3.59 \pm 0.10	4.77 \pm 0.20
w (g m ⁻³)	0.21 \pm 0.023	0.21 \pm 0.014	0.24 \pm 0.021
pH	2.86 \pm 0.030	3.27 \pm 0.018	3.95 \pm 0.032
[NO ₃] (μ eq l ⁻¹)	97.7 \pm 7.3	52.7 \pm 2.5	9.1 \pm 1.6
[SO ₄] (μ eq l ⁻¹)	1445.7 \pm 125.6	710.4 \pm 37.3	128.9 \pm 14.4

Table 2. Cloud pH, microphysical parameters and albedo for four orographic cloud events. The \pm values for the microphysical parameters were calculated based on the suggestions from Baumgardner¹⁴ and the \pm values for pH represent a 5% instrument error.

	June 7, 1993	June 14, 1993	June 18, 1993	August 4, 1993
N (cm ⁻³)	771 \pm 131	823 \pm 140	218 \pm 37	226 \pm 38
r _{ave} (μ m)	2.79 \pm 0.47	2.88 \pm 0.49	4.51 \pm 0.77	4.78 \pm 0.81
w (g m ⁻³)	0.16 \pm 0.05	0.18 \pm 0.06	0.19 \pm 0.06	0.15 \pm 0.05
pH	3.07 \pm 0.15	2.84 \pm 0.14	3.77 \pm 0.18	3.65 \pm 0.18
[NO ₃] (μ eq l ⁻¹)	45.4	40.7	24.8	24.6
[SO ₄] (μ eq l ⁻¹)	710.6	664.2	162.1	162.1
AVHRR albedo	0.53	0.58	0.47	0.45
in situ albedo	0.54	0.59	0.50	0.43

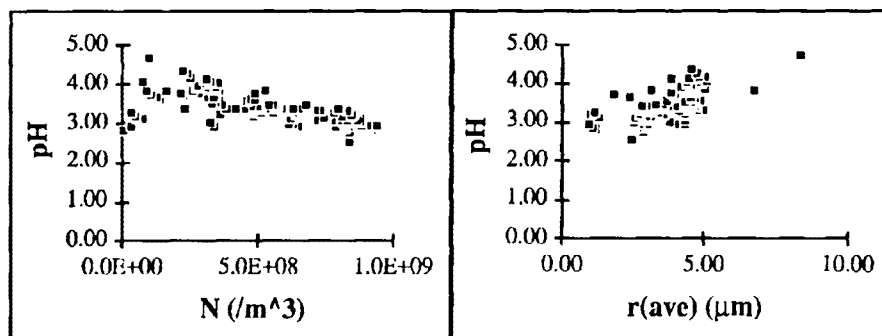


Figure 1. pH vs. Cloud droplet concentration for all 119 coincident data pairs.

Figure 2. pH vs. Average cloud droplet radius for all 119 coincident data pairs.

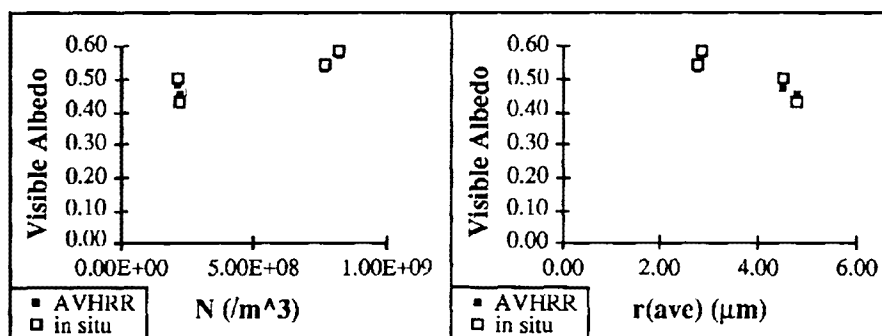


Figure 3. Albedo vs. Cloud droplet concentration for four orographic events.

Figure 4. Albedo vs. Average cloud droplet radius for four orographic events.

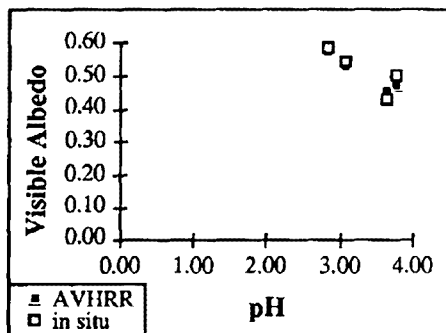


Figure 5. Cloud albedos vs. pH for four orographic events.

Aerosols as a Natural Tracer of Air Masses

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ABSTRACT

The chemical characteristics of marine, continental, and highly polluted air masses were studied by applying principal component analysis (PCA) to the cloud water data collected during field studies at a site located in Mt. Mitchell (2038 m MSL -35°44'05"N, 32°17'15"W) State Park, NC. The site is particularly advantageous for studying the effects of air pollution, since it intercepts air masses arriving from the East (marine), the West (continental), and the Northwest (polluted). PCA was used to study the relationship between the ionic constituents of the cloud water collected and the type of air mass that formed the cloud. By applying PCA to the cloud water chemistry, a set of highly intercorrelated variables was replaced with a set of uncorrelated principal components. It was found that PCA is most effective for identifying highly polluted air masses, where the variability among the ions is the greatest. The dominant source of the variance in continental air is the contrast between marine ions Na and Cl. For clean marine air, the variance among the different ionic constituents is minor. The sources of the air masses identified using PCA were compared to sources of the air masses assumed from back trajectory analysis measurements.

INTRODUCTION

Principal Component Analysis (PCA) has often been used in atmospheric research to help explain the relationship between aerosols and their source. In 1988 Elder¹ used PCA to identify the regions in the eastern U.S. that were the sources for SO₄²⁻ in precipitation. PCA has predominately been used in atmospheric research in the identification of the sources of dry aerosols collected by filtration as Mosher et.al.² did in Greenland in 1993. Recently a group in Sweden used PCA to examine the differences in the sources for interstitial and scavenged aerosols³. In this study the relationship between the ions present in the cloud water and different types of air masses is explored using PCA. PCA of cloud water chemistry is also used to augment existing techniques of using back-trajectory analysis and pH observation^{4,5} to determine the air mass history.

Experimental Site and Instruments

The site and the measurement capabilities are described by Saxena⁶ in a preceding paper in this volume. The main instrument used for this study was the ASRC (Atmospheric Science Research Center Albany, New York) passive string collector that collects cloud water. Cloud droplets were collected by the Teflon strings of the ASRC in a way that is analogous to the collision-coalescence process⁷. The cloud droplets that impact on the strings during a cloud event are collected in a water bottle once they become large enough to slide down the strings. Cloud water samples were collected every hour during cloud events and the pH of the samples was measured immediately after collection. In addition, part of the sample was stored at 4°C for later chemical analysis.

Cloud Water Chemistry Data

Pollution sources for Mt. Mitchell were categorized into three sectors by Saxena and Yeh⁴ using concentrations of SO_x and NO_x emissions. These sectors are shown in Figure 1 and are identified as highly polluted, marine and continental. Isobaric back-trajectories using the Hysplit3 model were calculated by Ulman⁸ for every cloud event that was sampled during June and August of 1993. For this study five cloud events were identified by their back trajectories as formed from air masses that were purely continental. Similarly three cloud events were identified as marine and three were identified as highly polluted. The back trajectories for these eleven cloud events are shown in Figure 1. To supplement this data, four highly polluted, six continental and five marine events were chosen from the 1986 and 19 field seasons at Mt. Mitchell. The back trajectories for these events are recorded in Saxena and Lin⁵.

Ion exchange chromatography was used to analyze the cloud water samples. Concentrations of cations NH_4^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and of anions SO_4^{2-} , NO_3^- , and Cl^- were measured. By examining the concentrations of the ions and pH of cloud water collected from highly polluted, marine and continental cloud events Saxena and Yeh⁴ made the following conclusions:

- The average acidity of the cloud water is the lowest for continental air masses.
- The average concentration of sulfate, nitrate and ammonium is less for clouds of mixed or oceanic origins when compared to clouds of urban origin.
- Higher concentrations of chloride, magnesium, potassium, and calcium are present in clouds of continental origin.
- An ionic balance between chloride and sodium is a good indication of an oceanic source.

The average pH of the six 1993 continental cloud events identified for this study was higher than the marine and polluted events as shown in Table 1. This supports Saxena and Yeh's first conclusion, but the pH range was also larger for continental cloud events with the lowest pH falling lower than any of the polluted or marine events. The average sulfate and nitrate are higher for highly polluted, but again the range overlaps with the continental and marine events. For continental events the average calcium is higher like Saxena and Yeh predicted, but chloride, magnesium and potassium are lower. Compared to the continental and polluted events the ionic balance between the average chloride and sodium is good, but for some marine events the concentration of chloride was over twice as large as the concentration of sodium. The point is that when considering individual cloud events the relationship between the cloud water chemistry and the source of the air mass is not always apparent. To further investigate the relationship between the source and the history of the air masses to the cloud chemistry, we have used principal component analysis on the cloud water data. PCA removes the correlation between highly correlated variables such as the ions found in the atmosphere or cloud water. By removing the dependence of the concentration of the ions on one another, we should get a clearer picture of how they are related to the type of air mass.

Principal Component Analysis

PCA takes a set of intercorrelated variables and replaces them with a set of uncorrelated principal components. These new variables are linear combinations of the original variables. The first principal component is the linear combination of the original variables that maximizes the variance between the original variables. The second principal component is a linear combination of the original variables that maximizes the variance to the extent that it is uncorrelated to the first principal component. The next principal component again maximizes the variance to the extent that it is uncorrelated with the first and second principal component and so on. In other words, by use of orthogonal rotations a set of correlated variables is turned into a set of uncorrelated variables. One method for finding these new uncorrelated variables is to use the correlation matrix. If the correlation matrix is diagonal then the variables are uncorrelated. Therefore the trick is to diagonalize the correlation matrix⁹. Diagonalization of a correlation matrix is done by finding its eigenvalues and eigenvectors. The eigenvalues and eigenvectors of a $(j \times j)$ correlation matrix is found by solving the eigenvalue problem

$$S\alpha = \lambda\alpha \quad (1)$$

where S is the correlation matrix, λ is the eigenvalue, and α is the eigenvector. The principal component z is then defined as

$$z = \alpha' x^* \quad (2)$$

where α' is the transpose of α and x^* is a standardized variable. The j th element of x^* is x_j/σ_j , where σ is the variance of x_j , the j th element of the original vector¹⁰.

PCA of Cloud Water

Principal Components of the cloud water cations NH_4^+ , Na^+ , Ca^{2+} , and of anions SO_4^{2-} , NO_3^- , and Cl^- were found using the correlation matrices calculated from the continental, mixed, and marine events. K^+ and Mg^{2+} were not included since they do not have a discernible influence on the pH. Since we have six variables it is possible to obtain up to six components. In all the events, the first two principal components accounted for at least 85% of the total variance, therefore they should be sufficient for explaining the relations between the ions and the air mass history. The highest eigenvector in the first

principal component represents the ion that best describes the variability of all the ions. NO_3 was the highest eigenvector for sixteen of the thirty-seven cloud events analyzed. Table 2 and 3 represent typical first two principal components for continental cases. In ten of the twelve continental cases a contrast between Na and Cl was indicated by opposite signs. The eigenvector for Cl is positive in the second principal component while the eigenvector for Na is negative for the example given in Table 2. The same is true in the second example, except the signs are reversed. June 29, 1993 and August 7, 1993 were the two cloud events where this contrast between Na and Cl did not occur. The correlation between Na and Cl for these two events was very high. Examination of the back trajectories for the two events shown in Figure 1, reveals that both have air masses that may have been influenced by the gulf. This influence might account for the high correlation between Na and Cl. Some variability was also accounted for by Ca, as shown in Table 3, where Ca has the highest eigenvector for the second principal component.

NO_3 accounts for the largest amount of variance in all the highly polluted events except one where Cl has a slight larger eigenvector for the first principal component. In five out of the seven events Na has the lowest eigenvector for the first principal component; Ca has the lowest eigenvector for the other two events. Na and Ca, both purely natural aerosols seem to have the least influence on the variability of the ion concentrations for the polluted events. Table 4 and 5 are examples of polluted events where Ca and Na have the lowest eigenvectors for the first principal component and NO_3 has the highest.

Table 6 gives the first principal component for a marine event that accounts for 92% of the total variance. For four out of the eight marine events analyzed over 90% of the total variance was accounted for by the first principal component. The first principal component accounting for almost all the variance indicates that the ions have nearly constant values for each of the observations made for the cloud event. Therefore the ions or original variables in these events are not dependent on one another¹⁰. In seven out of the eight marine events analyzed Ca had the lowest or second lowest eigenvector, which indicates that it accounts for the least amount of variance. The back trajectory for September 10, 1986, the one event where Ca did not have a low eigenvector compared to the other ions, shows the air mass starting southeast of Florida and traversing almost the total length of the state. This air mass probably spent more time over land compared to the other marine events, which would account for the increase in the importance of Ca.

Examination of the June 14, 1993 cloud event illustrates the usefulness of combining back-trajectory analysis and PCA to obtain a more accurate history of the air mass. The back-trajectory for this event shown in Figure 1 suggests this event is purely marine. Table 6 shows the first two principal components for the event which did not follow the pattern of low variability among the ion concentrations as the other marine events did. The first principal component for this event accounted for only 52% of the total variance, with NO_3 and SO_4 accounting for most of the variance. The correlation between Na and Cl for this event was 0.32. This low correlation is emphasized by the contrast between Na and Cl seen in the first principal component. Studying both the back-trajectory analysis and the PCA for this event reveals that the air mass was influenced by both marine and polluted sources.

CONCLUSION

PCA is a very useful tool for analysis of cloud water chemistry. Although SO_4 is very important in determining the degree of acidity of the cloud water, it is NO_3 that is more often the ion responsible for the largest amount of variability. The majority of the continental events exhibited a high contrast between Cl and Na, caused by a low correlation between them. Obviously, a marine component is lacking in continental air mass. A small contrast between Na and Cl is also occasionally evident in polluted and marine air masses, suggesting that marine aerosols are not the only source of Cl. The main characteristics of marine air are the small amount of variability among its ion concentrations and deficiency in Ca. Na and Ca account for the smallest amount of variability in polluted air. The most helpful ions in figuring out the type of air mass are Na and Ca. PCA was most effective in identifying the important factors in individual cloud event. By combining PCA and back-trajectory analysis a more reliable technique for identifying the sources of the air masses is obtained.

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Table 1. Summary of cloud chemistry for cloud events depicted in Figure 1. μ is the mean value and σ is standard deviation.

source		pH	NH ₄ ⁺ ueq/L	Cl ⁻ ueq/L	NO ₃ ⁻ ueq/L	SO ₄ ²⁻ ueq/L	Na ⁺ ueq/L	K ⁺ ueq/L	Ca ²⁺ ueq/L	Mg ⁺ ueq/L	Σ ion ueq/L
cont	μ	3.49	208.5	49.18	55.49	770.4	27.56	7.21	70.86	17.8	1207.22
	σ	0.43	135.2	27.20	40.48	515.7	26.90	6.15	81.82	16.8	794.49
pH range		2.49-3.99									
marine	μ	3.37	165.8	70.60	48.90	478.0	65.33	12.03	24.39	21.7	886.91
	σ	0.28	128.1	65.95	36.74	327.0	60.69	6.37	15.29	18.0	740.74
pH range		2.99-3.74									
polluted	μ	3.18	296.1	53.65	82.48	1070.	19.73	7.42	43.85	15.0	1588.76
	σ	0.17	77.98	18.02	28.14	253.8	18.87	3.80	20.70	5.44	326.90
pH range		2.95-3.34									

Table 2. Principal Components for continental event August 17, 1993.

	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	Ca ²⁺	NH ₄ ⁺	percent variance	cumulativ
1	0.43	0.43	0.31	0.41	0.43	0.43	88%	88%
2	-0.07	-0.06	0.92	-0.34	-0.10	-0.12	9%	98%

Table 3. Principal Components for continental event July 10, 1986.

	SO ₄ ²⁻	NO ₃	Cl ⁻	Na ⁺	Ca ²⁺	NH ₄ ⁺	percent variance	cumulative
1	0.44	0.44	0.44	0.41	0.22	0.45	78%	78%
2	-0.21	-0.16	-0.25	0.02	0.92	0.13	15%	93%

Table 4. Principal Components for polluted event June 24B, 1993.

	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	Ca ²⁺	NH ₄ ⁺	percent variance	cumulative
1	0.42	0.47	0.46	0.14	0.39	0.46	69%	69%
2	0.23	-0.12	0.19	0.85	-0.37	-0.22	18%	87%

Table 5. Principal Components for polluted event October 12, 1987.

	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	Ca ²⁺	NH ₄ ⁺	percent variance	cumulative
1	0.36	0.47	0.47	0.44	0.24	0.41	67%	67%
2	-0.55	-0.20	-0.09	0.28	0.75	0.08	20%	88%

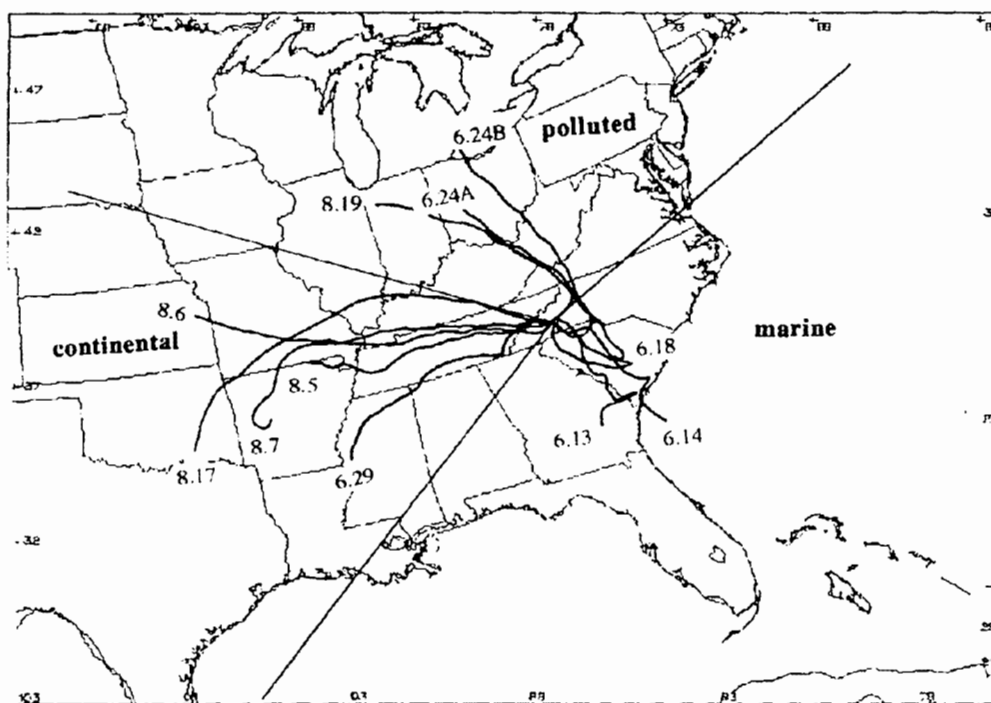
Table 6. Principal Component for marine event May 14, 1987.

	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	Ca ²⁺	NH ₄ ⁺	percent variance
1	0.41	0.42	0.42	0.42	0.34	0.42	92%

Table 7. Principal component for marine and polluted event June 14, 1993.

	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	Ca ²⁺	NH ₄ ⁺	percent variance	cumulativ
1	0.54	0.57	0.08	-0.03	-0.28	0.55	52%	52%
2	0.11	0.02	0.40	0.67	0.59	0.16	34%	86%

Figure 1 Back trajectories for continental, marine and highly polluted events from 1993. Each trajectory is identified by the month and day it occurred.



Greenhouse Warming, Acidic Deposition, and the Dilemma of Climate Change

by

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ABSTRACT

Tropospheric aerosols produce climatic perturbations through direct and indirect contributions to radiative forcing. Sulfate aerosols produce a cooling effect by elevating concentrations of cloud condensation nuclei (CCN) which enhance cloud-mediated albedo. Results from an ongoing field study at Mt. Mitchell, NC (35° 45'5" N, 82° 17'15" W, 2,038 m or 6,684 ft MSL) are presented. In response to the serious environmental problems due to acidic deposition, the Clean Air Act was amended mandating the reduction of fossil fuel emissions. Results presented here indicate a reduction in fossil fuel emissions that reduce acidic deposition could exacerbate greenhouse warming. Cloud reflectivity measured by the satellite based Advanced Very High Resolution Radiometer (AVHRR) from clouds with contrasting microphysical characteristics show varying radiative properties. This variation implies that the impact of enhanced CO₂ concentration on the temperature of the earth-troposphere system cannot be evaluated without accounting for the role of clouds in the same system.

INTRODUCTION

In an attempt to mitigate the serious environmental problems of global warming and "acid rain", the Amended Clean Air Act has mandated the reduction of both CO₂ and SO₂. The Amended Clean Air Act may actually exacerbate the magnitude of global warming while solving the dilemma of acid rain.

The role of SO₂ in the formation of hygroscopic nuclei is well known as is their capability of increasing the reflectivity of low level clouds.^{1,2,3} This increase in reflectivity in turn produces a cooling effect on the earth-troposphere system. The cooling effect may be significant enough to counteract greenhouse warming on a regional basis due to non-uniform distribution of sulfate aerosols. If sulfate cooling is currently counteracting greenhouse warming, reduction of SO₂ as mandated by the Clean Air Act will counteract cooling due to SO₂. The concentration of CO₂, however, will continue to rise for more than a century even if emissions are kept constant at present levels. It is known that an increase in the number concentration of cloud droplets causes an increase in the cloud lifetime and the cloud reflectance. Measurements such as those made under Project METROMEX (Metropolitan Meteorological Experiment) during the seventies have demonstrated that anthropogenic effluents cause an increase in the number concentration of droplets and precipitation in clouds formed downwind of urban industrial regions.⁴ However, it is not known what effect such effluents have on the shortwave albedo of these clouds. Modeling studies have shown that increases in the background pollution concentrations, in particular those that act as Cloud Condensation Nuclei (CCN), will result in changes in cloud reflectivity and evolution.^{5,6,7}

By observing the microphysico-chemical characteristics of both clouds and aerosols in clean and highly polluted air masses at Mt. Mitchell, NC (35°, 45'5" N, 82°, 17'15" W, 2038 m or 6684 ft MSL) the impacts of anthropogenic and natural tropospheric aerosols on the regional cloud reflectivity may be investigated by simultaneously analyzing cloud reflectivity data derived from the Advanced Very High Resolution Radiometer (AVHRR) aboard the NOAA spacecraft. The following features make Mt. Mitchell (designated as a United Nations Biosphere Reserve) a "barometer" for monitoring regional climate change

- the mountain encounters cloud 71% of days during the summer, on the average.
- the air masses arriving at the mountain could be highly polluted continental (pH of cloud water = 2.2) or clean maritime (pH of cloud water = 5.4) depending on the prevailing wind field.^{8,9}
- rates of cloud deposition were found to be in the range of 15-27 cm yr⁻¹.¹⁰ The deposition flux of sulfate ranged from 26-82 kg ha⁻¹ yr⁻¹.

METHODOLOGY

An intensive field campaign to Mt. Mitchell began on May 1, 1993. Besides meteorological measurements (Temperature, Pressure, Relative Humidity, Wind Speed and Direction) atop a 56 ft. (16.5

m) tall walk-up tower, the following observations were recorded: CCN activation spectrum (using Fukuta-Saxena CCN Spectrometer), cloud droplet size distribution (Forward Scattering Spectrometer Probe), and pH and ionic content of cloud water (collected by a passive collector and analyzed by Dionex system).

Cloud reflectivity is derived from the AVHRR instrument aboard the NOAA spacecraft. Raw AVHRR pass data containing channels 1 through 5 is processed into a 1024 x 1024 pixel subscene centered over Mt. Mitchell. Cloud reflectivity in the visible (0.63 μm) and near-IR (3.7 μm) are derived for daylight passes. Cloud reflectance at 0.63 μm depends on cloud thickness, liquid water content and droplet size. Cloud reflectance at 3.7 μm is controlled by droplet size alone. Cloud emissivity (3.7 μm) is derived for nighttime passes. Cloudy pixels in the vicinity of Mt. Mitchell are analyzed for reflectivity or emissivity depending on the time of day. Care is taken to exclude pixels that are contaminated by ice or contain fractional cloud elements.

RESULTS

Simultaneous analysis of AVHRR data and microphysico-chemical characteristics of clouds and aerosols during the period of June-October, 1993 (listed in Tables 1 and 2) have yielded the following evidence:

- 1) There is a strong relationship between visible cloud reflectance (0.63 μm) and the cloud droplet number concentration and pH of the cloud. In general, larger cloud droplet number concentration and lower pH (higher acidity) lead to a higher visible reflectance. The pH and the visible reflectance of the cloud (Fig. 1) are found to be strongly correlated (correlation coefficient = 0.98).
- 2) There is a strong relationship between cloud emissivity (3.7 μm) and cloud pH, cloud droplet number concentration, cloud droplet radius. In general, larger cloud droplet concentration, higher acidity (lower pH), and smaller cloud droplet radius lead to lower emissivity values. The pH and the emissivity (3.7 μm) of the cloud are found to be strongly correlated (correlation coefficient = 0.71).
- 3) The CCN number concentration at 1% Supersaturation in the air mass were found (listed in Table 2) to influence the emissivity of the ensuing clouds. In general, larger CCN concentrations lead to smaller emissivity values.
- 4) There is no relationship between the liquid water content of the cloud (listed in Tables 1 and 2) and the visible reflectance (0.63 μm) or emissivity (3.7 μm) of the cloud.

CONCLUSIONS

It is becoming increasingly apparent that the warming of the earth-troposphere system induced by greenhouse gases could be counteracted regionally by an increase in the cloud cover and/or cloud reflectivity.^{11,12,13} The results presented here illustrate the potential for analysis of clouds for microphysical effects at Mt. Mitchell and complement other studies of marine stratus clouds.^{14,15} The cloud systems are complex and conclusions about the relationships between cloud microphysical characteristics and cloud reflectivity will require careful statistical analysis of robust, long term datasets. Our first year observations followed by preliminary data analysis lead to the following inferences:

- 1) Clouds formed by clean air masses with higher pH (lower acidity) tend to have lower visible reflectances and higher emissivities.
- 2) Clouds formed by polluted air masses with lower pH (higher acidity) tend to have higher visible reflectances and lower emissivities.

The consequences of an emissions specific control policy intended to reduce global warming or "acid rain" could be to enhance global warming. Removal of SO_2 , and thus the hygroscopic nuclei formed by SO_2 , would remove any cooling effect on the earth-troposphere system. Observed increases in the number concentration of cloud droplets formed in polluted air masses indicate a cooling of 2-3 Wm^{-2} in eastern North America due to increased reflectivity of clouds.¹² These values are comparable to the estimated 2.5 Wm^{-2} heating due to anthropogenic greenhouse gas emissions up to the present.¹⁶ Model studies have calculated that a four fold increase in marine CCN concentrations could counteract greenhouse warming of

the earth-troposphere system caused by a doubling of CO₂.⁶ Climate models have shown significant climatic response whenever cloud-related parameters have been varied, especially with effective radius of cloud droplets.⁷

The data here have shown the radiative properties of clouds varying with differences in cloud microphysico-chemical characteristics; however, knowing the present radiative properties of clouds does not indicate the response of the regional climate to changes in cloud microphysico-chemical characteristics. The sensitivity of the climate system to changes in cloud radiative properties must be investigated before any strong conclusions may be drawn.

Acknowledgments:

This work is supported through the Southeast Regional Center of the National Institute for the Global Environmental Change by the U.S. Department of Energy under cooperative agreement No. DE-FC03-90ER61010.

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Table 1. Cloud microphysico-chemical properties with corresponding daytime Visible (0.63 μm) and Near IR (3.7 μm) reflectances.

Date 1993	Time (UTC)	pH	N (cm^{-3})	r (μm)	lwc (gm^{-3})	Visible Albedo	Near IR Albedo	Temp. ($^{\circ}\text{C}$)
June 14	2147	2.84	823	2.88	0.18	57.5	18.5	19
June 7	2132	3.07	771	2.79	0.16	53	13	11.2
June 18	2058	3.77	218	4.70	0.24	47	11	13
Aug 4	1415	3.65	226	4.78	0.15	45	19	12

Table 2. Cloud microphysico-chemical properties with corresponding nighttime emissivity (3.7 μm) values.

Date 1993	Time (UTC)	pH	N (cm^{-3})	r (μm)	lwc (gm^{-3})	Emissivity	CCN (1% S) (cm^{-3})	Temp. ($^{\circ}\text{C}$)
Aug 18	0013	2.97	750	3.22	0.16	0.672 ± 0.022	1100	13
Aug 19	1024	3.08	634	4.08	0.27	0.771 ± 0.052	1200	11.7
Aug 24	0125	3.24	515	4.37	0.27	0.848 ± 0.052	600	10
Aug 06	0942	3.79	462	4.93	0.3	0.863 ± 0.053	200	19
Oct 03	0940	4.74	54	8.3	0.29	0.875 ± 0.013	NA	6

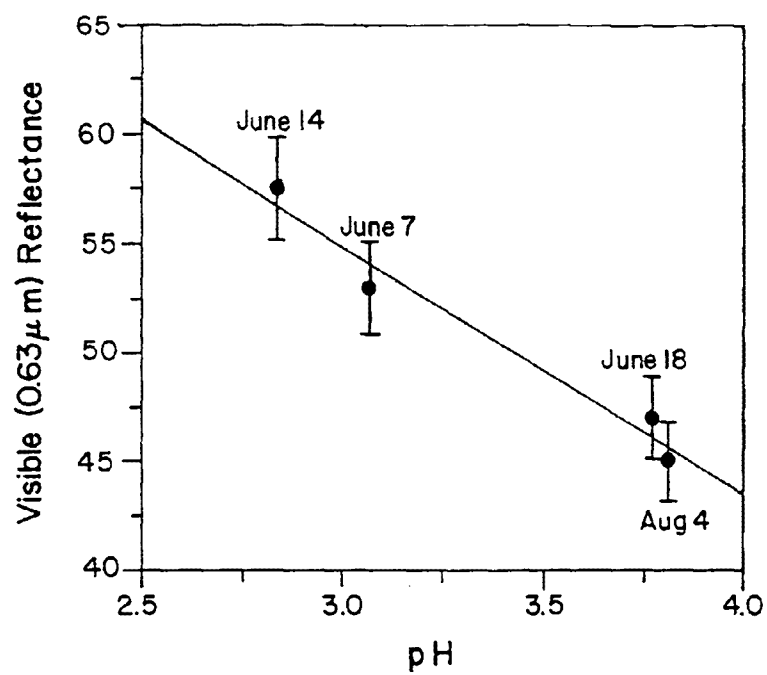


Figure 1. Cloud visible (0.63 μm) reflectance values vs. cloudwater pH. Error bars represent standard errors of pixel values averaged in the vicinity of Mt. Mitchell.

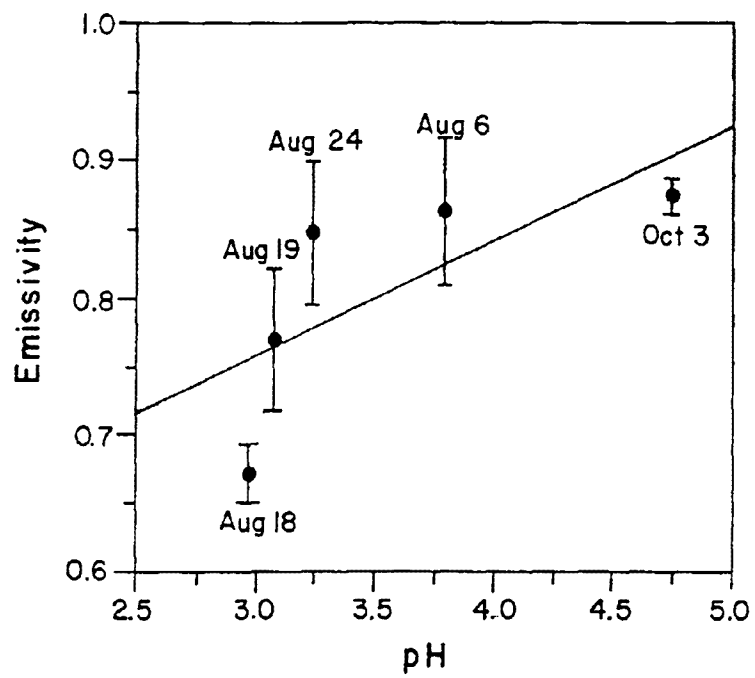


Figure 2. Cloud emissivity ($3.7\ \mu\text{m}$) values vs. cloudwater pH.

SAGE II Based Column Surface Area Measurements of the Mt. Pinatubo Aerosol Over the Eastern United States

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ABSTRACT

Since the increase in anthropogenic chlorine is estimated to be about 30-40% in the last 12 years, the eruption of Mt. Pinatubo during June 12-16, 1991 has the potential to possess the surface areas needed for the destruction of ozone on a large scale since it is the largest volcanic event recorded in recent history. The Pinatubo aerosol characteristics between 12-30 km and columnar characteristics in a unit column between 15-25 km are inferred from the Stratospheric Aerosol and Gas Experiment (SAGE) II measurements using a Randomized Minimization Search Technique (RMST) in the radii range of 0.1-0.8 μm in 0.1 μm increments. Results between 1991-94 indicate that the maximum surface areas observed were up to 48 $\mu\text{m}^2\text{cm}^{-3}$. The vertically averaged surface areas of up to 28 $\mu\text{m}^2\text{cm}^{-3}$ in February 1993 coincided with record lows of total ozone over the United States. The surface areas observed were also in the range found in the El Chichon aerosol months after the eruption which coincided with record lows of ozone in 1983.

INTRODUCTION

The role of ozone (O_3) in the atmosphere takes on 2 contrasting identities. In the troposphere, the presence of ozone is considered pollution and therefore a hindrance whereas in the stratosphere, the presence of ozone is needed in that ozone absorbs the sun's harmful ultraviolet (UV) radiation that can cause skin cancer and other biological damage. The role of stratospheric aerosols in relation to ozone depletion has stirred up considerable interest since the eruption of Mt. Pinatubo. Mt. Pinatubo (15.1° N, 120.4° E) in the Philippines erupted between 12-16 June 1991 and injected large amounts of ash, dust, and sulfur dioxide gas (SO_2) well into the stratosphere. The Pinatubo cloud was subsequently tracked by ground, airborne, and satellite sensors as it dispersed globally. The initial mass loading of SO_2 was estimated to be 20-30 megatonnes, the largest recorded in recent history (1). The SO_2 cloud reacted with water vapor (H_2O) to form a sulfuric acid aerosol ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}$). The e-folding time (the time it takes for this conversion) is about 35 days (2). Over time, the Pinatubo aerosol apparently stratified and was subsequently incorporated into the Junge layer where it still lingers to this date. The aerosol will coagulate and settle into the lower stratosphere and troposphere and eventually be removed by dry deposition, snowout, washout, and sedimentation.

Perturbations in the stratospheric ozone layer since the eruption of Mt. Pinatubo have been well documented. Column ozone decreases of 2-4% over mid-latitudes a few months after the eruption were attributed to additional heating in the lower stratosphere caused by the Pinatubo aerosol (3). Similar losses were observed after the El Chichon (17.22° N, 92.3° W) eruption in 1982 (4). Equatorial measurements derived from the total ozone mapping spectrometer (TOMS) show a 6% decrease from previous climatology (5). Lidar and ozonesonde measurements in the tropics showed maximum losses of up to 20% at an altitude of 24 km a few months after the eruption with a strong correlation to the peak aerosol loading at this height determined by the lidars (6). Ozone profiles over Wallops Island, Virginia and Boulder, Colorado depicted a 25% decrease in ozone between 12-22 km during the winter and spring of 1992-93 and was believed partially due to the heterogeneous chemical reactions on the surfaces of the Pinatubo aerosols (7). Heterogeneous chemical reactions on the surfaces of the resulting volcanic sulfate aerosol particles can render ozone more vulnerable to man-made chlorofluorocarbons (CFC's) (8). Since the increase in anthropogenic chlorine is estimated to be about 30-40% in the last 12 years, the eruption of Mt. Pinatubo has the potential to possess the surface areas needed for the destruction of ozone over tropical to mid-latitudes on the same order of magnitude as that of the seasonal losses over Antarctica (9).

It is the purpose of this study to investigate the temporal changes of the columnar and vertically averaged characteristics of the Pinatubo aerosol inferred from the Stratospheric Aerosol and Gas Experiment (SAGE) II measurements in the radii range of 0.1-0.8 μm between January 1991 to March 1994 in relation to ozone depletion.

SAGE II Data Base Description

NASA's SAGE II program has provided dependable stratospheric aerosol extinction measurements since the program's inception in October 1984. The SAGE II instrument is a self-calibrating, limb-scanning sun photometer on board the Earth Radiation Budget Satellite (ERBS) that measures vertical profiles of aerosol extinction coefficients at wavelengths of 1.02, 0.525, 0.453, and 0.385 μm , with one kilometer vertical resolution (10). The ERBS is a free-flying satellite with a 610 km circular orbit and a 57° angle of inclination. The SAGE II instrument measures 15 sunset and 15 sunrise measurements each day. The spacing is equal in longitude. The latitudinal spacing is roughly 0.5 degrees between measurements. Over a whole year, the SAGE II instrument covers from 75° S to 75° N (10).

The Pinatubo plume was sufficiently opaque in some areas that the solar intensity reaching the SAGE II instrument was zero (1). The height below the altitude of largest measurable extinction is truncated and referred to as the aerosol cloud top. Each data set was searched for untruncated layers and each layer was essentially counted for untruncated extinction measurements. The layers below 20 km were truncated the most indicating the most optically thick layers of the Pinatubo aerosol. Layers above 20 km were truncated only in a few areas. This phenomena is unique to the Pinatubo aerosol.

Randomized Minimization Search Technique (RMST)

The technique used for the inversion of the SAGE II spectral data for Mie particle theory is a modified randomized minimization search technique (RMST) (11 and 12). The extinction coefficient β_λ at wavelength λ is defined for Mie particles as

$$\beta_\lambda = \int_0^\infty Q(m_r, r, \lambda) \pi r^2 n(r) dr$$

where

Q = extinction efficiency factor for Mie particles

m_r = refractive index

r = particle radius in μm

$n(r)$ = number concentration in $\text{cm}^{-3} \mu\text{m}^{-1}$ between particle radius r and $r + dr$.

The RMST is a spectral inversion technique designed to find a size distribution whose optical properties have a minimum deviation from the measured properties. This deviation is quantified by a root-mean-square deviation. In this case, the RMST process is applied to the extinction coefficients β_λ provided by the SAGE II program at the four wavelengths λ (number of equations). To determine the inversion size interval, the ratio criterion of kernel functions is applied to the respective wavelengths. The ratio criterion states that if the ratios of kernel functions at different wavelengths remain constant in some size ranges, the information content cannot be provided in those ranges. To apply the RMST inversion algorithm, eight size intervals (number of unknowns) are selected with the middle points from 0.1 - 0.8 μm by 0.1 μm increments. The pre-mentioned criterion substantiates why the smallest ($< 0.1 \mu\text{m}$) and largest ($> 0.8 \mu\text{m}$) size intervals cannot be resolved by RMST. The Junge size distribution is used as an initial assumption to expedite the calculations. The aerosol particles are assumed to be comprised of a 75% sulfuric acid (H_2SO_4) and 25% water (H_2O) solution leading to an aerosol density of 1.65 g cm^{-3} . The refractive index for Mie particles used in the calculations is 1.45. Numerous inversion algorithms have been devised to invert spectral data. The main advantages of using RMST over other inversion algorithms are: 1) it is relatively fast, 2) no presumed size distribution is necessary, 3) RMST's ability to depict multimodal distributions, 4) smoothing and non-negative constraints, 5) no closure constraints (unknowns do not have to equal to the number of equations). The particular data base constraints are in essence, RMST's constraints. The efficacy of RMST was proven for the analysis of the severe ozone depletion episode over Antarctica during 1987 (12). In this study, columnar aerosol properties such as total number $N_c(\text{cm}^{-2})$, mass loading $M_c(\text{mg m}^{-2})$, surface area $S_c(\mu\text{m}^2 \text{cm}^{-2})$, and mean (R_m) and effective (R_e) radii in μm are derived in a unit column between 15 and 25 km. Vertically averaged characteristics are also derived at heights between 15-25 km. Retrieved spectra contain aerosol number distributions $n(r)$ between 12-30 km in the pre-mentioned size ranges. The temporal periods for this study are January 1991 for the background stratospheric aerosol profiles, June, July and November, 1991, February and July, 1992 and 1993, and March, 1994 for the volcanically perturbed stratospheric aerosol profiles between 25°-45° N and 90°-100° W.

DISCUSSION AND RESULTS

Tables 1 and 2 show the vertically averaged and maximum aerosol characteristics for each height between 15-25 km and 25°-45° N, 60°-80° W (i.e. the eastern U. S.), for January 1991 and February 1992 respectively. The January 1991 profiles depict the unperturbed background stratospheric aerosol characteristics. The presence of the Pinatubo aerosol is clearly evident in the 1992 profiles as the number concentration N increased by up to 10 times, the mass concentration M increased by up to 50 times, and the surface area concentration S increased by up to 25 times greater than the background levels in January 1991. The optically thickest layer appears to be between 18-22 km. Maxima in N of 173.8 cm^{-3} is found at 18.5 km, whereas S of $40.37 \mu\text{m}^2 \text{ cm}^{-3}$ and M of $8.45 \mu\text{g m}^{-3}$ are found at 19.5 km. The averaged peak value of N is 57.96 cm^{-3} at 20.5 km whereas the averaged peak values of S and M are $23.66 \mu\text{m}^2 \text{ cm}^{-3}$ and $5.19 \mu\text{g m}^{-3}$ respectively at 18.5 km. These observations suggest a greater concentration of smaller particles at 20.5 km. It must be stressed that these calculations are conservative estimates due to the large number of truncated measurements below 20 km and the retrieved size interval in that particles with $r < 0.1 \mu\text{m}$ and $r > 0.8 \mu\text{m}$ cannot be included in the calculations. The effective radius R_e (not shown) is the total volume to total surface area ratio and is helpful in determining the contribution of the larger particles. Values of R_e ranged between $0.29 \mu\text{m}$ at 24.5 km to $0.42 \mu\text{m}$ at 19.5 km compared to $0.14 \mu\text{m}$ and $0.18 \mu\text{m}$ in January 1991. Bi-weekly balloonborne particle measurements over Laramie, Wyoming (41° N) from June 1991 through May 1992 depicted maximum surface areas of $40 \mu\text{m}^2 \text{ cm}^{-3}$ approximately 180 days after the eruption and remained relatively homogeneous in time and altitude through May 1992 with maximum surface areas between $20\text{-}30 \mu\text{m}^2 \text{ cm}^{-3}$ (13 and 14). Aerosol volatility tests there approximately 1 month after the eruption showed that the Pinatubo aerosol was composed mainly of a 90% $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solution (13). It is quite evident that the values we derived here in Table 2 reasonably agree with those measured over Laramie in 1992.

Table 3 shows the same aerosol characteristics as in Tables 1 and 2 but for February 1993. The number of truncated measurements here is much less than in 1992 such that the heights that were truncated most were below 13 km. Therefore, the values listed here between 15-25 km are unaffected by the truncated measurements. The peak averaged N of 29.45 cm^{-3} is at 16.5 km as compared to 20.5 km in 1992. The peak averaged M and S of $2.82 \mu\text{g m}^{-3}$ and $12.38 \mu\text{m}^2 \text{ cm}^{-3}$ is at 15.5 km compared to 18.5 km in 1992. This lower height where the maxima are located illustrate the settling of the Pinatubo aerosol into the lower stratosphere. Maxima in S ranged from $1\text{-}48 \mu\text{m}^2 \text{ cm}^{-3}$ between 12-22 km and coincided with the record low decreases in ozone in 1993 between 12-22 km over the United States. The losses in ozone may be attributed to the heterogeneous chemical processing on the surface of the Pinatubo aerosol droplets (7). The mean values of S ranged from $1.5\text{-}28 \mu\text{m}^2 \text{ cm}^{-3}$ between 12-22 km. Values for R_e ranged from $0.2 \mu\text{m}$ at 24.5 km to a maximum of $0.52 \mu\text{m}$ at 14.5 km.

Figures 1a) through 1d) show sample columnar number distributions for a) February 1992, b) July 1992, c) February 1993, and d) July 1993 between 25°-45° N and 60°-80° W. The January 1991 profile is also shown in each figure to compare the unperturbed and volcanically perturbed stratosphere. The 1/91 profile can be fitted with a modified single mode lognormal distribution. The 2/92 and 7/92 profiles depict the perturbed stratosphere and contains 2 modes. The smaller mode has a corresponding radius of $< 0.2 \mu\text{m}$. There exists the possibility of a smaller radius of $< 0.1 \mu\text{m}$ but this may be due to the uncertainties of the SAGE II extinction coefficients at the smallest wavelength. Regardless, these profiles can be reasonably fit with the sum of 2 lognormal functions with the larger mode on the order of $0.4 \mu\text{m}$. The possibility of a third mode with radius $> 0.8 \mu\text{m}$ may be present in Figures 1b) and 1c). The 2/93 and 7/93 profiles can also be fitted with the sum of 2 lognormal functions. It is evident that the smaller radii intervals in Figure 1d) for 7/93 are approaching the background levels of 1/91. Larger particles are still present but smaller in total number. This can be attributed to the decay and sedimentation of the aerosol.

Table 4 shows the temporal history of the derived columnar aerosol characteristics over the eastern United States. Major increases in the derived characteristics are clearly evident in November 1991. The aerosol maintained columnar surface areas on the order of $100 \times 10^5 \mu\text{m}^2 \text{ cm}^{-2}$ from November 1991 to July 1992. The columnar mass concentrations increased almost 2 orders of magnitude between January and November 1991. The increase is due to a higher concentration of larger particles ($r > 0.3 \mu\text{m}$). The maximum surface areas coincided with the most optically thick layers. The surface areas, mean radii, and total number concentrations remained virtually constant through February 1993. A decrease on the order of 2 is evident between February and July 1993 for the derived characteristics N_c , M_c and S_c as the aerosol coagulates and settles into the lower stratosphere. The observed column surface areas between July 1992 to February 1993 are $50\text{-}100 \times 10^5 \mu\text{m}^2 \text{ cm}^{-2}$ and roughly coincide with record losses of ozone between 12-22 km (7). The effective radii R_e during this same interval ranged from $0.32\text{-}0.40 \mu\text{m}$. Similar results for longitudes between 80°-100° W were also found (not shown).

CONCLUSIONS

Columnar aerosol characteristics between a unit column of 15-25 km and mean aerosol characteristics between 12-30 km were inferred from SAGE II measurements between 25° 45° N and 60°-100° W. These characteristics were studied over time from 1991 to the present. The following conclusions result from this study:

- 1) Columnar bi-modal size distributions were prevalent from late July 1991 to July 1993 with small mode radii of less than 0.1 μm and large mode radii between 0.3-0.6 μm .
- 2) Vertically averaged surface areas were prevalent on the order of 10-26 $\mu\text{m}^2 \text{cm}^{-3}$ with maximums of up to 46 $\mu\text{m}^2 \text{cm}^{-3}$ at individual layers between November 1991 to July 1992.
- 3) Columnar bi-modal distributions with small mode radii approaching the background levels and large mode radii on the order of 0.35 μm are observed in March 1994 as the aerosol decays and settles. A larger mode with radii > 0.6 μm may be present.
- 4) Mean surface areas on the order of 1-28 $\mu\text{m}^2 \text{cm}^{-3}$ with maxima between 6-48 $\mu\text{m}^2 \text{cm}^{-3}$ were present and coincided with record losses of ozone over the United States between 12-22 km in February 1993.

ACKNOWLEDGEMENTS

This work was supported by NASA Langley Research Center under contract NAS1-18944. One of us (V.K.S.) is indebted to M. Patrick McCormick for making him interested in SAGE II.

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Table 1. Vertical profiles of averaged and maximum (max) aerosol characteristics between 15-25 km from 25°-45° N and 60°-80° W during January 1991.

Height(km)	N(cm^{-3})	Nmax	M($\mu\text{g m}^{-3}$)	Mmax	S($\mu\text{m}^2 \text{cm}^{-3}$)	Smax
15.5	4.01	16.26	0.12	0.22	0.96	2.49
16.5	5.57	19.12	0.13	0.23	1.19	2.85
17.5	4.71	23.78	0.13	0.27	1.10	3.56
18.5	5.40	17.24	0.12	0.21	1.13	2.60
19.5	5.82	15.75	0.11	0.17	1.13	2.27
20.5	5.62	17.31	0.09	0.15	1.04	2.38
21.5	4.50	14.21	0.07	0.13	0.82	1.91
22.5	3.68	12.64	0.06	0.12	0.67	1.74
23.5	2.47	11.61	0.04	0.10	0.48	1.55
24.5	2.78	12.17	0.04	0.10	0.47	1.68

Table 2. Vertical profiles of averaged and maximum (max) aerosol characteristics between 15-25 km from 25°-45° N and 60°-80° W during February 1992.

Height(km)	N(cm^{-3})	Nmax	M($\mu\text{g m}^{-3}$)	Mmax	S($\mu\text{m}^2 \text{cm}^{-3}$)	Smax
15.5	No Data	No Data	No Data	No Data	No Data	No Data
16.5	4.90	7.17	2.97	4.22	10.95	14.36
17.5	17.52	49.12	3.84	5.64	14.91	24.15
18.5	55.81	173.78	5.19	6.96	23.66	38.81
19.5	56.22	116.33	4.73	8.45	21.79	40.37
20.5	57.96	113.87	3.25	6.38	18.06	28.21
21.5	42.36	113.46	1.96	3.56	12.09	21.31
22.5	28.08	62.56	1.13	2.51	7.55	13.22
23.5	17.68	48.45	0.63	1.82	4.54	9.64
24.5	10.59	28.82	0.32	0.81	2.54	5.51

Table 3. Vertical profiles of averaged and maximum (max) aerosol characteristics between 15-25 km from 25°-45° N and 60°-80° W during February 1993.

Height(km)	N(cm^{-3})	Nmax	M($\mu\text{g m}^{-3}$)	Mmax	S($\mu\text{m}^2 \text{cm}^{-3}$)	Smax
15.5	24.05	70.12	2.82	4.93	12.38	24.63
16.5	29.45	81.49	2.42	4.21	11.61	21.82
17.5	26.11	78.11	1.93	3.73	9.79	18.72
18.5	22.34	63.64	1.28	3.19	7.24	15.64
19.5	19.58	54.41	0.78	1.90	5.21	12.15
20.5	16.31	43.42	0.43	1.13	2.96	8.96
21.5	6.07	34.54	0.23	0.85	1.69	6.18
22.5	3.87	18.07	0.11	0.36	0.93	2.87
23.5	1.27	5.59	0.05	0.18	0.40	1.30
24.5	1.63	10.38	0.04	0.14	0.56	1.46

Table 4. Columnar aerosol characteristics in a unit column between 15-25 km from 25°-45° N and 60°-80° W. The Re and Rm are averaged columnar properties.

Month(s) and Year	N(cm^{-2}) $\times 10^5$	M(mg m^{-2})	S($\mu\text{m}^2 \text{cm}^{-2}$) $\times 10^5$	Rm(μm)	Re(μm)
January 1991	50.1	0.90	9.1	0.11	0.17
June-July 1991	84.3	1.2	14.4	0.12	0.16
November 1991	258	19.6	100	0.16	0.29
February 1992	236	23.0	108	0.21	0.38
July 1992	193	21.6	95.2	0.19	0.40
February 1993	190	14.6	71.0	0.13	0.32
July 1993	106	7.5	38.4	0.14	0.31
March 1994	33.8	2.7	14.9	0.16	0.30

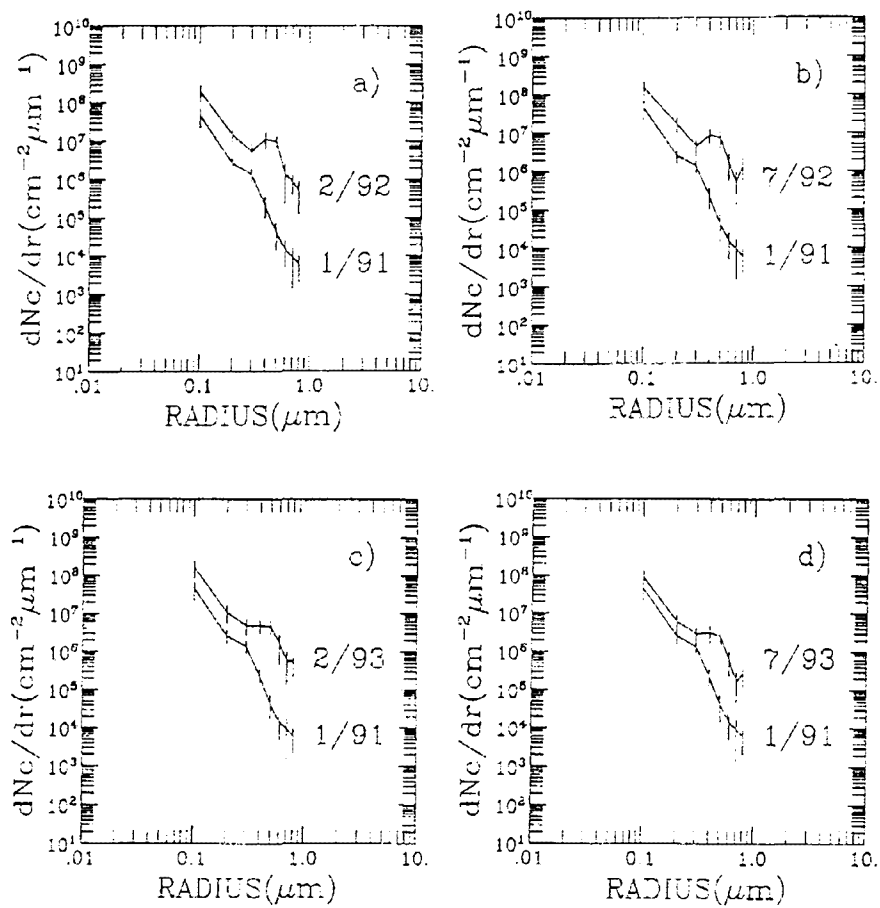


Figure 1. Comparison of the mean unperturbed January 1991 and volcanically perturbed a) February 1992, b) July 1992, c) February 1993, and d) July 1993 column number distributions between 25°-45° N and 60°-80° W in a unit column from 15-25 km. The error bars represent 1 standard deviation.

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SESSION 8:
MEASUREMENT METHODS

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A Study of Interferences in Ozone UV
and Chemiluminescence Monitors

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ABSTRACT

A study was conducted to examine interferences and other measurement anomalies in chemiluminescence and ultraviolet ozone monitors. Previous results had shown that there was a positive deviation in the chemiluminescence monitors and no direct interference with ultraviolet monitors due to the presence of water at non-condensing concentrations. The present study continues this effort, examining both potential positive and negative effects of moisture and other interferences on these monitors. Aromatic compounds and their oxidation products could potentially show a positive interference with ultraviolet monitors, and test measurements were made with aromatics such as toluene, benzaldehyde, and nitrotoluene to determine their possible retention in the ozone scrubber and their absorption in the cell as a function of the humidity. A detailed examination of the scrubbers used in ultraviolet ozone monitors has also been undertaken. Ozone scrubbers that have shown anomalous behavior in the field have been studied in various reduced-efficacy modes under controlled laboratory conditions. Longer term tests of unused scrubbers for possible ozone breakthrough under exposure to various simulated field conditions were initiated.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

INTRODUCTION

Ozone is formed in the atmosphere from photochemical reactions involving hydrocarbons (HCs) and oxides of nitrogen (NO_x). Adverse health effects and plant damage occur at high ambient concentrations. The Clean Air Act directed states and local pollution districts to monitor ambient ozone concentrations. Currently, many areas of the country are not in attainment of the national ambient air quality standard (NAAQS) for ozone. Therefore, accurate measurement of atmospheric concentrations is important because small differences in measured maximum ozone concentrations can change an area's nonattainment classification and profoundly affect its control strategies.

Current measurements of ozone use continuous monitors based on principles of chemiluminescence (CL) or ultraviolet (UV) absorption. The most prevalent chemiluminescence technique utilizes the reaction of ozone with ethylene, whereas the absorption approach uses the UV absorption of ozone at 254 nm. Because of its inherent instability, no primary ozone standards are available. NIST-traceable ozone standard monitors are available for accurate instrument calibration. Ambient interferences can cause significant ozone measurement errors with some types of monitors. This study investigates the role of water vapor and some aromatic photochemical pollutants in the measurement of ozone by chemiluminescence- and ultraviolet-based instruments. These results could have implications regarding the selection of the type of ozone monitoring instrument used in specific areas and the accuracy of the monitoring data obtained.

While most monitoring agencies in the US have had no apparent problems, measurement anomalies have been reported to the U.S. EPA by some local and state agencies. The response of both types of monitors to high levels of humidity has been questioned.¹ Also, the behavior of the scrubber canisters used in UV monitors to remove ozone from the sample (for zero reference) is not known. In order to test these monitors under controlled conditions, a manifold system capable of producing stable and known amounts of ozone, humidity and a variety of possible interferants was constructed. The current study has been designed to systematically examine the effect of various levels of absolute humidity on the response of several commercially available chemiluminescence and UV ozone monitors. In addition, the potential interference in UV instruments due to individual aromatic compounds present in ambient urban air has been examined.

EXPERIMENTAL METHODS AND PROCEDURES

A Teflon and glass manifold system was designed to fulfill the objectives of this study. The system, shown by the schematic in Figure 1, has been described previously². The only recent modification to this system has been the addition of a controlled inlet for the introduction of individual test compounds. Teflon source bags of these potential interferants were made from the same air source used to supply the manifold. The dilute test compounds could be introduced directly into the monitors or they could be added to the mixing manifold via a peristaltic pump. By using this system, the humidity, temperature, ozone and test compound concentrations remained extremely stable during experimental runs.

Several ozone monitors were used during the course of the study, but no more than six were tested at any one time. While the set of monitors tested do not represent the entire range of monitors available, they are probably representative of commercially available monitors, since the vast majority operate on the same principles. The UV instruments included two Dasibi Model 1003AH monitors (denoted in the text as Da031 and Da032), one Dasibi Model 1008AH monitor (Da08), two Teco Model 49 monitors (Teco1 and Teco2), and one Monitor Labs 9811 monitor (ML 9811). The UV instruments measure the difference in the ultraviolet radiation absorption of a low-pressure mercury UV source (254

nm) between the sample air and the sample air with ozone removed (or scrubbed). Ozone scrubbers in the analyzers generally consist of wire screens (or other media) coated with manganese dioxide enclosed in a canister through which the sample flows during half of the analysis cycle. The chemiluminescence monitors included a Bendix Model 8002 (Bendix) and a Monitor Labs Model 8410 (ML8410) instrument. Chemiluminescence occurs as a result of the reaction of ozone with ethylene, which is thought to generate an excited formaldehyde molecule through a minor pathway. The broadband emission with a maximum of 440 nm is detected by a conventional photomultiplier tube.

Ozone mixtures were also generated in a photochemical (i.e., smog) chamber from irradiations of hydrocarbon (HC)/NO_x mixtures. The reaction chamber is 23 m³ in volume and constructed of 5-mil Teflon film. A series of blacklights and sunlamps, which surround the cylindrical chamber, were used to simulate sunlight in the near UV spectral region. Samples for chemical analysis were taken from ports attached to the aluminum endplates. Other details of the chamber have previously been described².

Ozone calibrations were carried out by using a separate Dasibi Model 1003AII ozone monitor as a secondary (transfer) standard. This Dasibi ozone monitor was calibrated against U.S. Environmental Protection Agency (EPA) Standard Reference Photometer (SRP) #7, which is directly traceable to the standard ozone photometer operated by the National Institute of Standards and Technology (NIST). The calibration curve generated from the Dasibi transfer standard showed extremely good linearity ($R^2 = 0.999992$), and the resulting calibration curve was virtually identical (within 0.5%) to that obtained from previous calibrations against the SRP.

All of the monitors used in the study were calibrated against the standard Dasibi monitor by using the manifold system with ozone in dry zero air. Before the calibration, each of the monitors was adjusted for sample and reactant gas flows and electronic offset according to instructions given by the user manuals. During the calibration, 30 readings were taken from each of the instruments at five ozone concentrations between 0 and 400 ppbv. The monitor readings were then plotted against the true ozone concentrations, as determined from the standard Dasibi monitor. Calibration curves were generated for each of the instruments. The linearity of each of the instruments was excellent, giving R^2 values between 0.999984 and 0.999998. These multipoint calibrations were performed as necessary during the study.

For experimental measurements made with humid air or test compounds, the monitors were zeroed and spanned using dry dilution air immediately before and after the complete series of measurements each day. These measurements simply served as checks and were not used in subsequent calculations. When humid air was required, the dilution flow was directed through the water bubbler. Due to evaporative cooling, an external heat source (i.e., heating tape) was required to maintain the liquid reservoir at constant temperature. Ozone/humid-air flows were allowed to equilibrate for at least an hour before measurements were made. The readings from the monitors were entered into a spreadsheet template containing calibration information to generate absolute ozone measurements. In addition, all monitors were connected to individual chart recorders to provide a visual depiction of the stability of the system.

During efforts to examine the effect of condensed water on the monitors, the entire manifold system was heated to a temperature approximately 5 °C above ambient temperature. The monitors and sampling lines were maintained at ambient temperature during these experiments. All procedures were identical to those above, but data were obtained only with chart recorders.

As part of the study, HC/NO_x mixtures were irradiated in a smog chamber to generate ozone photochemically. Two different irradiated hydrocarbon mixtures, which have previously been used as

surrogates for urban atmospheres,³ were used to measure instrument and scrubber performance. The residence time in the chamber (10 hours) was selected so the concentration of ozone in the effluent was 120 - 150 ppbv. The major components measured during the irradiation included reactant hydrocarbons, organic and inorganic NO_x compounds, nitric acid, carbonyl compounds, and ozone. Selected carbonyls, dicarbonyls, other organic oxygenates were quantified. During the scrubber tests, the canisters were exposed to the smog chamber effluent continuously for 13 weeks. The flow through each scrubber was 1 L/min which is similar to the expected average flow for a normal monitor in the field. Both new scrubbers and used scrubbers reported to have previously malfunctioned (anomalous scrubbers) were tested for ozone breakthrough by placing the canisters in the sampling line of a chemiluminescence monitor, exposing the canister to various amounts of humidity and NO₂ at 200 ppbv ozone, and monitoring for ozone breakthrough. NO₂ was selected since it represents one of the most widespread inorganic pollutants found in photochemical smog and is generally found with ozone in moderate concentrations.

In another set of measurements, individual aromatic compounds were added to the manifold in the presence and absence of ozone to measure potential interferences. In these measurements, UV monitors were used in two configurations. Figure 2 shows the two different configurations for the Dasibi 1003-AH monitors. The bypass configuration was used for absorbance measurements of potential interferences. With this arrangement the absorbance of the test compound in the sample was measured against a known clean air reference. The normal configuration was used to measure the retention of the test compound in the scrubber and to determine the instrument response with the potential interferent present. Since many of the absorbance readings were low, the source bags were attached directly to the monitors to obtain adequate instrumental sensitivity.

RESULTS AND DISCUSSION

In the first phase of the study, experiments were conducted with the glass manifold system to determine whether systematic differences exist between the UV and the chemiluminescence monitors when ozone is measured in humid zero air. Initial checks were conducted to determine if a water vapor interference was present in the absence of ozone; no clear water vapor interference for either approach could be detected. Experiments using both types of monitors were then performed at known relative humidities for ozone concentrations of 85, 125, and 313 ppbv to see if an interference could be detected under these conditions, and if an interference existed, to determine the direction and magnitude of the interference. An independent ozone determination indicated that the UV monitors high reliable under these conditions. However, a positive deviation of 3.0% for each 1% (or 10,000 ppmv) of water in the sample was found for chemiluminescence instruments at dew point temperatures ranging between 11 and 23 °C. These experiments cover the range of dew points frequently seen in urban atmospheres. Moreover, the interference was found to be independent of the absolute ozone concentration. The result is similar to the results of several prior published and unpublished studies^{1,2,4}. However, in previous studies, no attempt was made to accurately quantify the magnitude of the interference.

The purpose of another part of the study was to determine whether condensed water in the instrument sampling lines could give rise to noisy conditions in which the UV instruments give systematically higher ozone values than the chemiluminescence instruments⁵. The outputs from the instruments were monitored on strip-chart recorders over periods of 5 hours for each experiment. Three experiments were performed under these conditions at nominal ozone concentrations of 330 ppbv, 325 ppbv, 125 ppbv. Figure 3 shows the chart recorder traces for each of the three instruments at a nominal ozone concentration of 325 ppbv and for a manifold RH of 85% at a temperature of 32.1 °C. During this experiment, the ambient laboratory temperature was 24.6 °C, and the dew point temperature of the mixture emanating from the manifold was on average 5 °C higher than the laboratory temperature. Chart

traces for other experiments in this series were similar in character to those of Figure 3.

As seen in Figure 3(B) and (C), the UV monitors appear to be noisier than usual. Moreover, Figure 3(C) indicates that the Teco UV monitor gave a periodic negative spike followed by a positive spike. These spikes appeared to have been synchronized with the air conditioning cycle, which strongly influenced the RH in the manifold, as the bottom panel indicates. Condensed water was present in the sampling lines during the times these spikes were observed. For the instruments tested, the increase in the noise at these high humidities appeared to be related more to a specific instrument, rather than a specific model type. It should be noted that overall the condensed water did not cause the integrated UV instrument readings to be higher than the chemiluminescence readings. Similar to previous measurements, the chemiluminescence instruments showed a higher average reading, but there was no observed increase in instrument noise. These results are relevant for cases in which the outdoor dew point is higher than the temperature of the monitoring station.

Two other measurement problems specific to the scrubber canisters used in UV monitors have also been reported. One problem involves breakthrough of ozone by the scrubber leading to a negative interference and the second involves retention of absorbing compounds (e.g., aromatics) on the scrubber leading to a positive interference. For correct operation of the UV monitor, the scrubber must remove 100% of the ozone, while retaining no compounds that absorb at radiation at 254 nm. Anomalous scrubbers from field monitors were tested for ozone breakthrough at approximately 200 ppbv ozone for various NO₂ concentrations (see above) and humidity levels. As seen in Table 1, there were several failures of these anomalous scrubbers to remove 100% of the ozone but the failures only occurred under humid conditions. Figure 5 shows the chart trace for a failing scrubber. In this case, when the air sample was dry which is normal during instrument calibration and span checks, the scrubber was found to remove ozone completely. Once water was added, ozone began to breakthrough the scrubber. In this particular test, the maximum loss of scrubbing efficiency was 40%. Under field conditions at the same relative humidity, this would result in an ozone reading that was 40% low if this scrubber were installed in a field unit. After the relative humidity of the sample was adjusted to 89%, the ozone breakthrough increased momentarily and then the scrubber returned to normal operation.

The chart trace in Figure 5 shows failure of the scrubber to remove 100% of the ozone under all conditions but, perhaps more importantly, the apparent transient nature of the problem. Since only previously deployed scrubbers showed evidence of humidity-assisted ozone breakthrough, new scrubbers were exposed to an irradiated synthetic urban air mix to find conditions under which they might fail. Four different types of canisters (Dasibi "gold", Dasibi "blue", Monitor Labs and Advanced Pollution Instruments) were exposed continuously for 13 weeks to the effluent from the smog chamber. Periodic tests of the scrubbers found no evidence of failure induced by synthetic smog mixtures. Therefore, the exact conditions which brought about the ozone breakthrough problems of the field units are unknown at the present time.

Experiments were also performed to test the degree to which the ozone scrubbers could retain compounds which absorb radiation at 254 nm. In an initial study,² measurements of ozone were made with a UV monitor from a mixture comprised of photochemically-derived products including ozone produced during irradiations of toluene/NO_x mixtures. The effluent from the irradiation was sent through two different scrubber cans as seen in Figure 4. Benzaldehyde and other aromatic ring-retaining photooxidation products (*o*-cresol, nitrotoluene, etc.) were almost completely removed from the sample by the ozone scrubbers.

However, in additional tests, it was found that products which deposit in the scrubber can be

reversibly emitted from the MnO_2 -coated screens when the humidity of the sample subsequently increases. In one test, two scrubbers were exposed for 20 minutes to a source bag of 2-nitrotoluene and then placed in the sample inlet line of a UV monitor. With a dry stream of clean air passing through the contaminated scrubbers there was a slightly elevated signal (Figure 6). When the humidity of the manifold sample increased to approximately 50%, the 2-nitrotoluene was flushed from the screen surfaces to a level that could be read on the UV monitor. Thus, depending on the timing of absorption and emission, the scrubber can produce either a positive or a negative measurement error when aromatic species are present in the sample.

Comprehensive studies of the effect of aromatic compounds on the UV measurement technique are sparse⁶. In this study, individual aromatic compounds were tested to determine the magnitude of an interference. To be an interference for the UV monitor, a compound must both absorb at 254 nm and be retained by the scrubber system. Results from this study for the compounds tested to date are given in Table 2. This list does not cover the entire range of compounds which have been found to absorb radiation at 254 nm, and additional compounds such as mercury, PAHs and nitroresols need to be tested. It is important to note that some chemicals give a greater response than ozone on a molar basis. Aromatic compounds present in the highest concentrations in ambient air (e.g., toluene) had relatively little effect on the UV monitor since they are weak absorbers and essentially pass through the scrubber. There may be numerous aromatic products (e.g. 2-nitrotoluene) present in low concentrations in ambient air (1-100 pptv) which absorb at 254 nm and are retained. If completely retained, a single product with a molecular weight of 150 g/mol can deposit 25 μg of material on the surface of a scrubber in one month at 100 pptv levels in the field. Normally UV monitors operate for several months without scrubber replacement. It is possible that one or more of these aromatic compounds can cause the anomalous behavior seen in suspect field scrubbers. Presently, it is impossible to speculate on the exact compounds or mechanisms which cause scrubber failure without ambient measurements of potential interfering compounds.

CONCLUSIONS

While this study has not been completed, it is possible to draw some preliminary conclusions from the data presented above. Both the chemiluminescence and UV ozone monitors are subject to measurement errors. The chemiluminescence monitor, which is based on the specific reaction between ozone and ethylene, appears to have a positive deviation with humidity. Calibration of this type of monitor at a representative humidity can minimize the error caused by water vapor in the sample. The UV technique has several different measurement interferences requiring further study. During times when the monitoring station is at a temperature below the dew point of the incoming sample, instrument noise increases significantly. The magnitude of the noise is instrument- rather than manufacturer-specific. The scrubbers used in the reference side of these instruments can cause both positive and negative measurement errors. Ozone breakthrough is a transient problem which can occur under humid conditions. Testing UV monitors in the field with a humidified ozone source is one method to detect anomalous ozone scrubbing efficiency. The interaction of aromatic compounds and the surfaces of the scrubber can cause positive measurement errors when the materials are retained and negative errors when the materials subsequently elute from the scrubber surface.

ACKNOWLEDGMENTS

Suspect scrubbers and reports on measurement anomalies were provided by Larry Ellibot (St. Louis Co. MO), Elton Erp (State of Virginia), Al Leston (State of Connecticut), and Charles Bellot (State of Louisiana). Valuable discussions were held with J.J. Bufalini, K.A. Rehme and C.F. Smith of the U.S. EPA. This work was supported by the U.S. EPA and the American Petroleum Institute.

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Table I. Summary of experiments to test the effect of NO₂ concentrations on the performance of suspect scrubbers in the presence of various levels of relative humidity. For each entry, the values represent, respectively, the number of scrubbers tested, the number failed, and the number of hours of exposure at an ozone concentration of 200 ppbv.

[NO ₂], ppbv	0%	25%	50%	75%	95%
0	3, 0, 20	1, 1, 2	1, 0, 5	1, 1, 2	1, 1*, 2
50	3, 0, 7	3, 0, 6	4, 2, 19	4, 3, 20	4, 0, 16
100	1, 0, 5	4, 2, 17	2, 0, 19	2, 0, 16	2, 0, 20
200	1, 0, 6	1, 0, 19	1, 0, 15	-	1, 0, 6

Table II. Measured absorbances at 254 nm in UV cell for selected aromatic compounds.

Compound	Absorbance (L/mol-cm)	% Retained by Scrubber	Signal (%)
Ozone	3200	100	100
Benzene	93.3	0	0
Toluene	137	0	0
<i>o</i> -, <i>m</i> -, <i>p</i> -Xylene	140-200	0	0
Benzaldehyde	230	< 10	< 1
Styrene	3600	100	113
2,5-Dimethylstyrene	4710	100	147
<i>o</i> -Cresol	599	98	18.7
2-Nitrotoluene	2590	97	78.4

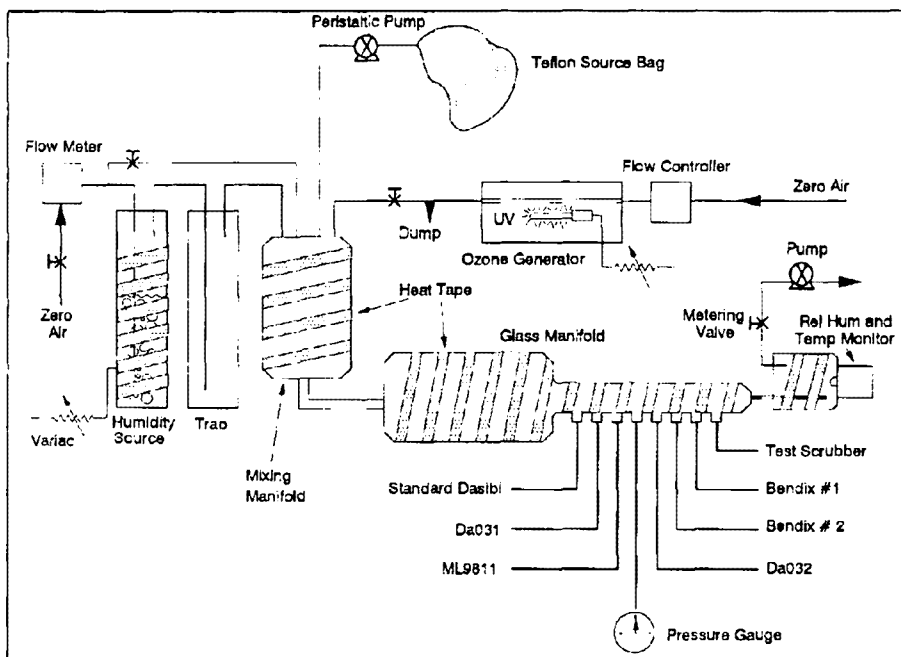


Figure 1. Experimental apparatus for measuring ozone interferences.

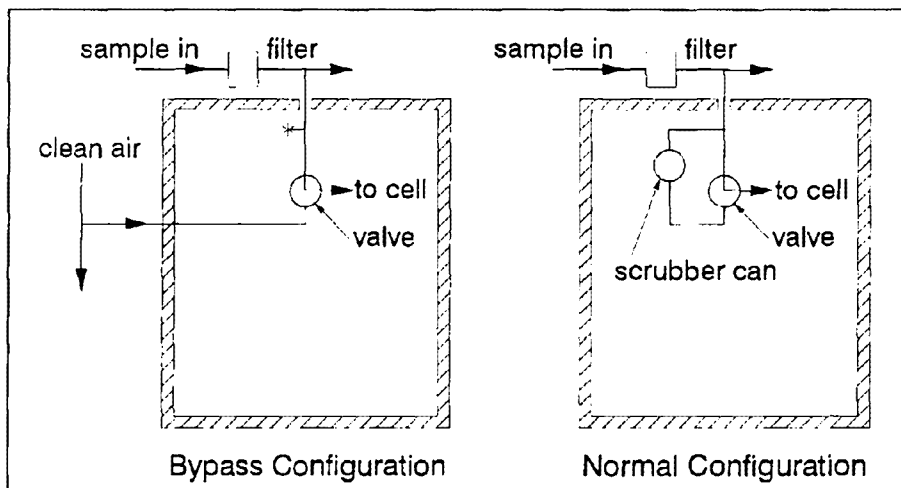


Figure 2. Schematic for measuring 254 nm absorbance and retention of test compounds.

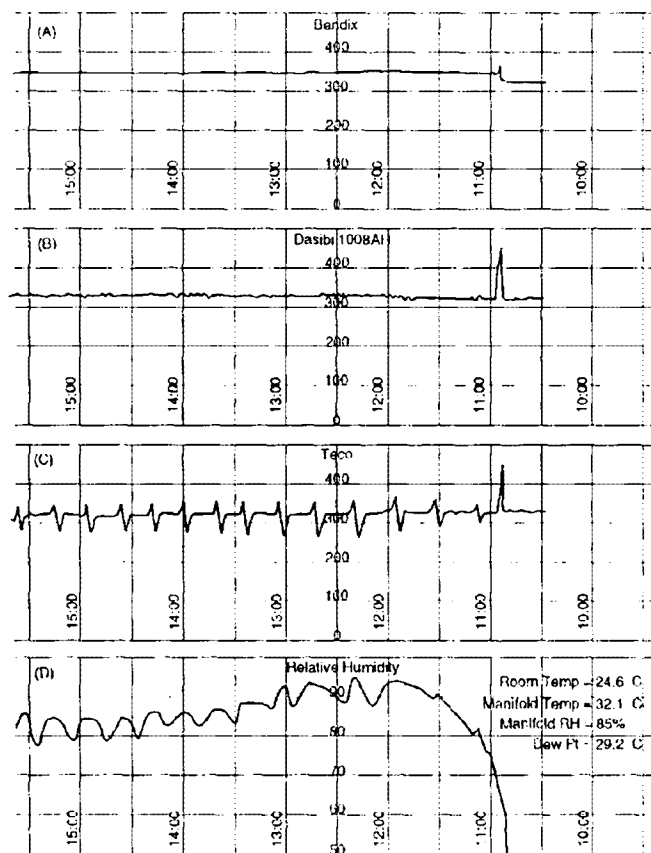


Figure 3. The effect of condensed water on ozone monitors.

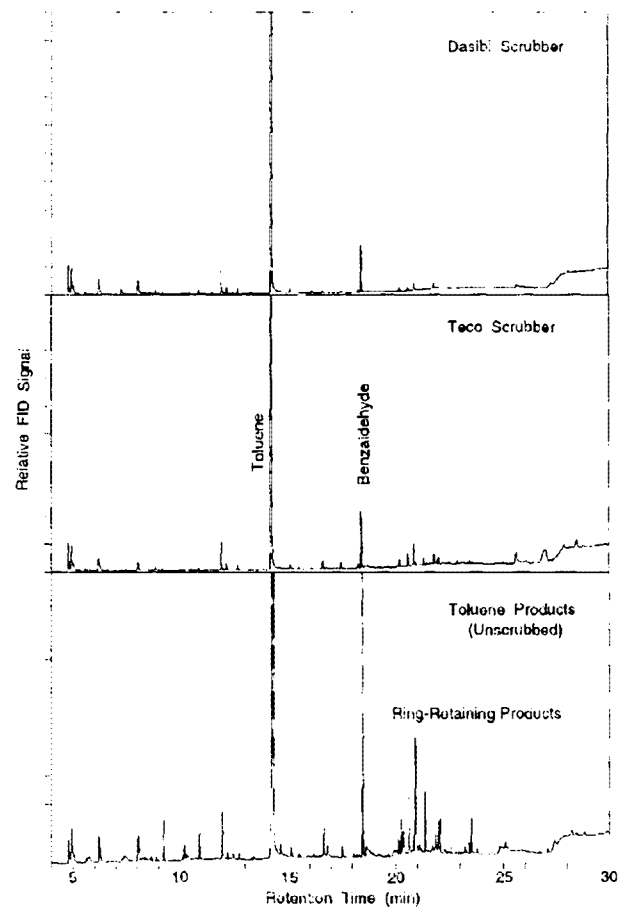


Figure 4. Retention of toluene photooxidation products on scrubber cans. Products generated from a toluene/ NO_x irradiation.

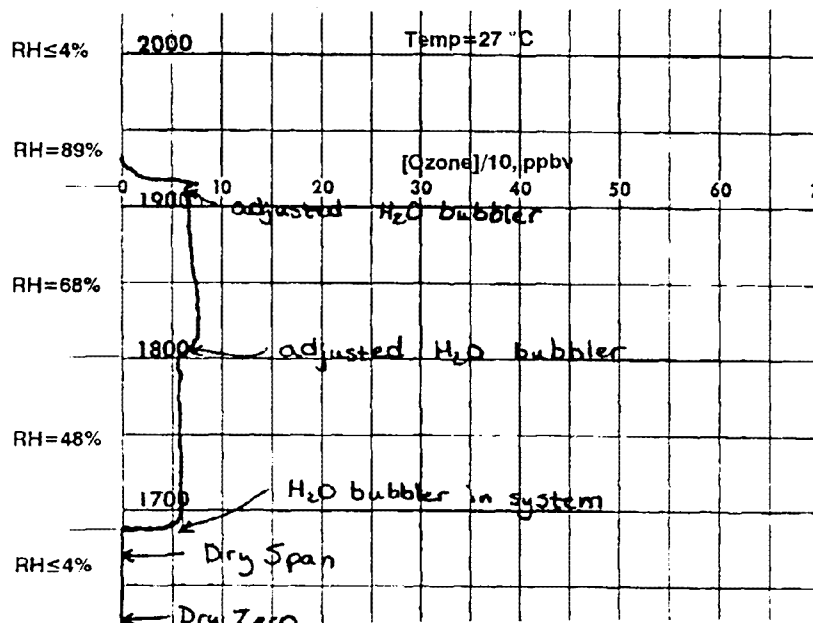


Figure 5. Chart trace showing ozone breakthrough from suspect scrubber can. (Vertical scale: Time; Horizontal scale: Ozone Concentration, 700 ppbv full scale)

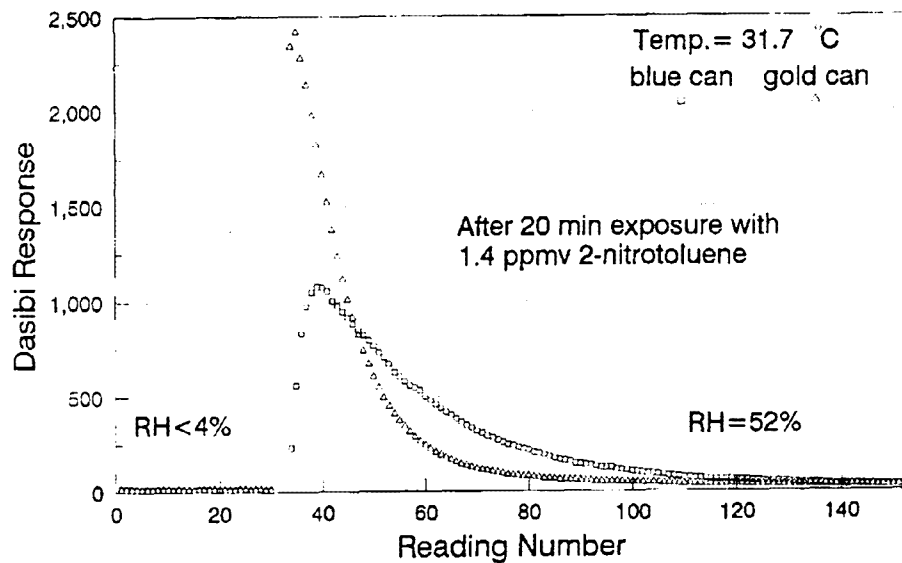


Figure 6. Instrument response from scrubber contaminated with 2-nitrotoluene. (See text for details; readings taken every 25 seconds.)

Real Time Electrochemical Measurement of Ozone in the Presence of Nitrogen Oxides

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Current regulatory models (USEPA/pNEM-03) estimate population ozone exposures within multiple microenvironments averaged over clock hour time periods. Validation of model algorithms requires measurement of personal ozone exposures of free-ranging individuals over hourly time frames within changing microenvironmental air quality. Ozone can be measured with electrochemical sensors at sensitivity limits of 5 ppb if the sensor is periodically corrected for baseline drift. The electrochemical sensor responds comparably to O_3 , NO_2 , and HONO. Initial attempts to measure ozone passively in the presence of nitrogen oxides by periodic ozone-scrubbed baseline drift corrections were unsuccessful due to the rapid changes in NO_x levels within several microenvironments. We have constructed a prototype active, battery-powered, data-logging personal monitor using two sensors in tandem with an ozone removal filter in between. The difference in the sensor signals is due to ozone; thus, corrections for NO_x interferences are made on-line in real time without sacrifice of sensitivity.

**The Development of an Active Personal Ozone Sampler
Using a Diffusion Denuder**

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Personal, microenvironmental and indoor ozone monitoring is currently carried out using a passive sampling device which is both light-weight and inexpensive. However, the collection properties of these samplers have been found to be sensitive to wind effects and sampler placement, thus limiting their potential use for personal monitoring. In addition, because of their relative insensitivity, these samplers cannot be used for short-term monitoring of ozone at low concentrations. In response to these problems we are developing a light-weight active ozone sampler which uses a single tube diffusion denuder for sample collection.

The new single tube diffusion denuder (STTD) consists of a 1.4 cm (ID) \times 10 cm etched Pyrex tube attached to a very small, low-flow, relatively low-cost personal pump. Tube diameter and length were chosen to maximize collection efficiency at a sampling rate of 65 mL/min. The tube is coated with a nitrite reagent which has been successfully used in the passive ozone samplers.

Variations in relative humidity, ozone concentration, and total ozone exposure have relatively small effects on the accuracy and precision of the STTD. In addition, the low limit of detection (LOD) of approximately 20 ppb-hrs gives a tenfold increase in sensitivity over the passive samplers for which a 200 ppb-hr LOD has been determined. This new active sampler thus makes possible both short-term personal and microenvironmental monitoring.

Evaluation of Passive Samplers for Field Measurements of Ambient Ozone in the National Parks

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ABSTRACT

In 1993 a follow-up study was conducted to the 1991 trials by the National Park Service of passive samplers for integrated measurement of ozone. A preliminary factorial design study was used to verify consistency between samplers and between analysis laboratories. It was found the significant differences in measured ozone were being introduced by the polypropylene rain shields that were used in the 1991 trials. PVC plastic rainshields were used subsequently.

For the main part of the 1993 study, five sites in two different national parks were used to compare passive sampler ozone measurements to average hourly exposures determined with UV-photometric ozone analyzers. Passive sampler measurements agreed well for each site and were within $\pm 10\%$ accuracy for each measurement period. The overall collection factor varied somewhat by site ($21.565 \pm 1.59 \text{ cm}^3/\text{min}$), had good repeatability at each site, but overall accuracy for multiple sites was $\pm 20\%$. The passive samplers generally met the criteria established prior to the study and appear to be suitable for field use to measure ambient ozone when used as part of a well designed ozone measurement program.

INTRODUCTION

Ambient air quality monitoring in remote locations such as national parks and wilderness areas using conventional instrumentation is hampered severely by the general lack of commercial AC power in these areas. Information on air quality levels in these areas is often necessary to address resource management issues related to the effects of air pollution on the natural resources of such areas.

Interest in personal exposure monitoring over recent years has resulted in the development of passive sampling devices that contain no moving parts and rely simply on the principle of gas diffusion. Although passive devices were designed initially to sample over durations of a few hours, they are now being tested over durations of a few weeks for use in ecological monitoring programs¹.

In 1991 a study was conducted by the National Park Service to evaluate the accuracy of the Ogawa passive ozone samplers during sampling durations of one week or longer under a variety of environmental and meteorological conditions. The passive samplers were deployed at eight NPS ozone monitoring locations with different average relative humidity, elevations, and ozone mixing ratios. Other variables, such as, temperature, winds, solar radiation, and site environment were also measured.

The conclusions of the 1991 study were that the accuracy exceeded $\pm 20\%$, that larger numbers of replicates were needed, and that differences in collection rates between parks were unacceptably large. A linear relationship between passive and continuous ozone measurements was obtained with an R^2 of 0.40.

Short exposures (1 week) of the passive samplers worked better than extended (4 -12 weeks) exposures. In light of those results, a second, more limited study with specific objectives was proposed.

A number of other field trials of the passive ozone samplers have been reported,¹⁻⁵ however, several of these have not appeared in the peer review literature as yet. Prior reports on field use of the passive samplers have indicated an accuracy of $\pm 20\%$, which is far from what is expected from a continuous ozone monitor. However, for areas where no ozone measurements are available, even the $\pm 20\%$ would be an improvement in the understanding of local ozone exposures.

EXPERIMENTAL

The 1993 study consisted of a preliminary experiment designed to resolve experimental problems that were noted in the 1991 trials and a main experiment designed to test accuracy, precision, and number of replicate samplers required. Multiple sites were chosen to test the variability of the passive samplers under field conditions.

The Ogawa passive samplers consist of a double-sided filter holder that is mounted on a "badge" with a clip on the back. Inside the filter holder are two nitrite coated filters. When the nitrite coated filters are exposed to the air, ozone diffuses through the end-caps and reacts with the nitrite to form nitrate. To protect the samplers from direct contact with water, a rainshield was made from 7.6 cm diameter PVC drain pipe, a PVC end-cap, and Teflon tubing for supports. The samplers are mounted so they are 1.3 cm about the open end of the rainshield.

A preliminary experiment was designed to study some of the variables that could effect passive samplers. A 2^3 factorial design was used to examine the effects of analysis by different labs, type of rain shield, and relative placement of the samplers within the rain shields. Eight combinations of the three factors were studied at a contractor's facility. Analyses of the coated filters were performed in laboratories at the Harvard School of Public Health and at Research Triangle Institute (RTI). Thus, 10 samples went to each lab from this preliminary study.

The main study plan was conducted in August at three sites within Great Smoky Mountains NP and at two sites within Sequoia-Kings Canyon NP. At each site there was a continuous ozone monitor for local calibration of the passive samplers and enough replicates were used to ensure that differences of 5 ppb ozone would be statistically significant between sites. Each exposure consisted of 5 passive samplers and 2-4 blanks. This allowed for subtraction of the blank for each set of samples and an estimate of the limit of detection for the method. Analysis were based on composites of coated filters from the two sides of each Ogawa device. All samplers had the same coating levels of nitrite and used the same extraction volumes in the analysis. The passive sampler badges were mounted inside PVC rainshields and the rainshields hung from PVC supports attached either to the monitoring site shelter or tower. Each passive sampler was located at the same height as the continuous ozone monitor intake and within five feet of the intake.

The sites differed by elevation and vegetation, both of which were expected to affect ozone levels and local winds. Although the projected ozone concentrations at the two parks were expected to be similar, the organic precursors for the formation of the ozone were expected to differ. Sequoia-Kings Canyon NP would generally be expected to have larger anthropogenic concentrations of volatile organic compounds (VOC) and Great Smoky Mountains NP to have larger biogenic concentrations of VOC. This difference challenges the passive samples more than if adjacent parks were used for comparison.

RESULTS AND DISCUSSION

Results from the preliminary study aided in the planning of the main study. A significant finding was that the polypropylene rainshield used in the 1991 study led to ozone values 30% high. The PVC rainshield gave results comparable to published reports² and had greater reliability. The other factors of badge location and analysis lab were found to contribute less than 2% error.

The unexposed passive samplers, here referred to as blanks, provided the baseline amount of nitrate on the filter pads. In the 1991 study the average one-week exposure blank was 156 ppb-hrs whereas in the 1993 study the average blank was 538 ppb-hrs. In general the blank analysis at RTI was consistent for the different weeks and about one-half the nitrate observed by the Harvard lab. The higher blanks obtained by the Harvard lab may be because they were analyzed a few weeks later or may indicate some analytical bias. The limit of detection (LOD), taken as three times the standard deviation of the blanks, was calculated as 1.5 ppb average ozone exposure over one week.

Reproducibility for the passive samplers was determined from the replicates. To remove the influence of different ozone levels, the relative standard deviation (RSD) was calculated as the percent where the standard deviation was divided by the average ozone mixing ratio. For the 1993 study, the RSD for the duplicates was 1.0% for Great Smoky Mountains NP (Table I) compared to the 5.0% in the 1991 study. At Sequoia-Kings Canyon NP, the present RSD was less than one-fifth of the value in the 1991 study. The lower variability was most likely due to use of the PVC rainshields, to use of a larger number of replicates over a shorter exposure time, and to improvements in the handling and analysis of the samples. An estimate for the precision (as the 95% confidence interval) of the passive was ± 1.0 ppb. This was better than expected from the results in the previous study.

Since each field site had a continuous ozone analyzer collocated with the passive samplers, a collection factor was calculated for each site by sampling period. In principle the collection factor should not change either with week being sampled or the sample location. In practice the results indicate a shift in the collection factor from an as-yet-to-be-identified interference. Table II shows the changes in the collection factors by site during the study and Table III summarizes the collection factors by week and park. Although the collection factors at Great Smoky Mountains NP suggests an elevation pattern (i.e., increasing collection factor with increasing elevation), the relationship does not hold for the samplers at Sequoia. It is likely that some influence other than atmospheric pressure is involved.

The best results were obtained when the average collection factor for multiple sites in one park were used for the samplers in that park. An overall collection factor of 21.565 ± 1.59 cm³/min (95% confidence limits) was used to compute the ozone exposures in the different parks. The 95% confidence limits for the collection factor were $\pm 7.4\%$ compared to $\pm 12.1\%$ for the 1991 study.

Direct comparison between the passive sampler and the continuous analyzer ozone concentrations are presented in Figure 1 for all of the sites and exposure periods. The linear regression line in Figure 1 is given as equation (1):

$$\text{Passive O}_3 = 0.963 \times (\text{Continuous Ozone}) \quad R^2 = 0.91 \quad (1)$$

This data set was not well suited for determining the response linearity of the passive samplers. However, as can be seen from Figure 1, all of the data falls within the $\pm 20\%$ values.

CONCLUSION

The results of this study indicate that the Ogawa passive ozone samplers can be used to measure ozone with an accuracy of better than $\pm 20\%$ and with enough precision to distinguish to better than 5 ppb between two sites within a park. The reproducibility of measurements is such that only 2 samplers need to be used at each measurement site to achieve this level of precision. Within these boundaries, the passive samplers appear to be suitable for low-cost spatial and temporal ozone measurements within a given park where there is a continuous ozone monitor to act as a reference.

With slightly less accuracy, the passive samplers can be used at widely separated parks when a common collection factor is used for the calculation of the ozone exposures. It is recommended that either a temporary continuous ozone monitor should be collocated with one of the sampling sites or the nearest existing ozone monitor should be used with collocated passive sampling as a check on the collection factor. The passive samplers can be used as screening devices for those locations where no prior ozone monitoring has taken place.

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Table I. Comparison of Passive Sampler Precision by Week and Site (ppb Ozone).

National Park	Individual Sites	First Week			Second Week		
		Std. Dev.	Average Ozone	RSD	Std. Dev.	Average Ozone	RSD
Great Smoky Mt.	Uplands	0.4	22.9	1.8%	0.7	23.5	3.1%
Great Smoky Mt.	Look Rock	0.8	58.0	1.3%	1.0	56.5	1.7%
Great Smoky Mt.	Cove Mt.	2.4	61.3	3.8%	0.8	58.2	1.4%
Sequoia-Kings Canyon	Lower Kaweah	--	--	--	0.6	74.0	0.8%
Sequoia-Kings Canyon	Grant Grove	--	--	--	0.4	67.3	0.6%

Table II. Calculated Collection Factors for Passive Samplers by Location (cm³/min).

National Park	Individual Sites	Site Elevation (ft)	Week 1	Week 2	Average	Std. Dev.
			Calculated Col. Factor	Calculated Col. Factor		
Great Smoky Mt.	Uplands	2,000	19.07	18.75	18.91	0.16
Great Smoky Mt.	Look Rock	2,700	20.98	24.29	22.63	1.66
Great Smoky Mt.	Cove Mt.	4,100	24.12	26.86	25.49	1.37
Sequoia-Kings Canyon	Lower Kaweah	6,200	--	19.43	19.43	--
Sequoia-Kings Canyon	Grant Grove	6,600	--	20.82	20.82	--

Table III. Summary of Collection Factors by Week for Each Park (cm³/min).

	Week 1	Week 2	Week 2
	Great Smoky Mountains	Great Smoky Mountains	Sequoia-Kings Canyon
Average	21.39	23.30	20.13
Std. Dev.	2.08	3.39	0.70
Range	5.05	8.12	1.39

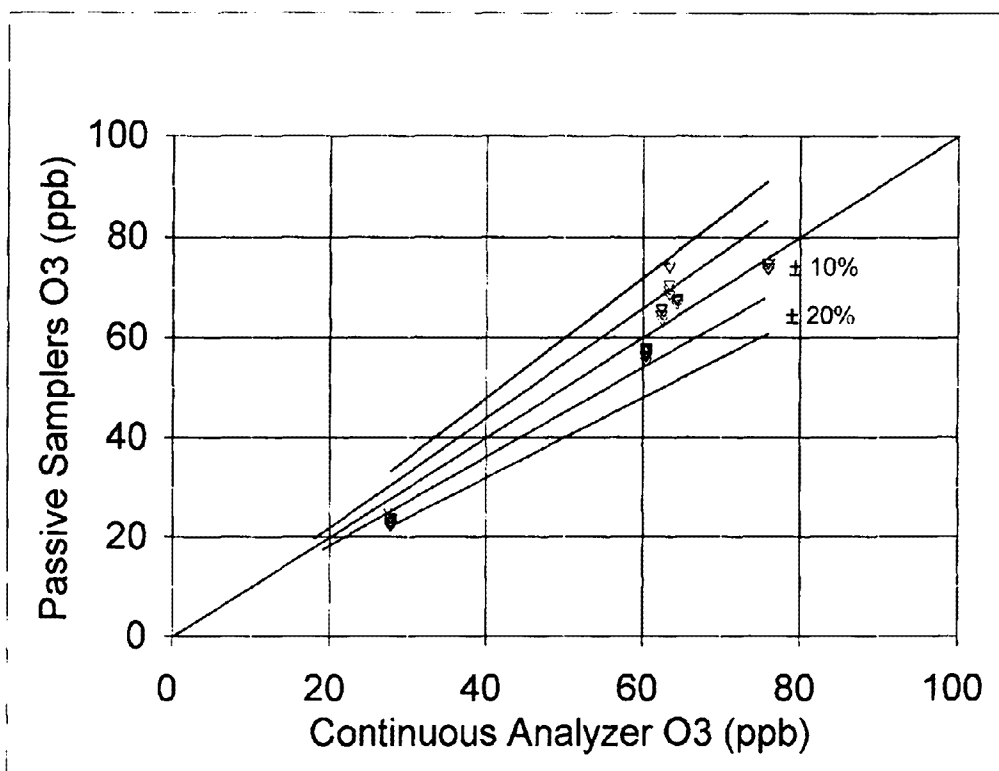


Figure 1. A comparison of continuous analyzer ozone and passive sampler results. The best fit regression line and $\pm 10\%$ and $\pm 20\%$ ranges are shown. Slope = 0.96, $R^2 = 0.91$

Development of a New Semi-Volatile Organic Compound Sampler

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A new sampler has been developed to sample semi-volatile organic compounds. The sampler utilizes the principle of virtual impactor to efficiently separate the particulate from the gas phases of organic compounds. The virtual impactor consists of a slit-shaped nozzle where the aerosol is accelerated, and another slit-shaped nozzle that collects the particulate phase of organics (plus a small and known fraction of the gas phase). The acceleration slit is 0.023 cm wide, the collection slit is 0.035 cm wide, and both slits are 11 cm long.

The virtual impactor's 50% cutpoint has been determined experimentally to be 0.12 μm . In addition, interstage losses have been determined (in all configurations tested, particle losses ranged from 5-15%). The impactor's sampling flow rate is 284 liters/minute, with a corresponding pressure drop of 100 inches H_2O . Higher or lower sampling flow rates can be achieved by increasing or decreasing the length of the slits. Tests for volatilization losses have been conducted by generating organic aerosols of known volatility, and comparing the impactor's collection to that of a filter pack sampling in parallel. The experiments demonstrated negligible volatilization losses (<5%) for the compounds tried.

Particles are collected on a filter connected to the minor flow of the impactor, followed by a sorbent bed to collect material that volatilized from the particles. The organic gas phases is collected on a sorbent bed, connected to the major flow of the impactor.

Outdoor Air NO_x Speciation by a Selective Denuder Collection System

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A series of interior coated hollow tubes has been studied for the collection and analysis of ambient air for gas phase nitric acid, nitrous acid, nitrogen dioxide, nitrosamines, and nitric oxide. The tube surface sequence consists of, in order, tungstic oxide, potassium-iron oxide, copper iodide, carbon, and cobalt oxides. Collected analytes are removed by heating the collection tubes with chemiluminescent detection for the analysis. Detection limits are in the fractional nanogram per sample range. Prior work has verified high collection efficiency and specificity of the sequential collection.

Results of the surface analysis of the coatings will be presented. Current work includes a study of interferences and application of the method. Possible interferences from carbon dioxide, carbon monoxide, ozone, formaldehyde, nitrous oxide were studied. Temperature and humidity effects were also studied. The analysis system has been applied to analysis of outside air in a producing orange grove area at which some impact from nitrogen oxides was suspected to have a serious impact. A contrast of indoor versus outdoor air will also be presented.

FIELD EVALUATION OF A GLASS HONEYCOMB DENUDER/FILTER PACK SYSTEM TO COLLECT ATMOSPHERIC GASES AND PARTICLES

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ABSTRACT

We have developed a glass honeycomb denuder/filter pack system to sample atmospheric inorganic gases and particles. The main feature of the sampler is the denuder component, which has a large number of small hexagonal glass tubes sealed inside an outer glass tube. Outdoor concentrations of nitric acid (HNO_3), nitrous acid (HONO), ammonia (NH_3), sulfur dioxide (SO_2), and fine-particle sulfate (SO_4^{2-}) and ammonium (NH_4^+) determined with the honeycomb denuder sampler were compared to those determined with a collocated Harvard/EPA Annular Denuder System (HEADS). The average collection of the HEADS sampler was higher than that of the honeycomb sampler for NH_3 and HNO_3 , whereas concentrations of SO_2 , HONO , and particulate NH_4^+ and SO_4^{2-} determined by both samplers were in excellent agreement.

INTRODUCTION

Tubular diffusion denuders have been used in several atmospheric studies to collect gaseous and particulate atmospheric pollutants (Ferm, 1979; Shaw et al., 1982; Forest et al., 1982; Braman et al., 1982). Possanzini et al. (1983) designed and characterized an annular denuder system that collects reactive atmospheric gases more efficiently, per unit length, than the tubular configurations. Koutrakis et al. (1988) designed and evaluated a glass impactor/annular denuder/filter pack system (HEADS) operating at 10 LPM. Measurements of SO_2 , HNO_3 , and HNO_2 gases showed mean collection efficiencies of 0.993, 0.984, and 0.952, respectively. The gas collection of the denuders and the fine particle mass and sulfate concentrations on the filter pack of this system was compared to an EPA sampler developed by Vossler et al. (1988) by conducting collocated studies. The gas and particle concentrations obtained from both the EPA and the HEADS samplers were in excellent agreement.

We have developed an alternative system which maintains and improves operational features, while being more compact (Koutrakis et al., 1993). The main, novel feature of the proposed system is the denuder component, (Figure 1), which is a cylinder with a height of 3.8 cm and a diameter of 4.7 cm, containing 212 hexagonal glass honeycomb tubes, with an inside diameter of 0.2 cm. The tubes are sealed inside an outer glass tube. The collection efficiency of the honeycomb denuder was compared to those of the annular denuder for HNO_3 and NH_3 for experiments simulating atmospheric conditions and were found identical. In addition, inlet losses of reactive gases in both systems were found to be insignificant. The capacity of the honeycomb denuders under simulated atmospheric conditions was found significantly higher than the capacity of annular denuders for tests using HNO_3 and NH_3 . Furthermore, laboratory and field experiments indicated that fine particle losses ($dp < 2.5 \mu\text{m}$) were less than

5% (Sioutas et al., 1994).

In this study we conduct a field evaluation of the new honeycomb denuder/filter pack sampler by comparing its performance with the performance of the previously developed HEADS system (Koutrakis et al., 1988). The concentrations of nitric acid (HNO_3), nitrous acid (HONO), ammonia (NH_3), sulfur dioxide (SO_2), and fine-particle sulfate (SO_4^{2-}) and ammonium (NH_4^+) determined with the honeycomb denuder sampler are compared to those determined with the collocated Harvard/EPA Annular Denuder System (HEADS).

METHODS

Design and description of samplers

The sampling flow rates in both the HEADS and the honeycomb denuder samplers are 10 LPM. A detailed description of the HEADS sampler is given in a paper by Koutrakis et al. (1988). Also, a detailed description of the honeycomb sampler can be found in a study by Koutrakis et al. (1993). Briefly, the HEADS system consists of a borosilicate glass impactor, two glass annular denuders, and a FEP Teflon filter pack. The impactor has been calibrated, and at a flow rate of 10 LPM its 50% cutpoint is $2.1 \mu\text{m}$ (Koutrakis et al., 1990). The design of the annular denuders is similar to that of Vossler et al. (1988). The denuder length is 26.5 cm, the outer diameter of the inner cylinder is 2.20 cm, and the thickness of the annulus is 0.10 cm. The first denuder is coated with Na_2CO_3 /glycerol to collect SO_2 , HNO_3 , and HNO_2 . The second denuder is coated with 2% citric acid:1% glycerol in a water:methanol solution to collect ammonia. Following the second denuder is a PTFE Teflon filter pack containing a Teflon filter to collect fine particles for fine particle mass, sulfate, and nitrate concentration measurements. The second filter is a 47-mm diameter glass fiber filter, coated with Na_2CO_3 to trap HNO_3 .

The honeycomb denuder/filter pack system, shown in Figure 1, has three essential features: a) an impactor to remove coarse particles ($d_p > 2.1 \mu\text{m}$) from the air sample; b) two glass honeycomb denuders; and c) a two stage filter pack to collect fine particles. The inlet has a short elutriator, which points downwards to help exclude the largest particles. The circular array of nozzles causes particles larger than $2.1 \mu\text{m}$ to impact on the impactor plate, a ring of sintered stainless steel, coated with mineral oil. A transition section allows the sample air to flow smoothly and have uniform flow through the individual honeycomb tubes of the first denuder. A Teflon coating minimizes internal surfaces from interaction with reactive gases. The first honeycomb denuder (coated with sodium carbonate/ glycerol to collect acid gases) is separated by an inert spacer from the second denuder (coated with citric acid/glycerol to collect basic gases). A stainless steel spring keeps the components in place. A third denuder can be placed, if desired. The two stage filter pack has a Teflon filter to collect fine particles (below $2.1 \mu\text{m}$) and a sodium carbonate-coated glass fiber filter to collect acid gases produced from the reaction of acidic fine particles with particulate ammonium salts of these acid gases. A third stage can be added in the filter pack if it is needed. Both the inlet and filter part components are connected to the sampler body using spring clips.

Sampling and analysis

Ambient air sampling experiments were conducted on the roof of the Harvard School of Public Health in downtown Boston during the summer of 1993. Two HEADS samplers with a flow-controlled pumps operating at 10 LPM sampled simultaneously with two honeycomb denuder/filter pack samplers, also equipped with flow-controlled pumps.

The upstream denuder in each of the collocated samplers (annular and honeycomb) was

coated with 1% Na_2CO_3 /1% glycerol in a 1:1 methanol/water solution, to collect acid gases (SO_2 , HNO_3 , HONO), whereas the downstream denuder was coated with 2% citric acid/1% glycerol in methanol, to collect ammonia. The collection efficiencies of both samplers for HNO_3 , HONO , SO_2 , and NH_3 were found to be 98% or higher (Koutrakis et al., 1988; Koutrakis et al., 1993). After being coated, the denuders were dried with clean dry air and capped to protect them from acid gases. After assembling the samplers, leak tests were done in the laboratory.

Only the Teflon filter in the filter packs (a 47 mm teflon filter, Gelman Sciences) was used in the field study, for both the Honeycomb sampler and the HEADS. The second and third filters are normally used to collect nitric acid and ammonia produced from the reaction of acidic fine particles with particulate ammonium salts, as well as the dissociations of these unstable salts. The amounts of HNO_3 and NH_3 on the second and third filters of the filter packs are used to determine the correct particulate nitrate and acidity (H^+) concentrations. The exact method for calculating these concentrations has been described elsewhere (Koutrakis et al., 1992). For the purposes of our field study, we excluded measurements on the second and third filters, since preliminary runs indicated that the ambient nitrate levels were lower than the limit of detection (equal to $0.06 \mu\text{g}/\text{m}^3$). In addition, determination of acidity (H^+ concentrations) was not necessary in comparing the performance of the two samplers for gas and particulate collection.

In the end of each experimental run, the samplers were disassembled and the annular and honeycomb denuders were extracted with 10 mL of ultrapure water. The aqueous extracts of the denuders were analyzed for NO_3^- , NO_2^- , SO_4^{2-} , and NH_4^+ by ion chromatography. The Teflon filters were wetted with 0.15 mL of ethanol and were sonicated with 6 mL of 10^{-4}N HClO_4 , similar to the method described by Koutrakis et al. (1988). The extracts of the Teflon filters were analyzed for SO_4^{2-} and NH_4^+ .

Laboratory blanks were used for quality assurance purposes. Gaseous NH_3 and particulate NH_4^+ concentrations were determined from quadratic regression equations for ammonium ion standards, while particulate sulfate, SO_2 , HNO_3 , and HONO concentrations were determined from linear regression equations for SO_4^{2-} , NO_3^- , and NO_2^- standards, respectively.

RESULTS AND DISCUSSION

The average concentrations for each pair of each type of sampler for HONO , HNO_3 , SO_2 , NH_3 , and particulate sulfate and ammonium are shown in Figures 2-7, respectively. In each of the figures, the concentrations determined using both samplers are plotted next to each other. The detection limits were 0.1 ppb for HONO , 0.2 ppb for SO_2 , 0.3 ppb for NH_3 , 0.2 ppb for HNO_3 , $0.14 \mu\text{g}/\text{m}^3$ for NH_4^+ , and $0.30 \mu\text{g}/\text{m}^3$ for SO_4^{2-} . Twelve field runs were conducted. In cases where fewer data points are reported (for example, in the case of HNO_3 , or NH_3), the omitted data corresponded to concentrations near the limit of detection. Table 1 shows the mean and the percentage differences of the two samplers for all the gas and particulate compounds measured. The mean percentage difference for a specific compound is defined as

$$(\%) \text{ Difference} = 100 \cdot \Sigma((\text{HEADS}_i - \text{HNY}_i) / \text{HEADS}_i) / N$$

where HEADS_i and HNY_i are the concentrations determined in the i -th run by the HEADS and the honeycomb samplers, respectively, and N is the number of runs. The mean difference is simply the average difference of the concentrations of the two samplers.

The SO_2 concentrations determined by the two samplers are in excellent agreement, as suggested by the results shown in Figure 2 and Table 1. The average collection of the Honeycomb sampler is 0.25% higher than that of the HEADS, while the average mean

concentration difference between the two samplers is 0.05 ppb. The HNO_3 concentrations in the two samplers, shown in Figure 3, indicate that the HEADS collection is on the average 11.9% higher than the Honeycomb sampler. The observed HNO_3 concentrations were very low (1-2.4 ppb) and several data points were omitted, since they were comparable to the detection limit. Since the performance of the Honeycomb denuder has been compared to that of the annular denuder in laboratory tests and found in excellent agreement (Koutrakis et al., 1993), the discrepancies are not likely be due to a decreased HNO_3 collection efficiency of the Honeycomb denuder. It is quite possible, however, that some HNO_3 was lost in the inlet surfaces of the Honeycomb sampler. The HNO_2 concentrations determined by both samplers (Figure 4) agree very well with each other. Although the observed levels were low (0.8-1.4 ppb), the average difference is 0.02 ppb, with the Honeycomb sampler collection being slightly higher (0.4%). The results for NH_3 (Figure 5) indicate that the concentrations determined by the Honeycomb sampler are on the average 18.4% lower to those of the HEADS, although the actual differences are quite small (0.25 ppb). The ambient NH_3 levels were quite low (1-2.5 ppb), and small differences tend to overestimate the actual performance difference of the two samplers. NH_3 losses on the inlet surfaces of the Honeycomb sampler are also possible, due to the large inlet surface area of the Honeycomb sampler (about 100 cm^2 , quite comparable to the collection surface area of the annular denuder, about 380 cm^2), and the relatively long residence time of the air samples (approximately 1 second compared to an air sample residence time of 0.1 second in the annular denuder).

The results of the comparison of the particulate sulfate and ammonium concentrations (Figures 6 and 7, respectively) demonstrate an excellent agreement between the two samplers. The mean differences between the Honeycomb sampler and the HEADS are approximately 0.1 $\mu\text{g}/\text{m}^3$ for both fine particulate sulfate and ammonium, with the concentrations determined by the Honeycomb sampler being 5.6% and 2.5% higher for NH_4^+ and SO_4^{2-} , respectively. The agreement in the particle collection between the two samplers should be expected, since particle loss tests conducted for annular denuders (Ye et al., 1991) and honeycomb denuders (Sioutas et al., 1994) indicated an overall loss on the order of a few percent (5% or less) for both types of denuders.

CONCLUSIONS

The performance of a new sampler that we have developed to sample inorganic particulate and gaseous pollutants has been compared to that of the HEADS in a field study. The key feature of the new sampler is the honeycomb denuder component, which has a large number of small hexagonal glass tubes sealed inside an outer glass tube. This design allows efficient collection of inorganic gases, such as HNO_2 , HNO_3 , and NH_3 , while keeping the length of the overall sampler short (the total length of the Honeycomb sampler is about 30 cm, whereas the length of just one annular denuder is 26 cm).

The field comparison results indicated an excellent agreement between the Honeycomb sampler and the HEADS in the concentrations of gaseous HNO_2 and SO_2 , as well as the concentrations of particulate sulfate and ammonium. For these compounds, the concentrations determined by both samplers agree within 5% with each other.

The Honeycomb sampler was found to collect less gaseous NH_3 and HNO_3 , compared to the HEADS. The average concentrations of NH_3 and HNO_3 determined by the Honeycomb sampler were on the average 18.4% and 11.9% lower, respectively, than those of the HEADS. Although the actual concentration differences in both cases were very small (on the order of 0.1-0.2 ppb), the observed ambient levels of HNO_3 and NH_3 were very small, thus the percent differences may be exaggerated. Nevertheless, it is quite possible that significant inlet losses can occur in the Honeycomb sampler, due to the combination of the relatively large inlet

surface area and the long air sample residence time at the inlet. This is clearly an area where the design of the Honeycomb sampler needs to be improved. We are currently designing and will evaluate a new impactor/inlet, whose surface area is considerably smaller than that of the original design.

ACKNOWLEDGEMENTS

We are grateful to Dr. Virgil Marple and Bernard Olson of the Particle Technology Laboratory of the University of Minnesota for the characterization of the impactor. The development and evaluation of the honeycomb denuder filter pack system was supported by U.S. EPA through the cooperative agreement #CR 816740. It has been subjected to the Agency's peer and administrative review and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. Finally, a patent application has been filed to the United States Patent Office, serial number #07/938,854.

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Table 1. Summary of the comparison between the HEADS and the Honeycomb samplers.

Chemical Species	Range ^A	Mean Difference ^B	Mean Difference (%) ^C
SO ₂	1.4-6.2	-0.05	-0.25
HNO ₃	0.9-2.4	0.11	11.90
HNO ₂	0.8-1.4	-0.02	0.40
NH ₃	0.9-2.7	0.25	18.44
Fine particle sulfate	1.05-11.81	-0.11	-5.64
Fine particle ammonium	0.54-3.78	-0.09	-2.55

A. Concentration ranges are expressed in (ppb) for the SO₂, HNO₃, HNO₂, and NH₃, and in (μg/m³) for particulate sulfate and ammonium.

B. Mean difference is the value for (HEADS-IINY). Mean differences are expressed in (ppb) for the SO₂, HNO₃, HNO₂, and NH₃, and in (μg/m³) for particulate sulfate and ammonium.

C. Mean Difference (%) = $100 \cdot \sum ((\text{HEADS}_i - \text{HNY}_i) / \text{HEADS}_i) / N$, where HEADS_i and HNY_i are the concentrations determined in the i-th run by the HEADS and the honeycomb samplers, respectively, and N is the number of runs.

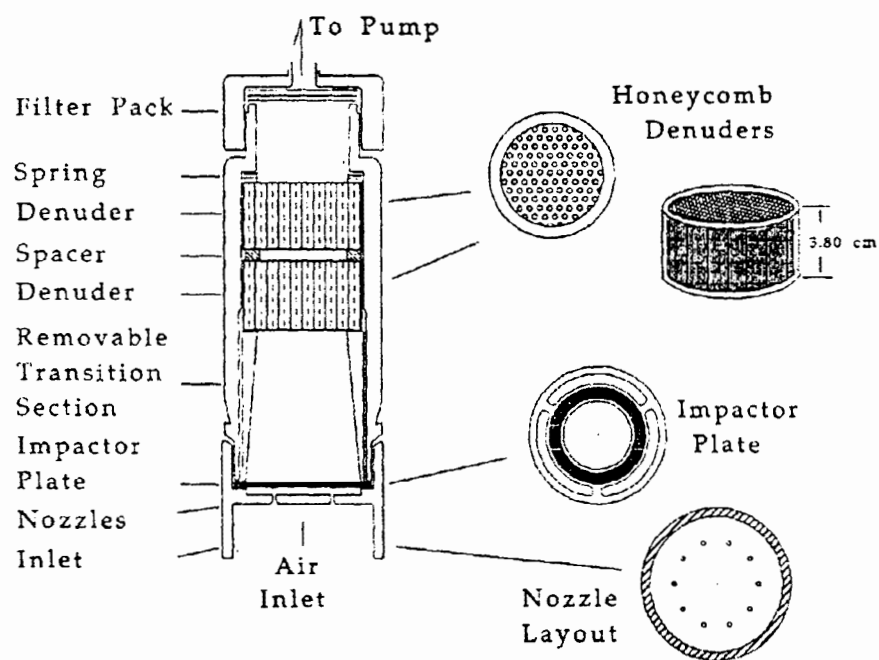


Figure 1. Schematic of the glass honeycomb denuder/filter pack sampler.

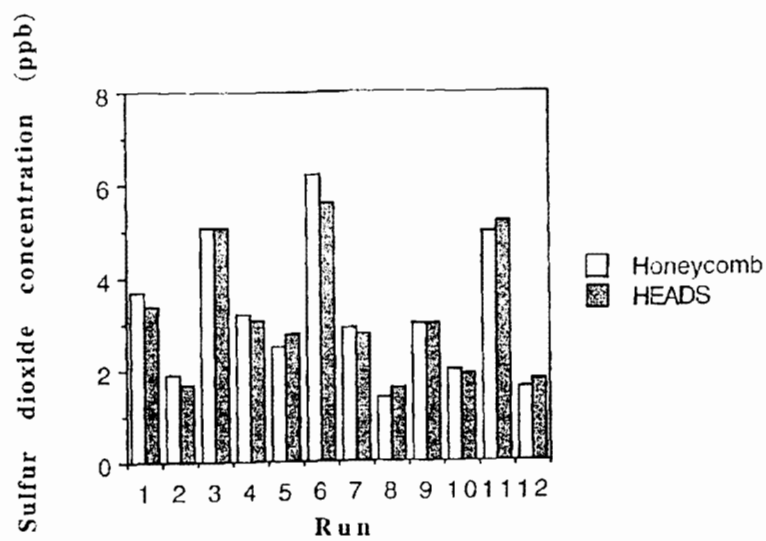


Figure 2. SO_2 concentrations measured by the Honeycomb sampler and the HEADS.

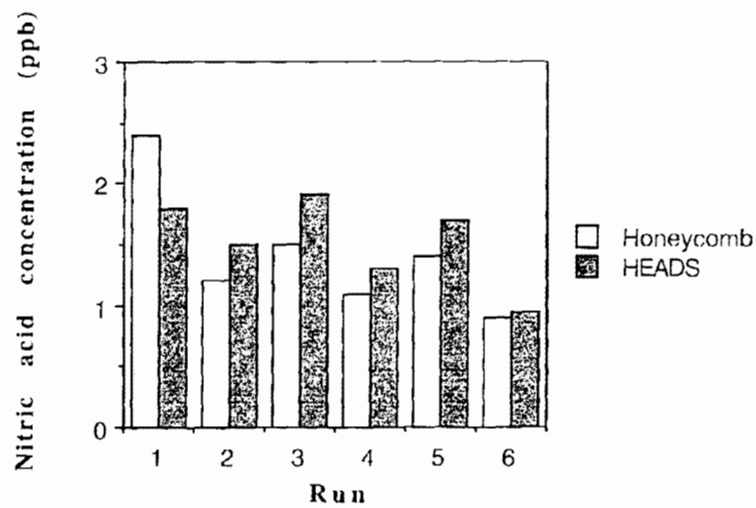


Figure 3. HNO_3 concentrations measured by the Honeycomb sampler and the HEADS.

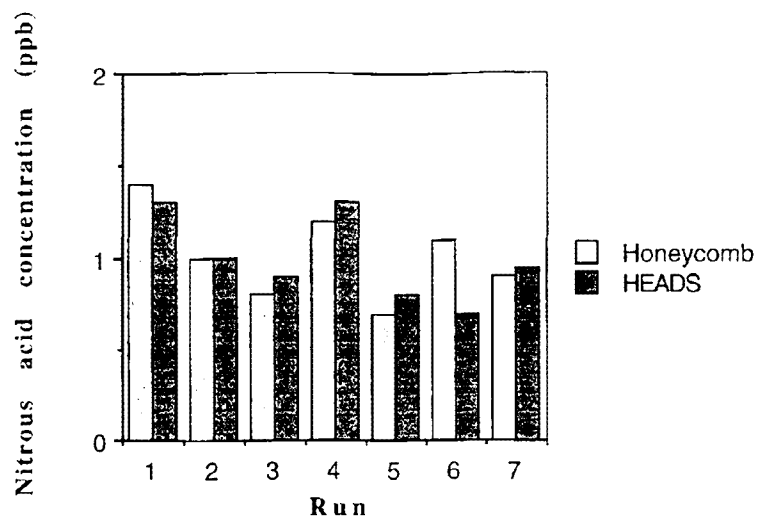


Figure 4. HNO_2 concentrations measured by the Honeycomb sampler and the HEADS.

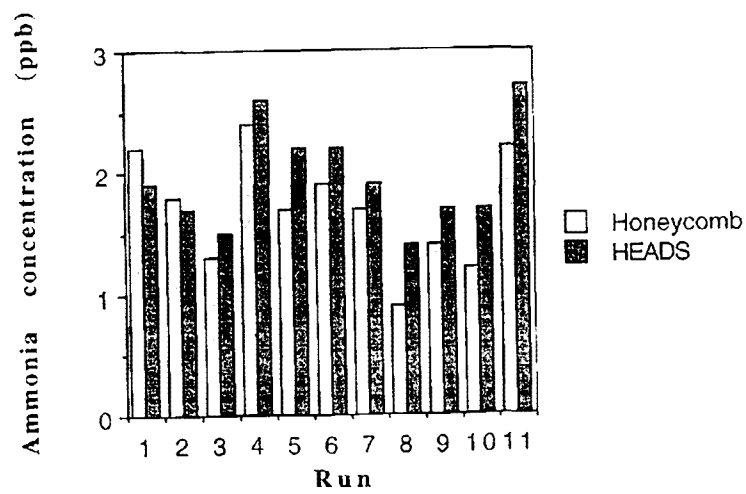


Figure 5. NH_3 concentrations measured by the Honeycomb sampler and the HEADS.

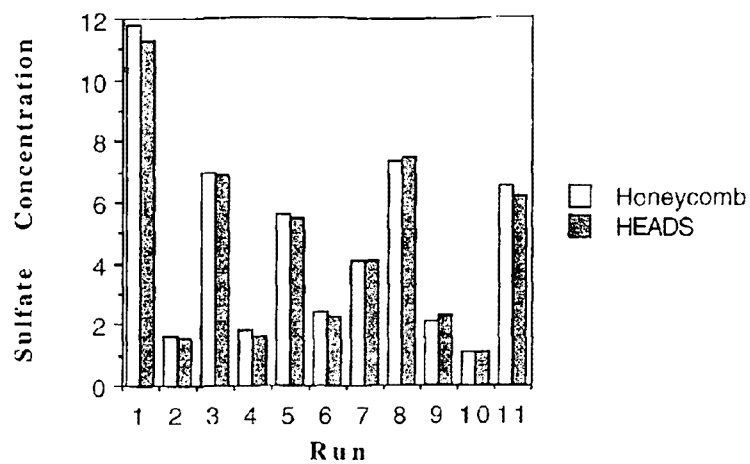


Figure 6. Particulate sulfate concentrations measured by the Honeycomb sampler and the HEADS.

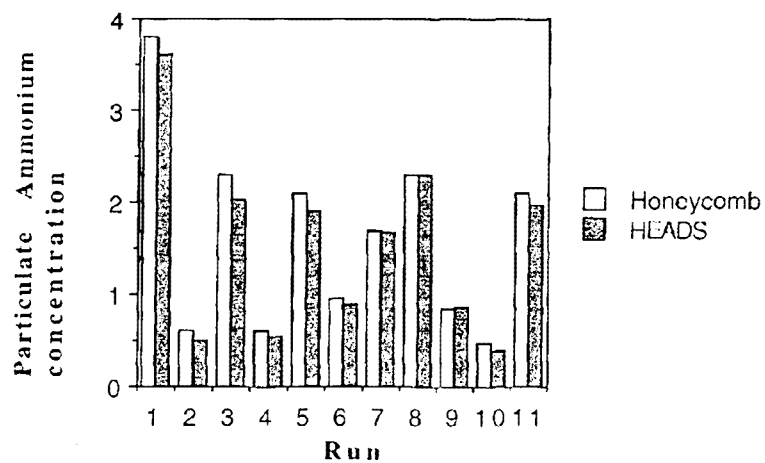


Figure 7. Particulate ammonium concentrations measured by the Honeycomb sampler and the HEADS

The Use of PM10 Anion-Cation Difference as an Index of Historical Aerosol Acidity

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The composition of particles in the air may have a significant influence on the health implications of inhaling these particles. Particulate matter less than $10\text{ }\mu\text{m}$ in aerodynamic diameter (PM10) has been routinely sampled throughout the U.S. and elsewhere in the world for years, but these samples are usually only weighed for total mass and summarily stored. However, these samples can be (and sometimes are) analyzed for their ionic composition (i.e. of sulfates, SO_4^{2-} ; nitrates, NO_3^- ; and ammonium, NH_4^+) via ion chromatography. Furthermore, it is hypothesized that the imbalance of these easily measured ions (i.e. anions-cations) may provide a useful estimate of the remaining unmeasured major particulate cation: aerosol strong acidity, H^+ . Conventional methods for directly measuring H^+ entail great care to protect the collected acid from neutralization by ambient ammonia, basic particles, or alkaline filter media, in order that all the H^+ show up via a pH determination. We have conducted such direct H^+ measurements side-by-side with state-run PM10 samplers in Albany, NY and in New York City, NY in order to test whether the PM10 ion difference estimates concur with the directly measured H^+ . Despite the lack of neutralization protection of the PM10 samples, it was found that the ion difference method yields H^+ highly correlated with, and not significantly different from, the directly measured H^+ . It is thought that the ion difference is maintained on these samples by the rapid neutralization of ambient H^+ by large basic particles coexisting on the PM10 filters, as well as by the weakly alkaline quartz filters themselves. This would preempt the conversion of particulate acids (e.g., H_2SO_4) to ammonium sulfates (e.g., $[\text{NH}_4]_2\text{SO}_4$) by ammonia gas, thereby maintaining the original sulfate-ammonium imbalance associated with the ambient H^+ . Archived PM10 samples therefore represent a potentially valuable resource regarding the nature of acid aerosol exposures throughout the U.S. and elsewhere.

**Passive Samplers for Ambient Ozone, Formaldehyde and Sulfur Dioxide:
Indoor, Outdoor, and Personal Exposure Applications**

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Time-integrated measurements of air pollutants have many applications in the context of regulations pertaining to indoor air quality, outdoor (ambient) monitoring, and personal exposure assessment. For several years, the passive samplers developed at DGA have been applied to cost-effective measurements of parts per billion levels of ozone, formaldehyde and sulfur dioxide. Examples of applications will be described. These include (a) formaldehyde measurements in indoor settings including museums, public buildings and personal exposure; (b) ozone measurements indoor (museums, cultural heritage buildings) and outdoor (Class I Wilderness areas; air quality surveys in Europe, Canada and Latin America. long-term monitoring of ozone exposure in forests) and (c) surveys of ambient levels of sulfur dioxide in several eastern European countries.

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SESSION 9:

**NC O₃ STATE IMPLEMENTATION PLAN,
MEASURING AND MODELING STUDY**

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Overview of the North Carolina UAM Project

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In 1992 North Carolina committed to perform photochemical gridded dispersion modeling to support the nonattainment state implementation plan (SIP) process. In particular, UAM results would be used to demonstrate attainment by 1996 for the three moderate nonattainment areas (Charlotte/Gastonia, Raleigh/Durham, and Greensboro/Winston-Salem/High Point). However, all areas measured clean air quality for ozone by 1992. The UAM project then was directed at developing a maintenance plan for the Charlotte/Gastonia area to support a redesignation request. This paper details the overall scope, organization, current status, and future plans for the North Carolina UAM project.

**The Sensitivity of Meteorological and
Emissions Uncertainties on Urban
Airshed Model Ozone Concentration
Results in North Carolina**

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ABSTRACT

This paper briefly summarizes the results of sensitivity studies conducted by the State of North Carolina on the use of the Urban Airshed Model (UAM) with the July 6-8, 1988 ozone episode. The purpose of this study was to determine model sensitivity to changes in emissions and meteorological inputs.

Hourly ozone concentrations from a base case run were compared with results from subsequent runs in which one or more inputs were varied. Fifteen sensitivity runs were performed, examined, and then ranked based on their effect on model results. It was concluded that for the July 6-8, 1988 ozone episode the UAM was most sensitive to changes in boundary conditions, mixing heights, and NO_x emissions. The model was less sensitive to changes in initial conditions, VOC emissions and elevated point source emissions.

The conclusions drawn from this study will serve as a guide to the correlation between model inputs and model sensitivity. In addition, knowledge of model sensitivity will result in more careful development of the critical inputs and provide a better understanding of how the model works.

INTRODUCTION

The Clean Air Act Amendments of 1990 require all ozone nonattainment areas, moderate and above to conduct photochemical modeling as part of a State Implementation Plan (SIP) attainment demonstration. Serious, severe, and extreme nonattainment areas are required to use the Urban Airshed Model (UAM). Moderate nonattainment areas can use either UAM or the EKMA model (EPA, 1991.)

In North Carolina, Raleigh-Durham, Greensboro-Winston Salem, and Charlotte were designated moderate ozone nonattainment areas. The North Carolina Air Quality Section decided to use UAM in preparation of a SIP attainment demonstration because UAM is the best modeling tool available to evaluate ozone and plan for future emissions reductions.

Over the last year, the Greensboro-Winston Salem MSA and the Raleigh-Durham MSA have been redesignated to attainment based on monitored air quality data and a maintenance demonstration. A redesignation request has also been submitted for Charlotte; however, UAM must be used to show maintenance of the ozone standard in Charlotte for the next 10 years. This demonstration is required because future emissions in Charlotte are expected to increase due to growth.

The UAM modeling domain was chosen to include all three urban areas and to be large enough to include all sources that may effect the areas and to lessen the influence of boundary conditions. The domain is 300 km X 450 km in size. The grid cells are 5km on a side, making the domain 60 X 90 grid cells. There are five vertical layers, varying in height with the mixing height, with 3 layers above the mixing height and 2 layers below. The top of the domain is set at 2400 meters.

The current modeling is being conducted with the original large domain, but attention is being focused on the Charlotte metropolitan area. The sensitivity analyses conducted in this study were applied to the full domain, but the maximum ozone concentration results are only applicable to a 25 X 25 grid cell area centered on downtown Charlotte. Figure 1 shows the North Carolina modeling domain with a box around the Charlotte subdomain.

The July 6-8, 1988 Ozone Episode

The first UAM episode to be modeled was July 6-8, 1988 and represents the highest ozone values ever measured in North Carolina. This ozone episode was characterized by strong transport from the north. A strong surface high and upper level ridge to the west, and an upper level low to the northeast created a northerly flow across the domain for the majority of the episode. Surface winds were light (1-3 m/s), but steady from the north and northeast on the 6th and 7th and veered to the southeast on the 8th. Upper level winds were also from the north and northeast throughout the episode with speeds ranging from 5-15 m/s in model layers 3, 4, and 5.

Temperatures were very hot during the period with highs steadily increasing from the upper 80's on the 6th to the upper 90's on the 8th. Skies were mostly clear, except for some clouds in Charlotte on the afternoon of the 7th. There was no precipitation in the domain until thunderstorms occurred on the evening of the 8th in Charlotte.

Ozone exceedences occurred throughout the domain on the 7th and 8th. Maximum ozone concentrations on the 7th were generally observed in the Greensboro-Winston Salem area with a high of 145 ppb. The highest monitored ozone on the 8th occurred in Charlotte with a reading of 169 ppb. Table 1 shows the maximum ozone values monitored in the three metropolitan areas.

Model Inputs to Base Case

There are 13 UAM input files which are roughly divided into 4 categories; emissions, meteorology, boundary conditions, and control files. A very brief explanation of input file development follows.

The emissions were processed using the EPA Emissions Preprocessing System (EPS 2.0). Mobile source emissions were calculated using MOBILE 5A. Area source emissions were calculated using EPA emission factors. Point source data was collected from the state regional air quality offices. Day specific emissions data were obtained from the electric utilities (Duke Power and CP&L) to estimate power plant emissions. Biogenic emissions were calculated using the UAM BEIS model.

Mixing heights were prepared using the RAMMET-X model. Upper air and surface meteorological data from Greensboro, NC and Athens, GA were used to process the mixing heights. RAMMET-X uses minimum and maximum daily mixing heights, and performs a temporal interpolation using hourly surface temperatures to produce 24 hourly mixing heights. The UAM preprocessor DFSNBK then spatially interpolates the mixing heights across the domain.

Wind fields were developed using the Diagnostic Wind Model (DWM). DWM spatially and temporally interpolates observed wind data. 21 surface stations and 4 upper air stations were used to develop the wind fields. DWM also uses a terrain file to adjust winds for terrain effects. The model was run with 13 vertical layers. The UAM preprocessor UAMWIND was then run to interpolate the DWM layers into 5 UAM vertical layers.

The initial, boundary, and top concentration data were supplied by the Regional Oxidant Model (ROM 2.2). ROM data was downloaded from the EPA mainframe and then processed into UAM files through the ROM-UAM interface (supplied with the UAM model).

For further discussion of the development of UAM inputs refer to the Charlotte redesignation demonstration and maintenance plan submitted to the EPA region IV office (NCDEHNR, 1993).

Model Performance-Base Case

Model performance for the July 6-8, 1988 episode was marginally acceptable. Statistical performance based on recommended EPA statistics (*EPA, 1991*) was acceptable although normalized bias was slightly higher than the recommended range of 5-15%. The model underpredicted ozone for most hours, especially on day 2. Table 2 shows the model performance statistics for the North Carolina domain. Figure 2 shows the base case ozone concentrations on day 3 at the hour of the domain-wide maximum.

A possible cause for the underprediction on the 7th is that ROM underpredicted boundary conditions on that day. The transport across the boundaries on this day was from the north. A preliminary performance evaluation of ROM results shows that ROM severely underpredicts ozone to the north of the North Carolina domain on the 7th (*EPA, 1994*). Based on observed wind speed and direction and past ozone values measured in the Piedmont area of North Carolina, ozone values of the magnitude measured on July 7th and 8th, 1988 are not likely to occur without transport from other areas.

SENSITIVITY RUN RESULTS

Table 3 lists each sensitivity run and results. Table 4 shows the percent relative changes between the base case and each sensitivity run. The model was run for 72 hours with the first day being a startup day. Day 1 is not used in the performance statistics and is not considered in the model results discussion.

Mixing Heights

Mixing height is defined as the height in the atmosphere below which similar diffusion characteristics occur. The RAMMET-X preprocessor was used to calculate mixing heights. The major shortcoming of this preprocessor is the overestimation of mid-morning and after sunset mixing heights. Over estimation of mixing heights leads to an increased model volume and, in turn, to diluted pollutant concentrations.

Two sensitivity runs were performed involving mixing heights. In the initial run, mixing heights were manually cut in half (figure 3). The winds, boundary conditions, top concentrations, and initial conditions were then rerun. The results indicate that predicted ozone concentrations are up to 60 ppb higher when mixing heights are reduced. The higher concentration of pollutants is due to decreased model volume. The areas of maximum ozone prediction shifted slightly, possibly because mixing heights are used to define the layers in the wind model. In addition to having an effect on the chemical volumes in the model, inaccurate mixing heights will also affect the spatial distribution and diffusion of species due to alterations in wind patterns at various levels.

In the next sensitivity run, mixing heights were multiplied by 1.5. The region top was adjusted from 2400 to 3600 meters to accommodate the higher mixing heights. The winds, boundary conditions, top concentrations, and initial conditions were then rerun. The UAM predicted lower concentrations of ozone when mixing heights were increased due to increased model volume. Spatially, the biggest decreases, up to 25 ppb, occurred very near the areas where high ozone was predicted by the base case.

Based on the sensitivity of maximum ozone concentration to changes in mixing heights, an accurate representation of mixing heights is critical. Also noted was that the wind fields will be altered by misestimation of the mixing heights, which may lead to errors in spatial distribution and diffusion. Checks against observational data should be performed where available to ensure that the models are doing a reasonable job of predicting mixing heights.

Wind Speeds

Wind speeds are important in calculating pollutant dispersion in the model. The stronger the wind, the greater the dispersion. The Diagnostic Wind Model (DWM) was used to process the wind fields for input into UAM.

Two sensitivity runs were performed involving changes to wind. In the initial run, surface and upper wind speeds were cut in half (figure 4). Decreasing winds reduced dispersion of ozone and precursors and reduced transport from urban to rural areas. The resultant modelled ozone predictions showed increases of up to 50 ppb in urban areas and decreases of up to 45 ppb in rural areas.

In the second run, surface and upper level winds were doubled. Doubling the winds caused greater dispersion of pollutants and increased transport from urban to rural areas. Transport of ozone across the northern boundary also increased. Ozone increased up to 30 ppb in rural areas. Decreases of up to 45 ppb occurred in urban areas.

Although higher winds will result in greater dispersion, not all areas will see an ozone decrease. Increasing the wind speeds causes an increase in transport as well as dispersion. Rural ozone is largely attributable to transport from urban areas.

Initial Conditions

Initial conditions refer to the concentrations present over the domain at the start of the model simulation. Ideally, the modeled effects of initial conditions will "wash out" as the episode progresses.

Two sensitivity runs were performed involving changes to initial conditions. In the first run, initial conditions were set to zero. This was accomplished by multiplying the ROM initial concentrations by 0.02, which was the smallest number by which we could multiply without encountering problems with floating point errors in the chemistry routines. ROM was used for boundary and top concentrations in both runs. Zero initial conditions reduced the predicted ozone maximum on day 2 by only 1 ppb. There was no change in the ozone maximum on day 3.

In the second run, clean background values (*EPA, 1991*) were substituted for each species in the initial conditions. Clean initial conditions had no effect on predicted ozone values.

Boundary Conditions

Boundary conditions refer to the concentrations present at the boundaries of the domain throughout the episode. The northern boundary of the North Carolina domain borders on the Northeast Transport Region, which contains many large industrial cities responsible for producing large amounts of ozone and precursors. The eastern, western, and southern boundaries are "cleaner" with the exception of a few large cities south and southwest of the domain. Since the July '88 episode was characterized by strong transport from the north, boundary conditions were thought to be critical.

Two sensitivity runs were performed involving changes to the boundary conditions. The first run assumed zero boundary conditions and resulted in domain wide decreases of up to 70 ppb (figure 5). ROM was used for initial and top concentrations. No increases in ozone were predicted.

The second run was with clean boundary conditions. Clean background values (*EPA, 1991*) were substituted for each species in the boundary conditions input file. Decreases in ozone were seen across the vast majority of the domain, with decreases of up to 40 ppb occurring along the boundaries.

Emissions Sensitivities

Seven emissions sensitivity runs were modeled, all using a domain-wide across the board emissions increase or decrease. These model runs identified which areas were most sensitive to NO_x or VOC changes and therefore which areas are NO_x or VOC limited. (In NO_x limited areas, ozone production is limited by the availability of NO_x . In VOC limited areas, ozone production is limited by the availability of VOC's.) But VOC limited areas in the base case may become NO_x limited in

future years or vice versa. The effect of potential future year control measures cannot be estimated using base case emissions.

Zero Emissions

All anthropogenic and biogenic emissions in the domain were set to zero. Initial, boundary, and top concentrations from ROM were not changed. This run tested the influence of ROM data on ozone concentrations within the domain.

Day two maximum concentrations in Charlotte decreased 55%. Day three concentrations only decreased 27%. With no emissions from within the domain, a much larger decrease in maximum ozone would be expected. A large amount of ozone is being transported into the domain along the northern boundary. The maximum concentration along the northern boundary is 138 ppb. The maximum ozone concentration in the Charlotte area with zero emissions was 104 ppb on day 3 (87% of the standard).

The results indicate that the specification of boundary conditions in this episode is critical to predicting the correct ozone concentrations within the domain. Also, emissions from within the domain are relatively unimportant in contributing to ozone formation.

NO_x Emissions

Two sensitivity runs were modeled to examine the effect of increasing or decreasing NO_x emissions. NO_x was initially increased by 50% and then decreased by 50% to show which areas are NO_x limited and therefore which areas may respond strongly to changes in NO_x.

When NO_x was increased by 50% the maximum ozone concentration in the Charlotte area increased by 4% on day 2 and 6% on day 3. The majority of the domain shows an increase in ozone which indicates areas that are NO_x limited. Areas within 5-50 km of power plants (depending on the size of the source) show a decrease in ozone of up to 20 ppb when NO_x is increased. This is due to ozone scavenging when NO_x concentrations become very high. Ozone concentrations in downtown Charlotte stay about the same indicating the area is not NO_x limited.

When NO_x was decreased by 50% the maximum ozone concentrations in the Charlotte area decreased by 20% on day 2 and 10% on day 3 (figure 6). The majority of the domain showed a decrease in ozone of up to 25 ppb. The largest decreases were in the urban areas where ozone levels were highest to begin with. Downtown Charlotte showed no change in ozone concentration indicating a small (~15km²) VOC limited area. Areas near power plants again showed an increase in ozone due to the removal of NO_x that was previously scavenging ozone.

The response to NO_x reductions was limited by the dominance of transported ozone and precursors into the domain. A larger reduction in ozone would be expected if the majority of ozone in the domain was a result of local emissions. The reduction in the ozone max was greater on day 2 than day 3 due to less transport on day 2.

VOC Emissions

Two sensitivity runs were modeled to examine the effect of increasing or decreasing VOC emissions. VOC's were initially increased by 50% and then decreased by 50% to indicate which areas are VOC limited and will respond to changing VOC emissions.

When VOC's were increased by 50% the maximum ozone concentration in the Charlotte area increased by 6% on day 2 and 5% on day three. Spatially, the areas where ozone increased were very small. Only small portions of the urban areas and areas near power plants showed ozone increases. These areas have relatively large NO_x concentrations, making them VOC limited. The additional VOC's in the sensitivity run were able to convert more NO to NO₂ than in the base case resulting in increased ozone formation. The maximum increase was 11 ppb of ozone in downtown Charlotte.

When VOC's were decreased by 50% the ozone maximum in the Charlotte area decreased by 11% on day 2 and 6% on day 3 (figure 7). Again, ozone decreased in the urban cores and near the

power plants. A decrease of 18 ppb was seen in downtown Charlotte on day 2 with around a 10 ppb decrease in the other VOC limited areas.

Reducing VOC's reduces the number of radical sources available to convert NO to NO₂ which is only important where excess NO exists. As would be expected, a reduction of up to 1 ppb of NO₂ was seen in the same areas which had lower ozone concentrations.

Isoprene Times Five

Isoprene emissions were increased by a factor of five in order to simulate an expected increase in the emission factors for isoprene in the BEIS model (*Pierce, 1994*). Isoprene represents the largest portion of biogenic emissions in the domain and is mainly emitted from deciduous trees. The changes in ozone concentrations as a result of the increase were very similar to the previous total VOC increase. The maximum increase was large in magnitude (63 ppb) but relatively small in affected area. The maximum ozone concentration in the Charlotte area increased 11% on day 2 and 15% on day 3. The increase was limited to urban core areas and near power plants. The largest domain wide increase occurred in the NO_x plume from a large power plant in Person County, NC.

Increases in ozone were greater spatially on day 2 which had less transport than day 3. The majority of the Charlotte metropolitan area was sensitive to increasing isoprene on day 2 with ozone increases of 5-20 ppb. Increasing isoprene has a greater impact on local emissions than on transported ozone. Estimating biogenic emissions could be important to modeling the ozone maximum especially in the urban areas. Increasing biogenics in rural areas will have little to no effect because the areas are already severely NO_x limited.

Zero Elevated Point Sources

All elevated point source emissions were set to zero. These are sources that have a potential plume rise greater than the minimum thickness of the first layer (50 meters). In the North Carolina domain, the majority of these sources are power plants. As a result, this sensitivity mainly reduces point source NO_x emissions.

The decrease in maximum ozone in the Charlotte area was 5% on both days 2 and 3. The maximum domain wide decrease was 61 ppb at the same power plant as when isoprene was increased. Ozone also increased by 45 ppb approximately 50 km downwind of the same power plant due to the lack of NO to scavenge ozone. Ozone decreased by 10-15 ppb along the path of the NO_x plumes from the power plants. The elevated point sources had a small effect on the urban areas and the maximum ozone concentration. If the NO_x plume is blown directly over an urban area, a larger effect on ozone concentrations can be expected. It is unclear whether large point sources will have a greater effect in other ozone episodes with less transported ozone. It will most likely depend on the path of the plumes.

CONCLUSIONS

The sensitivities performed for the July 6-8, 1988 UAM episode have shown how the model reacts to input changes and have revealed which uncertainties need to be studied further. Table 2 shows a ranking of relative increases and decreases in maximum ozone concentrations in the Charlotte area for each sensitivity run.

The zero boundary conditions model run clearly shows that the domain is dominated by ozone transported from the boundaries, especially on day 3. The majority of the transported ozone is coming from the northern domain boundary. It is impossible to predict the correct base year ozone values in this episode without accurate boundary conditions. The ROM boundary conditions are underestimated on day 2 and the result is a large underprediction of ozone in the entire domain. It is important to have accurate ROM results in the base year as well as the future years.

Initial conditions were derived from ROM data and had no effect on maximum ozone concentrations in the North Carolina domain on days 2 and 3. The initial conditions are washed out

of the domain by strong transport during the episode. It is not important to accurately estimate initial conditions for this episode.

Emissions from within the domain are less important than expected. When emissions are zeroed, an ozone maximum of 104 ppb still occurs in Charlotte due to boundary conditions. The ozone changes resulting from emissions changes are difficult to quantify due to the dominance of transported ozone.

In the base case, the majority of the domain is NO_x limited. Changes in NO_x emissions revealed large areas sensitive to both increasing and decreasing emissions. Downtown Charlotte and to a lesser extent other urban areas showed very little sensitivity to NO_x changes, indicating VOC limited areas. Ozone concentrations in grid cells near power plants increased when NO_x was decreased due to titration of ozone in the base case (making these areas VOC limited.) Due to the sensitivity of the model to NO_x changes, NO_x inventory estimates are important.

Changes in VOC emissions affected relatively small areas throughout the domain. Downtown Charlotte and grid cells within 50 km of power plants showed the greatest sensitivity to VOC changes. The maximum ozone concentration in the Charlotte area was slightly more sensitive to NO_x changes than VOC changes. Decreasing VOC's by 50% reduces ozone in these VOC limited areas, but unlike reducing NO_x , it does not increase ozone anywhere in the domain. Creating an accurate VOC inventory (including biogenics) is important in urban areas and near power plants, but not as important in the rural areas. If the biogenic VOC inventory in the rural areas is large compared to the NO_x inventory, the areas will be NO_x limited and therefore the exact amount of VOC emissions is not significant.

The model is sensitive to changes in mixing heights. Decreasing mixing heights had a greater impact than increasing mixing heights. Underestimating mixing heights will introduce bias into the model and may lead to compensating errors.

Changing wind speeds has a large effect on the spatial distribution of ozone concentrations. Increasing the wind speeds increases dispersion, and increases transport of ozone to rural areas. Increasing or decreasing wind speeds has only a moderate impact on ozone maximums, but has a large impact on model bias due to spatial shifts in ozone production.

The results of these sensitivities should not be used to make conclusions for other UAM episodes nor for future year model runs. The emissions reductions cannot predict future control strategies because the mix of pollutants in the future will change and ozone formation is highly non-linear.

In North Carolina, as in many areas, there is a lack of meteorological and precursor data from 1987 and 1988 to verify model input data and model performance. Increased monitoring of meteorological and pollutant data will reduce modeling uncertainties in the future. For the current modeling, improvements in the most sensitive model inputs will greatly reduce uncertainty and improve model performance.

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Table 1. Highest observed ozone (ppb) during the July 6-8, 1988 ozone episode.

	Charlotte	Raleigh-Durham	Greensboro-Winston Salem
July 6, 1988	81	94	103
July 7, 1988	143	142	145
July 8, 1988	169	115	153

Table 2. Model Performance Statistics July 6-8, 1988.

Unpaired Highest Prediction Accuracy	12.2%
Normalized Bias of all pairs > 60 ppb	17.1%
Gross error of all pairs > 60 ppb	24.4%

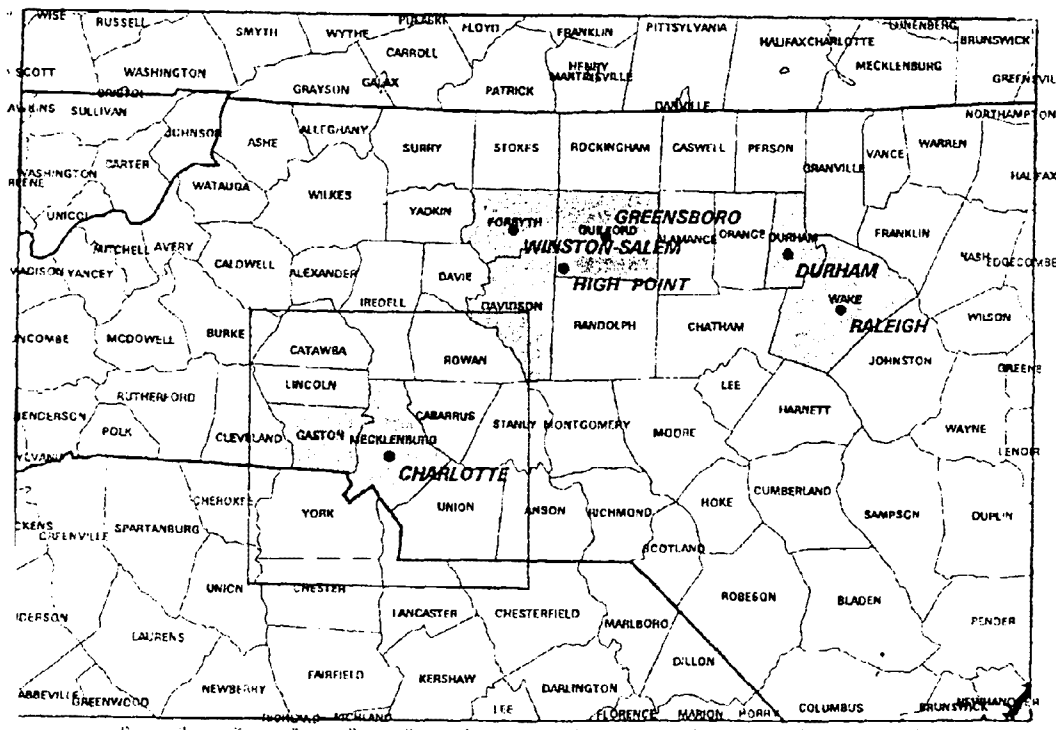


Figure 1. North Carolina UAM modeling domain.

Table 3. Daily maximums in parts per billion ozone

Scenario	Day 1	Day 2	Day 3
Base case	82	122	142
Multiply mixing heights by 0.5	94	154	170
Multiply mixing heights by 1.5	71	105	130
Halve surface and upper winds	100	146	149
Double surface and upper winds	72	105	143
Zero initial conditions	62	121	142
Clean initial conditions	83	122	142
Zero boundary conditions	75	79	68
Clean boundary conditions	84	123	110
Zero emissions	60	55	104
Zero elevated point sources	76	116	135
Multiply NOx by 1.5	91	127	151
Multiply NOx by 0.50	69	98	128
Multiply VOCs by 0.50	80	108	134
Multiply VOCs by 1.5	83	129	149
Multiply isoprene by 5.0	86	136	164

Table 4. Percent changes in ozone from base case.

Scenario	Day 1	Day 2	Day 3
Zero emissions	-27%	-55%	-27%
Zero boundary conditions	-09%	-35%	-52%
Multiply NOx by 0.50	-16%	-20%	-10%
Multiply mixing heights by 1.5	-13%	-14%	-08%
Double surface and upper winds	-12%	-14%	-01%
Zero initial conditions	-24%	-01%	0%
Multiply VOCs by 0.50	-02%	-11%	-06%
Zero point sources	-07%	-05%	-05%
Multiply mixing heights by 0.5	+15%	+26%	+20%
Halve surface and upper winds	+22%	+20%	+05%
Multiply isoprene by 5.0	+05%	+11%	+15%
Multiply NOx by 1.5	+11%	+04%	+06%
Multiply VOCs by 1.5	+01%	+06%	+05%
Clean boundary conditions	+02%	+01%	-23%
Clean initial conditions	+01%	0%	0%

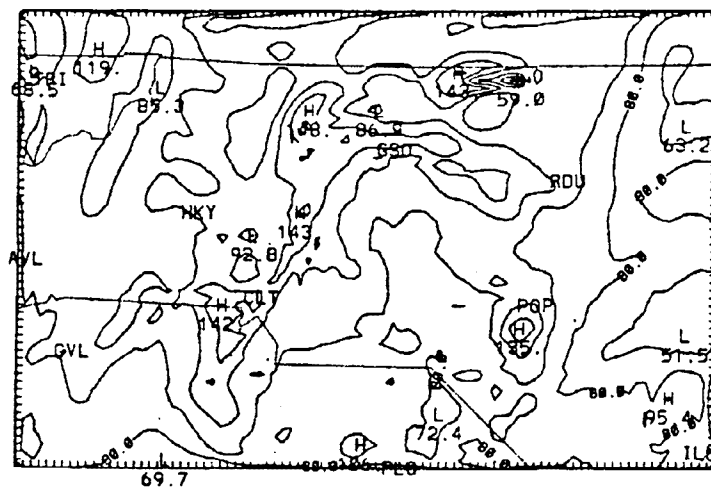


Figure 2. Ozone conc. in ppb for base case, day 3, hour 17.

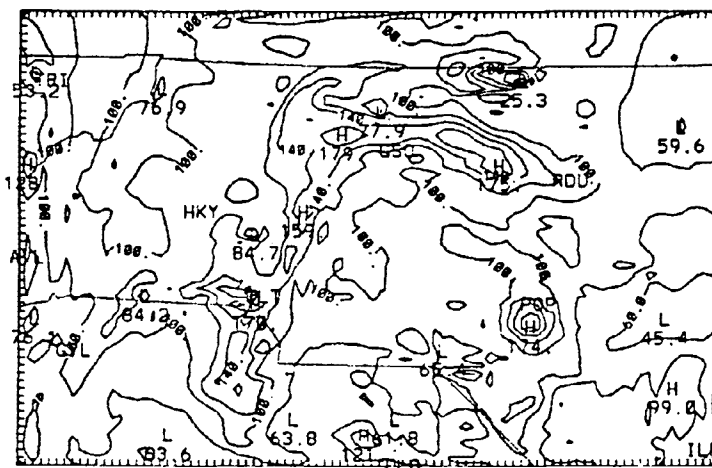
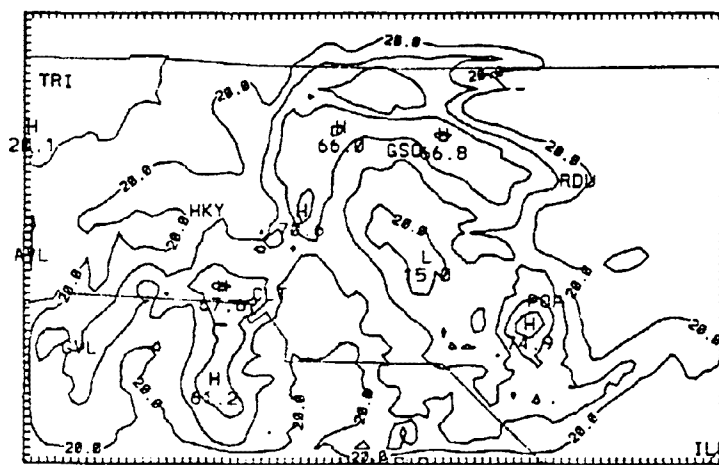
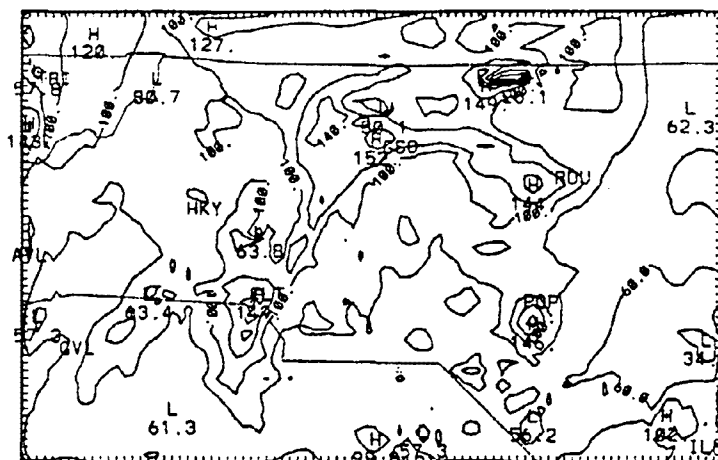
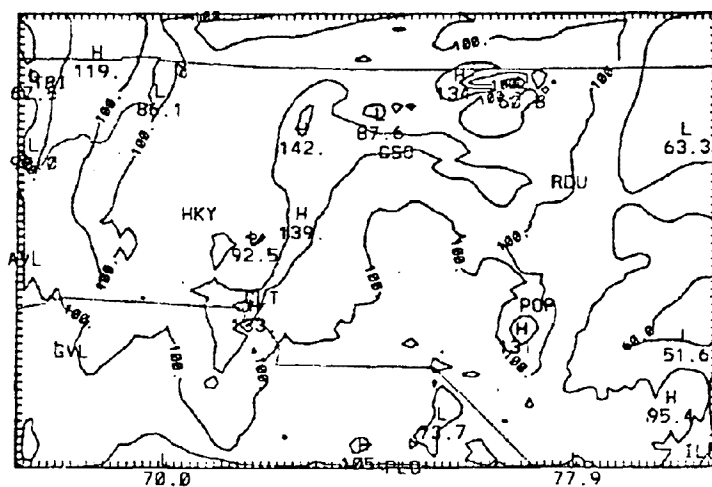
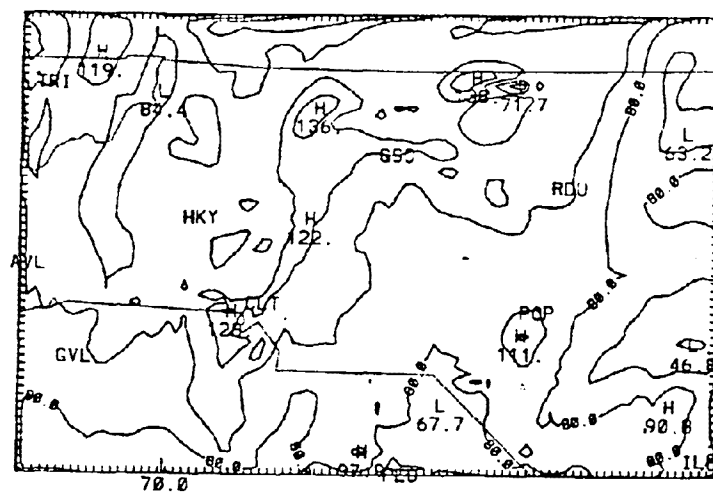


Figure 3. Ozone conc. in ppb with halved mixing heights, day 3, hour 17.





**Updated Land Use/Land Cover Data – Its Effects on Estimates of
Biogenic Emissions in the North Carolina Urban Airshed Modeling Effort**

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In North Carolina, emissions from vegetation comprise the bulk of the volatile organic compound (VOC) inventory. Estimation of these emissions will thus play a substantial role in the regulatory strategy suggested by modeling. The Urban Airshed Model (UAM), as available from the EPA, presently estimates biogenic emissions from land use/land cover data more than 20 years old. Recent data obtained from the U.S. Forest Service's periodic Forest Inventory and Assessment surveys have been gridded to the modeling domain. Emission estimates based upon these data will be compared with those from the older land use/land cover data set.

**Enhancements to the Emissions Inventory Inputs for the
North Carolina UAM Project**

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In an effort to better define and allocate both base year and projected emissions inventories, North Carolina Division of Environmental Management, Air Quality Section implemented a rigorous exploration of certain aspects of emissions inventory calculation, projection, and temporal allocation for use in an UAM analysis. In particular, a variety of growth factors were examined, several VMT projection methodologies were scrutinized, and default temporal allocation profiles for certain emissions categories were studied to determine if local data existed to develop alternative profiles. This paper presents the findings of each of the above mentioned studies.

Mobile Emission Calculations for the North Carolina UAM Project

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In development of highway mobile emissions for use in the North Carolina Urban Airshed Model (UAM) project, the Division of Environmental Management (DEM), Air Quality Section focused on the following aspects of the highway mobile emission calculations.

1. A method to estimate the inspection and maintenance (I/M) program influence in any of the North Carolina counties. The concept of I/M fractions was developed and implemented using North Carolina Accident Data from 1988-1992.
2. Use of the daily rather than hourly emission factors in calculation of highway mobile portion of UAM emissions inventories based on a comparative analysis of daily and hourly emission factors for a test case.
3. North Carolina specific vehicle age distribution developed to be used in Mobile5a runs to improve accuracy of highway mobile emission estimates.

This paper details the rationale for exploring these parameters as well as the justification for the final decision on the mobile emission calculations.

**Use of Link-Base Data to Add Definition to Highway Mobile
Emissions for the UAM**

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In developing highway mobile emissions for the Urban Airshed Model (UAM), the North Carolina Division of Environmental Management (DEM), Air Quality Section utilized link-based data, in addition to highway performance monitoring system (HPMS) data, in order to add definition to the mobile source emissions. HPMS data provided vehicle miles travelled by functional class per county. Link-base data allowed emissions to be calculated for each road segment, or link, for each of the top three functional classes.

The link-based mobile emission estimate method was selected for North Carolina because of the nature of the state. The majority of North Carolina's population is in three city clusters (Raleigh/Durham, Greensboro/Winston-Salem/High Point and Charlotte/Gastonia). These clusters are composed of medium-sized cities with an average of sixty miles between the clusters. With a concentration of population in three widespread city centers, the link-based emissions were thought to give a more accurate estimate of emissions and modeling results than simply allocating the emissions over each county on a population density basis without respect to the location of roads. This paper details the structure of the project, as well as the quality assurance process.

**Quality Assurance of the North Carolina Precursor of Ozone Inventories,
Emissions Preprocessor System and the Urban Airshed Model Output**

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The Urban Airshed Model (UAM) is being utilized in North Carolina as a tool for developing regulatory strategies. In order to have confidence in the results of the UAM output, the modeling inventories and the Emissions Preprocessor System (EPS) outputs needed to be rigorously quality assured. North Carolina Division of Environmental Management (DEM), Air Quality Section developed quality assurance strategies to ensure data integrity at all phases of inventory development and preprocessing for input into the UAM. This paper outlines the quality assurance strategies developed and implemented for the emissions inventories that were used in the UAM modeling effort.

Design of a Citizen Survey of Forest Plant Injury Caused by Exposure to Ozone

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ABSTRACT

The North Carolina Environmental Defense Fund has designed a citizen-based survey of forest plant injury caused by exposure to ozone. The first, pilot survey will run for ten weeks in July, August, and September 1994. The surveyors will be trained laypersons who are donating their time and effort. The scientific objective of the survey is to look for and collect evidence on the incidence and severity of ozone injury to the leaves of plants and trees (seedling- and sapling-sized plants) in the forests of western North Carolina. The educational objective is to discuss the facts and meaning of air pollution problems in the southern Appalachian Mountains. The third and equally important objective involves policy dialogue: specifically, our objective is to motivate the surveyors to participate in local and regional forums at which mountain air pollution is on the agenda.

INTRODUCTION

Although air quality monitoring, as currently practiced in the United States, accomplishes important and widely understood regulatory and scientific objectives, it fails to provide the "deep information" that is necessary for sustainable development. Deep information refers to the data and information structure that facilitates stewardship of resources for which the protection problem includes these characteristics: the most significant sources of injury are diffuse and numerous; the time frame over which severe and possibly irreversible injury occurs is long-term; and ignorance of the responses of ecosystems and human health to the stressors is high and unlikely to be substantially improved before the onset of pathology (1). Through broadly defining stakeholders and motivating public involvement in multi-stakeholder resource management enterprises (round tables, advisory committees), deep information creates the conditions for effective resource management by promoting exploration of the values that guide decisions and learning -- learning about the problem per se as well as learning about such institutional responses to uncertainty as the precautionary principle. In contrast, the information structure related to ozone air quality monitoring, for example, involves a highly technical dialogue about equipment and data collection; the parties are primarily the U. S. Environmental Protection Agency, state regulators, technicians, and atmospheric chemists.

The mismatch between the ozone information structure and the environmental problems that the pollutant causes is especially clear in the case of the southern Appalachian Mountains. In this rural area of the southeast, ozone levels consistently reach phytotoxic levels. Ozone injures vegetation in multiple ways, reducing its growth and its ability to tolerate natural stresses. One specific example must suffice to convey the environmental concerns that arise in this situation. Thirty species of plants native to Great Smoky Mountains National Park have been shown in laboratory studies to be sensitive to ozone at ambient levels, which typically are below the national ambient air quality standard of 0.12 ppm. Sixty years ago the nation expressed its devotion to the enduring preservation of the Smoky Mountains, and the Park's biological richness is world renowned, but its forests are threatened by ozone. Yet, the ozone information structure has not informed the public of the threats that the pollutant poses to forest ecosystems in the southern Appalachian Mountains.

The failings of the ozone information structure cannot be corrected simply by grafting "bio-indicator" monitoring onto the existing program of air quality monitoring. In fact, the U. S. Forest Service already conducts surveys of ozone injury to plants in wilderness areas and national forests (2) (3). Although those surveys are valuable, they neither include the public nor invite it to join scientific and policy dialogues concerning the future of the forests. At a minimum, sustainable development entails permanent protection of unique and irreplaceable special places such as Great Smoky Mountains National Park. At the process level, sustainable development requires participation of the public, as genuine partners, in efforts to understand environmental problems and the values at stake, and to develop solutions. Citizen-based environmental surveys are a means to meaningful public participation in sustainable development efforts.

SURVEY OBJECTIVES

The North Carolina Environmental Defense Fund (NCEDF) has designed a citizen-based survey of forest plant injury caused by exposure to ozone. The first, pilot survey will run for ten weeks in July, August, and September 1994. The surveyors for the pilot project will be trained laypersons who reside in mountainous western North Carolina, which is the general locale of the first survey.

Surveyors will learn that ozone can injure vegetation, and that ozone-induced injury of leaves is expressed in certain symptoms. After training, surveyors will recognize stippling (i.e., pigmentation often appearing as dark spots) and yellowing (chlorosis) as symptoms in broadleaf plants of exposure to ozone during the growing season. Stippling is the most significant symptom, being the "classic symptom" of ozone injury for broadleaf species (4). Also, the surveyors will see ozone-induced injury to vegetation in places that are important to them.

Thus the survey accomplishes the objective of teaching laypersons how to recognize ozone-injured forest vegetation. Another educational objective involves the multiple effects that exposure to ozone may cause. Ozone injury may adversely affect the whole plant by reducing photosynthesis and growth, and increasing susceptibility to natural stresses. Ozone has the potential to affect forest growth and species composition. This information and the experience gained from the project will provide surveyors with a background for appreciating hypotheses on the effects on forests of prolonged exposure to air pollution stress and the assertion, made by the National Acid Precipitation Assessment Program, that ozone is the most important pollutant for forest ecosystems (5).

The total experience offered by the survey will help to offset obstacles to public understanding of the mountain ozone problem. First, at common ambient concentrations, ozone is an odorless and colorless gaseous pollutant. Second, ozone is not emitted but formed in the atmosphere by reactions involving precursors which are emitted by widely dispersed biogenic and anthropogenic sources. The survey will assist ordinary citizens with understanding the threat of ozone to forest ecosystems by making the problem visible in a literal and tangible way.

Based on the history of other citizen-based environmental quality monitoring programs, NCEDF's survey may help build a constituency of citizens for effective air quality regulation at local and regional levels (6). Field trips and reports will provide good opportunities for media coverage of air pollution in the southern Appalachian mountains. The survey may help build a larger constituency around the nucleus formed by the surveyors.

SURVEY -- DESCRIPTION

Sources of Volunteers

To staff the pilot project, NCEDF in conjunction with western North Carolina groups of the Sierra Club will solicit volunteers from Asheville, North Carolina and environs. Sources of volunteers include, among other groups, garden clubs, Sierra Club, and NCEDF. A coordinator in Asheville working for NCEDF will assist with finding volunteers and making local arrangements for training, field trips, and publicity.

Training and Certifying Volunteer Surveyors

Surveyors must be able to collect two basic types of data: data on incidence and data on severity. Are symptoms of injury present? How bad is the injury?

Surveyors will receive training from the United States Forest Service and National Park Service. Training will follow a curriculum developed jointly by the Forest Service, National Park Service, and NCEDF. Surveyors will be taught how to identify the target bio-indicators; to select individual plants; to recognize symptoms of ozone injury and mimicking symptoms; to quantify visible ozone-induced injury; to select leaf samples; and to document observations.

The indicator species for the pilot project are the following plants and trees: black cherry, yellow poplar, sweet gum, blackberry, tall (poke) milkweed, winged sumac, crown-beard, and cutleaf coneflower. They are common in the southern Appalachians in meadows, woodland borders, and woodlands. All have been studied in fumigation experiments and hence their sensitivity to ozone and symptoms are known.

Interveinal stipple is the target symptom for the pilot project. This symptom appears as pigmented dots on the upper side of a leaf between veins. Another characteristic that in some situations aids diagnosis is "leaf shadow;" an upper, overlapping leaf reduces the sunlight reaching the lower leaf, greatly diminishing stippling, a photosensitive response. To reduce misdiagnosing leaf injury, surveyors will be trained to recognize mimicking symptoms which express normal leaf aging, site and soil conditions, and attack by pests and pathogens.

Surveyors will also be trained in two measures of severity: the overall amount of ozone injury to a plant and the degree of stippling. The first measure indicates the proportion of leaves on a plant that are injured. The second measure indicates, for an average of several most injured leaves, the proportion of leaf area that is stippled. Both measurements will be made according to the protocol of the Forest Health Monitoring Program; this protocol uses scales with six classes (7).

Training is scheduled to occur on July 30 at the Bent Creek Experimental Forest near Asheville. The training session will last about six hours. Every surveyor will be required to participate in the training session and to pass a written and laboratory examination before collecting data on ozone injury.

Data Collection Plan

NCEDF has established four criteria for data collection: 1) data that are usable by the federal land managers interested in improving mountain air quality; 2) site selection (geographical and temporal) that has the potential to illustrate the correlation of exposure with elevation and topographic position (e.g., on a ridge, in a cove); 3) repeated observation to monitor the progression of symptoms as exposure accumulates; and 4) volunteer direction of the survey.

By collecting data that will be used by federal land managers, the surveyors' efforts will complement the National Forest Health Monitoring survey and the Forest Service's Class I wilderness area surveys. The purposes of these surveys are to document the geographical distribution of ozone injury and to quantify the severity of injury. The volunteer surveyors will use the same quantitative injury standards and data collection forms as the Forest Service. Also, site selection for this project should either increase the thoroughness of the surveys or add to the territory that will be covered.

The location of sites at three elevations will suffice to convey how cumulative and peak ozone exposure tends to increase with elevation. Repeated observation at two-week intervals will ensure that surveyors see the progression of symptoms. Depending on the number of surveyors and their commitment, the actual scope of data collection may require some adjustment or truncation.

The surveyors will transfer data to the coordinator. The coordinator then will review and manage the data, store data sheets in files, and send copies of the records to participating federal land managers. The coordinator will also serve as the liaison between surveyors and data users; this function includes communication about the quality of the data.

Because the surveyors are partners in the project, their preferences should influence such important dimensions of the project as the timing of field trips and site selection. Data collection is scheduled to occur on three weekends: August 6, August 20, and September 3. Volunteers are free to choose either Saturday or Sunday in each weekend. To observe the progression of symptoms, volunteers will need to conduct surveys on all three weekends.

The project will be most effective if the volunteers survey plots in locations that are meaningful to them: for example, a ridge with a beautiful view, a favorite cove, a woodlands near their house. NCEDF and the Forest Service staff will work with surveyors to provide them with maximum freedom of choice while ensuring that their data are useful to federal land managers.

Quality Assurance and Quality Control

At this time, the objectives and procedures for quality assurance and quality control are still being developed. Nonetheless, some of the objectives are clear. Surveyors must be able to perfectly identify the bio-indicators and to measure severity within one class at least 80% of the time. Surveyors will collect leaf samples and send them to the Forest Service for verification. Incorrect species identification will result in rejection of data. Cross-crew checking may be employed.

Publicizing Survey Methodology and Results

An important goal of the project is to educate the public in western North Carolina about ground level ozone and other pollutants affecting the southern Appalachian mountains. Volunteer surveyors will quite likely help achieve this goal through ad hoc efforts--conversations with friends, informal discussions at Sierra Club meetings. To achieve the widest dissemination of results from the project, NCEDF will oversee the writing of a formal report at the conclusion of the pilot survey. This report will be distributed to the surveyors, federal land managers, government officials interested in mountain air quality, the general public, and the media. The report will assist surveyors with communicating about mountain air quality in more formal modes: discussions with government officials, letters to the editor and op-ed articles, speeches, and presentations.

CONCLUSIONS

Efforts to preserve the Great Smokies and other special places in the southern Appalachians by establishing national parks (and later wilderness areas) have failed to protect these areas from air pollution. As Tony Hiss observes in *The Experience of Place*, efforts to protect landscapes depend upon people who personally know places, through their own senses, and have reflected on their "responses, thoughts, and feelings to help us replenish the places we love" (8). I doubt that the public's involvement in any policy dialogue on the southern Appalachians can be widespread or meaningful as long the ozone problem remains invisible and intangible. A citizen-based survey of forest plant injury caused by ozone will help deepen the public's understanding of the ozone problem in the southern Appalachians. The survey will provide the conditions for citizens to rationally evaluate adding their own efforts to protecting the mountains from air pollution and will help to broaden the base of support for strengthening the policies that provide air quality protection for the southern Appalachians. A rigorous methodology will help ensure that the survey achieves all its objectives: scientific, educational, and motivational.

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Auburn Tower Ozone Study 1993

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ABSTRACT

The Raleigh-Durham area has been designated as a moderate non-attainment area for ozone because of measured excessive ozone concentrations. Redesignation proceedings are in progress for this area. The Auburn Tower, a 2000 foot broadcasting tower located about 10 miles southeast of Raleigh, provided the opportunity to perform multiple elevation atmospheric sampling. A study was designed to measure the ozone concentrations and organic compounds at three elevations. Three ozone monitors, hydrocarbon samplers and carbonyl samplers began sampling on July 23, 1993. Organic compounds were collected by contract laboratories who changed canisters and DNPH reagent cartridges and analyzed the samples. The organic sampling results are discussed in other related papers. Sampling continued until September 3, 1993 when all ozone equipment was audited and disconnected. Ozone was monitored continuously, 23 hours a day with one hour set aside for nightly automatic zero/span checks. Long sampling lines and probes were attached to the tower from each elevation down to the air conditioned room used for the ozone monitoring equipment. Heated lines and water traps were used inside this air conditioned room. The ozone concentrations measured are presented graphically. The normal diurnal pattern seen at ground level monitoring was not seen at 820 foot and 1420 foot elevation. Daily averages and maximums were larger at elevated levels. The average ozone concentration at ground level for August was .034 ppm and at 1420 foot level the average was .061 ppm. The maximums at ground level for August was .094 ppm versus the maximums for August at 1420 foot level was .105 ppm. The study will continue in 1994.

INTRODUCTION

The Air Quality Section of the North Carolina Division of Environmental Management is charged with protecting the ambient air quality within the state. Part of meeting this goal is to measure the amount of ozone in the ambient air. Ozone, a respiratory irritant, is regulated by both federal and state ambient air quality standards. The Raleigh-Durham area has been designated as a moderate non-attainment because of measured excessive ozone concentrations. The opportunity to perform upper air sampling in this area is of value in understanding the ozone problem and what ozone precursor pollutants are responsible for the ozone problem. The Auburn television tower, located about 10 miles south of Raleigh, North Carolina provided the opportunity to measure ozone, hydrocarbons and carbonyl compounds at near ground level, 820 foot level, and 1420 foot level. Access to the upper levels was by a two-man elevator in the center of the tower. The platform at each level was large enough to allow installation of sample probes and to support several small cabinets to house test equipment. The cabinets were used for hydrocarbon and carbonyl samplers. Ozone monitors and calibrators were located in a temperature controlled building at the base of the tower. Ozone sampling was done using long sample lines of FEP tubing to the ozone analyzers at ground level (approximately 320 feet above sea level). Access to the tower levels was limited to Tuesday through Fridays. The knowledge gained by others in a multi-level ozone study in California was helpful in designing this study (1)(2).

DISCUSSION

The sample probe assembly for the 820 foot and 1420 foot levels consisted of a 1/4" FEP line in a stainless steel tubular probe support. The quarter inch line connected to a 90mm Teflon® filter holder equipped with a Teflon® particulate filter which was connected to long 5/8" diameter FEP lines. Each probe support extended approximately 2 meters away from the tower platform with approximately a 60 degree downward bend to minimize precipitation entering the probe line. To further minimize the moisture/precipitation problem, the FEP lines stopped 2 feet inside the end of the stainless steel support. A contractor installed the sample lines and probes on the tower.

Ozone was measured using the ultraviolet photometric detection principle. A Dasibi 1003 AH analyzer was used for each level. These instruments are designated by EPA as "equivalent methods". A single, photometer-type calibrator was used to minimize variability in calibrations and routine checks. The output of the monitors were connected to a data logger and to a "back-up" data system.

Ozone Data Collection

The ozone monitors were installed at the tower on July 15, 1993. The instruments were allowed to warm up and stabilize with adjusted calibrations being done on July 20 and 21, 1993. All equipment and probes were connected and start-up officially began on July 23, 1993 about 16:00 hours. An audit was performed on July 30, 1993. Sampling continued until September 3, 1993 at 13:00 hours when all equipment was audited and removed. A total of 41 days of data were collected. The data completeness was excellent.

Ground level - 92.47% complete
820 foot level - 92.89% complete
1420 foot level - 96.54% complete

Water was noted in the ground level and 820 foot level sample lines early in the project as shown in Table 1. On August 12, heat tape was installed at the ground level probe assembly on the intake lines in the air conditioned building. No other water or moisture problems were noted. Some data was invalidated for these two levels for the days shown in Table 1.

Initial Calibration

The initial calibration of the ground level instrument was done on July 21, 1993 using a certified 1003 PC Dasibi calibrator.

The medium level (820') was calibrated on July 21, 1993 and the high level (1420') was calibrated on July 20, 1993 using the same calibrator. The percent differences from the data logger were noted after these calibrations (See Table 2). No data were reported until July 23, 1993, when the conditioned probe lines were installed and vacuum leak checked.

Calibrations are normally conducted quarterly (ninety-one days maximum). Since this project, only ran forty-one days, the initial calibrations were the only calibrations conducted. Two accuracy audits were performed on this project, on July 30, 1993 and on September 3, 1993. This was sufficient to support the quality of the collected data.

Routine Visits

Each ozone analyzer was subjected to an automatic zero and span check performed on a daily basis in the early morning hours (3:00 am until 6:00 am). These check results and the hourly ozone averages were reviewed daily via modem hook-up at the main office. The zero and span checks were used to determine whether a site visit was needed for further checking. To perform automatic zero and span checks, an artificial test atmosphere at zero and one span concentration was introduced into each analyzer. The span gas concentrations were about 70-90 percent of the analyzer's nominal operating range (.350 - .450 ppm).

Eighteen site visits were made during the 6 weeks of ozone monitoring. These visits were made by an Environmental Chemist in order to foresee any problems which might occur. All instrument checks, calibrations, and precision points followed EPA approved State SOP/QA procedures (3).

A special barometer was used to check the line pressure at the elevated levels. The line pressure was used to calculate each instrument's span number during the set up, calibrations, and routine checks. Upon completion of the checks, the span numbers were set to values based upon average barometric pressures at each level. These readings were used to show the line pressures were stable and that the particulate loadings on the up-the-tower particulate filters were not significant.

Precision/zero/span checks were performed biweekly by the site operator following approved procedures. Other routine operational checks were documented in the ozone monitor logbook during each site visit. The purpose of these checks were to ensure that the air monitoring station and all levels were operating properly and within prescribed parameters as indicated in the State SOP/QA Plan. Frequent manual zero/span checks were used to determine the need for analyzer adjustments. No adjustments were needed during this study. To perform the manual zero/span checks, artificial test atmospheres at zero and one span concentration (.350 - .450 ppm) were introduced into each analyzer through the 47mm particulate filter. During these checks, the analyzers operated in their normal sampling mode, except the span number for the two tower monitors, were adjusted to reflect average ground barometric pressure for the checks. These test gases were introduced to the particulate filter on the back of the analyzers via a solenoid valve and thus did not go through the particulate filter which was on the tower. Precision checks were performed in the same manner as manual span checks, except the precision check concentration was about 16-20 percent of the analyzer's full scale range (.08 - .10 ppm). The gaseous standards for the span and precision concentrations were obtained by an ozone generator with ozone concentrations determined by a currently certified ozone transfer standard.

Accuracy Audits

Accuracy is the difference between the analyzer response and the reference value obtained during the multipoint instrument audit. Accuracy audits were performed at the start-up and end of this project. The audits were performed by the Electronic and Calibration Unit (ECU) and not the normal site operator. The audit calibrator was certified against a primary standard quarterly. The monitors were operated in their normal sampling mode and the audit gas passed through the 47mm existing particulate filters on the monitor inputs.

After the analyzer and calibrator stabilized, ten analyzer readings, calibrator readings and recorder readings were taken. The average of the ten readings were compared to the average of the corresponding one minute data logger values. This procedure was used for each audit point.

The percent difference for each audit point was calculated following 40CFR58 Appendix A procedures. The accuracy audit results are shown in Table 3.

Sample Line Residence Times

The long FEP sampling lines (820 feet, 1420 feet) were .625" OD with .045" walls. The residence time for each level was calculated including the 130 feet of tubing to get the sample lines into the sampling building. The flow was 10 liters per minute using a helper pump. Both the inlet and outlet of the analyzers were connected to the lines from the tower. The monitor pumps were therefore not pulling against the vacuum created by the long sample lines. The sample residence times for the two elevated sample lines are found in Table 4. The ground level 1/4" FEP sampling line had a residence time of less than three seconds.

Ozone Line Loss

To minimize line loss, the .625 inch sample lines were conditioned with 2 ppm of ozone for seven days at a flow rate of 5 lpm prior to installation on the tower. Teflon® inlet filters were used on the lines near the intake on the tower to prevent particulate matter from entering the sampling lines. These filters were also conditioned with ozone to minimize the potential ozone scavenging.

Since the residence times are not within the time period recommended by EPA for the two elevated sampling locations, line loss ozone studies were conducted near the beginning of the project and at the end of the project. Line loss data was collected on July 30, 1993 and September 3, 1993 are shown in Table 5. The line loss tests were conducted by taking a certified calibrator to each

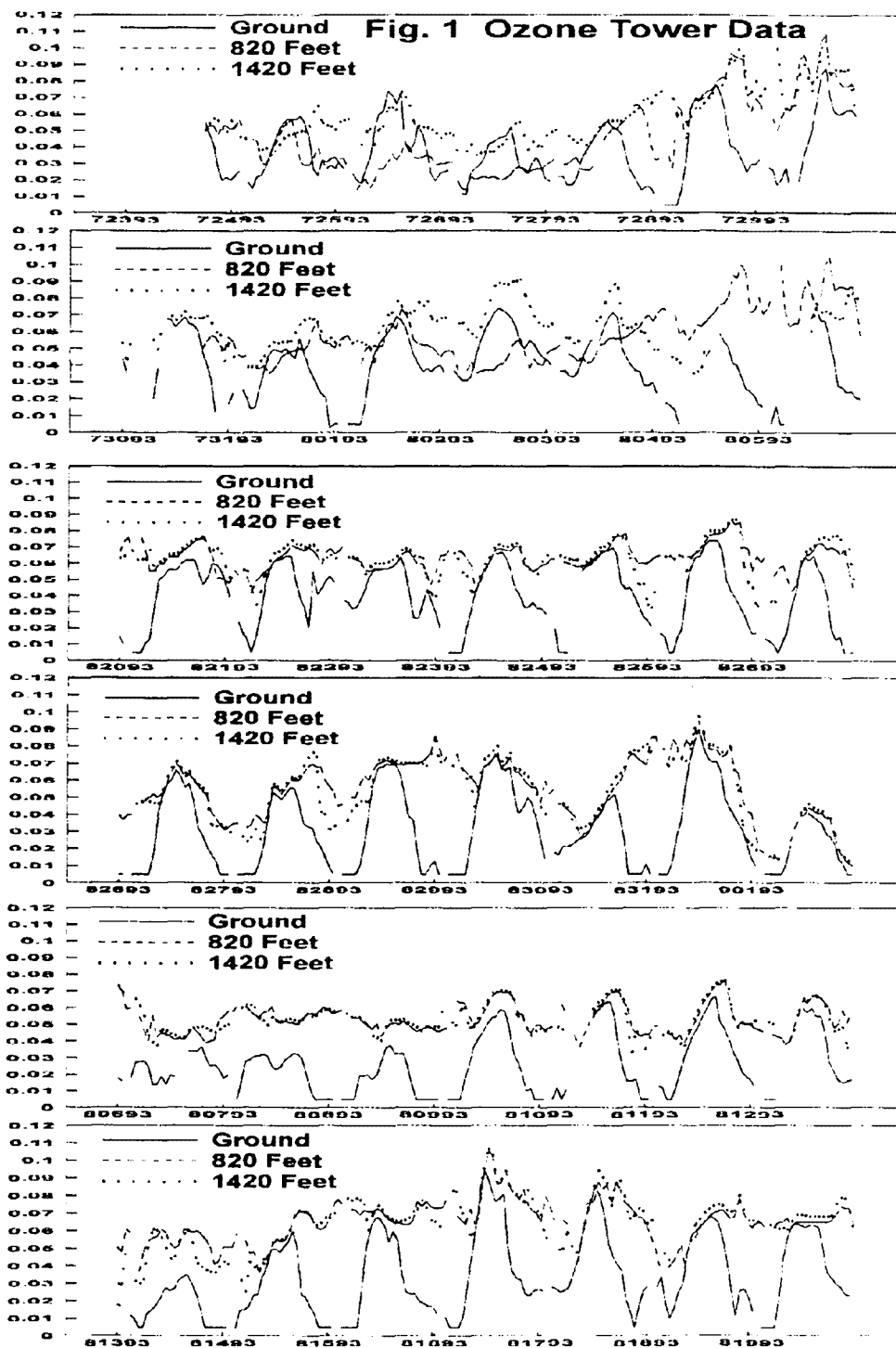


Table 1. Line Moisture

Date	Finding
August 4	Water in ground and 820 foot probe lines
August 5	Water in ground and 820 foot probe lines
August 6	Water in ground and 820 foot probe lines
August 10	Water in ground probe line
August 12	Water in ground probe line

Table 2. Calibration Difference from Datalogger

Calibration Point	Ground	Medium	High
Zero	0%	0%	0%
.450 ppm	.4%	0%	.5%
.030 ppm	0%	0%	.3%
.150 ppm	.7%	1.4%	0%
.050 ppm	0%	1.9%	0%

Table 3. Accuracy Audit Results

Location	Date	Audit Concentration Points (ppm)		
		.06-.08	.16-.18	.34-.45
		% Diff	% Diff	% Diff
Ground	7/30/93	-6.7	-2.9	-2.0
Ground	9/3/93	-2.7	-0.6	+1.0
820 feet	7/30/93	-2.7	-1.8	+1.0
820 feet	9/3/93	-1.4	+0.6	+0.5
1420 feet	7/30/93	+2.9	+1.8	+2.1
1420 feet	9/3/93	-1.4	+0.6	+2.0

Table 4. Residence Time

Tubing Size	Wall	Cross Sec.	Length	Volume	Residence
0.625	0.045	1.45	1550	68484	6.85
0.625	0.045	1.45	950	41974	4.20
0.25	0.030	0.18	15	81	0.04

Table 5. Auburn Tower Ozone Line Loss Results

Location	Date	% Difference
Ground	7/30/93	Monitor was 7.1 % lower than PC
	9/03/93	Monitor was 9.1 % lower than PC
820 feet	7/30/93	Monitor was 8.75 % lower than PC
	9/03/93	Monitor was 14.3 % lower than PC
1420 feet	7/30/93	Monitor was 17.9 % lower than PC
	9/03/93	Monitor was 5.6 % higher than PC*

* High winds and low ozone concentrations during this measurement.

level. The calibrator was warmed up for 30 minutes before any readings were taken. At each level, thirty (30) readings were taken from the calibrator while sampling ambient air. All values were corrected for zero off-set of the instruments. At the ground level, the thirty readings were recorded after waiting the calculated residence time to the nearest minute. The average results from the up-the-tower measurements from the calibrator were compared to the appropriate monitor average response to approximate the loss of ozone in the long sample lines. On both days, it was windy at the 1420 foot level. On September 3, 1993, a towel was draped over the calibrator to help retain the cell temperature. The cell temperature achieved on the tower was 33°C to 34 °C, which is lower than normal. The September 3rd measurements at 1420 feet were based on relatively unstable and low (~.02 ppm) ozone concentrations and are therefore not representative of most measurements during the study. Since September 3rd was the last day of tower availability, no further testing was performed.

CONCLUSIONS

Valid ozone information can be obtained using this technique, though quantifiable line loss occurs. The normal diurnal pattern seen at ground level monitoring was not seen at 820 foot and 1420 foot elevation. The patterns were flatter at the higher elevations. The daily averages and maximums were higher at elevated levels. The average ozone concentration at ground level for August 1993 was 0.034 ppm and at the 1420 foot level the average was 0.061 ppm. The highest daily maximum one hour reading at ground level for August 1993 was 0.094 ppm versus the maximum of 0.105 ppm at the 1420 foot level. The ozone data are presented graphically in Figure 1. These data are not corrected for line loss. This study will continue in 1994.

Note: The mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Vertical Distributions of Carbonyls in Urban North Carolina

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INTRODUCTION

Low molecular weight carbonyl compounds such as formaldehyde and acetaldehyde are intermediates in atmospheric photochemical processes as well as pollutants with well known human health risks.¹ Aldehydes arise from direct sources such as factory emissions and automobile exhaust as well as indirect sources such as the oxidation of hydrocarbons. The carbonyl compounds are precursors of the carboxylic acids and play a prominent role in free radical production.²

Numerous studies have reported diurnal variation of carbonyl compounds in both urban³ and rural areas⁴ but there have been few studies which explore the vertical profile of carbonyls. Since many carbonyl measurement technologies require either integrated sampling or equipment not amenable to aircraft platforms, the profiling of carbonyls, particularly formaldehyde, is problematical.⁵

This study takes advantage of a unique sampling platform for measuring the vertical profiles of carbonyls. The platform, known as the Auburn Tower, is a 610 meter television tower located approximately 15 km southeast of downtown Raleigh, N. C. The tower was equipped for sampling at the surface and at platforms located at 250 and 426 meter elevations.

METHODS AND PROCEDURES

Access to the tower was limited to four days per week, Tuesday through Friday, with a single integrated three hour sample collected between 0500-0800 hours. The carbonyl sampling system consisted of a pump (Parker Metal Bellows MB151) connected to the sampling cartridge which was in turn connected to a 1 meter, KI coated, copper, ozone denuder tube. An electric solenoid was located between the denuder tube and the cartridge. The pump and solenoid were connected to a timer for unattended operation and flow meters were used to calibrate the pump before and after sample collection.

Sampling was with Waters Sep Pak C-18 "Classic" cartridges coated with acidified 2,4-dinitrophenylhydrazine. The cartridges were prepared at the University of North Alabama, shipped to the field site for exposure and returned for elution and analysis by high performance liquid chromatography (HPLC). The HPLC was an LDC Milton Roy Constametric 3000 system equipped with a variable wavelength UV detector (360 nm) and a 10 μ L Rheodyne fixed loop injector. Isocratic elution with 60 : 40 acetonitrile-water was used for samples and standards. The HPLC was calibrated using 2,4-dinitrophenylhydrazone standards that were carefully weighed and serially diluted.

A method detection limit, defined as three times the standard deviation of the field blanks, gave the following results in which the μ g / cartridge value for each analyte has been converted to ppbv by assuming a 120 L air sample. Precision sampling

Detection Limits				
	Methanal	Ethanal	Acetone	Propanal
ppbv	0.166	0.159	0.208	0.115

experiments revealed no statistical difference (t-test) in the results obtained from each cartridge. Sequential gave good results on formaldehyde (>92 %) but resulted in considerable breakthrough with acetaldehyde, acetone and propanal.

The average concentration of each analyte at the three sampling elevations is shown in the following table.

Average Concentration of Analytes in Ambient Air (ppbv)

	Methanal	Ethanal	Acetone	Propanal	2-Butanone
426 Meters	2.54	0.14	0.09	0.04	0.01
250 Meters	2.63	0.13	0.05	0.04	0.01
Surface	0.80	0.08	0.05	0.03	0.01

RESULTS

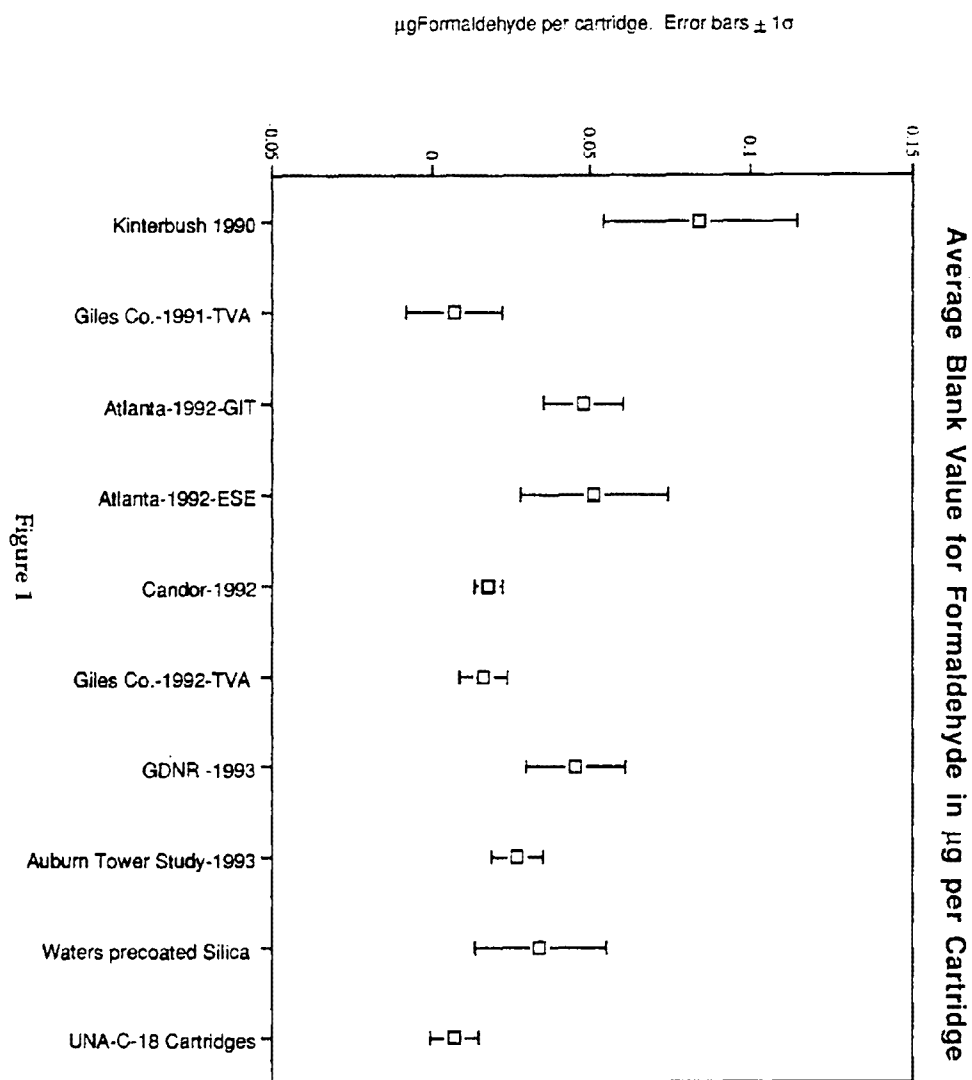
A major concern in this study was the background level of carbonyls in the blanks since the sampling cartridges were allowed to remain in the sampling apparatus, on the tower, for a minimum of 21 hours and in the case of samples taken on Tuesday, the cartridges were placed on the tower the preceding Friday. Blanks for this study were compared with the average blank levels for a number of other field studies, with carbonyls analyzed at the University of North Alabama, dating to 1990. The results for formaldehyde are shown in Figure 1, where the error bars represent one standard deviation. In the case of the commercial precoated silica cartridges and the LNA C-18 cartridges, the data shown is for laboratory blanks. The blank levels for formaldehyde in this study compare favorably to other studies where the cartridges were taken directly from and returned to a freezer before and after sampling.

The levels of formaldehyde at the surface averaged 0.80 ppbv but at higher elevations the concentration increased substantially as shown in Figure 2. The surface level results are not surprising given the fact that sampling occurred in the early morning hours after much of the ozone and formaldehyde had deposited. The ozone-formaldehyde correlations shown in Figure 3, show no correlation at the surface. At the higher elevations, probably above the inversion layer, the formaldehyde levels are higher and correlate better with ozone measurements taken at the respective levels on the tower.

An attempt was made in this study to determine the concentration of 2-butanone. Appropriate hydrazone standards were prepared but the field sample levels were so low (maximum value 0.14 ppbv) that this measurement appeared unreliable and no detection limit was established.

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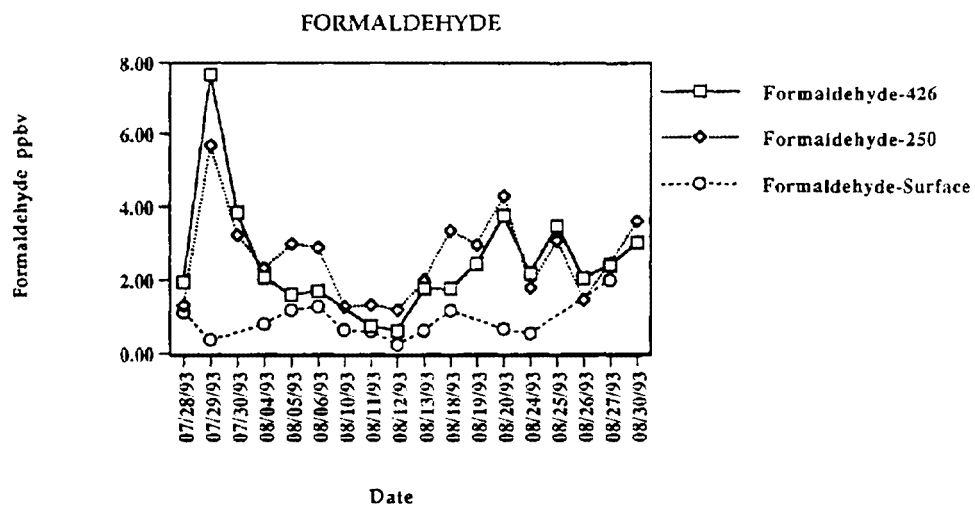


Figure 2

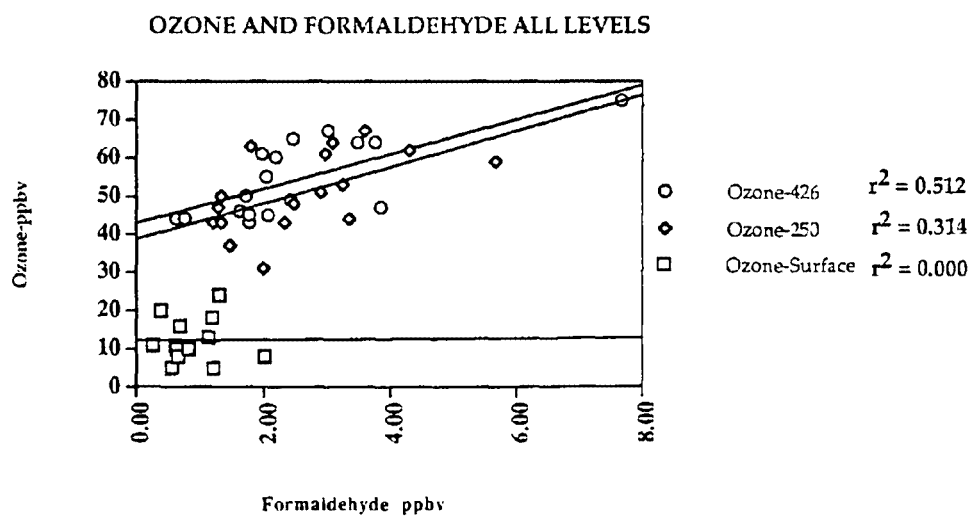


Figure 3

SESSION 10:
QUALITY ASSURANCE

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A Statistical Analysis of 40CFR60
Compliance Test Audit Data

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ABSTRACT

The U.S. Environmental Protection Agency (EPA) provides audit materials to organizations conducting compliance tests using EPA Test Methods 6 (SO₂), 7 (NO_x), 18 (organics by GC/FID), 25 (organics as ppm C), and 26 (HCl). These audit samples must be analyzed and the results reported to the regulatory agency along with the compliance test results. Each regulation specifies accuracy (% bias) limits that must be achieved on the audit samples. Failure to meet these accuracy limits may invalidate the compliance test results. A statistical analysis was done using the results from 5,926 compliance audits to determine if the limits will be achieved by most organizations. This analysis determined that they are likely to be achieved more than 90% of the time for Methods 6, 7 and 26 and also for some of the organics measured by Methods 18. However, they are not likely to be achieved even 50% of the time for Method 25 and for many Method 18 measurements.

INTRODUCTION

Our laboratory provides audit materials to organizations who are conducting compliance tests using EPA Test Methods 6 (SO₂), 7 (NO_x), 26 (HCl), 18 (organics by GC), and 25 (organics as ppm C).^{1,2} Each test method specifies accuracy (% bias) limits the organization being audited must achieve on these audit samples to demonstrate that it is proficient in using the test method. These limits are:

Method	% Bias Limits	
	Lower	Upper
6	- 5%	5%
7	-10%	10%
18	-10%	10%
25	-20%	20%
26	-10%	10%

If the audited organization fails to meet these limits, the regulatory agency may reject the compliance test results.

The EPA limits were established from small scale studies conducted while the compliance test methodology and the regulations were being developed. EPA's goal was to establish audit test limits that would be achieved at least 90 times out of each 100 tries. Was this goal achieved? We examined the 5,926 audit test results reported to date to answer this question.

DESCRIPTION of AUDIT MATERIALS

Method 6 (SO₂). The audit samples (2 per compliance test) are aqueous solutions of H₂SO₄ in glass ampoules. An aliquot of the audit sample is diluted with 3% H₂O₂ and this solution is then analyzed using the Method 6 titration procedure. When diluted the audit sample simulates a Method 6 stack sample equivalent to a stack gas concentration between 100 and 3000 mg SO₂ per dry standard cubic meter (DSCM).

Method 7 (NO_x). The audit samples (2 per compliance test) are aqueous solutions of KNO₃ in glass ampoules. An aliquot of the audit sample is diluted with the appropriate Method 7 sample collection solution and this solution is then analyzed by the same method as used for the compliance samples. When diluted, the audit sample simulates a Method 7 stack sample equivalent to a stack gas concentration between 100 and 2000 mg NO_x/DSCM.

Method 18 (Organics by GC). Each audit sample (one to two per compliance test) contains one organic compound at the ppm level in a compressed gas cylinder with N₂ as the balance gas. The auditee attaches his own regulator and transfer line to the cylinder and transfers a representative sample from the cylinder to his sampling train either directly (e.g., filling a Tedlar bag) or through a manifold. The collected sample is then analyzed exactly as the stack samples.

Method 25. (Organics as ppm C). Each audit sample (two per compliance test) contains three organic compounds at ppm levels and 5% CO₂ in a compressed gas cylinder. The balance gas is N₂. Two concentration levels are available (50 to 300 ppm C and 700-2000 ppm C). The auditee attaches his own regulator and gas transfer line to the audit cylinder and collects a representative sample in his Method 25 sampling train. The collected sample then is analyzed exactly as the stack samples are analyzed. The auditee reports the results as ppm C.

Method 26 (HCl). The audit samples (two per compliance test) are aqueous solutions of KCl in glass ampoules. An aliquot of the audit sample is diluted with 0.1N H₂SO₄ and this solution is analyzed for chloride by ion chromatography. When diluted, an audit sample simulates a stack sample containing between 10 and 50 mg chloride/DSCM.

STATISTICAL ANALYSIS of RESULTS

The bias statistic for each audit was calculated as follows: the expected concentration value was subtracted from the reported value and this difference was then divided by the expected value. Our statistical analysis procedure employed the bi-weight function of Mosteller and Tukey³. The center measure of the distribution of % bias was estimated as a weighted average.

$$\hat{y} = \sum w_i y_i / \sum w_i$$

where y_i is the % bias for the i^{th} audit with weights,

The median absolute deviation (MAD) is defined as

$$w_i = \begin{cases} 1 - \frac{|y_i - \text{med}(y_i)|}{6(\text{MAD})} & \text{when } \frac{|y_i - \text{med}(y_i)|}{6(\text{MAD})} < 1 \\ 0 & \text{otherwise.} \end{cases}$$

$$\text{MAD} = \text{median } |y_i - \text{med}(y_i)|$$

where med(y) is the median of the % bias values.

The MAD is approximately 2/3 the true standard deviation if underlying conditions are normal. Therefore, the bi-weight allows bias values that are within approximately ± 4 standard deviations to be averaged as a measure of the center of the % bias distribution.

The spread of the % bias distribution is estimated as the asymptotic variance of the bi-weight

$$s^2 = \frac{n \sum (y_i - \text{med}(y_i)) (1 - w_i^2)^4}{\sum (1 - w_i^2) (1 - 5 w_i^2) (-1 + \sum (1 - w_i^2) (1 - 5 w_i^2))}$$

This is indicative of the variability of % bias across a wide range of clients and audit levels. The uncertainty as to the true location of the center of the distribution is expressed in the 95% confidence limit

$$\hat{y} \pm t s/\sqrt{n}$$

where t is Student's t for 0.7(n-1) degrees of freedom.

The bi-weight is usually more robust and efficient (lower variance) than the arithmetic mean especially when things are less than perfect in the tails of the distribution. This means that the bi weight has a greater chance of being close to the true center than the mean. The same can be said for the median since the mean is more efficient than the median. To use the arithmetic average for Method 25 with the same efficiency as the bi-weight would require arbitrarily throwing out all % bias estimates greater than 125% in absolute value: four values at the high level and 26 values at the low level. There is no rational justification for discarding this many values as outliers. We used this approach for three reasons. First, there is no documentable reason in the data set for discarding even one result. Second, the results from this statistical technique are not affected by the actual distribution of the data. Third, it gives results similar to those from the more traditional outlier tests.

RESULTS and DISCUSSION

The question under review is "Are the % bias limits specified in each test method likely to be achieved at least 90% of the time?" The results presented in Tables 1,2 and 3 provide an estimate of the likelihood of this happening for each test method. In these tables

N is the number of audit results used to calculate the probability limits and U and L are the upper and lower probability limits, respectively. For example, Table 1 shows that 90 out of 100 Method 6 audit results will lie between +4 and -4% and that 90 out of 100 Method 7 results will lie between +10 and -10%.

Table 1 (Probability Limits for Method 6,7 and 26 Audits): Table 1 shows that more than 90% of the % biases for Methods 6,7 and 26 met the applicable acceptance limits and that the data are essentially symmetrically distributed about zero.

Table 2 (Probability Limits for Method 18 Audits): Thirty-one compounds have been used in Method 18 audits, but only 14 have been used in at least eight audits -- the minimum number of audit results required for calculating the probability limits. Table 2 shows that chloroform is the only one of these 14 that will yield % biases meeting the present Method 18 limits of $\pm 10\%$ at least 90% of the time. It also shows that with four exceptions (ethylene, methyl ethyl ketone, perchloroethylene and vinyl chloride) the % biases for these compounds will be approximately symmetrically distributed about zero with mean % biases less than 5%.

Table 3 (Probability Limits for Method 25 Audits): Table 3 shows that less than 75% of the % biases for the high concentration samples and less than 50% of the % biases for the low concentration samples will meet the Method 25 limits of $\pm 20\%$. It also shows that the mean % bias for the low concentration audit samples will be +16% and that for the high concentration samples will be -6%. Because the number of audit results used is large and since the influence of outliers has been neutralized, one has to assume that these biases are real.

CONCLUSIONS

Since the limits for Methods 6, 7 and 26 are being achieved routinely, they should remain unchanged. In contrast, the bases for the original limits for the majority of the Method 18 compounds and for Method 25 need to be examined to decide if new limits are required. For example, if the limits were simply widened to $\pm 30\%$, this audit limit would be achieved 90% of the time for 8 of the 14 compounds shown in Table II. Alternately, compound-specific limits could be established for Method 18 rather than using identical limits for all of the compounds. In the case of Method 25 any new limits should compensate for the biases present in Method 25. For example, the limits could be widened to $\pm 50\%$ and adjusted for the biases associated with each concentration level (i.e. high concentration -6%; low concentration +16%). Then, more than 95% of the high concentration audit sample and 75% of the low concentration audit sample results would meet these new limits.

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3. Mostellar, F., Tukey, J.E.; *Data Analysis and Regression*, Addison Wesley Publishing Co., Reading MA, 1977, pp 205 - 208.

DISCLAIMER

The information in this document has been funded wholly by the United States Environmental Protection Agency. It has been subjected to Agency review and approved for publication. Mention of trade names and commercial products does not constitute endorsement or recommendation for use.

Table 1. Probability limits for method 6, 7 and 26 audits.

Test	Compound	N	Mean % Bias	Probability Limits in % Bias							
				95/100		90/100		75/100		50/100	
Method				L	U	L	U	L	U	L	U
6	SO ₂	3598	-0.2%	-5	5	-4	4	-3	3	-2	1
7	NO _x	1665	0.6%	-11	13	-10	10	-6	8	-4	5
26	HCl	93	-0.9%	-12	9	-9	7	6	5	4	2

Table 3. Probability limits for method 25 audits.

Level	N	Mean % Bias	Probability Limits in % Bias							
			95/100		90/100		75/100		50/100	
			L	U	L	U	L	U	L	U
High ppm C	117	-6%	-43	32	-37	26	-28	16	-18	7
Low ppm C	127	16%	-66	98	-53	85	-32	64	-12	44

Table 2. Probability limits for method 18 audits.

<u>Compounds</u>	<u>N</u>	Mean <u>% Bias</u>	<u>Probability Limits in % Bias</u>							
			<u>95/100</u>		<u>90/100</u>		<u>75/100</u>		<u>50/100</u>	
			<u>L</u>	<u>U</u>	<u>L</u>	<u>U</u>	<u>L</u>	<u>U</u>	<u>L</u>	<u>U</u>
Benzene	104	0%	16	16	13	13	9	9	5	5
Carbon tetrachloride	8	0%	-98	98	-76	76	-49	49	-27	28
Chloroform	11	3%	-6	12	-4	10	-2	8	0	6
Ethylene	10	-8%	-54	38	-45	29	-32	16	-22	6
Hexane	15	-1%	-20	18	-17	15	-12	9	-8	5
Methyl ethyl ketone	11	-11%	-107	84	-88	65	-62	40	-40	18
Methylene chloride	14	1%	-90	92	-73	75	-49	50	-28	29
Perchloroethylene	16	10%	-59	79	-46	67	-28	48	-17	32
Propane	48	-2%	-19	15	-16	12	-11	8	-7	4
Propylene	12	3%	-27	20	-22	15	-16	9	-11	4
Toluene	34	-2%	-37	33	-31	27	-22	18	-14	9
Trichloroethylene	13	-2%	16	11	13	8	-10	5	-7	2
Vinyl chloride	19	-6%	-33	22	-28	17	-21	10	-15	3
-1, 3- Butadiene	11	-3%	-23	16	-19	12	-14	7	-9	2

ANALYSIS OF PROTOCOL GASES An On-Going Quality Assurance Audit

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ABSTRACT

In 1992, EPA's Atmospheric Research and Exposure Assessment Laboratory initiated a nationwide QA program on the suppliers of EPA Protocol Gases. The program has three goals: to increase the acceptance and use of Protocol Gases by the air monitoring community, to provide a QA check for the suppliers of these gases, and to help the users of these gases identify suppliers who can consistently provide accurately certified Protocol Gases. In this QA program which operates continuously, Protocol Gases are procured by EPA and the supplier's certification of the pollutant concentration(s) is verified by EPA. The results are published on the EPA Technology Transfer Network's electronic bulletin board. If a supplier's concentration differs from EPA's by more than 2%, the supplier is notified in writing immediately. The results obtained for SO₂, CO and NO Protocol Gases in single and multiblend mixtures are presented.

INTRODUCTION

The Atmospheric Research and Exposure Assessment Laboratory (AREAL) of the U.S. Environmental Protection Agency (EPA) has begun a nationwide audit of the vendors of Protocol standards. The intent of this program is as follows:

1. Increase the acceptance and use of Protocol Gases as secondary standards by the air monitoring community.
2. Provide a quality assurance check for the vendors of these gases.
3. Assist users of Protocol Gases to identify vendors who can consistently provide accurately certified Protocol Gases.

PROCEDURE

Either directly or through third parties, EPA procures Protocol Gases from commercial sources, checks the accuracy of the vendors' certification of concentration, and examines the accompanying documentation for completeness and accuracy.

The Protocol Gas procedure specifies two types of documentation that must accompany the gas cylinder: a Certificate of Analysis, which may be mailed separately or attached to the cylinder; and a cylinder tag which must be attached to the valve under the valve cap. Documentation is incomplete until the vendor provides every item shown in Tables 1 and 2 for the certificate and the tag, respectively.

Protocol Gases have a maximum allowable deviation of 2% from the certified value. Accuracy of the certification is checked using Standard Reference Materials (SRMs). If the difference between the EPA-determined and the vendor-determined concentration is more than 2%, the Protocol Gas' concentration likely is incorrect. This 2% limit accommodates the 1% uncertainty in the concentrations of NIST gaseous SRMs. **In other words if the difference between EPA's value and a manufacturer's value differs by 2% or less than statistically there is no difference between the two values because of the uncertainties in the total measurement system.**

When the difference between the EPA and the Manufacturer's values exceeds 2.0%, we send the Protocol Gases to a referee laboratory to confirm that this difference is real. If the referee analysis confirms the EPA results, EPA notifies the vendor of the Protocol Gas to resolve and correct the problem.

Results of EPA certification checks are placed on two bulletin boards. EMTIC (Emission Measurement Technology Information Center) and AMTIC (Ambient Monitoring Technology Information Center), on the Technology Transfer Network of the EPA's Office of Air Quality Planning and Standards.

Bulletin board entries are organized in tables by gas mixture and by vendor. Numerical data are supplemented by narrative footnotes explaining the results of any corrective action taken by the vendor. Thus the entries provide a continuous record of all audit activities. The bulletin boards are updated whenever EPA conducts a new audit or receives corrective action reports from a vendor. It allows users of Protocol Gases to easily review the comparative performances of the vendors.

Users who believe that their Protocol Gas has been certified incorrectly are encouraged to contact Ms. Avis Hines of ARFAL (919-541-4001) to request an EPA certification check. If EPA accepts the gas cylinder for testing, the results of these tests will also be posted on the bulletin boards. If you wish to access the EBB or need information on how to access the EBB contact Ms. Avis Hines.

RESULTS

Completeness of Documentation

The completeness of the documentation has increased dramatically since this program was initiated in July 1992, i.e.,

	<u>Complete Documentation</u>
July - December 1992	5 of 15 Gases (33%)
January - June 1993	5 of 11 Gases (62%)
July - December 1993	18 of 18 Gases (100%)

Accuracy Checks

Tables 3 and 4 summarize the results from the accuracy checks for single component and multi-component Protocol Gases, respectively. The results are presented by supplier and by pollutant. The results from the accuracy checks for single component Protocol Gases have been similar to the completeness of documentation checks, in that the percentage of the Protocol Gases within the 2% limits has increased for each six month period since July 1992.

The first group of multi component Protocol Gases was checked in November and December 1993 and the results for these mixtures were disappointing. In five of the 18 mixtures the EPA-determined SO₂ concentration differed by more than 2% from the supplier-determined concentration. It has now been determined that in at least four of the five cases incorrectly certified SRMs caused the difference. Once the suppliers had obtained the correct certified value for their SRMs, their revised SO₂ concentrations differed by less than 1% from the EPA-determined value.

CONCLUSION

The EPA QA program on the suppliers of Protocol Gases has brought dramatic improvements in the quality of Protocol Gases and in the completeness of the documentation. This program has been actively supported by both the users and the suppliers of Protocol Gases. Suppliers of Protocol Gases have found the program to be an effective external QA program for them and the users of Protocol Gases have found a data base containing information that is useful to them when deciding from whom to purchase a Protocol Gas. Based on these encouraging results and the support of the program from the supplier and user community, AREAL plans to continue this QA program including expanding it to other pollutant gases.

DISCLAIMER

The information in this document has been funded wholly by the United States Environmental Protection Agency. It has been subjected to Agency review and approved for publication.

REFERENCE

1. *U.S. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards (Revised September 1993)*, EPA 600/R03/224. U.S. Environmental Protection Agency; Research Triangle Park, NC 1993.

Table 1. Required Documentation for a Certificate of Analysis

Cylinder ID number	Reference standard data
Certified concentration of analyte	Protocol statement
Balance gas	Gas analyzer ID
Cylinder pressure	All analyzer readings
Certificate date	Calculations to three significant figures
Expiration date	Name and signature of analyst
Certification period (months)	

Table 2. Required Documentation for a Cylinder Tag

Cylinder ID number
Certified concentration of analyte
Reference standard data
Balance gas
Cylinder pressure
Certification date
Expiration date
Protocol statement
Laboratory ID
Name and signature of analyst

Table 3. Summary for Single Component Protocol Gases

Number of Gases Within 2%/Number Checked			
Supplier	NO	SO ₂	CO
AGA		1/1	
Air Products and Chemicals	1/1	1/0	1/1
Airco Industrial Gases	1/1	2/2	1/1
Alphagaz Spec. Gas. Div.	1/1	1/1	1/1
Matheson Gas Products	1/1	0/2	1/2
MG Industries Gas Products	1/1	0/1	1/1
National Specialty Gases	1/1	0/1	1/1
Scott Marrin Gases	1/1	2/2	1/1
Scott Specialty Gases	1/1	1/1	1/1

Table 4. Summary for Multi-blend Protocol Gases

Number of Gases Within 2%/Number Checked		
Supplier	SO ₂	NO
AGA	2/2	2/2
Air Products and Chemicals		
Airco Industrial Gases	1/2	2/2
Alphagaz Spec. Gas. Div.	1/2	1/2
Matheson Gas Products	2/2	2/2
MG Industries Gas Products	2/2	2/2
National Specialty Gases	1/2	2/2
Scott Marrin Gases	2/2	2/2
Scott Specialty Gases	1/2	2/2

Preparation and Evaluation of Representative Compounds in Small High Pressure Cylinders for Use as Audit Materials

by

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ABSTRACT

EPA currently regulates or plans to regulate over 130 organic and 20 inorganic gases as air pollutants. These compounds can be found in air matrices from 1 ppb to 1000 ppm and in different relative ratios. This presentation describes the evaluation of a gas transfer system that will allow an organization to prepare a wide variety of QA and QC audit gas mixtures using a small number of master gas mixtures. It has been used in our laboratory to prepare over 60 mixtures for use as performance evaluation and audit materials in support of the EPA regulations. The gas transfer system uses small, reusable, high pressure cylinders to prepare custom gas mixtures from large master cylinders. Experiments conducted to determine the maximum dilution ratio, and transfer efficiencies of organic compounds are described. Stability data are presented for compounds that have been contained in the small cylinders for more than one year. Additional experiments planned for the future are also described.

INTRODUCTION

Small quantities of certified gas mixtures are often needed by both the regulators and the regulated to verify the performance of sampling systems, analytical laboratories and pollution control equipment. To provide gaseous materials that can be used as audit samples, a gas transfer system (GTS) was assembled and tested.¹ The system uses static dilution of concentrated master gas mixtures with a pure diluent or other pollutant mixture (Figure 1) to prepare QA and QC samples in small, reusable, high pressure cylinders. In the earlier study¹, which was done to check the integrity of the GTS, no leaks were found and the GTS was found to be easy to clear using repetitive evacuation and pressurization with high purity nitrogen. Ancillary equipment used for performance evaluation studies was also tested for acceptable performance. No transfer bias due to the gas cylinder regulators was noticed, and both the audit cylinders and the regulators were easily cleaned after use¹.

Since this earlier study was reported, we have prepared over 60 mixtures of volatile organic compounds. The compounds chosen (Tables 1 and 2) represent a variety of hydrocarbons, halocarbons and polar analytes spanning a wide range of molecular weights and boiling points. They are representative of the compounds found on target lists associated with the RCRA, CERCLA (Superfund) and the Clean Air Act.

The GTS prepares certified mixtures in a variety of ways: (1) dilution of a concentrated mixture with pollutant free nitrogen; (2) mixing the contents of two or more master cylinders; and (3) injecting neat compounds into an evacuated cylinder and diluting to the desired levels. The study reported here describes our experiments to determine the accuracy of the mixing/dilution process, the stability of the compounds as a function of cylinder pressure, and transfer efficiency of the GTS as a function of compound and temperature.

GAS TRANSFER (GTS) SYSTEM

Currently, the GTS consists of a stainless steel manifold (Figure 1) containing eight diaphragm packless valves, one bellows valve, two pressure gauges (0-200 psi and 0-2000 psi) and fittings to attach five compressed gas cylinders.

All internal parts of the manifold have been treated with Scott Specialty Gases' Acuclean and Aculife processes. The manifold is mounted on a 3.2 mm thick aluminum plate which is mounted on a wall at MarTech Environmental Technology's Commercial Park West facility in Research Triangle Park, NC. To maintain a constant temperature, the GTS manifold is wrapped with heat tape covered with insulation. All tubing-to-tubing and tubing-to-valve connections are either orbitally welded or are of the VCR type.

The manifold can accommodate two master cylinders, a diluent cylinder and two receiver (audit) cylinders such as the 11 cm o.d. x 25.4 cm long aluminum cylinders we are now evaluating for use with this gas transfer system. These audit cylinders have been treated with Scott's Acuclean and Aculife processes and pressure tested to 3000 psi. Their nominal volume at one atmosphere is 1.5 L, which corresponds to 220 L at 2200 psi. They and the other compressed gas cylinders attach to the manifold using a CGA to VCR adapter.

EXPERIMENTS TO CHARACTERIZE THE GTS

Analytical System

The GTS can be used for inorganic and organic gas mixtures. Presently, we are studying only organic mixtures. Two or three samples are taken from each gas mixture (replicates) and analyzed as discrete samples using either a cryogenic concentrating system with a HP 5890 Series II/HP 5970 GC/MSD system or a GC/FID system. For the gas transfer efficiency studies, the GC/MSD system uses the master gas mixture as the reference standard. For most of the compounds in the gas mixtures being evaluated, the precision of the GC/MSD system is between 5 and 10% of the concentration and for the GC/FID system its less than 5%.

Maximum Dilution Ratio

To maximize the dilution ratio, and increase the accuracy of the system, the original analog psig gauges were replaced with digital electronic gauges. The original psig gauges were considered to be accurate to 1 % of full scale. Under the original circumstances the theoretical maximum dilution was approximately 100 fold. This was based on a diluent cylinder having a pressure of 2000 psig and the ability to read the analog gauge on the GTS accurately at 20 psig.

Digital replacements obtained from Omega Engineering Inc. are reported by the company to be accurate to 0.2 per cent of full scale, and capable of reading absolute pressure. When these gauges are used, the error associated with 5 psia is four per cent.

For most organic compounds this would not contribute greatly to the total analytical error.

Master cylinders containing series A and series B compounds (Table 2) at 20 ppm were diluted on separate occasions using VOC-free nitrogen. These dilutions required the operator to slowly fill the evacuated audit cylinders to 1.5 psia of pressure using the pollutant mix. The diluent nitrogen was then added to a final pressure of 1500 psia.

Recoveries were greater than 90%, as compared to the undiluted cylinders, for all compounds except acetonitrile and 1,4-dioxane. Only about 70 per cent of the acetonitrile and even less of the 1,4-dioxane was recovered. The result of this experiment demonstrated that even 1000 fold dilutions may be made accurately and with good recovery for most compounds studied.

Mixing at Low Concentrations

Another important potential advantage of the GTS is the ability to mix the contents of a number of master cylinders, even at low concentrations. The master cylinders containing series A and series B compounds (Table 2) at 20 ppb were used to evaluate this technique. Two hundred and fifty psia of each master cylinder were added to duplicate audit cylinders and the mixtures were analyzed using the system described previously.

Mean hydrocarbon recoveries were all greater than 90 per cent except for styrene which was 81 per cent. Halocarbon recoveries were greater than 90 per cent except for 1,2-dibromoethane which was 89 per cent. The polar analytes were recovered at less than 50 per cent. While overall the results were favorable, some of the analytes demonstrated marginal recoveries under these conditions when compared to the experiment which evaluated the maximum dilution ratio. (In the latter experiment, which used more concentrated materials, styrene and 1,2-dibromoethane demonstrated recoveries close to 100 per cent.) When the former experiment was repeated after modifying the heated zones to include the transfer lines from the master cylinder to the GTS and also the small cylinder valve and associated connection, recoveries of styrene and 1,2-dibromoethane improved to greater than 95 per cent.

Stability Tests

In March of 1993 a gas mixture was prepared by mixing three volumes of a gas mixture containing 20 aromatic and halogenated compounds at 5-10 ppb with one volume of another mixture containing 9 unique alkane compounds at 20 ppb. The resulting 800 psi mixture was re-analyzed after 379 days. Twenty one of the twenty nine compounds were within 10 per cent of their original value and Twenty four were within 20 per cent of their original value. Bromomethane, 1,2-dibromoethane and styrene were not detected. Ortho xylene and chlorobenzene were detected at 69 % and 72 % of their original value. In a separate experiment we investigated the effect of decreased cylinder pressure on stability. Two cylinders were originally pressurized to 1300 psi with 33 C2-C10 hydrocarbons at 45 ppbv. After forty one days the pressure was reduced in one of the cylinders to 650 psi. After more than 300 days under these conditions, 31 of the compounds demonstrated less than a 10 % difference in concentration between the two cylinders. For the other two compounds: acetylene differed by 20 % between the cylinders and 1,2,4-trimethylbenzene differed by 11 %.

Transfer Efficiency Tests

Quantitative transfer out of the cylinder and into the measurement system was also evaluated using field data from two intercomparison studies supporting EPA's Photochemical Assessment Monitoring Network (PAMS). In these intercomparison studies

the participants received audit cylinders containing PAMS target analytes which they analyzed with their PAMS measurement analytical system. Their analytical results indicate that the analytical conditions are important for full recovery of heavier compounds. For example, the mean per cent recovery of the higher molecular weight compounds was 5 to 10 % greater for those participants who transferred the gas from the audit cylinder into a humidified canister before introducing the sample into their analytical system than for those that who went directly from the cylinder to the analytical system. Because the reliable data sets are small, no statistical tests were applied to these data.

Our laboratory experiments have demonstrated that the difference between recoveries is not dependent on transfer out of the cylinder. The analyte is most likely lost in cold spots, dead volumes or other forms of active sites in the transfer lines to the measurement system. In this experiment, humidified canisters were prepared from the small audit cylinders by transferring the contents of the audit cylinder to the canister with a short length of 1/8 inch i.d. stainless steel tubing. The transfer took place over fifteen minutes and no flow control was used. The final pressure in the canister was about 30 psia and the relative humidity was approximately 50 per cent.

For ethyl benzene and other heavier compounds, recoveries were up to 40 per cent greater from the canisters than from the audit cylinders, and within 10 per cent of the theoretical value. This effect was only apparent on some analytical systems. Since the canisters were prepared directly from the small cylinders, near complete transfer must be taking place. A humid sample may overcome active sites in the measurement system to some extent.

CONCLUSIONS

After one year of use the GTS has proven to be a reliable method of preparing gaseous pollutant audit materials. Gases from stock cylinders containing binary or multicomponent mixtures may be diluted and mixed over a wide range of concentrations. Over 60 audit mixtures have been prepared and used in the field. Contamination of the GTS, cylinders and regulators has not been a problem and routine audits, using this system, have been scheduled for one program. Many hydrocarbon and halocarbon compounds have proven to be stable at the ppb level even after one year in the cylinder.

Due to improvements made to the original system, recovery for most compounds has increased to 95 per cent. Dilutions as high as 1000 fold are accurate to within 10 per cent and the mean per cent recovery for most compounds other than those that are polar has been greater than 90 per cent.

Using the GTS, organizations can prepare at relatively low cost a myriad of gas mixtures using a small number of master gas mixtures (\$200-\$10,000 each), a diluent gas (\$50-\$250 each) and reusable compressed gas cylinders (\$300-\$450 each). The GTS should be particularly useful when assessing emission control device performance. It should also be very useful for gas mixtures whose long-term stability is known only for concentrations 10 to 100 times higher than those needed for the measurement systems.

FUTURE WORK

Additional plans and experiments include the addition of a six port manifold to the system to increase the number of replicates produced. Direct liquid injections into the

cylinder, followed by the addition of diluent gas will be investigated and further characterization will help answer questions concerning the stability and recovery of problem compounds. More attention will be focused on methods of delivering the sample to the measurement system and vendor cylinder treatment processes will be evaluated.

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DISCLAIMER

The information in this document has been funded wholly by the United States Environmental Protection Agency. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Table 1. Representative compounds used to evaluate the GTS.

Hydrocarbons	Halocarbons	Polars
Ethane	Vinyl Chloride	Acetonitrile
Ethylene	Freon 11	Vinyl Acetate
Propylene	Methylene Chloride	1,4-Dioxane
Propane	1,2-Dichloropropane	
Hexane	Trichloroethylene	
1,3-Butadiene	Chlorobenzene	
Toluene	1,1-Dichloroethene	
Cyclohexane	Chloroform	
p-Xylene	1,2-Dichloroethane	
Styrene	Trichloroethylene	
Benzene	1,2-Dibromoethane	
	Tetrachloroethylene	
	Carbon Tetrachloride	

Table 2. Description of series A and B compounds.

Series A Compounds	Series B Compounds
Acetonitrile	Benzene
Benzene	1,3-Butadiene
Carbon Tetrachloride	Chloroform
Chlorobenzene	1,2-Dibromoethane
1,2-Dichloropropane	1,2-Dichloroethane
Ethylene	1,1-Dichloroethene
Halocarbon 11	1,4-Dioxane
n-Hexane	Ethane
Methylene Chloride	N-Hexane
Propane	Propylene
Styrene	Tetrachloroethylene
Toluene	Trichloroethylene
Trichloroethylene	Vinyl Acetate
Vinyl Chloride	p-Xylene
p-Xylene	Cyclohexane

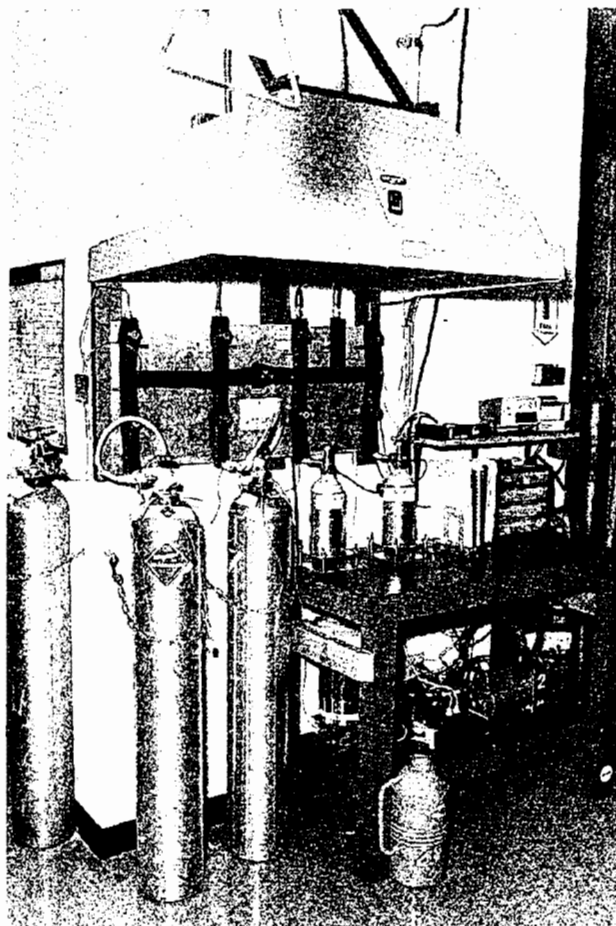


FIGURE 1. Gas transfer system.

**DATA HANDLING ISSUES AND TECHNIQUES ASSOCIATED WITH DATA
COLLECTED FROM AUTOMATED GC SYSTEMS USED FOR OZONE
PRECURSOR ANALYSIS**

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ABSTRACT

The 55 compounds designated by the U. S. Environmental Protection Agency as ozone precursors were monitored in the ambient air in Houston, Texas, from June 18 to November 30, 1993. Two Perkin-Elmer automated continuous gas chromatographic (GC) systems were used to monitor these compounds on an hourly basis throughout the day. A total of 48 data files were collected at each site daily. In addition, method, sequence, and the electronic logbook files were transferred from each site daily in order to process the data. Numerous data handling techniques were developed to process, verify, validate and transfer to the database the two to three Megabytes of data generated. This paper will describe the techniques and tools developed to process such a volume of data in a cost and time effective manner.

INTRODUCTION

Two sites in Houston, Texas were selected for deployment of Perkin-Elmer continuous GC systems for the hourly measurement of the 55 ozone precursor compounds. This effort was a portion of the Texas Natural Resources Conservation Commission (TNRCC) Coastal Oxidant Assessment for Southeast Texas (COAST) study. The objective of the COAST study was to improve the technical basis for designing effective ozone control strategies for the southeast Texas coast area (including Houston). The Clinton Drive site on the east side of Houston was selected to monitor the number of petrochemical industry sources in the vicinity and to aid in the assessment of the impact of hydrocarbon emissions from these sources on ozone formation. A second site, designated the Galleria site, was on the west side of Houston and represented a major vehicular traffic impact area, but contained little contribution from industry sources. A general overview of the continuous GC systems and the COAST project is provided in a companion paper.¹

The Perkin-Elmer Continuous GC systems are designed for unattended 24 hour operation. Each system utilizes dual columns and dual Flame Ionization Detectors (FID) to separate and detect the compounds of interest. Due to the differences in compounds detected, each detector requires separate calibration, processing and sequence methods. Therefore, two sets of methods are required for each analyzer. A total of 48 data files are produced each day with 96 data files for two sites. Since both raw and processed files are produced, a grand total of 192 data files are generated daily. Combined with the method files, sequence files and electronic logbook files required to rep-

data, two to three Megabytes of data is transferred daily from the field to Austin. Field operations and the data transfer procedures have been described in other papers.^{2,3}

Manual review of each of the chromatograms and data files produced each day is virtually impossible given the time and financial restraints which would result. Therefore, a number of tools were developed to quickly and efficiently review the data, compound identifications and concentrations, presence of outliers and proper instrument operation. In addition, it was desirable to quickly communicate problems with the analysis, quantitation or identification to the field operators for correction.

RESULTS AND DISCUSSION

Original instrument, calibration, method and electronic logbook files were electronically maintained on hard disk at the sites and on Bernoulli disks at the Consolidated Sciences offices. Data was automatically retrieved from the field sites each morning and transferred to a local host computer system at Consolidated Sciences as shown in the data flow schematic, Figure 1. These files were then compressed and automatically transferred via high speed modem and PC Anywhere software to Radian's Austin office. At times, problems were observed with the automated transfer of the data to Radian as evidenced by incomplete files or error messages. Many of these problems were attributed to the quality of the long distance telephone lines. When these problems were observed, Consolidated Sciences was contacted directly and the data was retransmitted manually.

Upon receipt of the compressed files at Radian, they were expanded, the processed data files from the two columns at each site were combined and the data were loaded into Radian's Oracle database. Quicklook reports were generated which consisted of:

- A report of the non-methane organic carbon (NMOC) and unidentified compounds (UNIDVOC) for each hour of the day;
- A calibration check and blank report for that day.
- The minimum, maximum, average and standard deviation for each of the target analytes for that day; and,
- Measured values for every compound at each hour of that day.

These files were used for primary review of the raw data. Data were screened for missing hourly files, missing compounds, apparent misidentifications, unusually high concentrations, or any data that generally looked suspicious. Data files which contained any of these items were marked for further investigation in the initial data verification.

Files which were determined from the Quicklook reports to have errors or suspicious data initiated a review of possible causes. Electronic log entries were reviewed to determine if instrument problems, down-time or deviations from scheduled sample collections are noted. Missing data files not addressed in the logs were retrieved from the host computer or from back-up disks. Field personnel were contacted to confirm missing data files, as necessary. Calibration logs were used to detail the installation of standards at the sites and provide theoretical concentrations of the standards' components. Method logs were screened to address modifications made to the data processing methods at the sites and to determine when response factors were updated.

Obvious data problems such as misidentifications or missed target analytes due to retention time drift were corrected by adjustments to the appropriate methods and batch reprocessing the data using the Perkin-Elmer Turbochrome software. Other problems were also noted such as UNIDVOC concentrations greater than 200 ppbC which typically indicated the presence of an electronic spike unless the associated NMOC was also very high. The chromatograms were reviewed for spikes and, if found, the data were qualified accordingly. Problems observed in the data could quickly be communicated to field personnel so corrective action could be taken at the sites, reducing the need for post-processing.

Compound concentrations were checked against the monthly cumulative averages. An hourly summary report which lists the concentrations of the ozone precursors over the 24 hour period for that day was checked for data reasonableness. Based on a solid knowledge of typical ambient air patterns and concentrations, the data validator reviewed data trends (e.g. conformity to traffic patterns), relative isomer ratios and concentrations, missing or atypically low concentrations for compounds ubiquitous in Houston ambient air (which may indicate sample shifting or misidentifications), and data outliers. Individual files containing questionable values were marked and the corresponding chromatograms were reviewed for accurate peak assignments and integrations. If the peak assignment and quantitation appeared to be correct, that observation was documented on the summary report. Otherwise, the data files were manually reprocessed or the data were later qualified. Daily averages summary reports which list the minimum, maximum, and average concentrations of each of the ozone precursors over a 24-hour period were also reviewed as an aid in identifying outliers.

As an illustration of the process, the NMOC and UNIDVOC concentrations of the data collected at the Clinton site on October 6th (Figure 2) were reviewed for anomalies. The NMOC concentrations for hours 20-23 appeared relatively high in relation to hours 01-19, especially after allowing for reduced traffic anticipated in the late evening hours. The UNIDVOC concentration appeared reasonable, suggesting that the high NMOC concentrations were not due to the presence of electronic spikes or system contaminants (unless interference with target analytes resulted). Review of the daily averages summary report (Figure 3) revealed extremely high levels of toluene during the 24-hour monitoring period. Review of the hourly summary report (a partial report is shown in Figure 4) confirmed uncharacteristically high toluene concentrations during hours 20-23 which did not follow the typical concentration pattern. The individual report and chromatographic files were examined and presence of toluene and the reported concentrations were confirmed (Figure 5). A note was made of this confirmation and forwarded to the senior chemist performing the final data validation to assist in their review/evaluation of the data.

In addition to the problem/suspected anomalous files, approximately 5% of the field processed data files/chromatograms were visually checked for accuracy of peak identifications, baseline integrations, peak resolution, baseline noise and drift, and the presence of system contaminants and spikes. Review of multiple files acquired over 2-3 week period assisted in determining the magnitude and extent of retention time shifting. Method modifications such as retention time window adjustments and baseline integrations, were tested on a subset of data files to ensure accuracy of peak assignments and quantitation. The data files were then batch-reprocessed with the optimized methods. The reprocessed data was then loaded into the database. Reprocessed files were placed in a designated directory which indicated the date of revision and revision number. All raw data and revisions of the data were archived for reference. Revised daily calibration and Quicklook summary reports were again generated for data review.

Revised calibration and sample data summary reports were reviewed in-depth for accuracy. Data validation comments made during the data review process were documented and filed with hard copies of the daily sample data summary reports. The comments were also used to prepare data qualification statements for the final report. All revised reports were validated by a senior chemist familiar with Houston ambient air patterns, compounds and compound concentrations. Any anomalies noted by this chemist were referred to the verification/reprocessing data analyst for further review of chromatograms and reports. Final revisions and/or data qualifiers were added and the revised data were loaded into the database. A final data validation for accuracy was performed and the data were reported to the COAST Program Management Contractor (Desert Research Institute) in a format specified for their database. Reports in AIRS format can also be provided.

CONCLUSIONS

Development of data handling techniques, such as the Quicklook reports, have resulted in efficient and cost effective means for handling large amounts of data generated from continuous monitoring field instrumentation. The tools developed provided techniques to quickly review, reprocess and report high quality data with a minimum of analyst interaction. In addition, it was possible to provide timely feedback to field operators so that problems with instrumentation or methods could be corrected to reduce the amount of post-collection processing needed. The use of these techniques also aided in meeting all project quality control requirements for continuing calibration check samples and audit samples. Data capture for the overall project was very good with 94% data capture from the Clinton site and 95% data capture from the Galleria site.

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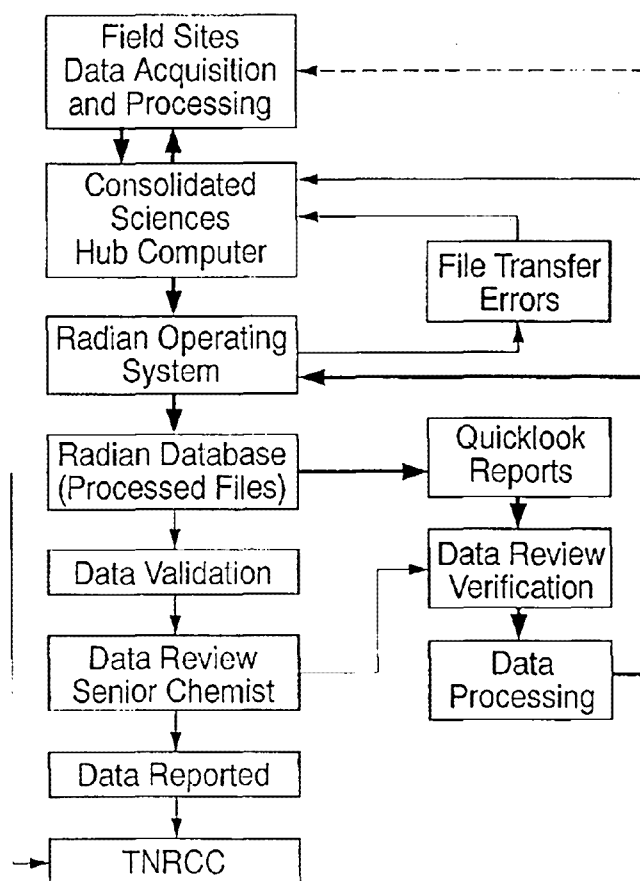


Figure 1. Data Flow Schematic

COAST CLINTON Wednesday, October 6th 1993

Hour	RADIAN SampleID	BP FileName	PL FileName	NMOC	UNIDVOC
01	A100693R-0059	ABSJ06B.RAW	APSJ06B.RAW	651.17	169.41
02	A100693R-0159	ABSJ06C.RAW	APSJ06C.RAW	575.01	148.09
03	A100693R-0259	ABSJ06D.RAW	APSJ06D.RAW	1044.11	323.55
04	A100693R-0359	ABSJ06E.RAW	APSJ06E.RAW	1193.35	444.07
05	A100693R-0459	ABSJ06F.RAW	APSJ06F.RAW	1014.88	316.72
06	A100693R-0559	ABSJ06G.RAW	APSJ06G.RAW	894.73	230.86
07	A100693R-0659	ABSJ06H.RAW	APSJ06H.RAW	778.25	170.28
08	A100693R-0759	ABSJ06I.RAW	APSJ06I.RAW	591.13	121.77
09	A100693R-0859	ABSJ06J.RAW	APSJ06J.RAW	298.41	65.09
10	A100693R-0959	ABSJ06K.RAW	APSJ06K.RAW	329.27	73.69
11	A100693R-1059	ABSJ06L.RAW	APSJ06L.RAW	429.57	81.08
12	A100693R-1159	ABSJ06M.RAW	APSJ06M.RAW	334.08	66.50
13	A100693R-1259	ABSJ06N.RAW	APSJ06N.RAW	292.98	63.47
14	A100693R-1359	ABSJ06O.RAW	APSJ06O.RAW	326.38	62.89
15	A100693R-1459	ABSJ06P.RAW	APSJ06P.RAW	312.61	86.57
16	A100693R-1559	ABSJ06Q.RAW	APSJ06Q.RAW	252.59	86.08
17	A100693R-1659	ABSJ06R.RAW	APSJ06R.RAW	325.21	91.82
18	A100693R-1759	ABSJ06S.RAW	APSJ06S.RAW	489.59	320.58
19	A100693R-1859	ABSJ06T.RAW	APSJ06T.RAW	362.15	83.14
20	A100693R-1959	ABSJ06U.RAW	APSJ06U.RAW	1601.53	239.89
21	A100693R-2059	ABSJ06V.RAW	APSJ06V.RAW	1659.18	228.14
22	A100693R-2159	ABSJ06W.RAW	APSJ06W.RAW	2034.21	265.15
23	A100693R-2259	ABSJ07A.RAW	APSJ07A.RAW	1572.42	243.78

				Min	252.59 62.89
				Max	2034.21 444.07
				Avg	757.13 173.24
				Stdev	533.53 108.93

Figure 2. NMOC and UNIDVOC Summary

COAST CLINTON Wednesday, October 6th 1993

No	Compound	Min	Max	Avg	Stdev
BPI Compounds					
65	n-Hexane	3.67	62.14	16.48	17.73
63	1-2-Hexene	0.00	14.87	1.85	3.74
71	cis-2-Hexene	0.16	3.65	1.50	0.97
73	Methylcyclopentane	1.51	19.01	6.10	5.33
75	2,4-Dimethylpentane	0.00	2.90	1.44	1.01
79	Benzene	3.72	19.09	10.58	5.28
83	Cyclohexane	0.55	8.42	3.16	2.01
358	2-Methylhexane	1.02	46.97	6.95	9.86
354	2,3-Dimethylpentane	0.36	6.25	2.07	1.78
97	3-Methylhexane	1.16	23.35	6.15	6.45
94	2,2,4-Trimethylpentane	1.86	14.05	6.57	3.82
95	n-Heptane	1.07	15.31	4.27	3.94
103	Methylcyclohexane	0.03	8.10	2.94	2.45
112	2,3,4-Trimethylpentane	0.42	34.44	3.55	6.87
111	Toluene	5.34	1075.29	159.79	324.49
355	2-Methylheptane	0.33	15.14	3.29	4.75
117	3-Methylheptane	0.38	14.79	3.02	4.20
124	n-Octane	0.44	4.53	2.02	1.30
129	Ethylbenzene	0.74	13.84	5.62	4.27
131	m,p-Xylene	2.49	34.56	15.16	10.45
134	Styrene	0.00	13.43	7.12	3.49
137	o-Xylene	0.81	53.70	11.50	15.30
139	n-Nonane	0.23	2.45	0.92	0.58
141	iso-Propylbenzene	0.20	1.45	0.72	0.33
146	n-Propylbenzene	0.26	2.04	0.94	0.59
142	α-Pinene	0.22	26.06	3.98	6.40
151	1,3,5-Trimethylbenzene	0.10	4.77	1.70	1.42
153	α-Pinene	0.52	9.21	3.90	2.93
155	1,2,4-Trimethylbenzene	0.37	28.08	5.39	7.65
Summed Compounds					
174	Total Unidentified VOC	62.89	444.07	173.24	108.93
300	Total NMOC	252.69	2034.21	757.13	533.53

Figure 3. Compound Specific Minimum, Maximum, Average and Standard Deviation Values

Compound	14	15	16	17	18	19	20	21	22
BPI Compounds									
n-Hexane	5.3	5.5	3.7	4.6	4.1	8.2	52.6	37.2	62.1
t-2-Hexene	0.5	0.3		0.5		0.7	7.5	1.8	14.9
cis-2-Hexene	1.7	1.0	0.3	1.8	0.8	1.8	3.6	1.2	3.7
Methylcyclopentane	2.4	2.3	1.8	3.4	1.7	4.2	17.9	11.1	19.0
2,4-Dimethylpentane	0.7	0.7	0.6	2.0		1.3	2.6	2.3	2.6
Benzene	5.2	5.2	4.5	4.4	3.7	5.5	18.3	13.9	19.1
Cyclohexane	4.6	0.8	0.6	0.7	0.9	1.1	2.4	2.1	2.1
2-Methylhexane	1.8	2.0	1.5	3.0	1.7	3.2	16.9	12.8	14.8
2,3-Dimethylpentane	1.1	0.7	0.7	1.4	0.6	1.3	6.3	5.2	5.4
3-Methylhexane	1.5	2.2	1.5	3.0	1.9	3.4	23.4	19.3	18.9
2,2,4-Trimethylpenta	5.2	4.6	3.8	12.3	3.3	5.0	6.3	6.8	4.2
n-Heptane	1.3	1.8	1.2	1.7	1.7	1.9	15.3	11.4	11.9
Methylcyclohexane	1.1	1.2	0.7	0.4	1.2	1.9	8.1	1.7	5.2
2,3,4-Trimethylpenta	1.8	1.5	1.6	4.3	1.0	1.6	1.9	2.1	1.1
Toluene	8.8	11.1	9.7	18.7	8.8	11.9	537.2	983.6	117.7
2-Methylheptane	0.5	0.7	0.5	1.2	1.0	1.1	13.6	14.9	15.1
3-Methylheptane	0.5	0.7	0.6	1.0	0.7	0.8	14.8	14.1	10.4
n-Octane	0.8	0.7	0.5	1.1	0.9	1.2	4.2	3.7	3.0
Ethylbenzene	1.2	2.0	2.0	5.2	1.6	2.2	10.3	12.7	12.7
m,p-Xylene	4.4	8.5	7.5	15.2	5.8	7.3	22.1	18.9	18.1
Styrene		0.0		0.4		0.2	7.1	3.7	9.8
o-Xylene	1.6	2.7	4.7	5.4	1.7	2.5	53.7	28.1	44.7
n-Nonane	0.3	0.5	0.3	0.6	0.6	0.6	1.2	1.0	1.0
iso-Propylbenzene	0.7	0.4	0.2	0.4	0.3	0.3	0.7	0.6	0.7
n-Propylbenzene	0.3	0.5	0.5	1.0	0.4	0.6	1.5	1.0	1.3
a-Pinene	0.4	0.7	0.6	1.2	0.9	0.5	1.6	1.6	1.9
1,3,5-Trimethylbenze	0.4	0.8	0.6	1.3	0.5	1.0	1.9	2.0	2.1
b-Pinene	0.8	1.7	1.5	3.7	1.5	2.4	4.9	0.9	5.1
1,2,4-Trimethylbenze	0.8	0.9	0.5	1.4	0.5	1.5	1.9	4.3	0.5
Summed Compounds									
Total Unidentified V	52.9	86.6	86.1	91.8	320.6	83.1	239.9	228.1	265.2
Total NHCC	335.4	312.6	252.7	326.2	490.0	362.2	111.8	111.8	111.8

Figure 4. Individual Compound Concentrations by Hour

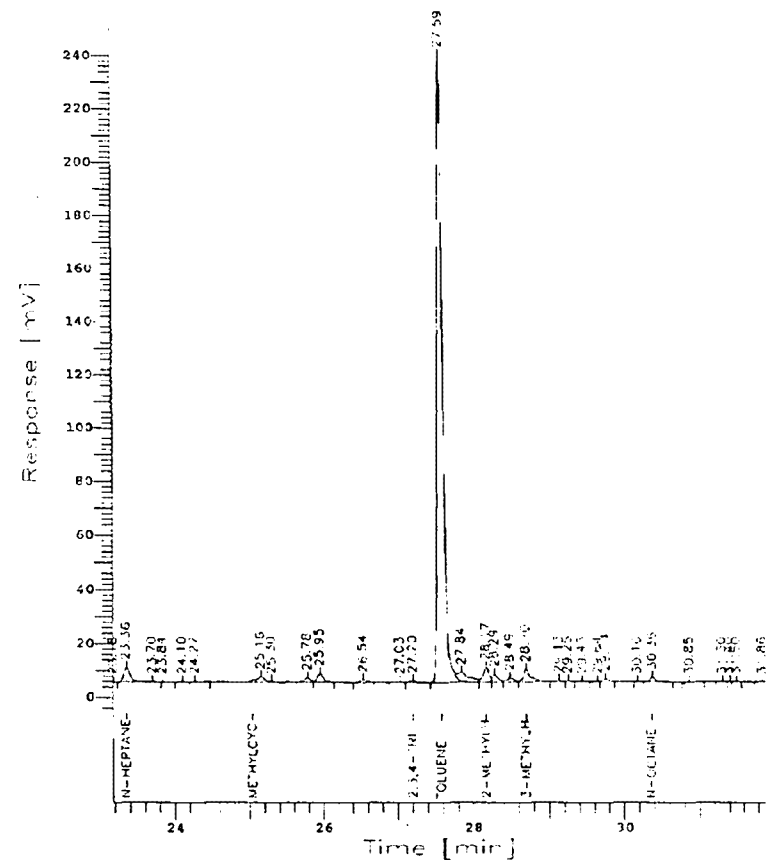


Figure 5. Chromatogram of Suspect Toluene

A Computer Controlled Dynamic Dilution System for Improved Accuracy and QA/QC in TO14 Standard Preparation

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Dynamic Dilution is the method of choice for preparing low level TO14 standards in canisters. One or more cylinders containing NIST certified standards can be blended together with a diluent gas under mass flow control to produce very consistent standards at ppb levels. Blending manifolds can be designed to maintain constant temperatures, pressures, and flow rates during the entire canister filling operation to insure that a proper mass balance is maintained.

One major source of error can exist when using Dynamic Dilution that can be significant in some cases. Manufacturers of mass flow controllers usually specify an absolute error of not more than $\pm 2\%$ of the full scale flow rate. This means that MFC's rated up to 100 sccm (standard cc per minute) could be off as much as 2 cc. At 100% of full scale, this results in an unfortunate but tolerable error of $\pm 2\%$. However, at 10% of full scale, a 2cc error corresponds to a 20% relative error which is not acceptable. Available dynamic dilution systems have been unable to perform automatic calibrations of mass flow controllers to account and correct for these inaccuracies.

A Dynamic Dilution system is presented that interfaces to a Windows™-based operating system allowing implementation of sophisticated flow calculations and feedback control. The dilution system is capable of using temperature compensated vacuum reservoir pressurization to calibrate up to 6 MFC channels unattended. Multiple calibration events can be set up to run sequentially with Means and %RSDs given for the data obtained for improved reliability. Calibrations over a several day period show the stability of mass flow controllers and can indicate the presence of unusually large drifts. These calibration factors are then used by the dilution system to make corrections in flow signals to provide very accurate ppb level standards. The preparation of multiple standards in different canisters without user intervention is also supported for making 2, 5, 10, 20, and 50 ppb level standards for TO14 instrument calibration.

Importance of Method Detection Limits in Air Pollutant Measurements

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ABSTRACT

Environmental measurements often produce many "less than" values or method detection limits (MDLs). MDL values may be used in determining compliance with regulatory limits, in the determination of emission factors (typical concentrations emitted by a given type of source), or in modeling efforts that feed into air measurement data bases. There is considerable technical discussion regarding definitions of, and methods for determining, detection limits. The definition and determination of MDLs are therefore important in planning an environmental measurement program. After an appropriate MDL has been determined, there are several ways to use the MDL value to calculate the mean concentration from a low level source. To avoid introducing high or low biases in the calculated mean, this paper proposes the use of look-up tables to fill in missing (less than MDL) values with statistically based estimates.

There are many approaches to dealing with the MDL issue, and the approach selected should depend on the end-use of the data. The MDL should be determined in the matrix that contains the analyte. Methods to calculate the MDL should be specified before the initiation of a measurement effort.

INTRODUCTION

An expanded understanding of the toxic effects of chronic low level exposure to air pollutants, regulatory mandates to improve workplace safety, and public pressure to eliminate all exposures to carcinogens have all focused attention on the need for accurate low level measurements of toxic materials in the air. These low level measurements often border on the limits of a measurement instrument's capability to detect the pollutant of interest. There have been technical discussions regarding how to define the detection limit, how to experimentally determine the detection limit, and how to use the detection limit values in subsequent calculations. This paper presents a brief overview of some current issues related to detection limits.

The manufacturer's stated MDL for a measurement instrument is frequently used as the estimated MDL, but this MDL is almost always too low. The manufacturer's MDL is often obtained experimentally under ideal conditions in a matrix such as zero air with minimal interferences. A more accurate MDL can be obtained by using a "real world" matrix that approximates the measured matrix. Accuracy of the MDL estimate is also improved by performing multiple determinations using the same laboratory personnel and instrumentation that will be used in the measurement project.

DEFINITIONS RELATING TO DETECTION LIMIT

Several definitions of the detection limit have been proposed by regulatory and professional groups. Concurrently, these groups have also proposed definitions and methods for determining the level of an analyte that can reliably be reported as an accurate number (quantitative detection limit). The following definitions appear frequently in the literature relating to detection limits:

Method detection limit (MDL) - The MDL is defined in the Code of Federal Regulations (CFR) (1) as "the minimum concentration of a substance that can be measured and reported with 99%

confidence that the analyte concentration is greater than zero." The MDL is calculated as the experimentally determined standard deviation, or s , times the Student's t -value for a 99% confidence level. This Student's t -value is approximately 3 for an experimental design with seven replicates.

Limit of detection (LOD) - The LOD is a term used by the American Chemical Society (ACS) (2) to describe the lowest concentration that can be determined to be statistically different from a blank. The LOD is generally equivalent to the MDL, although the limits of statistical probability can vary (e.g., 95% rather than 99%).

Limit of quantitation (LOQ) - The LOQ, as defined by the ACS, is the smallest true concentration where a single measurement used to estimate the unknown concentration in a sample would have an estimation error no greater than $\pm 30\%$ with 99% confidence (2). The LOQ, generally set at 10 s , is the concentration level at which the analyst has some measure of confidence that the analyte is present and that the reported value is accurate.

Minimum level (ML) - The ML is the level at which an analytical system must give a recognizable signal and an acceptable calibration point (3). An ML is generally set at 10 or 12 s and is rounded off to the nearest multiple of 2, 5, 10, 20, 50, or 100 to simplify the preparation of calibration standards.

Practical quantitation limit (PQL) - The PQL is the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operations (4). The PQL is generally greater than or equal to the LOQ and the ML. A recent paper advocated that no quantitative regulatory data be required below the PQL (5).

Detection Limits with Specified Assurance Probabilities - Several recent papers (6, 7, 8) describe statistical methods for determining detection limits using all of the calibration data and data from replicate analyses. Detection limits determined using these methods are dependent on the number of replicate analyses and the calibration design. Acceptable false negative and false positive rates are specified. These methods require the use of computer-assisted statistical packages and statistical expertise or the assistance of a statistician with knowledge of both the statistical methods and the technical limitations of the measurement technology. A description of these methods is beyond the scope of this paper.

In summary, four basic concepts relate to the determination of detection limits:

- The MDL and LOD describe the lowest level at which an analyte can reliably be differentiated from background noise. The MDL and LOD are generally equivalent, and both are generally set at 3 s .
- The ML and LOQ describe that concentration at which reliable quantitative information can be obtained. The ML and LOQ are generally set at 10 s .
- The PQL also describes a level at which reliable quantitative data can be obtained, but the PQL may be set at levels greater than the LOQ or ML.
- More rigorous statistical methods have been described that use all of the calibration and replicate analysis data to estimate a detection limit with acceptable false positive and false negative rates.

40CFR PROCEDURE FOR DETERMINING THE MDL

The method for determining the MDL as described in the 40CFR136 (1) serves as a model for the laboratory determination of detection limits. It contains many useful concepts that can be applied to the other methods described above. The CFR method contains the following steps:

1) The MDL should be determined in the same matrix as that which contains the analyte of interest *Different matrices can make significant differences in the level of an analyte that can be detected by a given method**.

2) The MDL is estimated as: (a) 2.5 to 5.0 times the noise level of a signal when a reagent blank is analyzed, (b) three times the standard deviation of replicate measurements of a reagent blank, (c) the region of a calibration curve where there is a significant change in the standard deviation of replicates, or (d) known measurement instrument limitations. *Use of available information can reduce the time and effort required to obtain reliable MDL data.*

3) The MDL is then determined experimentally by replicate analysis of seven aliquots of a sample containing a level of analyte equal to the estimated MDL. *Since the variance of replicate measurements can differ with concentration, it is important to determine variance at a concentration near the concentration of interest (i.e., near the MDL). The use of seven replicates allows for a more accurate estimate of this variance.*

4) The MDL is calculated as the standard deviation (s) of the seven replicate measurement values times the Student's t-value for a 99% confidence level at 6 degrees of freedom.

5) The CFR method also contains an optional iterative procedure to test the validity of the MDL determination. This procedure involves spiking the appropriate matrix with the analyte of interest at the initially determined MDL, repeating the seven replicate measurements, and calculating the variance (s^2) of the second set of replicates. An F-ratio (the larger variance value divided by the smaller variance value) is calculated. If the F-ratio is less than 3.05, the revised standard deviation is then calculated as the pooled standard deviation of the two experimentally determined standard deviations. If the F-ratio is greater than 3.05, the procedure is reiterated with a new sample set spiked at the most recently calculated MDL. *Some regulatory groups require this iterative procedure. It provides a greater degree of confidence that the MDL value is correct.*

6) If the most recently calculated MDL does not yield a signal of sufficient intensity for quantitation, then the revised MDL is reported as a value half way between the current and the previously calculated MDLs.

CHARACTERIZING LOW LEVEL SOURCES

One important use of detection limit data is in the characterization of low level sources. This situation is encountered frequently in measurements of environmental pollutants from ambient air samples. If, for instance, one wished to calculate a mean level of a pollutant from a given area, there might be several measurable values and several values that were below the MDL. Methods to estimate the mean value include:

- Discarding the values that are less than the MDL. *This leads to a false positive bias in the calculated mean.*
- Counting the <MDL values as zero. *This produces an artificially low mean.*
- Setting the <MDL values at the MDL. *If there are values below the MDL, this method gives a positive bias in the mean.*

* Material in italics represents the author's comments.

- Setting the <MDL values at half of the MDL. *The effect on the calculated mean is unknown, but this procedure probably gives a better estimate of the mean than the first three mentioned above.*
- Using numerical methods for the statistical calculation of the mean. *This method yields the most accurate estimate of the mean; however, it is beyond the capability of most chemical analysts, requiring considerable computing power and statistical expertise.*
- Estimating the mean using look-up tables that replace the <MDL values with estimates from the probability distribution. *These estimates are easily calculated with a portable calculator and generally give a better estimate of the mean than the first four items listed above. However, if there are more than 50% missing values, the accuracy of these estimates of mean and variance is low. Also, there are assumptions regarding the distribution of errors that may not apply to all data sets.*

With regard to the last item, several methods using look-up tables are described in the literature (9, 10, 11). Such methods generally give similar results (12, 13). To estimate an MDL using these tables, the "less than MDL values" are set at the MDL. Since these methods assume a lognormal distribution of repeated measurements from the same population (same area or same sampling site), the next step is to transform the measured values and the MDL values to their natural logarithms (which will have a normal distribution and be amenable to description by mean and standard deviation). Then the data are arranged in ascending order of magnitude. Coefficients are obtained from the table, based on the number of values in the measured set and the number of values below the MDL, and the products are calculated. The individual products are summed to give estimates of the mean and the standard deviation from the sampled population.

CONCLUSIONS

There does not appear to be one best way to address the definition of MDLs. It is important that an MDL be determined in the matrix that will contain the samples analyzed. It is also advisable that the MDL be determined using the same instrumentation and analyst as will be used to analyze the samples. Where the **accuracy of the analytical value** is of primary importance, the use of the PQL (10s) seems appropriate. Where **avoidance of risk** - such as possible chronic exposure to a highly toxic material or a material with a delayed effect - is the primary concern, the reporting of all values that can reliably be seen as non-zero values (MDL or LOD) may be appropriate. The actual MDL value may be used for conservative estimates in risk assessment models or in calculations for regulatory purposes (e.g., DREs or destruction removal efficiencies). When the goal is to **detect changes in pollutant concentration** with time, the more rigorous statistical methods, such as those proposed by Clayton et al. (6), are appropriate. Finally, to produce good quality data for long term monitoring, for regulatory applications and for database compilations, there needs to be a clear understanding of how the MDL is defined, experimentally determined, calculated, and used in calculating subsequent descriptions of the source of the sample.

ACKNOWLEDGEMENTS

Thanks to Ross Leadbetter (the University of North Carolina) for helpful discussions on the "look up tables," to Shri Kulkarni (Research Triangle Institute) for sharing technical papers and ideas, to Judy Ford (EPA/AERL) for many helpful suggestions and discussions, and to Larry Johnson (EPA/AERL) for useful discussions on practical problems relating to MDL use.

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Stability Evaluation of Multicomponent EPA Protocol Gases

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ABSTRACT

An assessment of specialty gas manufacturers' protocol gases was conducted by Research Triangle Institute (RTI) for the U.S. Environmental Protection Agency's (EPA's) Atmospheric Research and Exposure Assessment Laboratory (AREAL) in 1991 to evaluate the accuracy of the manufacturers' reported concentrations for multicomponent cylinder gases in two concentration ranges. The cylinders evaluated during this study were purchased from nine different manufacturers. Two cylinders were purchased from each manufacturer and contained both SO₂ and NO with a balance gas of nitrogen. Half of the cylinders contained SO₂ at 1500 ppm and NO at 900 ppm and the remaining cylinders contained SO₂ at 300 ppm and NO at 400 ppm.

These same cylinders remained in the custody of RTI after the audit and have been reanalyzed to evaluate the stability of multicomponent protocol gases over a two-year period. The results of this reanalysis were within $\pm 2\%$ of the 1991 analysis for all cylinders. No single manufacturer was found different from the others.

The stability of multicomponent cylinder gases is important because the EPA traceability protocol for certification of calibration standards specifies recertification intervals for gaseous standards. This paper presents the results of evaluating the extent to which the concentrations of multicomponent cylinder gases change over a two-year period. This paper also examines how much of a change would be required in order for it to be detected with statistical confidence.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has established quality assurance procedures for air pollution measurement systems that are intended to reduce the uncertainty in environmental measurements. One area of concern is the reliability of compressed gas standards used for calibration and audits of continuous emission monitoring systems. EPA's regulations require that the certified values for these standards be traceable to National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) or to NIST/EPA-approved Certified Reference Materials via a traceability protocol.¹⁻⁵ The protocol was published originally in 1978 and revised several times, with the most recent release in the fall of 1993.

An accuracy assessment of specialty gas manufacturers' protocol gases was conducted by Research Triangle Institute (RTI) for the EPA's Atmospheric Research and Exposure Assessment Laboratory (AREAL) in 1991 to evaluate the accuracy of the manufacturers' reported concentrations for multicomponent cylinder gases.⁶ Two cylinders were purchased from each of nine different manufacturers and contained both SO₂ and NO with a balance gas of nitrogen. Half of the cylinders contained SO₂ at 1500 ppm and NO at 900 ppm and the remaining cylinders contained SO₂ at 300 ppm and NO at 400 ppm. Because this was the eighth assessment of protocol gas accuracy, this work was referred to as "Cylinder Audit No. 8." The results of Cylinder Audit No. 8 were presented to the Air and Waste Management Association (AWMA) conference in May 1992.

The stability of multicomponent cylinder gases is important because the EPA traceability protocol for certification of calibration standards specifies recertification intervals for gaseous standards. The 1991

protocol procedure specified a 6-month recertification interval for multicomponent cylinder gases. Because this time interval was not practical for field operations, it was decided to evaluate the stability of multicomponent cylinder gases. This paper presents the results of evaluating the extent to which the concentrations of multicomponent cylinder gases change over a two-year period. This paper also examines how much of a change would be required in order for it to be detected with statistical confidence.

ANALYTICAL PROCEDURES

The cylinders were grouped according to their reported concentration (high and low), and the cylinder contents were analyzed by group. RTI measured the pollutant concentrations of the compressed gas standards by using instrumental monitors (IMs), ultraviolet fluorescence for SO₂, and chemiluminescence for NO. Both calibration standards (NIST SRMs) and compressed gas standards were sampled without dilution through a stainless steel, Teflon, and glass sampling manifold. Sample flow through the manifold was controlled by stainless steel solenoid valves, a needle valve, and a digital timer. Flow through the manifold remained constant during both IM calibration and cylinder audit analysis by maintaining a constant manifold pressure using the compressed gas cylinder regulator as indicated by a Heise gauge. The sample manifold allowed both the SO₂ and NO IMs to analyze cylinder gases simultaneously. Excess cylinder gas was vented from the laboratory through appropriate exhaust vents. The voltage outputs from the instruments were recorded by a data logger. Concentration calculations were made with averaged voltages from the data logger.

Multipoint calibrations were conducted with NIST SRMs. Linearity of the instruments' response was evaluated by using the multipoint calibration data. During analysis, the concentration of each cylinder gas was measured three times. Before and after each cylinder gas analysis, NIST SO₂ and NO SRMs were sampled by both the SO₂ and NO IMs. This routine provided data on the IM stability both before and after the cylinder gas analysis. Concentrations were calculated as specified by the EPA protocol procedure.¹ This procedure ratios the NIST SRM to its response when sampling the cylinder's contents.

The NIST SRMs were also used to determine if the presence of SO₂ affected the response of the NO IM or if the presence of NO affected the response of the SO₂ IM. This interference test was necessary because the NIST SO₂ and NO SRMs are single-component (i.e., SO₂ or NO in N₂) gases and the cylinder gas being analyzed contained both SO₂ and NO in N₂. The IMs were first calibrated with single-component NIST-SRMs, and then the interference response was tested by blending the SO₂ and NO NIST SRMs, generating a multicomponent gas.

ACCURACY ASSESSMENT SUMMARY

The accuracy of a manufacturer's certified concentration is defined as the percent difference between the manufacturer's certified concentration and RTI's corresponding mean measured concentration. Figure 1 is a graphical representation of these percent differences. The average differences for SO₂ were 0.8 and 1.5% with associated standard deviations of the differences of 2.8 and 3.7% for the 300 ppm and 1500-ppm concentrations, respectively. The average differences for NO were 0.2 and 0.3% with associated standard deviations of the differences of 1.0 and 1.4% for the 400-ppm and 900-ppm concentrations, respectively. In general, 72% of the results fell within the $\pm 2\%$ range, and 94% of the results fell within the $\pm 5\%$ range.

UNCERTAINTY ESTIMATES IN ACCURACY ASSESSMENT RESULTS

In estimating the uncertainty in the compressed gas cylinder concentrations that were determined during Cylinder Audit No. 8, several sources of error, both random and systematic, were considered:

- Uncertainty in the NIST SRMs.
- Error in measuring the effect of NO presence on the SO₂ measurements.
- Lack of linearity of the IMs.
- Memory effects of the IMs and uncertainty in correcting for these effects.
- Variability in repeated measurements on the same cylinder gas.

The results from Cylinder Audit No. 8 concluded that the first four sources of uncertainty combined to an estimated total of less than 2% at a 95% confidence level. The estimated relative standard deviation was less than 1%. The fifth source of uncertainty, repeated measurements of the same cylinder, is negligible because the relative standard deviation was less than 0.2% in each case. This 2% uncertainty estimate dictates that a difference greater than 2% between the audit concentration and the manufacturer's reported concentration

should be regarded as statistically significant. More specifically, results of an error analysis of the audit process indicated that for NO at 400 and 900 ppm, differences greater than 1.1% for both ranges may be regarded as statistically significant; for SO₂ at 300 and 1500 ppm, differences greater than 1.3 and 2%, respectively, may be considered statistically significant.

STABILITY EVALUATION

Results

The stability of the cylinder gas is defined as the percent difference between the concentrations measured in 1991 and 1993. Figure 2 is a graphical presentation of these percent differences. The average differences for SO₂ were -0.66 and +0.41% with associated standard deviations of the differences of 0.58 and 0.31% for the 300-ppm and 1500-ppm concentrations, respectively. The average differences for NO were -0.92 and -1.16% with associated standard deviations of the differences of 0.55 and 0.37% for the 400 ppm and 900-ppm concentrations, respectively. In summary, 100% of the results fell within the $\pm 2\%$ range, indicating that the concentrations did not change over the past two years.

The results were evaluated for differences between manufacturers for the different pollutants. This was accomplished by determining an average difference and comparing the difference of each manufacturer to this average difference for nitric oxide and sulfur dioxide. Figures 3 and 4 give a graphical presentation of how each manufacturer's difference compared to the average difference for nitric oxide and sulfur dioxide. Note that the confidence intervals all overlap zero percent difference. The half-width of the intervals represent the size of difference that would be required to be declared significant at the 5% level. These results indicate that no single manufacturer is different from the others.

One method used in the past to evaluate the stability of gases was to calculate the linear regression coefficients of concentration onto the time between analyses and evaluate the average slope calculated for each concentration range. These results indicated that SO₂ changed -0.082 ppm per month and +0.250 ppm per month with associated standard deviations of 0.072 and 0.186 for the 300-ppm and 1500-ppm concentrations, respectively. The results also indicated that NO changed -0.152 ppm per month and -0.439 ppm per month with associated standard deviations of 0.888 and 0.135 for the 400-ppm and 900-ppm concentrations, respectively.

Despite the fact that the statistical analysis results indicate no change in cylinder gas concentrations, the graphical presentations seem to indicate a trend for specific cylinder gas groups. Two kinds of systematic change can account for the apparent drift in cylinder gas concentrations: actual drift in the true cylinder gas concentration and drift or systematic change in the measurement system. Conventional statistics do not adequately differentiate between systematic changes. Professional judgement is a powerful tool, but its subjectivity does not necessarily fit with conventional statistics. Conventional least-squares regression analysis was performed on the data in an attempt to test whether the drifts of different manufacturers are different and to test for change in the measurement system. These tests were rather weak in that cylinder drifts would need to differ by more than 4% to have a fair chance of detection. One significant finding of the analysis is that the SO₂ measurement system behaved differently at the two levels tested (300 ppm and 1500 ppm). Aside from that, the analysis provided no clue as to whether the apparent drifts were caused by true drifts or measurement system changes. It would seem unusual to have so many different cylinders drift in the same manner.

Uncertainty Associated With Stability Evaluation

The same sources of error that existed during the accuracy assessment continue to exist during the stability evaluation. Additional sources of error, however, may include a shift in the NIST values, additional calibration errors, or a random error that appears, by chance, to be systematic. A shift in NIST values is minimized by conducting calibrations with multiple SRMs and defining linearity by using that portion of the instrument's response that represents $\pm 1\%$ at the 95% confidence interval. SRMs that are potentially different from other SRMs would become visible in this type of system. The 95% confidence interval for either the 1991 or 1993 analysis was $\pm 2\%$. Combining these analysis errors yields a stability evaluation error of $\pm 3\%$ at the 95% confidence interval.

CONCLUSIONS

The following conclusions were made from the stability evaluation:

- Cylinder gas concentrations appear to have changed as a group.
- No one manufacturer's cylinder was significantly different in terms of stability.
- Linear regression analysis could not conclude that the cylinder concentrations changed at all.
- The cylinder gas analysis was sufficiently sensitive to be able to detect instability of any single manufacturer whose drift may have differed from the group by more than 3%.

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract No. 68-D1-0009 to Research Triangle Institute. It has been subjected to Agency review and approval for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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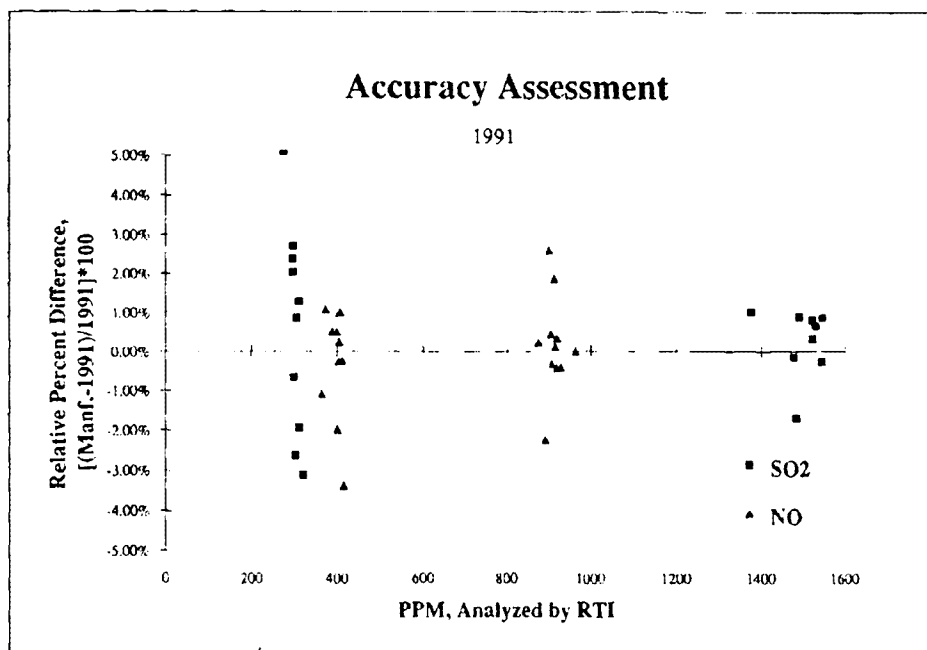


Figure 1. Protocol gas accuracy assessment.

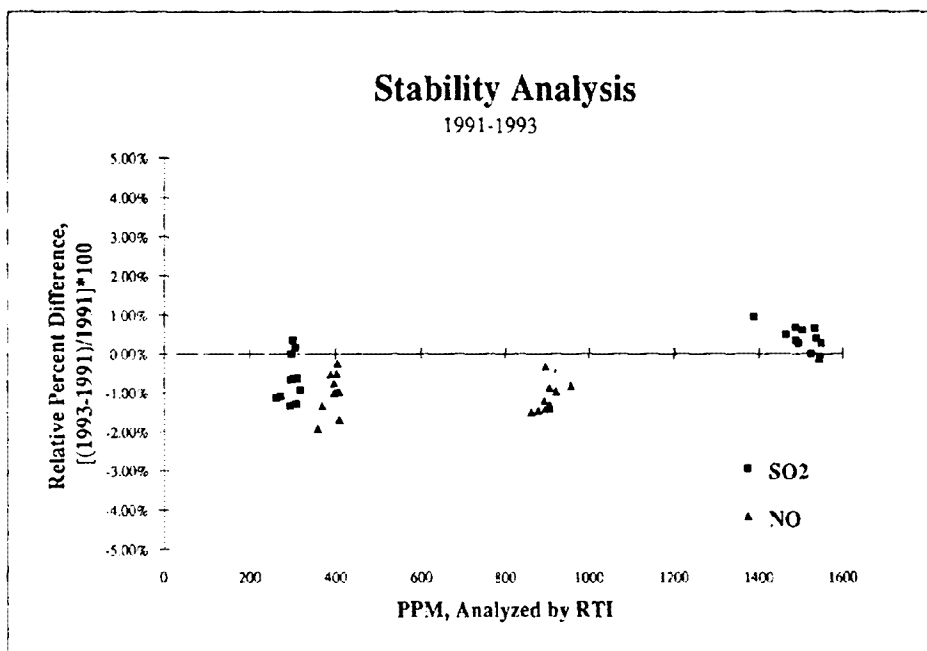


Figure 2. Protocol gas stability analysis.

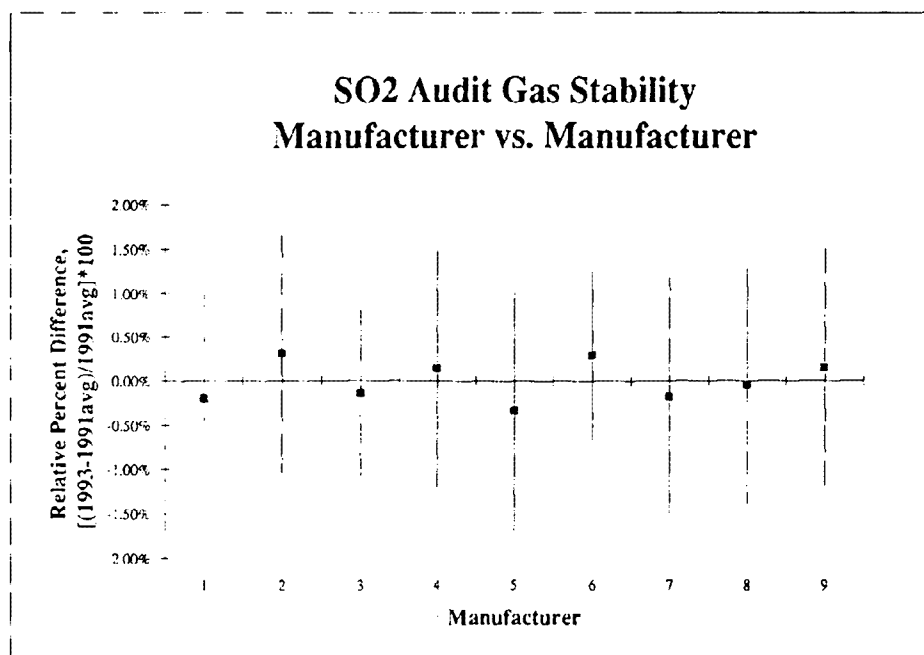


Figure 3. SO₂ cylinder gas stability by manufacturer.

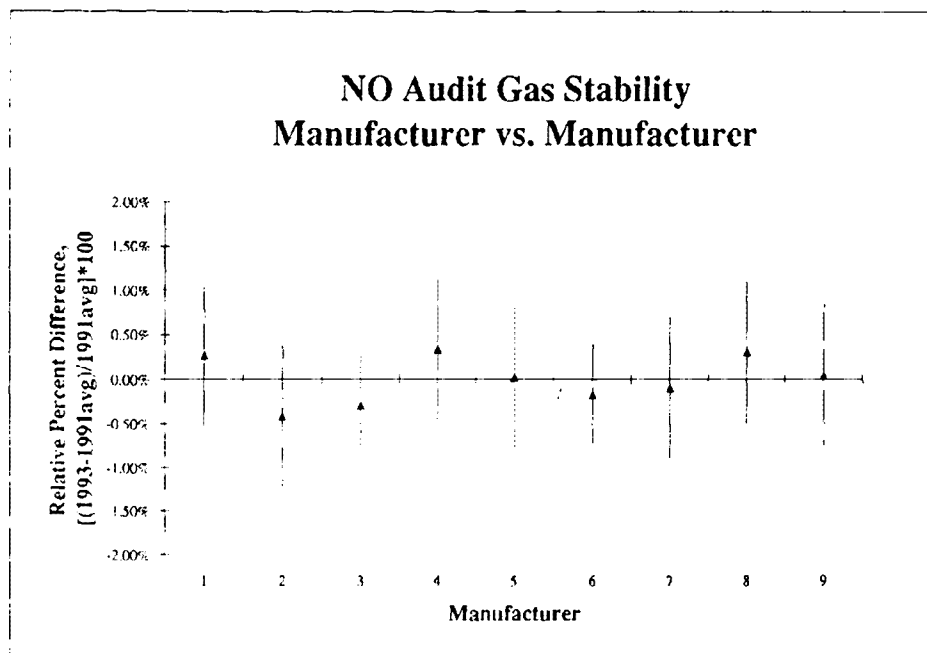


Figure 4. NO cylinder gas stability.

SESSION 11:
FTIR STUDIES

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Open Path FTIR Air Quality Measurements at a Petrochemical Complex in Brazil

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ABSTRACT

An open-path FTIR sensor was used to determine the characteristic air pollutants at ten different locations in a large petrochemical complex in Bahia, Brazil. These measurements were part of an initial survey in preparation for a measurement program which will use both open path FTIR and GC / MS analysis of collected air samples) to characterize the air quality within the complex and to obtain emission rates of the individual sources. In this initial survey, a total 17 different compounds were measured with the FTIR sensor, including the polar species, ammonia and acrylonitrile.

INTRODUCTION

An Open-path FTIR (OP-FTIR) was used to determine the characteristic air pollutants at ten different locations at the Camaçari Petrochemical Complex (Polo) in Bahia, Brazil. These measurements, using both OP-FTIR and GC / MS analysis of collected air samples, comprise the initial survey phase of a CETREL program to characterize the air quality within the complex and to obtain and characterize emission rates of the individual sources.

CETREL - Empresa de Proteção Ambiental S.A. is an environmental engineering company which is working with the State of Bahia CRA (environmental agency) to develop a Source Pollution Control Program (SPCP) to cover the entire Complex. CETREL operates a centralized waste treatment plant, treatment and disposal facilities and an incineration unit. In addition to their remediation services, CETREL also provides soil, water and air quality monitoring services.

Over the last few years, the interest in applying OP-FTIR techniques, to air quality measurements in the United States, has accelerated.¹ These techniques have been investigated for different applications, including Superfund remediation monitoring,² emergency response,³ waste water treatment⁴ and sludge treatment monitoring,⁵ fence line monitoring,⁶ production facility monitoring,⁷ measurements in DOE treatment, storage and disposal facilities,⁸ and industrial hygiene⁹ and other indoor¹⁰ applications. In the present study, OP-FTIR is used to survey fugitive chemicals in a large petrochemical complex in Brazil.

MEASUREMENTS

The OP-FTIR used in this study was used in a unistatic configuration with a single 12 inch Cassegrain telescope. A retroreflector array was used to return the beam. The resolution of the infrared spectra was 1 cm⁻¹. Chemical concentrations were obtained from the spectral data with a multicomponent least-squares (CLS) algorithm.

The measurements were made at ten different locations within the Complex in this initial phase of the program, which took place in the period from August 28 to November 3, 1993. Figure 1 shows the locations of the ten measurements on a map of the petrochemical complex. The locations of the

* At the time of these measurements, author was with MDA Scientific, Inc.

measurements are indicated by the labels P1 to P10, where the P designates the program label, POLO. Each location was chosen because it was downwind of a suspected emission source at the time of the measurement. A list of the chemicals detected with the OP-FTIR at the ten individual sites and the range of the concentration measurements are given in Table 1

A 115 volt, 1 KW gasoline generator was used to provide power to the instrumentation at the ten measurement sites. The resolution of the spectral measurements was 1 cm^{-1} and the signal-average times ranged from 45 seconds to 10 minutes. The system was typically configured along the side of roadways with the infrared beam at a height of ~ one meter. The one-way pathlengths, for the infrared beam, ranged from 27 to 165 meters and were chosen to optimally encompass the plume (as identified by odors). Since suspected emission sources were widely distributed around the complex, it was not feasible to measure "upwind" background spectra. At each site at least one "zero-path" background was measured. During these measurements, the retroreflector array was placed in front of the telescope tube at a distance of several inches. A disadvantage to using "zero-path" backgrounds is that they do not contribute to the cancellation of the interfering water vapor lines, so that one must rely totally on the matchup of the water vapor reference spectrum, used in the multicomponent CLS analysis, to the water vapor lines appearing in the field sample spectra. In order to improve the analysis, a spectrum made of local "clean air" was converted to a water vapor reference spectrum to be used in the analyses.

We further enhanced the data from the first site, (POLO1), by using one of the field sample spectra as the background. The preliminary analysis of the 23 field sample spectra, using a "zero-path" background, indicated that the twenty secondth single-beam file, labeled s3108v, did not have any measurable absorption due to the three measured species (ethylene, cyclohexane, and n-hexane). This was probably due to a momentary change in the wind direction. The use of s3108v as a background improved the results considerably over the preliminary analysis. One must be careful in using this technique since any absorption present in the spectrum used as a background will result in a negative bias. However the maximum magnitude of this bias should be less than the detection limits* of the species in question in the initial analysis of the field absorbance spectrum using the "zero-path" background. There have been occasions when the this type of analysis (using a spectrum from the data set as the background) resulted in detecting the presence of certain species which were not detected in the initial analysis. An example of this is in Run 1 at the fifth site (POLO5), where we detected benzene using this technique. The benzene was not detected in the preliminary analysis. Aside from POLO1 and Benzene in POLO5, the determinations reported in this paper were obtained using a "zero-path" background.

Figure 1 shows the locations of the ten measurements on a rough map of the Petrochemical Complex. The measurement locations P1 to P10 correspond to the labels, POLO1 to POLO10 (see Table 1 for the summary of measurement results at these 10 sites)

Figure 2 shows a comparison of the field absorbance spectrum from POLO5, Run 3 to the reference spectra of two of the species which have absorptions in this region of the field spectrum, methyl formate and methanol. The water vapor reference spectrum was subtracted from the field spectrum to better display the underlying absorption bands. However this subtraction was not necessary for the multicomponent CLS analysis, since the water vapor references was included in the analysis. The CLS analysis was performed separately for these two species, since their absorptions do not overlap. The results of the two separate analyses are 219 (19) ppb methyl formate and 691 (24) ppb methanol.

DISCUSSION

Table 1 shows a summary of the results obtained at the ten different sites at the Complex. Included in this table are the range of OP-FTIR concentration measurements. The measured concentrations at two of the sites, POLO5 and POLO8, are shown in Tables 2 and 3, respectively.

* The detection limits are measured using the error residuals of the CLS analysis.

A total of fifteen species have been measured at Polo. Several of these (ammonia, acrylonitrile and methanol) are polar molecules and are therefore difficult to measure using a sampling technique, due to losses on the walls of the collection vessel and the walls of the plumbing used in the GC / MS equipment. The OP-FTIR technique is being investigated because it offers the advantage of continuous monitoring over an uninterrupted path and providing a real time response to any high level fugitive emission. The gas sampling techniques are not amenable to this type of temporal and spatial coverage. The fact that the OP-FTIR detection limits, for many species, are higher than they are for the conventional air sampling techniques is strongly mitigated by the ability to provide real-time feed-back on the chemical environment, and to allow an emergency response to an accidental release of dangerous levels of chemicals.

Measurements made by other techniques indicate that benzene and other BTEX (Benzene, Toluene, Ethylbenzene and Xylenes) compounds are present at the Complex. Because of the health hazards relating to these compounds, it is important to include BTEX in the OP-FTIR measurements. In the present set of measurements, with the exception of one, the concentrations of these compounds were below the detection limits. We measured the detection limits at some of the locations for benzene, toluene and m-xylene, and obtained values which ranged from 11 to 240 ppb, 12 to 450 ppb, and 17 to 550 ppb, respectively. These values varied because of changes in the path length, humidity levels, interfering species other than water vapor, and signal to noise. However we did obtain one measurement of benzene at POI.05, in an optimized analysis where Run 2 (with little or no benzene) was used as the background for Run 1. The results of the analysis of benzene for Runs 1, 3 and 4 are shown in Table 2. The results degraded Runs 3 and 4 for two reasons. The pathlengths for these two runs was increased from 65 to 125 meters, one way, so the background from Run 2 does not optimize this two Runs because of imperfect water vapor cancellation. The second reason may be even more important. Methanol has an interfering absorption spectrum at 1031 cm⁻¹. This band completely overlaps the benzene band at 1037. In Run 1, methanol was below the detection limit of 18 ppb. In Runs 3 and 4 methanol was present at the concentrations 691 and 284, respectively. The detection limits for benzene for these two runs (< 148 ppb and < 68 ppb, respectively), seem to correlate with the methanol concentration. Because of the importance of the BTEX compounds, we may initiate a program to investigate developing an analytical algorithm to improve the detection limits on benzene by lowering the residuals due to the water and methanol absorption.

This program was preliminary and was performed in order to acquire information on the chemical environment at Polo to facilitate the future programs which include a complementary use of air sampling and OP-FTIR. The main purpose of the present measurements was to perform a survey. At this stage, validation of the data was not necessary, so no quality assurance procedures were used. Quality Assurance procedures will be developed in the later stages of the program.

CONCLUSION

This preliminary study lays the groundwork for establishing a continuous air quality monitoring program which will use both the OP-FTIR sensor and air sampling - GC / MS techniques in a complementary fashion and for intermeasurement quality checks. Quality assurance (QA) procedures for the OP-FTIR will be developed in the next phase of the program.

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TABLES

Table 1. The range of concentrations measured with the OP-FTIR at the ten POLO sites.

Site	Date	Methanol	Cyclo- Hexane	Ammonia	Ethylene	Propylene	n- Hexane	Methyl Formate
	1993	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
P1	8/31				7 - 450		3 - 180	
P2	9/17	74 - 210	2 - 260	60 - 600				
P3	9/24	74 - 170		60 - 270				
P4	9/28	44 - 1770						85 - 150
P5	9/28	280 - 690	10 - 75	20 - 41				220
P6	9/28	18 - 27	7	21 - 240				
P7	9/28	34 - 68	11 - 25		35 - 160	81		
P8	10/29	33 - 131	33 - 45		17 - 130	150 - 620	265	
P9	11/02					48 - 69	42 - 581	
P10	11/03			7 - 50		81 - 127		

(Table 1 continued)

Site	Date	Methyl Acetate (ppb)	Acrylo- Nitrile (ppb)	Form- aldehyde (ppb)	Dimethyl Ether (ppb)	Iso- butanol (ppb)	CHClF ₂ (ppb)	Propane (ppb)
P1	8/31							
P2	9/17							
P3	9/24							
P4	9/28	110 - 190		36 - 40	85 - 260			
P5	9/28							
P6	9/28							
P7	9/28							
P8	10/29							
P9	11/02					15 - 18		150 - 220
P10	11/03		64 - 101				8.4 - 19	

Table 2. Table of OP-FTIR concentration determinations at POLO5. With the exception of benzene, "zero-path" backgrounds were used. The benzene absorbance spectrum was created using the single-beam spectrum from Run 2 (File A280902). The numbers in the parentheses are equal to three times the estimated standard deviation.

File	Time	Path Length (m.)ow	Benzene (ppb)	Ammonia (ppb)	Methanol (ppb)	Methyl formate (ppb)	Cyclo- hexane (ppb)
POLO5	9/28/93						
A280901	7:48	65	6.0 (1.9)	20.3 (1.6)	< 18	< 567	64.4 (4.9)
A280902	7:53	65	- -	41.6 (1.6)	< 20	< 61	75.9 (8.4)
A280903	8:05	125	< 148	37.1 (2.9)	691 (24)	219 (19)	18.8 (4.6)
A280904	8:15	125	< 68	19.3 (2.9)	284 (13)	< 57	9.9 (1.9)

Table 3. Table of OP-FTIR concentration determinations at POLO8. All results shown here are from CLS analyses of absorbance spectra created using "zero-path" backgrounds. The numbers in the parentheses are equal to three times the estimated standard deviation.

File	Time 10/29 1993	Path Length (m) ow	Ethylene (ppb)	Propylene (ppb)	Methanol (ppb)	Cyclo- hexane (ppb)	n- hexane (ppb)
POLO8							
A29A3001	11:39	140	78.3 (5.9)	297 (35)	107.6 (9.9)	32.9 (7.2)	482 (18)
A29A3002	11:44	140	81.2 (5.7)	616 (54)	< 30	< 12	59 (12)
A29A3003	11:50	140	56.8 (5.7)	356 (38)	72.0 (8.3)	< 13	177 (13)
A29A3004	11:52	140	108.9 (8.0)	521 (57)	77 (11)	< 12	200 (13)
A29A3005	11:55	140	48.8 (4.6)	153 (23)	104.6 (9.1)	< 12	213 (12)
A29A3006	12:09	140	17.1 (5.6)	< 69	124.3 (9.1)	< 13	193 (10)
A29A3007	12:10	140	108.0 (7.4)	181 (23)	115 (11)	44.7 (9.2)	581 (21)
A29A3008	12:11	140	128.8 (8.5)	456 (58)	76 (11)	< 16	479 (17)
A29A3009	12:12	140	32.5 (4.1)	229 (23)	33.4 (8.3)	< 10	71 (10)
A29A3010	12:13	140	31.3 (4.8)	192 (23)	64.4 (9.1)	< 10	43 (10)
A29A3011	12:15	140	81.3 (7.2)	279 (40)	131.1 (11)	< 12	160 (12)

FIGURES

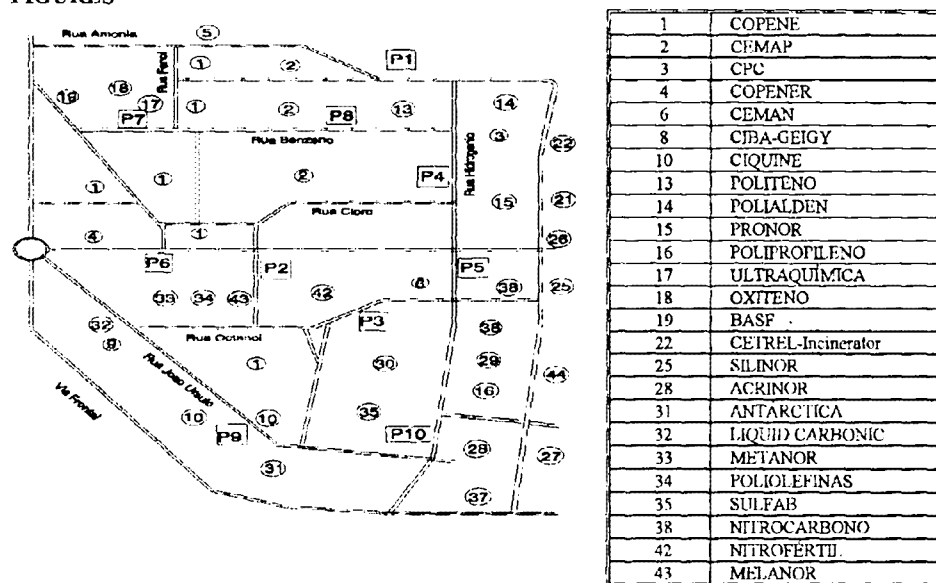


Figure 1. A Map of the Petrochemical Complex showing the Ten Measurement Locations (P1 to P10). The individual plants within the complex are designated with the encircled numbers. The names of the plants in the vicinity of the measurements are listed on the right. Table 1 gives the names of the gaseous chemicals detected with the OP-FTIR at the ten locations and the range of concentrations measured.

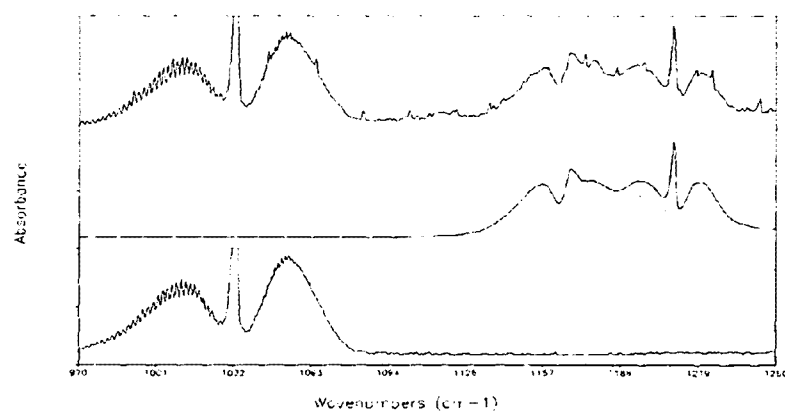


Figure 2 Comparison of the field absorbance spectrum from POI.05, Run 3 to two of the reference spectra used in the CLS analyses. Top trace: field spectrum over 125 meter one-way path, middle trace: 533 ppm-meter methyl formate reference, bottom trace: 27 ppm-meter methanol reference. The water vapor reference spectrum was subtracted from the field spectrum in order to better display the shape of the methyl formate band. The field spectrum was averaged for 5 minutes and a "zero-path" background was used to create the absorbance spectrum. The CLS analysis was performed separately for these two species, since the absorptions do not overlap. The results of the analyses on this portion of the field spectrum are 219 (19) ppb methyl formate and 691 (24) ppb methanol.

Open-Path FTIR Absorption Measurements at Urban and Industrial Sites in Germany - Two case studies

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ABSTRACT

Open-path FTIR absorption measurements have been performed at urban and industrial sites in Germany. The first direct intercomparison in Germany between open-path FTIR measurements and the official measurement network of the environmental state agency will be presented. Moreover the results of ammonia measurements in the complex atmosphere of a refinery plant will be addressed.

INTRODUCTION

The FTIR open-path measurement technique has already found various applications in the USA. In Germany interest in this method is steadily growing. In the Fachhochschule Düsseldorf the method is being exploited for various applications at industrial urban and rural sites in order to make it usable not only for research, but even for official tasks in the air pollution surveillance. Our experience will be brought into the standardization of this method in a German and maybe a European standard.

We used a commercial system with one wave number resolution for our measurements. The measurement was monostatic in every case. Monostatic means. The infrared light was sent out by a transmitter/receiver telescope towards a retroreflector, typically separated by an absorption path of several hundred meter. The reflected light was recollected again by the telescope and analyzed in the FTIR spectrometer, thus giving the time-averaged concentration of the air pollutants of interest. The method is described in more detail e.g. in [1,2].

Intercomparison Measurements at an Urban Site

The urban measurement site was situated at the outskirts of the German city of Cologne. This measurement site was chosen because it was known that sometimes very high methane concentrations could be found there and, additionally, photo-chemical smog situations in summer were noticed. Several potential sources of air pollution could be found in this region, for instance industrial plants, traffic, waste sites and waste-water treatment basins.

An official station of the Environmental State Agency of North Rhine-Westphalia, equipped with standard monitoring systems, was placed at this site as part of the air pollution measurement network for continuous measurements of the state, so that we were able to intercompare our results with the data of the official network of the state.

The first aim of our measurements was to find out how well our results matched the official measurements of the state agency. The second aim was to find out what the most important source of the high methane concentration was.

We made the measurements on two different days at that site with a temporal delay of about two weeks to enhance representativeness. For these measurements the spectrometer was placed near the station of the Environmental State Agency so that direct intercomparison of the two systems was possible. Down in a street a retroreflector was installed about two hundred meters away from the spectrometer down in a street. In the street, where we made our measurements, there was only little traffic. However, a main street with heavier traffic was situated nearby.

The measurements between both systems intercompared very well although the weather conditions changed from snowfall to rain and sunshine. The atmospheric temperature changed between -2 °C and +6 °C. On the first day (Fig. 1,3) the mean difference between both measurements was less than the difference of both measurements during the second day (Fig. 2,4). This can easily be explained by the fact that for the evaluation of the data of the second day the same synthetic background had been used, which was derived from the spectra

of the data of the first day. For this reason the shift of the baseline caused by the strong absorption of CO₂ and water vapor in the second measurement was not compensated as well as in the first measurement. Another reason is the continuously changing wind direction during the second day. This stresses the differences between point-sensor and a path-integrating system.

The measurement of methane showed a better agreement than the measurement of CO.

The very strong increase in the CO emissions, caused by a larger number of cars in the mainstreet in the afternoon hours, can clearly be seen (Fig. 1).

Figure 2 demonstrates the CO measurements of the second day. Again you can see a good agreement between both measurement systems. The overall trend of the concentrations increased in parallel.

In the measurement of the second day, slightly higher concentrations at about noon and in the late afternoon can be seen. The first concentration maximum could be correlated to an enhancement of traffic in the small street, where the measurements had been performed. The second maximum was due to the increased work traffic on the main street nearby.

Again it should be stressed at this point that the agreement between the FTIR open-path measurements and the measurements of the official measurement station were very satisfactory. So it could be clearly demonstrated that the FTIR-method can produce reliable results. Moreover, it was possible to make measurements even during heavy snowfall needing only about half an hour from arriving at the measurement to the beginning of the measurements.

In addition to the CO measurements we evaluated the spectra for the measurement of methane, which was the compound the people in that area were mostly interested in. Fig. 3 demonstrates the measurements of methane of the point monitor of the official network in comparison to our measurement. Again a very good agreement of the two measurement systems within a few percent could be registered. By the way, the dip in black line is caused by a big garbage truck.

The methane concentration at that day remained fairly constant just above the normal atmospheric value, so no alarming feature could be found in the measurements during that day.

During the second measurement day the methane concentrations showed a very dramatic increase during a certain period. For the time of one hour, between 2:30 pm and 3:30 pm, both measurement systems show a significant increase. In order to find out the reason for this feature we correlated the measured concentration with the wind data. The direction of the wind is plotted in Fig. 4 as well. So by correlating the wind data with the concentration data a waste water treatment basin, about two miles from the measurement site, could clearly be identified as the source of the high methane concentrations in that day, whereas the waste site as well as industrial areas could be excluded as the methane source.

This measurement shows that the general trend of changing concentrations is still visible even when background is not exactly matched to the measurement situation. This is important for continuous automatic monitoring over several days where the trend of the emissions is often more important than the exact value.

We will perform additional measurements at this urban site during this summer, in order to get data in the situation of photo-chemical smog.

In conclusion, we could prove at this urban site that the open-path absorption system can deliver reliable results for methane and CO in an on-line mode even under adverse weather conditions. As all we know, this is the first direct intercomparison between an open-path FTIR system and official measurement systems in Germany. Therefore it was of high importance that there was a very good agreement between our data and data of the official measurement network. This will surely increase the confidence in these innovative methods.

Measurement at an Industrial Site in Germany

We performed different measurements at industrial sites in Germany. In this paper we want to demonstrate a measurement which had been taken at an ammonia tanking facility within the area of a refinery. We chose this industrial site to demonstrate that with this method it is possible, to get results even in a dirty industrial atmosphere with many interfering compounds.

At that site, ammonia storage tanks were refilled from railway tank waggon. We had positioned our spectrometer on a little hill, about 380 m away from the tanking facility. The retroreflector was sited in such a position that the measurement path was downwind of the potential emission source of the tanking facility.

At the beginning of the measurement you can see nearly a constant level of ammonia concentration (Fig. 5). The measured concentration of about 7.5 ppb (5.7 µg/m³) was just above the normal atmospheric

centration, which usually is given as 5 ppb ($3.8 \mu\text{g}/\text{m}^3$). The black line represents the concentrations, which are evaluated using the Hanst library for the reference spectra. We got the dotted line by using the MDA library, in which all reference spectra were measured in the laboratory with an spectrometer identical to ours.

However, for a very short time interval of about one minute we could detect a very sudden and drastic increase. We were able to monitor this increase on-line at the site. As we heard later on, this ammonia emission is caused by the fact that just at that time the tanking hose was removed from the waggon so that a part of the mains of the ammonia in the hose could be released. If you refer the measured signal to the approximate dimension of the tanking facility of about 50 m, you get a peak concentration of the release of about 600 ppb ($45 \mu\text{g}/\text{m}^3$). It is remarkable, that this short emission could be detected by us on-line even at a distance of 30 m outside the plant.

With this measurement we successfully demonstrated the potential of the method to monitor one compound in an industrial environment.

CONCLUSION

The first direct intercomparison in Germany of FTIR open-path measurements with official measurements of carbon monoxide and methane is very satisfactory. We planned additional measurement campaigns together with the environmental state agency to extend the evaluation of the FTIR open-path system also for other compounds like e.g. ozone in an urban area.

At the industrial site we successfully demonstrated the benefit of the FTIR open-path absorption method for on-line and remote monitoring even of sudden emissions.

Moreover, it could be shown that this measurement method can have advantages over point monitors for measuring fugitive emissions in a complex industrial situation. The measurements at the industrial site will be continued.

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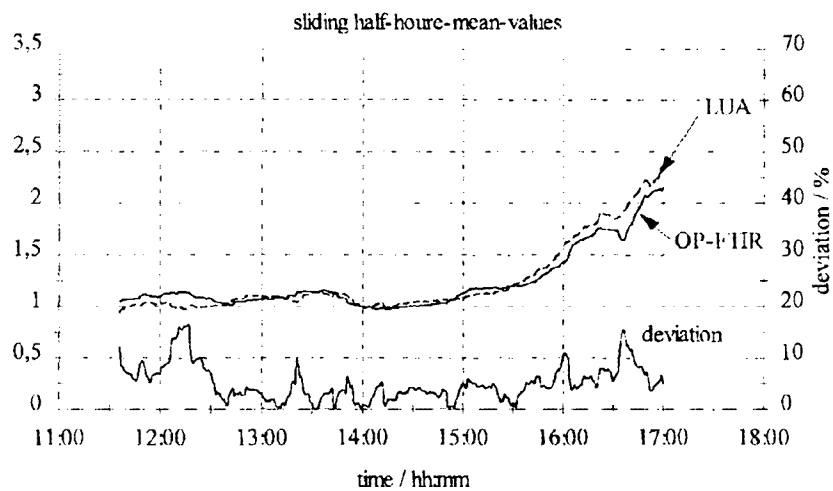


Figure 1. Carbonmonoxide measurement at urban site, first day.

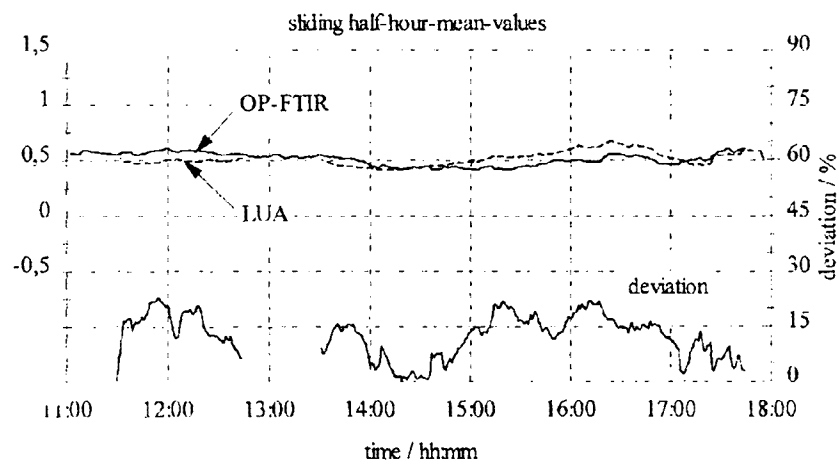


Figure 2. Carbonmonoxide measurement at urban site, second day.

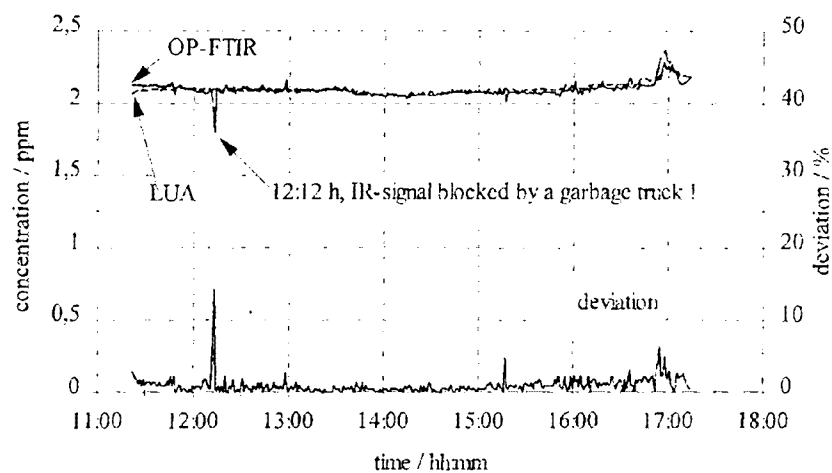


Figure 3. Methan measurement at urban site, first day

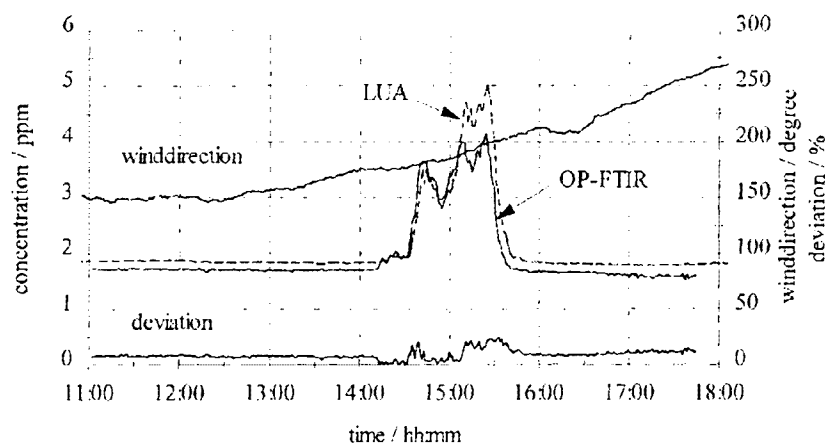


Figure 4. Methan measurement at urban site, second day

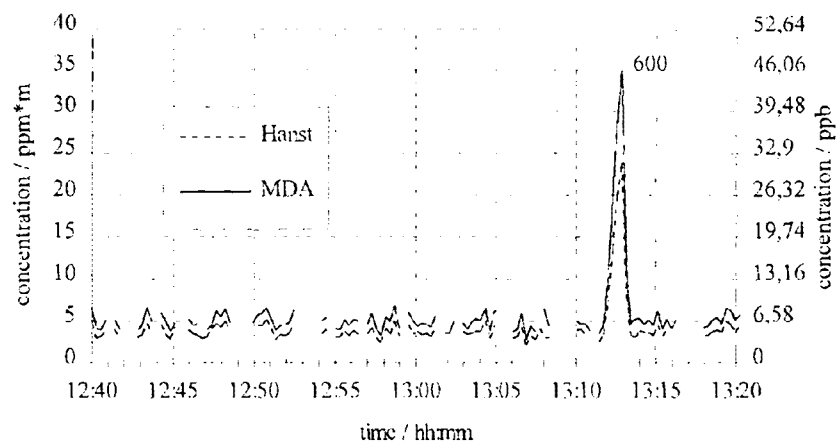


Figure 5. Ammonia measurement at tanking facility, 380 m

Development of Quality Assurance Procedures in Open-Path FT-IR Monitoring

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ABSTRACT

Data were collected over a period of two and one-half months as part of an ongoing program to develop quality assurance (QA) procedures in open path Fourier transform infrared (FT-IR) monitoring. A semi-permanent monitoring site with an FT IR system in the monostatic configuration was established over a grassy field with a total path length of 414 m. Spectral measurements were made by acquiring 5-min co-averaged spectra at 15-min intervals over 7 to 8 h starting in the morning and continuing through the afternoon. Measurements were also taken continuously over a 36 h period. A daily protocol that included measuring the instrumental electronic noise, the magnitude of the single-beam return signal, the baseline noise, and the repeatability of the position and full width at half height of selected water vapor absorption bands was followed. Ancillary measurements, including relative humidity, ambient temperature, and wind direction, were also made. The ambient concentrations of carbon monoxide, methane, and nitrous oxide were measured to assess the stability of the instrument and to investigate the feasibility of using ambient gas concentrations for QA purposes.

INTRODUCTION

For open-path Fourier transform infrared (FT-IR) spectrometry to become an accepted method for environmental monitoring, proper quality assurance (QA) procedures must be established. Kricks et al.¹ have discussed QA issues concerning the operation of open-path FT-IR spectrometers during field applications and identified several potential sources of error in the measurements. Russwurm^{2,3} developed a synthetic data set to illustrate the effects of spectral shifts and interfering species on errors in least-squares-fitting (LSF) analyses and has examined the effects of water vapor on the measurement of toluene. Weber et al.⁴ have addressed the need to develop experimental performance characteristics in optical remote sensing. Despite the attention that this topic has generated, however, there is currently no consensus regarding the proper QA procedures required to validate open-path FT-IR data.

One of our primary goals is to develop procedures to determine the quality of data taken with FT-IR monitors. The study described here was designed to evaluate the stability of the instrument and the precision and accuracy of concentration measurements. The following criteria were used to assess the stability of the instrument: electronic noise, the magnitude of the return signal, the root-mean-square (rms) baseline noise, and the repeatability of the position and full width at half height (FWHM) of selected absorption bands. Ambient concentrations of methane (CH₄), nitrous oxide (N₂O), and carbon monoxide (CO) were measured to test the use of these data for determining the precision and accuracy of the FT-IR open-path monitor. Measurements were made daily over two and one-half months, from November 1993 to mid-January 1994.

EXPERIMENTAL METHODS

Spectral data were acquired by using an MDA (Norcross, GA) monostatic FT IR monitor equipped with LabCalc software (Galactic Industries Corporation, Salem, NH). Each spectrum consisted of 64 co-averaged scans recorded at a nominal 1-cm⁻¹ resolution. Triangular apodization was used. The collection of each spectrum required approximately 5 minutes. A spectrum was taken every 15 minutes.

Single-beam spectra were typically acquired over a 7- to 8-h time period. Absorbance files were created by ratioing the single-beam spectra to a synthetic background spectrum generated from a 2048-scan single-beam spectrum recorded over the 414-m path. This background spectrum was recorded at the beginning of the experiment and was used throughout the study. The data were analyzed by using the MDA LSF package and reference spectra from a commercial library (Infrared Analysis, Inc., Anaheim, CA).

The site is located near I-40, one of the main traffic arteries for the Research Triangle Park, NC, area. The instrument was kept in a climate-controlled shed, which is heated during the winter months and cooled during the summer months. The total path length was 414 m, and it extended over an open, grassy field and a small parking area with very limited traffic. The beam path rose from about 6 ft to 42 ft above the ground as it was directed from the FT-IR instrument to the retroreflector, which was mounted on a tower.

RESULTS AND DISCUSSION

The instrumental electronic noise was measured each morning before the detector was cooled with liquid nitrogen. This signal typically ranged between 600 and 620 counts. Shortly after the detector was cooled, the instrument was aligned and the maximum return signal was recorded. The return signal was recorded again (without realignment) around noon to check the stability of the signal. On clear days the return signal ranged from 10,500 to 13,500 counts. (See Figure 1.) Certain atmospheric conditions caused the return signal to vary from day to day. For example, the return signal dropped by 20-30% during fog. On some mornings, when humidity was close to or below the dew point, condensation or ice formed on the retroreflector, resulting in a lower return signal in the early morning measurement. As the condensation evaporated, an increase in return signal counts was measured. To remedy the problem of condensation, a heat lamp was mounted on the tower and directed at the retroreflector. After the heat lamp was installed on December 10, the noon and early morning return signals were nearly the same. Also, use of the heat lamp did not cause an increase in noise or detected IR signal.

The rms baseline noise measured over 26 days is illustrated in Figure 2. The baseline noise was determined by collecting two back-to-back, 64-scan, co-added spectra. One spectrum was ratioed against the other to obtain an absorbance file. The rms noise (in absorbance units) was calculated over three spectral regions: 980-1020, 2480-2520, and 4380-4420 cm^{-1} . During operations when condensation did not form on the retroreflector, the baseline noise was on average approximately 2×10^{-4} for the 980-1020- cm^{-1} region, 2.5×10^{-4} for the 2480-2520 cm^{-1} region, and 9×10^{-4} for the 4380-4420- cm^{-1} region. During measurement periods when condensation formed on the retroreflector, the baseline noise for these regions increased to 9.7×10^{-4} , 5.5×10^{-4} , and 2.9×10^{-3} , respectively.

The wavenumber stability of the instrument was determined by monitoring the peak position and the FWHH of the water vapor singlet at 1014.2 cm^{-1} . Band positions typical of data collected at the beginning, in the middle, and near the end of the study are depicted in Figure 3. No shift in the frequency was observed during this time period. Also, no shifts were observed in the 1- cm^{-1} spectra collected under a variety of weather conditions, including rain, freezing rain, sleet, snow, and low (single-digit) temperatures. To determine if the water vapor singlet at 1014.2 cm^{-1} broadened, a spectrum collected at the beginning of the experiment was subtracted from a spectrum in the middle and end of the experiment. No broadening was evident during the middle of the experiment; however, a slight broadening for some of the spectra at the end of the experiment was observed. The FWHH of the water vapor singlet in spectra taken during different atmospheric conditions was also examined. When a clear day spectrum was subtracted from any of these spectra, no broadening was evident.

The feasibility of using ambient gases for QA purposes was investigated. Ambient concentrations of N_2O , CH_4 , and CO were measured on a daily basis. Each morning between 0715 and 0930 the concentrations of these gases increased, then steadily decreased during the remainder

of the day. However, concentrations of N_2O and CH_4 remained within their expected ambient levels, 250 ppb and 1.7 ppm, respectively. To determine whether the increases in concentration during the first 3 h of operation were due to an instrument effect or to the proximity of the site near a major highway, data were collected continuously for 36 h.

Data were collected from November 17 at 0730 until 1730 on November 18. The CH_4 concentration data exhibited scatter during an early morning fog episode and decreased steadily during the day. (See Figure 4A.) A step in the CH_4 concentration measurement was observed when the liquid nitrogen in the detector was depleted at approximately 2345 on November 17. The CH_4 concentration value was 1.70 ppm just before the liquid nitrogen was depleted, increased to 1.9 ppm after liquid nitrogen was refurbished, and remained 10% higher compared to the previous levels. The concentration data for CO showed a similar, stepped increase.

The CH_4 concentration data exhibited irregular behavior during a 6 h period shortly after the detector Dewar was refilled with liquid nitrogen. To determine if the instrument was operating properly during this time period, the single-beam intensity at 987 cm^{-1} was measured from archived spectra. The single-beam spectra had a lower intensity during the fog episode, then leveled off until the detector ran out of coolant. (See Figure 4B.) After this sudden drop, the single beam intensity returned to its original reading and remained relatively constant throughout the remainder of the experiment. This indicates that the instrument was working properly during the episode of high measured CH_4 levels.

One other observation during this time period was that on November 17 a cold front moved through the area in the late evening and the water vapor pressure dropped rapidly. Because the water vapor spectrum is used as an interfering species in the LSF concentration analysis for CH_4 , the sudden change in water vapor pressure could have had an effect on the CH_4 concentration measurements. The relative concentration of water vapor along the path was determined by measuring the peak area of the absorption band at 1014.2 cm^{-1} . Likewise, the relative concentration of CH_4 was determined by measuring the peak area of the absorption band at 2998.8 cm^{-1} . This peak was chosen because the water vapor bands do not interfere with it. As shown in Figure 5, the relative water vapor concentration decreased rapidly when the front moved through the area. The relative CH_4 concentration increased during this period. Similar trends were observed between plots of the CH_4 peak area and CH_4 concentrations determined by the LSF concentration analysis. This indicates that the change in water vapor concentration did not greatly affect the LSF analysis for CH_4 , and the fluctuations in the CH_4 concentrations were real.

CONCLUSIONS

The data collected in this study indicate that for this particular FT-IR monitor the return signal and baseline noise are repeatable and are instrumentally stable over extended periods, but are subject to variations due to weather conditions. The peak positions and the FWHMs of the water vapor singlet at 1014.2 cm^{-1} were repeatable from day to day and were not affected by rain, freezing rain, snow, or single-digit temperatures. The variability in the concentrations of ambient gases limits their use in instrument stability studies and for QA purposes. A step in the concentration measurements associated with the depletion and refurbishment of detector coolant is not yet understood. Future experiments using a QA cell with surrogate standards are planned to further investigate this effect.

ACKNOWLEDGMENT

Although the research described in this paper was funded wholly or in part by the United States Environmental Protection Agency through Contract 68-D0-0106 to ManTech Environmental, this paper has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

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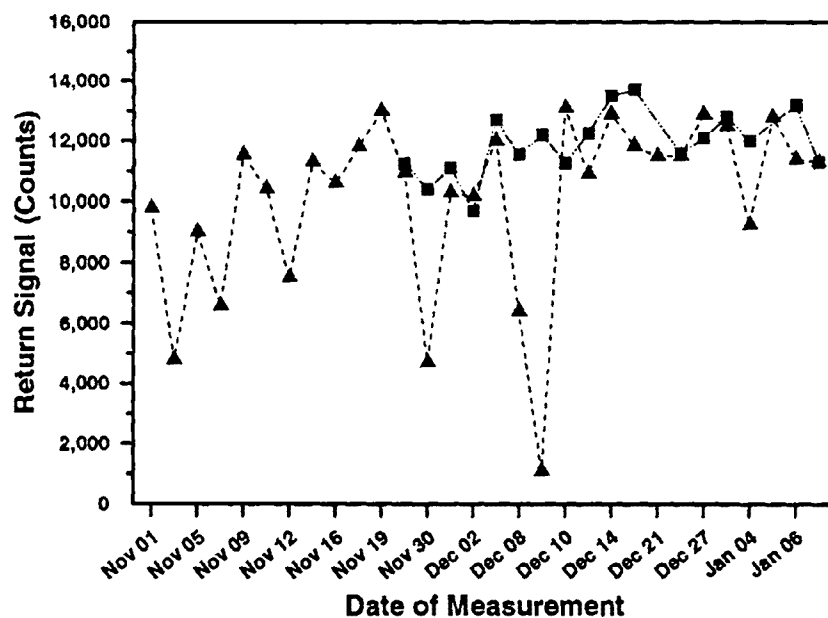


Figure 1. Return signal magnitude of the FT-IR monitor measured daily at 0700 (▲) and 1200 (■).

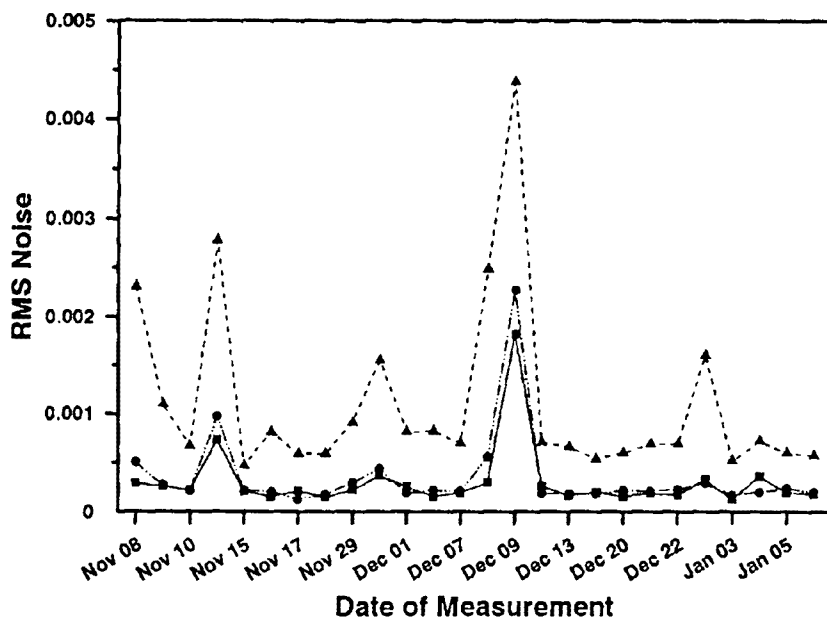


Figure 2. The rms baseline noise measured between 980 and 1020 cm^{-1} (■), 2480 and 2520 cm^{-1} (●), and 4380 and 4420 cm^{-1} (▲).

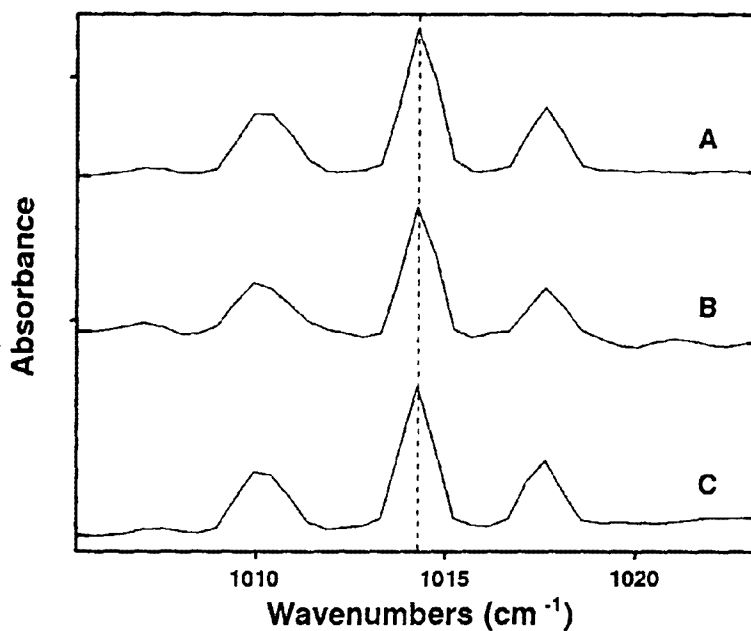


Figure 3. Repeatability of the position of the water vapor singlet at 1014.2 cm^{-1} measured on (A) November 10, 1993, (B) December 22, 1993, and (C) January 4, 1994.

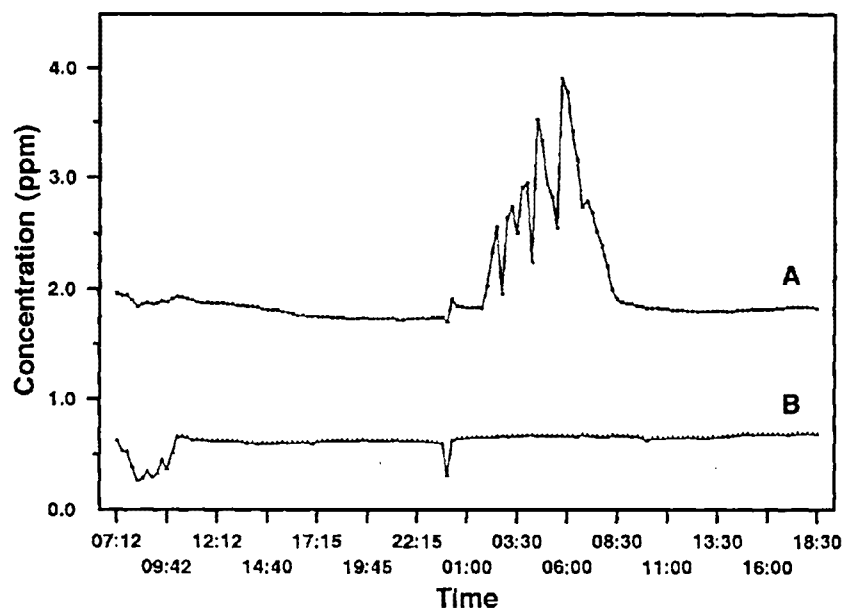


Figure 4. Measurement of (A) ambient methane concentration and (B) single beam intensity at 987 cm^{-1} on November 17 and 18, 1993.

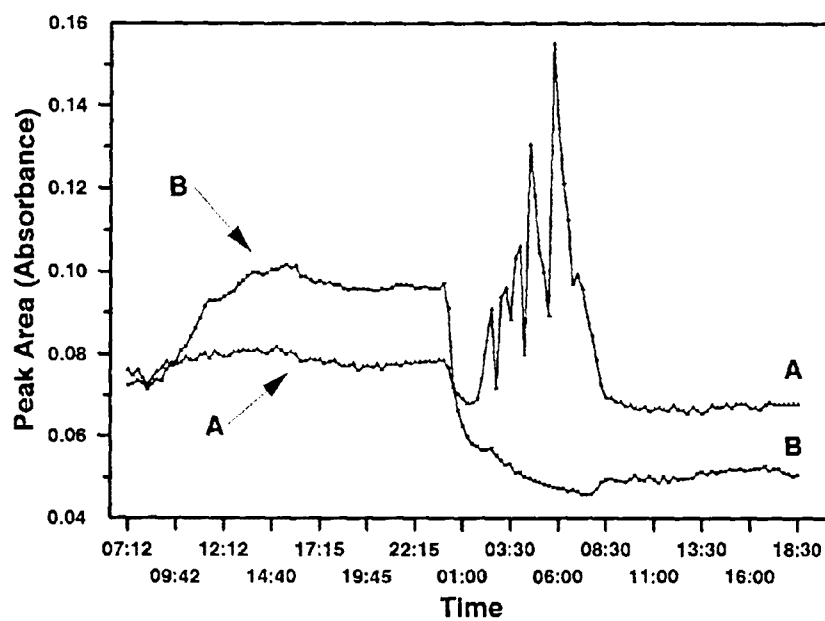


Figure 5. Measurement of the peak area of the 2998.8-cm^{-1} absorption band of methane (A) and the 1014.2-cm^{-1} absorption band of water vapor (B) on November 17 and 18, 1993.

Adaptation of a Military FTS to Civilian Air Toxics Measurements

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Abstract:

In many ways, the military problem of chemical agent detection is similar to the civilian problem of toxic and related air pollutants detection. A recent program to design a next generation Fourier transform spectrometer (FTS) based chemical agent detection system has been funded by the U.S. Army. This program has resulted in an FTS system that has a number of characteristics that make it suitable for applications to the civilian measurement problem. Low power, low weight, and small size lead to low installation, operating and maintenance costs. Innovative use of diode lasers in place of HeNe reference sources leads to long lifetimes and high reliability. Absolute scan position servos allow for highly efficient offset scanning. This paper will relate the performance of this system to present air monitoring requirements.

Introduction:

The US Army has been developing field-rated spectroscopic sensors for chemical agent detection for nearly 25 years. One of the first systems to be developed was LOPAIR (Long Path InfraRed). This system was a low resolution system using circular variable filter technology. A small number of these systems were built and used in conjunction with fairly basic spectral pattern recognition algorithms based on the Simplex technique. A good deal of confidence was developed in the application of these techniques to this massive detection field problem. Limited resolution and sensitivity of the LOPAIR systems prompted the examination of FTS systems, the first of which was called COIN (Correlation Interferometer). This was a single system built to address the practicality of FTS for field use as well as to provide a platform for the early study of extracting the detection information directly from the interferogram without going through the transform process. Both the LOPAIR and COIN systems were built by Block Engineering. Showing promise as a next generation technology for the Army's detection problem, an advanced FTS system was developed at Honeywell Electro-Optics Center. It consisted of a series of quasi-headboard instruments, the BMS (Background Measurement System) designed to collect the necessary field data for the development of algorithms; and the XM-21 system, a fully field rated FTS. Both of these systems were designed to operate in spectrum space. In 1986, the XM-21 went into production as the M-21 chemical agent detector. Brunswick Corporation purchased the Honeywell operation producing the M-21 and now manufactures these systems for the Army and other Department of Defense components. The latest in this series of FTS instruments is the L-SCADS (Lightweight-Standoff Chemical Agent Detection System). This is an interferometer system initially designed for use on an un-manned aerial vehicle and is intended to provide a standoff detection capability for battlefield commanders. An essentially identical version of the L-SCADS system is also being built as part of the Army's Armored Systems Modernization Program. L-SCADS was jointly developed by OPTRA and IMO/Baird. As with many of the military programs today, contractors are encouraged to develop dual-uses for the technology

embodied therein. The application of this sensor to monitoring and control problems in the civilian sector is a natural response to these urgings.

The instrument developed under this program is described in detail elsewhere. (See reference 1.) L-SCADS is a moderate resolution spectrometer using the classical Michelson configuration of two flat mirrors and a compensator/beamsplitter pair in a 45/45 degree configuration. Table 1 is a list of performance specifications. The spectrometer is designed for use from 700 to 1400 wavenumbers, the fingerprint region of the infrared spectrum. It is provided with variable resolutions from a high of 2 wavenumbers to a low of 16 wavenumbers. It operates in a continuous scan mode at a constant velocity for all resolutions providing a range of scan rates (interferograms/second). The interferometer has an aperture of 0.5 inch diameter and a field of view of 3 x 3 degrees. A 2X afocal telescope transforms this into an aperture and field of view of 1 inch diameter and 1.5 x 1.5 degrees respectively. The system is quite small (6 x 7 x 10 inches); it weighs less than 13 pounds; and draws less than 24 watts at 28 volts DC input power. The output of the system is an analog interferogram. Digitization, processing and data storage are all done by other units.

Signal to Noise Ratio:

One objective of dual-use programs is to consider the application of the military systems in a manner that minimizes additional engineering. Hence, an unmodified L-SCADS sensor is used as the basis for the following performance analysis. A bistatic system as shown in Figure 1 will be analyzed. The system consists of an unmodified L-SCADS interferometer spectrometer observing a continuum source which is collimated and projected by a 30 cm diameter (12 inch) optical system located 200 meters from the spectrometer. Furthermore, in an attempt to relate this analysis to a real problem, the analysis of the system performance will be done for the spectral interval of 780 cm^{-1} to 900 cm^{-1} , which is the spectral region often used for detection of phosgene, a pollutant of some interest. (See reference 2).

In such a closed system the performance figure of merit is the radiometric signal to noise. When that number is known the minimum detectable concentration path length of different materials can be determined. The system signal to noise ratio can be expressed as

$$\text{SNR} = \frac{N_s}{\text{NESR}} \quad (1)$$

where SNR = the signal to noise (unitless),
 N_s = the source radiance ($\text{w/cm}^2\text{-ster-cm}^{-1}$), and
 NESR = the system noise equivalent spectral radiance defined at the source ($\text{w/cm}^2\text{-ster-cm}^{-1}$).

$$\text{NESR} = \frac{\sqrt{A_d}}{D \cdot n \cdot \theta \cdot \Delta v \cdot \sqrt{\Delta t}} \quad (2)$$

where A_d = the area of the detector (cm^2),
 D^* = the detector detectivity ($\text{cm-Hz}^{1/2}/\text{watt}$),
 n = the system efficiency (unitless),
 θ = the system etendue ($\text{cm}^2\text{-ster}$),
 Δv = the spectral resolution (cm^{-1}), and
 Δt = the integration time (sec).

Combining equations (1) and (2) yields

$$\text{SNR} = \frac{N_s \cdot D^* \cdot n \cdot \theta \cdot \Delta v \cdot \sqrt{\Delta t}}{\sqrt{A_d}} \quad (3)$$

Since this analysis anticipates the use of an L-SCADS instrument, certain terms in equation (3) are fixed and others are variable. Each term is discussed below.

N_s , Source Radiance: Without being specific, the source chosen for this analysis will operate at 1000 K. Spectral radiance values for this temperature source over the 780 to 880 cm^{-1} spectral range are on the order of 3×10^{-4} watts/ $\text{cm}^2\text{-ster}\text{-cm}^{-1}$, slightly less than this amount at 780 cm^{-1} and slightly more at 880 cm^{-1} .

D^* , Detector Detectivity: A peak D^* (at 12 μm or 833 cm^{-1}) of 4×10^{10} $\text{cm-Hz}^{1/2}/\text{watt}$ is assumed even though the L-SCADS MCT detectors are somewhat better than this. Shorter and longer wavelength values follow the usual D^* curve.

n , System Efficiency: Over the spectral interval under consideration the system efficiency of the L-SCADS interferometer is approximately 0.2.

θ , System Etendue: The etendue (or area - solid angle product) of a system numerically describes the geometric light gathering capability of the system. The etendue of the system under discussion will be determined by the interferometer entrance aperture and the projector aperture and their respective separation by the relation

$$\theta = \frac{A_i \cdot A_p}{R^2} \quad (4)$$

where θ = the etendue for the system ($\text{cm}^2\text{-ster}$),
 A_i = the interferometer collector area (cm^2),
 A_p = the source projector area (cm^2), and
 R = the source-interferometer separation (cm).

Since

$$A_i = 5.07 \text{ cm}^2$$

$$A_p = 7.07 \times 10^2 \text{ cm}^2,$$

$$R = 200 \text{ m} = 2 \times 10^4 \text{ cm, then}$$

$$\theta = 8.96 \times 10^{-6} \text{ cm}^2\text{-ster.}$$

Δv , Spectral Resolution: For the analysis, the highest resolution of the L-SCADS (2 cm^{-1}) will be used.¹

¹ From modulation efficiency considerations, the maximum allowed obliquity angle within the interferometer is given as

$$u^2 = \frac{\Delta v}{v}$$

where u = the obliquity half angle (radians),
 Δv = the spectral resolution (cm^{-1}), and
 v = the highest optical frequency (cm^{-1}).

At, Integration Time: Assuming an observation efficiency of 0.8 and an observation time of 10 seconds, the integration time for this analysis is 8 seconds.

Ad, Detector Area: L-SCADS has a square detector of linear dimension 5×10^2 cm.

Using the values from above, equation (4) can be used to generate the SNR curve shown as Figure 2.

Minimum Detectable Concentration

The absorbance at specific wavelengths is related to the concentration path length as

$$A = M \cdot c \cdot d \quad (6)$$

where A = the absorbance (unitless),
 M = the absorptivity (ppm-meter)¹,
 c = the concentration (ppm), and
 d = the path length (meter).

From measured spectra the absorbance is quantified as

$$A = -\log_{10} \left\{ \frac{I}{I_0} \right\} \quad (7)$$

where I = the spectrum obtained in the presence of an absorber, and
 I_0 = the "clean air" spectrum taken under the same conditions as I .

Since the noise in each spectrum is a constant, I and I_0 are related to their respective SNR's by the same factor equation (7) can be rewritten as

$$A = -\log_{10} \left\{ \frac{\text{SNR}_i}{\text{SNR}_0} \right\} \quad (8)$$

By defining the minimum detectable absorbance as that which reduces the transmission by 3 times the noise level, from equation (8)

Together with the interferometer mirror area this defines the maximum allowed system etendue

$$\theta_{\max} = A_m \cdot \pi \cdot u^2$$

where A_m = the interferometer mirror area (cm²).

For L-SCADS the interferometer mirror radius is 0.635 cm giving

$$\theta_{\max} = \pi \cdot (0.635)^2 \cdot \pi \cdot \left[\frac{2 \text{ cm}^{-1}}{780 \text{ cm}^{-1}} \right]^2$$

$$\theta_{\max} = 1.02 \times 10^{-2} \text{ cm}^2\text{-ster}$$

Since equation (4) yields a system throughput of $8.96 \times 10^{-6} \text{ cm}^2\text{-ster}$ this condition is clearly met.

$$A = -\log_e \left[\frac{SNR_o - 3}{SNR_o} \right] \quad (9)$$

Using the SNR's from Figure 2, a plot of A_{min} is presented as Figure 3. Across the band, A_{min} is approximately 10^{-3} .

From the earlier discussion regarding etendue it is noted that the system throughput could be increased by slightly more than 10^3 times leading to an improvement in A_{min} of the same magnitude. The right hand axis of Figure 3 represents A_{min} for a system which would include a modest 25cm (10 inch) diameter collector on the interferometer.

Conclusions:

The L-SCADS sensor has the potential for operating as a transmissometer system element. The minimum detectable absorbance projected for this system compares very favorably with systems that are substantially larger and heavier and less suitable for field use.

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Table I

Performance Specifications

Spectral Range:	700 - 1400 cm-1
Resolution:	2, 4, 8, 16 cm-1
Scan Rate:	5, 10, 20, 40 scans/second
Field of View:	3 x 3 degrees
Spectrometer Aperture:	0.5 in diameter
Operating Mode:	Passive (Emission)

Figure 1

Transmissometer System

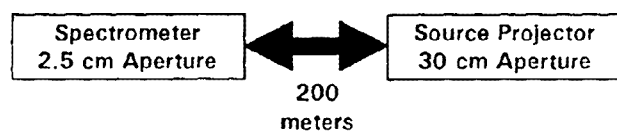


Figure 2
Signal to Noise Ratio
(2 cm⁻¹, 10 sec Observation, 200 m)

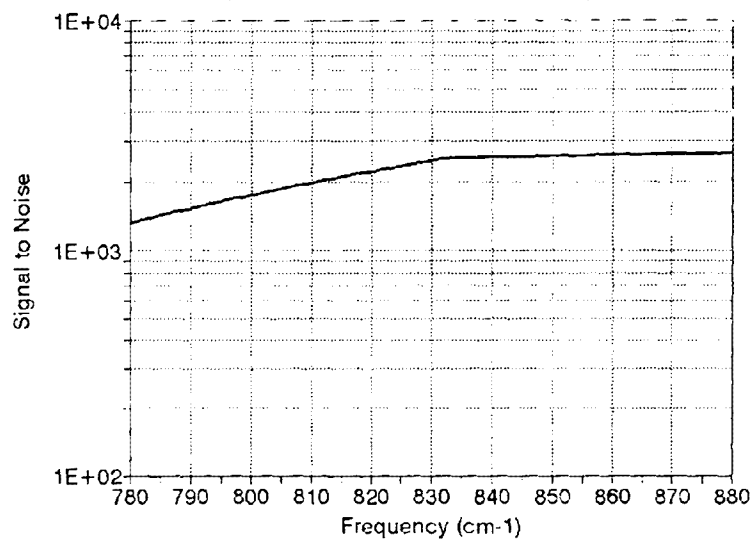
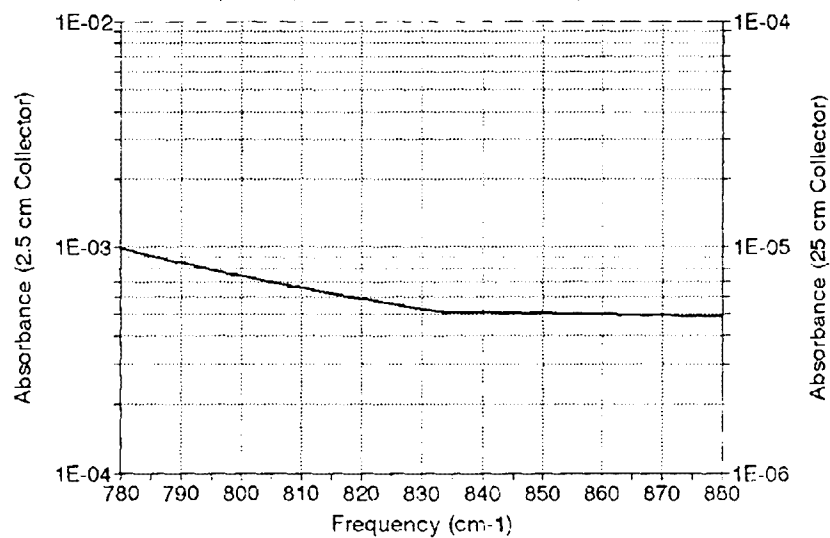


Figure 3
Minimum Detectable Absorbance
(2 cm⁻¹, 10 sec Observation, 200 m)



Joint Observations of the ETL Ozone Lidar and MPS System during the Los Angeles Free-Radical Study

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ABSTRACT

Lidar systems measuring ozone concentration and aerosol profiles in the lower troposphere can make significant contributions to the understanding of chemical and transport processes for regional air quality assessment and control. The Environmental Technology Laboratory of the National Oceanic and Atmospheric Administration has developed a compact, efficient, transportable lower troposphere ozone lidar, which is capable of continuously measuring ozone concentration profiles from near the surface to about 3 km with high range resolution, and aerosol backscatter profiles from near the surface to about 10 km. The ozone lidar was deployed in two field experiments in California in 1993. The second field experiment, discussed here, was the Free Radical Study in the Los Angeles basin during September 1993. The ETL Mobile Profiling System (MPS), co-located with the lidar during the study, continuously measured surface and profiles of meteorological parameters using remote and in-situ techniques. The meteorological information is combined with the ozone lidar measurements to provide valuable insight into the complexity of the ozone profiles.

INTRODUCTION

The Los Angeles Free-Radical Study (LAFRS) (3 Sept.- 22 Sept. 1993) was co-sponsored by EPA and the California Air Resources Board to study the formation of ozone (O_3) in the Los Angeles basin. During the experiment, the multi-wavelength ETL ozone lidar measured ozone profiles and aerosol profiles, while the MPS provided meteorological support for the air chemistry portion of the study and meteorological data for input to air pollution models and comparison with the co-located ozone lidar. Operations were conducted in Claremont, California, 5 km south of the San Gabriel Mountains and 20 km east of downtown Los Angeles, a major source region for precursors to O_3 . The experiment site was located on the eastern edge of the Los Angeles basin, some 60 km from the coast.

THE DIFFERENTIAL ABSORPTION LIDAR SYSTEM (DIAL)

The compact, transportable differential absorption lidar (DIAL), specifically designed for ozone and aerosol profiling in the lower troposphere (from near surface to about 3 km), was developed at the National Oceanic and Atmospheric Administration's Environmental Technology Laboratory (ETL), formerly Wave Propagation Laboratory (WPL). The ETL ozone lidar (Zhao *et al.*, 1993) transmits four wavelengths simultaneously. Two UV wavelengths at 266 and 289 nm are used for ozone profiling from ~100 m to ~3 km above the

surface with high range resolution. Another two wavelengths at 532 and 266 nm are for aerosol profiling from the surface to about 10 km. The maximum detection range for ozone is comparable to or greater than much bigger and more powerful lower tropospheric ozone lidar systems. The near range coverage is unique (Zhao *et al.*, 1992). The efficiency and the compactness of the lidar due to the innovative hardware design and improved signal processing technique (Zhao, 1990) make the system inexpensive and easily transportable.

A block diagram of the ozone lidar is shown in Fig. 1. The transmitter and the receiver are assembled on an optical breadboard 1.65 m long and 0.75 m wide. The height of the transmitter and receiver are about 0.6 m. The optical layout of the transmitter is shown in Fig. 2. A Continuum Nd:YAG laser (Model NY61-10) is used in the transmitter. The 10-Hz Nd:YAG laser is frequency-doubled (532 nm) and quadrupled (266 nm) and exits the output aperture as a single, three-color beam. The output energy at 266 nm is adjusted to be much lower than the maximum output (within the range of 20 to 40 mJ) to save the down-stream optics. The energy at 289 nm, which is generated from the residual energy at 532 nm using Raman shift and sum-frequency-mixing techniques, is in the range of 0.5-4 mJ. The two UV beams are adjusted to be collinear with an angle difference less than 50 μ rad. This angle is further reduced by a 3X beam expander to less than 17 μ rad. The receiver consists of a well-baffled Newtonian telescope with an 8 inch diameter off-axis parabolic primary mirror and a field of view of 1.0 mrad. The output beam of the telescope is then directed into a four-wavelength detector package. The transmitted beams are precisely aligned to the receiver using lateral transfer retroreflectors and periscopes to an accuracy of better than ± 50 μ rad. Calibration of the system is carried out in the horizontal direction during periods when the atmosphere is assumed to be horizontally homogeneous.

At present, a temporary data acquisition and processing system based on an IBM-486 personal computer is employed. Lidar signals at 532 and 1064 nm are digitized by a two-channel, 8-bit, 64 MHz digitizer, and the UV signals are digitized by a two-channel, 12-bit, 10 MHz digitizer.

The lidar is installed in a mobile laboratory, modified from a 20-foot sea-container. Thus the lidar is easily transportable. A movable temporary scanning mirror set can be installed on top of the sea-container to steer the beams in the horizontal direction (with a $\pm 15^\circ$ scanning capability) for horizontal and low-elevation observations and system calibrations. The system will be modified to include a full scanning capability within the next few years.

MOBILE PROFILER SYSTEM

The System Demonstration and Integration Division of the National Oceanic and Atmospheric Administration's (NOAA) Environmental Technology Laboratory (ETL) (Boulder, CO) in conjunction with the Battlefield Environment Directorate of the U.S. Army Research Laboratory (ARL) (White Sands Missile Range, NM) designed and built the Mobile Profiler System (MPS, Moran and Weber 1993, Wolfe *et al.* 1994). The purpose of MPS is to supplement existing rawinsonde data and improve thermodynamic and wind profiles with nearly continuous integrated data from an array of ground-based and satellite-borne sensors.

The MPS sensors include a 924-MHz phased-array wind and temperature profiler, a four-channel microwave radiometer, a surface meteorological tower and a satellite receiving station for processing satellite radiometer data. Data can be displayed or analyzed from each instrument separately or as blended thermodynamic and wind profiles. Some technological advances incorporated in MPS include improved methods of wind profiler and RASS sampling and processing and near real-time wind profiler quality control (Weber et al. 1992).

JOINT OBSERVATIONS OF THE OZONE LIDAR AND THE MPS IN THE LAFRS EXPERIMENT

The ozone lidar, the MPS, and other instruments were co-located at a site (elevation 433 m MSL) approximately 60 km east of downtown Los Angeles, in Claremont, California. During the experiment period, we experienced the highest surface ozone episode observed during 1993 in the Los Angeles basin. A series of ozone profiles taken during the highest ozone day, 9/9/93, are shown in Figs. 3a-3f. Atmospheric backscatter profiles at 532 nm are shown in Figs. 4a-4f. Balloon soundings of temperature and humidity profiles are shown in Figs. 5a-5d. The lidar observations confirm that both ozone and aerosol distributions are significantly affected by the meteorological conditions.

Keith (1980) describes climatological conditions typically found within the Los Angeles basin. The basin is characterized by a marine air influence and temperature inversion, especially during the hot summer months. Strong diurnal heating generates a consistent land/sea breeze. On-shore flow from the Pacific ocean is modified as it moves inland toward the experiment site. Therefore, the strength of the marine inversion is highly dependent on the strength and duration of the westerly winds. The westerly sea breeze increases in strength toward mid-afternoon to around $4\text{--}6\text{ ms}^{-1}$.

Previous studies (Roberts and Main, 1993) have shown that high concentrations of O_3 often exist aloft. Mechanisms for this include undercutting of the mixed layer by the sea breeze, slope flows along the mountains and their resulting return flow back toward and over the LA basin, and penetration of low-level polluted air into the inversion layer. Urban Airshed Models (UAM) have experienced difficulty in modeling these conditions due to the complexity of these patterns. The MPS and the O_3 lidar present a unique opportunity to observe the atmospheric structure and O_3 profile simultaneously, with temporal and spatial resolution providing a better description of these processes than conceivable in the past.

Figure 6 is a time series of 30-min average wind directions at three heights observed during a high pollution day as part of LAFRS (9 September 1993). Not shown is the height of the marine inversion or the mixing depth. The inversion, as monitored continuously by profiler/RASS and confirmed by balloon launches, is shallow and surface-based, extending to a height of 0.6 km. Surface heating lifts the base of the inversion, but is not able to completely break through the shallow strong inversion. Early morning surface winds are from the north-northeast, consistent with a drainage off the San Gabriel mountains. As local heating begins, the winds first shift to the southeast before becoming westerly. Wind speeds are light during this transition period. Winds above the surface (0.2 km), but below the inversion, exhibit a more easterly component corresponding to the larger scale land

breeze. This air appears to be riding over the colder local drainage off the mountains. Wind directions above the inversion (0.5 km) are consistent with those at 0.2 km, except for an earlier and more rapid shift from the easterly land breeze to a westerly sea breeze.

Figure 7 is a time series of the measured surface O_3 and the low-level peak in O_3 taken from the profiles observed by the lidar for the same time period as Fig. 6. This peak varied in height from 0.15 km to 0.35 km beginning just after sunrise. Absolute values of the lidar profile have not been aerosol corrected at this time. In Fig. 7 we see that the low-level peak in O_3 has an early morning maximum corresponding in time with the winds, below the inversion, shift in response to the inland heating. This maximum is believed to be transported O_3 trapped within the inversion layer. Surface O_3 is also rising at this time, but in a slower and steadier fashion consistent with local production. We start to see surface O_3 levels reflect the vertical mixing, represented by a slight decrease in O_3 , and the transport of higher levels of O_3 from the downtown Los Angeles area as the mixed layer grows and the winds become more westerly. Upper-level O_3 shows a similar pattern, but can not be fully explained by the winds. The mid-morning (1800 UTC) minimum is possibly the result of relatively clean air, cut-off from the surface, transported from Los Angeles. As heating increases the mixing depth over Los Angeles, O_3 is carried aloft and detected by the lidar as it advects downwind. This would explain why the elevated O_3 so closely follows the trend in O_3 at the surface. This analysis is for only one day with strong local heating and a well defined land/sea breeze, but similar data sets can be used to examine other days during LAFRS with different wind patterns and vertical mixing.

SUMMARY

As can be seen from the comparison for a single day during LAFRS, the complexity of the region and its meteorology increases the possible pollution scenarios. Further analysis is needed to obtain a better understanding of the transport of O_3 within, into, and out of the Los Angeles basin, especially because of the correlation seen between changes in both surface and elevated O_3 levels and wind direction. The role vertical stability plays also needs to be examined further through use of the continuous RASS temperature profiles. The O_3 lidar and MPS together should lead to a better understanding of the mechanisms involved.

ACKNOWLEDGEMENT

The joint ozone lidar - MPS observations in the LAFRS were supported by the California Resources Board (CARB). The authors wish to thank Robert Weber, Dick Cupp, and Judy Schroeder for their hard work in participation of the experiment, and to Bart Croes, Lowell Ashbaugh, and Ash Lashgari of CARB for their encouragement and help.

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BLOCK DIAGRAM OF THE OZONE LIDAR

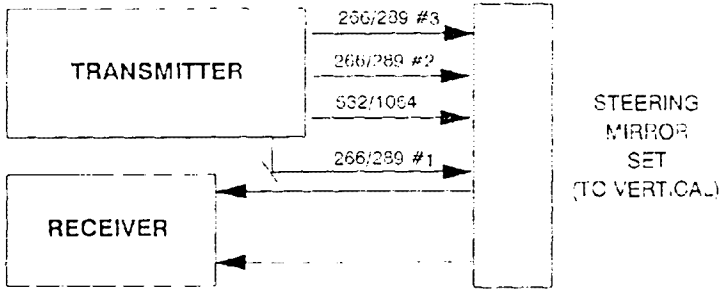


Fig. 1

OPTICAL LAYOUT OF THE OZONE LIDAR TRANSMITTER

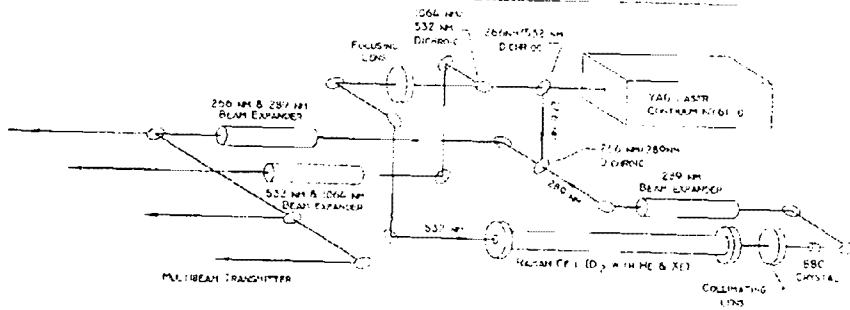


Fig. 2

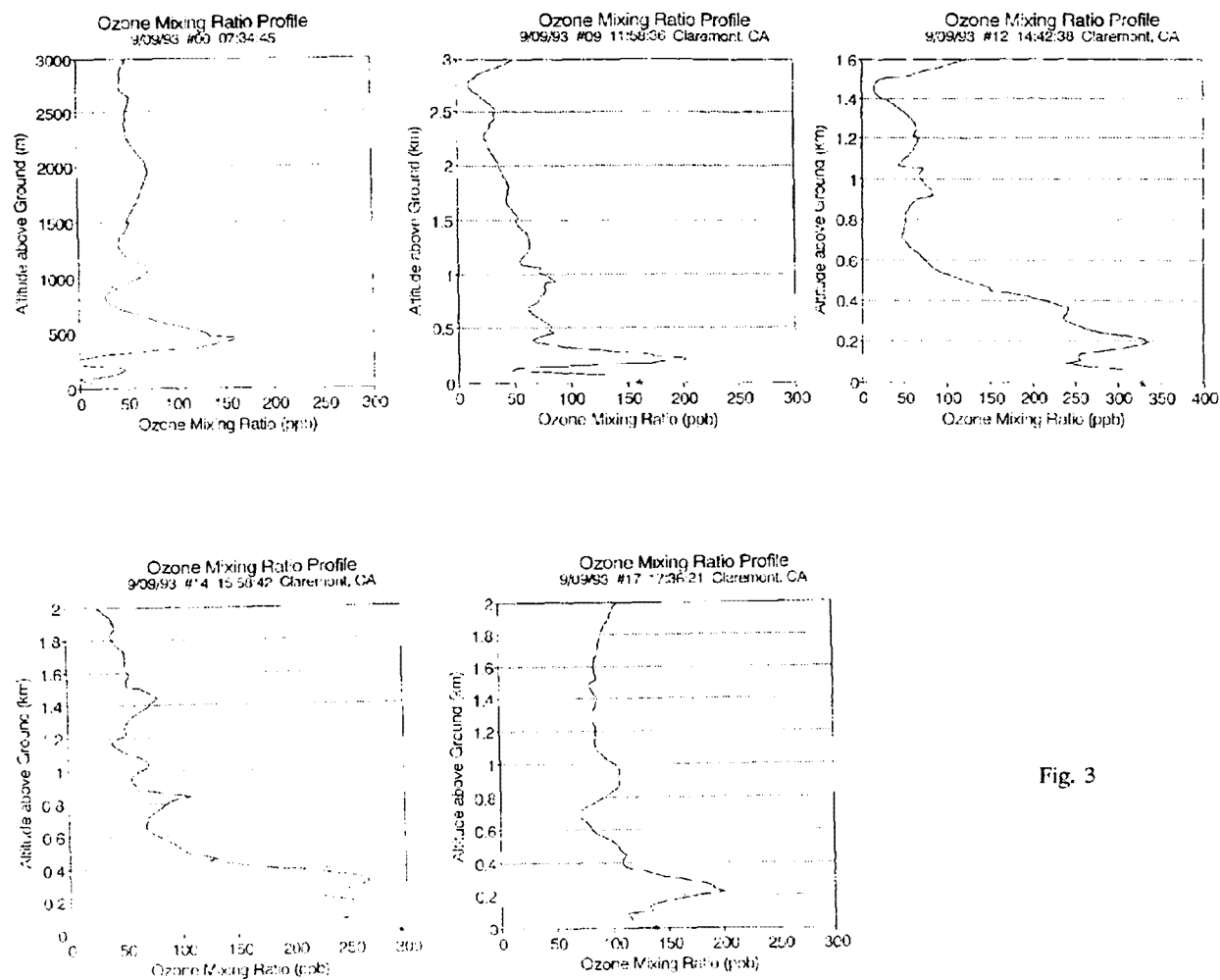


Fig. 3

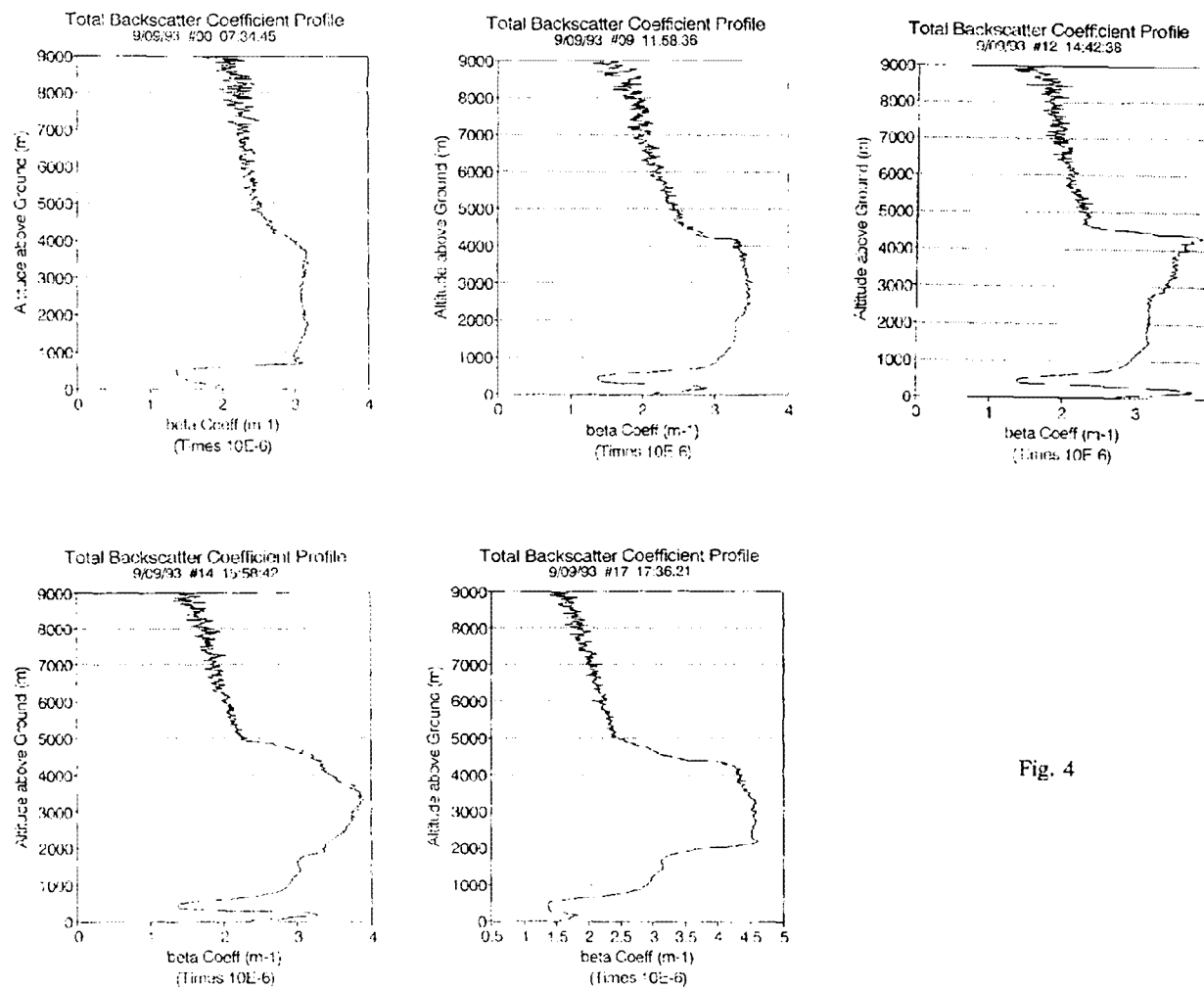


Fig. 4

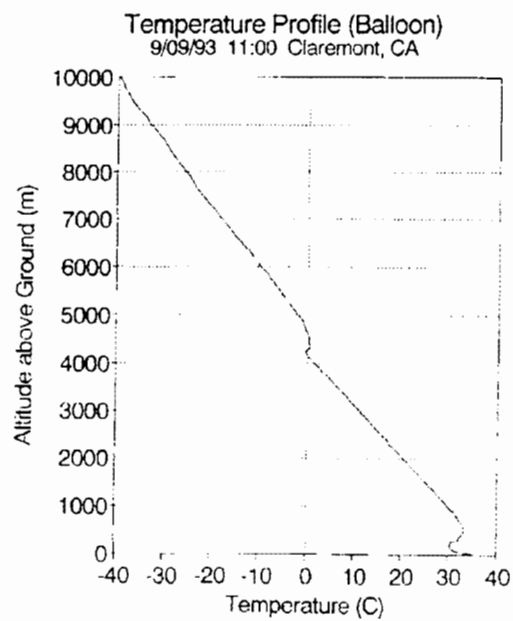
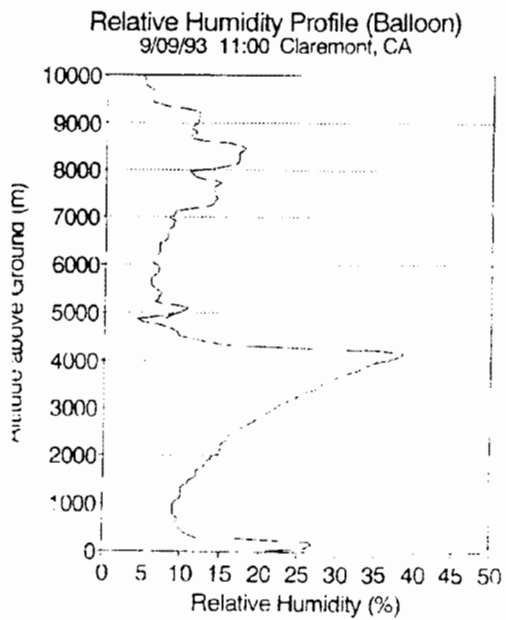
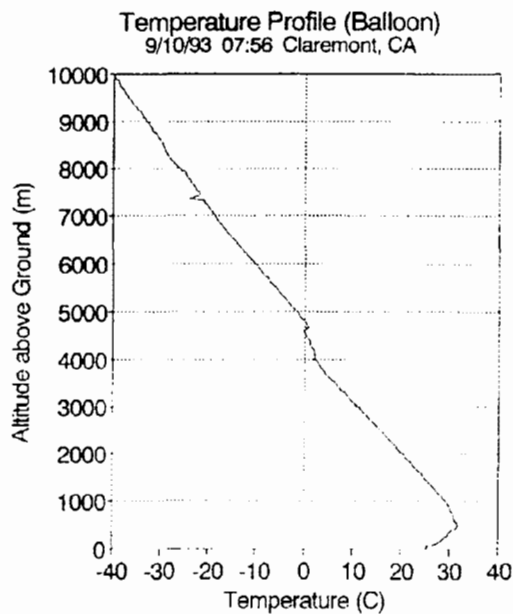
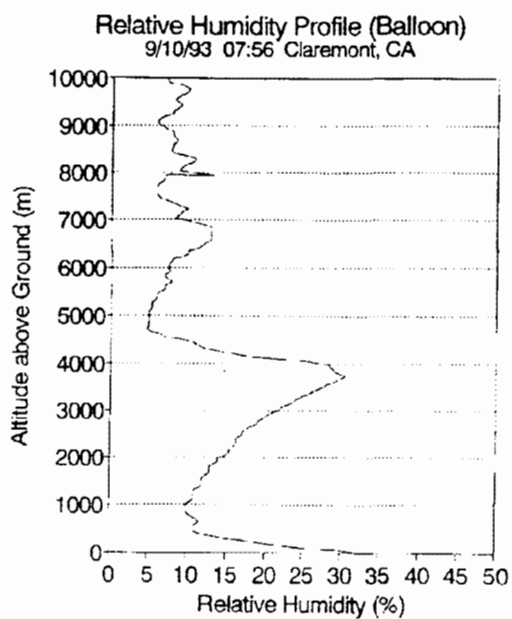


Fig. 5

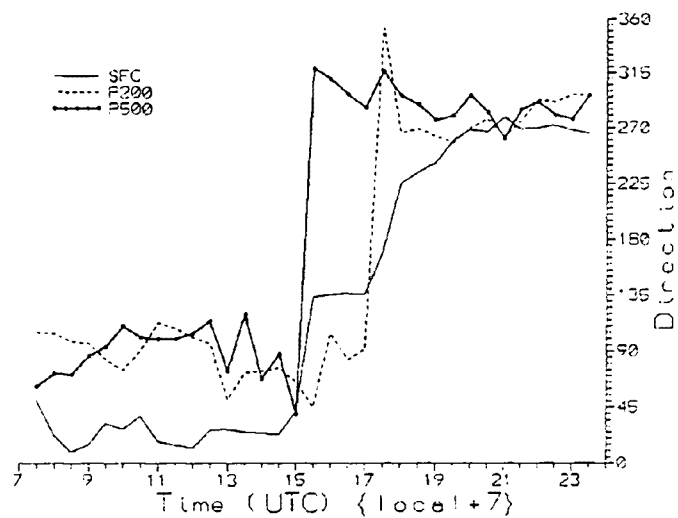


Fig. 6 Time series of 30 min average wind directions (surface and profiler 0.2 and 0.5 km AGL) at 0700 UTC 9 September until 0000 UTC 10 September 1993. Local time equals UTC-7 hrs.

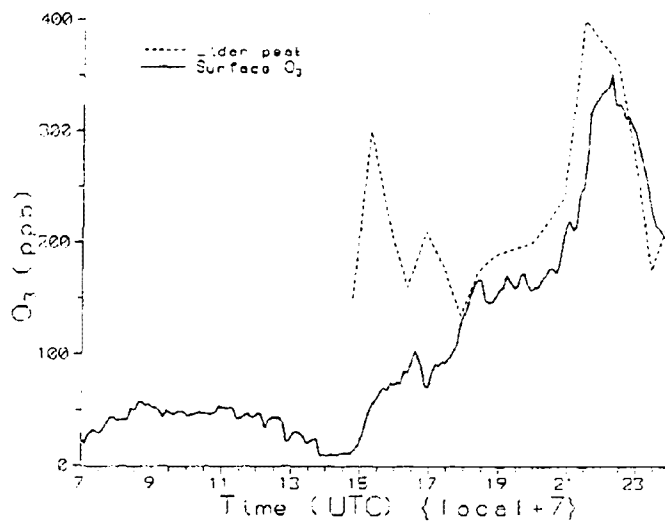


Fig. 7 Time series of surface O_3 and peak low-level O_3 taken from the lidar profiles for the same time period as Fig. 6. Low-level peak represents 7 min vertical sample every half-hour.

Fourier Transform Microwave Spectroscopy: A Potential New Analytical Tool For Trace Gas Species

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ABSTRACT

A pulsed molecular beam Fabry-Perot microwave spectrometer has been developed that has demonstrated sensitivities to most polar gas-phase molecular species that are in the low parts-per-billion (ppb) range. The highest sensitivity is obtained using neon or argon carrier gas but nitrogen or air can also be used with some loss in sensitivity due to the less efficient cooling in the molecular beam with diatomic gases. The minimum detectable concentrations for several representative compounds has been determined. These include SO_2 , propene, acrolein, and methyl t-butyl ether. Considerable attention has been given to making the instrument robust for use in industrial laboratories. The instrument is controlled using a standard Intel 486 based computer. A Graphical User Interface (Windows-type) operating system has been developed that makes the instrument extremely user-friendly allowing all instrument control functions to be carried out using a mouse.

INTRODUCTION

The technique of Fourier transform microwave spectroscopy (FTMS) was pioneered in the late 1970's and early 1980's by Balle and Flygare¹. Our first instrument at NIST was constructed in 1985². Since that time many improvements have been made to this instrument, some of which have been previously described³. These new improvements have increased the sensitivity of the instrument as well as made it much easier to use. A software package has been developed that allows all instrument control functions to be accomplished using a standard computer mouse.

EXPERIMENTAL

Instrument

A block diagram of the instrument is shown in Figure 1. The instrument consists of a Fabry-Perot microwave cavity formed by two diamond-turned aluminum mirrors that are 35 cm in diameter. The mirrors are housed in a vacuum chamber that is approximately 1 m in length and 60 cm in diameter. The vacuum chamber is pumped by an 8000 l/s diffusion pump and a 2.5 m³/min roughing pump. A commercial pulsed molecular beam valve has been modified with two 1.5 mm inlet lines that allow gas to enter the valve near the valve tip. The flow through these inlet lines is controlled by mass flow controllers. Excess gas flows out the top of the pulsed valve allowing a continuous fresh sample at the nozzle tip. In a typical experiment the gas to be analyzed is entrained at low concentration levels (up to several %) in an inert carrier gas stream such as air, nitrogen, neon or argon. The expansion of the gas from the high pressure side of the nozzle into the vacuum chamber cools the molecules in the gas pulse to near 1 K. At this temperature only the lowest few rotational energy levels of the molecules are populated. Thus by probing rotational transitions from these low lying energy levels, a tremendous increase in signal to noise is obtained compared to a room temperature sample. This enables one to study larger gas phase species with complex rotational spectra with the ease that one usually associates only with light diatomic and triatomic species.

The pulsed valve can be mounted to pulse either perpendicular to the Fabry-Perot cavity or collinear with the cavity axis. For the results reported here, the valve was mounted on the back side of one of the Fabry-Perot cavity mirrors and pulses the gas through a 1 mm diameter hole

through the mirror parallel to the cavity axis. The positions of both mirrors are controlled with computer-driven motor micrometers. The microwave radiation enters the cavity through a L-shaped coaxial antenna located at the center of the mirror.

Microwave radiation from a microwave synthesizer is synchronously pulsed into the microwave cavity by opening a microwave switch for a short time (1-5 μ sec) when the molecules from the nozzle are in the cavity. This generates Fourier components of the microwave radiation that cover ~ 1 MHz in bandwidth. If the molecules in the molecular beam have a rotational transition within the bandwidth of the cavity they are "pumped" by the Fourier components of the microwave radiation that has been pulsed into the cavity. After a few microseconds of delay, the molecular emission signal from the cavity is digitized for several hundred microseconds as the molecules that were pumped by the original microwave pulse relax back to their original state. Once the decay signal has been stored in the computer it can then be Fourier transformed into the frequency domain. This entire process can be repeated at 2-10 Hz for signal averaging or real-time monitoring of polar trace-gas species. A typical Fourier transformed signal is shown in Figure 2. The two Doppler components of the signal arise because the molecular beam is traveling in one direction down the cavity axis while the microwave radiation is traversing the cavity in both directions, thus generating a forward and reverse Doppler component of the molecular signal. The true rotational frequency is the average of the two frequency components.

Sample Preparation

Initial tests have been performed with several compounds in order to assess the minimum detectable concentration for each molecular species. In these tests, identical samples were prepared by filling aluminum cylinders with approximately 533 Pa [4 torr] of the gas of interest. The cylinders were then pressurized to 0.65 MPa [80 psi] which makes the final concentration approximately 816 ppm. In most cases this sample concentration provides signals that are too intense to be measured accurately. In order to determine the Minimum Detectable Signal (MDS) for each species, rotational transitions from some of the less abundant naturally-occurring isotopes were recorded. The natural abundances of the various isotopic species are given in Table 1. These rare isotopes provide a built-in measure of relative intensities that spans several orders of magnitude. The only restriction is that an isotopic species has been previously studied so that the frequencies of the transitions are known.

Since some variation in rotational transition strength with carrier gas is expected, three identical samples were usually prepared. Samples were prepared using neon, argon, and nitrogen as the inert carrier gas. The most intense signals are obtained using neon, followed by argon and then nitrogen. Indications are that neon provides good cooling and very little complexation while argon provides good cooling but it also tends to form more bimolecular complexes with the sample of interest. Nitrogen does not cool as well as the monatomic gases and hence provides the weakest molecular signals. The signal strength in nitrogen typically is a factor of ten weaker than in neon. Variation of signal strength is shown in Figure 3 where the same rotational transition of a ^{13}C isotopomer of acrolein (8.6 ppm) is shown for the three different carrier gases.

Figure 4. shows a rotational transition of one of the deuterated isotopomers of acrolein in neon which is present in natural abundance in the 816 ppm sample at 122 ppb. The upper trace shows the results of one gas pulse from the nozzle while the lower trace shows the results of averaging 100 gas pulses (50 seconds of integration). The signal-to-noise ratio improves as the square root of the number of pulses so the lower trace should be a factor of ten better than the upper trace.

Sulfur Dioxide Experiments

Sulfur dioxide is a common emission product in many combustion processes. Its rotational spectrum is rather sparse in the spectral region accessible by the current FTMS thus, the only transition that can be monitored is the $2_{02} \leftarrow 1_{11}$ transition in the vicinity of 12 GHz. Unfortunately

this transition is approximately 60 GHz higher in energy than the lowest energy transition. Thus in the cold molecular beam, the lower state is not well populated. However, the signals are still reasonably intense and good sensitivities can be obtained. A number of Standard Reference Gas samples of SO₂ in nitrogen are available from NIST as Standard Reference Materials (SRMs). Several of these samples were used to assess the linearity of response of the instrument. SRMs of approximately 50, 500 and 1000 ppm of SO₂ in nitrogen were used to obtain the data in Figure 5. A least squares fit of the three data points indicates that the instrument response is linear over more than an order of magnitude in signal strength. Currently, an 8-bit digitizing board is being used, however, installation of a 12-bit digitizer would greatly extend the linear range of the instrument. The signal indicated at 360 ppm is a sample that was prepared to test the gas variation (Ne, Ar, and N₂). This illustrates how the instrument can be calibrated using SRM samples.

Carrier Gas Blending

A set of experiments was carried out using the $J = 1 \leftarrow 0$ rotational transition of carbonyl sulphide (OCS) to see if blending varying amounts of Ne or Ar could be used to enhance the signal strength of a sample in a nitrogen carrier gas stream which would be the typical carrier gas in most industrial process streams. In these experiments, commercial mass flow controllers were used to blend the gases in our flow nozzle. Figure 6 shows that an increase in signal strength is obtained by blending up to approximately 50% Ne or Ar. In this plot, the normalized signal intensity ($\mu\text{V/ppm}$) is plotted vs the % of inert gas added to the total carrier gas stream. With Ne, an order of magnitude increase is obtained while with argon only a factor of five is realized. It is not certain why the signal intensity drops after the addition of 50% inert gas but it may be due to inefficient mixing of the two gases at the nozzle tip. The important point however is that the signal strength can be increased by an order of magnitude just by diluting with neon carrier gas.

Searching for Unknown Molecular Species

The software package available with our instrument allows completely automated, unattended searching with the instrument. This is advantageous if unknown chemical species are present in the process gas stream. Of course if certain molecular species are expected it is quite simple to just program the computer to quickly jump between a given set of frequencies to check for any number of different compounds.

CONCLUSIONS

Table II lists several compounds that have been studied to determine the minimum detectable signal for each species. All of the compounds studied to the present time have detection limits that are in the low to mid ppb region when neon carrier gas is used and 100 gas pulses are averaged. This list is currently being expanded to include a number of different classes of compounds. Additional improvements to the software and hardware of the instrument should allow us to realize another order-of-magnitude improvement in sensitivity of the instrument.

In addition to the real-time analysis capability of the instrument, all the standard water management and concentration techniques commonly used in gas chromatographic-mass spectrometric applications can also be employed with the FTMS method, thus, easily extending the minimum detectable signals down into the parts-per-trillion region. The high sensitivity of the FTMS technique coupled with the 100% species selectivity should make it an attractive procedure that could be used in a variety of process monitoring and control situations as well as a competitive extractive stack-gas sampling technique for trace gas analysis.

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Table I. Natural abundance of a number of the isotopic species.

Isotopic species	% Natural abundance. ^a	Concentration. (ppm)
¹⁶ O	99.76	816
¹⁸ O	0.2	1.63
¹⁷ O	0.04	0.333
¹² C	98.89	816
¹³ C	1.11	9.090
¹ H	99.99	816
² H	0.015	0.122

a. The natural abundance is relative to each individual atom, ie O, C, and H.

Table II. Minimum detectable signals in the FTMS instrument for several molecular species.

Compound	Formula	MDS ^a (ppb)
Acrolein	$\text{H}_2\text{C}=\text{CHCHO}$	3
Sulfur Dioxide	SO_2	13
Propionaldehyde	$\text{CH}_3\text{CH}_2\text{CHO}$	100
Methyl t-Butyl ether	$\text{CH}_3\text{OC}(\text{CH}_3)_3$	190
Propene	$\text{CH}_3\text{CH}=\text{CH}_2$	250

^a Minimum Detectable Signal for the following set of parameters: Neon carrier gas; average of 100 gas pulses taken at a 2 Hz repetition rate (50 sec total integration time) assuming a signal-to-noise ratio of 1.

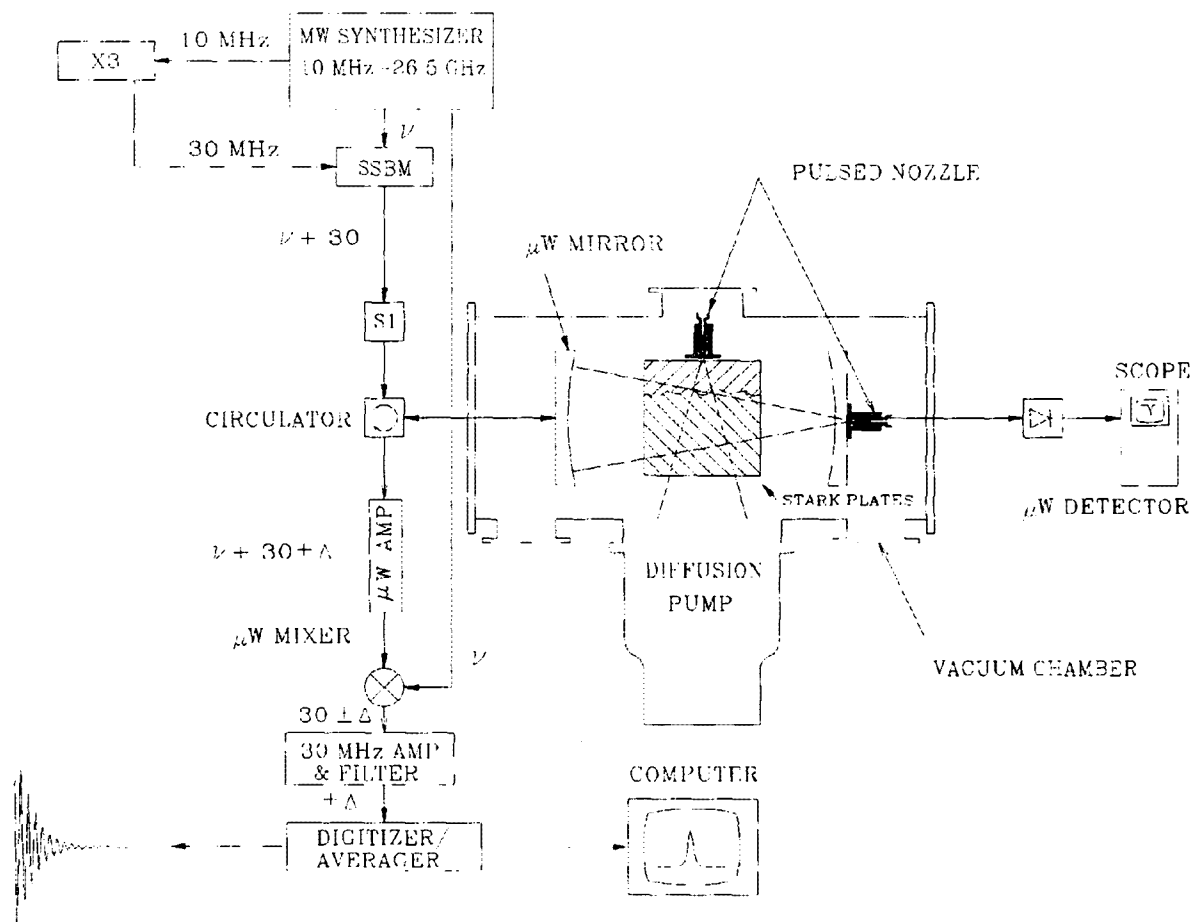
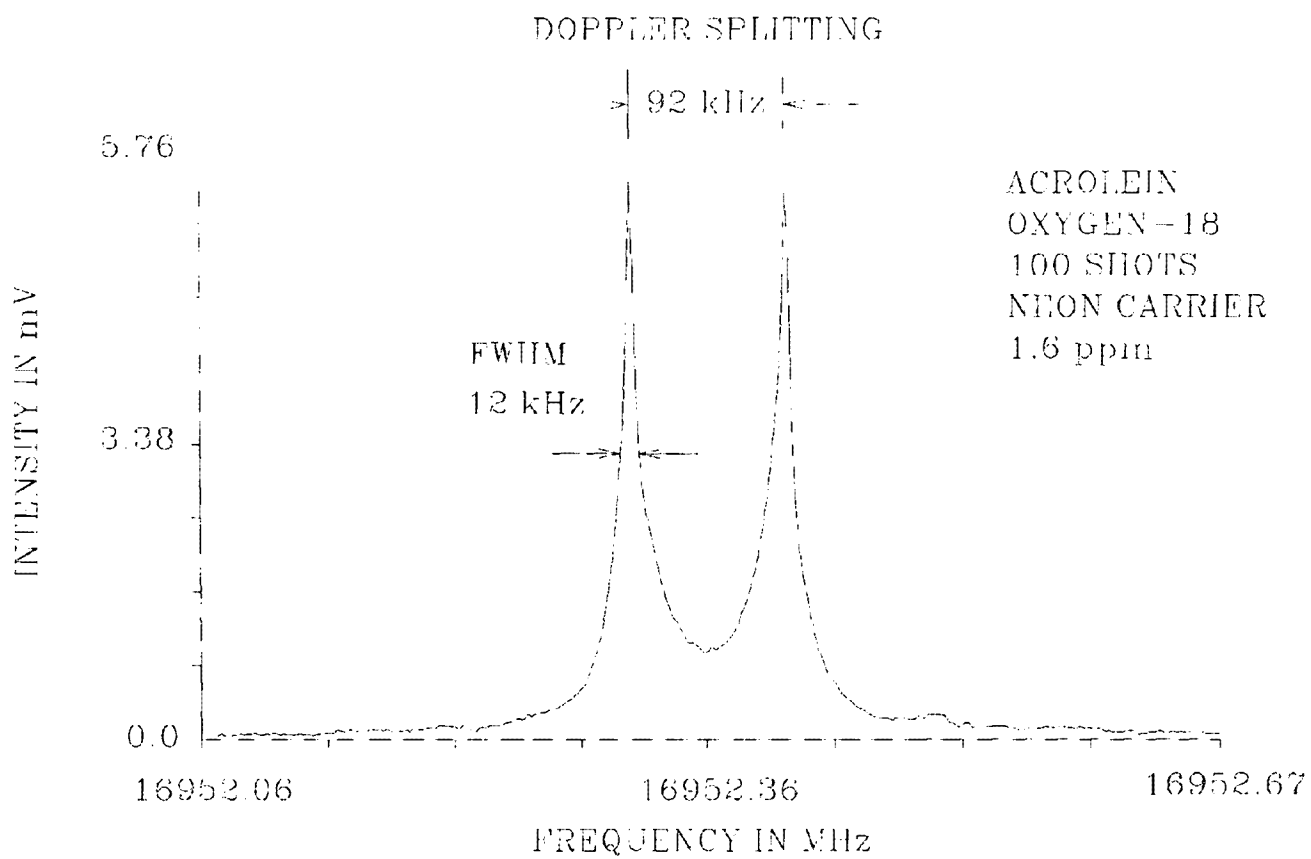


Figure 1. Schematic diagram of the Fourier transform microwave spectrometer.

Figure 2. Sample spectrum of a frequency domain signal from the FWS.



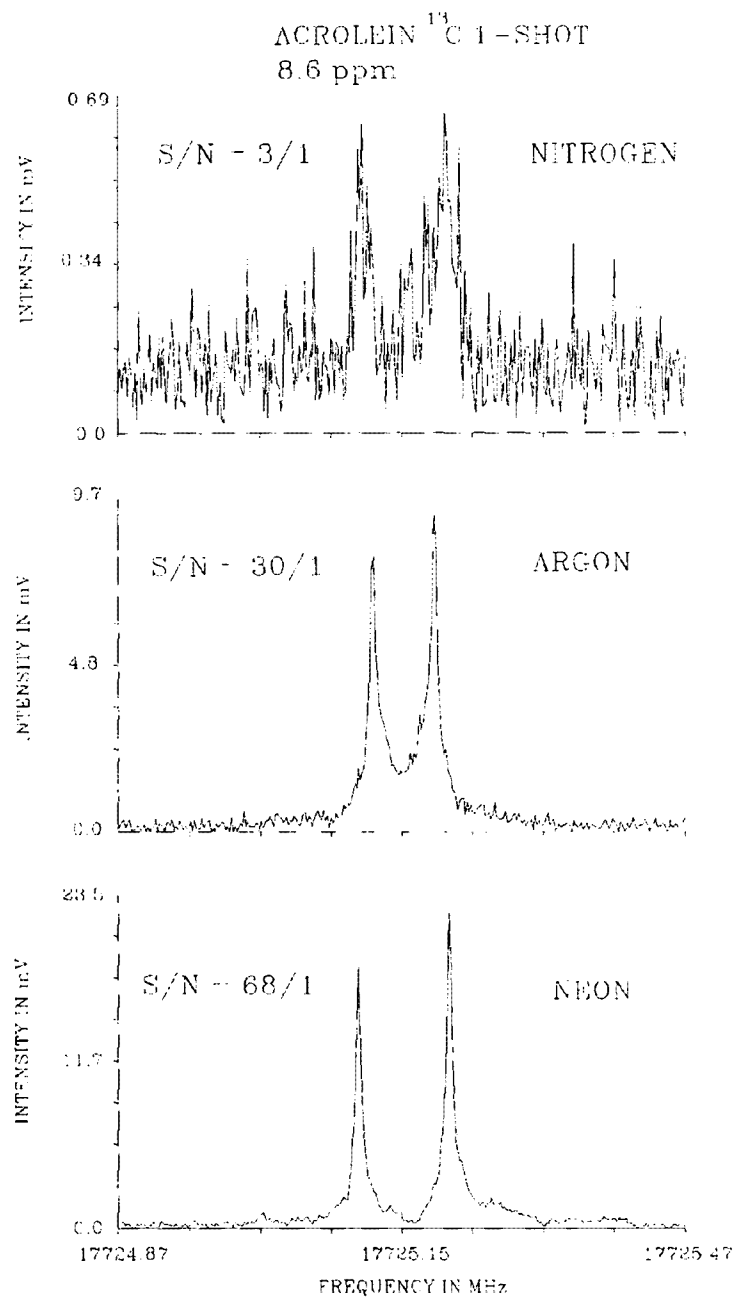


Figure 3. Frequency domain spectra of a ^{13}C isotopomer of acrolein showing the signal intensity variation with carrier gas (one gas pulse in each case).

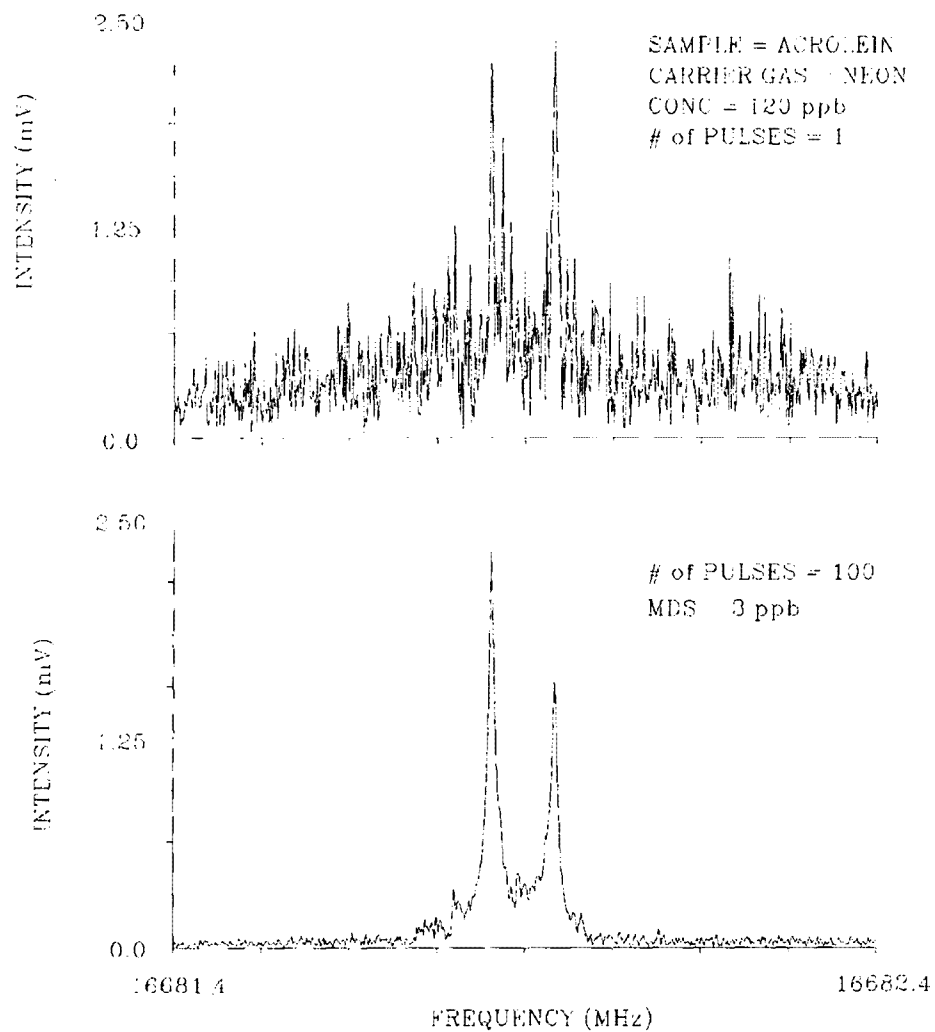


Figure 4. Frequency domain spectrum of a deuterated isotopomer of acrolein in natural abundance (120 ppb). This figure shows the signal-to-noise improvement obtained with averaging.

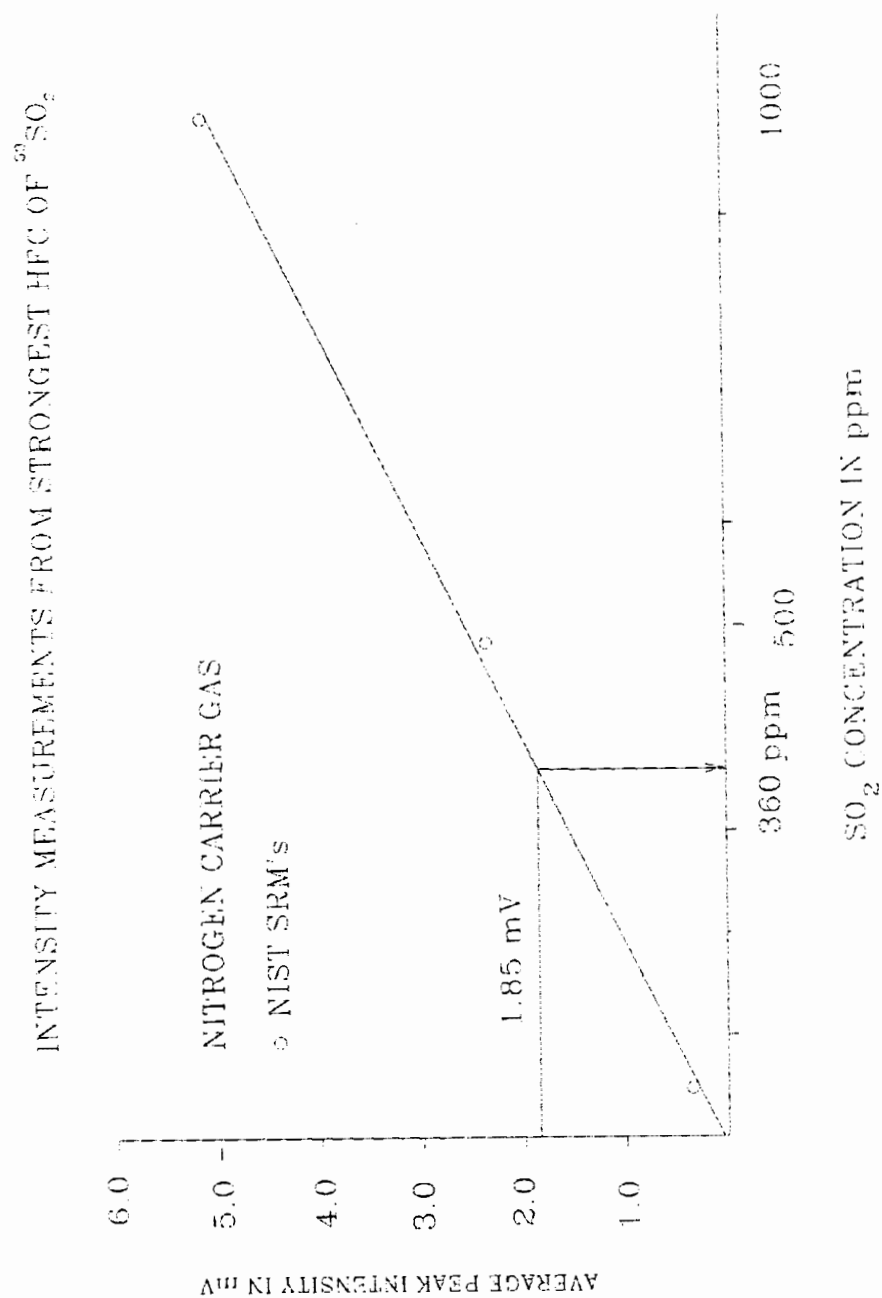


Figure 5. A plot of signal strength versus SO₂ concentration obtained using three different NIST SRMs. The 360 ppm plot indicates how the plot was used to determine the concentration of an unknown sample.

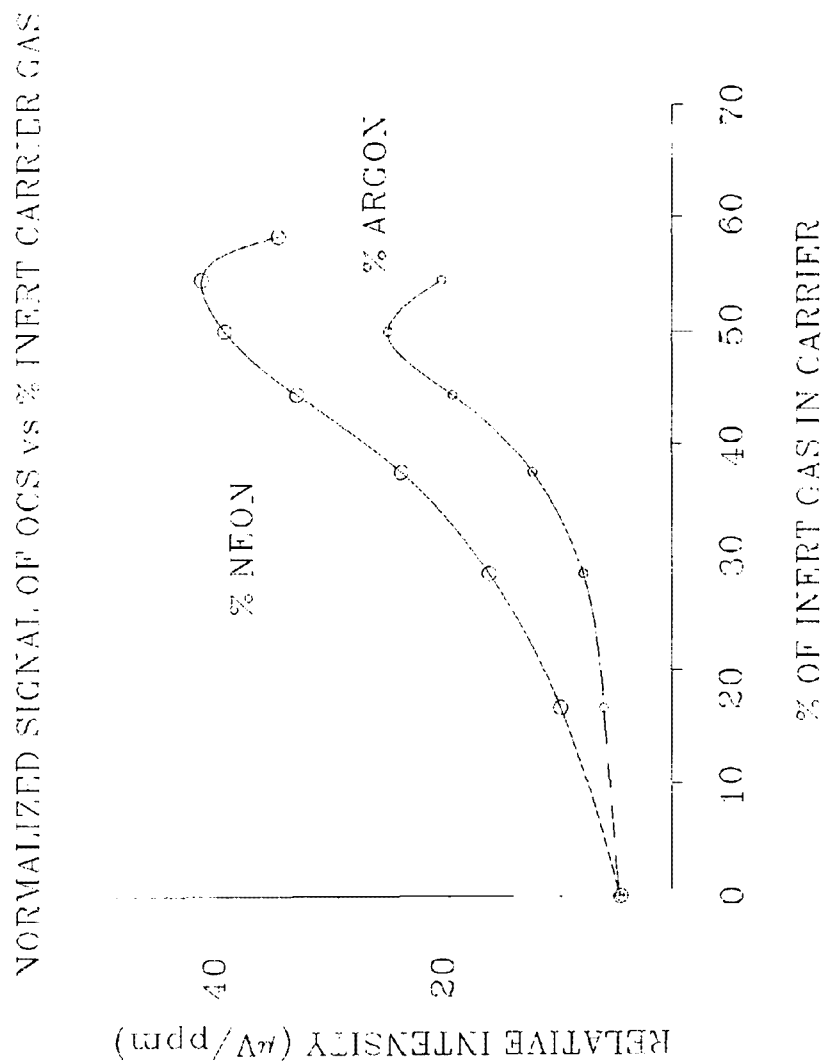


Figure 6. A plot of the normalized signal strength ($\mu\text{V/ppm}$) versus percent of Ne or Ar blended into a N_2 carrier gas stream. An order of magnitude improvement in signal strength is obtained by blending 50% Ne into the N_2 carrier gas.

Monitoring Air Pollutants by Molecular Beam Microwave Spectroscopy

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The molecular beam Fourier transform microwave spectroscopy has been proved to be a very powerful tool to determine molecular parameters in the gas phase with high precision and high resolution. It will be shown that this method is also suitable for quantitative analysis, this means the evaluation of concentration of single components in complex gas mixtures like pollutants in air.

Microwave spectroscopy is mainly restricted to the investigation of polar molecules. Many industrial solvents, chlorofluoromethanes or other air pollutants belong to this group of substances. Presently about 2000 molecules have been analyzed and their parameters published. Many of these gases may be monitored with only one instrument. To switch from one substance to another takes about one minute.

Due to the high resolution of the apparatus there is nearly no cross sensitivity. The usable range of concentration is from percent to the lower ppm at least, but may be lower depending on the gas. The total measuring time ranges from seconds to minutes depending on concentration and substance.

The method and the apparatus will be presented and some features of instrument will be discussed.

**The Effect of Temperature on the Ability to Collect Data:
The MDA Scientific Open-Path Fourier Transform Infrared Spectrometer**

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ABSTRACT

The experience of several users of the MDA Scientific, Inc. open-path Fourier Transform Infrared spectrometer has shown that the system has difficulty collecting data at low temperatures, especially when the instrument is subjected to long periods at low temperatures when the instrument is not turned on. The interferometer needs to be sufficiently warm to find its zero point before data collection can begin. Since delays in data collection can result in costly delays in beginning operations at a clean-up site or loss of data for an industrial study, it is important to understand the parameters of the temperature effects and how to reduce their effect on delays in data collection. For this reason, Remote Sensing=Air, Inc. (**RS=A**) decided to test its instrument under varying temperature regimes to document the temperature at which the instrument would begin collecting data and the best ways to attain that temperature to avoid unnecessary delays. The instrument was set up in an unheated area of a basement and the ambient temperature and the temperature of the instrument below the interferometer were collected and recorded every minute.

Data are presented showing the temperature at which the instrument begins collecting data, the increase in final equilibrium temperature due to operation of the instrument, to adding heating pads, and to adding insulation. These data should help determine which means of increasing the temperature will be effective under various low temperature regimes. Coincident with the **RS=A** study, a group at ManTech Environmental Technologies, Inc. (ManTech) performed a similar test with their MDA system with very similar results. The results of both studies are presented.

It should be noted that other OP-FTIR instruments may also have trouble collecting data when cold; however, MDA Scientific instruments were available for the two studies reported.

INTRODUCTION

Open-path optical remote sensing has been used very successfully over the last several years in monitoring air quality at industrial facilities^{1,2,3,4} and at hazardous waste sites.^{5,6,7} During such monitoring programs, it has been noted that there is difficulty in collecting data with the MDA Scientific open-path spectrophotometer at low ambient temperatures especially when the instrument has been exposed to these low temperatures while the instrument is not

turned on. Since delays in data collection can result in costly delays in beginning operations at a clean-up site or loss of data for an industrial study, it is important to understand the parameters affecting the influence of temperature on data collection and how to reduce delays in data collection. For this reason, Remote Sensing=Air, Inc. (RS=A) decided to test its instrument under varying temperature regimes to document the temperature at which the instrument would begin collecting data and the best ways to attain that temperature, thus, avoiding unnecessary delays.

METHODS AND MEASUREMENTS

Both the RS=A and ManTech studies used MDA open-path spectrometers and a means of determining the ambient and instrument temperatures simultaneously. The RS=A OP-FIR system has the detector cooled using a Stirling engine while the ManTech system uses liquid nitrogen for cooling the detector.

RS=A Study

Purpose and Goals

The purpose of the study was to gain an understanding of the parameters involved in determining the time that it would take for the system to begin collecting data under various temperature regimes. The goals were:

- To be able to predict how long it would take the OP-FIR to start collecting data under various low temperature regimes.
- To be able to control the time needed to initiate data collection (i.e. shorten it) through the use of insulation and/or heating devices.

The following questions were to be answered by the study:

- At what temperature does the instrument begin collecting data under various cold temperature regimes?
- What is the increase in final equilibrium temperature provided by having the instrument on?
- What is the increase in final equilibrium temperature provided by using insulation with the instrument on?
- What is the increase in final equilibrium temperature provided by using a heating pad?
- How long does it take for the instrument to reach the temperature required for collecting data under various cold temperature regimes?
- Once collecting data, will the instrument continue to collect even if the temperature drops?

Temperature Determinations

Temperatures were monitored continuously using a DataBear® datalogger and sensors (LPT#1400) using the Sense-Your-World!® software (Langan Products, Inc.) for transfer of data to RS=A's analytical programs. The DataBear® datalogger allows simultaneous collection of temperature data at two locations with the data determined each second and saved at

intervals from one second to a maximum of 32767 seconds. Temperatures were also determined using a standard thermocouple voltmeter and from Radio Shack. Temperature data were collected 24 hours per day except when dumping the data. The usual interval was every 10 minutes.

OP-FTIR System and Set-up

The **RS=A** open-path FTIR instrument studied was a MDA Scientific, Inc. open-path FTIR (model 282000) with a Stirling engine cooler for the detector. The system was configured in the unistatic mode using a 35 cm x 35 cm retroreflector. Data were collected using the continuous monitor application developed by MDA. This application made it possible to determine exactly when data collection began by recording the time of the spectra collected. The instrument was set up in an unheated and poorly insulated area of a basement during a very cold time in St. Louis (January 1994). The path-length was necessarily short due to space restrictions; the path length varied from 7 m to 3 m during the study. Data collection times varied between five minutes and one hour. The computer was set up in a warmer section of the basement and connected to the spectrometer with 250 meters of fiber optic cable.

ManTech Study

Purpose and Goals

The ManTech data reported here are part of a larger, on-going study to develop a database of information on data collected over a long time span in one location. In addition to the spectra collected, operating parameters related to the data collection were also collected. These operating parameters included instrument and ambient temperature data.

Temperature Determinations

Temperatures were determined simultaneously inside the OP-FTIR instrument, in the shack in which the OP-FTIR was housed, and the outside of the shack using a Rustrack Ranger II® datalogger with three probes (National Instrument LM35CZ). The ambient relative humidity was also monitored and logged using the datalogger. One of the temperature probes was inserted inside the instrument and hung just above the interferometer while the top of the OP-FTIR instrument was left unscaled. Temperature data were collected every minutes 24 hours each day.

OP-FTIR System and Set-up

The MDA Scientific system used by ManTech was similar to that used by **RS=A**; however, the ManTech unit used liquid nitrogen for cooling the detector rather than the Stirling cooler used by the **RS=A** unit. Also, because the ManTech unit is opened frequently, it is not under constant nitrogen pressure as the **RS=A** unit is.

The ManTech OP-FTIR system was set up in a shack at one end of an open field near the EPA complex with the retroreflector on a tower at the other end of the field. The shack was heated and was kept closed at night (5 pm to 8 am) and opened each morning to allow the OP-FTIR beam to access the retroreflector. The instrument was left on over night but was not collecting data. Data collection occurred from 8 am to 5 pm except for special overnight studies not reported in this paper.

DATA ANALYSIS AND RESULTS

Both the **RS=A** and ManTech data from the respective dataloggers (temperature, date and time) were transferred to QuattroPro® for graphing and analysis. The difference in the temperature between the ambient air and either under the interferometer (**RS=A**) or above the

interferometer inside of the instrument (ManTech) was determined for each data set. For the **RS=A** data, the time of increase and final temperature difference when the instrument was turned on, when the heating pads were turned on, and when insulation was used was determined for each data set. These data were used to answer the questions posed above and presented in the Conclusions and Recommendations section of this paper.

Temperature of Start of Data Collection

In order to determine the temperature at which the instrument would begin data collection, the instrument was turned off at night and left in the cold area of the basement. Sometimes the instrument was turned off but with insulation and/or the heating pad on. The instrument was turned on in the morning and the Continuous Monitor software started. The set up could then be left unattended and the spectra and concentration data were automatically saved as data began to be collected. Plots of data from three days of monitoring are shown in Figures 1 - 3. A time series plot of temperature of first data collection and ambient temperature is presented in Figure 4. As can be seen, the temperature under the instrument at which the instrument begins collecting data is very consistent even at widely different ambient temperatures. The time to reach that temperature does vary with ambient temperatures and whether the instrument is heated and/or insulated. Since the ManTech instrument was usually left on all of the time and kept in a heated shack during the night, there was usually no problem in initiating data collection. However, on a few occasions they encountered similar problems with initiating data collection at low temperatures.

Once the instrument began collecting data, the temperature could drop significantly and data would still be collected (see Figures 5 and 6). Neither the **RS=A** group nor the ManTech group observed any differences or problems with data collected at low temperatures (below those at which data collections could be initiated).

Increase in Final Equilibrium Temperature Provided by the Instrument Running

The increase in final equilibrium temperature provided by the heat produced by having the instrument turned on can be seen in Figures 2, 3, and 5 for the **RS=A** study and Figures 6 and 7 for the ManTech Study. The ManTech data indicate a slightly higher difference than the **RS=A** data. This higher difference is likely due to the positioning of the probe inside of the instrument rather than having it taped to the outside as done for the **RS=A** study. The 10 to 12 °C increase due to having the instrument on is usually enough to allow data collection under cool but not cold conditions. Again, the plots show that the final difference appears to be independent of the ambient conditions.

Increase in Final Equilibrium Temperature Provided by External Heating and Use of Insulation

The temperature of the instrument was significantly increased by the use of heating pads attached under the instrument just below the interferometer. The rate of increase observed by the **RS=A** group may be misleading since the heating pad and probe were both attached under the interferometer and the probe (even though separated from the heating pad by styrofoam) was likely to have been affected more quickly than the interior of the instrument. Figures 1-3 indicate the effects of the heating pads and/or insulation.

The temperature at which data collection occurs and the final temperature rise for various heating and insulation scenarios do not depend on the ambient temperatures. However, the rate of rise and, thus, the time before data can be collected does appear to depend on the ambient temperature. Because the **RS=A** probe was not inside the instrument, the rates determined are probably skewed toward faster rates for external heating. At ambient temperatures from -10 to 0°C, it took between 3 and 5 hours to start data collection with both the instrument and heating pad on.

CONCLUSIONS AND RECOMMENDATIONS

It is concluded that there are several ways of ensuring that the instrument will be at the proper temperature for data collection and that it is useful to understand the capabilities of each. The answers to the questions posed at the beginning of the paper are presented below.

Answers to Questions

- The **RS=A** OP-FTIR instrument began collecting data at approximately 22 °C (72 °F) with an standard deviation of 2 °C. The variation appears to be due to the variation in the location of the taping of the probe under the instrument or possibly the slipping of the styrofoam placed between the probe and the heating pad.
- The increase in final equilibrium temperature provided by having the instrument on was 10 °C (50 °F) with an uncertainty of 2 °C for the **RS=A** study. For the ManTech study, the increase was 12 °C (54 °F) with an uncertainty of 0.5 °C for the April 11 data with slight changes in ambient temperature and an uncertainty of 4 °C for the January 19 data with large changes in ambient temperature.
- A cotton cover provided a final equilibrium temperature increase of 5 °C (41 °F). Insulation with aluminum foil next to the instrument, a layer of foam rubber and a wool blanket provided a final equilibrium temperature increase of 12 °C.
- The heating pad provided a temperature rise of 10 to 15 °C (50 to 59 °F) depending on whether set at medium or high.
- A minimum of four hours should be allowed for the instrument to warm up if it has been left turned off and equilibrated at temperatures below 10 °C.
- There was no indication in the data collected in either the **RS=A** or the ManTech study of any differences or problems with the spectra collected at temperatures below that needed to initiate data collection once data collection had begun.

Solutions to Data Collection at Low Temperatures

Below are listed some methods that have been used to allow data collection at low temperatures.

- If no ac power is available and generators need to be used, keep the instrument warm when not being used, turn on the instrument as soon as it is set up and use a heating pad or hair dryer to warm up the interferometer quickly.
- ManTech keeps their instrument on continuously in a heated shack.
- Blasland, Bouck and Lee, Inc. uses a timer to turn the instrument on several hours before it is needed, if there is power available. They also use a "jacket" made of rubber and attached with velcro which has been used for data collection at temperatures of -29 °C (-20 °F).⁸

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RSA TEMPERATURE DEPENDENCE STUDY

10 January 1994

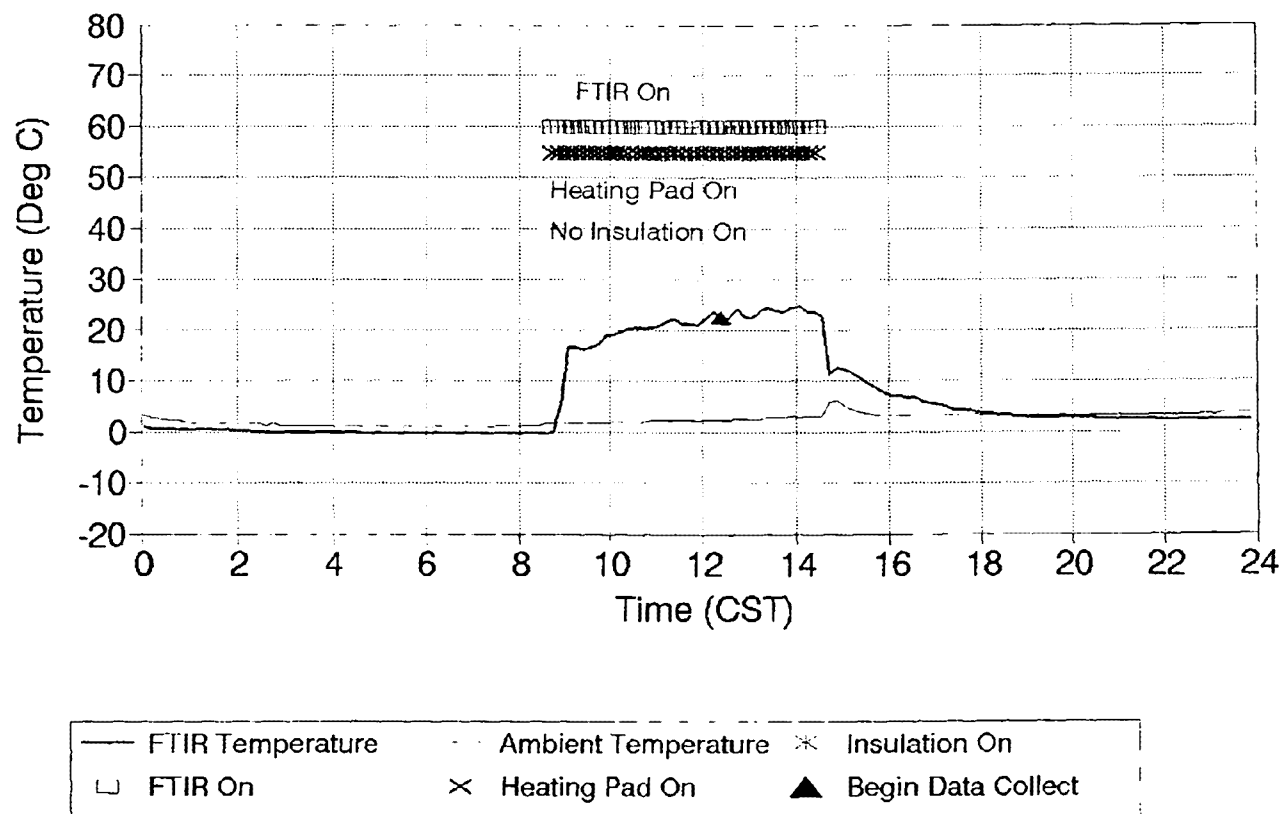


Figure 1.

RSA Study on 10 January 1994 - Temperature of instrument, ambient temperature, and temperature at which data collections occurred.

RSA TEMPERATURE DEPENDENCE STUDY

11 January 1994

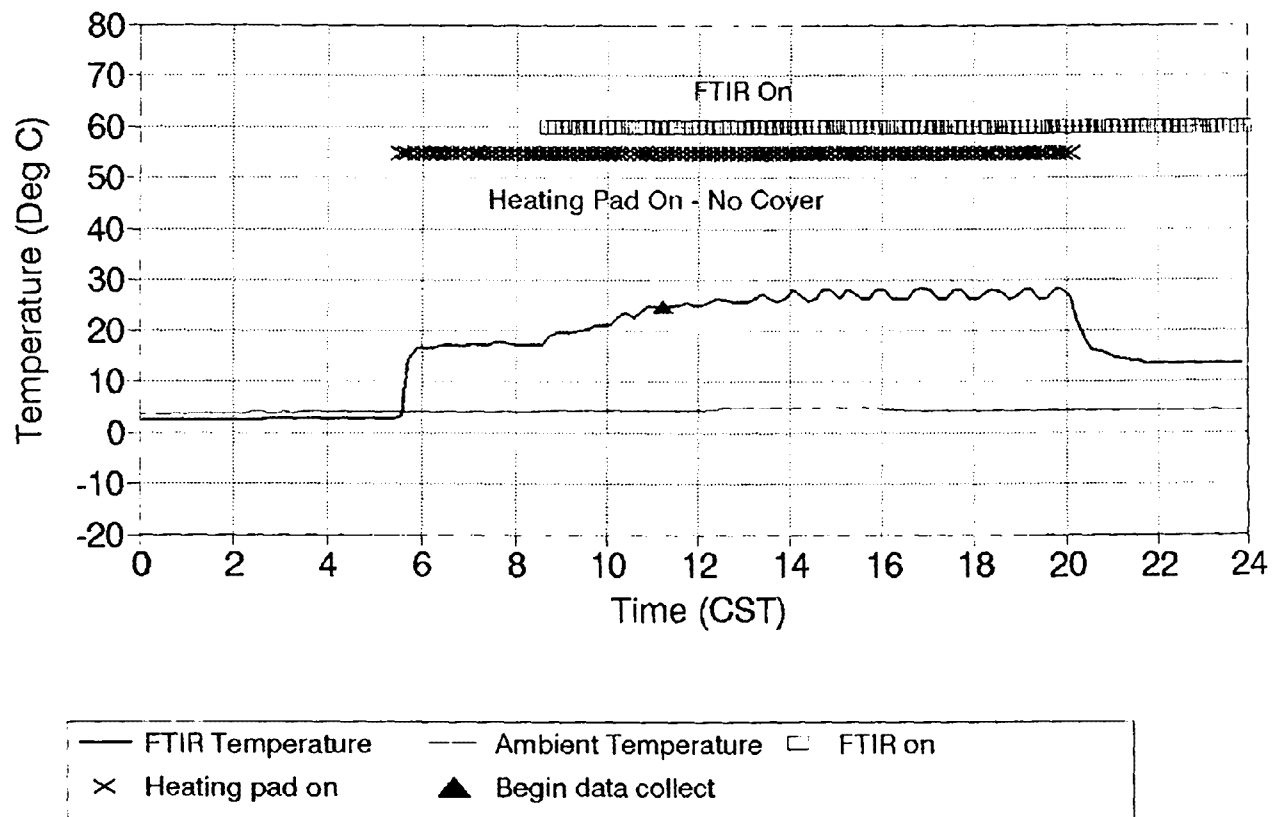


Figure 2.

RS=A Study on 11 January 1994 - Temperature of instrument, ambient
 and time at which data collections occurred.

RS=A TEMPERATURE DEPENDENCE STUDY 13 January 1994

571

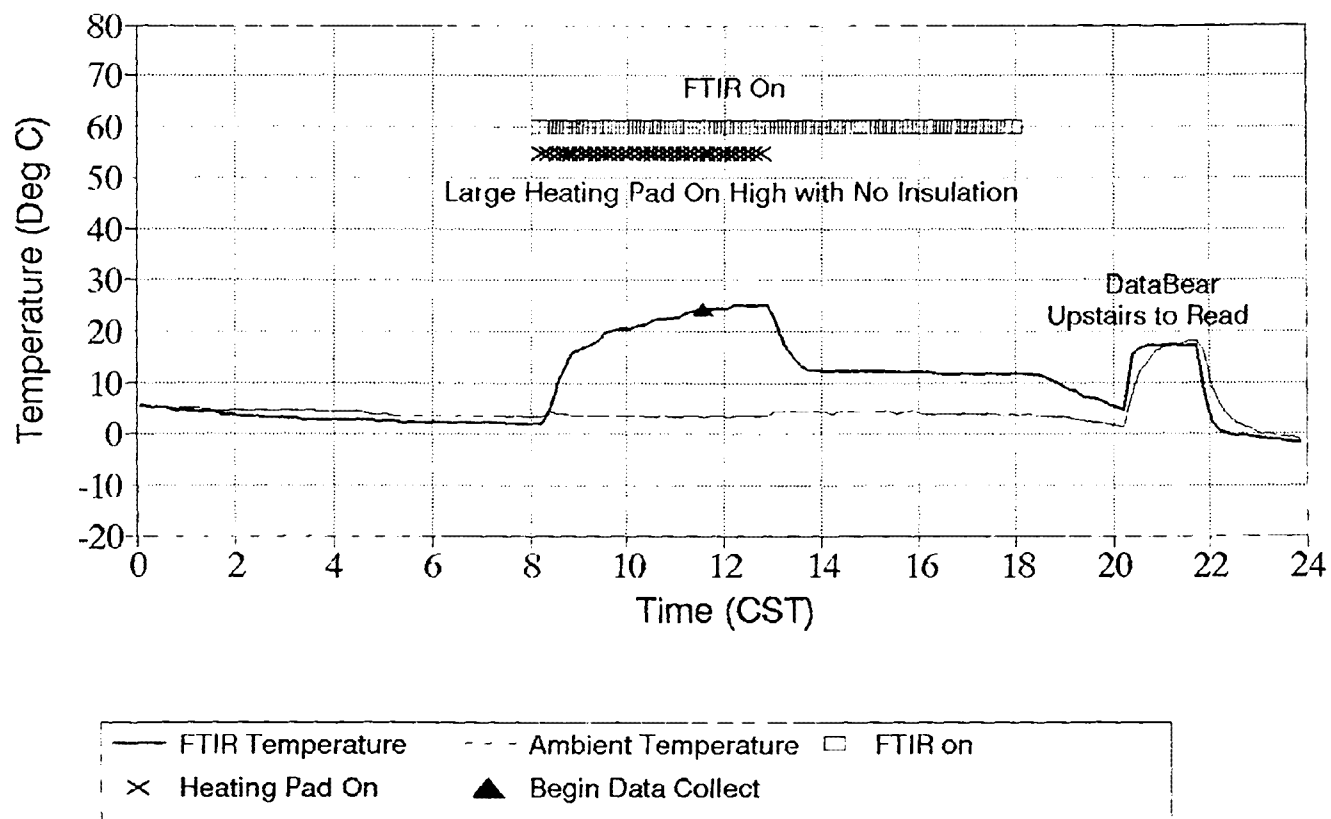


Figure 3.

RS=A Study on 13 January 1994 - Temperature of instrument, ambient temperature, and temperature at which data collections occurred.

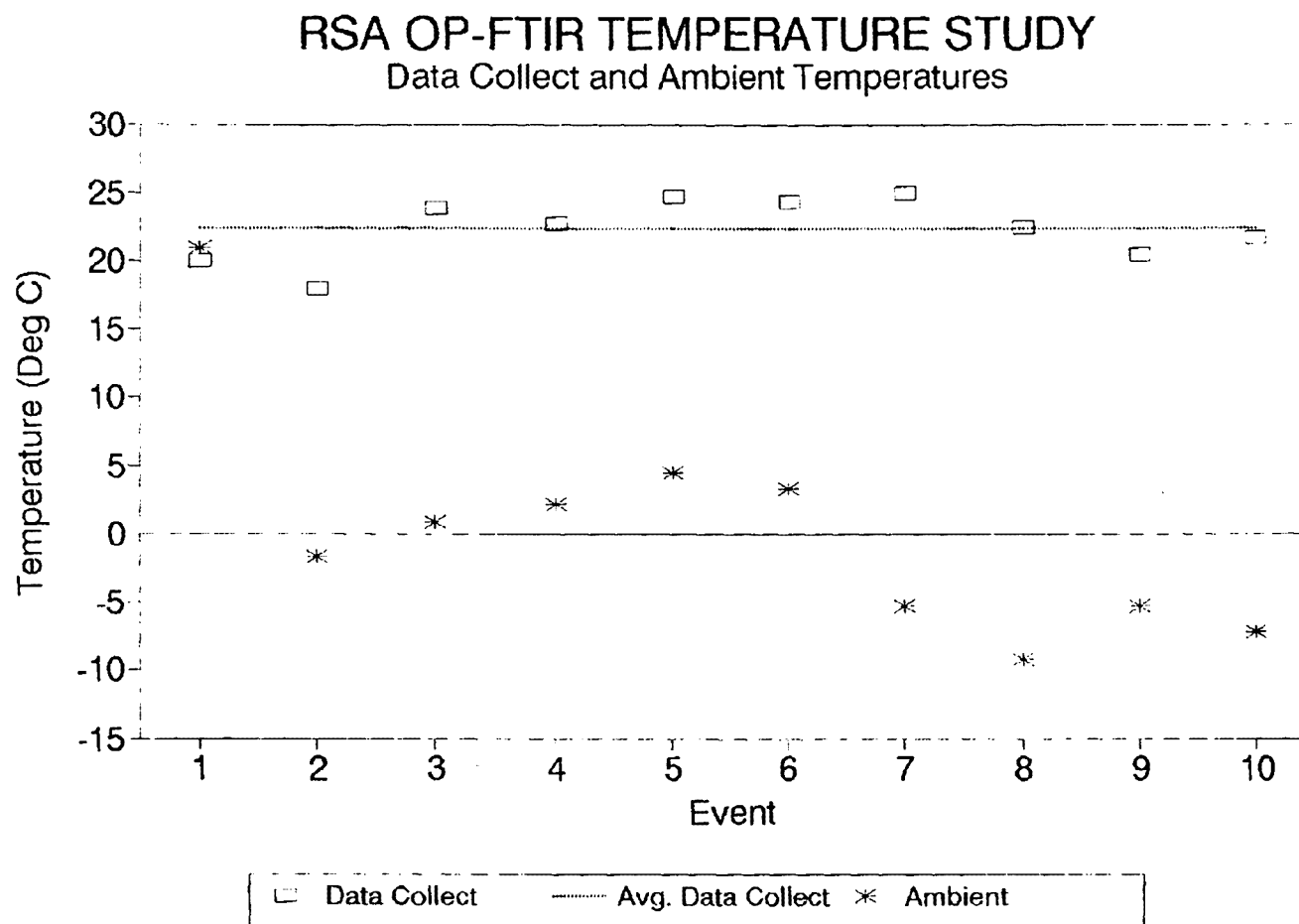


Figure 4. **RSA Study** - Comparison of the temperature at which the instrument was used for 10 of the **RSA**

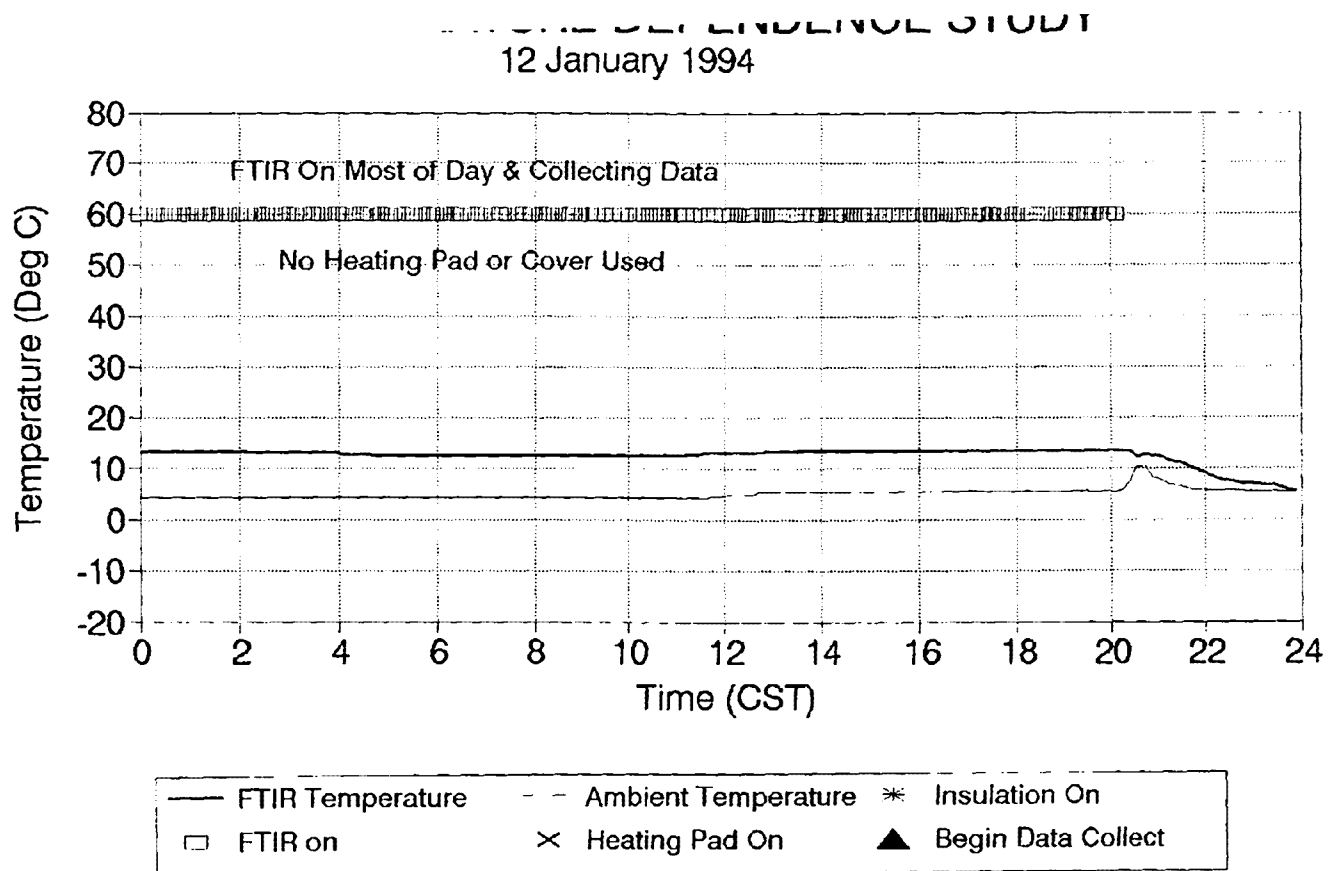


Figure 5.

RS≡A Study on 12 January 1994 - Temperature of instrument and ambient temperature. Note that the instrument remained on all night and day collecting data even at temperatures below those needed for initiating data collection.

MANTECH TEMPERATURE COMPARISON

19 January 1994

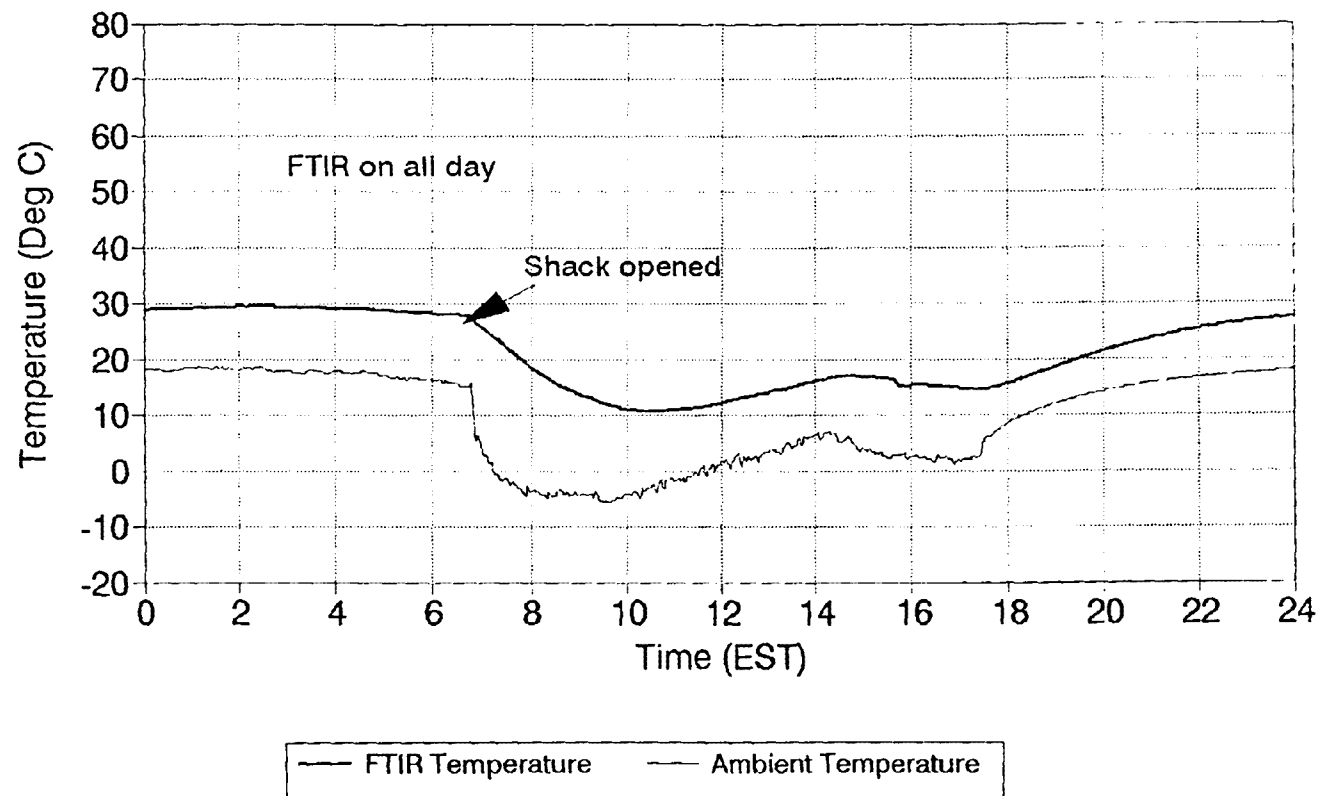


Figure 6.

ManTech Study on 19 January 1994 - Temperature of instrument and ambient temperature. Note that the instrument remained on all night and day and began collecting data when shack was opened about 7 am and continued to collect data even at temperatures below those needed for initiating data

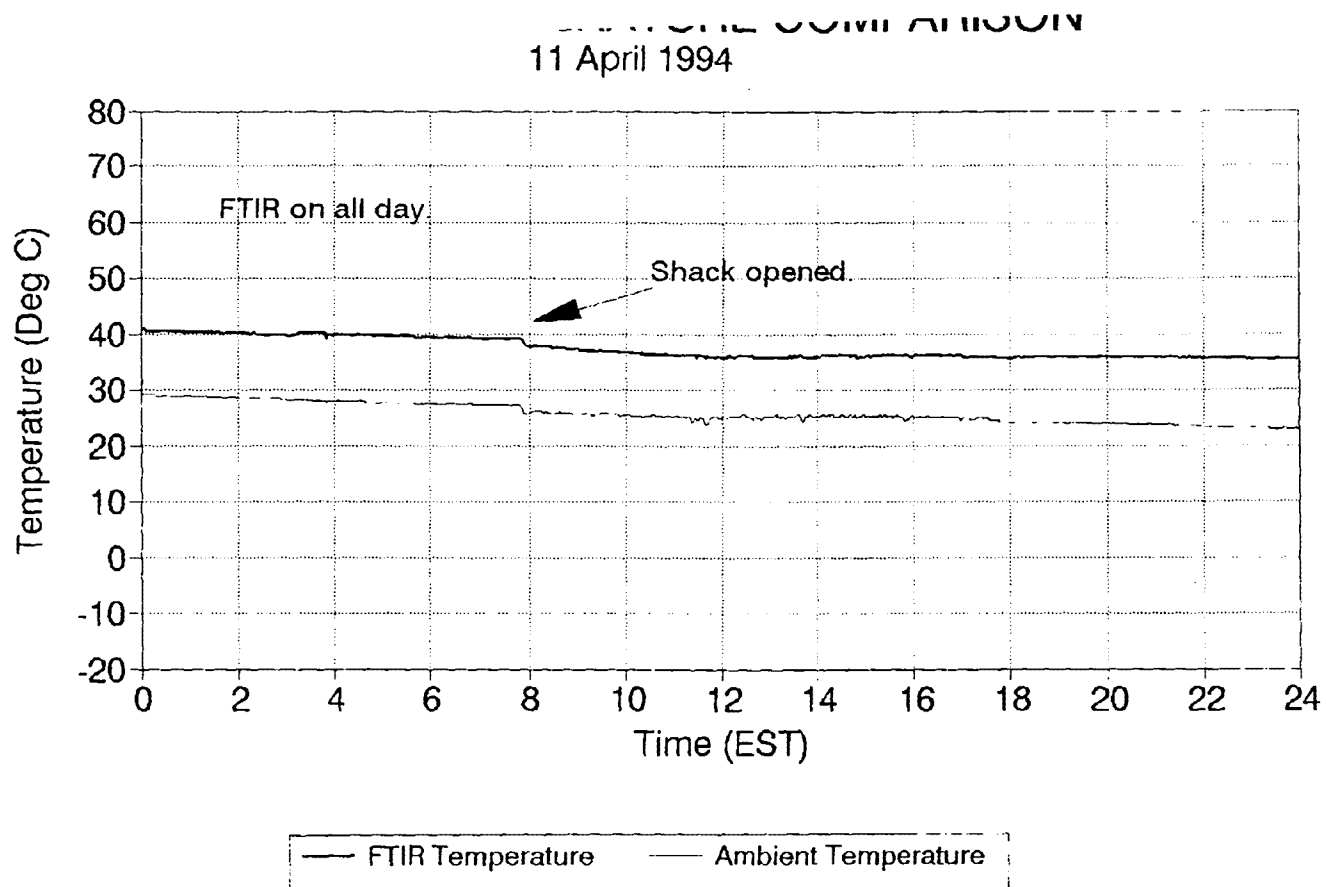


Figure 7.

ManTech Study on 11 April 1994 - Temperature of instrument and ambient temperature. Note that the difference between instrument temperature and ambient temperature remained steady throughout the day and the same as on the very cold day (19 January 1994).

PHOTOLYSIS ASSISTED POLLUTION ANALYSIS (PAPA)

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ABSTRACT

Photolysis Assisted Pollution Analysis (PAPA) combines the infrared method of gas measurement with a boost of high-speed photochemical activity. PAPA goes beyond standard infrared absorption techniques by using a compound conversion process that selects reactive gases from among the non-reactive and reveals their spectra. At the same time the technique renders invisible the spectra of water and carbon dioxide. In PAPA, three infrared spectra are recorded: the first through an empty absorption cell, the second through the cell containing sample, and the third through the cell with sample, after photochemical transformation. The photochemical activity is initiated by ultraviolet radiation from a quartz-mercury lamp. Ozone molecules, oxygen atoms and hydroxyl radicals are formed. These cause oxidation of the reactive pollutant molecules. From the three spectra, the computer extracts the concentrations of pollutant gases. In a single experiment, many gases may be measured. When a ratio plot is made from the second and third spectra, high visibility is conferred on reactants and products. At the same time, unreactive molecules, including water and carbon dioxide, are allowed to remain invisible. The unreactive molecules are measured in a ratio plot made from the first and second spectra. In PAPA, no calibration chemicals are needed. The calibration comes from the software package, which contains a library of digitized quantitative reference spectra. The PAPA method can measure pollutant gases down to parts-per-billion concentration levels, including especially: (1) nitrogen oxides and other nitrogen containing pollutants, (2) organic pollutant gases, including acids, aldehydes, ethers, esters, ketones, hydrocarbons, and halogenated compounds, (3) isoprene, pinenes and other reactive hydrocarbons, (4) benzene and other aromatic compounds, including halogenated species, and (5) hydrogen sulfide, carbon disulfide, mercaptans and other sulfur-containing pollutants.

Introduction

All gaseous polyatomic and heteronuclear diatomic molecules can be measured by their infrared absorption, but some are more difficult to measure than others. Some compounds are difficult to measure because of weak absorption bands, while others that have strong absorption bands are difficult to measure because of interference by water and carbon dioxide. (Ref. 1).

The first problem--that of the weak bands--has not yet had much attention. At first consideration it might appear that not much could be done for improvement. In the past, compounds with weak bands, such as hydrogen sulfide, have only been measured by infrared when at relatively high concentrations. We describe here, however, a method of converting weakly-absorbing compounds into new compounds that have strong, easily measured infrared bands.

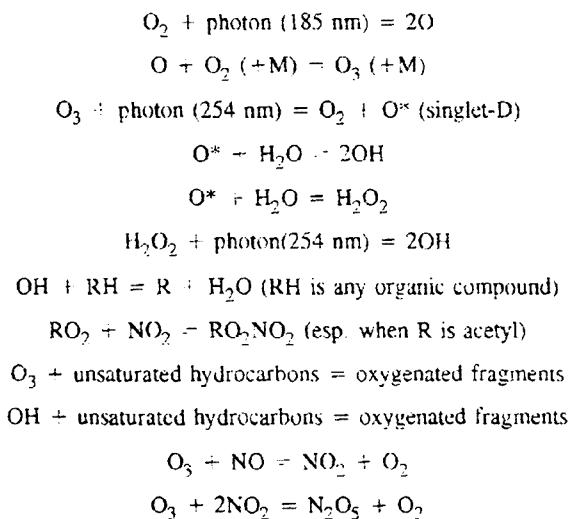
The second and larger problem --that of interference by water and carbon dioxide--has had much effort devoted to it, but proposed solutions have not been easy to apply. The most used solution is to ratio the sample spectrum against a reference spectrum of a gas mixture that contains water and carbon dioxide at the same concentrations as in the sample. Unfortunately, absorbance law failure at low resolution makes it necessary to use many different reference spectra to accommodate the wide range of humidities encountered in the air. The compound conversion system we describe here eliminates the need for these spectra. Our new method has the effect of using the sample itself as its reference mixture.

How the PAPA Technique Works

The PAPA method uses ultraviolet radiation to transform the trace gases in an air sample. The radiation creates oxygen atoms, ozone molecules and OH radicals, which are then mainly responsible for the transformation of the pollutant gases. A ratio plot of spectra obtained before and after transformation reveals (in one direction) the spectra of gases removed and (in the other direction) the spectra of gases created.

The source of the radiation is a medium-pressure quartz mercury resonance lamp. This type of lamp emits one or two percent of its radiation in the 185 nm. mercury line and about 90 percent in the 254 nm. line, with the remainder in lines that fall in the near ultraviolet and visible. The 185 nm. photons dissociate oxygen molecules. The resultant oxygen atoms react mainly with molecular oxygen to form ozone. The ozone can then react with other molecules, or it can absorb the 254 nm. photons and be photo-dissociated, giving oxygen atoms in the energetic singlet-D state. These energetic atoms react with water to produce hydroxyl radicals. The ultraviolet photons can also directly photo-dissociate pollutant molecules. Here are some

of the reactions that take place in an air sample.



There are many possible reactions beyond those shown above. (Ref. 2). It does not appear to be practical to try to explain everything that can happen to air pollutants in this case. The important point is that reactive molecules will be transformed in the air sample, but water and carbon dioxide will not be transformed. When the before-photolysis spectrum is then divided by the after-photolysis spectrum, only the changes in sample composition are revealed, and the water and CO₂ lines are cancelled out.

Products of the transformation of organic compounds include water and CO₂ as well as partially-oxidized intermediate compounds. The newly-created water and CO₂ are unobtrusive in the spectrum, because they are only a small increment on the large amounts already present. The most prominent products of the photolysis are the ozone and hydrogen peroxide, but their bands can be subtracted out. The ozone-H₂O₂ spectrum needed for the subtraction may be created through photolysis of a sample of clean air.

Since some important molecules are stable under the photolysis, a full analysis of air will require examination of the spectrum before photolysis as well as examination of the ratio of the before-photolysis and after-photolysis spectra. The amounts of reactants and products may be determined by the interactive subtraction technique, using digitized quantitative reference spectra. When the PAPA technique is carried out in a long path absorption cell while using the best of the infrared detectors, detection sensitivity can extend down to the parts-per-billion level (10⁻⁹ atm.).

Components of a PAPA System

A PAPA system has three main parts: (1) an FT-IR spectrometer, (2) the PAPA cell, and (3) the quantitative analysis software. The system used in the present tests and demonstrations included the following components, as sketched in Figure 1.

- (1) A MIDAC scanning interferometer of 0.5 cm^{-1} resolution.
- (2) A Nernst glowbar source.
- (3) A permanently-aligned multiple-pass cell manufactured by Infrared Analysis, Inc. Cell length was 1.5 meters; inside diameter was 0.15 meters. The optical path was 62 meters.
- (4) Two 40-Watt medium pressure quartz mercury lamps mounted inside the cell.
- (5) LAB-CALC spectroscopic software.
- (6) The Infrared Analysis, Inc. library of digitized quantitative reference spectra.

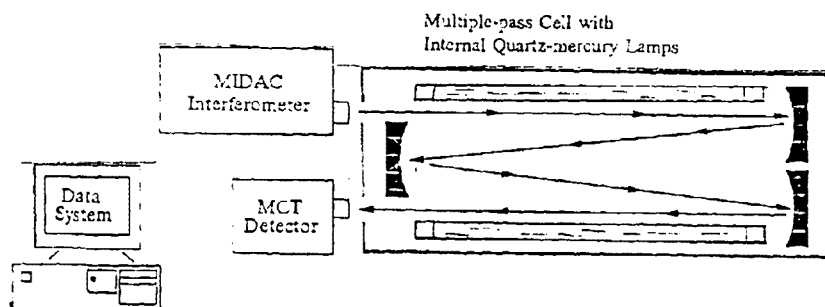


Figure 1. PAPA System Components.

A Demonstration with Aromatic Hydrocarbons

Benzene and the other gaseous aromatic hydrocarbons are readily measured in PAPA. This includes halogenated species. Benzene in air is normally difficult to measure because its strongest band (at 674 cm^{-1}) is hidden by CO_2 lines. In PAPA, however, the CO_2 remains invisible while benzene is revealed by removal of its strong band.

The detection of benzene, toluene and ortho-xylene are illustrated in Figures 8 and 9. Figure 2. Pathlength was 45 meters. The changes in the spectra due to photolysis are not readily apparent in the single-beam plots, while in the absorbance-type plot of PAPA, the bands of the aromatic pollutants are clearly revealed.

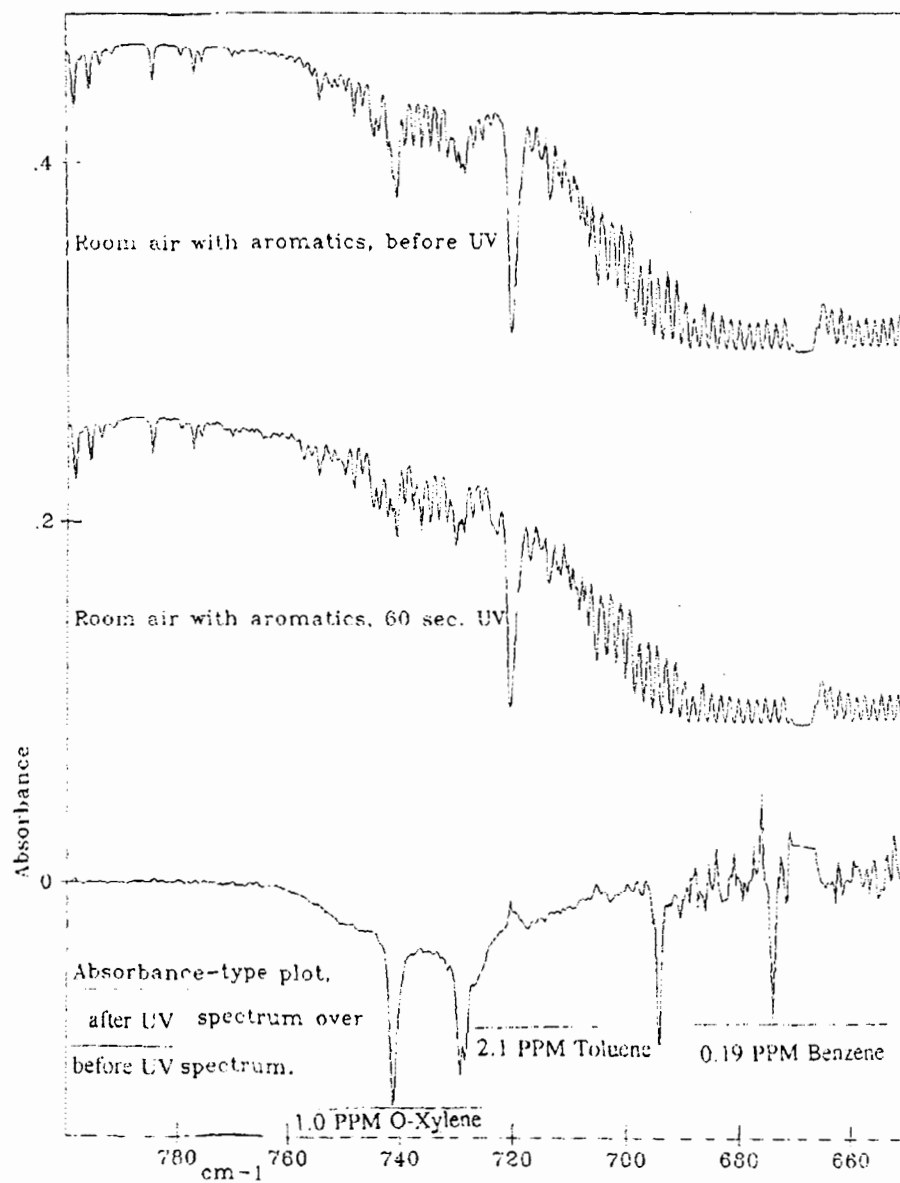


Figure 2. PAPA Technique for Aromatic Hydrocarbons. 45 Meter Cell.

Advantages and Applications

Advantages of the PAPA measurement technique include:

- (1) PAPA can be quick. Only a few minutes time is required to produce the results of the analysis.
- (2) It is simple. No chemicals are needed in the analysis. No measurements of flow or pressure are required. No calibrations are called for. The calibration is inherent in the use of the digitized reference spectra.
- (3) It is sensitive. With just a modest-sized PAPA cell, detection limits for most compounds are on the order of a few parts-per-billion.
- (4) PAPA does things that no other analytical method can do, such as convert compounds to more easily measured forms.
- (5) A PAPA system can be used in its special applications, and then without modification it can be used in regular infrared applications.

Here are some of the special applications envisioned for the PAPA system.

- (1) Measure nitrogen oxides and other nitrogen-containing pollutants in air and in combustion effluents.
- (2) Measure organic pollutant gases in air and in combustion effluents.
- (3) Measure isoprene, pinenes and other reactive natural hydrocarbons in air.
- (4) Measure hydrocarbons and other impurities in ground water.
- (5) Measure hydrocarbons and other impurities in soil samples.
- (6) Measure sulfur-containing pollutants in air, combustion effluents, soil, and water.
- (7) Measure impurities in carbon dioxide, including sulfur-containing pollutants.

Future Work

The potential of the PAPA method has not yet been fully explored. Topics for further study include the following.

- (1) The benefits of working at pressures lower than one atmosphere.
- (2) The relationships between spectral resolution and detection limits.
- (3) Gains from working at longer optical paths.
- (4) The possibilities of measuring homonuclear diatomic molecules by observing their reaction products, such as ozone from oxygen, hydrogen chloride from molecular chlorine and hydrogen fluoride from molecular fluorine.
- (5) Improving the data processing programs for the spectra so that the subtractions and quantitative analyses may proceed with only minimal operator interaction.

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FTIR Transmission Spectroscopy for Quantitation of Ammonium
Bisulfate in Fine Particulate Matter Collected on Teflon Filters

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ABSTRACT

A quantitative measurement method for fine particle bisulfate in ammonium bisulfate collected from the ambient air onto Teflon filters is described. Infrared absorbance measurements of the Teflon filters are made before and after particle collection. Subtraction of the two spectra reveals the absorbance spectrum for the particulate. The presence of bisulfate is identified by characteristic and unique spectral features including prominent absorption bands at 1050 cm^{-1} and 870 cm^{-1} . The area seen under of the absorption band centered at 870 cm^{-1} is calibrated for the bisulfate ion by measuring the hydrogen ion concentration for a series of ammonium bisulfate calibration standards. An indirect measurement of the bisulfate ion is made by inference from measurement of the sulfate ion concentration as determined by ion chromatography. The lower limit of detection (LLD) for the bisulfate ion is 150 nanomoles. This corresponds to the total ammonium bisulfate which would be collected from an air volume containing 1.2 micrograms/ m^3 sampled for 24 hours at 10.0 L/min. This method provides a specific, nondestructive, direct measurement of ammonium bisulfate. As such, the method has distinct advantages over indirect methods involving ion balance in solution.

INTRODUCTION

A large percentage of sulfate in the ambient air exists in the fine (< 2.5 microns) particle fraction, originating from the gas phase through chemical reactions in the atmosphere. Fine particles can be separated from coarse particles using size fractionating, particulate sampling devices such as dichotomous samplers¹, or in-line filter packs with size fractionating inlets². For these samplers, particles are collected using Teflon filters over sampling intervals of several hours to one week. Filters are generally subjected to nondestructive elemental analysis by X-ray fluorescence³ followed by water extraction and analysis by ion chromatography⁴ and/or ion selective electrode for cations and anions.

The potential usefulness of FTIR transmission spectroscopy for the identification of ammonium, sulfate, bisulfate and other ions has been noted in the literature⁵⁻¹⁰. Special studies with a limited number of samples have shown the utility of the method^{5,10} for sulfate measurement in ammonium sulfate. These studies used samples from an archived filter bank. For such samples no attempt was made to preserve the acid sulfate and hence the sulfur present was in the form of neutral ammonium sulfate.

RESULTS

A typical spectrum of ammonium bisulfate collected on to a Teflon filter is shown in Figure 1. Bisulfate bands occur at 870 cm^{-1} , 1050 cm^{-1} and 1215 cm^{-1} . The 870 cm^{-1} band is in a region that contains no significant Teflon absorption bands and is free from other overlapping spectral bands seen in typical environmental samples. The integrated area centered at $870\text{ cm}^{-1} \pm 36\text{ cm}^{-1}$ is thus used for quantitative purposes. The area is measured and compared to a calibration curve to obtain the amount of bisulfate present in the sample. To obtain the most accurate measurement of absorbance, the filters are indexed with respect to their position in the filter holder. This practice lowers the detection limit¹⁰ and tends to eliminate the effect of asymmetric scattering from the uneven stretch patterns in the Teflon filter.

CALIBRATION

A calibration response for the system was obtained by measuring the absorbance of standards prepared with a TSI Model 3706 aerosol generator and sampled from a manifold using an in-line Teflon filter pack. Standard filters were loaded with ammonium bisulfate ranging from $85\text{ }\mu\text{gm}$ to $350\text{ }\mu\text{gm}$ each. The absorbance spectrum was taken from 4000 to 400 cm^{-1} and the area centered at $870\text{ cm}^{-1} \pm 36\text{ cm}^{-1}$ was integrated for the bisulfate measurement. The filters were then extracted with 20 ml of water using ultrasonification for 60 minutes. A 0.5 ml aliquot of the sample

was then analyzed using an Orion Model 511 ion selective electrode for direct determination of hydrogen ion. Measurements of sulfate were also made on a Dionex Model 4000 ion chromatograph. Since the measurement of sulfate was considered very reliable, sulfate was used as a surrogate for hydrogen ion. Based on the respective slopes, the calibration curve generated from the direct determination of hydrogen ions is on average 10.6% lower than the hydrogen ion calibration curve generated from equivalent sulfate ion values. This difference may be due to the difficulty in making low level hydrogen ion determinations using the ion selective electrode. Another possible explanation could be the neutralization losses that occur with acidic samples due to the presence of ambient ammonia. The FT-IR analysis LLD computed for a 3/1 signal to noise ratio was 150 nanomoles of bisulfate ion. This computation was made by computing the FT-IR integrated area for a known calibrated standard. The LLD was then computed for a theoretical area having a 3/1 signal to noise ratio, based on the aforementioned standard. This method of determining the LLD was necessary because of the inability to accurately determine hydrogen ion concentrations using traditional wet chemical means at extremely low levels. The LLD stated corresponds to a collected sample weight of 17.3 ug of ammonium bisulfate on a standard 37mm teflon filter.

CONCLUSION

The applicability of FT-IR transmission spectrometry to the quantitative and qualitative determination of ammonium bisulfate has been demonstrated. The method is nondestructive and provides a direct measure of ammonium bisulfate. Qualitative indicators for the presence of ammonium bisulfate are absorption bands at 870 cm^{-1} and 1050 cm^{-1} . These bands along with the spectral shift that occurs for the neutral sulfate band normally seen at 620 cm^{-1} confirm the presence of ammonium bisulfate. The integrated area of the 870 cm^{-1} absorption band when calibrated against standard wet chemical techniques can be used to determine the concentration of bisulfate ion present in ambient aerosol. The lower detection limit cited at this stage of development is 17.3 ug (150 nmoles) of sample collected as ammonium bisulfate on a 37 mm Teflon filter. The limiting calibration factor in the method is the uncertainty that exists with the wet chemical determinations. The slope of the calibration curve for bisulfate determination is 10.4% lower using direct hydrogen ion measurements as compared to the use of sulfate ion as a surrogate for hydrogen ion. As with other methods used to analyze particulate matter collected on filters, the sample integrity cannot be assured because of interaction among particles. However, this is minimized by removal of the coarse particles and by protection of the bisulfate from neutralization by basic gases such as ammonia.

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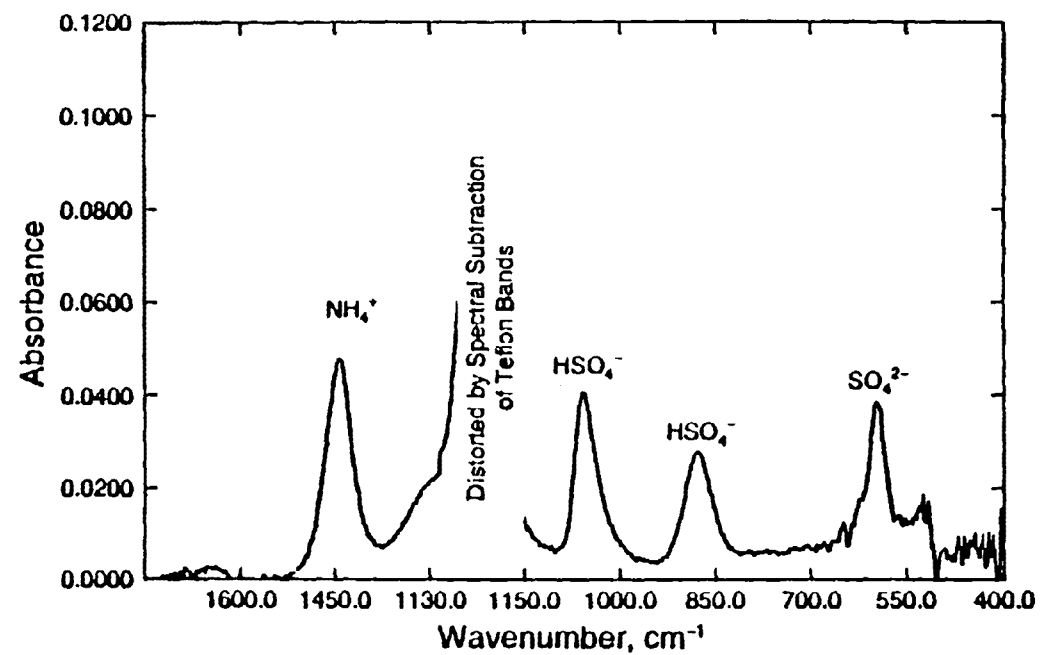


Figure 1. Absorbance Spectrum of Ammonium Bisulfate Standard

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
FOURIER TRANSFORM INFRARED SPECTROSCOPY
TEST PROGRAM FOR EMISSIONS MEASUREMENT

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ABSTRACT

The U.S. Environmental Protection Agency (EPA) published amendments to the Clean Air Act (CAA) November 15, 1990. Title III of the CAA amendments included a list of 189 hazardous air pollutants (HAP's) for which emission test procedures must be established.

An extractive emission test method, using Fourier Transform Infrared (FTIR) spectroscopy, is being developed for measuring HAP compounds. The FTIR procedure has the potential to detect over 100 of the listed compounds plus additional compounds such as criteria pollutants. This procedure has the ability to detect multiple compounds simultaneously and will provide near real-time data.

Since the development of the extractive FTIR procedure, many source categories have been screened for HAP emissions using this technique. Modifications to the procedure have been made and validation testing has been performed. Currently, this technique is being used to collect data for maximum achievable control technology (MACT) standard development.

INTRODUCTION

This paper focuses on the application of FTIR to emissions testing of various air pollution sources. This involves extracting samples from stacks or ducts in industrial sources. (See figure 1.) The development of the testing program has involved several phases. The first phase involved the development of sufficient reference spectra, software, and an FTIR Protocol¹ to guide in making these measurements. The second phase involved the development of sufficient sampling systems and performing screening tests at several source categories to evaluate the protocol and potential sampling systems. The third phase involved the validation of this technique for 46 HAP's at a

coal-fired boiler. Currently, the extractive FTIR technique is being used to collect emission data in support of MACT standards.

EXTRACTIVE FTIR DEVELOPMENT AND TESTING PROGRAM

Phase 1

Due to the lack of sufficient reference spectra for the HAP's, the Emission Measurement Branch sponsored Entropy Environmentalists, Inc., to develop reference spectra for over 100 HAP's. These spectra are available through the emission measurement technical information center (EMTIC) bulletin board system². The FTIR Protocol, noted previously, serves as a guideline for the use of extractive FTIR systems in emission testing. It provides a basis for the source-specific integration of sampling procedures, reference spectra and software development, and quality assurance/quality control procedures. The protocol specifies extractive sampling guidelines and calibration transfer techniques. The protocol is currently designed for users with extensive FTIR training, but a practical FTIR test method must be suitable for performance by an operator with less experience. The transition between the protocol and a test method will require that suitable reference spectra and user-friendly software be made generally available.

Phase 2

After the development of appropriate reference spectra, software, sample conditioning systems were developed. Sample conditioning systems are necessary to deliver the stack gas to the FTIR sample cell in a condition that will not damage the FTIR cell and optics and will reduce spectral interference. This involves filtering particulate, and, in certain cases, removing moisture. These sample conditioning systems were (1) the hot/wet system, (2) the perma-pure system, (3) the condenser system, and (4) the preconcentration system. The first three systems listed are considered direct sampling systems. The hot/wet system draws the sample through a heated filter and heated teflon line. The perma-pure and condenser system remove moisture. The preconcentration system involves sample collection in a sampling train (Method 0010³) which uses tenax as an absorbent. The tenax is thermally desorbed into the FTIR sample cell for analysis.

After the development of these systems, screening tests were performed to gain preliminary "qualitative" emission data on potential HAP's from these sources and to evaluate the FTIR procedure (sample conditioning systems and analysis). Source categories, where screening testing was conducted, included pulp and paper, portland cement, wool fiberglass, primary aluminum, secondary aluminum, secondary lead, and utility boilers. Certain source categories were of particular interest because of the upcoming MACT standard development. Based on these screening

tests, modifications to the sample conditioning systems were made, based on target compounds and expected concentration levels of these compounds at these sources.

Results of phase 1 and phase 2 were presented in more detail at the Air and Waste Management Association annual meeting in June of 1992.⁴

Phase 3

In January and February of 1993, validation testing was performed at a coal-fired boiler following Method 301 procedures⁵. The validation testing involved dynamically spiking 46 HAP compounds. Dynamic spiking involves spiking the sample gas at the sample probe (immediately prior to the filter) and was conducted using known concentrations of the target compounds. The compounds chosen were those that were available as cylinder gases to be used as the standards. Three of the sample conditioning systems were tested: the hot/wet system, the condenser systems, and the preconcentration system. Of the systems which were tested, the hot/wet and condenser sampling systems, together, validated for 32 of the 46 compounds. The preconcentration system validated for 11 of the compounds. Data for a number of other compounds did not meet the Method 301 criteria; however, they demonstrated more than adequate performance of the FTIR technique for use as a screening procedure.

Utility study and MACT standard development.

The FTIR procedure has been used to gather information for the utility report to Congress and to gather information for MACT standard development. In all cases, both controlled and uncontrolled emissions from the various processes were of interest. The preconcentration system was developed because of the low levels (low part-per-billion) of HAP's from utility boilers. Five utility boilers were tested: two coal-fired boilers, two gas fired boilers, and an oil-fired boiler.

Two portland cement facilities were tested using FTIR to gather data to set a MACT standard. The target compounds for this source category were acetaldehyde, benzene, bis(2-ethylhexyl)phthalate, carbon disulfide, chloromethane, formaldehyde, hydrochloric acid, naphthalene, phenol, styrene, toluene, and xylenes. The HAP's that were detected at the first plant were benzene, carbonyl sulfide, formaldehyde, hydrochloric acid, and naphthalene. All compounds were detected with the preconcentration train at high ppb levels, except HCl, which was detected with one of the gas phase systems (parts-per-million level detection limit). Emissions were evaluated at the inlet to a carbon injection system and baghouse (in series) and the outlet of the baghouse. The HAP's, detected at the second facility,

were benzene, chlorobenzene, hexane, naphthalene, styrene, toluene, and o-xylene. All compounds were detected with the preconcentration train, except hexane and xylenes which were detected in the gas phase system. The emissions were sampled from a rotary kiln both before and after a multiclone and baghouse (in series), and before and after a scrubber. Other compounds, detected at both facilities which are not HAP's, included sulfur dioxide, nitric oxide, methane, and ethylene.

Emissions from two mineral wool fiberglass facilities were also evaluated for MACT standard development using the extractive FTIR procedure. Target compounds for the FTIR were phenol, formaldehyde, and methanol. The test reports for these facilities have not been completed. However, preliminary results indicate that phenol, formaldehyde, methanol and carbonyl sulfide were detected at both facilities. For the first test, the emissions from a bonded line were sampled at the inlet and outlet of a baghouse, which controlled the cupola emissions. The inlet and outlet emissions of a filter house, which controlled the collection drum, were evaluated. The inlet and outlet of an incinerator, which controlled the curing process emissions, and the uncontrolled emissions from the cooling process were also evaluated.

For the second test, both emissions from a bonded line and a nonbonded line were sampled. Emissions from the incinerator and baghouse, controlling the cupola emissions, were also sampled. For the bonded line, the emissions from a filter house, controlling the collection drum emissions, were evaluated. Emissions from an afterburner, controlling the curing process emissions, were evaluated, and emissions from a common stack for the baghouse and filter house, mentioned above, were evaluated. For the nonbonded line, the emissions from a filter house, controlling the collection drum emissions, were evaluated.

CONCLUSIONS

The FTIR procedure has provided extremely promising results. This technique has been validated for many of the HAP compounds at a coal-fired boiler and is currently being used to collect data in support of MACT standards. Future plans for FTIR testing include a wool fiberglass facility and a secondary aluminum facility.

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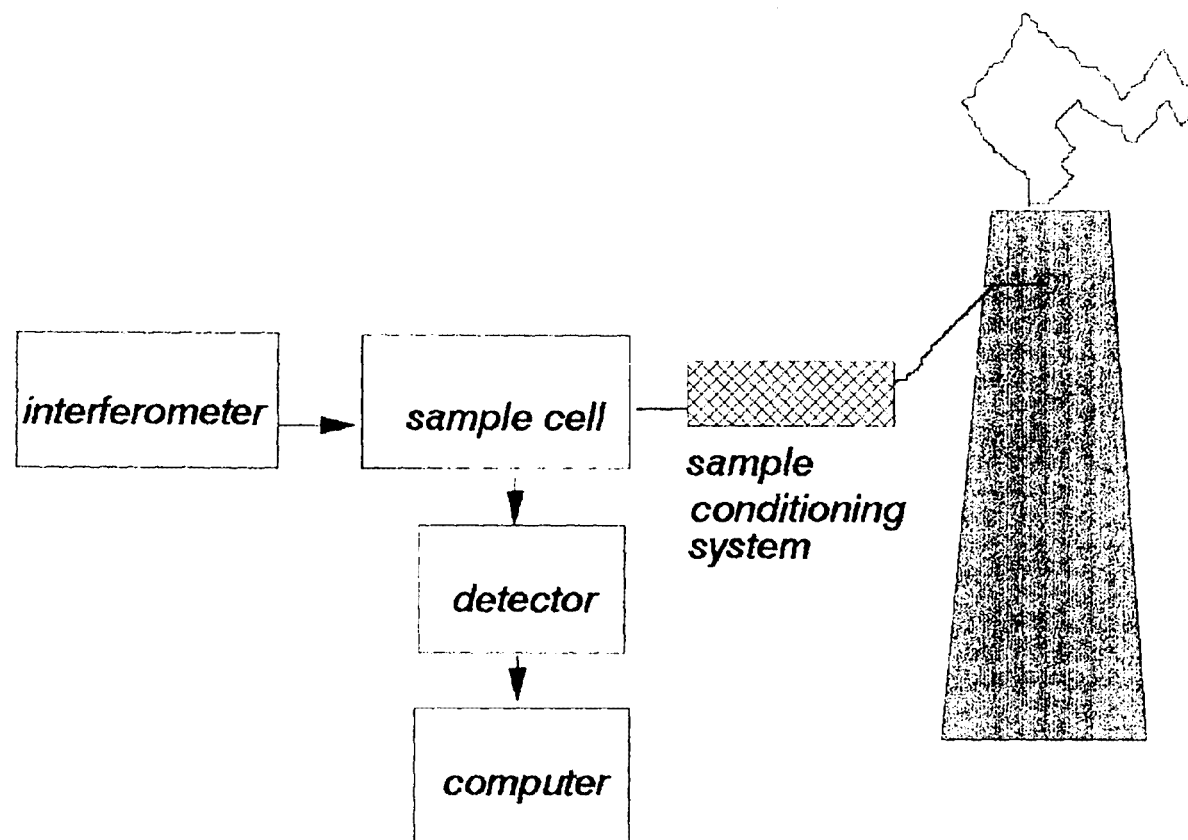


Figure 1. FTIR Extractive Sampling Schematic

SESSION 12:
NEW METHODS FOR VOCS

**The Concentration and Measurement of Air Pollutants by GC/MS;
A Comparison of Sorbent Versus Cryo Trapping**

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The measurement of toxic air contaminants and ozone precursors in ambient air is gaining more importance as the 1990 Clean Air Act Amendments (CAAA) take effect. Simple, reliable and low maintenance instrumentation is needed to detect the more than 100 volatile organic compounds (VOCs) in ambient air at low or sub ppb levels as specified in the CAAA.

A Saturn GC/MS ion trap system equipped with an inboard concentrator (SPT) was used to study the advantages and disadvantages of cryo and sorbent trapping of the pollutants. The cryo trapping was carried out on glass beads at -150°C or -180°C, using liquid nitrogen as coolant. The sorbent trapping took place at or around ambient temperatures employing custom selected sorbent traps and liquid CO₂ for cooling. Sample volumes of 60ml and higher were concentrated, and after separation on a capillary column, full scan detection was performed.

System precision, detection levels and linearity data will be presented for different compound groups and results of ambient air samples will be shown.

A Real Time Sorbent Based Air Monitoring System For Determining Low Level Airborne Exposure Levels to Lewisite

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ABSTRACT

The Real Time Analytical Platform (RTAP) is designed to provide mobile, real-time monitoring support to ensure protection of worker safety in areas where military unique compounds are used and stored, and at disposal sites. Quantitative analysis of low-level vapor concentrations in air is accomplished through sorbent-based collection with subsequent thermal desorption into a gas chromatograph (GC) equipped with a variety of detectors. The monitoring system is characterized by its sensitivity (ability to measure at low concentrations), selectivity (ability to filter out interferences), dynamic range and linearity, real time mode (versus methods requiring extensive sample preparation procedures), and ability to interface with complimentary GC detectors.

This presentation describes an RTAP analytical method for analyzing Lewisite, an arsenical compound, that consists of a GC screening technique with an Electron Capture Detector (ECD), and a confirmation technique using an Atomic Emission Detector (AED). Included in the presentation is a description of quality assurance objectives in the monitoring system, and an assessment of method accuracy, precision and detection levels.

INTRODUCTION

Lewisite (2-chlorovinylchloroarsine) is a toxic arsenical compound of historical military interest (Table 1). Since Lewisite is a suspected carcinogen, it is necessary to monitor vapor concentrations to protect worker safety in areas where the chemical is stored or that contain items that may have been exposed to the chemical, and in former manufacturing areas during installation restoration activities.

Historical Methodology

Because of the need for accurate assessments of exposure levels, a number of analytical methods for the detection of Lewisite have been developed. The thermal instability of the compound and its reactivity with water have complicated the search for quantitative measurement techniques and are reported extensively in the literature¹. Since attempts to analyze Lewisite directly via gas chromatography result in severe deterioration of the chromatographic column and metal surfaces of the detector, most accepted methods rely on

indirect measurements of either elemental arsenic or a reaction product. One conventional measurement analyzes trace arsenic by graphite furnace atomic adsorption², another quantifies trace levels of acetylene formed during the alkaline decomposition of the chemical³. A current approach uses high pressure liquid chromatography with UV and electrochemical dual detection to analyze hydrolyzed Lewisite (2-chlorovinylarsonous acid, CVAA)⁴.

Limitations

Each of these traditional approaches can be limited by the presence of interfering substances, i.e. naturally occurring arsenic collected and reported as Lewisite. Similarly, Lewisite derived acetylene is indistinguishable from acetylene that enters the sample stream as a background constituent. It has been reported that headspace samples of acetylene generated from Lewisite typically contain water vapor artifacts, a 9:1 ratio of water vapor to acetylene, that reduce the sensitivity of the analytical detector, limiting detection levels⁵. Also, all of these methodologies involve collection of samples by passing air through a liquid filled impinger (bubbler) or filter media, which is labor intensive and costly, can impose a delay of several hours to several days before analytical results are obtained, and requires expensive decontamination and disposal procedures of waste water and solvent.

In search of more accurate, reliable and cost effective methodology, the Edgewood Research, Development and Engineering Center (ERDEC) at Aberdeen Proving Ground, MD, and other research organizations at APG have funded various studies investigating other Lewisite reactants, specifically with thiols. Jakubowski⁶ et.al. and Albro⁷, continuing with derivatization techniques suggested by Peters⁸ and reported by Fowler⁹ developed GC methods for analyzing the derivative of Lewisite and hydrolyzed Lewisite after derivatization with 1,2 ethanedithiol (EDT). They described the use of more sensitive and selective GC detectors, the flame photometric detector (FPD) and electron ionization mass spectroscopy (EIMS), and introduced elemental analysis with the Atomic Emission Detector (AED) to further extend the lower concentration range at which quantitative measurements of Lewisite could be obtained. Most of this body of work concentrated on measurements of the purity of Lewisite standards in solvents, and detection of Lewisite in water and soil samples. EDT derivatization as a means of measuring vapor concentrations in air were basically obtained by analyzing water from samples collected through bubblers.

Technical Approach

This method's approach utilizes sorbent tube technology for the monitoring of airborne Lewisite. The solid sorbent Tenax is substituted for bubblers, with subsequent thermal desorption into a GC column. Sensitivity increases, since all of the collected sample is available for analysis, instead of an aliquot of the extracted bubbler medium. After desorption, sorbent cartridges are reusable, with no costs incurred in the disposal of waste water or solvents.

Due to Lewisite's thermal instability, derivatization was seen as an excellent means of producing a stable compound analyzable by GC. The derivatizing agent, most likely reacting with hydrolyzed Lewisite due to the moisture in the air, converts it to a compound that retains its Arsenic molecule, in combination with other molecules that allow both an AED and Electron Capture Detector (ECD) to respond to the reaction product with sufficient sensitivity without interference from the derivatizing agent (Figure 1). 1,4 thioxane was substituted for 1,2 ethanedithiol because of problems with EDT purity that limited detector

response on the FPD and Electron Capture Detector (ECD). Derivatization was accomplished by injecting the derivatizing agent directly on the tube containing the airborne adsorbed Lewisite hydrolyzate.

A Dynatherm ACEM 900 thermal desorber, coupled with a Hewlett Packard 5890 GC with an ECD serves as a *prescreening* system during analysis of the sampling tube. It saves approximately 75% of the sample so that subsequent analysis of the *same sample* can be made on the *confirming* system, consisting of an ACEM 900 and HP 5890 GC with an Atomic Emission Detector. The ACEM has an integral sample saver that splits the sample during thermal desorption between the column on the prescreening GC and a second sorbent tube. If the screening GC generates a positive response, the saved portion of the sample on the auxiliary sorbent tube is available for analysis on the confirmation GC. Both the ECD and AED give quantitative as well as qualitative results. [The Dynatherm / HP-GC / HP-AED system has been previously reported in the literature¹⁰].

EXPERIMENTAL

Precision and accuracy studies (P&As) performed to validate the method specified a minimum range of .25 - 1.5 times the Time Weighted Average (TWA), currently set at .003 mg/m³ (.35 ppb), and required 5-point calibrations, in duplicate, over a four day period. A CASARM Lewisite standard was diluted to a concentration of 1.08 ng/ μ l in methanol. The derivatizing agent, 1,4 thioxane, was made up in a 1.2% solution in methanol. Standards may be introduced to the sorbent collection tube either as a liquid or gaseous injection. A liquid Lewisite standard was used for the P&As because it appeared to have better stability over longer periods of time. Table 2 lists the injection amounts relative to the percentage of TWA, with 1 TWA based on a 1.6 liter air sample.

After the standard was injected through a special injection port adapted for the Dynatherm Six -Tube Conditioner, Model 60, the sorbent tube was purged with nitrogen at 600 cc/minute for 3 minutes. This was followed by injection of the derivatizing solution, purged at the same rate for twice the time. A sleeve heater slipped over the tube during the derivatizing process maintained an elevated temperature of 70°C to ensure consistency of reaction and remove residual water and solvent. After loading with the derivatized standard, the tube was transferred to the ACEM 900 for thermal desorption into the GC/ECD system.

The ECD and AED systems were calibrated with the same sample, split via the ACEM sample saver, and the curves from both detectors plotted. It was necessary to verify that neither detector was adversely affected by the splitter or concentration changes. Each detector gave a linear response within the required range, with correlation coefficients ranging from .996 - .999 (Figures 2 and 3).

Column information and temperature, time and flow conditions for the ACEM 900, GC oven and detectors are presented in the parameters log (Table 3).

The only interferences predictable from the P&As are those compounds associated with the Lewisite standard and derivatizing agent, reflecting less than 100% purity levels of both chemicals. Though background compounds appear in the chromatograms of both the ECD and AED systems, none appear at or near the same retention time of the peak of interest. Since the ECD does not have the elemental selectivity of the AED, interferences introduced during actual field sampling are possible. Should an interference appear within the ECD retention time window, it will be subject to investigation on the AED system. Only a compound producing an arsenic response within the AED retention time window will be

confirmed as positive. The likelihood of such an interference is remote.

The turnaround time with either the ECD or AED system is approximately 15 minutes, an analysis rate of 4 per hour. Only positives generated on the ECD system require analysis on the AED system.

Detection limits on both systems are well within current exposure limits. Under the conditions described for the P&As, the lowest concentration analyzed by the ECD system was less than .25 ng on column. Area counts were in excess of 150000, with a high signal to noise ratio. Sensitivity of the AED when monitoring at 189 nm for arsenic was also very high. Note also that sample volumes are based on a response to 1.6 liters of air at 1 TWA. Given the structure of the derivatized compound and the surface area of the Tenax adsorbent, one could predict good collection efficiency at 4 to 6 times current sampling volumes. Based on these factors, there is a high probability that exposure levels could be monitored at significantly lower vapor concentrations than current TWA. Determination of the minimum detection level of this method would require study of absolute detector sensitivity for the ECD and AED, establishment of breakthrough volume on the adsorbent tube, and the effect of higher concentrations and sampling volumes on derivatization efficiency.

CONCLUSIONS

The method as described for the analysis of Lewisite and/or its hydrolyzed product through solid sorbent collection of airborne vapors, derivatization to a chromatographable compound, and analysis by two specific GC detectors offers high sensitivity and selectivity. The risk of false positives due to environmental interferences should be low. Detection levels are such that measurement of exposure values below current TWA can be investigated. Significant cost savings through elimination of waste products can be obtained.

Field tests of the method to date have been promising, though no positive response other than to spiked samples has been recorded. Operator skill levels, while requiring some familiarization with gas chromatography and analytical capability, are not excessively high.

Future research suggested by the success of the current approach will be devoted to adaptation of the method to real time continuous monitoring. The same analytical equipment described in this method could also collect and analyze air samples unattended with the addition of a fixed amount of derivatizing agent in gas form. The basic format and instrumentation of the Army RTAP mobile laboratory, already fielded at a number of storage depots and in use by Monitoring Branch for worker exposure assessments, could be modified with the appropriate equipment for Lewisite analysis. The dual methodologies, for sampling with easily portable sorbent tubes and unattended monitoring with a real-time monitor, would present an ideal solution to the various difficulties encountered in Lewisite vapor exposure assessments to date.

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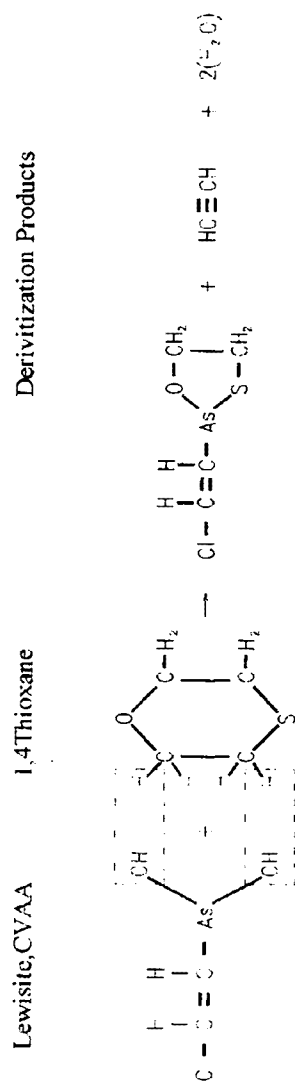


Figure 1. Products formed when hydrolyzed Lewisite, CVAA, is derivitized with 1,4 Thioxane

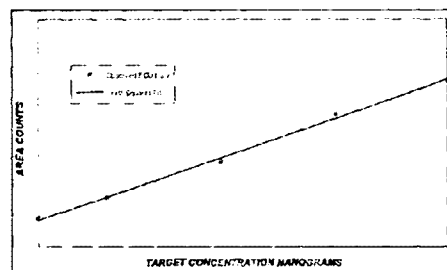
Figure 2. **Linearity During 4-Day P&A Study**
ECD Detector

Day 1

Regression Statistics

$$\text{Area} = 89205(\text{Amt}) + 68232$$

$$r^2 = 0.996608073$$

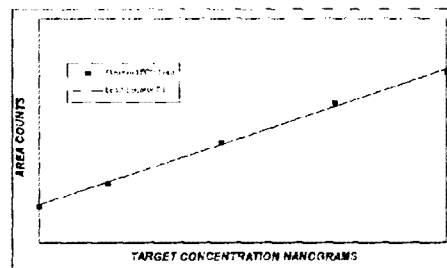


Day 2

Regression Statistics

$$\text{Area} = 87871(\text{Amt}) + 131573$$

$$r^2 = 0.996611364$$

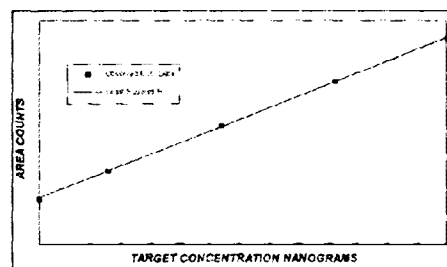


Day 3

Regression Statistics

$$\text{Area} = 103163(\text{Amt}) + 168951$$

$$r^2 = 0.999695326$$



Day 4

Regression Statistics

$$\text{Area} = 109476(\text{Amt}) + 209927$$

$$r^2 = 0.999021548$$

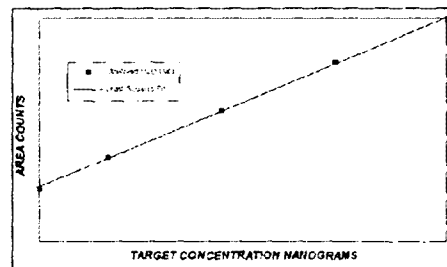


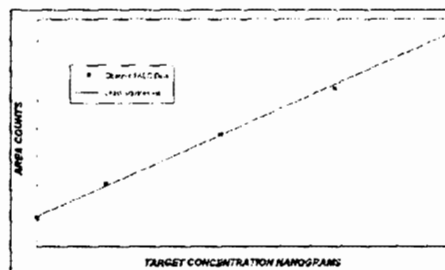
Figure 3. **Linearity During 4-Day P&A Study**
AED Detector

Day 1

Regression Statistics

$$\text{Area} = 1250.85(\text{Amt}) + 652.28$$

$$r^2 = 0.998851517$$

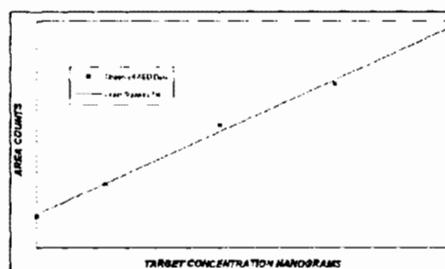


Day 2

Regression Statistics

$$\text{Area} = 1280.40(\text{Amt}) + 795.82$$

$$r^2 = 0.99764992$$

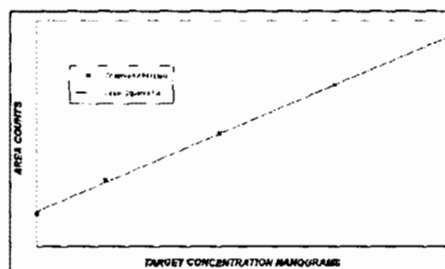


Day 3

Regression Statistics

$$\text{Area} = 1204.25(\text{Amt}) + 967.79$$

$$r^2 = 0.999529939$$

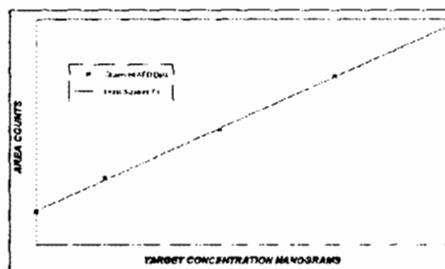


Day 4

Regression Statistics

$$\text{Area} = 1273.45(\text{Amt}) + 867.63$$

$$r^2 = 0.999738575$$



Lewisite: Dichloro-(2-chlorovinyl)arsine

Molecular Formula: $C_2H_2AsCl_3$

Molecular Weight: 207.35

Boiling Point: 190°C

Vapor Pressure: 0.394mm Hg at 20°C

Table 1. Physical properties of Lewisite

Workplace Exposure Level (TWA) $0.003\text{mg}/\text{m}^3 = 0.35\text{ppb}$

Fraction of TWA	20%	50%	100%	150%	200%
Amount Injected					
in μl	1.0	2.3	4.6	7.0	9.3
in ng	1.08	2.48	4.97	7.56	10.04

Table 2. Injection amounts related to TWA

Table 3		ACEM 900 / HP 5890 II GC System Parameters Log			
Method:		Lewisite Derivatization / DAAMS Tube / ECD Screen and AED Confirmation			
Operator: Uday Mehta		Date: 1/31/94			
Flow Settings					
Sampling Flow (ml/min)	<input type="checkbox"/> Vacuum <input type="checkbox"/> Pressure <input checked="" type="checkbox"/> O ₂ -Line	Sample Saver	ECD system only	<input checked="" type="checkbox"/> ON <input type="checkbox"/> O-F	
		Split Ratio	5 ml/min to focus trap 15 ml/min to sample saver		
Sample Tube	Nitrogen	Focus Tube	Nitrogen	<input type="checkbox"/> EPC <input checked="" type="checkbox"/> Flow Controlled	
Purge/Desorb Flow	20 ml/min	Desorb/Column Flow	4 ml/min		
Sorbent Tube Data					
Tube	Part Number	Materials	O.D.	I.D.	
Sample Collect	MX-08-2111 / 20-35	Tenax-TA, 20-35 mesh, 150 mg	6 mm	4 mm	
Sample Saver	MX-06-2111 / 20-35	Tenax-TA, 20-35 mesh, 150 mg	6 mm	4 mm	
Focus Trap	AC-08-5229	Tenax-TA, 20-35 mesh / AWS glass beads, 60/80 mesh	6 mm	9 mm	
Temperature Setpoints					
Valve	225 °C	<input type="checkbox"/> OFF	Transfer Line	250 °C	<input type="checkbox"/> OFF
Tube Desorb	350 °C	<input type="checkbox"/> OFF	Trap Desorb	350 °C	<input type="checkbox"/> OFF
Tube Idle	°C	<input checked="" type="checkbox"/> OFF	Trap Idle	°C	<input checked="" type="checkbox"/> OFF
Time Setpoints					
Ex. Sample	0 minute(s)	<input type="checkbox"/> OFF	Tube Cool	2 minute(s)	<input type="checkbox"/> OFF
Tube Dry	4 minute(s)	<input type="checkbox"/> OFF	Trap Heat	1 minute(s)	
Tube Heat	3 minute(s)		Sys. Recycle	0 minute(s)	<input type="checkbox"/> OFF
Other Controller Module Settings					
GC/Data System	Both systems set ON	<input checked="" type="checkbox"/> ON	Cycles	Both systems set OFF	<input checked="" type="checkbox"/> OFF
Remote Start		<input type="checkbox"/> OFF	# of Samples		
Sample Saver	ECD system set ON	<input checked="" type="checkbox"/> ON			
Split Function	AED system set OFF	<input checked="" type="checkbox"/> OFF			
GC Column Data					
Phase	I.D.	Length	Film Thickness		
J & W DB-5	.53 mm	30 meters	1.5 µm		
GC / ECD Conditions					
Initial Temp.	80 °C	Final Temp.	275 °C		
Initial Hold	1 minute(s)	Final Time	0 minute(s)		
Rate 1 (A)	15 °C/minute to 140°C / 0 minutes	Detector 1	Electron Capture Detector		
Rate 2 (E)	25 °C/minute	Detector Temp. 350°C	Make-up Flow: 30 ml/min Nitrogen		
GC / AED Conditions					
Initial Temp.	70 °C	Final Temp.	250 °C		
Initial Hold	0 minute(s)	Final Time	0 minute(s)		
Rate 1 (A)	15 °C/minute	Detector 1	Atomic Emission Detector		
Rate 2 (B)	0 °C/minute	Element	Arsenic		
GC Block/Trans Line	250 °C	Cavity Block	270 °C		
Min. Peak Width	0.04 minutes	CRT WIND	10 minutes		
Sol. Vent Open	0.5 minutes	Sol. Vent End	7.8 minutes		
CRT 2'S	CRT Offset 5%	Element 1	Wavelength: 189.092	Reagent Gas: H ₂ F No Filter	

IDENTIFICATION OF AMBIENT AIR SAMPLING AND ANALYSIS METHODS FOR THE 189 TITLE III AIR TOXICS

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ABSTRACT

The state of development of ambient air measurement methods for the 189 Hazardous Air Pollutants (HAPs) in Title III of the Clean Air Act Amendments was surveyed. Measurement methods for the HAPs were identified by reviews of established methods, and by literature searches for pertinent research techniques. Methods were segregated by their degree of development into *Applicable*, *Likely*, and *Potential* methods. This survey identified a total of 183 methods, applicable at varying degrees to ambient air measurements of one or more HAPs. As a basis for classifying the HAPs and evaluating the applicability of measurement methods, a survey of a variety of chemical and physical properties of the HAPs was also conducted. The results of both the methods and properties surveys were tabulated for each of the 189 HAP. The current state of development of ambient measurement methods for the 189 HAPs was then assessed from the results of the survey, and recommendations for method development initiatives were developed.

INTRODUCTION

The 1990 Clean Air Act Amendments (CAAA) accelerated the pace of regulating toxic air pollutants by establishing a list of 189 Hazardous Air Pollutants (HAPs). The HAPs are a remarkably diverse group of compounds, including metals, pesticides, chlorinated and hydrocarbon solvents, industrial chemicals and intermediates, combustion byproducts, complex chemical mixtures, and chemical groups such as polychlorinated biphenyls. Some of the HAPs are volatile organic compounds commonly measured as air pollutants. Many other HAPs are widely recognized as toxic, but have previously only been addressed in workplace environments. Some of the HAPs are not single compounds, but rather complex mixtures or groups of chemicals spanning broad ranges of chemical and physical properties. A few HAPs, such as titanium tetrachloride, phosphorus, and diazomethane, are unlikely to exist in ambient air because of their reactivity.

To meet the CAAA goals of defining and reducing human health risks from HAPs, ambient measurements are needed. However, ambient measurement methods for the HAPs are generally lacking, possibly because of a lack of adequate measurement methods and the diversity of the HAPs. A recent survey of ambient HAPs data conducted for U.S. EPA showed no ambient data for 74 of the 189 HAPs,¹ and furthermore found less than 100 ambient measurements for 116 of the HAPs.

The present study was conducted to identify existing and potential ambient measurement methods for 189 HAPs. This study differed from similar previous surveys^{2,3} in that the physical and chemical properties of the HAPs were compiled, and used as the basis for evaluating the applicability of measurement methods. This survey also identified novel research methods, rather than relying solely on official compilations of standard methods. Finally, this survey categorized the HAPs measurement methods by their state of development, distinguishing workplace, laboratory or stack emission methods from methods actually tested in ambient air. The project final report⁴ provides complete details of the survey methods, results, assessment and recommendations; this paper presents highlights of the study.

SURVEY METHODS

HAPs Properties

The chemical and physical properties of interest in this survey are those that affect the sampling and measurement of HAPs in the atmosphere. To organize the compilation of properties, the HAPs were divided into groups. As a starting point, the 189 HAPs were first divided into organic compounds and inorganic compounds. This initial distinction was based largely on the designation of chemicals in the CRC Handbook of Chemistry and Physics, and on the known nature of the HAPs. The primary properties then obtained for all the HAPs were vapor pressure (VP in mm of Hg at 25°C) and boiling point (and/or melting point) temperature. The vapor pressure data were used to categorize and rank the HAPs. Quantitative vapor pressure criteria were set up defining very volatile organic and inorganic compounds (VVOC and VVINC).

VP > 380), volatile compounds (VOC and VINC: VP from 0.1 to 380), semivolatile compounds (SVOC and SVINC: VP from 10^{-7} to 0.1), and nonvolatile compounds (NVOC and NVINC: VP < 10^{-7}). These vapor pressure criteria are similar to those used in similar previous categorizations,⁵ except for the very volatile categories. The vapor pressure criteria are somewhat arbitrary, and compounds with vapor pressures near the criterion values generally fall into "gray areas" that define gradual transitions from one volatility class to the next. For the volatile and very volatile HAPs, further chemical and physical properties were compiled, consisting of electronic polarizability, water solubility, aqueous reactivity, and estimated lifetime relative to chemical reaction or deposition in the atmosphere.

The primary information sources used for the HAPs properties survey were handbooks and published reports of chemical and physical properties (references provided in the project report), including computer data bases specifically addressing the 189 HAPs.⁶ Whenever possible, inconsistencies and errors were corrected by comparisons of data from various sources, searches of the STN (Beilstein file) computer data base, and through consultations with EPA staff.⁷

HAPs Measurement Methods

The search for measurement methods for the HAPs was intended to be as wide-ranging as possible. Information sources included standard compilations of air sampling methods, such as EPA Source Test Methods, EPA Contract Laboratory Program (CLP) and Compendium (i.e., TO-) methods, as have been used in previous surveys.^{2,5} However, this study also reviewed standard methods designated by the Intersociety Committee on Methods of Air Sampling and Analysis, the National Institute of Occupational Safety and Health (NIOSH), the Occupational Safety and Health Administration (OSHA), and the American Society for Testing and Materials (ASTM). Additional sources of information were the two surveys recently conducted by Battelle for EPA on the ambient concentrations and atmospheric transformations¹ of the HAPs. The ambient concentrations survey was especially useful as a guide to measurement methods for HAPs, and assured that methods were identified for all HAPs that have been measured in ambient air. In addition, reports, journal articles, and meeting proceedings known to contain information on HAPs methods were obtained and reviewed. In general, highly complex and expensive spectroscopic research methods were considered unsuitable for widespread monitoring and were not included in this survey.

The measurement methods identified for the 189 HAPs were organized into three categories, depending on the degree of development of the method:

Applicable - An *Applicable* method was defined as one which has been reasonably established and/or documented for measurement of the target HAP in ambient air; designation as an *Applicable* method does not necessarily imply that the method has been approval or certified by U.S. EPA for measurement of the target HAP in ambient air. In most cases, methods identified as *Applicable* have actually been used for ambient measurements. In other cases, a method was identified as *Applicable* for a specific HAP because of the degree of documentation and standardization of the method, even though no ambient data were found. The identification of a *Applicable* method does not guarantee adequate measurement of the pertinent HAP(s) under all circumstances; simply, the method was evaluated to be capable of being applied to ambient air measurements of the HAP. Further development and evaluation may be needed to assure sensitivity, freedom from interferences, stability of samples, precision, accuracy, etc., under the range of conditions found in ambient measurements.

Likely - Two types of *Likely* measurement methods were defined. The most common type is a method which has been clearly established and used for the target HAP in non ambient air, such as OSHA or NIOSH methods established for HAPs in workplace air. The second type of *Likely* method consists of techniques identified as *Applicable* for one HAP, and consequently inferred as *Likely* for another HAP based on close similarity of chemical and physical properties.

Potential - A *Potential* method was defined as one which needs extensive further development before application to ambient air measurements will be justified. Many *Potential* methods have been evaluated for the target HAP in sample matrices other than air (e.g., water, soil). *Potential* methods were inferred for some HAPs, based on *Applicable* or *Likely* methods found for other HAPs of somewhat similar chemical and physical properties. The degree of similarity of properties between HAPs was used as the guide in designating *Potential* methods in those cases.

For HAPs for which no *Applicable* or *Likely* methods were found, further searches were conducted beyond the reviews outlined above. For such HAPs, detailed literature searches were conducted using the files of Chemical Abstracts Service (CAS) and the National Technical Information Service (NTIS). The computer searches were not restricted to English language publications. In all method searches and reviews, the chemical and physical properties compiled in this study were valuable. The quantitative similarity of properties such as vapor pressure, solubility, and reactivity of HAPs was used to suggest *Likely* and *Potential* methods, and the degree of similarity of properties determined the choice between designation as a *Likely* or *Potential* method.

Detection limits or ranges of measured concentrations were indicated for each method and HAP as reported in the respective methods. Supporting information such as the approximate sampled air volume was also compiled. An effort was made to indicate the detection limit for at least the most fully developed method(s) for each HAP, but detection limits were not estimated when not explicitly stated in the method. The detection limits reported were meant primarily as a guide to the relative capabilities of the various methods. Reference and method citations in the methods survey were aimed at providing the user of the survey with enough information to review at least the basics of the identified method, and to locate further information if needed. No effort was made to compile all possible information on each method.

RESULTS

HAPs Properties

The first result of the survey of HAPs properties was the assignment of HAPs to the various volatility classes, using the vapor pressure criteria discussed previously. The 189 HAPs were categorized into VVOCs (15), VOC (82), SVOC (64), NVOC (5), VVINC (6), VINC (3), SVINC (2), and NVINC (12), where the numbers of HAPs in each class are shown in parentheses. HAPs that are actually compound classes were categorized on the basis of the most volatile species likely to be present in ambient air. The volatile and semivolatile compound classes comprise the majority of the 189 HAPs, with organic compounds (166 chemicals) predominating over inorganic compounds (23 chemicals).

The project final report⁴ presents the complete results of the properties survey, in two different tabular forms. The first table lists the 189 HAPs in the same order as in the CAAA, with the HAP name, CAS number, molecular weight, volatility class, vapor pressure, boiling point, and water solubility. The second table lists properties for VVOCs and VOCs only, and includes some of the information from the first table, but also includes electronic polarizability, aqueous reactivity, and lifetime in ambient air.

HAPs Measurement Methods

The HAPs method survey is presented in the project final report⁴ in the form of a comprehensive table that presents the 189 HAPs in the same order as they appear in the CAAA. A portion of the complete table is shown in Table 1 of this paper. For each HAP, the name, CAS number, and major volatility class are shown. The ambient methods information is listed in successive columns for *Applicable*, *Likely*, and *Potential* methods. The respective methods identified for each HAP are indicated by standard method designations (e.g., TO-5, CLP-2, NIOSH 5514), or by citations to the pertinent literature (e.g., R 1, R-2, etc.). The limits of detection for selected methods are provided, together with explanatory comments. The methods and literature citations compiled in conducting the methods survey are cited in a reference list following the complete methods table. HAPs consisting of compound classes were addressed by identifying methods for the most and least volatile species of each class likely to be present in ambient air.

In all, this survey identified 183 methods pertinent to ambient measurements of the 189 HAPs, comprising of 15 TO- methods, 51 NIOSH methods, 30 OSHA methods, 3 EPA screening methods, 4 CLP methods, and 80 reference methods. A summary of the methods survey results was then prepared to examine whether the most fully developed method for each HAP falls within the definition of *Applicable*, *Likely*, or *Potential*. This summary, presented in the form of a table in the project report,⁴ lists each HAP together with its volatility class assignment, and indicates the current status of methods identified for the HAP. In the summary table, *Likely* and *Potential* methods are each sub-divided into two categories, one for methods inferred on the basis of HAP chemical and physical properties, and the other for methods established for the particular HAP. The total number of HAPs in each method development column was determined from this summary table, with Figure 1 showing a graphical overview of the results.

Figure 1 shows that for 126 HAPs (two-thirds of the HAPs list), *Applicable* ambient measurement methods were found. Figure 1 also shows that for 53 HAPs, *Likely* methods were found, but no *Applicable*

methods. Most of these *Likely* methods were specific to the HAP in question, but for 7 HAPs the identification of *Likely* methods was inferred based on HAP properties. For 6 HAPs only *Potential* methods could be identified, and of those, 3 were inferred on the basis of chemical and physical properties. For 4 HAPs, no measurement methods could be identified at any level of development. The finding of 126 HAPs with *Applicable* methods is consistent with a recent survey⁵⁻⁷ which found ambient data from urban areas in the U.S. available for 115 of the HAPs. Note, however, that in considering Figure 1, the definition of a *Applicable* method must be stressed. An *Applicable* method is one which is targeted for the indicated HAP in ambient air, and which has been developed and documented to a reasonable degree. This does not mean that all *Applicable* methods have actually been used for ambient measurements of the indicated HAPs, or that all sampling and analysis difficulties have been solved. An overly optimistic view of the state of HAPs measurement methods could result if Figure 1 is interpreted without these reservations.

A more detailed evaluation of the methods summary was also conducted with respect to the most developed methods available by class of HAPs. For most of the volatility classes, *Applicable* methods were identified for the majority of the HAPs. In total, *Applicable* methods were identified for 109 of the 166 organic compounds, and for 17 of the 23 inorganic compounds. However, for the 5 NVOCs and 2 of the 3 VINCs, no *Applicable* methods were found. In all volatility classes, most compounds with no *Applicable* methods could be associated with one or more *Likely* methods. This result appears to suggest that for the great majority of the HAPs, promising methods at least exist from which ambient methods may be developed. However, for 6 HAPs, namely *Acetamide* (SVOC), *2-Acetylaminofluorene* (NVOC), *Benzotrichloride* (SVOC), *Chloramben* (SVOC), *1,2-Diphenylhydrazine* (SVOC), and *N-nitroso-N-methyl urea* (VOC), only *Potential* methods could be identified. Finally, for 4 HAPs, namely, *Acrylic acid* (VOC), *Ethyl carbamate* (VOC), *Hexamethyl phosphoramide* (SVOC), and *Titanium tetrachloride* (VINC), no methods of any kind were identified.

SUMMARY AND RECOMMENDATIONS

For 126 of the 189 HAPs, measurement methods designed for use in ambient air were identified. Most, but not all, of these methods have actually been used for ambient measurements of the pertinent HAPs. For 53 other HAPs, measurement methods were identified which are likely to be applicable to ambient air after some further development. Based on these observations, ambient measurement methods appear to be achievable for the great majority of the 189 HAPs. For 6 HAPs, existing measurement methods would require extensive further development before application to ambient air can be considered. For 4 HAPs, no measurement methods in any state of development were identified. Cumulatively, these latter 10 HAPs comprise the greatest gap in measurement capabilities for the HAPs.

In terms of method development needs for the HAPs, the most cost-effective approach would probably be further development of the *Likely* methods that exist for the 53 HAPs with no *Applicable* methods. The definition of a *Likely* method means that a reasonable degree of further development should result in a method applicable to ambient air. Of the 53 HAPs with only *Likely* methods, 44 are VVOCs, VOCs, or SVOCs. These three groups are the largest classes of HAPs, so further development of methods for such compounds would be particularly beneficial. In addition, the large number of *Applicable* methods already available for volatile and semi-volatile organics should enhance development of methods for additional compounds. Continued evaluation of measurement methods for all the HAPs would be worthwhile. An important goal of such an effort should be to consolidate and simplify the variety of methods available into a smaller number of well-characterized and broadly applicable methods. Further verification of HAPs methods is needed, even for *Applicable* methods, particularly for the research methods identified.

The 10 HAPs identified previously for which only *Potential* methods or no methods were found would seem to indicate the greatest current need for ambient method development. These 10 HAPs are relatively unusual compounds, not normally regarded as ambient air contaminants and some are highly reactive and not likely to be present for long in the atmosphere.¹ There are no ambient air concentration data for these 10 HAPs,² and virtually no information on potential atmospheric reaction products.³ Consequently, it is difficult to determine whether they or their reaction products cause a significant health risk in ambient air. Method development should be pursued for these 10 HAPs, but should be prioritized based on information on the emissions, reactivity and products of these HAPs. This approach will avoid spending time and resources on method development for a HAP or HAPs that are, for example, too reactive (e.g., titanium tetrachloride) or emitted in quantities too small to be present at measurable levels in the atmosphere. This linkage of method development with other information should in general be valuable for all other HAPs.

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ACKNOWLEDGMENTS

This work was conducted by Battelle under the sponsorship of the U.S. Environmental Protection Agency's Atmospheric Research and Exposure Assessment Laboratory (EPA/AREAL), under Contract No. 68-D0-0002, Work Assignment 44. The Work Assignment Manager was Dr. William A. McClenny. This paper has not been subjected to Environmental Protection Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. We gratefully acknowledge the involvement and technical insight of Drs. McClenny and Robert G. Lewis of EPA in the work.

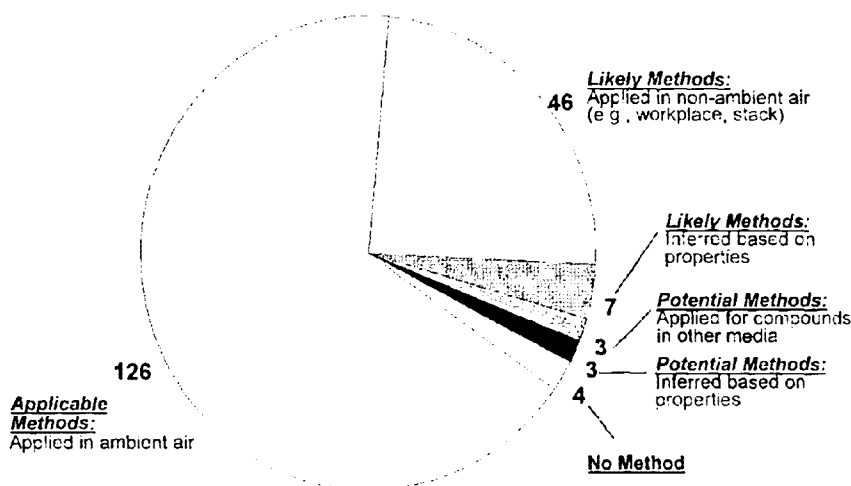


Figure 1. Distribution of the 189 HAPs by the most developed type of ambient measurement method currently identified for each HAP.

Table 1. Partial listing of the ambient measurement methods table for the 189 HAPs presented in the project final report.⁴

Compound	CAS No.	Compd. Class ^a	Ambient Measurement Method			Limit of Detection ^{a,2,3,4,5}	Comment
			<i>Applicable*</i>	<i>Likely</i>	<i>Potential</i>		
Acetaldehyde	75-07-0	VVOC	TO-5 TO-11	R-4 [14]		TO-5: 1 ppbv; TO-11: 1 ppbv [14]; 30 ppmv	
Acetamide	60-35-5	SVOC			OSHA CIM [A625, R-37; R-47]		[A625]: not a validated method; R-47: method developed for analysis of water
Acetonitrile	75-05-8	VOC	R-1, CLP-1A, R-3	TO-15		R-1: 1 ppbv	
Acetophenone	98-96-2	VOC	CLP-2		TO-15	CLP-2: 37 ng/m ³ (0.007 ppbv)	
2-Acetylaminofluorene	53-96-3	NVOC			OSHA CIM [C065]		[C065]: not a validated method

* Designation as an *Applicable* method does not necessarily imply certification or approval by U.S. EPA as an ambient air measurement method

**Direct Trace Analysis of Volatile Organic Compounds in Air Using
Filtered Noise Field Ion Trap Mass Spectrometry**

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There is increasing interest in the development of field portable mass spectrometers to monitor environmental pollutants in real time. A direct air sampling filtered noise field (FNF) ion trap mass spectrometer has been evaluated in the laboratory under controlled conditions with an environmental test chamber serving as the source of the target compound mixtures at known concentrations. The FNF ion trap technology developed by Teledyne has been used with direct sampling interfaces (semipermeable membrane; glow discharge ionization source) to measure nonpolar and polar VOCs at trace levels. This ion trap is capable of true selective ion monitoring and, when operated in the MS/MS mode, provides a unique means of simultaneously isolating individual target compounds in complex mixtures with high sensitivity and specificity. The device is small and light-weight, and can be easily deployed in the laboratory or the field. Using the combination direct sampling/ion trap system, experiments have been carried out to evaluate the specificity, sensitivity, response time, and effects of relative humidity on the detection of 44 nonpolar and 15 polar VOCs of environmental interest.

A System for the Determination of Trace-Level Polar and Non-Polar Toxic Organic Compounds in Ambient Air

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ABSTRACT

A gas chromatographic system is described for the determination of toxic organic compounds in ambient air. These compounds include all those specified within the U.S. EPA Compendium Method TO14 and some polar additional analytes under consideration for the proposed TO15 Method. The system supports both on-line and off-line (passivated canisters and adsorption tubes) methods for sampling air -- providing a fully automated analysis. A key feature of the system is that liquid cryogen is not required for either the analyte preconcentration or the subsequent chromatographic separation. Water management is achieved by dry-purging an adsorbent trap upon which the sample analytes have been retained.

The performance of the system is demonstrated with conventional detection systems (electron capture and flame ionization) and with a mass spectrometer.

INTRODUCTION

A companion paper [1] discussed the various aspects of water management associated with the collection and analysis of ambient air. This paper examines the instrumental considerations of a system for the analysis of volatile toxic organic compounds in air. Several key requirements identified for such a system are listed below:

- Should be applicable to the U.S. EPA TO14 target analytes and polar compounds proposed for the pending TO15 method
- Should support on-line and off-line (passivated canisters and adsorbent tubes) sampling methods
- Should enable sub-ppb detection limits
- Should be compatible with capillary chromatography
- Should eliminate the need for a liquid cryogen
- Should eliminate the effects of water
- Should be compatible with conventional and mass spectroscopic detection systems

INSTRUMENTATION

Operation

Figure 1 provides a schematic overview of the instrumental components of the system. This basic configuration is intended to be used, with minor changes, both with conventional detection systems such as flame ionization and electron capture and with a mass spectrometric detection system.

The operational sequence starts with the air sample or the effluent from a heated adsorbent tube being passed into an adsorbent trap held at a near-ambient temperature. The volatile organic compounds are retained within the adsorbent trap along with some of the water within the sample. After analyte preconcentration, a flow of dry purge gas is passed through the adsorbent to remove most of the residual

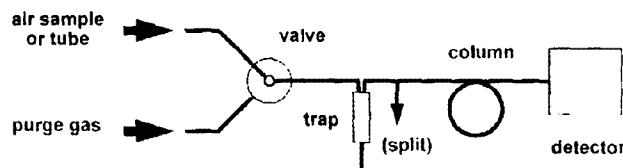


Figure 1. Overview of instrumentation

moisture. The adsorbent trap is then heated and a flow of carrier gas in the reverse direction backflushes the analytes, using splitting if required, into the chromatographic column. Chromatography then commences. The system is fully automated for on-line and off-line (canister and tube) analyses and is designed to enable the next sample to be collected while chromatography of the current sample is still in progress.

System with conventional detectors

System description

Table 1 lists the instrumental conditions for a system that uses flame ionization and electron capture detection systems. Chromatographic separation is important with these detectors so a long, very low phase-ratio column is used to retain the early eluting components at 40°C. To reduce the analysis time a high carrier gas flow rate (5 to 6 ml/min.) is applied. Although this is not normally considered optimum for chromatographic efficiency, the faster rate does result in a more efficient desorption of analytes from the trap and thus improve the chromatography of the early eluting components. The system employs the dry-purge technique described previously [1] to remove much of the water collected in the trap. Note that no split is applied to the trap effluent as it passes into the chromatographic column.

Table 1. Experimental conditions for the system using conventional detectors.

Chromatograph	Perkin Elmer AutoSystem
Column	100 m x 0.32 mm x 5.0µm methyl silicone, Scientific Glass Engineering
Oven	40°C for 10 min., then 5°C/min. to 250°C, hold for 8 min.
Detector	a) Flame ionization at 300°C b) Electron capture at 300°C
	Column effluent split 300:1 FID:ECD
Thermal Desorption System	Perkin Elmer ATD 400
Adsorption Trap	Perkin Elmer Air Monitoring Trap, 27°C during sample collection (15 min. at 30 ml/min.) and dry purge (3 min. at 30 ml/min.), 325°C during desorption for 10 min. with no split
Carrier Gas	Helium at 25 p.s.i.g. (5 ml/min. flow rate through the column)

Results

Figure 2 shows typical chromatography from the system for 450 ml of a mixture of 10 ppbw TO1 target analytes from a canister. Good peak shape is apparent for all the peaks and good chromatographic separation is achieved for all components except m-xylene/p-xylene and o-xylene/1,1,2,2-tetrachloroethane. Table 2 includes a list of the analytes and the quantitative precision exhibited by the system over a series of repetitive analyses.

Table 2. Quantitative precision of the system for TO14 analytes under different operating modes

Analyte #	Analyte Name	% RSD of Peak Areas, FID/ECD & Canister, (n=12)	% RSD of Peak Areas, MS & Canister, (n=9)	% RSD of Peak Areas, MS & Tube, (n=5)
1	Freon 12	+9.75	1.97	2.85
2	methyl chloride	6.34	2.70	6.39
3	Freon 114	13.71	1.52	3.81
4	vinyl chloride	1.56	1.78	3.95
5	1,3-butadiene*	3.08	2.35	13.01
6	bromomethane	23.63	9.51	16.55
7	ethyl chloride	10.56	5.88	5.71
8	Freon 11	+0.85	2.14	2.94
9	vinylidene chloride	1.07	3.31	5.54
10	dichloromethane	1.33	4.60	7.68
11	3-chloropropene	1.31	3.33	6.50
12	Freon 113	+0.70	3.71	3.01
13	1,1-dichloroethane	1.07	2.02	4.13
14	cis-1,2-dichloroethylene	3.11	2.06	3.75
15	chloroform	+0.48	2.46	3.66
16	1,2-dichloroethane	3.43	2.45	5.36
17	methylchloroform	+0.70	2.03	2.50
18	benzene	0.75	3.88	5.68
19	carbon tetrachloride	+0.79	2.43	1.83
20	1,2-dichloropropane	1.03	2.74	4.01
21	trichloroethene	+0.65	3.57	4.05
22	cis-1,3-dichloropropene	1.63	7.89	17.57
23	trans-1,3-dichloropropene	0.76	9.64	17.83
24	1,1,2-trichloroethane	1.67	3.28	3.53
25	toluene	1.02	2.58	3.69
26	1,2-dibromomethane	+0.55	8.54	14.73
27	tetrachloroethene	+0.57	1.98	1.12
28	chlorobenzene	1.02	2.37	4.14
29	ethyl benzene	0.49	2.12	4.16
30	m,p-xylenes**	0.39	2.56	3.88
31	styrene	0.31	2.22	2.48
32	1,1,2,2-tetrachloroethane	+1.18	2.63	3.56
33	o-xylene	***	2.03	3.84
34	ethyl toluene	0.62	2.15	3.21
35	1,3,5-trimethylbenzene	0.95	1.69	3.58
36	1,2,4-trimethyl benzene	1.18	1.81	2.78
37	benzyl chloride	2.73	1.69	4.55
38	m-dichlorobenzene	1.68	2.76	2.36
39	p-dichlorobenzene	1.90	2.72	0.90
40	o-dichlorobenzene	2.29	1.33	2.04
41	1,2,4-trichlorobenzene	5.59	2.05	1.27
42	hexachlorobutadiene	+6.08	2.89	1.37

* ECD data; all others in this column are from the FID

1,3-butadiene is not included in the USEPA TO14 list of target analytes

* These components cannot be separated on this column or by mass spectrometry, so the data is combined

** O-xylene co-elutes with 1,1,2,2-tetrachloroethane and so cannot be quantified on the FID

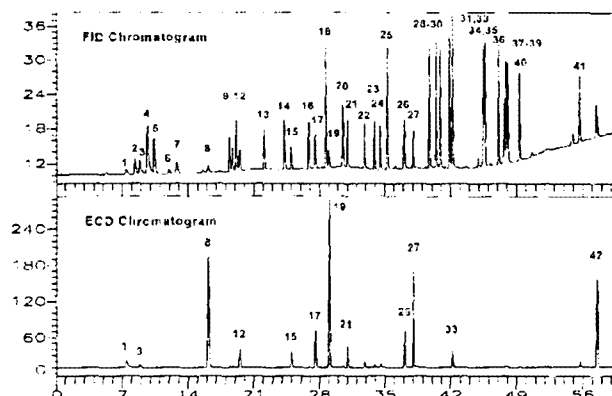


Figure 2. Typical chromatogram of 10 ppbv TO14 analytes from system with conventional detectors. The identities of the peak numbers are given in Table 2.

System with a mass spectrometer

System description

Table 3 lists the instrumental conditions for a system that uses a mass spectrometer as the chromatographic detection system. The system is very similar to that for the conventional detectors. The carrier gas flow rate must be restricted to approximately 1 ml/min. for efficient detector operation. Chromatographic separation, however, is less critical as peaks may be discriminated by selective mass chromatograms. Therefore, to reduce both the flow rate and the analysis time, a shorter column of the same type is employed. The mass spectrometer is much less tolerant of water than the conventional detectors so the amount of water is further reduced by taking a larger sample volume and applying a small split on the trap effluent as described previously [1]. It was found that the carbon-based adsorbents used in the trap generated carbon dioxide in use. To minimize this effect, the trap was heated to the lower temperature of 280°C with no apparent degradation in the shape of the early eluting peaks. The ion with m/z 44 was excluded from the total ion chromatograms to further reduce the effects of the carbon dioxide on the visualized chromatography.

Table 3. Experimental conditions for the system using a mass spectrometer.

Chromatograph	Perkin Elmer Autosystem
Column	50 m x 0.32 mm x 5.0µm methyl silicone, Scientific Glass Engineering
Oven	40°C for 10 min, then 5°C/min to 250°C, hold for 8 min
Detector	Perkin Elmer QMASS 910, scan acquisition mode, 30 to 300 a.m.u.
Thermal Desorption System	Perkin Elmer ATD 400
Adsorption Trap	Perkin Elmer Air Monitoring Trap
	a) Canister sampling: 27°C during sample collection (50 min at 20 ml/min) and dry purge (3 min at 30 ml/min)
	b) Tube sampling: 27°C during tube desorption/dry purge (10 min : ml/min)
	280°C during trap desorption for 10 min with 6:1 outlet split
Carrier Gas	Helium at 5 p.s.i.g.
Tube	Perkin Elmer Air Monitoring Sample Tube
Tube Desorption	280°C for 10 min at 30ml/min desorption flow

Results

Figures 3 and 4 show typical total ion chromatograms from the system for 1000 ml of a mixture of 10 ppbv TO14 target analytes from a canister and a number of adsorbent tubes (loaded from the same canister) respectively. Good peak shape is apparent for all peaks upon a clean, flat baseline signal.

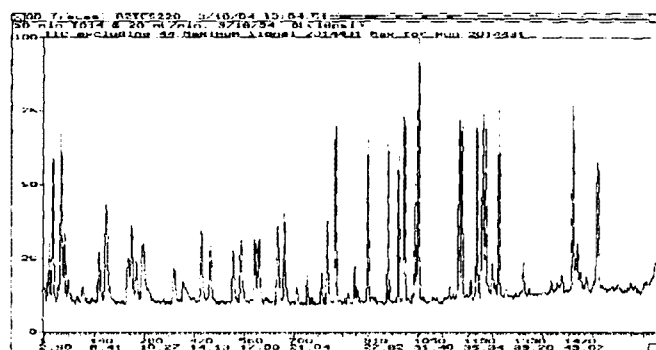


Figure 3. Typical total ion chromatogram of 10 ppbv TO14 analytes from canister sample

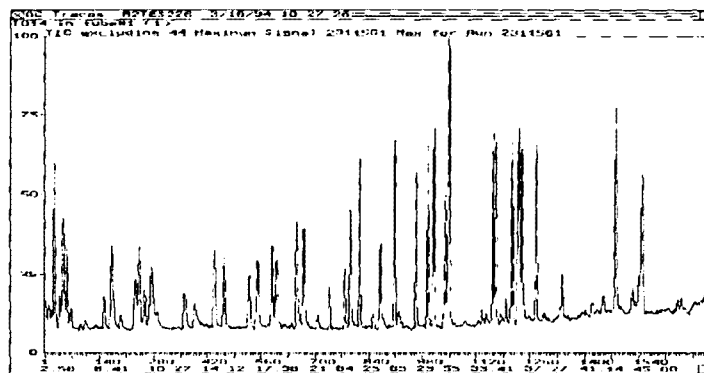


Figure 4. Typical total ion chromatogram of 10 ppbv TO14 analytes from tube sample

One concern to many analysts is equivalency between canister and tube sampling. Figure 5 shows plot of absolute areas, for selective ion peaks, for both canisters and tubes. Good agreement between the two sampling methods is evident.

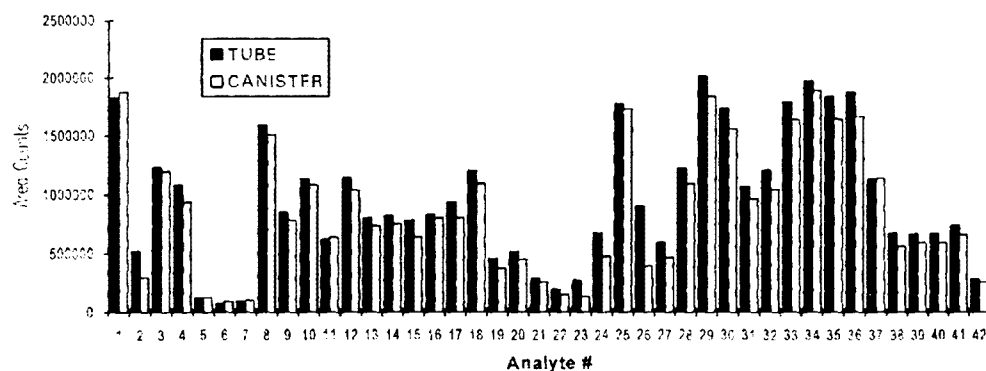


Figure 5. Comparison in analyte recovery between canister sample and tube sample. The analyte identities are given in Table 2.

A second concern is the generation of artifacts or carry-over effects. *Figure 6* shows chromatograms (same scale) of two analyses of the same tube in succession. No artifact or carry-over effect is apparent in the second chromatogram.

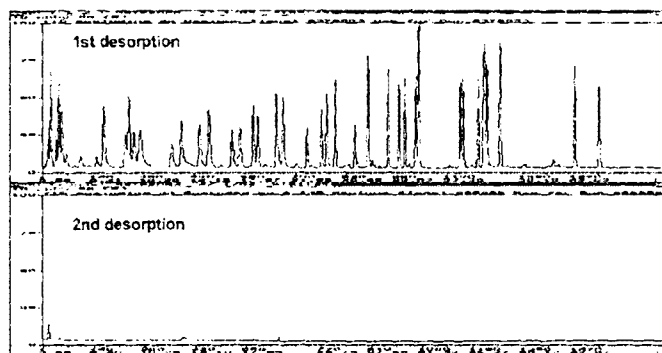


Figure 6. Lack of artifact and carry-over effects from an adsorbent tube

Table 2 includes the quantitative precision for samples taken from canisters and tubes. In all case these values are less than 20% and in most cases they are less than 5% and are very similar to those obtained from the conventional detector system.

Figure 7 shows selective mass chromatograms of a ~2 ppbv mixture of TO14 analytes. These eluting analytes are the 'worst-case' components for detection limits because of their reduced response factors and because of increased background noise (because of traces of water and carbon dioxide). The chromatograms clearly show that detection limits will be below the 1-ppbv level.

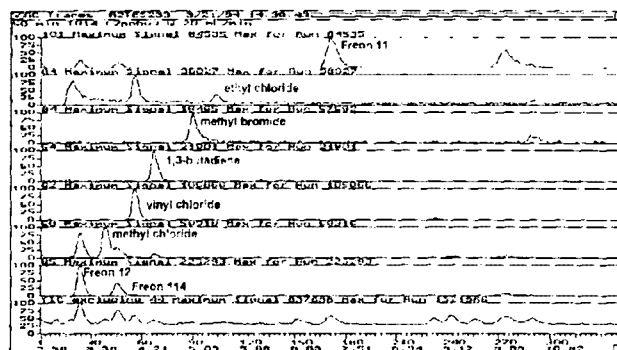


Figure 7. Selective mass chromatograms of early eluting TO14 analytes at 2 ppbv from a canister

Figure 8 shows normalized plots of detector response versus volume of sample up to 2000 ml. These data provide an indication of the retention capabilities of the adsorbent trap and also an indication of the system's quantitative linearity. All the data appears satisfactory except for methyl chloride, methyl bromide and 1,2-dibromomethane. These analytes are known to be highly reactive and are known to readily hydrolyze in water at low temperatures [2,3]. The effect appears to be less pronounced with the volume adopted for this analysis (1000 ml).

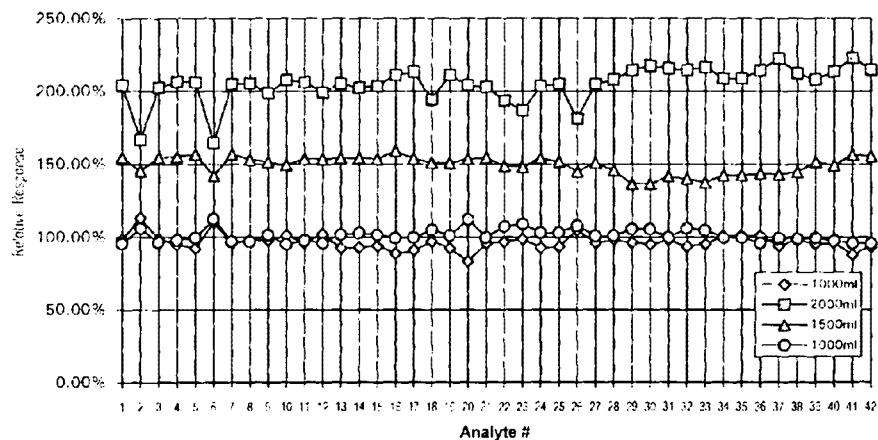


Figure 8. Normalized plots showing variation in response with sample volume from 10 ppbv TO14 canister mix. The analyte identities are given in Table 2.

Figure 9 shows a total ion chromatogram of several polar analytes at the 10 ppbv level extracted on an adsorption tube. Note that even methanol is easily visualized.

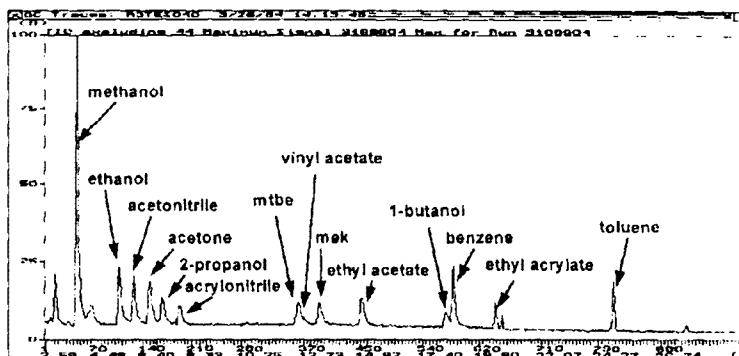


Figure 9. ~10 ppbv polar analytes from an adsorption tube

Figure 10 shows chromatograms of an ambient air sample in which the presence of methyl t-butyl ether (MTBE) is suspected. Figure 11 shows the mass spectrum of the highlighted peak that was easily confirmed to be MTBE.

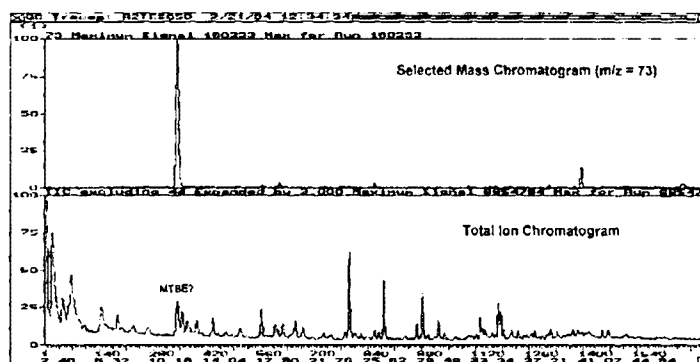


Figure 10. Chromatogram of ambient air taken on-line at Wilton, Ct on 2/21/94

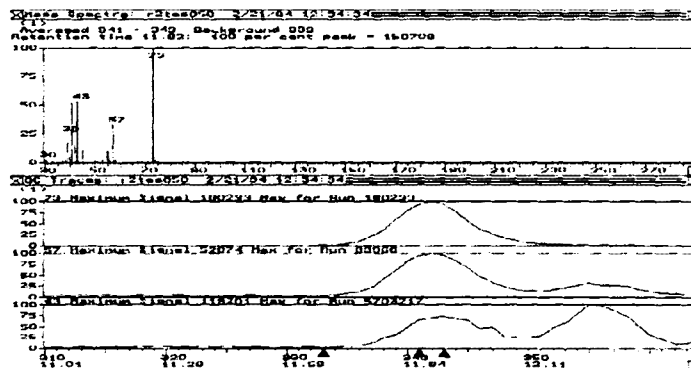


Figure 11. Mass spectrum confirming identity of MTBE peak

CONCLUSIONS

These data demonstrate the practical application of a multimode instrumental system for on-line and off-line (using canisters or tubes) sampling methods. The extraction and preconcentration of analytes from the air and the subsequent chromatography is performed without the need for a liquid cryogen. The dry-purge technique coupled with a small desorption split, removes sufficient water to enable detection by mass spectrometry. The dry-purge does not exclude polar analytes from the analysis and as a result, compounds such as MTBE have been detected at low levels in ambient air.

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Water Management in Capillary Gas Chromatographic Air Monitoring Systems

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ABSTRACT

Capillary gas chromatography is an excellent technique for the speciated quantitation of low-level volatile organic compounds (VOCs) in ambient air.

Although GC detectors have excellent sensitivity, some sample pre-concentration will be necessary to enable detection of VOCs at sub-ppb levels. This process normally employs a cooled and/or adsorbent trap to retain the analytes from a large volume of sample air. For very volatile VOC's, a very retentive trap is used and this may also retain water present as vapor in the sample. This trapped water causes significant problems with the chromatography and detector operation and methods must be sought to remove it or eliminate its effects.

This paper investigates the magnitude of the problem and examines the various alternatives for managing the trapped water. The application of some of these techniques is demonstrated in a method for the determination of volatile polar and non-polar toxic organic compounds in ambient air.

INTRODUCTION

This paper is intended to serve as an introduction to a companion paper [1] to be presented and published in the same forum. It is designed to consider the various aspects of water management and to provide the basis for practical instrumentation to perform analytical methods such as the U.S. EPA Compendium Method TO14 [2] and proposed polar analytes to be included in the pending TO15 method [3].

The first questions to address in considering water management, are:

- how much water is collected
- what happens to water inside the analytical system
- what options are available to remove water

Amount of water in the air

The amount of water in the air sample depends on three factors:

- Sample humidity
- Sample temperature
- Sample volume

The first two of these cannot be controlled by the analyst as they depend on climatic conditions. The analyst is able, however, to choose the volume of sample to be collected. The main factor that dictates the amount of sample to be taken is the detection limits of the gas chromatographic detection system to be used. For typical detectors this means that a sample volume of 100 ml to 1000 ml must be taken in order

collect sufficient mass of the analytes to be detected. *Figure 1* shows a plot of the water content of air at 75 % and 100 % relative humidity (R.H.) over a range of temperatures [4].

This plot shows that, for example, if a 420-ml sample was taken at 20 °C at 75 % R.H., approximately 6 mg of water also would be collected.

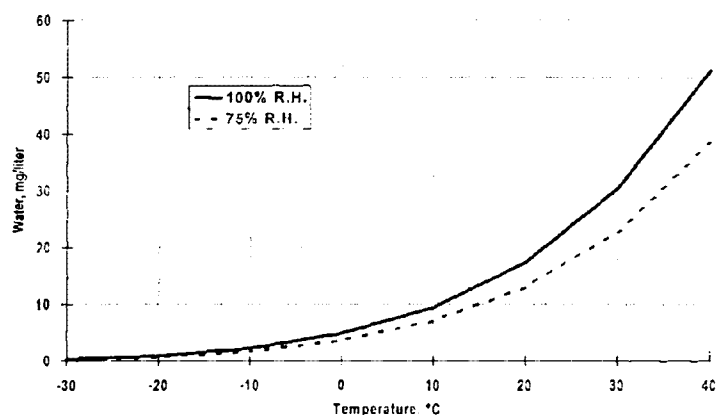


Figure 1. Water content of air at 75 % and 100 % R.H. over a range of temperatures

Effects of water

A typical capillary column requires a gaseous sample volume of about 50 μ l at its inlet for efficient operation. This means that the analytes in the sample must be preconcentrated by a factor of about 10,000 prior to chromatography. This preconcentration is readily effected using a trapping device as shown in *Figure 2*. The trap may be cooled or packed with an adsorbent or both of these in order to retain the analytes as the sample is drawn through. A cooled trap will retain most of the moisture from typical air samples as a result of simple condensation. *Figure 3* shows the amount of water that would be collected from a range of sample volumes on an unpacked trap cooled to various temperatures.

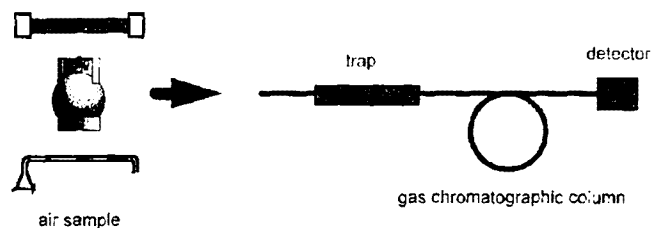


figure 2. Overview of air preconcentration technique

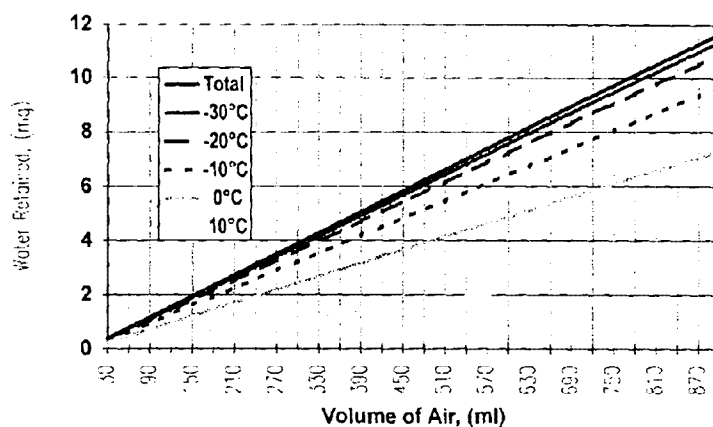


Figure 3. Condensation of water from air at 20 °C and 75 % R.H. onto a trap cooled to a range of temperatures

If no efforts are made to reduce this water, it may cause significant problems in the analysis as shown in the list below:

- Potential Blockage of Cold Trap
- Possible Reduction in Trapping Efficiency
- Possible Reduction in Desorption Efficiency
- Disturbance in Chromatographic Carrier Flow
- Spurious Chromatographic Peaks
- Smearing of Chromatographic Peaks
- Degradation of Chromatographic Column
- Detector Quenching or Degradation
- Obscuration of Peaks of Interest

Options for water reduction

High trap temperature

The easiest way of preventing the condensation of water within the trap is to maintain it at a temperature above that of the sample during collection. To retain analytes at such a temperature, the trap must be packed with a suitable adsorbent.

Hydrophobic adsorbents

There are many adsorbents currently available from a variety of suppliers that have been used successfully by many analysts for sample collection without experiencing problems with water. These have been generally applied to components less volatile than n-C4 [5,6]. Analytes such as those specific in the TO14 method [2] require stronger carbon-molecular sieve based adsorbents that are slightly hydrophilic and will retain significant amounts of water.

Smaller sample volumes

Taking smaller volumes of sample will directly reduce the amount of water entering the analytical system. Although this may address problems associated with ice formation in cold traps, the ratio of the amount of water to analyte (typically 1,000,000:1) will not be reduced. More sensitive detection systems will be required to detect the lower analyte levels and, if these are sensitive to water, problems may still be experienced in handling chromatographic peaks that co-elute with the water. Collecting samples at flows below about 5ml/min may be unreliable and introduce additional errors into the analysis. Thus taking small volumes may not be possible in instances where long sampling times are required to determine time-weighted average analyte concentrations.

Condensation

Water will be removed from the air sample by condensation if it is taken below the dew point. This can be achieved by lowering the sample temperature or increasing the sample pressure. However, it is also possible for target analytes to condense with the water or for them to partition into the water and so causing quantitative errors as a result.

Sample Splitting

With a semi-hydrophilic adsorbent, at above-ambient temperatures, the trap may become saturated with water after, for example, 500 ml of air have passed through it during sample collection. If further sample is taken, the amount of water will not increase but the amount of analyte will increase. This has the effect of reducing the ratio of water to analyte on the trap. By splitting the effluent from the trap during thermal desorption, the amount of water entering the column is reduced to a more practical level while maintaining the required analyte levels.

Semi-permeable membrane dryers

Perfluorinated membrane dryers (NAFION, Du Pont) have been successfully employed in the TO14 [2] and Ozone Precursor [7] analyses. They are easy to use and give excellent performance especially with aliphatic and aromatic hydrocarbons [8]. They can, however, remove polar analytes from an air stream as shown in *Figure 4*.

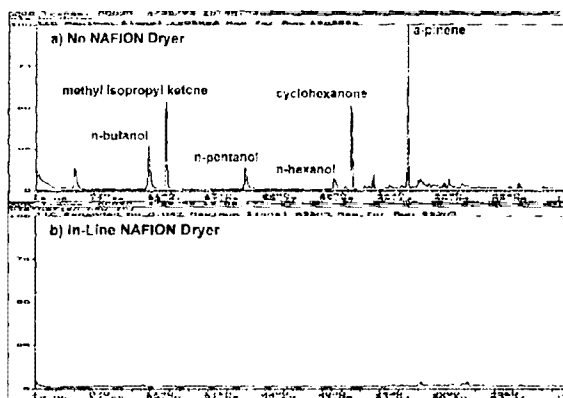


Figure 4. Loss of Polar Analytes on NAFION Dryer

Inorganic desiccants

Inorganic desiccants have been successfully applied by several workers [10] in abstracting water from air streams. They tend to be selective in their application and quickly become saturated with water.

Dry purge of the adsorbent

When a semi-hydrophilic adsorbent is used for sample collection at above-ambient temperatures, the residual water left by the sample may be reduced by passing a dry gas through the adsorbent and out to a vent [3,9,11] as shown in *Figures 5a to 5c*. The only requirement is that none of the analytes should elute from the trap during this purging process.

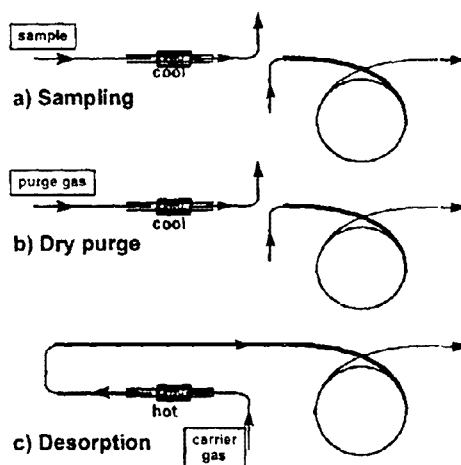


Figure 5. Operational Sequence of Dry Purge Technique

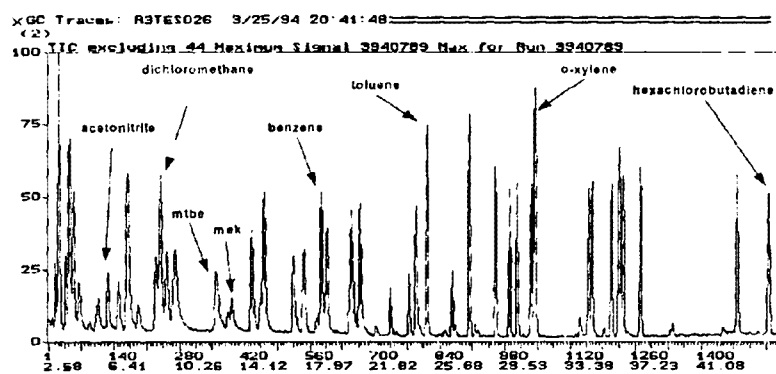


Figure 6. Total ion chromatogram of ~10 ppbv TO14 target analytes and added polar compounds

This approach offers the maximum flexibility in terms of sample volume, sampling method (on-line, passivated canister or adsorption tube), analyte range (non-polars and polars) and detection systems. The dry purge technique may also be combined with trap outlet splitting as required.

The practical application of the water removal technique for a complex and demanding analyte range is shown in *Figure 6*. This shows a total ion chromatogram of TO14 and polar analytes using a combination of dry purging and trap outlet splitting obtained using the conditions listed in *Table 1*. *Figure 7* shows some selective mass chromatograms that illustrate that analytes such as methanol, acetone and methyl t-butyl ether can be easily visualized and quantified using this technique.

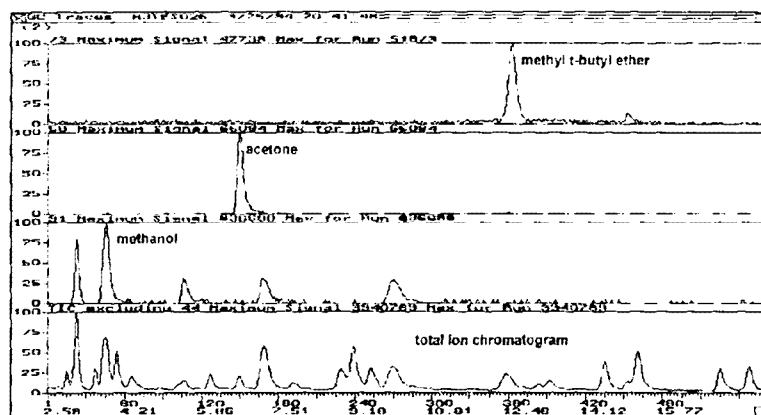


Figure 7. Selective mass chromatograms of early eluting polar analytes in ~10 ppbv mixture of TO14 target analytes and added polar compounds

Table 1. Experimental conditions for the determination of TO14 and Polar Analytes in ambient air using the dry purge technique.

Chromatograph	Perkin Elmer Autosystem
Column	50 m x 0.32 mm x 5.0µm methyl silicone, Scientific Glass Engineering
Oven	40°C for 10 min., then 5°C/min to 250°C, hold for 8 min.
Detector	Perkin Elmer QMASS 910, scan acquisition mode, 30 to 300 a.m.u.
Thermal Desorption System	Perkin Elmer ATD 400
Adsorption Trap	Perkin Elmer Air Monitoring Trap, 27°C during sample preconcentration and dry purge (10 min.), 280°C during desorption with 6:1 outlet split
Carrier Gas	Helium at 5 p.s.i.g.
Sample	Perkin Elmer Air Monitoring Sample Tube Loaded with 1000 ml (50min at 20 ml/min) 10 ppbv TO 14 analyte mix with added polar analytes
Sample Desorption	280°C for 10 min. at 30ml/min desorption flow

Further experimental details of the instrumentation, its operation and performance are given in the companion paper [1].

CONCLUSION

A method has been developed that offers potential for the gas chromatographic determination of both non-polar and polar analytes in ambient air without the inherent problems traditionally associated with water even when using a mass spectrometer as a detector.

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**The Perkin-Elmer ATD-400 System for Monitoring of Ambient
VOC Ozone Precursors**

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The systems described were used in the Texas Natural Resource Conservation Commission (TNRCC) Coastal Oxidant Assessment for Southeast Texas (COAST) program. Continuous VOC monitoring programs were implemented in June through November of this year in Houston. This Perkin-Elmer developed monitoring system included a dual capillary column chromatographic application in an 8700 GC with a modified ATD-400 sampling system. The resulting separations are monitored and quantified using Turbochrom (ver. 3.2) chromatographic data handling software. The key element to this system is the thermal desorption device which is capable of concentrating VOCs from ambient air then desorbing them directly to the gas chromatograph on a continuous cycle. The ATD-400, unlike other similar devices, contains an activated carbon trap which is electrically cooled during collection via Peltier technology. This eliminates the need for cryogenic liquids or compressed air (vortex) for sample collection and makes unattended field operation more feasible than previous systems. The entire system is integrated to provide a completely automatic sample collection cycle, gas chromatographic analysis and data collection, reduction and report generation. Reliability and repeatability data suggest that the system is robust. Good correlation between systems and quality audits confirms data from the manufacturer. Modifications which are being implemented to the chromatographic system, system sites, and operator behavior to enhance the system performance will also be presented.

**System Operation: Continuous Volatile Organic Compound Air
Monitoring of 56 Ozone Precursors with the Perkin-Elmer 8700 GC
and Automatic Thermal Desorption System**

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As part of the Coastal Oxidant Assessment for Southeast Texas (COAST) program, two sites were chosen by the Texas Natural Resource Conservation Commission (TRNCC) and equipped with a Perkin-Elmer VOC system composed of the 8700 Gas Chromatograph, ATD-400 Automatic Thermal Desorption and Turbochrom III Data system on DEC computers. The systems were equipped with a dual capillary column application capable of resolving 56 distinct target ozone precursors. These components were separated and quantified on an hourly basis 24 hours each day. Each system generated 96 data files and approximately 30 documentation files each day totaling nearly 3 megabytes of information. The system was fully automated and monitored rigorously via high-speed modem communication. The modem communication proved to be essential in the handling of the large volume of data generated each day. A fully automated data transfer system was developed to allow unattended file archiving thus eliminating many problems associated with manual handling of files and facilitating the rapid evaluation of the data. This paper will identify the major issues in operation and maintenance of these systems (not including the chromatographic application). Problems which were encountered can be subdivided into two categories, a) hardware system problems such as power failures, equipment malfunction and temperature/humidity fluctuations, and b) software issues: capability/incompatibility, bugs, communication problems and a plethora of computer or computer-related issues (confusion).

SESSION 13:

**APPLYING TOTAL HUMAN EXPOSURE
METHODOLOGIES TO ADDRESS
ENVIRONMENTAL HEALTH ISSUES ALONG THE
U.S.-MEXICO BORDER**

Session cancelled.

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SESSION 14:
PARTICLE STUDIES

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**The Role of Size-Dependent Dry Deposition of Sulfate Aerosol in
a Three-Dimensional Eulerian Air Quality Model**

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The Regional Particulate Model, a three-dimensional Eulerian air quality model, was developed to investigate aerosol particle issues of importance to the U.S. EPA and to meet the demands of the Clean Air Act Amendments of 1990. In addition to aerosol dynamics such as growth and coagulation, the model includes photochemistry, transport, and deposition. A new formulation of dry deposition as a function of the aerosol size distribution has been incorporated into the model. This formulation allows for the representation of dry deposition of total particle number and total particle mass by deposition velocities specifically formulated for these two quantities as a function of particle size. Results for the dry deposition of sulfate mass from the new model will be compared with those from the Tagged Species Engineering Model (McHenry, et al., 1992) for a variety of local conditions. The behavior of the aerosol size distribution responding to the new formulation will also be discussed.

McHenry, J.N., Binkowski, F.S., Dennis, R.L., et al.
(1992) *Atmos. Environ.*, **26A**:1427-1443.

¹On assignment to the Atmospheric Research and Exposure Assessment Laboratory, U.S. EPA.

Size Distributions Parameters and Hygroscopic Growth of Aerosol Particles Bearing V

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Size-segregated submicrometer aerosol particles were collected with microorifice impactors (MOI) at three sites in the heavily urban, but nonindustrialized Washington, DC. metropolitan area, during a 40-day period in August and September of 1990, when atmospheric V was principally derived from commercial and utility oil combustion. Results for 34 MOI samples, analyzed for V by instrumental neutron activation analysis, were fit with a least-squares technique which used impactor calibration data to determine log-normal distribution parameters, i.e., mass median aerodynamic diameter (mmad) and geometric standard deviation (σ_g) for fine-particles bearing V. The median mmad for 19 College Park (CP) samples was 0.361 ± 0.006 μm . At this site mmads for samples collected in the absence of rain and with V concentrations >0.61 ng/m^3 increased continuously with increasing RH from 56 to 79% according to the equation $d_p^{-3} = 0.02168 \pm 0.00325 \cdot \ln(a_w) - 0.0130$. Mmads for samples collected at the other sites were characteristically smaller than those determined at CP at comparable RH, possibly, due to the influence of nearby oil-fired boilers. Vanadium aerosol data for rural Chesapeake Bay sites will also be presented.

**Measurement and Speciation of Gas and Particulate Phase
Organic Acids in an Urban Environment**

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Organic acids are important contributors to ambient acidity, in both gas and particulate phase. Particulate phase organic acids represent an important fraction of organic particulate matter. This paper presents the results of a field study conducted in Philadelphia, PA, during the summer of 1992, to measure the concentrations of gas and particulate phase organic acids. Formic acid was found to be the most abundant gas phase organic acid, with acetic and propionic acids detected at lower concentrations. Organic acids constituted approximately 5% of the particulate fine mass, whereas sulfate and ammonium constituted 40% and 15%, respectively. Dicarboxylic acids and even-carbon monocarboxylic acids were found to account for a large fraction of particulate weak acidity; odd-carbon monocarboxylic acids accounted for a very small fraction. The pronounced even carbon preference of the monocarboxylic acid distribution suggests a biogenic origin; the dicarboxylic acid distribution may suggest that primary emission is more important than photochemical production. This paper discusses the measurement and analytical techniques used in this study and the chemistry and origins of organic acids.

Philadelphia Diesel Particulate Matter Monitoring Study

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ABSTRACT

This paper summarizes the results of a monitoring study conducted in Philadelphia to learn more about the contribution of diesel particulate emissions to particulate matter concentrations in urban areas. Saturation monitors and a dichotomous sampler collected data for 28 days in two traffic corridors. The results indicate that higher particulate matter concentrations occur where there are higher bus counts and traffic volumes. The daily operation of the study is described and average bus counts and quality assurance results are discussed. The monitoring method used in this study proved to be reliable with a 95% data capture of ambient particle mass.

INTRODUCTION

Because of the nature of their use, heavy duty diesel buses are predominately found in heavily populated metropolitan areas. They discharge up to 70 times more particulate than gasoline-powered vehicles, thus contributing to known air quality problems and a widespread consensus on the health risks associated with exposure to their emissions.¹ During the period of October 19 to November 18, 1993, a study was conducted to monitor diesel particulate emissions in and around the Center City section of Philadelphia, PA. The purpose of this study was to monitor particulate emissions in an urban street canyon-like area influenced by diesel bus traffic. This paper summarizes the methodology used and the particulate matter data obtained during the study period.

EXPERIMENTAL

Sampling Sites

The monitoring network consisted of 15 saturation monitor sites (one collocated with a dichotomous sampler) in the City Hall/Dilworth Plaza section of Philadelphia (see Figure 1). An additional saturation monitoring site, Site 16, was located approximately six blocks south of the City Hall area. Sites 1 through 8 are primarily located along Market Street where it meets East Penn Square. Sites 9 through 15 are located along the Chestnut Street Transitway which functions as a one way dedicated bus corridor. These two areas, referred to as Market Street and Chestnut Street, represent typical urban streets bordered on both sides by tall buildings, thus creating a corridor or canyon effect. Site 16 would be considered a non-canyon monitoring site.

All saturation monitors were hung on streetlight poles at 3.2 to 3.4 meters above the sidewalk level and generally within 3.0 meters from the roadway. Collocated saturation monitoring sites were Sites 1, 4, 10, and 14. The dichotomous sampler and a saturation monitor were located at Site 2 at the corner of Commerce and Juniper Streets.

Saturation Monitor and Dichotomous Sampler

The saturation monitor is a non reference portable battery powered sampler that is often used to determine approximate particulate matter concentrations in short duration studies. The Airmetrics (Springfield, OR) saturation monitor was used to collect samples for measurement of particles with an aerodynamic diameter less than or equal to a nominal 10 micrometers (PM-10). Samples were collected on a 47 mm Pallflex (Putnam, CA) Teflon®-coated glass fiber filter. Particle separation is achieved by impaction. The monitor operates at a flow rate of 5 L/min at ambient conditions. The monitor is equipped with a programmable timer to automatically start and stop sampling.

The Anderson (Atlanta, GA) dichotomous sampler is a low-flow-rate (16.7-L/min) sampler that divides the air stream passing the 10- μm inlet into two portions, which are filtered separately. The sampler cuts the 0- to 10- μm total sample into 0- to 2.5- μm (fine) and 2.5- to 10- μm (coarse) fractions, which are collected on separate 37-mm Millipore (Bedford, MA) Teflon® filters. The coarse and fine fractions are combined to give a total sample.

Bus Counts

Bus counts were taken at the Market Street and Chestnut Street (note B on the map in Figure 1) areas over four days at four different time intervals covering morning and evening peak traffic rush hours. Market Street has unrestricted two-way traffic with approximately 115 to 150 buses per hour during traffic rush hours. Buses on Market Street include both Philadelphia city buses and interstate commuter buses. Chestnut Street is restricted to one-way Philadelphia city bus traffic with approximately 25 buses per hour during traffic rush hours.

Sampling Schedule

The saturation monitors at Site 1 and Sites 3-16 were set on automatic timers to turn on at 2:00 p.m. and turn off the following morning at 10:00 a.m. The batteries and filter holders were changed between 10:00 a.m. and 2:00 p.m. daily. Collocated saturation monitors operated for one-week periods to obtain integrated samples at Sites 1, 4, 10, and 14. The dichotomous sampler and the saturation monitor at Site 2 collected 24-hour samples. Filter, filter holder, and battery changes were performed daily around 9:45 a.m.

Filter Handling and Weighing

All weighing was performed in the laboratory at Research Triangle Park (RTP) according to EPA quality assurance specifications. After the initial weighing of filters for the saturation monitors and the dichotomous sampler, the filters were placed in individual, labeled plastic storage dishes. After sampling, the filters were placed in their original dishes and returned to RTP for final weighing at the end of the study. The filters were weighed on a Cahn C-31 microbalance (Cerritos, CA) located in an environmentally controlled chamber. All filters were placed in the chamber a minimum of 24 hours prior to both initial and final weighing.

RESULTS AND DISCUSSION

Saturation Monitor and Dichotomous Sampler Data

The PM-10 mean concentrations for saturation monitor Sites 1 and 3-8 (Market Street) and Sites 9-15 (Chestnut Street) are presented in Figure 2. The average number of buses per hour during peak traffic hours is also indicated for each area. Market Street PM-10 mean concentrations range from 38.4 $\mu\text{g}/\text{m}^3$ to 48.2 $\mu\text{g}/\text{m}^3$ with an average bus count of 130 buses per peak traffic hour. Chestnut Street PM-10 mean concentrations range from 31.8 $\mu\text{g}/\text{m}^3$ to 34.0 $\mu\text{g}/\text{m}^3$ with an average bus count of 25 buses per peak traffic hour. It appears that the higher PM-10 mean concentrations in the Market Street area are related to the higher bus counts and volume of traffic. Site 16 is the non-canyon site with a mean concentration of 34.7 $\mu\text{g}/\text{m}^3$.

The PM-10 concentrations for selected Sites 1,4,6,8,10 and 14 by sample day of week are shown in Figure 3. These sites represent concentrations in both the Market Street and Chestnut

Street areas. During the study period, the measured PM-10 concentrations consistently fluctuate and track each other regardless of site location. The PM-10 concentrations for weekends are consistently lower than average weekday PM-10 concentrations.

The total particle mass collected by the dichotomous sampler peaked at $70.4 \mu\text{g}/\text{m}^3$ and resulted in a mean concentration of $36.9 \mu\text{g}/\text{m}^3$. The PM-10 mean concentration for the collocated saturation monitor at Site 2 was $34.5 \mu\text{g}/\text{m}^3$. When comparing the collocated saturation monitor and dichotomous sampler PM-10 concentrations, 88% of the values agree within 20% of each other. The dichotomous sampler fine fraction averaged 68% of the total PM-10 sample for the 28 sample days.

Quality Assurance Results

The dichotomous sampler flow and saturation monitor flows were checked daily and adjustments were made if necessary. Blank dichotomous filters, both fine and coarse, and normal and field saturation monitor filter blanks were collected. There were no appreciable changes in the before-study and after-study filter weights (less than 0.009% difference). Quality assurance in the filter weighing procedure was also conducted and recalibrations of the balance were made as appropriate.

Saturation monitors were collocated for one-week periods at sites 1, 4, 10, and 14. Comparative concentration results of the collocated monitors under ambient conditions indicate an average percent difference of 5.1% between the main monitor and the collocated monitor.

The overall percent data capture for the study for both the saturation monitors and the dichotomous sampler was 95%.

CONCLUSIONS

The results of this study confirmed that saturation monitoring can be a useful screening tool. There was good agreement between the PM-10 concentrations measured by the dichotomous sampler and its collocated saturation monitor. Furthermore, the saturation monitoring method used in this study proved to be reliable for collecting atmospheric particle mass data (95% data capture overall). The quality assurance practices conducted in this study resulted in a weighing precision that is well within acceptable limits.

Based on the comparison of PM-10 mean concentrations at the Market Street and Chestnut Street areas, it appears that higher PM-10 concentrations are measured where there are higher bus counts and traffic volumes, thus more tailpipe emissions and particle resuspension off roadway surfaces.

During the 28-day study period, PM-10 concentrations measured on weekends were consistently lower than the average weekday, regardless of site location. Fluctuations in day-to-day PM-10 concentrations were consistent for all site locations.

The PM-10 mean concentration at the non-canyon site is higher than the PM-10 mean concentration for the Chestnut Street area. This may be due to the much greater volume of traffic, thus tailpipe and resuspended particulate matter emissions, at the non-canyon site.

For the dichotomous sampler and its collocated saturation monitor, 88% of the measured concentration agree within 20% of each other. Two-thirds of the total sample measured with the dichotomous sampler is in the fine fraction for this study period.

Future monitoring studies may further our understanding of the impact of diesel emissions on particulate matter concentrations. For example, ambient particulate concentrations and traffic volumes collected using continuous sampling methods and video surveillance equipment would provide real-time data for time-series analyses. Because of the renewed interest in fine particulate matter concentrations in urban areas, consideration should be given to conducting saturation monitoring studies using a $2.5\text{-}\mu\text{m}$ cut point indicator for collecting real-time or diurnal data.

ACKNOWLEDGEMENTS

This paper is based on work performed by ManTech Environmental Technology, Inc. for the U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards and the Atmospheric Research and Exposure Assessment Laboratory.

DISCLAIMER

Statements made in this paper are those of the authors and do not necessarily represent the views of the U.S. Environmental Protection Agency or ManTech Environmental Technology, Inc.

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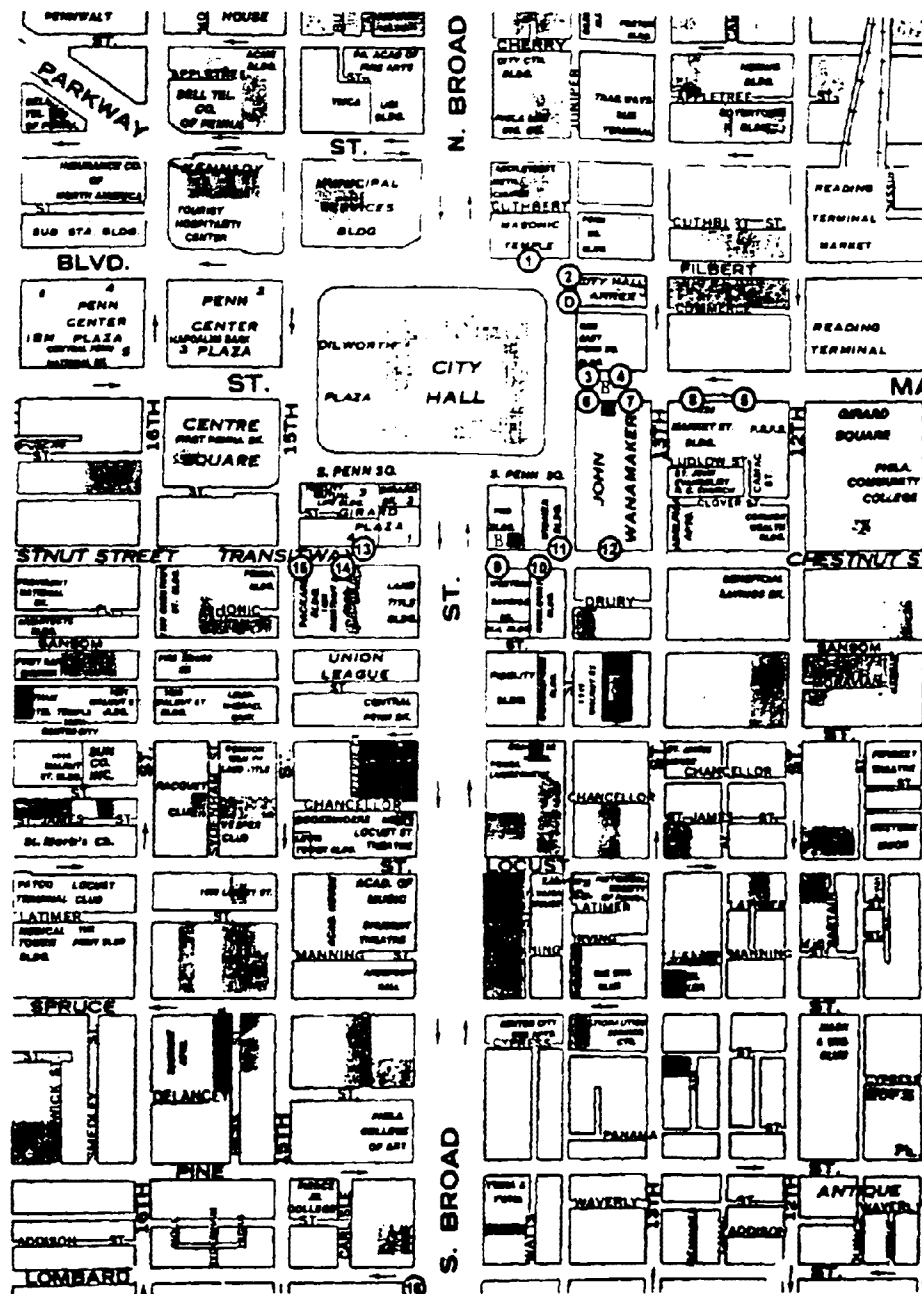


Figure 1. Map of sampling area in Philadelphia, PA.

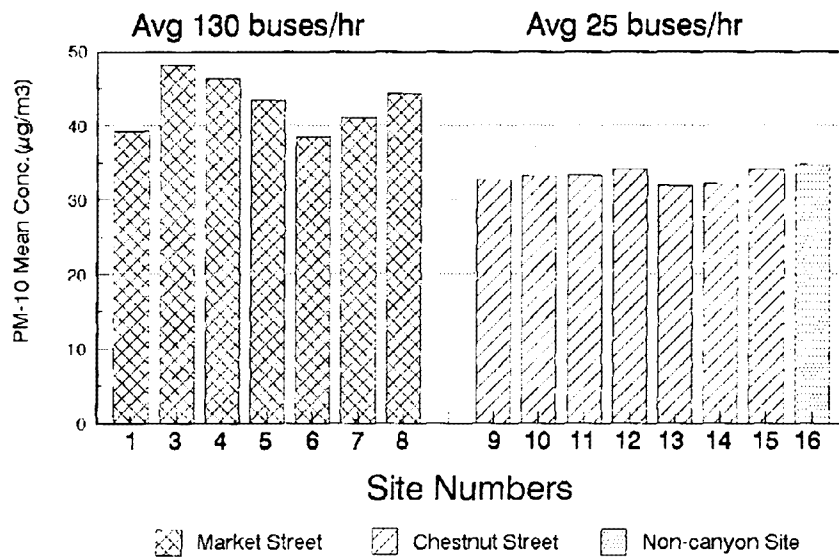


Figure 2. Market Street vs. Chestnut Street saturation monitor results.

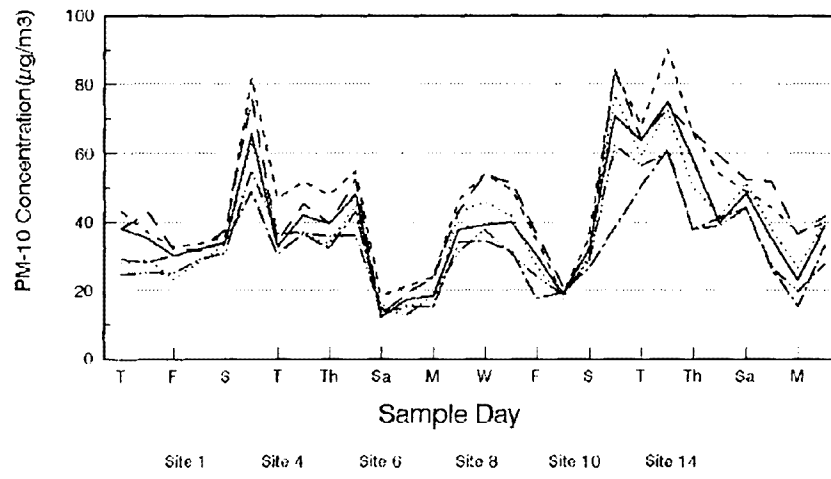


Figure 3. Tracking daily concentrations for Sites 1, 4, 6, 8, 10, and 14.

Diurnal and Elevational Variations in Ozone and Aerosol Concentrations in New Hampshire's Class I Airsheds

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ABSTRACT

Ozone and fine mass aerosol concentrations on New Hampshire's Mount Washington, situated adjacent to both the Presidential/Dry River and Great Gulf Wilderness Class-I Airsheds, exhibit distinct diurnal and elevational patterns. These patterns are attributed to regional pollutant transport dynamics, nocturnal atmospheric stratification, mountain meteorological phenomena and scavenging. A well-defined planetary boundary layer (PBL) forms at about 1 km elevation at night as demonstrated by nocturnal ozone monitoring along the Mount Washington Auto Road. The PBL provides an effective elevational barrier at night, isolating the valleys from the regionally transported air pollutants present above the mixing layer. During the daytime, the PBL breaks up due to convective processes and katabatic winds resulting from solar heating in the valley. This process creates a diurnal mixing cycle with ozone maxima recorded near mid-day in the adjacent valley. In contrast, fine mass concentrations are higher at the valley site, attributed to local source inputs, and the lack of strong nocturnal scavenging processes, compared with ozone. How aerosol concentrations are related to the PBL and how they are affected by diurnal mixing remains unclear largely due to current sampling methods. Exposure to ozone is generally greater above treeline in the two airsheds.

INTRODUCTION

The White Mountain National Forest (WMNF) and its two Class-I Airsheds are located in northern New Hampshire about 200 kilometers north of the metropolitan Boston area. The area experiences 7 million visits per year. Many visitors enjoy hiking along the ridgelines of the Presidential Mountain Range above treeline with its abundant rare arctic plant species. Mount Washington, easily accessed by its summit road and public facilities, is centrally located between the Great Gulf Wilderness (0.5 km north of Mount Washington) and Presidential/Dry River Wilderness (1 km. south of Mt. Washington) Class-I Airsheds, providing an ideal location for assessing air quality impacts. This joint AMC and HSPH study began in 1986 to examine the dynamics of ozone and fine mass aerosols with elevation as a part of a hiker health study and to provide baseline pollutant monitoring to protect the two Class-I areas in cooperation with the White Mountain National Forest.

Methodology

The AMC and HSPH ozone monitoring site on the summit of Mount Washington in New Hampshire's White Mountain National Forest has operated during summer months since 1987 in the Mount Washington Observatory at an elevation of about 1914 m. Data from the site, audited monthly for quality assurance by the state of New Hampshire Air Resources Division (NHARD) and EPA, is submitted to the EPA AIRS retrieval system through NHARD. An AID 560 portable chemiluminescent ozone analyzer was used to acquire elevational ozone data on the Mount Washington Auto Road. While the summit ozone monitor operates continuously from mid-May to mid-

October, the standard analysis period is July/August. Additional detail on ozone monitoring methods may be found in Hill and Allen (1994). Data from the valley site was provided by W. Manning of the University of Massachusetts.

Acid aerosol and fine mass aerosol monitoring is conducted at a high and a low elevation site using Harvard protocol denuder samplers (Koutrakis *et al.* 1988; Marple *et al.* 1987.) Monitoring is also conducted during a standard July/August period. Daily average fine mass and acid aerosol concentrations are taken from nominal 10-hour daytime samples. The valley monitoring site is situated at the AMC Camp Dodge facility at an elevation of about 451 m. At this site fine mass (PM_{2.5}), acid aerosols and sulfate data are collected. At the high elevation site, located at the AMC's Lakes of the Clouds facility at 1,540 m., fine mass, sulfate and acid aerosol concentrations are measured using techniques described in Hill and Allen (1993).

RESULTS OF THE STUDY

Ozone and Fine Mass Aerosols

Typically, higher ozone concentrations are recorded with elevation, on Mount Washington. For the cumulative monitoring period (1987-1993), mean hourly ozone during the standard July/August period was 45 ppb at the summit site and 30 ppb at the valley site. Similarly, the maximum hourly average concentration recorded at the summit, 148 ppb, exceeded the National Ambient Air Quality Standard (NAAQS) in 1988. A considerably lower 105 ppb maximum was recorded at the valley site in 1991. Similar elevational relationships in the Swiss and Austrian Alps have been reported by Samson (1978), Wunderli and Gehrig (1990), and Puxbaum *et al.* (1991). The top of a visible haze layer beneath the summit of Mount Washington is located at the same elevation as the PBL. This haze is composed of fine mass aerosols with nominal 10-hour daytime sample concentrated as high as 81 $\mu\text{g}/\text{m}^3$. Chemical analyses suggest sulfate is 52-64% of the total fine mass aerosol and that sulfate is partially neutralized to ammonium bisulfate.

Elevational Profile of Ozone

Elevational profiles on Mount Washington (Hill and Allen, 1994) indicate nocturnal atmospheric stratification. Radiational cooling forms a valley-bottom inversion layer. In addition, a second layer develops at about 1,000 m. elevation, interpreted to be the PBL. Figure 1 are daytime and a nighttime ozone and temperature profiles for August 3, 1993. The nocturnal profile demonstrates a steady increase in ozone from 26 ppb in the valley bottom to about 1,100 m. where the ozone concentration flattens out at about 56 ppb. Note, also, the temperature inflection at the same elevation for the 5 am. run. This elevation is interpreted to be the PBL. The presence of a visible early morning layer below the summit, and a strong relationship between visibility and aerosols supports this hypothesis. In contrast, the daytime profile indicates homogenous ozone concentrations in the atmosphere from summit to valley due to mixing related to the diurnal thermal cycle.

Diurnal Variations in Ozone on Mount Washington

Figure 2 shows average ozone concentrations for the summers of 1987-1993 broken down by hour at the two sites. The summit curve (n=17,100 hours) exhibits higher overall concentrations and is depressed (reversed) near mid-day. Peak ozone concentrations are commonly recorded between midnight and 6 am at the summit. Based on 1988 data, peaks compared for a HSPH Newtown, CT site and the summit site indicate that ozone travels north and reaches the WMNF after a time lag of about half a day under

conditions of southerly airflow. This relationship, combined with higher concentrations recorded at the summit site, suggest that ozone is regionally transported above the PBL. The base site curve ($n=12,350$ hours) shows a strong diurnal cycle with maxima near mid-day, a pattern nearly identical to the solar heating cycle, and similar to patterns described in the valley bottoms of the Swiss Alps (Wunderli and Gehrig, 1990.) The valley diurnal cycle displays a similar pattern to urban diurnal cycles created by photochemical reactions and the solar cycle. The mountain valley diurnal pattern is, to a lesser extent, the result of photochemical reactions and nighttime scavenging combined with daytime mixing of the concentrated high elevation air down into the valley. Depressed summit concentrations near mid-day temporally coincide with peak diurnal ozone at the valley site and suggest this mechanism. However, because year-to-year trends in valley ozone concentrations do not follow summit trends, there may be a significant influence of local emissions sources on valley ozone conditions. Thus, the differences in ozone concentrations recorded at two sites are attributed to: 1) nighttime stratification and formation of the PBL and attendant regional transport resulting in higher concentrations above the PBL, 2) daytime breakup of the PBL by convectively-driven mixing of summit and valley air, and 3) possible significant local sources for valley ozone.

High and Low Elevation Aerosols

Daytime fine-mass aerosol concentrations from high and low-elevation sites correlate well (Figure 3). The high elevation site, however, shows consistently lower concentrations compared to the valley site. A correlation of fine mass $PM_{2.5}$ between the high elevation and low elevation sites for 1990-1992 data (Figure 3), exhibits a strong correlation with a slope of unity (ANOVA $r^2=0.83$, $p<.0005$) and a $5 \mu g/m^3$ (std. error 0.827) intercept on the base site axis. Higher $PM_{2.5}$ concentrations at the valley site may be a result of emissions from local sources trapped below the PBL and by possible localized mobile source input nearby the monitoring site. In 1993 the site was relocated to reduce any influence of local source emissions. Because aerosol measurements are made during the daytime, high and low elevation aerosols have been influenced by mixing, based on the relationships in the ozone data. In 1994, further nighttime aerosol measurements will aim at discerning the PBL in the aerosol data.

CONCLUSIONS

In summary, we draw the following conclusions:

- 1) Summit ozone data are strongly influenced by regional transport above the PBL; peak ozone concentrations measured at night result from regional transport and an approximate half-day time-lag from emissions sources.
- 2) The valley site is isolated from the higher nighttime ozone concentrations resulting from regional transport due to nocturnal atmospheric stratification. Mid-day peak ozone concentrations in the valley result from: 1) the strong diurnal cycle associated with convective mixing of air and katabatic winds from higher elevations, and 2) possible local sources in New Hampshire; valley minima are the result of radiational cooling and scavenging.
- 3) Daytime aerosol concentrations at high and low elevation sites correlate well and show no apparent PBL influence. Higher concentrations in the valley are attributed to mobile emissions sources but may also be related to a valley haze inversion at night.

- 4) This work demonstrates significant deterioration of air quality in the two Class-I areas. Exposure of hikers and plants to the pollutant ozone is generally greater above treeline.

ACKNOWLEDGEMENTS

This work was partially funded by a WMNF Recreation Cost Share Agreement. The Mount Washington Observatory provided monitoring support at the summit site. Gene Likens provided funding through a grant from the Andrew Mellon Foundation. AMC interns Marion Hourdequin and Sarah Whitney and Jim Liptack are acknowledged for collecting and processing of data. Dr. Petros Koutrakis is acknowledged for support for the project at HSPH. Kenneth Kimball reviewed this manuscript.

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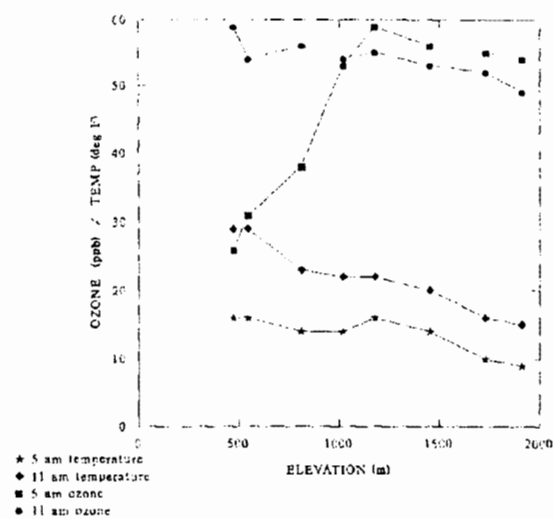


Figure 1: Elevational profiles on Mount Washington, August 3, 1993. 5 a.m. curve indicates increasing ozone concentration with elevation until about 1,200 m. Note inflection in temperature at same elevation. 11 a.m. curve indicates atmospheric mixing and breakup of PBL by mid-day.

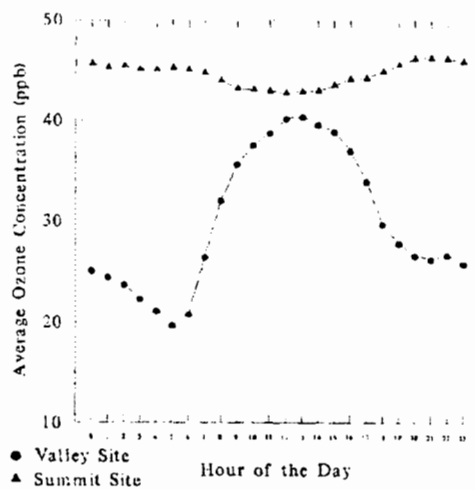


Figure 2: Plot of diurnal ozone cycle at both summit and valley sites July/August 1993 (valley site data courtesy, W. Manning, University of Massachusetts). Valley site shows strong cycle peaking near mid-day, summit site concentrations are higher with a less pronounced depression near mid-day, probably due to convective mixing.

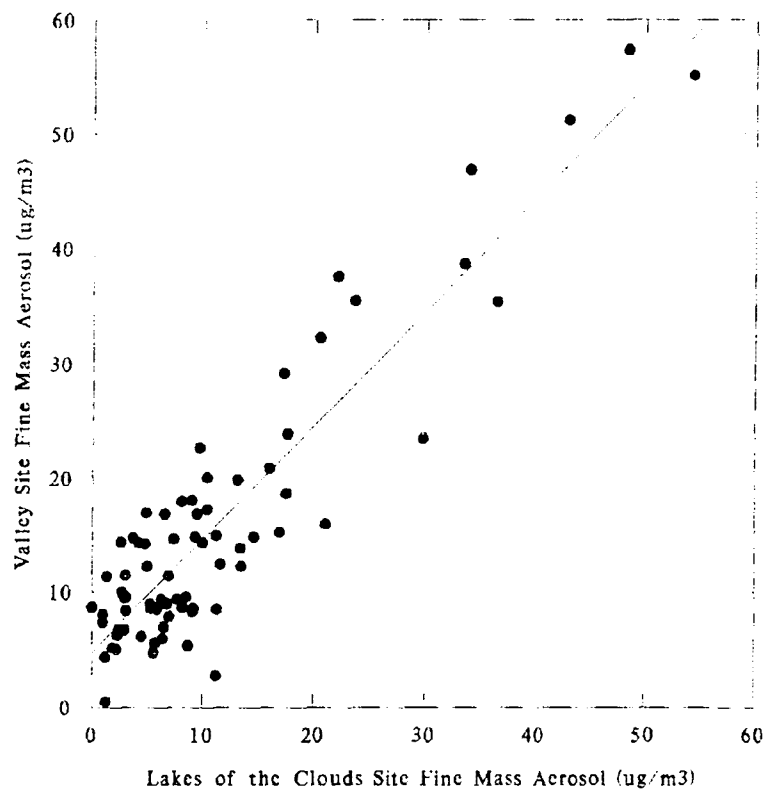


Figure 3: Linear regression of paired nominal 10-hour daytime fine mass aerosol concentrations from high elevation Lakes-of-the Clouds site and valley site 1990-1992 (ANOVA $r^2 = 0.83$, $n=75$, $p < .0005$; intercept=4.747 std. error 0.821.) Indicates average higher daytime fine mass concentrations in valley.

Temporal and Spatial Characteristics of Particle Mass in Metropolitan Philadelphia

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Particle mass concentrations ($PM_{2.5}$ and PM_{10}) were measured daily or every other day at seven residentially oriented sites in Philadelphia, PA during the summers of 1992 and 1993. Samples were collected for 24-h periods using $10\text{ L}\cdot\text{min}^{-1}$ Harvard Impactors for mass. Coarse mass concentrations ($2.5 < d_p < 10\text{ }\mu\text{m}$) were determined by subtraction of $PM_{2.5}$ from PM_{10} . To allow improved temporal characterization during periods of elevated particle mass concentration, continuous or semi-continuous methods for mass, sulfate, and black carbon were also used at one site for the first summer.

Concentrations of PM_{10} and $PM_{2.5}$ were reasonably uniform across the urban area, reflecting the regional nature of summertime transported secondary aerosols typical of summer months in the northeast US. Temporal variation in 24 h concentrations of $PM_{2.5}$ and coarse particle mass are compared and contrasted for a 12 week period at the two sites. Fine mass is shown to dominate the daily and short term (6 to 12 h) temporal variation of PM_{10} concentrations. The relative contribution of elemental carbon and sulfate to the total fine particle mass concentration is contrasted for short term periods of high fine mass concentrations relative to similar periods of non-episodic concentrations, as well as for the 24 h duration samples.

SESSION 15:
STAINLESS STEEL CANISTER
SAMPLING AND ANALYSIS

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SUMMA Canisters - Do They Need to Be Cleaned for TO-14 Analysis?

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Once properly cleaned, should Summa canisters undergo the riggers of cleaning once again when used to collect ambient air samples? The importance of thorough and proper cleaning of stainless steel canisters is known for the proper collection and analysis of ambient air samples. The need for continual cleaning of each canister before use for collection of ambient air samples when used previously for ambient air will be discussed.

BEYOND CANISTER CLEANING...WHAT ABOUT THE SURFACE CHEMISTRY?

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There exists a need for a rapid, definitive test for measuring the surface activity of a canister. The test must meet four criteria: (1) the test solution must be stable in and of itself, (2) the test must be rapid (i.e., less than 10 minutes), (3) the test must be a simple GC test and (4) the test must discriminate between "inert" and "active" surfaces.

Results will be presented using different test probes and a number of new canisters, from two different manufacturers. Test probe recovery as a function of time demonstrates the variability in the surface of the new canisters and also allows the calculation of a statistically derived "inert" surface data base. A variety of older canisters were evaluated in order to demonstrate the utility of the test to identify inert and active canister surfaces.

This chemical test provides the laboratories with an additional means of demonstrating the inertness of a canister to prospective data users. It serves to add validity to the data set.

INTRODUCTION

TO-14 is one of the methods included in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*. The Compendium was first circulated in 1984 and later updated in 1986 and 1988. Much has changed since 1988 and the use of TO-14 for the analysis of volatile organic compounds (VOCs) has been extended to include a more comprehensive list of target compounds and sample matrices beyond ambient air. In addition, risk assessment determinations have made it necessary to measure many toxic compounds at the pptv level and TO-14 is often specified as the method of choice.

Beyond the obvious difficulties associated with accurately detecting a compound at the pptv level, there are a number of other factors which must be considered, understood and managed before the data can be considered meaningful. The addition of polar, (i.e., more reactive) compounds to the target compound list (TCL) necessitates that the sampling equipment (sampling line, critical orifice particulate filter and canister) be inert as well as clean. The fact that Summa canisters are often used for matrices other than ambient air means that the canister surface is often exposed to corrosive compounds such as hydrochloric acid, high levels of humidity and samples which may have a number of non-volatile compounds (at room temperature and ambient pressure). The accumulation of these non volatile compounds (which may or may not polymerize during the normal canister cleaning process) will degrade the Summa surface. It is fair to assume that once a canister has been in service for over a year that the Summa surface has been compromised, the degree of which is currently not monitored by most commercial laboratories.

Some laboratories recognize the dangers of using damaged canisters (i.e., canisters whose surface have been exposed to non-ambient sample matrices) for low level ambient air determinations and segregate their canisters into "ambient" and "other". This approach is not only expensive but often impractical given the degree of sophistication required of the canister tracking program and the fact that "ambient" is a relative term and is often mis-applied to a given set of samples.

TO-14 specifies that the sample be collected and stored in a Summa canister prior to analysis and it provides guidance on how to clean and certify canisters. However, there is essentially nothing available on the chemical characterization of the canister surface. Concerns about surface adsorption are addressed primarily by varying the humidity within the canister prior to sampling and the temperature during analysis. Studies of recovery versus humidity / temperature always fail to take into account the variability found in real world samples. The conclusions of the studies are invariably valid only for ambient air and fail to consider the effects of other sample matrices on the Summa surface.

Canister cleaning protocols utilize exponential dilution, heat (often in the presence of moisture and oxygen) and vacuum to remove VOCs and moisture from the canister. At the end of the process the canister is free of VOCs and very "dry". The two most common methods of "certifying" canisters (TO-14 and TO-12) simply measure the residual level of volatiles remaining after the "cleaning" process. They answer the question: Are there VOCs in the canister? They do not measure the inertness of the SUMMA surface. This may be fatal short coming if the canister is used to acquire and store a sample for which the TCL includes a number of polar compounds and pptv data is requested.

The recovery of reactive compounds in a complex matrix at the pptv level requires a chemical characterization of the canister surface. While humidification of the surface may "mask" the chemical activity of the surface in the short term, its effects on recovery over time are difficult to predict. This situation is analogous to that which exists in the world of gas chromatography. The importance of measuring the residual chemical activity of a gas chromatographic column has long been acknowledged by chromatographers. All column manufacturers test each column with a "polarity mix" to measure the chemical nature of the column surface. If a general purpose column like DB-5 adsorbs (usually indicated by peak tailing, a decrease in peak height or, in severe cases, peak abstraction) the phenol or the alcohol, it is rejected. Most laboratories monitor column performance as a means of determining when the column has degraded to the point where it must be replaced. This same approach can be applied to testing the surface of a canister.

One injects a "polarity mix" into a clean canister. If the surface is chemically active, or if there is a residue on the surface, one or more of the active compounds in the mix are adsorbed. The degree of adsorption serves to characterize the surface. Using this approach canisters can be classified into two groups: "inert" and "active".

EXPERIMENTAL

In order to be practical the test must have the following characteristics: (1) it must be a simple gas chromatographic test. That is, the sample is injected using a gas tight syringe - no cyrotrapping. The column should separate on the basis of boiling point (DB-1 or DB-5) in order to facilitate peak identification. A conventional flame ionization detector is used because of its universal response and general availability. (2) the test must be relatively quick, that is, less than 10 minutes and (3) the results must be easily interpreted. Canister classification is based on peak height relative to one of the inert (e.g., 2,2,4-Trimethylpentane or benzene) compounds. Because of the relative nature of the measurement it is not necessary to calibrate the gas chromatograph.

One of the most difficult aspects of developing a test mix with a multiplicity of functional groups is to find compounds which are both miscible and stable in solution. Should the compounds react or decompose (a common problem with amines) the findings

Figure 1 shows a typical chromatogram along with peak identification. The oven was program from 40°C to 110°C at 10°C/min. Column: 30m X 0.53, DB-5.

Three different studies are summarized below:

- (1) Recovery as a function of humidity using new canisters.
- (2) Recovery as a function of hold time. Obviously the goal is to develop a test which provides sufficient information to classify a canister in the least amount of time.
- (3) A demonstration of the tests ability to classify canisters.

A large group of canisters have been evaluated including new canisters (from two manufacturers), canisters which have been in use for 1-5 years and canisters which have been exposed to hydrocarbon process streams containing high levels of sulfur compounds. Glass surfaces were also investigated.

RESULTS AND DISCUSSION

New canisters were used to establish the "baseline" statistics for a freshly prepared Summa surface. Canisters from two manufacturers were used in order to eliminate any bias due to manufacturing variations. No attempt was made to differentiate canisters on the basis of vendor; however, there are significant differences between the two groups of canisters and it is a simple manner to identify the manufacturer on the basis of the test. This study was run using both humidified and dry canisters. It is clear from Table II that the common TO-14 analytes are well behaved and can be used as indicators of a valid test, while the polar compounds are less predictable and, as expected, humidity plays as strong albeit transitory role in recovery. The data in Table II is a summary of the average relative response taken at 30 minutes, 60 minutes, 90 minutes and 18 hours after injection into the canister.

Table II. AVERAGE RESPONSE USING NEW CANISTERS (n=6)

TEST PROBE	R _f - DRY CANISTER	R _f - HUMIDIFIED CANISTER
1-Propanol	1.4±0.19 (14% RSD)	1.3±0.015 (5.0% RSD)
Chloroform	0.34±0.006 (2.0%)	0.34±0.005 (1.5%)
Benzene	2.0±0.048 (2.3%)	1.9±0.056 (3.0%)
2,2,4-Trimethylpentane	INTERNAL STD.	INTERNAL STD.
Methylisobutylketone	1.2±0.13 (11%)	1.2±0.42 (3.3%)
Benzaldehyde	4.7±2.2 (46%)	4.1±1.3 (33%)
Phenol	2.7±1.2 (41%)	1.4±0.94 (65%)

The relative response for benzaldehyde and phenol is bi-modal. Both the magnitude of the relative response and its associated standard deviation varies between the two manufacturers. Canisters from a single manufacturer yield much better precision than is indicated above for the combined canister set.

For comparison purposes a number of glass bulbs were evaluated in order to compare the test performance on, what is normally considered to be a more inert surface than "Summa". The glass surface was not specially treated or silanized prior to testing. Any benefit of such treatments have been demonstrated to be transitory in nature and certainly not of any value as a surface treatment prior to taking an air sample. In fact, inorganic acids (e.g., HCl) and water readily attack a silanized surface. The subsequent formation of silanes and cyclic-siloxanes will often complicate the VOC analysis.

While this study can hardly be considered definitive, results indicate that for common (i.e., non-polar) TO-14 target compounds there is no difference between a "Summa" surface and an untreated borosilicate surface (2.9% R_f difference for

are of questionable value. For example, during the course of this study attempts were made to use benzaldehyde and butyl amine as test probes. These two compounds react invalidating the test results despite the fact that they appear to be ideal test probes. Such problems require the mix to be made daily which adds a level of inconvenience and threatens the incorporation of the test into every day use.

The probes selected must be volatile; it is essential that the test probe have a boiling point under 175°C otherwise there may be difficulty removing it from the canister upon completion of the test. The ideal candidate is, first of all, not a common TO-14 target compound and, secondly, has a boiling point between 60 and 150°C.

Table I lists the molecular probes utilized during the course of this study; Figure 1 shows a typical chromatogram of this test mix. The test mix is made up in methanol at approximately 80mg/mL. 0.5 mL was injected into the canister. 0.5mL was injected into the gas chromatograph which was, in turn, split approximately 100:1. As previously mentioned, other probes were investigated but found to either be unstable in the mix or of limited value. The compounds have a range of polarities in order to provide a range of possible surface interactions. For example, the alcohol will easily hydrogen bond; the acidic compound, phenol, provides a good measure of the acid/base nature of the surface. The aldehyde is very reactive. These three compounds were selected because they are reactive and often appear on TCLs. The inert compounds serve as internal standards and provide a demonstration of test validity. This mix, when stored in the freezer, is stable for up to 8 weeks.

Table I. TEST PROBES FOR CANISTER SURFACE ACTIVITY

TEST PROBE	BOILING POINT	DIPOLE MOMENT
1-Propanol	97°C	1.68
Chloroform	61°C	1.01
Benzene	80°C	0
2,2,4-Trimethylpentane	98°C	0.18
Methylisobutylketone	118°C	NA
Benzaldehyde	178°C	2.7
Phenol	182°C	1.45

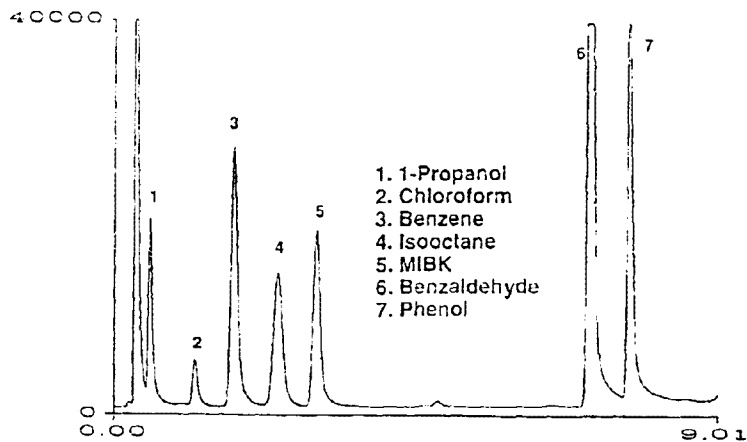


Figure 1 shows a typical chromatogram along with peak identification. The oven was program from 40°C to 110°C at 10°C/min. Column: 30m X 0.53, DB-5.

chloroform and 0% R_f difference for benzene) with respect to recovery over time. However, the data clearly suggests that glass, with its high population of surface silanols adsorbs the polar, less volatile analytes more than does a Summa surface (e.g., there is a 66% difference in R_f for both benzaldehyde and phenol). These relative response factors were gathered over 2 hours. More work needs to be done on other "glass" surfaces using a variety of surface deactivation techniques such as humidification in conjunction with a variety of matrices and analytes.

RECOVERY FROM DRY, USED CANISTERS

The used canisters were all characterized without humidity. The presence of moisture in the canister very effectively masks the surface for most organic compounds in the short term and makes the distinction between surfaces much more obscure. Two canisters which had been exposed to hydrocarbon process streams containing a significant amount of organic sulfur were also tested. The canister surfaces were, in fact, black.

While the vast majority of canisters tested performed very much like the new canisters, a few provided a clear demonstration of the value of surface characterization. Figure 2 shows three chromatograms acquired from a single canister after a period of 90 minutes. It is clear from the changes in peak height, See Table III, that the surface is quite active. Virtually all of the methanol solvent is adsorbed. All of the polar compounds show a decrease in recovery with time while the non-polar, TO-14 analytes such as chloroform and benzene are unaffected. This canister is clearly not suitable for the determination of polar analytes at low levels. It is interesting to note that in every case where surface activity was found, the recovery of the non-polar target compounds was unaffected.

Table III. AVERAGE RESPONSE (n=6) FOR AN "ACTIVE" SUMMA CANISTER

TEST PROBE	R _f @ 30 MIN.	R _f @ 60 MIN.	R _f @ 90 MIN.
1-Propanol	1.3	0.34	0.30
Chloroform	0.34	0.34	0.34
Benzene	2.0	2.0	2.0
Isooctane	INTERNAL STD.	INTERNAL STD.	INTERNAL STD.
MIBK	1.3	0.93	0.91
Benzaldehyde	6.9	2.0	0.86
Phenol	3.2	1.7	0.82

RECOVERY USING HUMIDIFIED CANISTERS

It has been well documented that the recovery of polar compounds is enhanced if the canister is humidified prior to sampling. The question must be asked, will a layer of water render an active canister surface inert? Two of the canisters which had been classified as "active" were cleaned, humidified and re-tested. The results for one such re-test is presented in Figure 3. Note that the recovery of the non-polar TO-14 target compounds is unaffected by humidity; however, the recovery of the polar compounds is greater from the humidified canister although recovery decreases over time. This work, en mass, clearly supports the body of work that shows that polar compounds are best recovered from a humidified canister rather than a dry canister. This work also suggests that recovery is more dependent on humidity than the residual chemical activity of the surface. More work needs to be done in order to determine the duration of the enhanced recovery on a humidified surface. For example, what is the hold time of a sample containing polar analytes on a Summa, or for that matter, any surface?

RECOVERY AS A FUNCTION OF HOLD TIME.

It is important to determine the length of time necessary to differentiate the canister surfaces. In this study the canisters were analyzed at 30 minutes, 60 minutes, 90 minutes and 120 minutes. Several tests were performed after 18 hours, but 18 hours falls outside the realm of being a practical test. The data changed very little between 60 and 120 minutes. The 30 minute data is suspect because the relative response for the polar compounds was often lower than that obtained after 60 minutes. The mixing in the canister takes a finite time that increases with decreasing compound volatility. A meaningful surface test requires at least a 1 hour hold time prior to analysis. Because the analysis only takes 8 minutes, 6 to 8 canisters can be evaluated/hour.

SUMMARY

Canisters should be differentiated on the basis of the TCL and not the source of the sample. Regardless of the nature of the surface it appears that non-polar TO-14 compounds can be recovered at levels approaching 100%. In addition, the recovery is constant over time (at least up to 14 days). The recovery of polar compounds mandates that the surface be humidified; however, the increased recovery appears to be transitory and is clearly a function of the surface chemistry.

Chemical characterization of the canister surface can be accomplished in a little more than 1 hour. It provides the laboratory with a basis for quantitatively grouping canisters into active and inert. This test provides an additional level of QA to the laboratory and helps ensure data quality when polar compounds are of interest.

The value of periodically characterizing the surface of each canister in use has been demonstrated. In our laboratory each canister is evaluated after 5-6 cycles to the field except for those instances where high level of organics or sulfur compounds have been found. In these instances each canister from the project is subjected to a test and a judgment made with regards to its utility in the future. It also helps to find those canisters which contain non-volatile material.

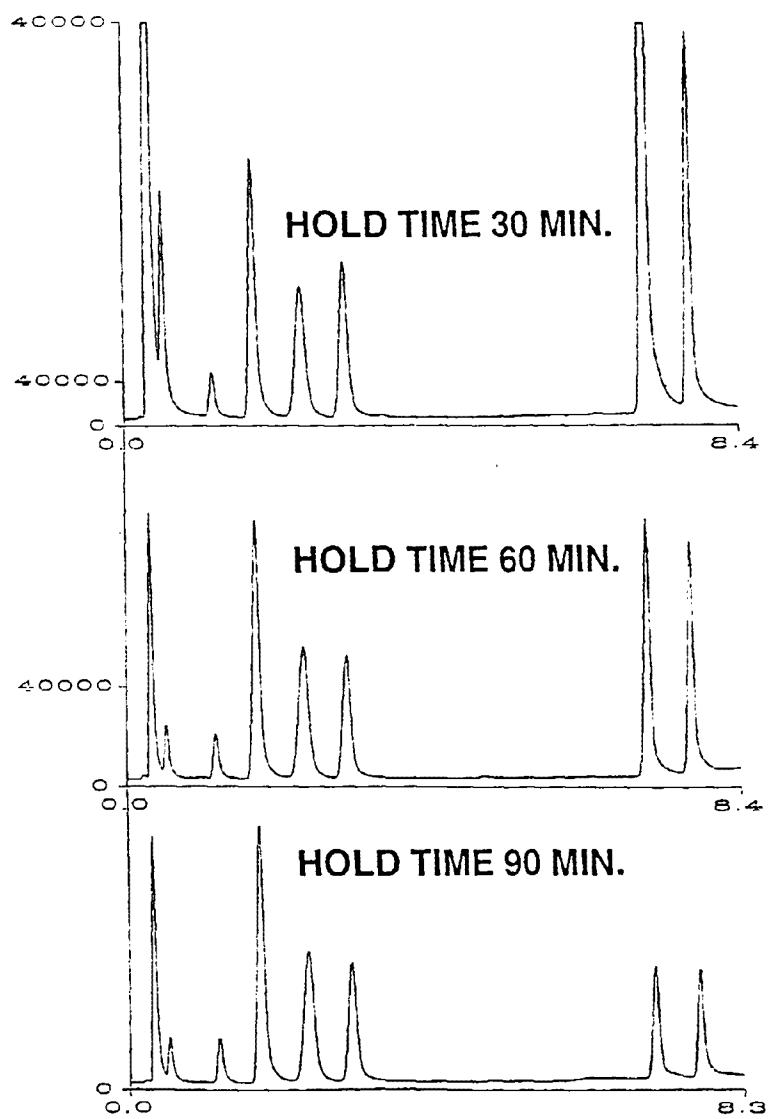


Figure 2. Three chromatograms from an "active" canister. See Figure 1 for peak identification

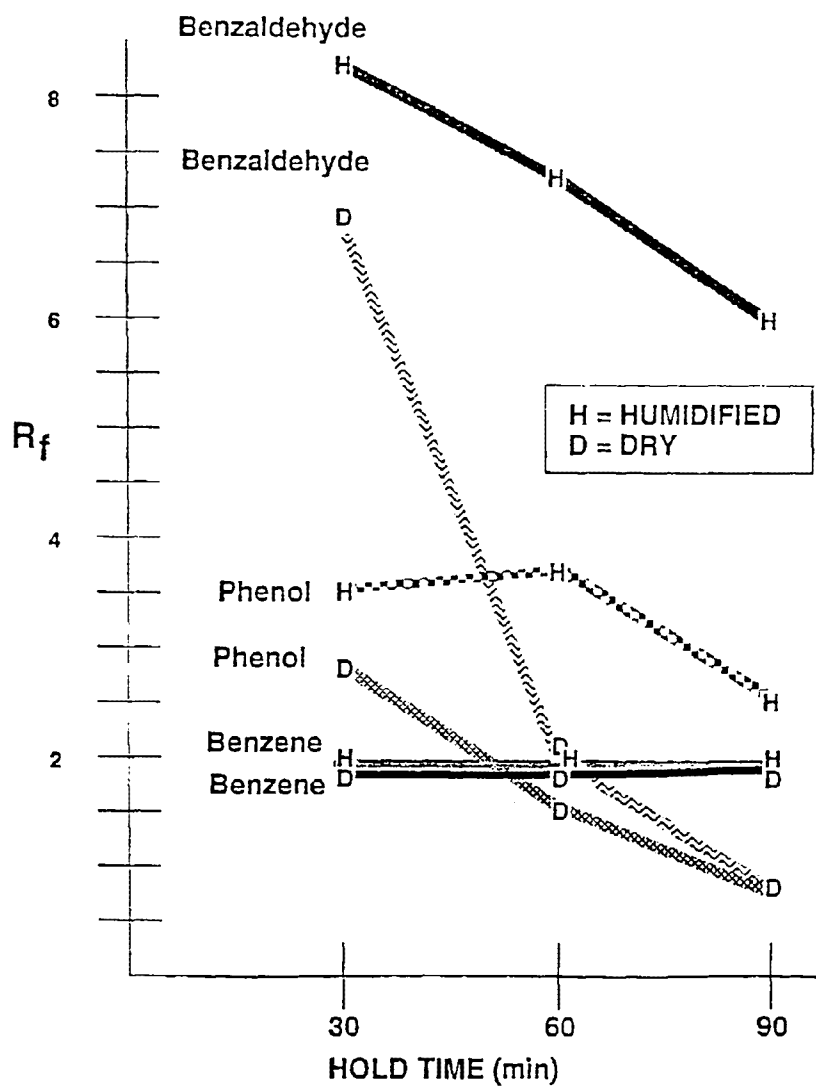


Figure 3. Relative Response for three test compounds (Benzene, Benzaldehyde and Phenol) using an "active" canister. The canister was tested both dry and humidified.

DEVELOPMENT AND VALIDATION OF A HEATED CANISTER-BASED SOURCE SAMPLING METHOD

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ABSTRACT

In response to the Clean Air Act Amendments of 1990, the United States pulp and paper industry through the American Forest and Paper Association (AF&PA) has instituted a program to characterize hazardous air pollutant (HAP) emissions from a variety of sources at 16 facilities. To meet some of the specific needs of this program, a method has been developed, based on EPA Method 18, that uses a heated sampling system to transfer source gas samples to a heated stainless steel summa polished canister. After sampling, the canister is kept hot in an insulated box and transferred to an on-site mobile laboratory. All of the analyte system components are also heated so that the moisture is not allowed to condense in the sample before it is analyzed. An initial mill screening study, laboratory evaluation/validation, and an EPA Method 301 validation on pulp mill sources have all been completed with acceptable results. This method is being used to quantitate 26 VOCs, e.g., methanol, acetone, methylene chloride, chloroform, benzene, methyl ethyl ketone, and methyl isobutyl ketone.

BACKGROUND

The heated canister-based source sampling method described in this paper was developed to meet the specific needs of the American Forest and Paper Association Maximum Achievable Control Technology Study (AF&PA MACT Study). This study was organized by the AF&PA and NCASI to meet the information needs of the pulp and paper industry relative to the implementation of the 1990 Clean Air Act Amendments (1).

The project is managed by NCASI. Roy F. Weston, Inc., Auburn, Alabama was contracted to perform the testing. In this study speciated VOC emissions, primarily HAPs, were measured at 16 facilities over a 14½ month period. Approximately 20 sources were tested at each facility. The analyte list included 26 compounds.

A method was needed that could quantitate individual VOC emissions to ≤ 0.1 lb/hr emission rates. This corresponds to an approximate quantitation limit of $\approx < 0.1$ ppmv. We also desired to quantitate lower emissions when possible. Definitive qualitative analysis and the ability to identify any major VOCs not on the calibration list were required. Fast data turn around, within 24 hours, was a requirement. This meant that on-site analysis in a mobile laboratory was required. Fast data turn around was required to allow us to make decisions in the field about: which samples to run on the GC-MS, additional tests on sources which yielded questionable results, and deletion of tests on sources found to have insignificant emissions. An additional requirement of the method was sampling train mobility. In the initial planning for the project, the determination of source variability by intermittent sampling over a multi-day period was envisioned. Thus, the sampling

trains would need the mobility to be rotated from source to source around the mill. The method chosen for this study was required to collect an integrated sample. Finally, we needed a method that was validated by EPA Method 301 (2). Unfortunately, no methods were validated for VOC HAP measurements in pulp and paper mill sources. Thus, we would have to validate the method we chose for this project.

The sources to be tested in this study included pulping, bleaching, and combustion sources at kraft, sulfite, and semi-chemical pulp and paper mills. These sources are often high temperature, high moisture, and contain corrosive gases, e.g., SO_2 , Cl_2 , ClO_2 , NO_x .

The target analytes for this study are listed below.

TARGET ANALYTE LIST

methanol	chloroform	benzene
acetone	dichloromethane	toluene
methyl ethyl ketone (MEK)	1,2-dichloroethane	xylene
acetaldehyde	1,2-dichloroethylene	styrene
methyl isobutyl ketone (MIBK)	1,1,1-trichloroethane	terpenes
acrolein	1,1,2-trichloroethane	methyl mercaptan
formaldehyde	1,2,4-trichlorobenzene	dimethyl sulfide
total hydrocarbons (THC)	tetrachloroethylene	dimethyl disulfide
carbon tetrachloride	trichloroethylene	
chlorobenzene	hexane	

We could not find an existing developed method to meet our desired method's characteristics, therefore we decided to develop a new method that best fit the specific needs of this project.

METHOD DESCRIPTION

We decided that a canister-based method would be ideal for the needs of this study except for the problem that the condensed moisture would cause when the source gases cooled to ambient temperature. Thus, we decided to try an approach in which we kept the canister hot so that the moisture is not allowed to condense. Additionally, the sampling and analytical system components are kept hot so that moisture is never allowed to condense in the sample. This method is really a variation of the heated sample line option of EPA Method 18 (3).

Figure 1 diagrams the sampling system. The sampling system consists of four major components: probe, filter box, flow control module, and canister module, all of which are heated to 30°C . At the conclusion of the test period, the canister module is removed from the sampling system and transported to the mobile laboratory where it is maintained at 130°C pending analysis. Canister vacuum draws the sample. The canisters are constructed of summa polished stainless steel. Canister volume is six liters; metal bellows valves are used for closure. Typically, samples are

collected at a 50-70 mL/min flow rate for 1 hour. Flow control is via a micrometer-type needle valve and vacuum gauge.

The following text describes sample collection procedures.

Once an acceptably clean canister is obtained, it is evacuated and heated to 130°C. The pressure in and temperature of the canister are measured with an electronic manometer and digital pyrometer, respectively. These data are recorded for sample volume calculation purposes. The summa canister is connected to the flow control module, and the sampling train is positioned at the sample location. All components are then heated to the sampling temperature of 130°C.

Once all components have reached the required temperature, a leak check is performed on the HSCSST by attaching a pressurized canister to the probe tip and pressurizing the system to approximately five pounds per square inch (psi). During the leak check procedure, the valve on the pressurized canister is opened until the pressure in the sample train reaches 5 psi. After the desired pressure is obtained, the valve on the pressurized canister is closed. The valve on the evacuated canister that is used for sample collection remains closed during all leak check procedures. A leak rate of less than one percent of the sampling rate was considered acceptable.

After an acceptable leak check has been obtained, the HSCSST is ready for operation. Immediately before sampling begins, the HSCSST is purged by attaching a vacuum pump to the purge port. The system is purged with source gas at a flow rate of 200 mL/min for a period of three minutes. When the purging operation is complete, the three-way purge port valve is rotated to complete the sampling circuit and close the purge circuit.

Sampling is initiated by opening the bellows valve on the heated summa canister. A needle valve is used to adjust the sampling rate during the sample period. The canister vacuum gauge and train component temperature values are recorded by the sampling train operator at the beginning and end of the sampling period and at five minute intervals during the sampling period.

At the completion of each sampling run, the bellows valve on the heated canister is closed. A post-test leak check is performed in the same manner the pre-test leak check was performed. The run is considered acceptable if the post-test leak check is acceptable.

After the leak check is completed, the summa canister is disconnected from the HSCSST and immediately transferred to the on-site transportable laboratory. Canisters are transported such that the canister temperature does not drop below 100°C. Once at the laboratory, the summa canister is maintained at 130°C pending analysis.

The analytical system, schematically depicted in Figure 2, consists of the equipment necessary to interface the summa canister to both a cryogenic sample concentrator and a rotary sample valve. The cryogenically concentrated sample can be delivered to both a GC/FID and an optional GC/MSD. Additionally, a whole gas sample can be delivered to the other channel of the GC/FID.

The analytical system employs two separate GCs. One GC is equipped with dual FIDs. The other GC is equipped with the optional MSD. Table 1 summarizes the operating criteria for the gas chromatograph systems.

Each channel of the GC/dual FID is fitted with several megabore capillary columns connected in series. One channel is plumbed to a rotary sample valve for introduction of whole gas

samples. The other channel is plumbed to one of the two outlets from the cryogenic concentrator for introduction of cryogenically concentrated samples. The use of two columns and two different sample application techniques significantly extends the analytical range of the system as compared to the use of a single sample application system. This chromatographic system is calibrated to yield quantitative data.

For the purposes of this study, the concentrator quantitation limit was chosen to be equal to the level of the lowest calibration standard. The system is capable of quantitating lower concentrations than the quantitation limits used in this study. The heated valve quantitation limits were determined by the analyst's judgement of the smallest chromatographic peak area that would yield reasonable quantitation limits in pulp and paper mill sample matrices. The concentrator and heated valve ppbvd quantitation limits are listed in Table 2. These values assume canister dilution factors of one and two for the concentrator and heated valve systems, respectively.

METHOD EVALUATION/VALIDATION

The heated canister method evaluation/validation was a three step process which included a field feasibility study, a laboratory evaluation, and an EPA Method 301 validation exercise.

Figure 3 diagrams the sampling apparatus used in the field feasibility study. The sample was drawn through a heated probe, filter box, and through a heated transfer line into a heated box. Inside the heated box the sample line is connected to a manifold. Four sets of flow control apparatus were connected to the manifold. A set of flow control apparatus consisted of a high temperature variable area flow meter, a fine metering valve, and a vacuum gauge. Heated transfer lines connected the outlets of the flow control apparatus to the six liter canisters contained in heated boxes.

At the conclusion of each feasibility study sampling period, two of the four canisters were spiked with a mixture containing the 20 compounds listed below.

FEASIBILITY STUDY SPIKE COMPOUNDS

methanol	toluene
ethanol	ethyl benzene
acetone	m/p-xylene
isopropyl alcohol	o-xylene
dimethyl sulfide	cumene
methyl ethyl ketone	α -pinene
chloroform	β -pinene
benzene	3-carene
bromodichloromethane	p-cymene
dimethyl disulfide	

Feasibility study results obtained from sampling a brownstock washer filtrate tank vent, a each plant scrubber outlet, and a kraft recovery furnace are contained in Tables 3, 4, and 5, respectively. In the interest of conserving space, only the results for methanol, acetone, MEK,

chloroform, and benzene are shown in these tables. Precision was calculated as the percent difference (see equation below) between the two spiked samples.

$$\text{percent difference} = \left(\frac{|\text{sample 1} - \text{sample 2}|}{(\text{sample 1} + \text{sample 2})/2} \right) \times 100 \quad (1)$$

Spike recovery was calculated from the average of the spiked and unspiked canister results, as shown in the equation below.

$$\text{percent recovery} = \left(\frac{\text{avg. spiked conc.} - \text{avg. unspiked conc.}}{\text{spike conc.}} \right) \times 100 \quad (2)$$

Storage stability was calculated from the difference in initial and subsequent analyses, as shown in the equation below.

$$\text{storage stability, percent} = \left(\frac{\text{subsequent conc.} - \text{initial conc.}}{\text{initial conc.}} \right) \times 100 \quad (3)$$

The results from the feasibility study were promising so we proceeded with a laboratory method evaluation. The laboratory evaluation included the analysis of a synthetic stack gas with 30 percent moisture at 130°C. The synthetic stack gas was simultaneously sampled with four trains. This was repeated four times. The synthetic stack gas analytes are listed below.

SYNTHETIC STACK GAS ANALYTES

methanol	benzene
acetone	MIBK
methylene chloride	toluene
methyl ethyl ketone	α -pinene
chloroform	β -pinene

The range of synthetic stack gas theoretical analyte concentrations and the percent recoveries are listed in Table 6.

With the exception of α - and β -pinene, which seem to react on the heated canister surfaces the results of the laboratory evaluation were acceptable, thus we proceeded with the EPA Method 301 validation of the heated canister method on pulp and paper mill sources.

The EPA Method 301 validation procedure for an individual source requires that six runs be conducted with four simultaneously operated sample trains with collocated probes. Two of the canisters from each quadruplicate run are spiked at the conclusion of the run. Bias and precision are statistically calculated from the results of the six quadruplicate runs. For a method to be acceptable, the bias correction factor must be between 0.7 and 1.3, and the precision (relative standard deviation) must be within ± 50 percent. The Method 301 validation was conducted on the five following sources: brownstock washer hood, bleach plant scrubber inlet, smelt dissolving tar recovery furnace, and lime kiln. Eight compounds, which were considered to have the highest potential for release from pulp and paper mill sources and which were considered to be

representative of the types of other compounds released in trace amounts, were chosen as the target compounds for the Method 301 validation. The results obtained from the EPA Method 301 validation are contained in Tables 7 through 11. All of the results for the bleach plant scrubber inlet (Table 7), brownstock washer vent (Table 8), and the smelt dissolving tank vent (Table 9) are in the acceptable range. All of the results for the lime kiln (Table 10) and recovery furnace (Table 11) are acceptable except for the bias correction factors for benzene from both sources and the bias correction factors for toluene and MEK from the lime kiln. The uncertainty associated with measurement of the very low concentrations of benzene and toluene in both the spiked and unspiked samples probably caused the error which resulted in the apparent high recoveries from the sources. The low recovery of MEK from the lime kiln (correction factor 1.38) was likely due to canister degradation.

DISCUSSION

It is important to caution the potential user of this method about some of the major problems that will be encountered when using this method. Degradation of sampling train, canister, and analytical system surfaces is a constant problem. In the early stages of surface degradation, MEK, MIBK, and 1,1,1-trichloroethane recoveries are reduced. As the degradation becomes more severe, the recovery of other compounds may be affected. New canisters need to be screened before use; we have found about one out of four new canisters has active surfaces.

In the AF&PA MACT study, we have sampled approximately 320 sources at 16 facilities. Typically, four test runs were conducted on each source with calibration for 26 compounds. Relative to the specific needs of this study, we have generally been satisfied with the method performance. As of the date of this writing, we have not thought of a method or combination of methods that would have better allowed us to accomplish the goals of this study.

There is still much potential for further research relative to the development, improvement, and extension of this method. The sampling, storage, and transfer temperature of 130°C was chosen on the basis of scientific judgement. The project time frame did not allow for determination of an optimum temperature; rather, 130°C was chosen because it was thought by the people involved to be a temperature that would allow the goals of the project to be accomplished. The method could be extended to other compounds. An area of potential research that would be very useful is the potential evaluation and development of hot sampling, cold canister storage, and hot analysis. If the canisters could be stored at ambient temperature between sampling and analysis, it would allow the test team to ship the canisters to a remote laboratory for analysis which would significantly decrease the cost of doing this type of testing. Finally, research into techniques for regenerating degraded sampling system, canister, and analytical system surfaces would be very useful.

LITERATURE REFERENCES

Clean Air Act Amendments of 1990, "Title III - Hazardous Air Pollutants," **November 15, 1990**, Public Law 101-549.

Appendix A to Part 63 - Test Methods, Method 301 - "Field Validation of Pollutant Measurement Methods from Various Waste Media," *Federal Register*, **December 29, 1992**, 57, 61998.

"EPA Method 18 - Measurement of Gaseous Organic Compound Emissions by Gas Chromatography," *Code of Federal Regulations*, Part 60, Appendix A.

**TABLE 1 TYPICAL OPERATING CRITERIA FOR THE
GAS CHROMATOGRAPH SYSTEMS**

GAS CHROMATOGRAPH/DUAL FLAME IONIZATION DETECTORS	
Column	0.53 mm ID x 30 m SPB 1 (5 μ m film) followed by 0.53 mm ID x 30 m SPB 5 (5 μ m film) followed by 0.53 mm ID x 2 m CARBO WAX (1.2 μ m film)
Carrier	Ultra high purity helium, regulated via electronic pressure control (EPC). 10 mL/min.
Hydrogen	30 mL/min
Air	300 mL/min
Injector Temperature	175°C
Detector Temperature	250°C
Temperature Program	40°C for 5 minutes; ramp to 250°C at 8°C/minute; hold at 250°C for 5 minutes
GAS CHROMATOGRAPH/MASS SELECTIVE DETECTOR	
Column	0.2 mm ID x 30 m SPB 1 (0.8 μ m film) followed by 0.2 mm ID x 30 m (SPB 5 (0.8 μ m film)
Carrier	Ultra high purity helium, regulated via electronic pressure control. 1.0 mL/min.
Temperature Program	40°C for 5 minutes; ramp to 250°C at 8°C/minute; hold at 250°C for 5 minutes
Detector Vacuum	4.5×10^{-5} Torr
Mass Range Scan	28 AMU - 250 AMU
CRYOGENIC PRECONCENTRATOR	
Sample Drying	None
Sample Volume for Calibration	100 mL
Cryotrap Temperature	-120°C
Cryofocus Temperature	-120°C
Desorb Temperature	150°C
System Bakeout	150°C for 5 minutes

**TABLE 2 HEATED CANISTER METHOD QUANTITATION LIMITS
USED IN THE AF&PA MACT STUDY**

ANALYTE	QUANTITATION LIMIT, ppmv	
	Heated Valve	Concentrator
acetaldehyde	-0.14	-0.04
methanol	-1.64	-0.12
methyl mercaptan	-1.00	-0.50
acetone	-0.10	-0.03
dimethyl sulfide	-1.00	-0.50
methylene chloride	-0.36	-0.09
1,2-dichloroethylene	-0.16	-0.03
methyl ethyl ketone	-0.14	-0.04
n-hexane	-0.10	-0.01
chloroform	-0.40	-0.12
1,2-dichloroethane	-0.14	-0.04
1,1,1-trichloroethane	-0.10	-0.03
benzene	-0.12	-0.01
carbon tetrachloride	-0.24	-0.12
trichloroethylene	-0.12	-0.03
methyl isobutyl ketone	-0.10	-0.01
dimethyl disulfide	-1.00	-0.50
1,1,2-trichloroethane	-0.10	-0.03
toluene	-0.08	-0.01
tetrachloroethylene	-0.66	-0.03
chlorobenzene	-0.12	-0.01
m,p-xylene	-0.14	-0.01
o-xylene	-0.14	-0.01
styrene	-0.08	-0.01
terpenes		-0.01
1,2,4-trichlorobenzene	-0.02	-0.01
acrolein	-0.10	-0.03

TABLE 3 FEASIBILITY STUDY RESULTS - BSW FILTRATE TANK VENT

SELECTED COMPOUNDS	AVERAGE CANISTER, ppmv		PERCENT			
	Unspiked	Spiked	Precision	Recovery	1 Day Storage Stability	6 Day Storage Stability
methanol	340	1136	6	97	+9	-2
acetone	2.3	131	5	103	+30	+30
MEK	0.45	115	9	102	+22	+24
chloroform	0	225	5	108	+3	0
benzene	0.14	73	1	106	+8	+7

TABLE 4 FEASIBILITY STUDY RESULTS - BLEACH PLANT SCRUBBER OUTLET

SELECTED COMPOUNDS	AVERAGE CANISTER, ppmv		PERCENT		
	Unspiked	Spiked	Precision	Recovery	1 Day Storage Stability
methanol	36	42	4	104	0
acetone	0.59	4.8	15	115	+8
MEK	0	4.2	13	85	-4
chloroform	22	8.3	0	114	+1
benzene	0.15	3.0	1	107	-5

TABLE 5 FEASIBILITY STUDY RESULTS - RECOVERY FURNACE

SELECTED COMPOUNDS	AVERAGE CANISTER, ppmv		PERCENT		
	Unspiked	Spiked	Precision	Recovery	1 Day Storage Stability
methanol	6.9	46	15	90	-11
acetone	0	5.3	1	94	+14
MEK	0	4.6	11	58	+52
chloroform	0	9.0	26	95	-3
benzene	0.40	2.9	NA	118	-11

TABLE 6 RESULTS OF SYNTHETIC STACK GAS ANALYSIS

ANALYTE	RANGE OF THEORETICAL CONCENTRATIONS, ppmv	AVERAGE RECOVERY, PERCENT
methanol	6 - 13	117
acetone	1 - 2	108
methylene chloride	2 - 3	85
methyl ethyl ketone	0.7 - 1.3	88
chloroform	2 - 4	88
benzene	0.9 - 1.7	88
MIBK	1 - 2	86
toluene	0.5 - 1.2	87
α -pinene	1.3 - 1.5	61
β -pinene	0.9 - 1.4	39

TABLE 7 SUMMARY OF EPA METHOD 301 VALIDATION RESULTS, BLEACH PLANT SCRUBBER INLET^a

SOURCE	STATISTICAL PARAMETERS				
Compound	RSDs	RSDu	CF	SPIKE CONCENTRATION, ppm	AVERAGE EMISSION CONCENTRATION, ppm
methanol	2	11	1.07 ^b	172.63	56.22
acetone	10	31	NR	40.43	0.53
methylene chloride	2	2	1.12 ^b	64.35	0.78
methyl ethyl ketone	2	2	1.13 ^b	24.50	0.30
chloroform	2	10	1.14 ^b	74.11	11.35
benzene	3	2	1.16 ^b	31.62	0.26
methyl isobutyl ketone	6	2	1.13 ^b	31.78	0.22
toluene	6	2	1.02	18.69	0.17

RSDs = Relative Standard Deviation of Spiked Samples, %

RSDu = Relative Standard Deviation of Unspiked Sample, %

CF = Correction Factor

NR = Non-Required

^aHeated Valve Used for Sample Application^bSignificant Bias^cUnacceptable

TABLE 8 SUMMARY OF EPA METHOD 301 VALIDATION RESULTS, BROWNSTOCK WASHER VENT^a

SOURCE	STATISTICAL PARAMETERS				
Compound	RSDs	RSDu	CF	SPIKE CONCENTRATION, ppm	AVERAGE EMISSION CONCENTRATION, ppm
methanol	8	3	1.06	486.30	387.16
acetone	4	16	0.96 ^b	113.90	8.34
methylene chloride	6	12	0.95 ^b	181.28	0.69
methyl ethyl ketone	8	6	0.94 ^b	69.03	0.60
chloroform	4	12	NR	208.78	0.76
benzene	6	12	0.98	89.07	0.23
methyl isobutyl ketone	16	12	0.88 ^b	89.51	0.19
toluene	19	14	0.79 ^b	52.65	0.15

RSDs = Relative Standard Deviation of Spiked Samples, %

RSDu = Relative Standard Deviation of Unspiked Sample, %

CF = Correction Factor

NR = Non-Required

^aHeated Valve Used for Sample Application^bSignificant Bias^cUnacceptable

TABLE 9 SUMMARY OF EPA METHOD 301 VALIDATION RESULTS, SMELT DISSOLVING TANK VENT^a

SOURCE	STATISTICAL PARAMETERS				
Compound	RSDs	RSDu	CF	SPIKE CONCENTRATION, ppm	AVERAGE EMISSION CONCENTRATION, ppm
methanol	12	6	1.17 ^b	123.84	63.49
acetone	8	6	0.94 ^b	28.09	1.21
methylene chloride	8	5	NR	92.16	0.72
methyl ethyl ketone	11	5	0.87 ^b	36.08	0.28
chloroform	9	5	NR	119.80	0.80
benzene	10	5	NR	9.98	0.24
methyl isobutyl ketone	13	5	0.90 ^b	12.46	0.20
toluene	11	5	NR	8.39	0.16

RSDs = Relative Standard Deviation of Spiked Samples, %

RSDu = Relative Standard Deviation of Unspiked Sample, %

CF = Correction Factor

NR = Non-Required

^aHeated Valve Used for Sample Application^bSignificant Bias^cUnacceptable

TABLE 10 SUMMARY OF EPA METHOD 301 VALIDATION RESULTS, LIME KILN^a

SOURCE	STATISTICAL PARAMETERS				
Compound	RSDs	RSDu	CF	SPIKE CONCENTRATION, ppm	AVERAGE EMISSION CONCENTRATION, ppm
methanol	20	20	NR	4.64	1.00
acetone	26	35	NR	1.21	0.21
methylene chloride	23	12	0.81 ^b	2.65	0.39
methyl ethyl ketone	37	12	1.38 ^{b,c}	1.40	0.17
chloroform	26	12	0.72 ^b	4.22	0.51
benzene	21	14	0.48 ^{b,c}	0.45	0.04
methyl isobutyl ketone	30	12	0.79 ^b	0.57	0.04
toluene	22	12	0.54 ^{b,c}	0.38	0.04

RSDs = Relative Standard Deviation of Spiked Samples, %

RSDu = Relative Standard Deviation of Unspiked Sample, %

CF = Correction Factor

NR = Non-Required

^aEntech Concentrator Used for Sample Application^bSignificant Bias^cUnacceptable

TABLE 11 SUMMARY OF EPA METHOD 301 VALIDATION RESULTS, RECOVERY FURNACE^a

SOURCE	STATISTICAL PARAMETERS				
Compound	RSDs	RSDu	CF	SPIKE CONCENTRATION, ppm	AVERAGE EMISSION CONCENTRATION, ppm
methanol	28	33	NR	38.07	5.89
acetone	18	27	0.82 ^b	9.92	0.19
methylene chloride	23	12	NR	21.70	0.36
methyl ethyl ketone	49	25	NR	11.45	0.16
chloroform	19	12	0.78 ^b	34.52	0.48
benzene	9	12	0.46 ^{b,c}	3.70	0.04
methyl isobutyl ketone	47	12	NR	4.64	0.04
toluene	16	12	0.72 ^b	3.12	0.04

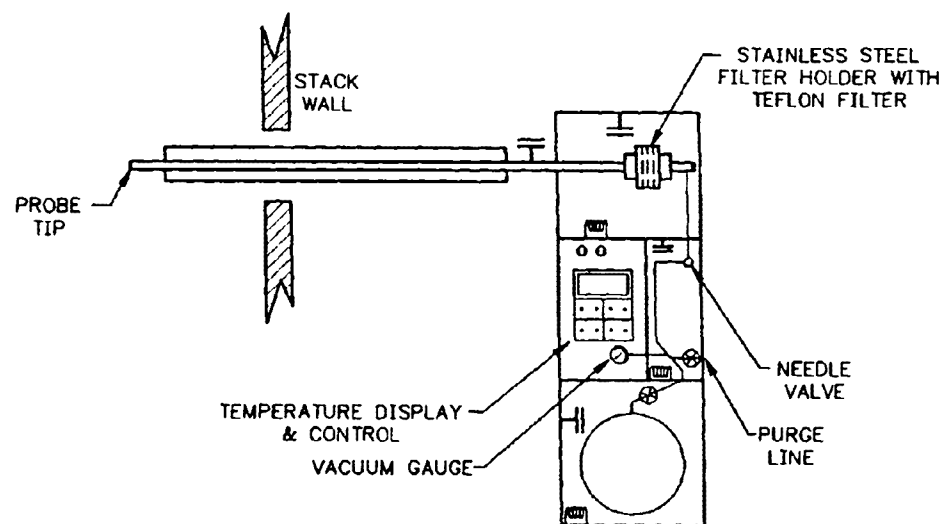
RSDs = Relative Standard Deviation of Spiked Samples, %

RSDu = Relative Standard Deviation of Unspiked Sample, %

CF = Correction Factor

NR = Non-Required

^aEntech Concentrator Used for Sample Application^bSignificant Bias^cUnacceptable



- ⊗ VALVE
T THERMOCOUPLE
H HEATER

FIGURE 1 HEATED SUMMA CANISTER SOURCE SAMPLING TRAIN (HSCSST)

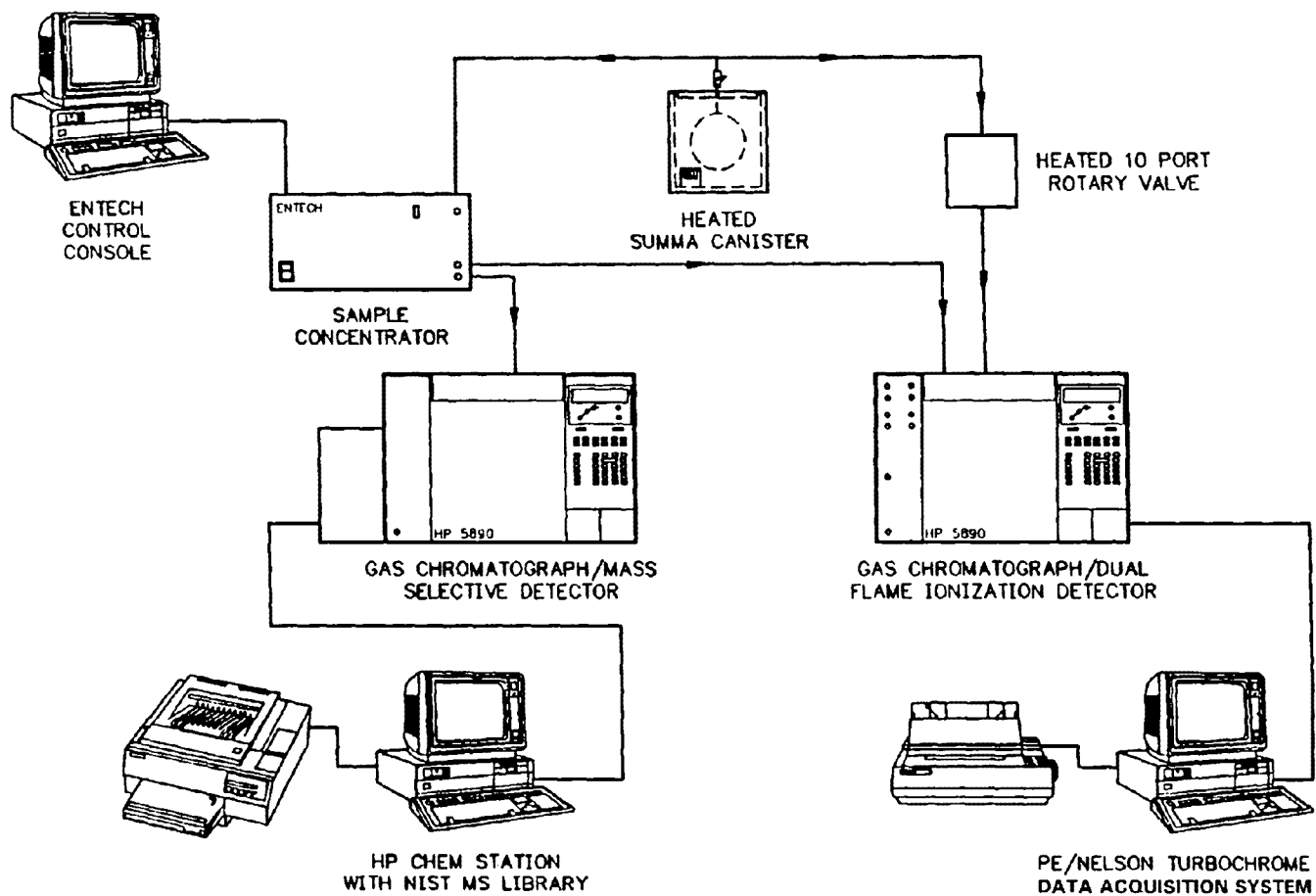


FIGURE 2 SCHEMATIC OF HEATED SUMMA CANISTER ANALYTICAL SYSTEM

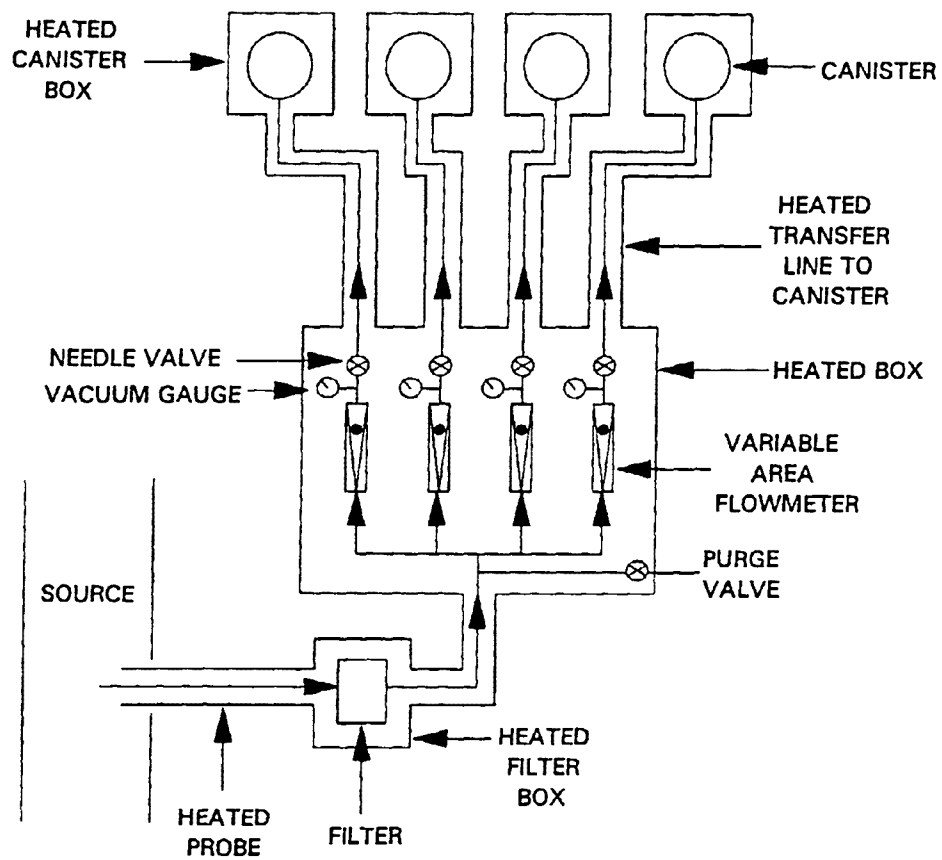


FIGURE 3 FEASIBILITY STUDY SAMPLING APPARATUS

Recovery of Oxygenated Organics from SUMMA Canisters

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It is well known that the atmospheric reaction products of many anthropogenic and biogenic hydrocarbons are oxygenated organics. Many analytical techniques have been used to monitor and determine ambient air concentrations of these species with limited success. Collection of oxygenated organics and recovery in various sampling residues have been used but because of the sticky nature of these compounds to adhere to surfaces, analytical results have been questioned. The use of Summa canisters to collect oxygenated organics and their recovery for analysis will be discussed.

**Analysis of Selected Polar Volatile Organic Compounds
via TO-14 and Modified TO-14 Method**

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SUMMA canister based sampling and analytical system (TO-14 method) has gained wide acceptance for the collection and analysis of integrated whole ambient air samples containing volatile organic compounds (VOCs). This method has been very well developed for most non-polar volatile halogenated hydrocarbons and hydrocarbons.

The studies are concentrated on suitability of TO-14 method for several polar VOCs, including ketones, ethers, sulfur contained compounds, etc. Studies on alternate technical approach and method modification are also conducted. The results on humidity effect, interaction between parameters, time dependent stabilities, and comparison of different modifications are presented.

Why Is It So Difficult to Measure Terpenes in Ambient Air?

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Biogenic compounds and in general Terpenes make up a large fraction of the volatile organic compounds emitted into the ambient atmosphere. The measurement of Terpenes is of importance in knowing the biogenic contribution to the atmospheric loading of organic compounds. The ambient concentrations of Terpenes are usually low in the ambient atmosphere which may in itself result in difficulties in their analysis. The chemical and physical nature of the Terpenes may also lead to difficulties in their analysis. Ambient air samples collected in Summa canisters under conditions in which Terpenes should be present, and results of experiments with Terpenes in Summa canisters will be discussed.

Certification of VOC Canister Samplers for Use at the Waste Isolation Pilot Plant

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ABSTRACT

The Waste Isolation Pilot Plant (WIPP) site is designed to demonstrate safe disposal of transuranic (TRU) mixed waste. An air monitoring program has been established at the WIPP site to verify that volatile organic compounds (VOCs) do not migrate out of the disposal unit. In this air monitoring program, modified commercially available dual canister samplers are used to collect air samples for VOC analysis. Sampler certification, sample collection, and sample analysis are performed based on the procedures contained in U.S. Environmental Protection Agency's Compendium Method TO-14. The canister samplers are certified for cleanliness by passing humid zero air through the entire sampling system and collecting a sample in a canister over a 24-hour period. In addition, each canister sampler is certified for target compound recovery efficiency by passing a humid calibration gas standard through the entire sampling system and collecting a sample in a canister over a 24-hour period.

In this paper, we discuss the techniques developed for meeting the stringent certification requirements of the monitoring program and present data to support the need for these stringent requirements.

INTRODUCTION

The effort to locate a permanent disposal site for TRU waste began over 30 years ago when the National Academy of Sciences recommended that radioactive waste be permanently disposed of in salt beds. After a decade of review of potential sites by the Atomic Energy Commission, the Oak Ridge National Laboratory, and the U.S. Geological Survey (USGS), the WIPP site was selected.

The WIPP repository, an underground mine, is located approximately 2,150 feet below the surface in the Salado Rock-Salt Formation southeast of Carlsbad, New Mexico. The Salado formation is a 2,000-foot-thick salt bed that extends laterally for approximately 36,000 square miles. The land in the vicinity of the WIPP is owned by the Federal Government and administered by the Bureau of Land Management. The 4-mile by 4-mile plot of land overlying the repository has been temporarily withdrawn from public use by the Department of Interior; it is now under the control of the U.S. Department of Energy (DOE).

In March 1989, the DOE submitted a no migration variance petition for test activities to be conducted at the WIPP facility. DOE has designed the WIPP as a permanent repository for TRU wastes that are generated and stored at the DOE sites around the country. These wastes consist of a variety of materials, including tools, equipment, protective clothing, and other material contaminated during the production and reprocessing of plutonium; solidified organic and inorganic sludges; process and laboratory wastes; and items from decontamination and decommissioning activities at DOE installations.

Section 268.6(a) of 40 CFR states that "petitioners for a no migration variance must demonstrate, to a reasonable degree of certainty, that hazardous constituents will not migrate from the disposal unit or injection zone for as long as the waste remains hazardous."¹ EPA proposed to interpret this standard to mean that the hazardous constituents cannot migrate from the unit at hazardous levels.² In other words, to show "no migration," the petitioner must demonstrate that constituents released from the unit do not exceed health-based standards at the point where they exit from the unit. EPA considers the point where the exhaust shaft of the mine meets the surface as part of the WIPP unit boundary.³ VOC concentrations are monitored at this and other locations throughout the facility to ensure no-migration via the air pathway.

The WIPP VOC Monitoring Plan⁴ provides for sampling and analysis to be performed using the guidance in EPA Compendium Method TO-14.⁵ This method is capable of detecting the hazardous constituents targeted for quantitation with a sensitivity below 1 part per billion by volume (ppbv). Samples are collected in 6-liter SUMMA[®] passivated stainless steel canisters. The method requires that all samplers, including pumps, valves, and peripheral equipment, be certified to ensure cleanliness and reliable sample recovery. Samples are analyzed by high-resolution gas chromatography followed by full scanning mass spectrometry (GC/MS/SCAN) to provide the capability to identify a wide variety of VOCs.

Method TO-14 also requires that all samplers be removed from service for routine maintenance and be leak tested and certified with humidified zero air and humidified gas calibration standards. The monitoring plan submitted by DOE indicates that all samplers will be certified on a quarterly schedule.

SAMPLING PROGRAM

Eleven sampling locations originally were proposed to demonstrate no-migration from the repository. At this time, three stations are operational. Biweekly samples are being collected to gather baseline concentration data at VOC-1 (exhaust shaft), VOC-2 (air intake shaft), and VOC-8 (underground).

Commercially available, dual-canister samplers are used to collect air samples for VOC analysis.⁶ A schematic of the WIPP multicanister samplers and the sampler certification system is presented in Figure 1. Dual-canister samplers are expandable to accept secondary sampling modules. In this configuration, up to four canisters can be installed to allow unattended sampling over any desired period, such as a long weekend or holiday, either continuously or on alternating days. In addition to unattended sampling, the multichannel digital timer and switching solenoid valves enable simultaneous or collocated sampling for the purpose of estimating sampling precision. The samplers were modified with a bypass and a 3-way valve to enable simultaneous certification of all sampling ports. Sampler certification of all sampling ports is important to ensure defensible data for any sampling port used. In the event that one or more sampling ports fail as a result of mechanical problems, the remaining ports can still be used with confidence.

SAMPLER CERTIFICATION

Although many steps are required to complete VOC canister sampler certifications (Figure 2) as specified in the WIPP VOC Monitoring Quality Assurance Project Plan (QAPjP),⁷ only two are considered data-generating steps. These steps specified in Method TO-14 are the Humid Zero Air Certification and the Humid Calibration Gas Standard Certification.

The total flow rate through the dual canister samplers is about 2.5 L/min. The majority of this flow is vented through the bleed air-out port. This high flow rate helps dilute any contaminants present in the sampler pump and decreases the residence time in the sampler inlet tubing and peripheral equipment. Approximately 8 cm³/min of sample flow is directed into the SUMMA® canister via the flow controller, yielding a final canister pressure of approximately 15 psig after 24 hours. Because integrated 24-hour samples are being collected at the WIPP facility, the certification time criteria for both humid zero air and humid calibration gas was set at 24 hours. Although this 24-hour certification criterion presented several logistical challenges for the successful completion of the sampler certifications, it was deemed necessary to ensure the integrity of the data for the DOE WIPP VOC monitoring program. Section 11.2.3.8 of Method TO-14 states that "at the end of the sampling period (*normally same time period used for anticipated sampling*), the sampling system canister is analyzed and compared to the reference GC-MS or GC-multidetector analytical system to determine if the concentration of the targeted VOCs was increased or decreased by the sampling system." In addition supplying sufficient, humidified, high-quality ultra zero ambient monitoring (UZAM) air for extended periods was a significant challenge. Reliable, unattended operation of the certification system (for 24-hour periods) was another design concern. UZAM cylinders connected by a manifold were used as the first solution to the zero air supply problem. Later, a commercially manufactured UZAM generator was purchased and tested to assure the quality and reliability of the system. Electronic mass flow controllers, improved humidification chambers, and computerized data acquisition systems were added to facilitate the reliable, unattended operation of the certification system.

Five target compounds most commonly present in the wastes are currently used in the sampler certification program: 1,1,1-trichloro-1,2,2-trifluoroethane (Freon 113), methylene chloride, 1,1,1-trichloroethane (1,1,1-TCA), carbon tetrachloride, and trichloroethene. If other compounds are measured at the WIPP facility at a specified frequency, they will be added to the sampler certification target list.

Based on the guidance in Method TO 14, the WIPP VOC Monitoring Program criteria have been established and adhered to for all sampler certifications. Only canister samplers that meet the established program criteria are placed into service; therefore, completeness for the sampler certification program is always 100 percent.

CERTIFICATION DIFFICULTIES

Of the five target compounds for the WIPP VOC monitoring project, by far the most difficult to remove from the samplers is 1,1,1-TCA. In an effort to eliminate 1,1,1-TCA from the VOC canister samplers, a number of procedures have evolved that are designed to overcome contamination. The methods used to remove sampler contamination included internal purging with methanol and deionized water vapor; heating and purging the sampler under vacuum; and complete sampler disassembly, washing with laboratory soap, and baking selected parts in an oven before reassembling. None of these methods was completely successful in removing sampler contamination.

Because of individual component testing and the high flow rate through the sampler pump, the sampler pump was eliminated as a probable cause of the majority of the sampler contamination. Separate component testing indicated that the two components most likely to cause contamination problems were the solenoid valves and flow controllers. Two manufacturers of solenoid valves had different methods for lubricating their o-rings. One of the manufacturers used a spray lubricant, whereas the other manufacturer applied the o-ring lubricant by hand. The spray lubricant was found to contain 1,1,1-TCA, which permanently contaminated the o-rings. The lubricant applied by hand was free of 1,1,1-TCA and did not contaminate the samplers.

In order to eliminate any chance of contamination from lubricants, a literature search was conducted to find an o-ring that would seal without the use of a lubricant. An o-ring manufacturer indicated that Viton® o-rings (normally used in solenoid valves) are mechanically superior to other materials; however, they are permeable and will absorb compounds such as 1,1,1-TCA. Engineers

from the o-ring manufacturer confirmed that heating is beneficial for cleaning metal parts, but detrimental for cleaning elastomer-containing porous materials such as o-rings and diaphragms. Heating actually increases the permeability of these porous materials. The realization that use of this cleaning method for porous materials was actually worsening the problem prompted an immediate change in procedure. New porous materials were ordered to replace any material that had been previously heat treated. New Teflon[®]-coated Viton[®] o-rings were ordered to replace the Viton[®] o-rings in the solenoid valves. Subsequent zero air certification samples showed that the Teflon[®]-coated o-rings made a significant improvement; however, several samplers were still contaminated with 1,1,1-TCA.

Further discussion with the manufacturing engineers revealed that the flow controller diaphragms are made with Kel-F[®], a plastic similar to that used to produce 2-liter soft drink bottles. This plastic, although strong, is very permeable and virtually impossible to clean when contaminated.

As a result of this information, a plastics distributor was requested to fabricate new Teflon[®] flow controller diaphragms to replace the Kel-F[®] diaphragms. The low permeation rate for Teflon[®] seemed to eliminate the problem associated with the Kel-F[®] diaphragms. Results of the subsequent blank checks on two test samplers confirmed that the Teflon[®] diaphragms were superior to the Kel-F[®] diaphragms for cleanliness.

OBSERVATIONS

Section 11.2.2.3 of Method TO-14 states that the humid zero gas stream passes through the calibration manifold, through the sampling system, and then to the analytical system at 75 cm³/min. The certification methodology for the WIPP samplers uses a 8 cm³/min flow rate.

As shown in Table 1, the analytical results from one sampler varied greatly depending on the flow rate through the sampling system. Humid zero air pumped through the canister sampling system at the Method TO-14 suggested rate of 75 cm³/min produced analytical data indicating that the sampling system was clean and ready for field use. The same sampling system was then challenged with a test stream of humid zero air at 8 cm³/min for a 24-hour period. Analytical results indicated that the same "previously clean" sampler had concentrations of 1,1,1-TCA in excess of 4 ppbv. This concentration did not meet the WIPP certification criteria, and was therefore rejected for field use.

CONCLUSIONS

When stringent sampler certification requirements must be met, it is necessary to pay close attention to small details that can adversely affect the representativeness of monitoring data. Thus, both sampler integrity and certification procedures should be carefully evaluated before a VOC monitoring program is initiated. Close attention must be paid to individual sampler components as part of the certification process.

Sampler certification data collected from this program suggest that VOC sampler certifications conducted at high flow rates with shortened time intervals could produce misleading data about the cleanliness of a sampling system. Subsequent field sampling at low flow rates over a 24-hour period may produce erroneous data with concentrations of target compounds that are perceived as actual ambient air values. A portion of the measured concentrations may be attributed to sampler contamination.

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Table 1. Target Compound Concentration vs. Sample Flow Rate

Target Compound	Concentration (ppbv) @ 75 cm ³ /min	Concentration (ppbv) @ 8 cm ³ /min
Frcon 113	ND ^b	ND
Methylene chloride	ND	ND
1,1,1-TCA	ND	4.69
Carbon tetrachloride	ND	ND
Trichloroethane	ND	ND

^a ppbv - Parts per billion by volume.

^b ND = Not detected. Detection limit is 0.20 ppbv.

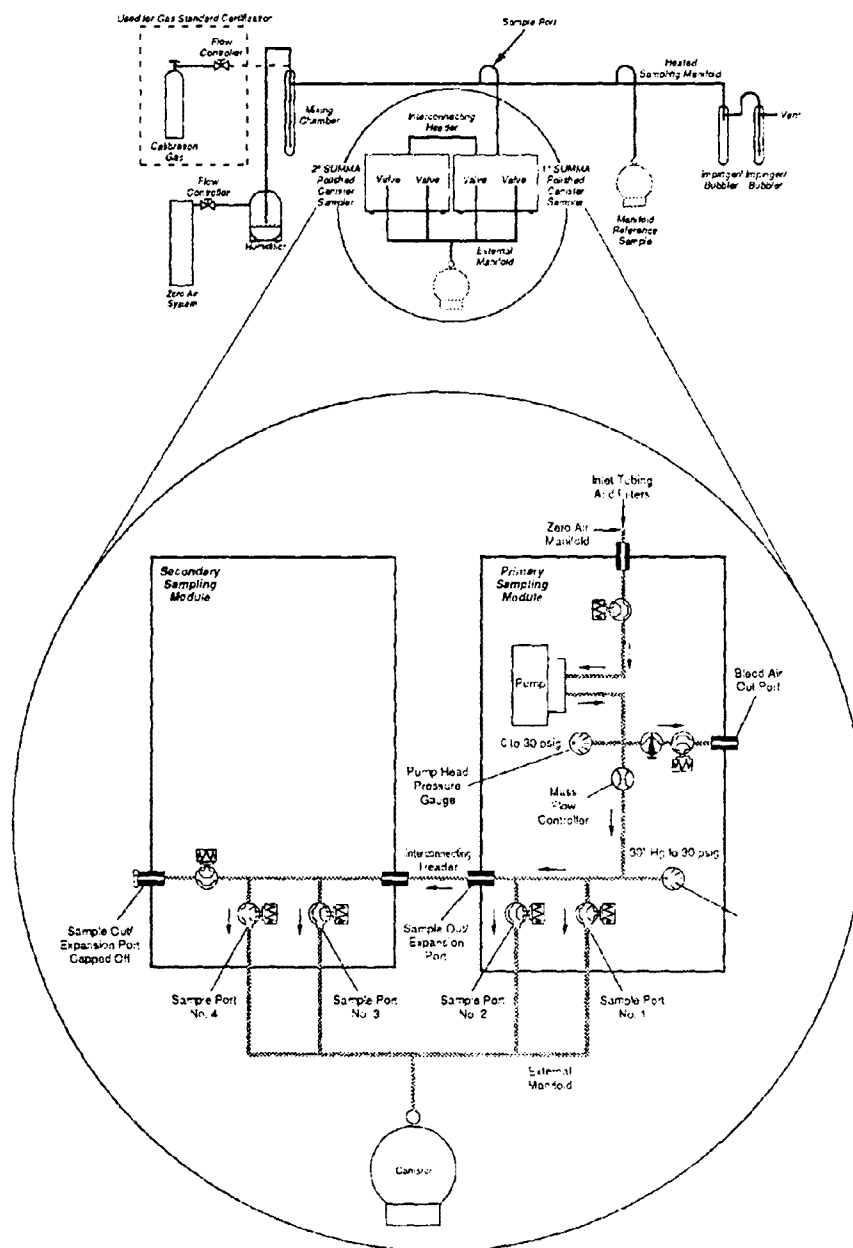


Figure 1. Schematic diagram of WIPP Multi-Canister Samplers and Sampler Certification System.

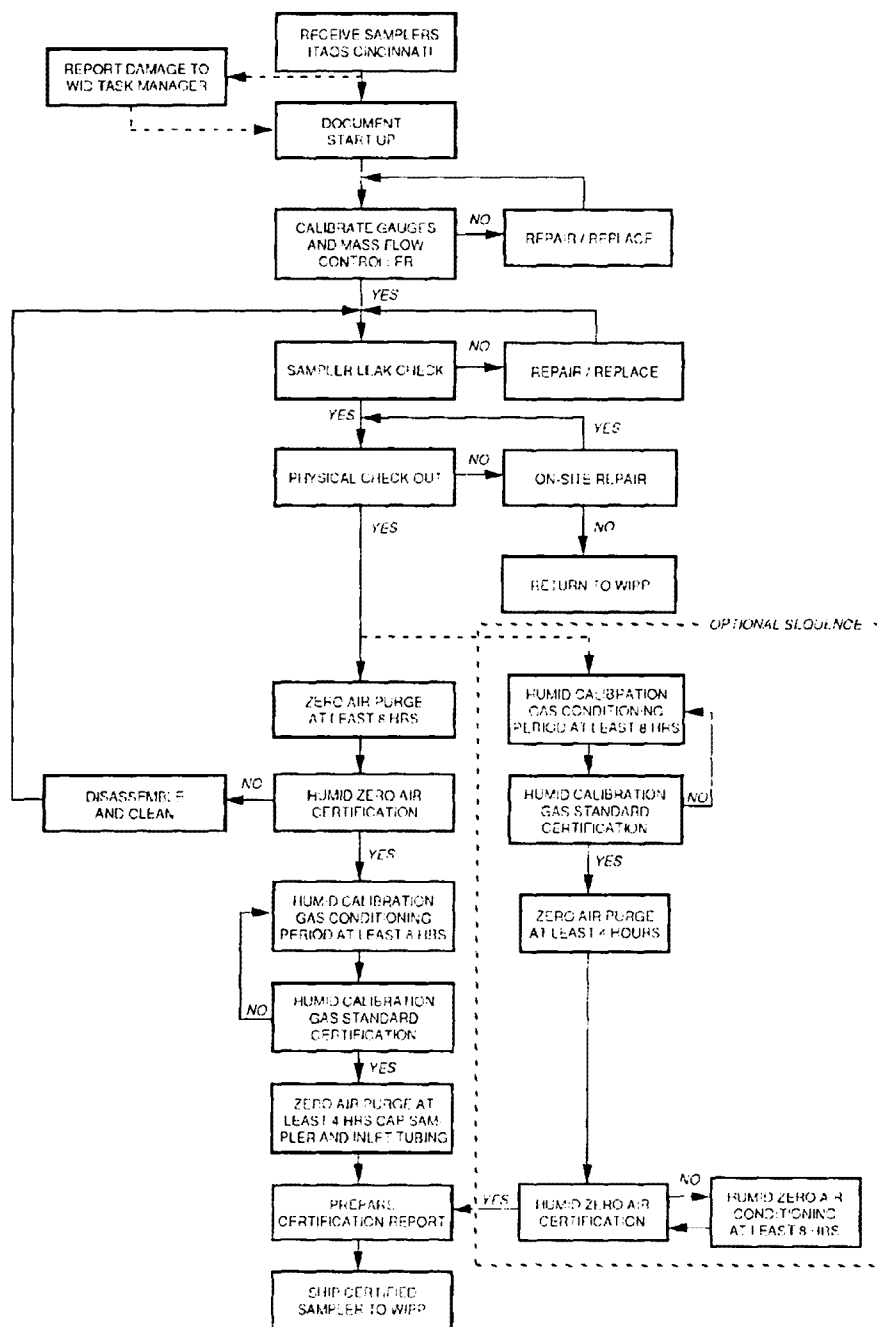


Figure 2. Certification algorithm.

A Fully Automated SUMMA Canister Cleaning System for Method TO14

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Cleaning SUMMA passivated canisters used in EPA method TO14 is required to prepare them for reuse as a field sampling container. This process requires several cleanup and quality assurance steps, including initial leak checking of the manifold after canister attachment, preliminary evacuation of the manifold with valves closed to insure leaktight valves, cycling between filling and evacuation to flush out contaminants, high vacuum pump down to finish contaminant removal, and standby monitoring to verify the absence of leaks in the canister welds. This procedure can require a lot of technician attention and is subject to human error when cleaning large numbers of canisters.

A system is presented that automatically performs the functions described above while recording all pressures and vacuums to a QA report. The only interaction required by the operator is to open the canister valves after the first round of valve leakchecking is completed. The canister cleaner uses a molecular drag pump to perform evacuation of 8 to 12 canisters simultaneously down to 10-20 mtorr. Flexible, all stainless tubing is used to connect each canister to the 3/8" diameter manifold allowing canisters of virtually any size and shape to be cleaned. Canister heating and humidification of flush gas are performed to assist in displacing heavy or polar VOCs from canister surfaces. Discussions will be focused around the improvements in quality assurance and cleaning consistencies relative to manually operated systems.

Networking an Entire TO14 Laboratory into a Single Windows-Based Control System

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EPA Compendium Method TO14 specifies the analysis of Volatile Organic Compounds (VOCs) in ambient air as collected in SUMMA passivated stainless steel canisters. In order to perform Method TO14, provisions must be made for field collection of samples in canisters, preconcentration and analysis of the VOC fraction in the canister, cleaning of the canisters for reuse, and preparation of analytical standards for method validation and GC/MS response factor determination. The temporary or long term loss of any of these capabilities within a laboratory will cause a bottleneck and ultimately delay operations until alternatives can be found. Even when successfully completing each of these tasks, a laboratory's ultimate efficiency and profitability will be determined by sample throughput which will be hindered by the task that is the least automated.

A novel approach to instrument communications is presented that makes it possible to monitor and control field sampling, canister cleaning, standard preparation, and preconcentration and analysis systems in a TO14 laboratory using a single IBM compatible PC operating under Windows™. The network permits communication with microprocessor based devices, such as 32-position aldehyde/sorbent tube samplers and 16-position canister field samplers, for transfer of new program information and recovery of field collected data. Canister cleaning operations are improved by providing feedback and control of leak-checking operations, mass dilution canister cleaning, and final high vacuum evacuation without user intervention. Generation of standards by dynamically diluting an NIST traceable ppm level standard to ppb levels is supported with provisions for autocalibration of mass flow controller channels for ultra-accurate VOC blends. Full communication and control of a 3-stage TO14 preconcentrator is also supported with extended QA/QC protocols and diagnostics for improved uptime and performance. An overview of the system will be presented with primary attention paid to enhancing TO14 laboratory productivity.

**Advanced Surface Treatment and Cleaning Techniques for the
U.S. EPA Method TO-14 Grab Sampling Containers**

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Increased demands and an expanding list of toxic organic compounds, including oxygenated organics and other special groups, e.g., organic sulfur compounds, require modifications and improvements to the existing sampling and measurement hardware. One critical area is the passivated stainless steel surface of the grab sampling containers. The established and proven electropolishing (SUMMA passivation) works well for the sampling of hundreds of organic and inorganic volatile compounds. However, there are instances (i.e., some oxygenated organics) where the normal passivation falls short of the required stability and storability requirements. Recent R&D efforts show some promising avenues of improvement for the surface treatment and cleaning of the sampling containers. The passivated surface can be coated with several inorganic materials to enhance its performance. The initial work shows performance improvements for some groups of organics, but not an across-the-board enhancement. The effect of surface saturation with water vapor and other materials has also been investigated. Some novel surface cleaning techniques have been explored with encouraging results. This paper will attempt to bring the audience up to date on some of the above discussed efforts.

SESSION 16:
AMBIENT AIR MEASUREMENTS OF VOCS

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Determination of Volatile Organic Compounds in Ambient Air with Gas Chromatograph-Flame Ionization and Ion Trap Detection

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ABSTRACT

Two new techniques are utilized to integrate the following three equipments: an Entech 2000 automated air concentrator, a Hewlett Packard gas chromatograph (GC) with flame ionization detector (FID) and an ion trap mass spectrometer detector (ITD). This combined analytical system is used to determine low ppb level volatile organic compounds (VOC) in ambient air. The first technique is to configure the inlet system of the GC, so that the pressure regulated flow control system of the GC injection port is used to control the flow of both the desorb gas of the automated air concentrator and the carrier gas of the GC column. The injection port still can be used to inject gas and liquid samples directly. The second technique is to split the effluent of GC column at a 1:1 ratio to the ITD and the FID. In this way, both FID and ITD data can be obtained for each analysis. For ambient air non-methane hydrocarbons monitoring, the FID detector is widely used. Oxygen containing and halogenated organic compounds cannot be differentiated by FID detector and would be quantified as coeluting hydrocarbons. However, volatile organic compounds other than target hydrocarbons can be identified by ITD. This analytical system is very valuable research tool for non-methane hydrocarbons and urban air toxic monitoring. The performances of this developed system have been presented.

INTRODUCTION

The Environmental Research Institute of the University of Connecticut has been conducting a cooperative monitoring program with the Air Toxic Group of the Bureau of Air Management, Department of Environmental Protection, State of Connecticut. In the volatile organic monitoring, in addition to the determination of the concentrations of toxic compounds (halogenated, aromatic and other common solvents) and ozone precursors (non-methane hydrocarbons), confirmation analyses for back-up canister sample from field continuous monitoring in PAMS (photochemical atmospheric monitoring study) study is also required.

In air toxic monitoring, mass spectrometer (GC/MS) is usually required. In the GC/MS method, target compounds are identified and quantified by combining the information of retention time from gas chromatograph and characteristic ions from mass spectrometer. Non-target compounds can be also identified tentatively. But in a low resolution mass spectrometer, nitrogen and carbon dioxide background ions, may interference the analyses of ambient level C2 to C3 hydrocarbons, since the masses of their fragment ion are very close. In the PAMS study, C2 to C10 hydrocarbons in the ambient air sample are analyzed using a gas chromatograph with a flame ionization detector (FID), retention time is the only information for qualification. Since the response of a FID for a hydrocarbon is proportional to the number of carbon in its molecule, this simplifies the calibration procedures for quantification. However, a compound other than target hydrocarbons may be misidentified as a target hydrocarbon, if retention times of these two compounds are close enough.

In this work an analytical instrument system and a methodology have been developed to analyze both C2 to C10 hydrocarbons and air toxic compounds. Two new techniques were utilized to integrate the following three equipments: an Entech 2000 automated air concentrator, a Hewlett Packard gas chromatograph (GC) with flame ionization detector (FID) and an ion trap mass spectrometer detector (ITD). The first technique was to configure the inlet system of the GC, so that the pressure regulated flow control system of the GC injection port can be used to control the flow of both the desorb gas of the automated air concentrator and the carrier gas of the GC column. The injection port still can be used to inject gas and liquid samples directly. The second technique is to split the effluent of the GC column at 1:1 ratio to the ITD and the FID. In this way, both FID and ITD data can be obtained from each analysis. An open split interface was used to combine GC and ITD. The interface was optimized by the manufacture to introduce less than 1 ml/min column flow into ITD, the rest is vented. The GC column flow was around 2 ml/min. After 1:1 splitting, the flow enters the ITD is around 1 ml/min, so about same amount of analytes introduced into ITD and no significant sensitivity loss. As both inlets of ITD and FID are near to atmospheric pressure, the split ratio can be easily controlled by using two pieces of deactivated fuse silica tubing with the same inner diameter and length. This analytical system is a very valuable research tool for hydrocarbons and air toxic compounds monitoring. The performance of this developed system is evaluated.

EXPERIMENTAL

Instrumental

Automated Concentrator An Entech 2000 Canister Automatic Concentrator (Entech Inc. Simi Valley, Ca) with a micro-purge and trap module. Air sample is first trapped in a liquid nitrogen cryogenic trap packed with glass beads. The trap is then heated up to room temperature. A small nitrogen flow is used to purge the trapped organic compounds onto a sorbent trap. In this step, only small amount water is transferred. A dry gas flow is used to further remove moisture on the sorbent trap. The sorbent trap is then thermally desorbed. Organic compounds are cryofocused on a liquid nitrogen trap before injected into GC column. The temperature and flow conditions are as following:

Glass bead trapping temperature:	-160°C.
Sorbent trap temperature:	-50°C.
Cryofocusing trap temperature:	-130°C.
Glass bead trap desorb temperature:	30°C.
Glass bead trap desorb flow:	125 ml (at 25 ml/min).
Sorbent trap desorb temperature:	170°C.
Sorbent trap desorb time:	4.0 min.
Sample injection:	2.5 min at GC column flow.

Gas Chromatograph Hewlett Packard 5890 gas chromatograph equipped with a splitless injection port, a flame ionization and a liquid nitrogen oven cooling valve. An HP-5 capillary column (made by Hewlett Packard Inc.) with 0.32 mm inner diameter, 50 m long and 1.0 µm film thickness, was used for the analysis. Head pressure of the column is 15 psi, column flow rate is about 2 ml/min.

The temperature program are as following:

Initial temperature:	-15 °C for 2 min
Step 1:	to 0 °C at 15°C/min, held for 2.0 min.
Step 2:	to 60°C at 4 °C/min.
Step 3:	to 200°C at 7 °C and held for 4.0 min.

Ion Trap Mass Spectrometer Detector. A Perkin-Elmer ITD Ion Trap Detector with an open split GC interface was used. The ITD is tuned to 1,4-Bromofluorobenzene criteria. The mass scanning range is from 26 to 350 m/z at 1.0 second/scan. The multi-points external standard method was used for quantitative analyses.

System Configuration. Figure 1 shows the diagram of the system. The injection port of the GC is unmodified and fully utilized. A piece of 0.53 mm ID deactivated fused silica tubing is installed to the outlet of the injection port as a normal capillary column, its end is connected with the carrier gas inlet line of the Entech 2000 automated sampler via a union. The sample transfer line from the Entech 2000 is connected with the inlet of the analytical column using a zero dead volume union. At the outlet of the analytical column a stainless steel Swagelok 1/16 Tee is used to split the column flow. At each end of the Tee, a 0.32 mm id, 0.5 m long deactivated fused silica is connected. The other ends of the two pieces of fused silica tubing are connected to FID and ITD respectively.

Calibration Standards

Stock Vapor Standards. The vapor standards with concentrations at ppm level were prepared with the static dilution method. A few microliters of each neat liquid compound is injected into a 2.00 liter static dilution bottle containing carbon filtered nitrogen. The mass of a compound added can be calculated from the volume injected and the liquid density. A 2 ppm VOC standard gas mixture (ALPHAGAZ Division of Liquid Air Corp.) containing 42 target compounds in air toxic monitoring is also used as stock standard.

Working Standards. Working standards at lower ppb level are prepared by injecting small amount stock standards into an evacuated Summar canister and then filling the canister with humidified carbon-filtered zero grade air. The total dilution volume is calculated from the volume and the final pressure of the canister. A concentration of 10 ppb working standard mixture in a Summar canister is used to prepare at least a four-point calibration curve by introducing volume of 200 to 1000 ml. Another standard prepared separately is used as a calibration verification standard. A calibration usually can be used for a month. Two types of standard mixtures are used, one contained 42 target compounds of method TO-14 plus bromodichloromethane, chlorodibromomethane, bromoform and 5 polar compounds, which are acetone, acrylonitrile, 2-butanone (methyl ethyl ketone MEK), methyl isobutyl ketone (MIBK) and methyl methacrylate. The second standard mixture contains C2 to C10 hydrocarbons, which are target compounds in PAMS study. Both standard mixtures are analyzed under the same conditions. An unknown sample is analyzed once and calibrated against each group of standards. Two sets of results can be obtained.

Reference Standards. A standard vapor mixture containing 18 volatile organic compounds at 5 ppb, which are traceable to National Institute of Standards & Technology (NIST) primary standard, is used as reference standard to check the standard prepared in the laboratory.

RESULTS AND DISCUSSIONS

Recoveries of Reference Standard

Table 1. shows typical recoveries of both FID and ITD. In our laboratory, 70 to 130 percent recoveries are used as quality control criteria. In most cases, these criteria can be achieved. Sometimes, after repeated preparation of standards from stock standard.

Comparison Criteria

The values of a compound from the same analysis but two different detectors, FID and ITD, always has difference. The question often asked is what difference can be considered significant. Criteria need to be established, before the evaluation of the data. The following procedures were used to establish the criteria in comparison of the values of the same compounds from the two detectors.

- 1) Estimate the standard deviation of every compound on both detectors respectively by repeatedly analyzing the same concentrations and using the following equation:

$$s^2 = \sum (X - \bar{X})^2 / (n - 1)$$

Where: s - standard deviation.

\bar{X} - average of individual measurements X_i .

n - number of repeatedly analyses

- 2) Calculate standard error of the difference between two measurements for each compounds:

$$s_{(x_1-x_2)}^2 = \sqrt{s_1^2 + s_2^2}$$

- 3) Estimate the difference with the confidence level of 95%:

$$Z_{(1-\alpha/2)} s_{(x_1-x_2)}^2 \text{ (here the } Z = 1.645)$$

When the difference of two values from ITD and FID for the same compound is equal to 1.646 times of standard error, the difference can be considered as greater than zero with 95% confidence level

A standard mixture with concentration around 1 ppb, common concentrations for a volatile organic in ambient air samples, was analyzed 7 times. The standard error of the difference between FID and ITD measurements for each compounds is calculated using the above equations. Figure 2 and Figure 3 illustrate the results. The standard errors for most compound are less than 0.4 ppb. When the difference of FID and ITD measurements for a compound, which concentration is around 1 ppb, is less than 0.4 ppb, the difference can be ignored. In Figure 2, no data for methylene chloride, carbon tetrachloride, cis-dichloropropene and chloromethylbenzene, due to unresolved peaks. The difference for m-xylene is twice that of the other compounds because in the standard mixture contains both m-xylene and p-xylene. The ITD is not capable of differentiating, the actual combined concentration is about 2 ppb, so the standard errors is also doubled.

Comparison of Results from Different Calibrations

In PAMS study, the calibration is simplified by using an average response factor (ppbc/peak area) of a few compounds to calculate all other compounds concentration in a sample. This simplified calibration method is based on the fact, that the response factor of FID is about the same for all hydrocarbons, when the concentration is expressed as ppbc, ppv multiplied by the number of carbon in a hydrocarbon molecule. In our work each hydrocarbon is calibrated individually, using multi-points calibration prepared from standard of the compound. The simplified calibration method is also used to calculate the pph concentration by dividing the ppbc concentration with the carbon number of the compound. Results from different calibration methods are tabulated in Table 2. In the table for unresolved two peaks, the both ppbc and individual FID results are calculated as first compounds. The last column, range, indicates the largest difference among reference value, ppbc/c, ppb by FID and ppb by FID. A range, which is greater than 40% of reference value need be

examined closer, is denoted by an asterisk. Large differences are often caused by unresolved peaks in FID, in this case ITD shows some advantages. The ppbc results for compounds which retention time is longer than toluene, show relatively low concentrations. The possible reason is that these heavier compounds have relatively lower transported efficiencies. This effect can be compensated for by using an individual calibration, because standards also suffer the same processes, but not by using a universal response factor method.

Conclusions

This analytical system has the following advantages:

- 1) The original GC column flow control system is fully utilized.
- 2) Injection port still can be used for direct injection.
- 3) Both ITD and FID results can be obtained in one analyses.
- 4) A routine method is provided for both air toxic and hydrocarbons analysis.

This analytical system is a good tool for VOC analyses in air and for real time comparison of FID and mass spectrometer in VOC analysis. More ambient sample analytical data are needed to evaluate this system.

Acknowledgements

We thank David Gregorsky, Jim Ellis, Louis Scarfo and Michael Murphy, of the Air Management Bureau, Department of Environmental Protection, State of Connecticut, who provide full support for this work.

Table 1. Recoveries of Reference Standards Tracable to NIST Primary Standards

Compounds	Cert. Conc.	ITD		FID	
	ppb	Conc.	% Rec.	Conc.	% Rec.
Vinyl chloride	4.91	4.85	98.8	4.81	98.0
Bromomethane	5.27	5.27	100.0	4.95	93.9
Trichlorofluoromethane	5.20	4.84	93.1	4.75	91.3
Methylene chloride	4.56	4.48	98.2	4.94	108.3
Chloroform	4.91	4.41	89.8	4.29	87.4
1,1,1-Trichloroethane	5.45	4.85	89.0	4.58	84.0
1,2-Dichloroethane	4.87	5.12	105.1	4.78	98.2
Benzene	4.93	4.84	98.2	4.43	89.9
Carbon tetrachloride	4.08	4.85	118.9	4.43	108.6
Trichloroethene	5.12	4.69	91.6	4.59	89.6
1,2-Dichloropropane	4.70	4.75	101.1	4.59	97.7
Toluene	5.05	5.04	99.8	4.90	97.0
1,2-Dibromoethane	4.84	4.07	84.1	3.94	81.4
Tetrachloroethene	5.01	4.90	97.8	5.70	113.8
Chlorobenzene	5.10	5.03	98.6	4.89	95.9
Ethylbenzene	4.89	4.88	99.8	4.46	91.2
o-Xylene	5.30	5.17	97.5	4.73	89.2

Cert. Conc. - certified concentration

%Rec. - percentage recovery

Table 2. Comparison of Results from Different Calibrations

Compound	REF ppb	#C	ppbc	ppbc/c	ITD ppb	FID ppb	Range ppb
Ethylene	10.1	2	21.1	10.5	11.2	11.1	1.1
Ethane	10.1	2	29.0	14.5	22.0	30.0	19.9 *
Propylene	10.0	3	22.6	7.5	9.0	9.4	2.5
Propane	10.1	3	47.8	15.9	9.0	10.8	6.9 *
1-Butene	10.3	4	43.9	11.0	9.1	10.2	1.8
n-Butane	9.9	4	46.6	11.6	9.0	10.1	2.6
trans-2-Butene	9.2	4	36.4	9.1	8.4	9.1	0.8
cis-2-Butene	9.2	4	35.2	8.8	8.6	9.1	0.6
3-Methyl-1-Butene	15.0	5	79.1	15.8	14.0	14.8	1.9
Isopentane	16.1	5	89.1	17.8	14.6	16.2	3.2
1-Pentene	10.0	5	44.8	9.0	8.4	9.7	1.6
n-Pentane	10.0	5	51.1	10.2	8.8	10.0	1.5
Isoprene (1)	18.7	5	139.8	28.0	15.5	34.7	19.1 *
trans-2-Pentene (2)	17.3	5			15.2		2.1
cis-2-Pentene	17.3	5	69.3	13.9	15.9	16.7	3.5
2-Methyl-2-Butene	17.6	5	68.3	13.7	15.7	17.1	4.0
2,2-Dimethylbutane	14.1	6	87.8	14.6	12.9	14.0	1.7
Cyclopentene (1)	18.0	5	119.1	23.8	16.2	32.1	15.9 *
4-Methyl-1-Pentene (2)	14.8	6			12.6		2.1
2,3-Dimethylbutane	14.4	6	78.8	13.1	12.7	14.2	1.7
Cyclopentane	20.0	5	99.2	19.8	18.5	20.0	1.5
2-Methylpentane	14.2	6	84.5	14.1	12.9	13.9	1.3
3-Methylpentane	14.4	6	85.4	14.2	13.0	14.2	1.4
2-Methyl-1-Pentene	15.1	6	58.7	9.8	14.2	15.0	5.3 *
n-Hexane	9.9	6	34.5	9.1	9.1	10.2	1.1
trans-2-Hexene	7.0	6	30.0	5.0	7.8	6.6	2.8 *
cis-2-Hexene	20.1	6	81.1	13.5	19.1	18.0	6.6 *
Methylcyclopentane (1)	16.6	6	188.1	31.3	16.0	28.7	15.3 *
2,4-Dimethylpentane (2)	12.5	7			11.2		1.3
Cyclohexane (1)	17.3	7	193.7	27.7	16.2	39.1	22.9 *
Benzene (2)	21.0	6			21.6		0.6
2-Methylhexane	13.0	7	81.3	11.6	11.7	12.6	1.4
2,3-Dimethylpentane	13.0	7	97.7	14.0	12.0	12.7	1.9
3-Methylhexane	12.8	7	85.5	12.2	11.3	12.5	1.5
2,2,4-Trimethylpentane	11.3	8	93.7	11.7	10.0	11.0	1.7
n-Heptane	12.8	7	69.4	9.9	12.2	13.4	3.5
Methylcyclohexane	14.7	7	100.1	14.3	13.2	14.2	1.5
2,3,4-Trimethylpentane	11.8	8	90.8	11.4	10.5	11.4	1.2
2-Methylheptane	11.4	8	79.5	9.9	11.3	11.1	1.5
3-Methylheptane	11.4	8	82.8	10.4	12.5	14.9	4.5 *
Toluene	17.6	7	78.2	11.2	16.0	15.9	6.4 *
n-Octane	11.5	8	70.1	8.8	10.3	11.7	3.0
Ethylbenzene	15.3	8	69.0	8.6	14.3	15.7	7.1 *
m/p-Xylene	12.0	8	78.5	9.8	13.7	15.5	5.7 *
n-Nonane (1)	10.5	9	113.9	12.7	9.9	26.5	16.7 *
Styrene (2)	16.2	7			14.0		2.2
o-Xylene	15.5	8	97.8	12.2	14.2	15.4	3.3
Isopropylbenzene	13.4	9	83.2	9.2	12.3	13.3	4.2 *
alpha-Pinene	11.8	10	99.4	9.9	11.3	11.2	1.8
n-Propylbenzene	13.4	9	72.6	8.1	12.4	13.4	5.4 *
1,3,5-Trimethylbenzene	13.4	9	74.4	8.3	13.5	13.7	5.4 *
beta-Pinene	11.8	10	85.4	8.5	10.9	11.3	3.2
1,2,4-Trimethylbenzene	13.8	9	66.6	7.4	13.6	14.1	6.7 *

NOTE: * indicates a range is greater than 40% of its reference value.

(1) peaks not resolved with GC, reported as sum of two compounds for FID results

(2) peaks not resolved with GC, only ITD result available

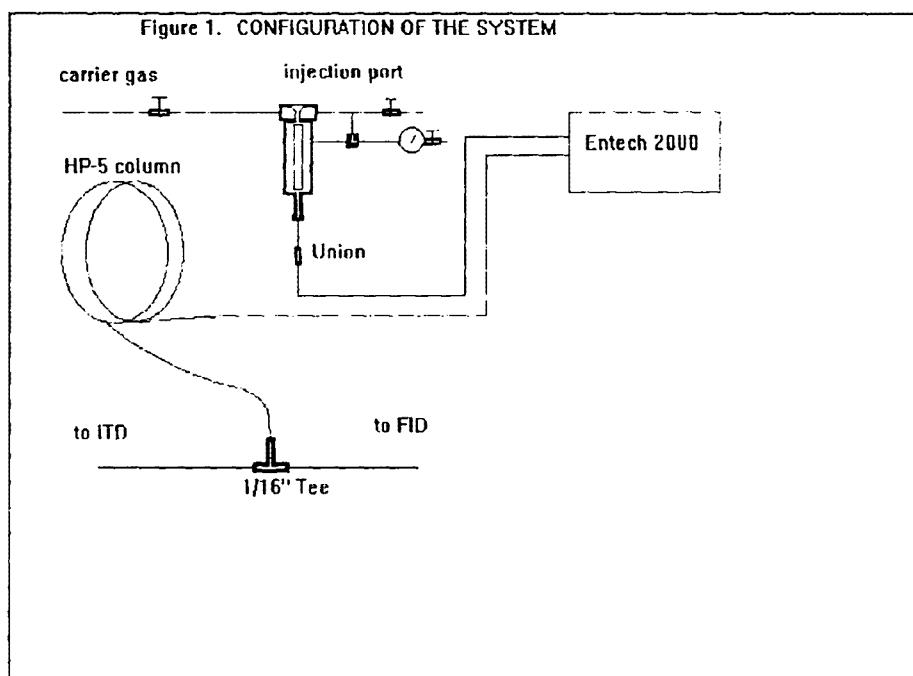


Figure 2. Difference with 95% Confidence at 1ppb

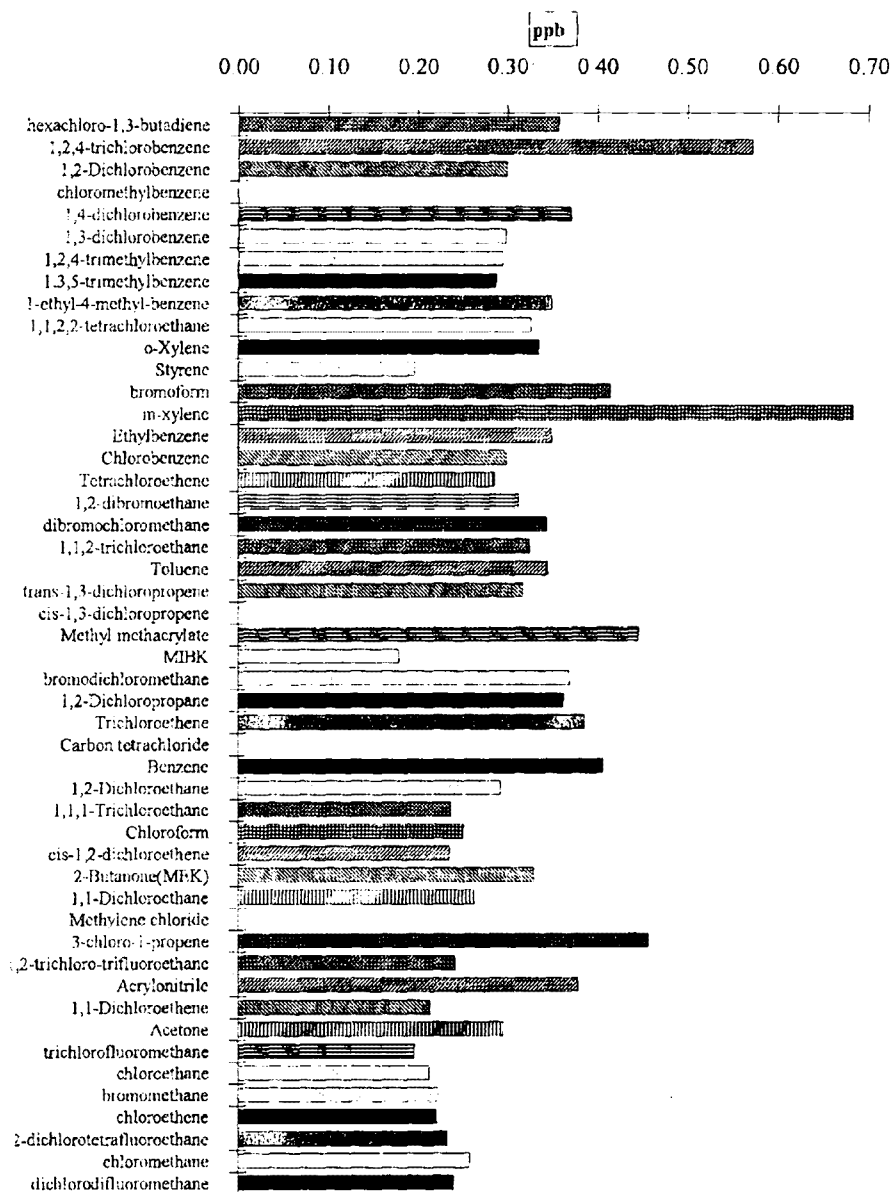
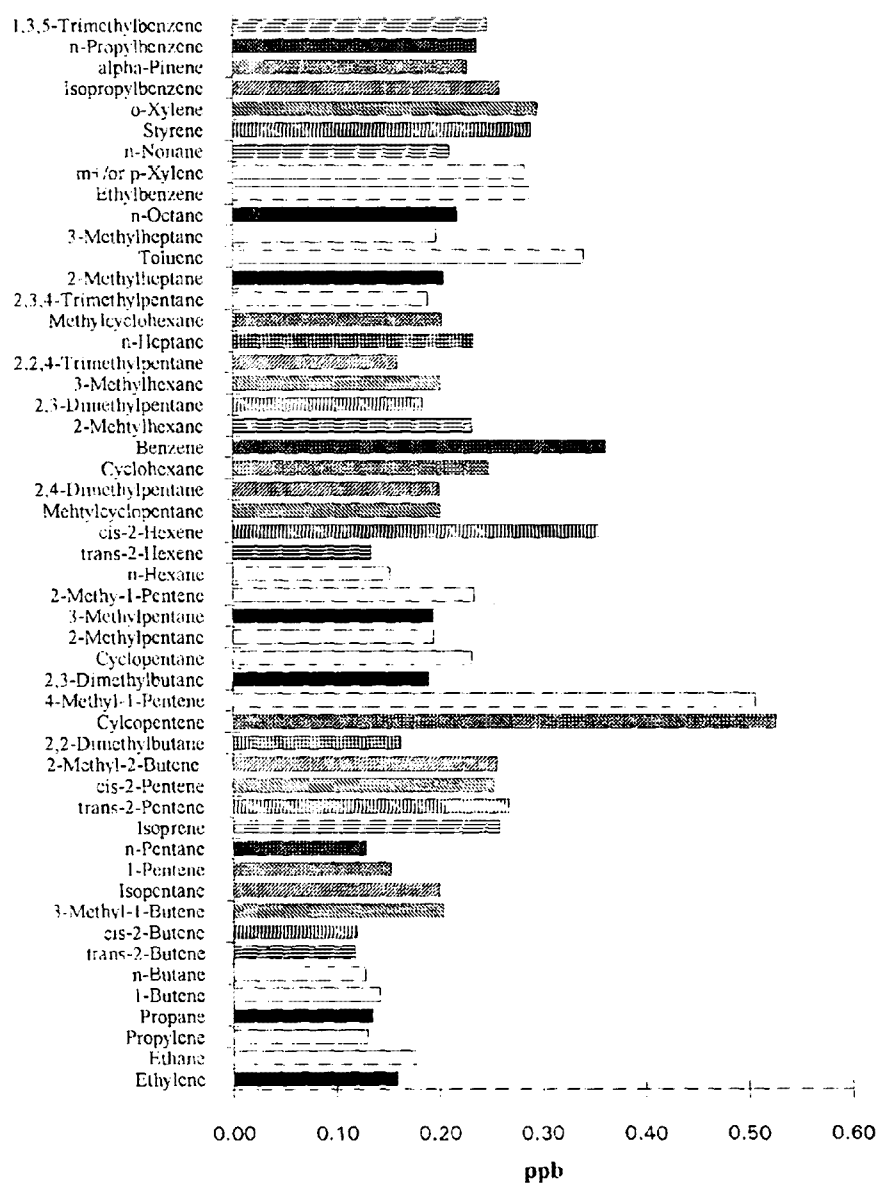


Figure 3. Difference with 95% Confidence at 1 ppb



Exposure to Evaporative Gasoline Emissions

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INTRODUCTION

Exposure to evaporative gasoline emissions that occur in selected microenvironments or during specific activities can contribute significantly to the daily volatile organic compounds (VOCs) exposures an individual receives. Three microenvironments/activities that are influenced by evaporative gasoline emissions are residential garages, public parking garages and activities surrounding refueling of an automobile. In addition, exhaust emissions contribute to public parking garage air concentrations. The emissions that occur within a residential garage can also penetrate into the attached home. This penetration has been observed within samples collected as part of the TEAM study. Gasoline emissions are one of the major sources of general population VOC exposures, acute higher environmental exposures and as VOC sources into the home indoor microenvironmental. The data presented are preliminary results from a study designed to measure the potential VOC exposures in the above mentioned microenvironments and obtain a data base suitable for evaluating mathematical models describing human exposures from mobile sources.

EXPERIMENTAL

Measurements of the benzene and toluene air concentrations were made within each microenvironments/activity using integrated adsorbent trap samples (trilayer adsorbent of Tenax GC, Carboxen 569 and Carbosieve SIII) analyzed by thermal desorption (PTD400) coupled with GC/MS (HP 5890-MSD) and/or with a portable gas chromatograph (MSI 301) that collects an air sample approximately every eight minutes. The latter is being used to evaluate temporal changes within the microenvironment. In addition to provided average concentrations the adsorbent trap thermal desorption/GC/MS method provides a quality control check on the peak identification and concentration measured by the portable GC. The integrated samples were collected using a constant flow, personal air sampling pump whose calibration was verified before and after use using a bubble flow meter and whose flow rate was adjusted to provide between 0.5 and 3 liters of air, based on the predicted sampling time. A minimum of a five point calibration curve was prepared for each compound to be measured by GC/MS and the calibration curve check daily. A blank trap was transported to the field each sampling day and analyzed to assure that no contamination of the traps were present. The MS settings were checked using bromo-fluoro benzene, as outline in EPA method 625. A multi-point calibration curve is prepared and saved in the memory of the portable GC. The response of the portable GC was verified daily by use of an air sample with a known concentration. The zero response of the portable GC was check by attaching a tube containing activated charcoal to its intake port.

RESULTS

Residential Garage Study

The benzene and toluene air concentrations within a residential garage and the room adjacent to the garage in the attached home were measured before and after an automobile

entered the garage and the garage door was closed. These studies were done during the summer months, since evaporation from the fuel tank is increased when the ambient temperature is higher. The air concentrations of both benzene and toluene were elevated in the garage after a car was parked in it, to as much as $50\mu\text{g}/\text{m}^3$ and $150\mu\text{g}/\text{m}^3$, respectively, (figure 1). This elevation represented an increase of two to ten times the concentrations present in the air before the car entered. Air concentrations within the home also increased, approximately twice the concentration present before a car entered the garage (figure 2). The increase in the air concentration is rapid and reaches a maximum value that is a function of the emission rate from the automobile and the air exchange out of the garage. The concentration subsequently declines in an exponential fashion (figure 3). The integrity of the fuel system affects the emission rate and thus the maximum concentrations obtained in the garage. Samples collected during the summer of 1992 using an older vehicle whose controls systems had probably been comprised resulted in mg/m^3 levels being measured in the garage, two orders of magnitude greater than presented here.

Public Parking Garage Study

Air samples were collected within a multi-level public parking garage. The upper two levels were open on two sides, while the lowest level was enclosed on all four sides, with the access ramp in the middle of the garage. The garage chosen is usually full to capacity during the day time hours with a mixture of individuals who use the garage for the entire day and those that park for short time periods of less than one hour. Automobiles often idle within the facility while waiting for a parking spot to be available. The air concentrations have contributions that are expected to be a mixture of exhaust and evaporative emissions, with the latter more prevalent during the warmer months, and a heavier odor of gasoline is apparent during the summer months. Levels of benzene exceeded $150\mu\text{g}/\text{m}^3$ and of toluene $500\mu\text{g}/\text{m}^3$ within the garage (figure 4). The air concentrations were higher in the summer months than the winter, suggesting the importance of an evaporative emission contribution to the observed levels. The variability in the concentration within a three hour time period on a single day, on two levels with different ventilation was measured using the portable GC. A greater concentration, along with greater variability in that concentration was observed on the level that had less ventilation (figure 5). These measurements indicate that "high" acute exposures can occur within a public parking garage but that design of the facility to minimize the air concentration can be accomplished by not enclosing the facility completely.

Refueling Study

Adsorbent trap air samples were collected within an automobile prior to, during and after refueling and a personal sample was collected from an individual who either refueled his/her own car or stood next to the service station attendant during the refueling operation. The automobile interior samples collected prior to refueling were similar to values that we have collected previously within an automobile being driven in New Jersey. The concentration in the interior of the automobile was higher during and after refueling than before refueling. The personal samples were highest (figure 6). An examination of the ratio of benzene to toluene in the air samples indicated that a ratio greater than 1, was present during and after refueling, while a ratio more typical of ambient, air 0.3, was observed prior to refueling. This difference is best explained by an increased contribution of evaporative emissions compared to exhaust emissions to the during and post refueling samples, since benzene is a more volatile compound than

toluene, even though toluene is present in the fuel in a higher percentage. Refueling of gas tank results in an acute exposure to gasoline derived VOCs, which can persist within the automobile following refueling.

Exposure Estimates

Daily estimates of benzene exposures can be made based on concentrations and time spent in various microenvironments and compared to what might result from the microenvironments/activities studied here (Table 1). The largest exposures to VOCs occur indoors, since the majority of a person's time is spent there. Driving in traffic has been shown to contribute more than 10% of a person's exposure. Spending 10 minutes in a residential garage, with a well maintained car could contribute an additional 4% and infiltration to a home another 8%. If the automobile used has a compromised control device on the fuel tank or if the more time is spent in the garage the exposure level can be considerably higher. Walking within a public parking garage to and from a car and driving to find a parking spot could contribute more than 10% of the daily exposure, with the type of ventilation within the garage being an important controlling factor in the exposure. An individual who refuels a car can receive as much as half of the daily benzene exposure accumulated on that day from that five minute activity. A small contribution can also result to individuals who remain in their automobile during refueling.

SUMMARY

Three specific microenvironments that are impacted by gasoline emissions were studied and each found to have elevated concentration of VOCs because of those emissions, relative to ambient air and indoor air. Even spending a small amount of time in these microenvironment could make a measurable contribution to a persons exposure to VOCs. Additional work is ongoing to collect data in these microenvironments to evaluate models that predict overall exposures to VOCs from gasoline emissions.

ACKNOWLEDGEMENT

Although the research described in this article has been funded wholly or in part by the US EPA-AREAL under a cooperative agreement (CR82035-01) to UMDNJ-RWJMS-EOHSI, it has not been subjected to the Agency's peer and administrative review and therefore may not necessarily reflect the views of the Agency and no official endorsement is to be inferred.

RESIDENTIAL GARAGE STUDY

Benzene & Toluene Concentrations
adsorbent trap - GC/MS

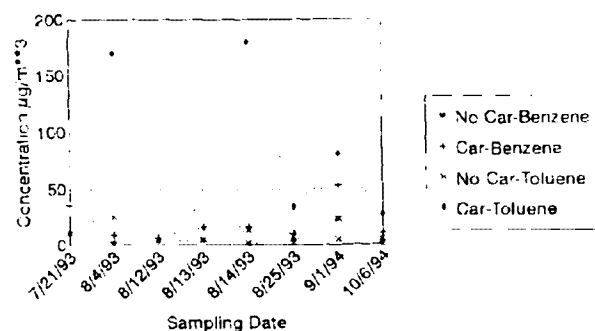


Figure 1

RESIDENTIAL GARAGE STUDY

Benzene Concentrations
portable GC

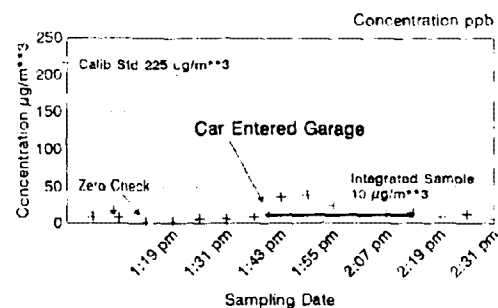
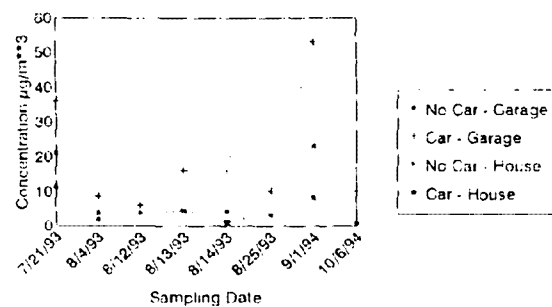


Figure 3

RESIDENTIAL GARAGE STUDY

Benzene Concentrations
adsorbent trap - GC/MS



PUBLIC PARKING GARAGE

Benzene Concentrations
absorbent traps - GC/MS

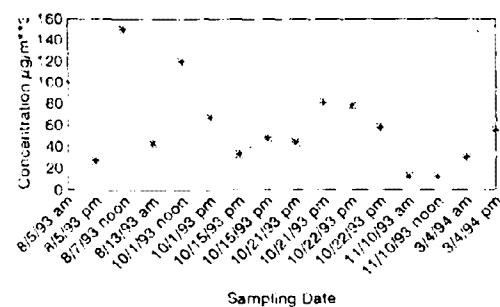


Figure 4

REFUELING STUDY

adsorbent trap - GC/MS

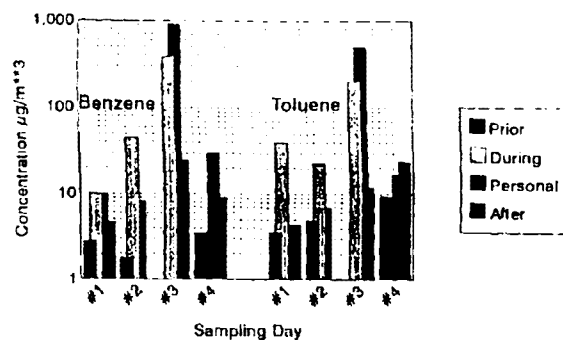


Figure 5

PUBLIC PARKING GARAGE

Benzene Concentrations
portable GC

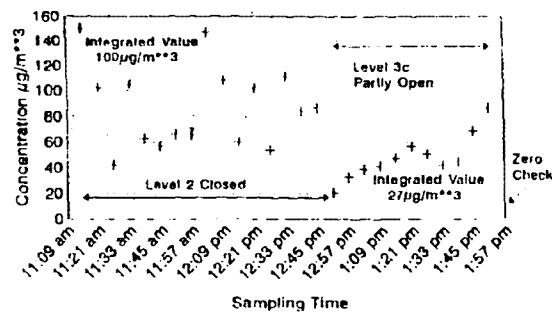


Figure 6

Table 1

DAILY BENZENE EXPOSURE ESTIMATES

- Influence of residential garage:
in garage for 10 minutes
 $25 \mu\text{g}/\text{m}^3 \times 0.2 \text{ hours} = 5 \mu\text{g}/\text{m}^3$
increase in house for 2 hours
 $5 \mu\text{g}/\text{m}^3 \times 2 \text{ hours} = 10 \mu\text{g}/\text{m}^3$
- Public parking garage
in garage for 20 minutes
 $60 \mu\text{g}/\text{m}^3 \text{ for } 0.3 \text{ hours} = 18 \mu\text{g}/\text{m}^3$
(ventilation affects conc. - time to
find a parking space and walking)
penetration into attached building ???
- Refueling an automobile
self service for 5 minutes
 $1000 \mu\text{g}/\text{m}^3 \times 0.08 = 80 \mu\text{g}/\text{m}^3$
in car full service
 $50 \mu\text{g}/\text{m}^3 \times 0.08 = 4 \mu\text{g}/\text{m}^3$
+ post refuel residual exposures

Hydrocarbons in the C8-C20 Range Measured During COAST Study in Texas

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ABSTRACT

Hydrocarbons in the C8-C20 range were collected using Tenax-TA solid adsorbent cartridges during the Coastal Oxidant Assessment for Southeast Texas (COAST) field study, carried out in the Houston-Galveston and Beaumont-Port Arthur areas. Ambient samples were collected at the Galleria, Clinton and Port Arthur sampling sites, from August 26 to August 30, 1993. In addition, a number of Tenax samples were collected in the vicinity of major industrial complexes (such as Exxon, AMOCO Oil, Union Carbide, Dow Chemical) and in an urban tunnel. All samples were analyzed with high resolution capillary column gas chromatography with flame ionization detection (GC/FID) for quantification and selected duplicate samples were analyzed with combined gas chromatography/Fourier transform infrared/mass spectrometry (GC/FTIR/MS) for identification of individual compounds. The results of these analyses are presented.

INTRODUCTION

In order to improve the technical basis for designing effective ozone control strategies for the Houston-Galveston and Beaumont-Port Arthur-Orange areas of southeast Texas, the Texas Natural Resource Conservation Commission (TNRCC) has sponsored the Coastal Oxidant Assessment for Southeast Texas (COAST) project. The purpose of the COAST project was to develop a comprehensive air quality and meteorological data base for southeast Texas which can be used to enhance the understanding of the relationship between emissions and spatial and temporal distributions of pollutants so that air quality simulation models and, ultimately, air quality management strategies can be improved. An important component of the COAST study was the characterization of the composition and concentrations of the organic precursors of ozone - mainly non-methane hydrocarbons (NMHC) in the C2-C12 range, collected by the canister sampling method (U.S. EPA, 1991¹).

However, in some airsheds the fraction of hydrocarbons with carbon number > C12 existing in the gas phase, so-called semi-volatile hydrocarbons (SVHC), could be significant. These airsheds include areas strongly influenced by diesel emissions or other fossil fuel-type emission sources, as is the case in southeast Texas. It has been shown in a recent study conducted in the Fort McHenry (Baltimore, Maryland) and Tuscarora (Pennsylvania) Tunnels that the total NMHC concentrations measured in the tunnels increased by up to 60% when the concentrations of SVHC in the range C10-C20 were added to those of volatile C2-C12 hydrocarbons obtained from canister samples (Zielinska et al., 1993,² 1994³). It has been also shown in the SJVAQS/AUSPEX study (1989) that canister samples collected within an oil production area (Kern River Oil Field, CA) exhibited an unusually high number of peaks eluting in the range >C8. However these peaks were not identified or quantified.

Clearly, a complete analysis of all gas-phase hydrocarbons is necessary in order to determine the relative importance of SVHC in relation to traditionally measured gas-phase total NMHC. In recognition of this need, a limited number of Tenax samples analyzed for C8-C20 hydrocarbons were collected during the summer 1993 COAST study, in parallel with canister samples analyzed for C2-C12 hydrocarbons. In addition to ambient air measurements, a number of Tenax samples were

collected in the vicinity of the main industrial complexes and in an urban tunnel. This paper describes the preliminary results of Tenax samples analysis.

EXPERIMENTAL METHODS

Sampling

Ambient Tenax samples were collected at the Galleria, Clinton and Port Arthur sampling sites from August 26 to August 30, 1993. The Galleria site was located in Bellaire City, in the Houston-Galveston metropolitan area. The site was surrounded by local streets and the busy I-610 freeway was located ~210 m east. This was a typical urban site, impacted by motor vehicle emissions. The Clinton site was located in an industrial suburban Houston area with a major refinery plant no more than 1 km from the site. It was surrounded by residential streets and the I-610 freeway was ~750 m away. The Port Arthur sampling site, located in Port Arthur, approximately 60 miles southeast of Houston, was situated in a flat field, ~400 m away from Highway 365. It was a rural site, except that a big refinery (Texaco) and a pulp mill were situated not far away. The samples were collected during 1-hour sampling periods, starting at 0300, 0700 and 1500 hr, in parallel with canister sampling. Over a three-day sampling period, 22 Tenax samples were collected (plus 22 duplicate and 44 back up Tenax cartridges).

Source samples were collected during the period September 1 through October 8, 1993. Motor vehicle exhaust emission samples were collected in the Baytown Tunnel, a motor vehicle tunnel on Highway 146 situated under the Houston Ship Channel and connecting Baytown and La Porte. Samples were collected inside the tunnel and, in parallel, in the ventilation building intake room to account for the background ventilation air. In addition, samples were collected upwind and downwind of vehicles in the Houston AstroDome parking lot during a major sporting event. Simultaneous upwind and downwind samples were also collected at a number of industrial clusters. These included: Exxon Baytown facilities (between Bay Way Drive and Highway 330), AMOCO Oil (Texas City), Union Carbide (Texas City, adjacent to AMOCO), Dow Texas Operation (Plant B facility and Oyster Creek facility in Freeport), and Texaco (Port Arthur). Biogenic emission samples were collected at the major forests around the study area, namely at Brazos Bend State Park, located some 40 miles southwest of Houston (mixed oak/hardwood river bottom forest) and at Sam Houston National Forest, about 60 miles north of Houston (mostly pine forest). Approximately 25 source Tenax samples were collected (not counting duplicate and back-up cartridges).

Ambient and source air samples were collected using glass cartridges filled with Tenax-TA solid adsorbent. Prior to use, Tenax-TA solid adsorbent was cleaned by Soxhlet extraction with hexane/acetone mixture (4/1 v/v), packed into Pyrex glass tubes (4 mm i.d. x 15 cm long, each tube contained 0.2 g of Tenax) and thermally conditioned for four hours by heating at 300 °C under nitrogen purge. After heating, the cartridges were capped tightly using clean Swagelok caps (brass) with graphite/vespel ferrules, and placed immediately in metal containers with activated charcoal on the bottom and stored in a clean freezer. The cartridges were used for sampling within two weeks after preparation. The sampling units drew two parallel streams of air at ~0.5 l/min per stream. Since each Tenax sample can be analyzed only once by the thermal desorption method, two parallel Tenax samples were always collected. In order to assess the possible breakthrough effect, two Tenax cartridges in series were employed for each sampling period (hence, four cartridges per unit). After sampling, the Tenax cartridges were capped tightly with Swagelok caps, placed in their metal containers with activated charcoal on the bottom, and kept on ice until transported to a laboratory freezer.

Analysis

Tenax samples were analyzed by the thermal desorption-cryogenic preconcentration method, followed by high resolution GC separation and combined Fourier transform infrared/mass spectrometric (FTIR/MS) detection (GC/IRD/MSD; Hewlett Packard 5890 II GC with 5979 MSD and 65B IRD) or flame ionization detection (Hewlett Packard 5890 II GC/FID) of individual

hydrocarbons. The Chrompack Thermal Desorption-Cold Trap Injection (TDCT) unit, which could be attached to either the GC/FID or the GC/FTIR/MS system, was used for sample desorption and cryogenic preconcentration. The desorption parameters were as follows: desorption temperature 280°C, held for 8 min; trapping temperature -140°C; He flow 15 mL/min. A 30-cm piece of fused silica capillary tubing (0.52 mm id), packed with a small amount of glass wool, was used as a cold trap. After the cycle of desorption was completed, the cold trap was heated to 280 °C within seconds and held for 2 min at this temperature. A 60 m (0.32 i.d., 0.25 µm film thickness) DB-1 capillary column (J&W Scientific, Inc.) was used and the chromatographic conditions were as follows: initial column temperature of 30 °C for 2 min, followed by programming at 6 °C/min to a final temperature of 290 °C and held isothermally for 5 min.

Several duplicate Tenax cartridges from each sampling location were analyzed by the GC/IRD/MSD technique in order to identify individual hydrocarbons. Identification of individual components was made based on their retention times, mass spectra, and infrared spectra matching those of authentic standards. If authentic standards were not available, the National Institute of Standards and Technology (NIST) mass spectral library (containing over 43,000 mass spectra) and the U.S. EPA infrared spectral library were used for compound identification. The quantification of hydrocarbons collected on all remaining Tenax cartridges was accomplished by the GC/FID technique. For calibration of the GC/FID, a set of standard Tenax cartridges was prepared by spiking the cartridges with a methanol solution of standard SVHC, prepared from high purity commercially available C9-C20 aliphatic and aromatic hydrocarbons (Alltech Associates, Inc.). 1,3,5-trimethylbenzene and n-dodecane were used in the concentration range from ~7-8 ng/Tenax up to 200-300 ng/Tenax. The solvent was then removed with a stream of N₂ (5 min, 100 ml/min at room temperature) and the Tenax cartridges were thermally desorbed into the GC system, as described above. At least three concentrations of each standard compound were employed. Area response factors per nanogram of compound were calculated for each concentration and each hydrocarbon and then the response factors were averaged to give one factor for all hydrocarbons measured. In addition, Tenax cartridges spiked with a mixture of standard paraffinic (in the C9-C20 range) and aromatic (C4-, C5-, and C6-benzenes) hydrocarbons were periodically analyzed by GC/FID to verify quantitative recovery of these hydrocarbons from the cartridges.

Identification and quantification of individual species from the GC/FID analyses were based on the DRI laboratory calibration table, which contains ~200 species. GC/FID outputs are connected to a data acquisition system (ChromPerfect, Justice Innovations, Inc., Palo Alto, CA). The software performs data acquisition, peak integration and identification, hardcopy output, post-run calculations, calibrations, and user program interfacing. Acquired data are automatically stored on a hard disk. Peak integration is generally hand checked for accuracy and an integration output file is generated by the ChromPerfect software and stored to disk as an ASCII file. This file is imported into a custom designed data-base management system (running under FoxPro version 2.5, Microsoft Corp., Redmond, WA) that is used to confirm peak identifications. This system requires the user to manually identify 12 or fewer peaks which are then used for a correlation analysis with observed retention times to compare with the calibration file. The adjusted retention times are used to assign peak identifications for all detectable peaks. The retention time adjustments and peak assignments are executed automatically by a subroutine of the program. The ChromPerfect and subsequent confirmatory peak identifications are then compared and discrepancies are resolved by the analyst based on peak patterns or confirmatory identification by GC/MS. In the final step, the validated data are appended to the master data base. Each sample appears as a record within the data base and is identified by a unique sample identification number, site, date, and time and as a primary, collocated blank, spiked, or replicate sample. Typically, over 85% of the detectable C8-C20 hydrocarbon mass was identified and quantified.

RESULTS AND DISCUSSION

Compound Identification

In order to identify as many individual SVHC as possible, selected duplicate Tenax samples from each sampling period and sampling location were analyzed by the GC/FTIR/MS technique. From a single analysis, this system gives three dimensions of data for positive compound identification: retention times, infrared spectra, and mass spectra. The Fourier transform infrared technique proved to be very helpful in the identification of non-hydrocarbons, especially oxygenated compounds, due to the high sensitivity and selectivity of IR spectroscopy to these types of compounds. For example, in several ambient samples collected in the Clinton and Port Arthur areas, a number of aliphatic C9-C10 alcohols were identified, based on their FTIR and mass spectra. In the source samples collected upwind of Dow Chemical (Oyster Creek facility) a high concentration of phenol and tert- and sec-butyl phenol derivatives was found. However, the Schenectady Chemical plant, situated upwind of Dow Chemical, is probably responsible for this chemical presence. Samples collected in the vicinity of petroleum plants, such as AMOCO and Exxon, showed the presence of alkyl- (mostly C2-C4) substituted cyclohexanes. These compounds were also found in Tenax samples collected upwind of Union Carbide. However, the Union Carbide facilities in Texas City are adjacent to AMOCO Oil facilities.

Compound Quantification

Tables 1 and 2 show the concentrations of paraffinic, olefinic, aromatic and total hydrocarbons in the C8-C20 range, for ambient and source Tenax samples, respectively. It can be seen from Table 1 that the highest ambient concentrations of C8-C20 hydrocarbons were generally observed in Clinton, and the lowest ones in Port Arthur. The sample collected in Clinton on August 26 from 0700 to 0800 hr shows an unusually high proportion of paraffinic hydrocarbons. This is due to the presence of a number of C11-C12 paraffins, which suggests the influence of a nearby refinery. Two morning Clinton samples collected on August 29 (0300-0400 and 0700-0800 hr) show unusually high concentrations of m/p-xylene, 84 and 159 ppbC, respectively. These high concentrations, not accompanied by proportionally high concentrations of ethylbenzene and o-xylene, cannot be due to motor vehicle emissions. In addition, the sample collected at 0700 to 0800 hr contained a significant amount of C9-C10 aliphatic alcohols. The same alcohols are also present in a sample collected on the same day from 1500 to 1600 hr.

The Galleria samples show the highest concentrations of C8-C20 hydrocarbons in the samples collected from 0700 to 0800 hr, during morning rush-hour traffic. The hydrocarbon pattern is typical of a site impacted mainly by motor vehicle emissions.

The highest C8-C20 hydrocarbon concentrations for Port Arthur are observed in the samples collected in the early morning, from 0300 to 0400 and 0700 to 0800 hr. Samples collected on August 29 from 0300 to 0400 hr, as well as those collected on August 30 from 0300 to 0400 and 0700 to 0800 hr, contain the significant amount of C9-C10 aliphatic alcohols. These samples also show relatively high concentrations of naphthalene, 1- and 2-methylnaphthalenes, dimethylnaphthalenes and biphenyl.

In the source samples, the highest concentrations of C8-C20 hydrocarbons were observed in the Baytown Tunnel (see Table 2), reaching nearly 3 ppmC during peak traffic hours. The lowest concentrations were recorded for the biogenic emission impacted sites, namely Brazos Bend and Sam Houston National Forest. Although all Tenax samples collected in these locations show the presence of biogenic hydrocarbons (mainly α - and β -pinene, limonene, and sabinene), the obtained concentration values are not quantitative. These compounds, particularly α -pinene, show significant breakthrough during sampling of large volumes of air with Tenax (~30-35 L in our case). Biogenic hydrocarbons, such as α - and β -pinene, and limonene were also observed in most of the Tenax samples collected in all three ambient air sampling locations.

Tenax samples collected downwind of Exxon (Baytown) and AMOCO Oil (Texas City) show relatively high concentrations of C8-C20 hydrocarbons, especially the samples collected on

September 9 and 28 from 1540 to 1640 and 1725 to 1825 hr, respectively. The proportions of paraffinic hydrocarbons in these samples in relation to total hydrocarbons are relatively high. This is due to the high concentration of n-alkanes in the C8-C14 range. All Exxon and AMOCO downwind samples show also the presence of C2-C4 alkyl cyclohexanes.

The C8-C20 compounds identified in the source samples may prove useful in the development of emission profiles for these sources. However, due to the very limited number of Tenax samples collected during this study, it is not possible to develop such profiles at present. The compositions and concentrations of C8-C20 hydrocarbons found in the individual ambient and source Tenax samples are presented in detail elsewhere (Zielinska et al., 1994⁴).

CONCLUSION

Semivolatile organic compounds in the C8-C20 range collected by means of Tenax-TA cartridges during the COAST study in Texas, occur in appreciable concentrations in ambient and source samples. Some of these compounds may prove useful in the development of emission profiles for local sources.

ACKNOWLEDGEMENTS

Financial support for this study was provided by the Texas Natural Resource Conservation Commission. The authors thank Eric Fujita, Desert Research Institute, for helpful discussions.

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Table 1. Summary Table for Ambient Tenax Samples

Sampling date	Sampling time	Sampling location	Total (CR C20) in ppbC			
			paraffins	olefins	aromatics	hydrocarbons
26-Aug-93	700-800	CLINTON	175.3	5.7	78.7	259.7
29-Aug-93	300-400	CLINTON	40.4	10.4	231.5	282.3
29-Aug-93	700-800	CLINTON	57.5	9.7	293.6	360.8
29-Aug-93	1500-1600	CLINTON	27.4	3.0	81.1	111.8
30-Aug-93	300-400	CLINTON	18.3	13.2	108.5	140.1
30-Aug-93	700-800	CLINTON	15.0	2.7	103.1	120.8
30-Aug-93	1500-1600	CLINTON	54.7	3.9	108.5	167.1
26-Aug-93	700-800	GALLERIA	22.0	5.0	111.8	138.9
26-Aug-93	1500-1600	GALLERIA	11.8	1.7	51.8	65.3
29-Aug-93	300-400	GALLERIA	10.5	3.0	61.3	74.8
29-Aug-93	1500-1600	GALLERIA	7.1	1.9	35.0	44.1
30-Aug-93	300-400	GALLERIA	10.9	3.0	46.7	60.6
30-Aug-93	700-800	GALLERIA	43.8	18.3	220.4	282.4
30-Aug-93	1500-1600	GALLERIA	5.9	1.3	25.1	32.2
26-Aug-93	700-800	PORT ARTHUR	9.0	2.9	31.4	43.2
26-Aug-93	1500-1600	PORT ARTHUR	4.2	1.0	7.5	12.6
29-Aug-93	300-400	PORT ARTHUR	13.5	4.8	53.9	72.2
29-Aug-93	700-800	PORT ARTHUR	12.6	6.5	67.6	86.7
29-Aug-93	1500-1600	PORT ARTHUR	4.8	0.4	4.9	10.1
30-Aug-93	300-400	PORT ARTHUR	5.9	2.6	24.8	33.2
30-Aug-93	700-800	PORT ARTHUR	8.2	3.4	44.5	56.1
30-Aug-93	1500-1600	PORT ARTHUR	3.2	0.7	8.4	12.2

Table 2. Summary Table for Source Tenax Samples

Sampling date	Sampling time	Sampling location	Total (CR C20) in ppbC			
			paraffins	olefins	aromatics	hydrocarbons
21-Sep-93	700-800	BAYTOWN TUN.	180.1	14.8	2724.2	2919.2
21-Sep-93	700-800	BAYTOWN TUN. VENT	21.0	3.2	126.2	150.5
24-Sep-93	1800-1900	BAYTOWN TUN.	181.7	13.4	2516.8	2711.8
24-Sep-93	1800-1900	BAYTOWN TUN. VENT	9.9	1.4	21.4	32.7
10-Sep-93	1500-1539	BRAZOS REND	5.1	1.9	22.3	29.4
01-Oct-93	1320-1420	DOW (PLANT B) UW	9.6	2.5	21.5	33.6
01-Oct-93	1730-1830	DOW (OYSTER CR.) UW	33.2	4.4	50.8	88.4
01-Oct-93	1732-1832	DOW (OYSTER CR.) DW	9.8	1.0	19.8	30.6
02-Oct-93	1445-1600	TEXACO-UW	9.9	1.3	24.3	35.5
02-Oct-93	1445-1600	TEXACO-DW	11.6	1.6	27.1	40.4
11-Sep-93	1205-1305	ASTRO DOME-DW	16.3	1.2	66.2	83.7
11-Sep-93	1205-1305	ASTRO DOME-UW	21.5	6.5	108.2	136.2
30-Sep-93	1130-1230	UNION CARBIDE DW	16.1	1.6	38.9	56.6
30-Sep-93	1130-1230	UNION CARBIDE-UW	53.4	4.1	108.1	165.5
28-Sep-93	1415-1515	AMOCO-DW	21.9	2.5	60.3	84.7
28-Sep-93	1415-1515	AMOCO-UW	17.5	3.4	33.0	54.0
30-Sep-93	1615-1715	AMOCO-DW	34.4	3.3	74.4	112.0
28-Sep-93	1725-1825	AMOCO-UW	15.3	3.9	51.9	71.1
28-Sep-93	1725-1825	AMOCO-DW	112.3	8.8	194.5	315.6
09-Sep-93	1530-1630	EXXON-UW	11.5	0.4	26.5	38.4
09-Sep-93	1540-1640	EXXON-DW	111.3	2.0	166.9	282.2
09-Sep-93	1930-2030	EXXON-UW	21.1	0.8	76.0	97.8
09-Sep-93	1930-2030	EXXON-DW	27.2	10.9	77.6	115.7
04-Sep-93	1350-1450	S. HOUSTON NAT. FOR.	2.4	1.7	3.8	7.9
04-Sep-93	1625-1725	S. HOUSTON NAT. FOR.	3.8	4.1	6.5	14.3
04-Sep-93	1800-1900	S. HOUSTON NAT. FOR.	3.5	7.6	6.0	17.0

DW - Downwind, UP - Upwind

The Determination of Hazardous Air Pollutants with a Built-in Preconcentrator and Capillary GC

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Under the 1990 Clean Air Act Amendments industries identified as major sources of hazardous air pollutants must meet Maximum Achievable Control Technology standards within a certain time frame. The resultant reduction of emissions is enforced under the Title V permit program. This reduction may require monitoring of the source as well as at the fence line of the facility precursors. Multiple location monitoring is required during the remediation of certain hazardous waste sites to track the air pathways ensuring that pollutants are not transferred outside the site. Gas Chromatography and Gas Chromatography/Mass Spectrometry in combination with air sample preconcentration is the primary analytical technique used for these monitoring requirements since it provides the best sensitivity and quantitative reliability. One problem with this approach is the size as well as the complexity of these preconcentrator/GC systems.

A hazardous air pollutant GC system has been configured with a new built-in sample preconcentration trap (SPT) and associated valving capable of preconcentrating air samples of variable volumes. Since the preconcentrator is built into the GC, the system has a small footprint, simple interfacing, and control from one PC. The air sample is drawn either from a canister or directly from the ambient air through SPT adsorbent trap. The adsorbent trap is cooled to initial conditions using the option of a cryo or non-cryo technique. Following trapping, the air toxics are quickly desorbed with the fast heating (40° C/sec) SPT to a wide bore capillary column with detection by FID, PID, ECD, or a combination of detectors. No column oven cryogenics are required.

Optimization of the trapping and chromatographic parameters has been performed using a TO-14 air standard. The results of these studies and a description of the integrated system will be presented.

An Integrated Approach to Parts-per-Trillion Measurement of Volatile Organic Compounds in Air

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The quest for ever lower detection limits continues, with part-per-trillion (pptv) measurements of volatile organic compounds becoming the latest "Holy Grail" in air quality measurements. In particular, the 0.1 pptv level is a recent defacto benchmark in analytical performance. A unique combination of factors must be considered in any measurement made at this level. These factors include canister cleaning and certification, advanced analytical technologies, and adequate quality assurance. Assuming a 0.1 pptv detection limit, the canister and sampling system must be cleaned to at least that level or below. The analytical system must have correctly derived detection limits, and the usual quality assurance requirements (calibration using accurate standards, precision and accuracy, etc.) must be met for this level while taking into account the usual limitations such as inherent imprecision associated with each step in the process. Each of these factors alone will not assure success; it is the combination that provides the requisite analytical accuracy and precision.

High quality ambient air sampling and analysis is the obvious recipient of such performance goals, especially in light of the current unit risk factors in use for risk assessment. This paper will examine some of the factors that must be considered in order to generate pptv data. Specific measurements of low level concentrations of volatile organic compounds will be presented using this method, including ambient and indoor air, and emissions from various consumer products such as textile floor coverings, computers, and miscellaneous other materials in an environmental chamber. An integrated experimental approach to the sampling and analysis of pptv concentration values will be presented.

**VOC Quality Control Measurements in the
CASTNet Air Toxics Monitoring Program (CATMP)**

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The determination of volatile organic compounds (VOCs) in ambient air with acceptable precision and accuracy at concentration levels as low as 0.1 ppbV is the primary analytical requirement of the Environmental Protection Agency's (EPA's) Clean Air Status and Trends Network (CASTNet) Air Toxics Monitoring Program (CATMP). The CATMP was established in 1993 by EPA to reactivate and operate the Urban Air Toxics Monitoring Program (UATMP). The purpose of the program is to establish baseline toxics concentrations, develop air emission inventories, and to identify air toxic sources using chemical mass balance modeling techniques.

Samples are collected from 15 urban sites in passivated stainless steel canisters every 12 days and analyzed with a gas chromatograph/mass spectrometer (GC/MS) operated in the electron impact full-scan mode. 53 target VOCs are determined. Analytical procedures and instrument operating parameters are described in detail. The paper focuses on the analytical quality control (QC) measurements which accompany every batch of samples analyzed. These include the analysis of instrument performance check standards, calibration standards, NIST reference samples, canister blanks, replicates, and internal standards/surrogates. Results of QC measurements performed during 1993 are presented, including precision and accuracy determinations. Data for selected VOCs determined in network samples are also presented.

**An Automated GC Technique for Enhanced Detection of Organic Compounds
Monitored Using Passive Organic Vapor Badges**

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The principle use of organic vapor badges is for monitoring of exposure to organic compounds in the workplace, where the concentrations of target species are typically in ppmv to sub-ppmv range. When this passive device is used for monitoring of organic compounds in ambient air, the analytical method used must have good sensitivity and precision to allow the small amount of compounds collected to be measured. A Hewlett Packard 5840A gas chromatograph with an autosampler was configured for two-dimensional gas chromatography with intermediate cryo-trapping to measure species like benzene, toluene, PERC and MEK. The autosampler gave high injection precision. The primary column was used for separating the large solvent peak from target compounds. Heart-cutting and cryo-focusing allowed target species to be analyzed with capillary column with good sensitivity. The technique was used in several monitoring programs and showed very good precision. Findings will be presented and discussed.

Background Monitoring Of Air Toxics At The Waste Isolation Pilot Plant

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ABSTRACT

The Waste Isolation Pilot Plant (WIPP), located southeast of Carlsbad, New Mexico, has been constructed as a permanent repository for containerized solid or solidified transuranic (TRU) mixed waste. The repository is constructed in a massive salt bed formation, 2,150 feet below the surface. The WIPP has been granted a No-Migration Variance by the U.S. Environmental Protection Agency (EPA) according to the requirements of 40 CFR 268.6.

As part of the variance, a detailed air monitoring program has been developed for the facility. The purpose of the program is to detect airborne releases of hazardous constituents at the earliest practicable time. Routine background monitoring for volatile organic compounds (VOCs) has been performed at WIPP for the last two years. The monitoring program routinely quantifies airborne concentrations of five VOCs in the ventilation airstream of the underground facility, using Compendium Method TO-14. This paper describes the monitoring program in-place at the facility and presents a summary of the monitoring results for the last two years.

INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) is a research and development facility designed to demonstrate the safe transport, handling, and disposal of transuranic (TRU) waste resulting from defense activities and research programs of the United States government. By definition, TRU waste contains radionuclides with an atomic number greater than 92 (uranium), such as plutonium, americium, and curium. Approximately 60 percent of the TRU waste is categorized as mixed waste, because it contains hazardous constituents regulated by the Resource Conservation and Recovery Act (RCRA). The waste will be placed 2,150 feet below ground in a deep, bedded salt formation (Figure 1) located approximately 26 miles southeast of Carlsbad, New Mexico.

The WIPP is defined as a land disposal facility under RCRA Section 3004(k). Land disposal includes the placement of hazardous waste in a salt-bed formation. The term placement encompasses both storage and disposal of waste in a land disposal unit. The land disposal of hazardous materials is restricted by the provisions of EPA regulation 40 Code of Federal Regulations (CFR) Part 268¹. However, in accordance with 40 CFR 268.6, land disposal facilities may, by virtue of site characteristics and/or the properties of the waste they will receive, be granted a variance from the land disposal restrictions. To be granted a variance, the owner/operator of the unit must successfully demonstrate "to a reasonable degree of certainty, that there will be no migration of hazardous constituents from the disposal unit . . . for as long as the wastes remain hazardous" [40 CFR 268.6(a)]. A no-migration determination (NMD) by the U.S. Environmental Protection Agency (EPA) allows untreated restricted wastes to be placed in a land disposal unit, pursuant to the conditions and limitations of the determination.

On November 14, 1990, the EPA issued a conditional NMD for the WIPP test phase (55 Federal Register [FR] 47700²), according to the requirements of 40 CFR 268.6. This NMD allows the DOE to place untreated restricted wastes for experimental uses in the facility and specifies conditions and limitations of the determination.

WIPP BIN-SCALE TEST

Until October 1993, the WIPP facility was to serve as an experimental pilot plant. Tests would be performed during this phase to collect, interpret, and refine data necessary for the performance assessment required by EPA for radioactive waste disposal. Data gathered during this phase would also be evaluated to determine if any additional measures are necessary to ensure that no migration of hazardous constituents will occur beyond the unit boundary.

The planned WIPP bin-scale tests involved testing of repackaged TRU waste in specially designed, transportable sealed bins after a series of detailed characterization and examination steps. A bin is a metal box with sampling ports and instrumentation. Each bin would accommodate the equivalent of four to six 55-gallon drums of TRU waste.

Bin-scale tests were scheduled to be performed underground during the test phase. The bin-scale tests were designed to provide information concerning gas production, gas composition, and gas depletion rates from actual TRU wastes. The waste would be representative of the general TRU waste inventory.

In October 1993, the DOE announced that the bin-scale tests would not be performed at the WIPP. Tests involving radioactivity will be performed at other laboratories. Physical and facility tests are now planned for WIPP while the waste experiments are completed. When the results of all testing have been obtained and after meeting all regulatory requirements, WIPP will move directly to the disposal phase.

VOLATILE ORGANIC COMPOUND MONITORING

As part of the WIPP No Migration Variance Petition, a detailed air monitoring program was developed for the test phase at the facility. This program is intended to fulfill the monitoring requirements of 40 CFR 268.6. Presently, there are five volatile organic compound (VOC) sampling stations installed at the WIPP facility. Four of these sampling stations are defined to be air monitoring stations and use commercially available portable VOC sampling equipment. The fifth station, VOC-10, was defined to be a source monitoring station and uses sampling equipment developed specifically for the facility.

The sampling and analysis program that was established in anticipation of the bin-scale experimental phase, includes provisions for measurements of direct VOC releases to air from the bin-scale experiments (the source monitoring station). Measurements of airborne VOC concentrations also were planned for the other four locations. These stations (Figure 2) are located at the top of the facility ventilation exhaust shaft (VOC-1), near the ventilation air intake shaft (VOC-2), in the Panel 1 air intake passageway (VOC-8), and in the Panel 1 air outlet passageway (VOC-9). VOC-10 sampling activities had stopped due to cancellation of the bin-scale tests. Currently biweekly sampling is being performed at VOC-1, VOC-2, and VOC-8.

Media other than air are not considered viable contaminant transport pathways and are not monitored under this program. In the NMD, EPA defined migration at WIPP to be releases of VOCs from the repository to the atmosphere at concentrations above health-based levels at the unit boundary. Annual average concentrations of individual VOCs above background are used for this determination.

Generator knowledge of the wastes and process by which they are generated, in addition to available analytical data, indicate that there are five VOCs most commonly present in the wastes. These compounds and their established health-based levels are:

Carbon tetrachloride (0.03 micrograms per cubic meter [$\mu\text{g}/\text{m}^3$])

Methylene chloride (0.3 $\mu\text{g}/\text{m}^3$)

- Trichlorethylene (TCE) [0.3 $\mu\text{g}/\text{m}^3$]
- 1,1,1-Trichloroethane (TCA) [10,000 $\mu\text{g}/\text{m}^3$]
- 1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113) [30,000 $\mu\text{g}/\text{m}^3$]

VOC sampling and analysis are performed at WIPP using guidance in the EPA Compendium Method TO-14, Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Summa® Passivated Canister Sampling and Gas Chromatographic Analysis³. Integrated 24-hour samples are collected in six-liter passivated stainless-steel canisters. The VOC samplers are operated by WIPP facility personnel, and sample analyses are performed by a contract laboratory.

The VOC monitoring program activities are documented annually in a report to the EPA. Sampling results for a 12 calendar month period ending August 31 are summarized in each annual report. The monitoring results for the sampler at the facility ventilation exhaust shaft over the previous two years are described below.

RESULTS

Figures 3 and 4 presents a frequency distribution of the results of the monitoring program for one of the air monitoring stations at the facility. This station (VOC-1) is located at the top of the repository ventilation exhaust shaft. The nominal air flow at this point is approximately 425,000 cubic feet per minute.

The data in Figures 3 and 4 reflect the day-to-day variability in concentrations at the facility due to ongoing activities and are not due to activities involving TRU mixed waste. The facility is not yet accepting waste. Figures 3 and 4 also includes the average and maximum concentrations of each VOC measured over the two-year period. Concentrations less than 0.2 parts per billion by volume [ppbv] have been estimated by the laboratory based on mass spectral data that indicated the presence of the compound, but where the results were less than the laboratory reporting limit. When a particular VOC was not detected in a sample, one-half of the laboratory reporting limit for the compound was reported for the sample. This substitution was made so that annual average concentrations could be calculated as required by the NMD. Because of this substitution, the calculated annual average concentrations may be overestimated. The laboratory performs method blank analyses as part of routine sample analysis. Over 100 method blanks were analyzed during the two-year period. All of the blank results were less than 0.2 ppbv for the five VOC target compounds.

The lowest value in the frequency distribution represents the sampler cleanliness certification limit (0.5 ppbv). Measured values above this lower limit demonstrate that elevated concentrations of three VOCs are present in the facility. These concentrations are attributed to use of various paints and solvents within the facility for ongoing operations. As shown in the table, TCA concentrations are highly variable. The highest TCA concentration measured over the two-year period was 670 ppbv. The highest concentration measured for the other VOCs was 15 ppbv for Freon 113.

The calculated average concentrations are at least four orders of magnitude lower than the standards established for the protection of workers. However, the average concentrations for three of the compounds (carbon tetrachloride, methylene chloride, and TCE) are greater than the health-based limits established by EPA in the NMD. These results show that background concentrations must be carefully considered in the calculation of annual concentrations for determination of no-migration for the facility. The past and ongoing monitoring at the facility to establish baseline variability in and magnitude of measured concentrations will be crucial for determining whether migration has occurred once waste is received at the facility.

QUALITY CONTROL AND QUALITY ASSURANCE

A number of quality control and quality assurance (QC/QA) activities are performed as part of the overall monitoring program. These activities include: sampler certifications, collection of duplicate samples, duplicate laboratory analyses, evaluation of field and laboratory accuracy, and

data validation audits. A brief discussion of these activities is included below.

Sampler Certifications

All VOC samplers are calibrated and certified after every three months of operation to ensure cleanliness and reliable sample recovery. Each air monitoring station has a spare sampling system, allowing one sampler to be recertified while the other is in operation. The sampler flow rate projected for routine monitoring is used for the entire certification process. The process entails two steps for each sampler. First, a sample of ultra high purity air is collected in a canister after passing through the entire sampling system (inlet and sampler) to evaluate sampler cleanliness. Second, a sample of humidified calibration gas is collected in a canister after passing through the sampling system to evaluate target compound recovery.

The zero air certification for air samplers requires that the samplers contribute 0.5 ppbv or less of each target compound detected in the zero air sample. The comparable limit for the source monitor is 5.0 ppbv. The calibration gas recovery for any individual target compound must be between 75 and 120 percent, with the additional stipulation that the average recovery for all target compounds must be between 90 and 110 percent. (Note: WIPP sampler cleaning and certification activities are described in a paper entitled, "Certification of VOC Canister Samplers for Use at the Waste Isolation Pilot Plant", also presented in this symposium).

Program Precision

Field precision is evaluated from laboratory analysis of duplicate samples collected with the sampling systems. Relative percent difference (RPD) is calculated for each set of duplicate samples. The calculated RPDs ranged from -23 to 36 percent over the two-year period, and 88 percent of the calculated values were within +/- 15 percent.

The contract laboratory reports laboratory precision based on duplicate analyses of individual samples. Calculated RPDs ranged from -24 to 33 percent with 95 percent of the values between +/- 15 percent.

Program Accuracy

A procedure has been developed to evaluate method relative accuracy for the sampling systems. Sampling systems are challenged with an audit gas in the field. Both a matrix spike and a concurrent matrix duplicate sample are collected. The matrix duplicate samples are obtained so that the accuracy evaluations can be adjusted for background concentrations present in the facility. Accuracy evaluations performed over the two-year period have demonstrated an overall range of -13 to 34 percent for the method.

The contract laboratory tracks internal accuracy weekly for five compounds: 1,1-dichloroethene, benzene, TCA, toluene, and chlorobenzene. Over the two year period, 98 percent of the accuracy values have been within 90 to 110 percent.

Program Completeness

Completeness for the field effort was determined based on the sampling at the ventilation exhaust shaft. This station had the only scheduled routine sampling over the entire period. For the two-year period 100 percent of the scheduled samples were collected and the field data validated. Data validation is also routinely performed on the analytical data packages.

CONCLUSION

Concentrations of VOCs measured at the WIPP facility ventilation airstream demonstrate are highly variable for three of the five VOC target compounds. The measured concentrations at the facility are attributed to ongoing facility operational activities and not to any activities involving DU mixed waste.

The data obtained to date represent a reasonable database of concentrations that can be used

for the design of a disposal phase monitoring program.

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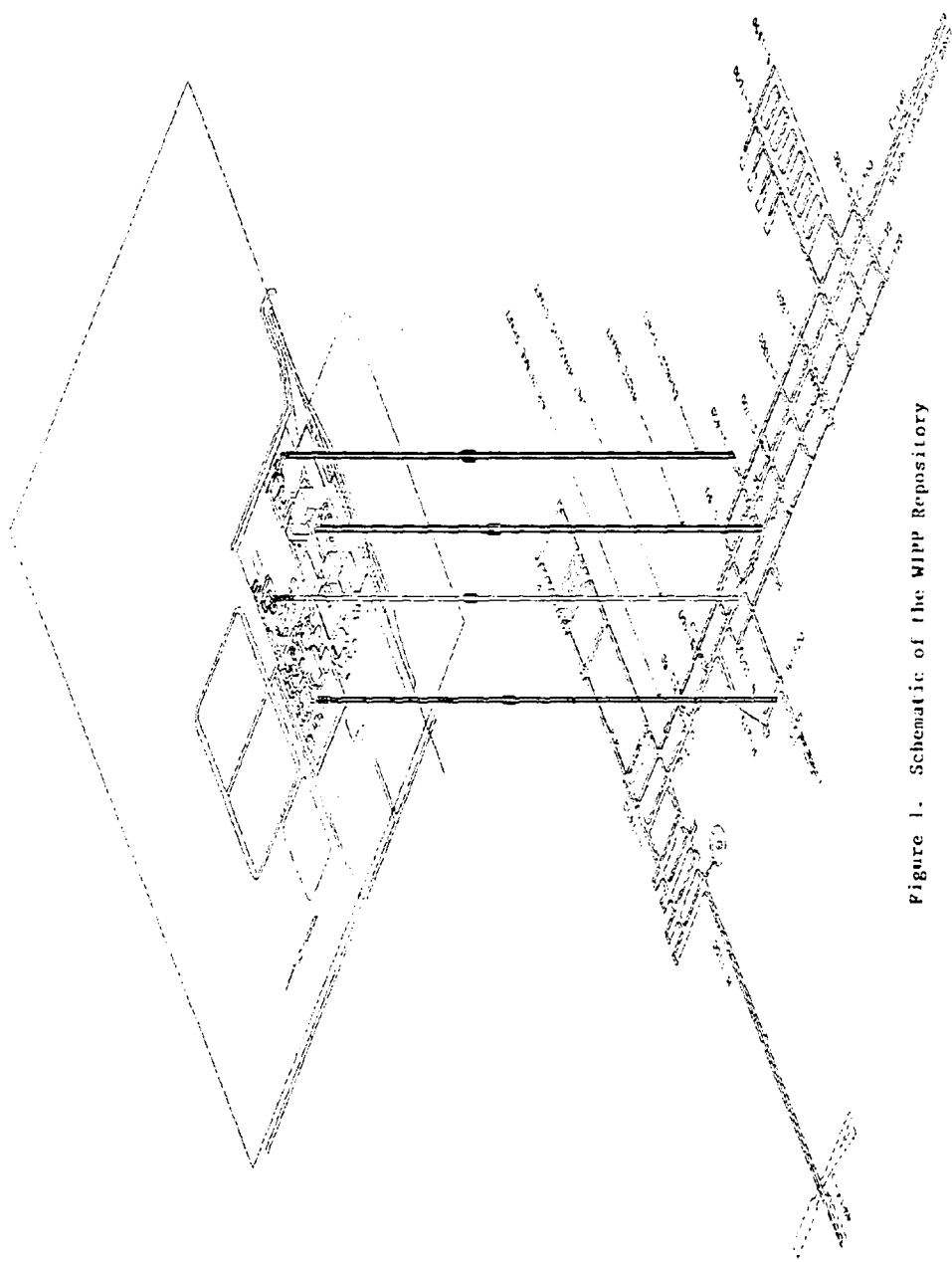


Figure 1. Schematic of the WIPP Repository

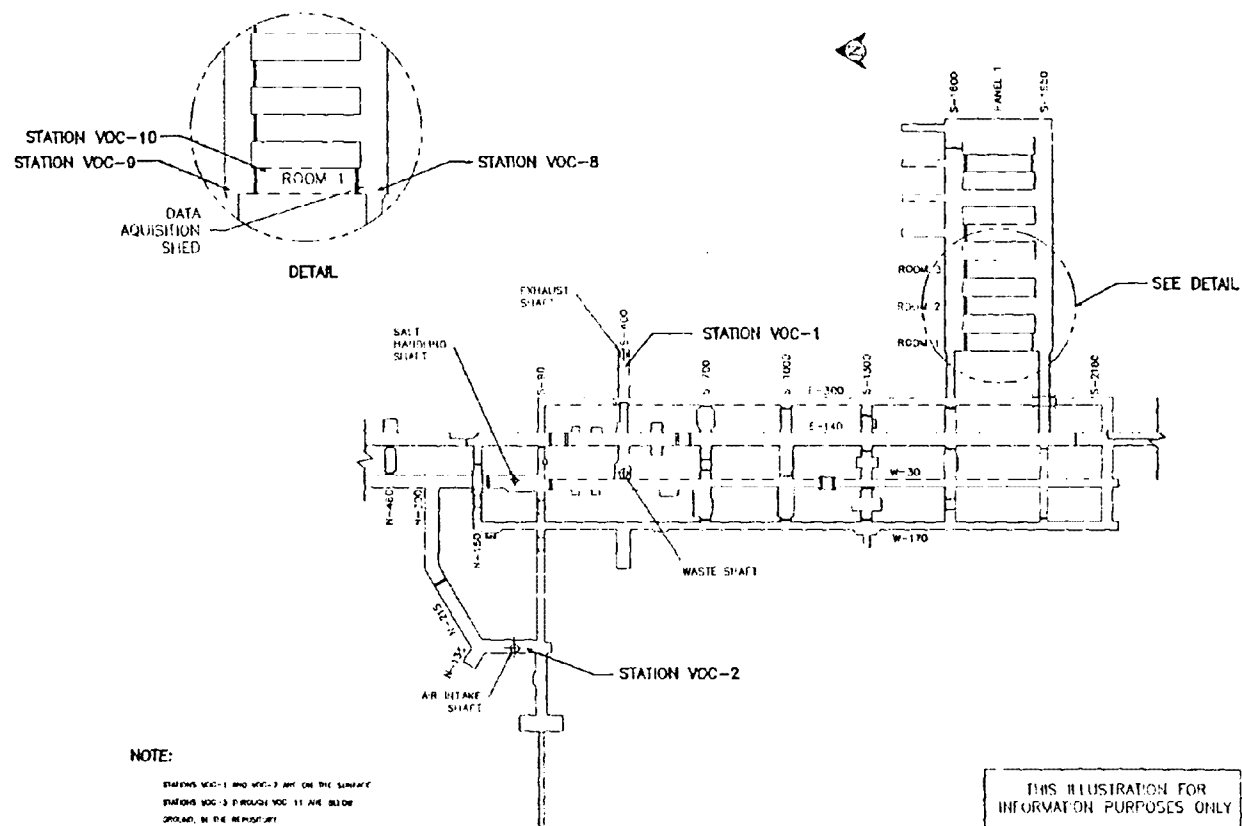


Figure 2. VOC Monitoring Station Locations

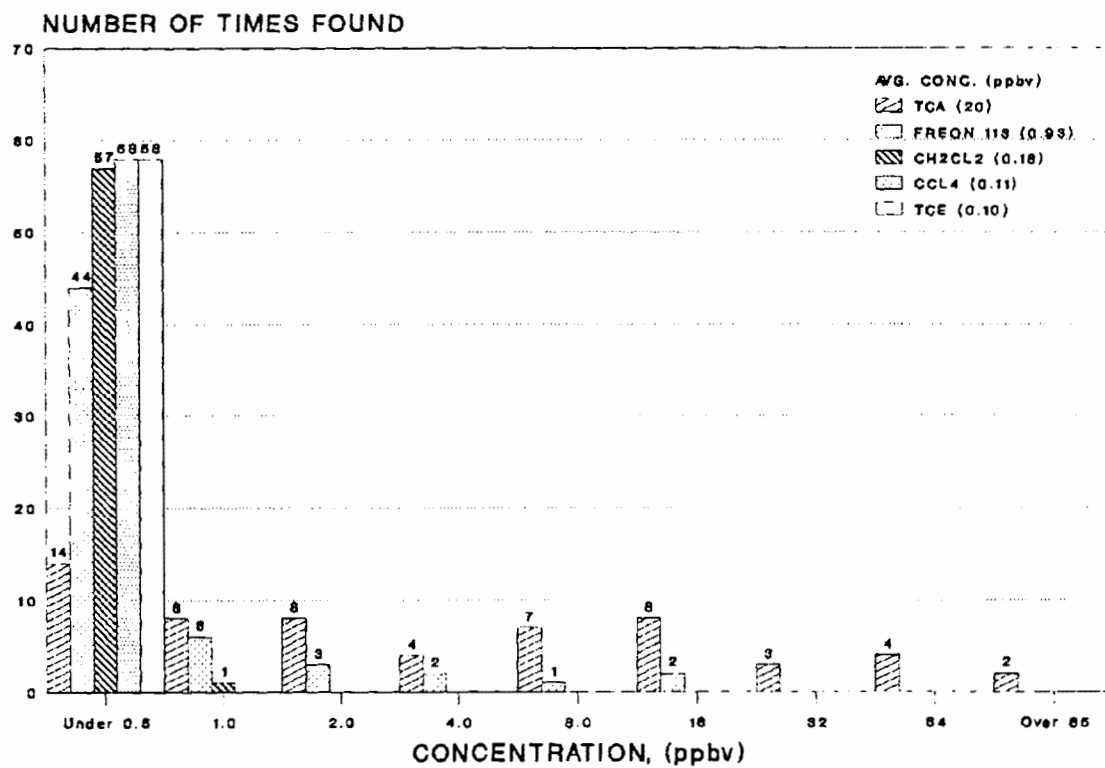


Figure 3. VOC Monitoring Data Summary
Frequency Distribution 1991-1992 Data

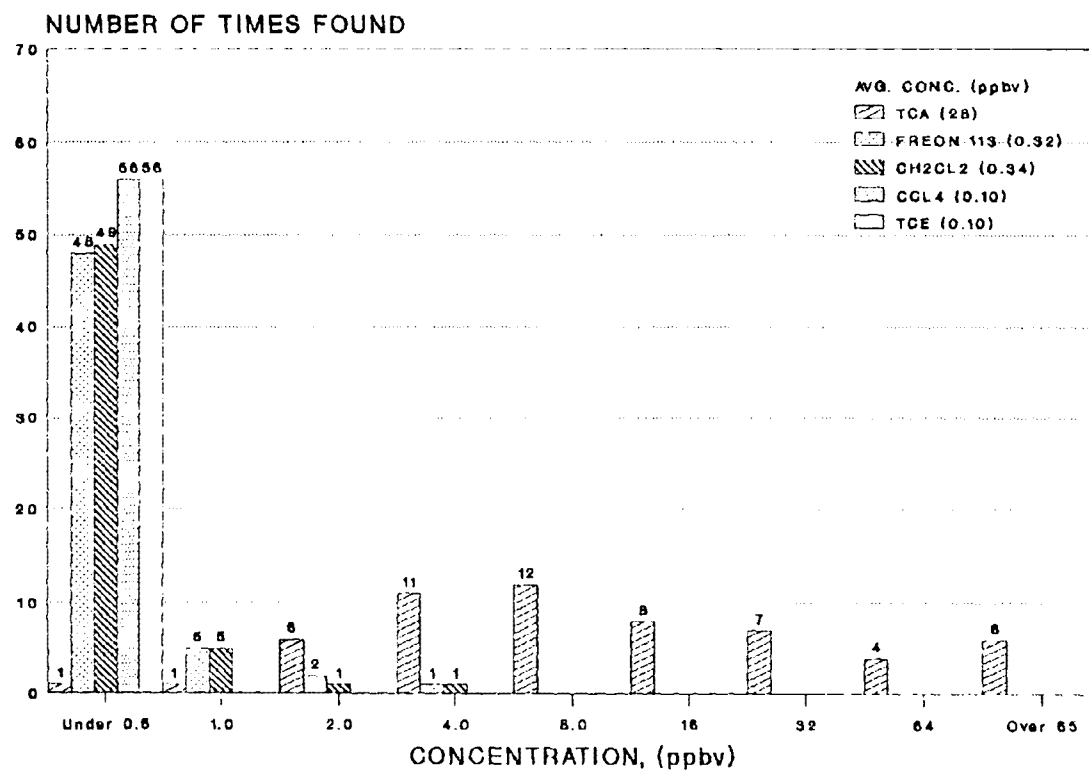


Figure 4. VOC Monitoring Data Summary
Frequency Distribution 1992-1993 Data

Experience in Establishing Portsmouth Photochemical Assessment Monitoring Station

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Abstract

The 1990 Clean Air Act Amendments (CAAA) stipulate that tropospheric ozone non-attainment areas with "serious" or higher classification must implement a network of Photochemical Assessment Monitoring Stations (PAMS) to quantify and speciate volatile organic compounds (VOCs) considered to be one of the prime precursors of tropospheric or ground-level ozone. Data that will be gathered will include ozone, nitrogen oxides, VOCs, carbonyls, and meteorological parameters. This paper describes the approach used by the NH Department of Environmental Services (DES) to implement this monitoring program.

1 - Background

Ozone is the primary component of smog which is produced during hot summer weather by the chemical reaction in the atmosphere of precursor pollutants from many sources. These pollutants include nitrogen oxides (NO_x) and volatile organic compounds (hydrocarbons) such as gasoline, chemical solvents, products of combustion and some consumer products. These pollutants emanate from many sources, including smokestacks, automobiles, industrial process vents, painting and metal parts cleaning operations. Ultraviolet solar radiation promotes reactions in the atmosphere between the various pollutants resulting in free radicals of oxygen which lead to the formation of tropospheric ozone.

It is not uncommon for these pollutants to be transported great distances by the wind. Tropospheric ozone levels may be significantly higher many miles downwind of the sources of the pollutants as a result of this transport. Based on the 1990 CAAA, the United States Environmental Protection Agency (EPA) and the states have identified ozone non-attainment areas. These areas are categorized into one of five classes based on ambient monitoring data. These non attainment classes and the corresponding ppb of ozone are: marginal (121-137), moderate (138-159), serious (160-179), severe (180-189), and extreme (190-280).

Those areas of the U.S. which are classified as being in the "serious" or higher category of ozone non-attainment must come into attainment of the National Ambient Air Quality Standards (NAAQS) for ozone by the year 1999. These areas must also implement a PAMS program for certain volatile organic compounds which are suspected of contributing to the elevated levels of tropospheric ozone. EPA's immediate task is to collect a large volume of air monitoring data. The data will be used to evaluate, and if need be, redefine acceptable levels of those compounds determined to be precursors of tropospheric ozone.

Tropospheric ozone has deleterious effects on human and animal health and damages sensitive plant species. EPA's primary goal in implementing the PAMS program is to achieve the primary health standards for ozone in a cost-effective manner. Strategies have

been developed to reduce ground-level ozone. These strategies include the use of reformulated gasoline, the use of vapor recovery systems at gasoline stations, motor vehicle inspection and maintenance (I/M) programs and additional controls on industrial processes and power plants. Continuous monitoring of ozone precursors is necessary to assess the impact of these strategies.

This paper discusses the progress that has been made by the State of New Hampshire in implementing the monitoring requirements of the CAAA. Specifically, we will review our experience with the continuous gas chromatograph (GC) being used to monitor VOCs on an hourly basis at the air monitoring station downwind of Portsmouth, NH in Kittery, ME.

2 - Siting Consideration

The federal regulations for PAMS (CFR, 1993) require that as many as four different site types be established around the metropolitan statistical area/ consolidated metropolitan statistical area (MSA/CMSA) that has been classified as "serious", "severe", or "extreme" for ozone non-attainment. The number of site types required is based on the population of the MSA/CMSA. The Portsmouth-Dover-Rochester MSA/CMSA has been classified as "serious" for ozone non-attainment. Based on population, NH must install two enhanced ozone monitoring stations in the Portsmouth area, one upwind of the central business district (CBD) and one downwind of the CBD. The first site type which must be installed is designated as "Type 2". This Type 2 site is expected to be the point at which the highest levels of volatile organic compounds being emitted to the atmosphere from the CBD of the primary site in the MSA/CMSA will be monitored.

Portsmouth has been designated as the primary city in the MSA/CMSA and the monitoring network is being designed around it. The site of maximum ozone precursor impact for the city of Portsmouth has been determined to occur at a point in Kittery, Maine, about two miles northeast of the central business district of Portsmouth.

It is expected that the site will "see" VOCs and NO_x from motor vehicle traffic in the CBD and on I-95, industrial and commercial sources, and the emissions from two fossil fueled power plants located upwind.

3 - Equipment Housing

The NH Type 2 PAMS is intended to be an on-line, in-the-field laboratory to continually monitor VOC ozone precursors, ozone, nitrogen oxides, carbonyls and numerous meteorological parameters. The equipment will be housed in an 8' x 16' field office trailer which will be temperature controlled (68°-86°F) and have counter space designed specifically for this monitoring application. Meteorological instrumentation will be located atop a ten meter aluminum tower located behind the trailer. Data management will be handled by an on-site PC with telemetry capabilities through a high speed modem to computers located at University of New Hampshire in Durham, and at the Air Resources Division in Concord.

Ambient samples will be directed into the trailer by a borosilicate glass manifold equipped with an induced draft fan to move air through the manifold. Exhaust gases from the ambient monitors will be ducted to the outside via the discharge side of the manifold.

The trailer will have two 12,500 Btu/h air conditioners and baseboard heaters for temperature maintenance. All temperature functions are thermostatically controlled.

The total cost to construct and install the trailer at the Kittery site, including the GC system, the meteorology tower, and the site preparation is estimated to be \$171,000.

4 - Planned Ambient Air Sampling

EPA has an extensive list of needs which the PAMS site and data have to fulfill (EPA, 1991). Data on the distribution and concentration of VOC precursors of ozone and of total nonmethane organic compounds (TNMOC) are required. The minimum acceptable sampling frequency for VOCs at a "Type 2" PAMS site are:

Pollutant	Sampling Frequency	What to report
VOC	Eight 3-hour samples every day during the ozone season, June, July and August.	55 VOC precursors of ozone and TNMOC
	One 24-hour sample every sixth day year-round. This is done by collecting the sample in a canister.	
Carbonyl	Samples of 3-hour duration are to be taken 8 times per day during the same months (June, July and August).	Aldehyde precursors

N.H. will attempt to achieve 75% data capture in the 24-hr period, 75% data capture in a month, and 75% data capture in a quarter. This means that within each 24 hr period a maximum of 6 hours may be used to do calibration, validation, or blank runs. The sampling at the N.H. Type 2 PAMS site in Kittery, ME will start in June 1994.

5 - Gas Chromatograph Hardware

The VOC precursors of ozone will be measured continually by a GC equipped with two flame ionization detectors. While the trailer is being installed and the site prepared, UNH is working under a contract with the N.H. Air Resources Division to install and test the hardware and software of the VOC portion of the PAMS. The installed equipment include:

- Perkin Elmer (PE) GC 8000 with Taxan Supervision 787, 14" color monitor. The PE-GC is equipped with two columns, BP1 (50 m long x 0.22 mm i.d., with 1 micrometer film) to detect C₆ to C₁₂ components, and a Porous Layer Open Tubular (PLOT) fused silica capillary column (50 m long x 0.45 mm o.d., 0.32 mm i.d) to detect C₂ to C₅.
- Perkin Elmer automatic thermal desorber (ATD) 400 with air flow controller (Tylan RO-32), and pumps (Charles Husten pumps CAPIX 1.2C)
- Air compressor (GAST ROA-P106T-AA)
- Balston TOC air generator (78-30 TOC), equipped with a gas receiver (Balston 72-007 TOC) and a Perkin Elmer unit, PE-Express (PE N930-1178).
- Hydrogen generator (Packard 9200). The output H₂ pressure is maintained at 36 psi.
- Perkin Elmer GC-to-computer interface (PE Nelson, analog-to digital, 900 Series Interface) equipped with a memory buffer for data acquisition and temporary storage.
- Helium gas (99.9999% purity) tank with Matheson 3014C-580 gas regulator. Helium is the carrier gas. Its flow is adjusted to be 2.4 ml/min. through the PLOT column.
- Digital DEC PC 433 dSLP computer with 14400 bps MNP zoom fax modem.

The air sample enters the system through a stainless steel line from the glass manifold. It first enters the ATD 400 at the rate of 15 ml/min and is collected on a cold trap which is cooled to -30°C by a Peltier cooler. At the end of the sample collection period (40 minutes), the trap is heated and the sample is transferred to the GC via a heated transfer line. The sample first passes through the BP1 column to detect the C₆ and heavier compounds. The sample is then split, and passed through the PLOT column to detect the C₂ to C₅ component.

The 1/8" stainless steel sample line from the glass manifold to the ATD 400 is approximately one meter in length. A stainless steel 2 micron sintered filter has been placed in the sample path to prevent particulate material from entering and contaminating the system.

The ATD 400 and GC operate simultaneously. The ATD 400 collects sample air for 40 minutes out of every hour and then transfers the collected sample to the GC for analysis. The GC analyzes the sample while the ATD 400 recycles and begins collection of a sample for the next hour. The cycle is repeated continuously, resulting in 24 hourly samples per day.

The trap which is used in the ATD 400 is dual-bed glass and is packed with 64 mg of Carboxive SIII and 40 mg of Carbotrap C. The trap is cooled to -30°C using an electronic (Peltier) cooler rather than a liquid cryogen, i.e., liquid nitrogen. The concentrated sample is transferred from the ATD 400 to the GC through a heated fused silica transfer line.

6 - GC Software

The software used for automated GC analysis of ambient air in real time is the PE Nelson Turbochrom 4.0 package. It has the following capabilities:

- Control supported chromatographs through serial communications.
- Acquire analog or digital chromatography data from chromatographs.
- Analyze the raw data and report results.
- Automatic acquisition and analysis of data from large batches of samples.
- Store the raw data and the calculated results.
- Create methods that define acquisition and analysis parameters.
- Optimize analysis parameters through graphics, then use the improved parameters to reprocess raw data.
- Use graphics application to compare chromatograms.
- Communicate with other software applications.

7 - Calibration Standard and Blank

The Perkin Elmer GC 8000 can be configured to automatically draw a calibration standard, or a blank gas, through a separate port. We set the sequence in Turbochrom to do 2 hrs ambient air sampling, followed by 1 hr of sampling of either a blank or a standard. We are using a Mantech retention time standard, and ultra pure nitrogen gas, 99.9999% for blank. Chromatograms were produced by the output function of the Turbochrom software.

8 - Our Observations to Date

1 - Gas Consumption

We are monitoring the use of Helium gas to determine its consumption, and to time the replacement of the cylinder. Over a period of two months of continuous running, the Helium pressure dropped from 2500 psi to 2250 psi.

2 - Balston TOC Gas Generator

The TOC gas generator manual indicates that: 40 minutes are needed to warm up, and 12 hours are needed to regenerate itself at first start-up. When the unit was shut off, it took us altogether about 3 hours to be in operation.

3 - Hydrogen Generator

Deionized water is needed. Our preliminary experience is that about half of the deionized water is consumed in a period of one month.

4 - Instruments Manuals

The manuals supplied with the GC have a wealth of information. We found them to be reasonable, but some sections need more details. For example: "Seal On", "Bus Error" error messages appeared on the ATD board. These were not found in the manual.

5 - Data Telemetry

We are using PCanywhere. We had a limited success in accessing remote PCs and moving files back and forth. We encountered difficulties with Gateway computer running DOS 5.0.

6 - Analysis

We ran analysis of ambient air in the lab. We obtained several peaks. Copies of the chromatograms of the BP1 and PLOT columns are shown in Figure 1. We have also found no excess carryover from one analysis to the next.

9 - Plans for the Near Future

These include:

- GC calibration for retention time and for speciation
- Continual data acquisition
- Data integration and analysis
- Data telemetry
- Establishing what to be included in a written log

10 - Conclusions

N.H. is making considerable progress towards enhanced monitoring, as specified in the CAAA of 1990. The plans for a "Type 2" PAMS site are underway. While the Kittery site is being prepared, the GC system has been assembled at UNH and is being tested for ozone VOC precursors. Further testing, calibration, data integration and analysis still remain.

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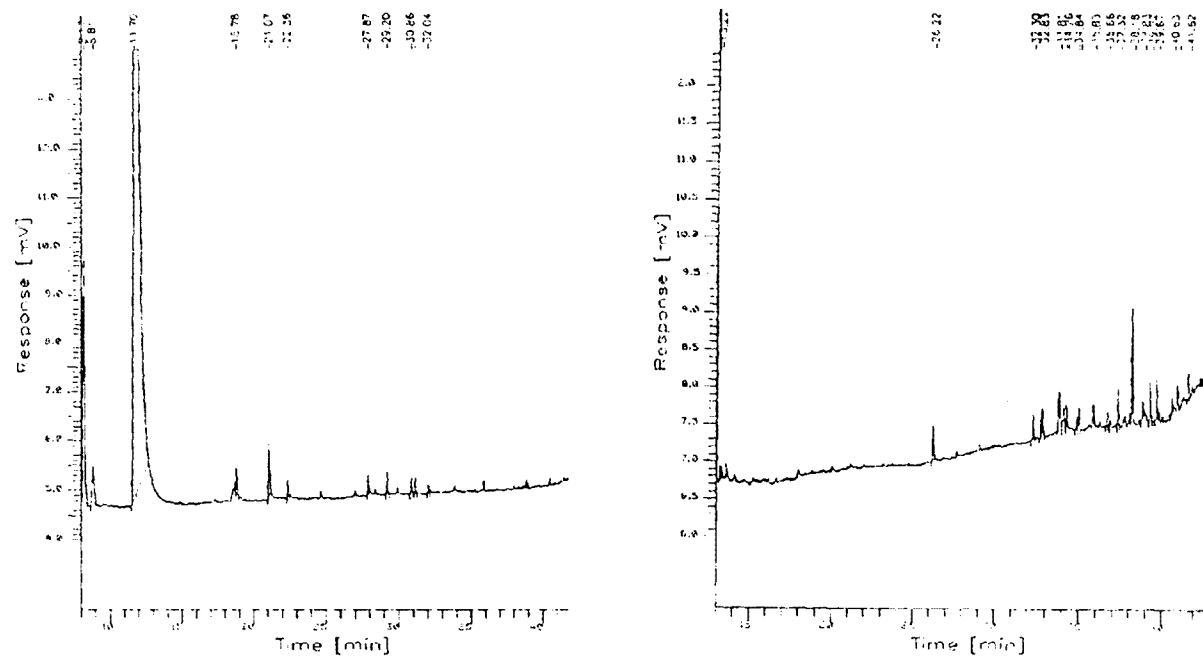


Figure 1: Chromatograms of ambient air. Left: the PLOT column (C₂-C₅). Right: the BP1 column (C₆-C₁₂)

Comparison Studies of Ozone Precursors in Phoenix, Arizona

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This paper will present the comparison of the ozone precursors monitoring program for Phoenix, Arizona during 1992 and 1993. Specific details and methodologies will be presented involving collection of air samples and analysis of speciated measurements for reactive VOC and carbonyl precursors responsible for ozone formation. Quality control and quality assurance techniques will also be discussed.

Implementation of a Risk-Based Air Monitoring Program Using Integrated and Continuous Air Monitors

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ABSTRACT

A risk-based air monitoring program was conducted during excavation activities at a Superfund site. The objectives of the air monitoring program were to (1) ensure that the air emissions would not adversely impact the health and safety of workers and the surrounding community; (2) allow excavation activities to proceed without cumbersome engineering controls that might be required by regulatory agencies in the absence of such an air monitoring program; (3) evaluate the reliability of continuous VOC and particulate air monitoring equipment in ensuring compliance with risk-based ambient air criteria; and (4) provide a basis for revising air monitoring instrumentation and procedures, as necessary.

Personal air samples were collected within the Exclusion Zone using integrated and continuous air monitors. Ambient air monitoring was conducted at seven stations using nine integrated air samplers and three continuous air monitors. Three mobile stations were positioned at the perimeter of the work area, and four permanent stations were installed along the site boundary. Integrated air samples collected each day were evaluated on the basis of the site activities, results from the concurrent continuous air monitoring, and the previously developed risk-based action levels.

This paper presents the methodologies and procedures used in an EPA-approved risk-based air monitoring program and the subsequent air monitoring results. Development of the risk-based action levels and the correlation between the integrated and continuous air sampling results are discussed. The risk-based air monitoring program was found to provide protection to the workers and nearby residents, and allow for the remediation to be performed in a more cost-effective and efficient manner.

INTRODUCTION

As part of a Superfund site remediation program, excavation was proposed at several locations where elevated levels of both metals and volatiles had been detected. Although the site is in a relatively remote area, concerns were expressed by both the state and federal regulatory agencies regarding the potential adverse health effects associated with emissions during these excavation activities.

An air monitoring program was established at the site to ensure that emissions during the limited excavation activities would not pose an unacceptable risk to the off-site community or to on-site workers. This program consisted of the following main elements:

- The development of risk-based criterion concentrations in off-site air for individual chemicals of concern;
- Atmospheric dispersion modeling to determine on-site concentrations in air corresponding to the off-site criterion concentrations; and
- The development of on-site risk-based action levels for a continuous, real-time monitoring program to ensure that off-site criterion concentrations would not be exceeded.

The off-site criterion concentrations were developed for specific chemicals of concern. Based on these criterion concentrations and a site-specific air dispersion analysis, action levels to be enforced at the work area were developed. Continuous air monitoring was then performed near the work area to ensure compliance with these on-site action levels. Available continuous air monitoring equipment was not capable of monitoring specific chemicals of

concern at the site, so action levels were developed for surrogate parameters that could be measured on a real-time basis. By continuously monitoring for the surrogate parameters, and periodically measuring for the specific compounds of concern, it was possible to proceed with excavation activities without major disruption, and without posing unacceptable risks to the off-site community.

DETERMINATION OF RISK-BASED ACTION LEVELS

Chemicals of Concern and Surrogate Parameters

Based on data from previous waste sampling, the primary chemicals of concern were identified as arsenic, aniline, and various volatile organic compounds (VOCs), including xylenes and benzene. Sampling results indicated that the waste contained arsenic at a maximum of 16% (160,000 ppm), with a weighted average of approximately 10%; aniline was detected at a maximum concentration of approximately 11%. Based on a consideration of concentration, toxicity and physical/chemical properties, arsenic was determined to be the primary chemical of concern for potential particulate emissions, while xylenes and benzene were determined to be the primary concern in vapor emissions.

It was determined that real-time, continuous monitoring of the individual chemicals of concern was not feasible. Surrogate parameters more amenable to continuous monitoring than the individual chemicals themselves were therefore identified. Respirable particulate matter (PM₁₀) was selected as the surrogate parameter for arsenic. Total VOCs was selected as the surrogate parameter for xylenes and benzene. These surrogates were chosen because the arsenic would tend to be adsorbed to particulates, while xylenes and benzene would be emitted almost exclusively as vapors. Aniline could be emitted either in the vapor or particulate phase.

Risk Characterization and Development of Criterion Concentrations

Toxicity Evaluation. EPA-verified toxicity benchmarks, including Reference Doses (RfDs) for noncarcinogens and Cancer Slope Factors (CSFs) for potential carcinogens, were identified from EPA's Integrated Risk Information Service (IRIS) data base or from EPA's *Health Effects Assessment Summary Tables*¹. Inhalation-specific toxicity benchmarks were used when available; otherwise, oral benchmarks were applied.

Exposure Assessment. Populations at risk of exposure to chemicals emitted during excavation activities were identified, and reasonable hypothetical scenarios regarding the nature of their exposures were developed. Direct inhalation of chemicals emitted during excavation activities was identified as the primary route of exposure. Specific exposure assumptions were derived based primarily on standard EPA references.

Development of Criterion Concentrations. The term "criterion concentration" was defined in this study as the chemical concentration in air at the maximum exposure location that results in a target risk level established for the excavation activities. Criterion concentrations were developed using risk assessment methodologies outlined by EPA. For noncarcinogens, criterion concentrations correspond to the maximum chemical concentration in off-site air to which an individual may be exposed on a repeated basis without experiencing adverse health effects. For potential carcinogens, criterion concentrations in off-site air were derived based on a cancer risk level of 1×10^{-6} , i.e., that the maximally exposed hypothetical individual would have an incremental risk of less than one chance in a million of developing cancer as a result of the exposure. If concentrations based on both carcinogenic and noncarcinogenic effects can be estimated, the criterion concentration allowable at the receptor location is the more conservative of the two concentrations.

Criterion concentrations were first developed for each of the chemicals of primary concern (xylenes, benzene, and arsenic). Criterion concentrations for surrogate parameters (total VOCs and PM₁₀) were then calculated based on the assumed composition of the PM₁₀ and VOCs.

Criterion PM₁₀ concentrations were calculated as 10 times the criterion concentration for arsenic because respirable particulates associated with excavated waste are assumed to contain 10% arsenic. Criterion VOC concentrations were derived from the criterion concentration calculated for xylenes and benzene assuming these chemicals would be present in a 6:1 ratio. On-site, risk-based action levels were derived from criterion concentrations at the receptor by applying the appropriate correlation factor from the air dispersion modeling, as described below.

Air Dispersion Modeling

Three sources of potential emissions were identified: the buried waste area; the buried drum area; and the waste storage building. Dispersion modeling of emissions associated with excavation and storage was undertaken using the Industrial Source Complex (ISC) model² for estimating off-site air concentrations. The area source option of the ISC model was employed to simulate the effects of emissions from the waste area excavation and buried drum area excavation. The volume source option was used to simulate the effects of fugitive emissions from the proposed waste storage building. The selection of the area and volume source models is consistent with EPA's recommendations on source configuration categorization for Superfund sources³.

Modeling Parameters. Five-year (1985-1989) continuous hourly surface meteorological data recorded at a nearby international airport were processed in conjunction with concurrent upper air data⁴ to provide consecutive hourly meteorological data for the ISCST modeling. The rural mode option was chosen in the dispersion modeling because within a 3-km radius around the source area, less than 20 percent of the land can be described as light-moderate industrial, compact residential, or commercial using the meteorological land use typing scheme proposed by Auer⁵. Major model input parameters are shown in Table 1, and Figure 1 shows the locations of all individual receptor locations around the site. In addition, a 961-receptor grid was selected to cover the impact area.

Calculation of Chemical Concentrations in the Environment

Waste Area Excavation. The waste area excavation was designed to be conducted sequentially. At any given time, only a fraction of the waste area would be disturbed. Therefore, a time scaling factor, T_j/T , was used to scale the emission rate resulting from disturbance of the j^{th} fraction of the vault waste, where T_j is the time required to excavate subarea j and T is the total time required for excavating the entire waste area. It was estimated that the excavation would take place sequentially at three subareas. During each excavation, only half of the subarea would be disturbed and exposed to the atmosphere, while the other half would remain undisturbed and covered.

- **Annual Average Concentrations in Air.** For emissions produced during excavation, emissions from source j would persist only for a period of time T_j during the whole excavation time, T . Therefore, the chemical concentration averaged over T would be T_j/T of the air concentration during excavation. In the current assessment it is assumed that $T_j = 1/6 T$.

- **Time-Varying Emission Rates.** Emissions resulting from the waste area excavation were expected to occur primarily during the day. It was conservatively assumed that excavation would occur seven days per week between 8:00 a.m. and 6:00 p.m. for a period of six months. The exposed waste surface would be completely covered at the end of each work day. Therefore, emissions would occur only during the day and there would be no significant emissions between 6:00 p.m. and 8:00 a.m. each day.

Buried Drum Area Excavation. Excavation at the buried drum area was expected to be completed in one month. It was assumed that the whole area would be remediated at the same time. Therefore, there was no time scaling factor for the source emission rates in the dispersion modeling. However, the time-varying emission rates were applied because the excavation was

assumed to be conducted 10 hours per day, the same as the work schedule for the waste area excavation.

Waste Storage. It was assumed that the waste storage piles will continuously emit chemical vapors. Therefore, no time scaling factors or time-varying emission rates were applied in the air dispersion modeling.

Estimate of Off-site Concentrations

Off-site Air Concentrations. The ISCST modeling results showed the maximum one-hour average concentration for the nearest resident, $854 \text{ } (\mu\text{g}/\text{m}^3)/(\text{g}/\text{s}\cdot\text{m}^2)$, occurred at a northern receptor. The results also indicated that the annual average concentration is approximately 400-fold less than the maximum one-hour average concentration at that location.

The maximum annual average concentration at the nearest receptor resulting from fugitive emissions from the storage building was found to be $27 \text{ } \mu\text{g}/\text{m}^3/(\text{g}/\text{sec})$. For waste storage buildings, emissions are expected to be confined within the building and discharged to the atmosphere by the building ventilation system or through doors, windows, and leaks. Therefore, the work area perimeter air monitoring should be conducted within the building, which can be best characterized by the concentration at the ventilation outlet. Based on a building ventilation rate of 10,000 acfm, the average concentration at the ventilation outlet would be $0.212 \text{ g}/\text{m}^3/(\text{g}/\text{sec})$.

Correlation Matrices for Dispersion Factors. The dispersion factors estimated from ISCST air modeling were used to establish correlation factors for exposure concentrations of various durations at locations of off-site exposed individuals (MEI) and at work area air monitors, which were located between the sources and the receptors. Based on the correlations between long-term (annual) MEI concentrations and short-term (1-, 2-, 3-, and 8-hr) work area concentrations, a set of on-site "action-level concentrations" of various durations at the work area were established from "criterion concentrations" at the off-site MEI to ensure that activities under normal operations would not result in unacceptable risks to off-site residents. The "action-level concentration" is the chemical concentration in air at the work area perimeter that would result in a criterion concentration at the MEI locations based on the air dispersion modeling.

FIELD MEASUREMENTS, INSTRUMENTATION AND LABORATORY ANALYTICAL METHODS

Meteorology Monitoring

Meteorological monitoring was conducted at a MetStation (Climatronic EWS System) located at the southwest corner of the site, approximately 30 feet inside the fenceline. Meteorological data (wind speed, wind direction, and temperature) have been recorded continuously on a strip chart recorder since the MetStation was installed. A commercially available hygrometer, G. Lufft Model 5804, was added later to record the ambient humidity. Humidity monitoring was designed to provide information that could be used to quantify the impact of condensing humidity on the continuous PM_{10} air monitors for particulates less than $10 \text{ } \mu\text{m}$ (PM_{10}).

Personal Air Sampling

Personal air sampling for arsenic and aniline was conducted twice weekly during waste excavation activities. Samples were collected in the breathing zone of the most exposed individuals for the duration of their activities in the work area.

Sampling was performed using constant flow sample pumps (SKC 224-43XR) equipped with sorbent sample tubes for aniline (silica gel) or mixed cellulose-ester filter cassettes for arsenic. A flow rate of approximately 2,000 ml/min was used for arsenic sampling; a flow rate of approximately 100 ml/min was used for aniline sampling. A primary standard (Gilian

Instruments Bubble Generator) was used with a collection device in-line to measure the flow rates before and after sampling.

Samples were analyzed by an American Industrial Hygiene Association-accredited laboratory. In general, analysis for total arsenic was performed using NIOSH Method 7901 (modified). Analysis for aniline was performed using NIOSH Method 2002.

Work Area Air Monitoring

Work area air monitoring was performed at three mobile stations. A fixed station was positioned in-line between the specific work area and the most sensitive off-site receptor. The most sensitive off-site receptor was determined based on site-specific air dispersion modeling and a health-based risk evaluation, as discussed in the previous sections. A downwind station was located approximately 50 feet directly downwind of the excavation area. The exact location of the downwind station was determined each day by the site manager and the air monitoring operator based on the prevailing wind direction that day. During calm conditions (when the wind speed was less than 1 m/sec, or 2 mph), the wind direction was determined based on the prevailing wind direction of previous hours and the previous day. An upwind station was located approximately 50 feet upwind of the excavation area. Unlike the downwind station, the location of the upwind station was flexible, the only requirement being that it be located away from and upwind of the excavation area. These stations remained within the Exclusion Zone throughout the excavation activities.

Continuous Air Monitoring. Each of the work area stations was equipped with a Thermo Environmental Instruments Inc. Organic Vapor Monitor (OVM) Model 580B, an MIE Real-time Acrosol Monitor (RAM-1), a PDL-10 Data Logger for use with the RAM-1, a strip chart recorder, also for use with the RAM-1, and a heating coil unit for use with the RAM-1 when the relative humidity was above 70%. Both the OVM and the PDL-10 Data Logger were programmed to average continuous readings over one-hour time intervals.

The OVMs were calibrated at the beginning of each day with 250 ppm span gas, and were checked with the same span gas at the end of the day to determine if the initial calibration was accurate and if any drift had occurred during the sampling period. Each RAM-1 was calibrated at the beginning of each day with a manufacturer-supplied reference scatter. If the relative humidity was high (approximately $\geq 70\%$), a heating coil unit was used in each station to reduce the condensing humidity that might interfere with the RAM-1 readings.

While excavation was underway, the hourly information recorded by the OVMs and Data Loggers was relayed from the Exclusion Zone to the air monitoring field personnel in the Support Zone by the Site Health and Safety Officer (SHSO). Thus, air monitoring and health and safety personnel were always aware of the continuous instrument readings.

Integrated Air Monitoring. Integrated samples for PM_{10} and VOCs were collected at the fixed and downwind stations, with duplicate samples in the downwind station. Constant-flow sample pumps were used in conjunction with cascade impactors in the air monitoring program. Ambient air was drawn through the cascade impactor at a flow rate of 2,200 ml/min for approximately 8 hours. The flow rate was calibrated each day prior to sampling and maintained at $2,200 \pm 5\%$ ml/min throughout the day. A total volume of approximately 1.0 m³ of air was passed through the substrates and backup filters, resulting in a detection limit of 0.01 mg/m³.

The VOC sampling required one Tenax tube, conditioned by the laboratory, and one SKC pump, calibrated to a low-flow rate of approximately 25 ml/min. Calibrations were performed at the beginning and end of each sampling period using a Gilibrator.

When integrated samples were being collected at the work area stations, the SHSO would check every hour that the SKC pumps were functioning normally and relay the readings on the rotometers of the high-flow pumps to the field air monitoring operator.

Perimeter Air Monitoring

Perimeter air monitoring consisted of integrated sampling at four stations at the site fenceline (Figure 1). As with the sampling in the work area, integrated samples were collected for PM₁₀ and VOCs.

Perimeter air monitoring was performed every day when there were soil/waste disturbance activities at the site. Five 8-hour air samples (four regular samples and one duplicate sample) were collected each day. At the end of each day, the air monitoring operator and the SHSO determined if laboratory analysis of these samples was necessary. Laboratory analysis was required if the work area air concentrations on that particular day exceeded the action levels; otherwise, the samples were discarded.

Storage Area Air Monitoring

Continuous monitoring of the air quality in the waste storage area was performed periodically with an OVM to determine if any volatiles were escaping from the overpacked drums. Whenever any readings above 2 ppm were observed, Sensidyne detector tubes for aniline and amines and/or integrated volatile samples were taken to determine if these contaminants were present in the building.

QUALITY ASSURANCE/QUALITY CONTROL

Quality control was enforced via the standard operating procedures for sample custody. Sample custody procedures were followed through sample collection, transfer, analysis, and ultimate disposal. The overall data quality for the air monitoring samples was determined to be very good. Any data requiring qualification are flagged in the data summary tables. However, field blanks for ambient volatile organic analyses (EPA Method TO1) showed a significant level of contamination, as discussed below.

Sample Precision and Accuracy

The largest relative percent difference (RPD) between two detected duplicate PM₁₀ samples was found to be 139 percent. The smallest difference was 67 percent. The largest difference between a detected sample and a nondetect was 0.09 mg/m³. The duplicate differences were within the range anticipated for co-located ambient samples. Small sample weights were associated with larger differences but were still within acceptable limits, given the small magnitude of the measurements.

With only one exception, all arsenic samples and duplicates were nondetect. The RPD for the one pair for which a comparison was possible was 50 percent. The RPDs for volatile sample duplicates ranged between 0 and 189 percent. Large differences were frequently associated with low concentrations and suspected laboratory contaminants.

Completeness

Under normal sampling and analysis conditions, it is expected that only 80 to 85% completeness may be realistically achieved. By use of backup measurement systems and sampling efforts, at least 99% completeness was achieved.

Field Blanks

The field blanks associated with the TO1 analyses for VOCs showed a significant level of contamination. The contamination probably occurred either between conditioning and shipping or during packing and shipping. Benzene, toluene and xylenes, as well as other compounds detected during the analyses, are associated with a hydrocarbon fraction, possibly diesel fuel, while styrene may have been introduced during shipping. It was determined that use of tyrofoam peanuts in the shipping of the Tenax tubes was not acceptable and the practice was immediately stopped to prevent potential sample contamination during shipping.

RESULTS AND DISCUSSION

Health and Safety Air Monitoring

Volatile organics and PM_{10} readings on real-time monitors in the work area did not exceed the action levels in place for workers in Level B PPE (the initial level of PPE) at any time during waste excavation. Results from four of the five integrated arsenic samples were less than the limit of detection; 8-hour time-weighted average (TWA) concentrations were less than approximately 5% of the OSHA-PEL for inorganic arsenic of 0.01 mg/m^3 . These results are consistent with results from the integrated samples collected at the work area stations during the same time period; all the work area results were below the detection limit for arsenic. One personal air sample indicated levels equal to the OSHA-PEL for inorganic arsenic. Results from integrated samples collected from the fixed and upwind work area stations on the same day were below the limit of detection for arsenic, while arsenic was detected in the integrated sample from the downwind work area station at about 0.0005 mg/m^3 , approximately 25 times less than the TWA concentration at the excavation.

Aniline results for all samples were less than the limit of detection. Eight-hour TWA concentrations were less than approximately 3% of the OSHA-PEL of 2 ppm (7.8 mg/m^3).

Work Area Air Monitoring

PM_{10} Air Monitoring. Continuous hourly PM_{10} concentrations at the work area and the relative humidity at the site were recorded. The RAM-1 readings were sometimes affected by the ambient humidity, as discussed below. Integrated air monitoring was conducted on the first day of intrusion into a new portion of the waste area and on other days when significant disturbance of the material was expected. Table 2 shows the PM_{10} and arsenic concentrations detected in the air samples. The PM_{10} concentrations continued to be low due to well controlled excavation activities. The arsenic concentrations were less than the detection limit, except for two samples.

VOC Air Monitoring. Continuous VOC air monitoring took place at the same three work area stations. Integrated VOC air monitoring was performed concurrent with the PM_{10} air monitoring. Chemical concentrations were consistently found to be below levels of potential concern.

Perimeter Air Monitoring

PM_{10} Air Monitoring. Integrated air samples were collected at the four perimeter stations during the excavation. The samples were analyzed if the work area continuous monitoring indicated exceedance of action levels, or if any unusual conditions occurred. Based on the results of work area air monitoring, none of the perimeter samples required laboratory analysis. However, one round of samples was analyzed because humidity interference with the RAM-1 readings was severe at the beginning of that day. Nevertheless, the concentration levels observed from all perimeter stations were extremely low and consistent with the regional background concentrations, indicating that the disturbances caused by the excavation activities generated relatively insignificant amounts of dust.

VOC Air Monitoring. VOC samples were collected concurrent with the collection of PM_{10} samples. One round of samples was analyzed for volatiles and semi-volatiles for possible humidity interference with the OVM. Only toluene, benzene, and tetrachloroethene were detected, and only at levels not believed to pose a significant health risk.

Storage Area Air Monitoring

Continuous VOC Air Monitoring. Continuous monitoring for volatiles in the storage area was conducted during the excavation. Readings on one particular workday were relatively high, likely due to excessive vehicular traffic in the building, and offgassing from the recently painted

cement floor. The readings were highest when many vehicles were driving in and out of the building. Instantaneous readings decreased to almost 0 ppm when the instrument was raised up to the breathing zone, away from the floor paint.

An OVM left in the storage area overnight gave an average reading of 2.3 ppm for one night. The next night, one OVM was placed in the same location, and an additional OVM was placed in the opposite corner of the building. Though these two averaged less than the 2.3 ppm measured on the previous night, the drum area was checked with Sensidyne detector tubes for aniline and amines on the next day; both tubes showed nondetect.

Integrated VOC Air Monitoring. Integrated VOC samples were taken whenever continuous readings in the storage area indicated the possibility of volatile contaminants escaping from the overpacked drums. VOCs were found to be comprised primarily of xylenes, ethylbenzene, and 4-methyl-2-pentanone.

The Impact of Relative Humidity on the RAM-1 Readings

Figure 2 presents all hourly upwind RAM-1 readings in terms of relative humidities. The PM_{10} concentrations observed at the upwind station were comparable to the regional (0.028 mg/m^3) and local (0.016 mg/m^3 from the pre-remediation air monitoring results) background air concentrations, since the upwind air concentrations remained unaffected by the downwind excavation/soil disturbance activities. The background concentrations are represented by four horizontal lines in Figure 2. It is apparent from the figure that the RAM-1 readings were comparable to the background air concentrations when the relative humidity was less than 65%. As shown, the RAM-1 readings appeared to be high (in the range of 0.09 to 0.20 mg/m^3) at high humidities (i.e., above 65%). It has been observed during humid days with the heating coil operating that the PM_{10} concentration detected by RAM-1 dropped from 0.35 mg/m^3 to 0.12 mg/m^3 . Although the heating coil was always turned on when the relative humidity exceeded 70%, this modification to increase the inlet temperature does not completely eliminate the humidity interference. A well controlled laboratory environment in which humidity, temperature, PM_{10} concentration, and particle size distribution can be carefully monitored would be required to fully understand and quantify the effect of humidity on the RAM-1 readings.

Based on the observations from pre-remedial design activities and current air monitoring, the RAM-1 functions normally at humidities less than 70%. At humidities above 70%, the RAM-1 tends to overestimate PM_{10} concentrations in air, but the humidity interference can be reduced to approximately 0.1 mg/m^3 by increasing the inlet temperature. To further offset the humidity interference, the background concentration or humidity interference (under high humidity condition) detected from the upwind RAM-1 air monitor was subtracted from the downwind reading. The differences between air concentrations reported from the upwind and downwind stations thus represents the ambient air concentration resulting from disturbances of the work area. The difference in downwind and upwind RAM-1 readings were found to be consistent with the results reported from the integrated air monitoring.

Comparison of Results from Integrated and Continuous Monitors

Table 2 summarizes ambient PM_{10} air concentrations obtained from the integrated and continuous air monitors during excavation activities. The eight-hour average PM_{10} air concentrations were very low because of light excavation activities, high soil moisture content, and the conglomerative nature of the vault waste.

All samples except one were below the National Ambient Air Quality Standards for PM_{10} of $150 \text{ } \mu\text{g/m}^3$ (for 24-hr average) and $50 \text{ } \mu\text{g/m}^3$ (for annual average). This sample taken at the downwind station detected an air concentration of $87 \text{ } \mu\text{g/m}^3$ while the duplicate sample, taken at the same station, detected an air concentration of less than $8 \text{ } \mu\text{g/m}^3$. The difference may have been caused by the turbulence-induced concentration fluctuation in the lower layer of the

atmospheric boundary layer, the spontaneous release of a dust puff that bypassed only one sampler, or laboratory instrumental/operating error in the gravimetric analysis of low concentrations. It is not unusual to occasionally observe variation of this magnitude in determining weights of PM_{10} using gravimetric methods. The concurrent perimeter air monitoring provided additional air sampling data from different downwind locations. However, the perimeter air monitoring results for the same day show that the ambient PM_{10} concentrations were all less than the detection limit of $10 \mu\text{g}/\text{m}^3$, and the arsenic concentrations were not greater than $0.3 \mu\text{g}/\text{m}^3$, indicating that the off-site residents could not be exposed to the same arsenic concentration level as the on-site workers (arsenic concentrations of more than $0.3 \mu\text{g}/\text{m}^3$) during that day and would not experience any adverse health impacts, based on the health-based risk assessment.

Results recorded by the continuous air monitors are consistent with those obtained from the integrated air monitors except on the days when humidity interference with RAM-1 appeared in all stations. For those days when integrated samples were collected in the work area and when the relative humidity was less than 70%, the continuous air monitors, in general, were able to measure PM_{10} concentrations consistent with those measured by the integrated air monitors to $\pm 0.050 \text{ mg}/\text{m}^3$. For those days with high relative humidity, all RAM-1s gave false high readings, in the range of 0.1 to $0.2 \text{ mg}/\text{m}^3$, regardless of the air monitor locations.

Activity-Specific Action Levels

Arsenic Content in the Airborne Particulates during Waste Excavation. The average arsenic concentration detected during waste excavation was less than $0.0028 \text{ mg}/\text{m}^3$. The concentration measured at the excavation was rapidly diluted or dispersed in the atmosphere. By the time the contaminants reached the work area air monitors, the average arsenic concentration in the air was reduced to less than $0.0003 \text{ mg}/\text{m}^3$. In addition, at the perimeter air monitors, no detectable arsenic concentrations were found. The rapid dispersion or depletion of arsenic contaminants is evident from the air monitoring results obtained on the "worst" day of excavation. The arsenic concentration observed that day was $0.014 \text{ mg}/\text{m}^3$ at the excavation, $0.0005 \text{ mg}/\text{m}^3$ at the work area, and less than the detection limit ($< 0.0003 \text{ mg}/\text{m}^3$) at all perimeter air monitors.

The average arsenic content in the airborne particulates was found to be less than the initially assumed values at the work area and the site perimeter. It is expected, then, that the arsenic content would be greatly reduced at the off-site residences.

Based on the above discussions, the initial arsenic content used in the development of site-specific action levels appears may be overly conservative.

Chemical Content of the VOCs during Waste Excavation. The preliminary VOC action levels were derived assuming that total VOCs are composed of xylene and benzene in a 6:1 ratio. Based on the concurrent OVM monitoring, the percentage of these chemicals in VOCs can be quantified as 0.5% benzene and 1.2% xylene.

ACKNOWLEDGMENTS

The authors wish to express their appreciation for the assistance received from Kirsten Findell, Caroline Czank, Brian Perkins, Arthur Bozza, Tom Fizzano, Mary Enard, and Jim Roy during the course of this study. The views expressed in this paper are those of the authors and not necessarily those of ENVIRON Corporation.

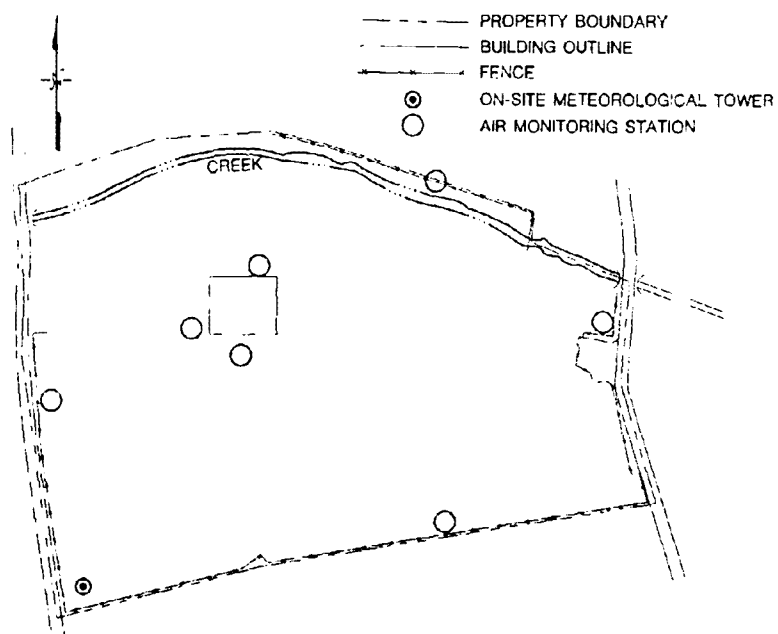
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TABLE 1 ISC Model Input Parameters			
Parameter	Waste Area Excavation	Buried Drum Area Excavation	Storage Building
Source Type	Area	Area	Volume
Emission Rate (g/s-m ² for area source, g/s for volume source)	1.0	1.0	1.0
Source Area (m ²)	937.5	231	--
Ambient Air Temperature (K)	293	293	293
Flagpole Receptor Height (m)	0	0	0
Terrain Elevation (m)	Yes	Yes	Yes
Urban/Rural Option	Rural	Rural	Rural
Building Downwash	No	No	Implicit
Initial Lateral Dispersion (m)	-- ⁽¹⁾	--	10.6
Initial Vertical Dispersion (m)	-- ⁽¹⁾	--	4.2
Note:			
⁽¹⁾ Automatically determined by the ISC model.			

TABLE 2 Summary of Daily Work Area PM ₁₀ Air Monitoring Results										
Date	Average RAM-1 Reading (mg/m ³)			Integrated Air Sample (mg/m ³)						
	Upwind Station	Fixed Station	Downwind Station	PM ₁₀			Arsenic			Humidity (%)
				Upwind Station	Fixed Station	Downwind Station	Upwind Station	Fixed Station	Downwind Station	
1-6-93	0.090	0.054	0.060*		0.009	0.020 0.020		<0.0009	<0.0009 <0.0009	**
1-11-93	0.011	0.043	0.104		0.020	0.050 0.009		<0.0003	<0.0003 <0.0003	**
1-27-93	0.053	0.053	0.035		<0.01	0.01 <0.01		<0.0003	<0.0003 <0.0003	63%
1-28-93	0.041	0.041	0.047		<0.01	0.05 0.01		<0.0003	<0.0003 <0.0003	43%
2-3-93	0.019	0.019	0.023		<0.009	<0.01 0.020		<0.0003	<0.0003 <0.0003	35%
2-8-93	0.095	0.072	0.076	<0.008	<0.008	<0.008 0.087	<0.0002	<0.0002	0.0003 0.0005	61%
Average	0.052	0.047	0.058	<0.008	<0.011	0.025	<0.0002	<0.0004	<0.0004	
Notes:										
* Value estimated from strip chart.										
** Hygrometer not available.										



NOTE: ALL AIR MONITORS ARE LOCATED APPROXIMATELY 6 FEET ABOVE THE GROUND SURFACE

FIGURE 1: SITE SKETCH

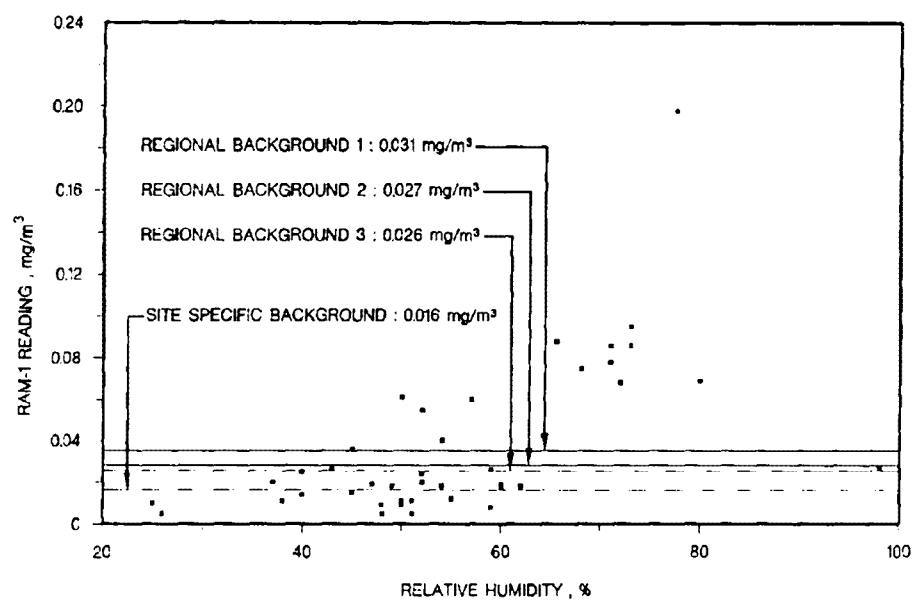


FIGURE 2 : RAM-1 READING VERSUS RELATIVE HUMIDITY

A Two Channel, 16-Position Canister Field Sampler for Improved Performance and Quality Assurance

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Current automated field samplers used to sequentially collect whole air into multiple SUMMA canisters contain many deficiencies that add suspicion to data quality. Mechanical mass flow controllers used have been shown to have temperature dependent flow rates resulting in different flow rates during day and night operation. With the absence of dynamic, on-line pressure measuring devices, canisters that have leaked since being evacuated in the laboratory would be analyzed with data reported without question. In addition, the lack of data showing whether sample flow into the canister dropped off before the end of the sampling period due to leak prepressurization of the canister or inconsistent sampling flow rates can result in a sample that may or may not be representative of the local VOC concentration during the entire requested sampling time.

A new programmable field sampler is presented that records sampling information for later retrieval by a Windows based PC. Collected data can include flow rate into each canister during the entire sampling event, beginning and ending pressures in the canisters, feedback verification that the correct canister was being filled at the correct date and time, and even the optional flow rate of surrogate into the canisters during sampling. Flow rates are controlled using electronic mass flow controllers that are unaffected by changing temperatures and pressures, with the added luxury of being able to record actual rather than theoretical flow rates. The canister sampler can be set up for collecting samples literally once a minute to once every week, depending on the mass flow controllers installed and the size of the canisters used. Samplers can be chained together so that the next sampler will commence as soon as the previous sampler has completed all 16 positions. Monitoring and control of the sampler can be achieved via modem link to improve implementation efficiency. Data collected during field sampling operations will be presented as well as a new procedure for unattended dilution sampling of high concentration samples (stack gas, landfill gas, etc.) which keeps target analytes well below saturation points for improved stability and recovery from canisters without heating.

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SESSION 17:

AIR POLLUTANTS IN GENERAL

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Temporal Variation of Fine Particle Mass at Two Sites in Mexico City

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Simultaneous sampling of fine mass ($PM_{2.5}$, using an integrated 24 hour gravimetric method) and the particle scattering extinction coefficient (b_{sp} , using a heated integrating nephelometer) were used to estimate continuous fine particle concentration at two sites in Mexico City. Linear regression analysis of the 24 h averages of b_{sp} and the $PM_{2.5}$ integrated samples was done on a seasonal basis. The coefficients of determination (R^2) between these methods ranged from 0.84 to 0.90 for the different sampling periods.

These data are the first attempt to describe the diurnal variation of fine mass in Mexico City. Distinct and different diurnal patterns were observed for both sites. For the site located near an industrialized area, a sharp peak occurred between 0700 and 0900 hours and a second smaller but broader peak occurred late at night. This site is characterized by the presence of primary pollutants, with PM_{10} annual mean concentrations exceeding $150 \mu g \cdot m^{-3}$.

The second site is located in a residential area down wind of the industrialized area, and is characterized by the presence of secondary pollutants with much lower PM_{10} concentrations (annual mean of under $50 \mu g \cdot m^{-3}$). The diurnal fine mass pattern at this site had a broad peak between 0900 and 1200 hours. On individual days, fine mass was sometimes highly correlated with ozone.

Ability of Fixed Monitoring Stations to Represent Commuter's Exposure to CO Revisited: The Case of Mexico City.

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ABSTRACT

In-vehicle concentrations of carbon monoxide (CO) were compared to concurrent measurements taken at fixed site monitoring stations (FSM) to assess if the FSM stations can be used to estimate commuters' exposure to this pollutant. CO concentrations inside private and public transport vehicles were consistently higher than those measured at FSM stations and indeed much higher than those reported in previous commuter studies for US cities. Simple regression models with considerable predictive power were developed to estimate in-vehicle CO concentrations using ambient CO concentrations, wind speed and travel speed data for different vehicle types.

INTRODUCTION

Taking CO measurements inside vehicles on a continuous basis is expensive and time-consuming. What has to be developed then, is a functional relationship between the ambient CO concentrations and the exposure experienced in the commuting microenvironments.

The objective of this paper is to evaluate if the FSM stations can be used to estimate commuters' exposure to CO. Commuter/fixed-site CO concentration ratios and differences will be calculated and compared with results from previous commuter studies. Finally, a number of regression models will be fitted for selected transport modes to assess the possibilities of predicting commuter exposures to CO using the data collected at the fixed-site stations.

METHODS

CO concentrations were measured inside public transport vehicles and private cars while travelling as a passenger along five standardized commuting routes during the morning and evening rush hours (6:30 to 9:30 and 17:30 to 20:30). Measurements were taken on weekdays between mid-January and mid-March of 1991, using six GE COFD-1 personal exposure monitors (PEMs) lent by the US EPA. The field work design, as well as the results of comparisons between transport modes, travel times, travel shifts and commuting routes were described in a previous paper[1].

Mexico City has an automatic network for atmospheric monitoring (RAMA). In 1991, the RAMA had 25 stations, of which 15 had CO monitors (NDIR technique). The five fixed-site stations located nearest to the commuting routes -- within 2 km at the nearest point -- were selected to compare their data with the in-vehicle measurements. These stations are: *Insurgente Taxqueña*, *Merced*, *Lagunilla* and *Plateros*. On the basis of their specific siting[2], *Insurgente Taxqueña* are roadside stations, located within 25 m from busy roads and therefore they are likely to receive strong influence from vehicular emissions of CO. Although *Merced* station is also a roadside station, the road in which is located does not have as much traffic volume and congestion as in the case of the other two stations. *Lagunilla* station is in a busy area, but is in quiet back-street. The nearest heavy traffic road is about 100 m away towards the south. Finally *Plateros* is located in a residential area, about 20 m away from a street with very light traffic. A thorough analysis of the selected stations has been given somewhere else[3].

RESULTS

Ambient CO

As shown in Table 1, ambient CO concentrations during the study period were very high. The five selected stations reported exceedences to the Mexican and US 8-h standards for CO (13 ppm and 9 ppm respectively). It should be noted that, during the same period, the 9 ppm standard was exceeded on at least 5 days at 14 of the 15 stations that measure CO in the City.

Figure 1 shows the hourly pattern of CO concentrations measured during the study period at the selected stations. From 7:00 to 9:00 CO concentrations reach a peak around 12 ppm. Concentrations then fall to values between 6-7 ppm approximately and remain relatively stable around this level from 12:00 to 19:00. From 20:00 ambient CO concentrations build up again, reaching another peak from 21:00 to 23:00. However, this second peak is much smaller than the morning one, reaching values of 8.0 ppm. The lowest CO concentrations of the day were registered between 3:00 and 5:00, but even at this time, mean ambient CO concentrations were still as high as 5 ppm. This characteristic hourly cycle of CO concentrations may be partially explained by changes in the wind speed during the day. The secondary y axis of Figure 1 shows the hourly average wind speed during the same period. This graph suggests that the peak of ambient CO concentrations is reached when two factors coincide: the lowest wind speed and the heaviest traffic of the day.

CO hourly averages from the five stations were extracted and processed to identify the records for each commuting monitoring day. These data were used to calculate a morning (06:00 to 9:00 inclusive) and evening (17:00 to 20:00 inclusive) average of one-hour values for each station. The averaging periods were selected to correspond with the measurement of in-vehicle CO concentrations. The average ambient CO concentrations during commuters' rush hours (combining morning and evening) by station were: *Lagunilla* 7.1 ppm; *Plateros* 9.1 ppm; *Merced* 9.6 ppm; *Insurgentes* 9.9; and *Taxqueña* 11.0 ppm. On the average, the morning values were 54% higher than the evening ones. The morning/evening ratios for each station were as follows: *Insurgentes* 1.2, both *Lagunilla* and *Merced* 1.6, *Plateros* 1.8, and *Taxqueña* 1.5.

In-vehicle CO

Significant differences in CO concentrations were found between different transport modes. The highest CO concentrations were found inside autos and *taxis colectivos* (both 9-seater "combi" van and 22-seater minibus), while metro trains, trolleys and buses had lower concentrations. In general, CO concentrations during the morning rush hour were higher than during the evening. Table 2 shows a summary of CO concentrations by transport mode. A complete analysis of results is provided in a previous paper[1].

In-vehicle/Ambient CO Ratios and Differences

The daily shift-average CO concentration (by route and transport mode) was calculated from the commuter trips and then matched to the concurrent ambient concentrations (using the average of the five selected stations). Since the in-vehicle concentrations for all transport modes were always larger than the concurrent ambient concentrations, the differences between them are always positive and the ratios are always greater than one.

Table 3 shows the differences and ratios between commuter and ambient concentrations by transport mode. On the average, commuters' exposure at rush hour was increased above ambient CO levels by 42 ppm in autos; 41 ppm in combi; 36 ppm in minibus; 21 ppm in bus; 17 ppm in trolley and 11 ppm in the metro. The magnitude of these values is much larger than the corresponding values for other cities studied before. For instance, Holland reported that commuting by automobile increased ambient exposures by an average of 3 ppm in Phoenix, 5 ppm in Denver, and 10 ppm in Los Angeles[4]. In Washington D.C., commuters increased their exposures above ambient CO levels by 7-12 ppm in automobile, 2-6 ppm in buses and 0-3 ppm

in rail vehicles[5]. It must be noticed that the Washington study included interstate, highway and arterial routes, while the one for Mexico City was conducted mainly on arterial routes.

On the average, the in vehicle/ambient ratios by transport mode were found to be as follows: auto, 5.2; combi, 5.2; minibus, 4.3; bus, 3.1; trolley 3.0; and metro, 2.2. When findings from other commuter studies are reviewed, one finds that some of the reported commuter/fixed site ratios for automobile are also very high. In Los Angeles, the ratio was found to be 3.9[6], in Boston 2.2 (calculated from ref. [7]), 3.9 in Raleigh[8] and 5.0 in Washington D.C. (calculated from ref. [5]). However, care must be exercised when comparing these data since the commuting routes and the reference fixed-site stations selected in every study may have completely different characteristics.

Regression models

The in-vehicle CO concentration data were matched with the ambient CO data from each of the five selected stations. This was to detect the station with the highest correlation with the in-vehicle CO concentrations for each transport mode. For simplicity, only the station with the strongest association with commuters' exposures was used for model building: Plateros station for the metro and bus models, and Insurgentes station for the auto and minibus models. A forward stepwise regression method was used (SYSTAT package) to develop models for prediction of commuters' exposures to CO. Data were arranged in a matrix, matching the in-vehicle concentration (time weighted average for every available trip) with the following potential predictors:

- FSM = Concurrent ambient CO concentration (in ppm).
- WSP = Concurrent wind speed measured at the centre of the city (in m s^{-1}).
- TMP = Concurrent temperature measured at the centre of the city (in Celsius degrees).
- SPD = Average speed for the trip measured in km h^{-1} .
- RUT = Variable indicating the number of the commuting route (1-5).

Table 4 summarizes the resulting regression models. The ambient CO concentration variable was always entered first into the regression model. Once this variable was in the model, the decisions on which predictor should next enter the model were based on the following standard criteria[9]: the variable with the largest partial correlation coefficient entered the model first, and then, an additional term was included only if: a) the F-statistic for the increment in R^2 was significant (p-value $< .05$); and b) the regression (beta) coefficients for all variables in the model were significantly different from zero (t-statistic $< .05$). Additionally, care was taken to prevent the development of models with serious multicollinearity among the predictors.

The resulting models offer a good combination of the available variables for prediction of the commuters' exposures under the circumstances described in this research (during the winter period, for the specific routes and at the rush hours). All the models have a fairly good predictive power, explaining between 49% and 71% of the variability in the exposure experienced by commuters.

DISCUSSION

As pointed by Cortese and Spengler in their seminal work[7], "the difference between person exposure and fixed location readings is, in part, caused by the fact that commuters are much closer to major sources of CO than are the fixed location monitors". In the MAMC, the effect of transport mode on the relative magnitude of differences and ratios between commuter and ambient measurements, confirms that commuters' exposures depend strongly on the mode of travel[1].

The fact that different monitoring stations and different variables proved to be more useful predictors for a particular travel mode raises two questions. Firstly, what station or stations

should be used for comparison and prediction of commuters' exposure to CO; and secondly, why do some transport modes seem to be more sensitive to variables such as wind speed or travel speed than others.

When using ambient data in exposure assessment studies, several monitoring stations should be evaluated to find out the most suitable station or group of stations for the specific purposes of the research, e.g. the estimation of CO exposures in a particular microenvironment (indoors residential, indoors office, outdoors near the roads, commuting, etc). In the Mexico City's study, a background station located in a road with light vehicular traffic (*Plateros* station) proved to be more appropriate to estimate exposure of metro and bus commuters, while a roadside station surrounded by streets with heavy traffic (*Insurgentes* station) was the most useful to estimate exposure of auto and minibas commuters.

In the future, the models presented here should be validated to determine their predictive power in two circumstances: firstly, on additional samples taken under similar conditions; and secondly, to explore their possible use under different conditions such as sampling at a different season of the year or on other commuting routes.

CONCLUSIONS

This paper has raised three main points. Firstly, the fact that exceedences of the ambient air quality standards for CO are frequently reported in the MAMC. Secondly, that in Mexico City, as in US cities studied before, measurements taken at the FSM consistently underestimate the CO concentrations experienced by commuters at rush hour. Thirdly, that, for commuters of some public transport modes (e.g. metro, minibas and bus), it is possible to develop predictive models with a reasonable explanatory power by means of using the appropriate FSM stations and other variables.

ACKNOWLEDGMENTS

The present study would have not been possible without the support of the Undersecretary for Ecology (SEDEU) in Mexico. In particular I thank the personnel involved in the operation, maintenance and data processing of the air pollution monitoring network (RAMA). Many thanks also to the US EPA for lending the CO monitors used in this study.

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Fixed-site Monitoring Stations	Daily maximum 8-h CO concentrations (in ppm)					Days exceeding AAQS (percent)	
	Days [#]	Min	Max	Mean	S.D.	8h>9 ppm	8h>13 ppm
<i>Taxqueña</i>	72	5.6	18.9	11.3	2.8	81.9	20.8
<i>Insurgentes</i>	71	3.5	14.7	9.6	2.4	60.6	9.9
<i>Merced</i>	83	4.9	15.0	9.2	2.0	50.6	8.4
<i>Plateros</i>	81	4.5	14.4	8.9	2.2	45.7	6.2
<i>Lagunilla</i>	60	2.3	22.4	7.2	3.1	15.0	3.3

Table 1. Daily maximum 8-hour CO concentrations during January-March 1991.
[#]Number of days with complete data sets.

Transport Mode	Trips	Min	25%	Median	75%	Max
Auto	34	34.9	48.3	57.5	63.7	83.7
Combi	35	23.2	44.4	58.6	65.1	90.7
Minibus	152	17.9	34.8	42.7	55.2	109.3
Bus	170	12.9	24.2	30.2	36.5	59.4
Trolley	47	14.8	21.6	25.6	33.5	42.4
Metro	111	12.0	17.5	20.6	25.5	33.5

Table 2. Percentiles of average CO concentrations (ppm) of terminus - to - terminus commuting trips by transport mode[1].

Transport Mode	Difference Vehicle-FSM (ppm)	Ratio Vehicle/FSM
Auto	36.5 - 47.4	3.0 - 7.0
Combi	28.5 - 51.6	3.6 - 7.7
Minibus	22.9 - 49.4	3.4 - 5.6
Bus	14.0 - 26.5	2.5 - 4.0
Trolley	15.1 - 19.1	2.5 - 3.5
Metro	9.0 - 12.7	1.9 - 2.5

Table 3. Comparison between in-vehicle and ambient CO concentrations.
Range corresponds to means for different routes and shifts.

METRO	$R^2 = .48$ $N=63$ $P. \text{ Reg. Model} < .001$ $COEXP = 13.27 + 0.69 \text{ FSM}$
BUS	$R^2 = .62$ $N=113$ $P. \text{ Reg. Model} < .001$
Route 1	$COEXP = 43.45 + 0.66 \text{ FSM} - 0.61 \text{ SPD} - 1.37 \text{ WSP}$
Route 3	$COEXP = 46.11 + 0.66 \text{ FSM} - 0.61 \text{ SPD} - 1.37 \text{ WSP}$
Route 4	$COEXP = 40.56 + 0.66 \text{ FSM} - 0.61 \text{ SPD} - 1.37 \text{ WSP}$
Route 5	$COEXP = 41.88 + 0.66 \text{ FSM} - 0.61 \text{ SPD} - 1.37 \text{ WSP}$
MINIBUS	$R^2 = .63$ $N=87$ $P. \text{ Reg. Model} < .001$
Route 1	$COEXP = 47.37^* + 1.17 \text{ FSM} - 2.91 \text{ WSP}$
Route 2	$COEXP = 46.59^* + 1.17 \text{ FSM} - 2.91 \text{ WSP}$
Route 3	$COEXP = 51.53^* + 1.17 \text{ FSM} - 2.91 \text{ WSP}$
Route 4	$COEXP = 49.06^* + 1.17 \text{ FSM} - 2.91 \text{ WSP}$
AUTO	$R^2 = .71$ $N=21$ $P. \text{ Reg. Model} < .001$
Route 1	$COEXP = 57.87^* + 1.70 \text{ FSM} - 1.28 \text{ SPD}^{**}$
Route 2	$COEXP = 63.28^* + 1.70 \text{ FSM} - 1.28 \text{ SPD}^{**}$

Table 4. Regression models by transport mode. All coefficients are different from zero at the $p < .001$ level, unless marked as follows: * $p < .05$; ** $p < .01$.

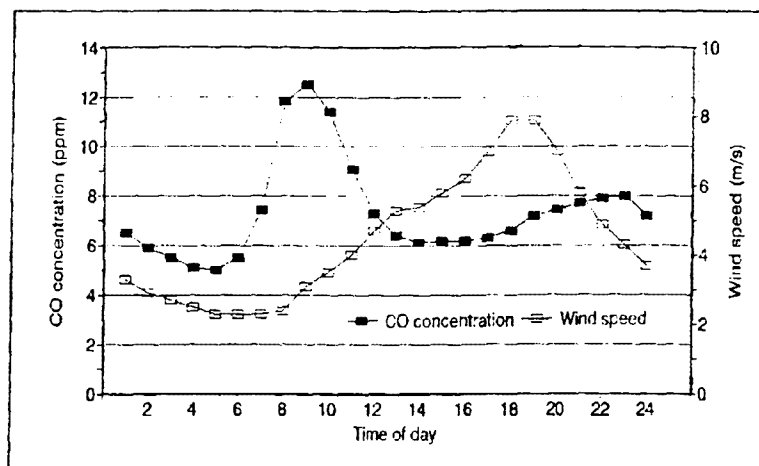


Figure 1. Hourly CO concentrations and wind speed in Mexico City during January-March, 1991 (average of 5 selected stations).

**Investigation of Spatial and Temporal Pattern of Ozone Concentration
within a Metropolitan Area Using Ozone Passive Sampler**

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The Canadian Research on Exposure Assessment Modeling (CREAM) pilot studies were conducted during the winter and summer of 1992 in Toronto, Ontario, Canada. In the pilot studies, personal, indoor, and outdoor samples were collected using passive ozone (O_3) samplers. Personal O_3 samples were taken from 89 participants from 50 different households. Indoor O_3 samples were taken from participants' homes and work places and a variety of non-residential buildings. The indoor samplers were located on a "sampling tree" that included a fan to maintain a constant air flow. Outdoor O_3 samples were collected by placing passive samplers outside participants' homes. Outdoor O_3 concentrations also were monitored simultaneously by continuous monitors at the 21 stationary ambient monitoring sites operated by the Ministry of Environment throughout Metropolitan Toronto, Central Ontario, and Hamilton. Approximately 20 duplicate passive samples per week were taken for quality control and quality assurance purposes. Air exchange rate of the homes were taken weekly using perfluorocarbon tracer gas method. Participants were asked to complete time-activity diaries throughout the monitoring period.

The performance of the passive sampler is evaluated for various weather conditions and various applications. Spatial variation of outdoor O_3 concentrations is examined using standardized scores and analysis of variance (ANOVA) techniques. Factors affecting O_3 outdoor spatial variation, indoor O_3 concentrations, and personal O_3 exposures are examined. A personal O_3 exposure model is developed by using home outdoor, home indoor, work place, and other microenvironmental O_3 concentrations.

A COMPARISON OF ACID AEROSOL AND OZONE EXPOSURE PATTERNS IN A SUMMERTIME STUDY OF METROPOLITAN PHILADELPHIA

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ABSTRACT

A study of acid aerosol and ozone exposure patterns was conducted for metropolitan Philadelphia between June and August 1992. Included in the study design were daily monitoring of particulate strong acidity (PSA), sulfate (SO_4^{2-}) and hourly ozone data (O_3) at a citywide network. A continuous sulfate thermal speciation analyzer at one site collected hourly concentration data for SO_4^{2-} aerosol. The current paper presents temporal patterns of continuous measurements for O_3 and SO_4^{2-} aerosol. Both pollutants had similar daily peak periods in the mid-afternoon, although the range for O_3 was much greater than for SO_4^{2-} aerosol. The daily peak values were also correlated for the two species during the study period. It seems that many of the same meteorological factors affect the spatial and temporal patterns for these lung irritants. Hence, the similarity in exposure patterns for O_3 and SO_4^{2-} aerosol is reason for concern, regarding possible synergism from coincident doses.

INTRODUCTION

Both O_3 and particle strong acidity are harmful to the lung, and, at levels currently observed in parts of the U.S., they each appear to cause measurable human health effects. To understand whether these two pollutants may act in concert, it is necessary to determine how their exposure patterns relate.

Because of its status as a Criteria Pollutant of the NAAQS, O_3 data are available for all U.S. metropolitan areas and most suburban and rural regions. At all sites in the NAMS and SLAMS works, measurements for O_3 are made and stored as hourly averages, 24 hours each day. Because the NAAQS for O_3 is a 1-hour standard, data are usually reported in terms of the maximum daily 1-hour concentration.

On the other hand, measurements for particle strong acidity (PSA) are not nearly as widespread. The priority of data on atmospheric levels of acidic particles has been produced in just the past few years. While it is now known that acidic sulfate concentrations (24-h) can be as high as $25 \mu\text{g m}^{-3}$ in the rural and suburban regions of eastern U.S. and Canada, data are notably limited in and around metropolitan

areas¹.

Particle acidity is found to be singularly associated with sulfate aerosol². It is observed that sulfate aerosol occurs at its highest levels in the summertime, associated with many of the same conditions leading to photochemical smog episodes. The data for PSA show that it is also associated with smog episodes, although the PSA fraction in sulfate aerosol is highly variable and site specific.

Ozone in the troposphere remains a resistant problem in much of the eastern U.S., as well as metropolitan regions in the rest of North America. In the summertime, elevated levels can occur on a daily basis over an extensive area. It is becoming clear that some of the same factors which elevate O₃ concentrations also have an influence on sulfate and acid aerosol levels. Day-to-day variability of O₃ depends chiefly on variation in meteorological conditions, such as mixing layer depth and temperature, while PSA levels further depend on the availability of sulfate precursors (SO₂) and their reactions and fate.

In order to determine the possibility of synergistic effects for exposure to O₃ and PSA during photochemical episodes, accurate exposure determinations are needed. In this paper, data for a field study in metropolitan Philadelphia are presented. Our interest is in the coincident exposure patterns in a polluted region, where there is a high density of people living and working.

METHOD

The field study was conducted in metropolitan area of Philadelphia from June through August 1992. A network of nine monitoring sites had HEADS (Harvard/EPA Annular Denuder Sampler) to measure acidic aerosol components (PSA and SO₄⁼ aerosol); five sites were collocated with O₃ monitors (Figure 1). In addition, at the Northeast Airport (N/E site) a CSTS (Continuous Sulfate Thermal Speciation) monitor was collocated with HEADS and O₃ monitors to measure hourly sulfate levels through the study period³.

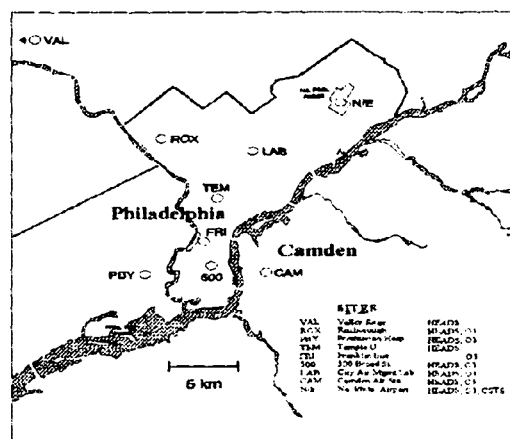


Figure 1. Sampling sites for Philadelphia study 1992

RESULTS

The summer of 1992 was notable cooler and less polluted than others of record. The average daily peak O₃ among the 7 sampling sites were from 50 to 68 ppb during the study period. The maximum level observed was 117 ppb at ROX site in August (Table 1). During the months June through August, there was not a single NAAQS exceedance (>120 ppb for 1 h) at any of the sites, while 10 to 15 exceedance days are more typical. Likewise, the levels of sulfate and PSA were relatively moderate. The average sulfate levels were from 63 to 100 nmole/m³ during the same period. PSA levels were only 10 to 30% corresponding sulfate levels; the average concentration ranged from 9 to 33 nmole/m³ among sampling sites. The PSA fraction in nearby New Jersey for previous summers was 20-40%⁴.

Table 1. HEADS measurements and hourly ozone data in Philadelphia summer 1992.

site	24h average (nmole/m ³)						hourly Ozone (ppb)					
	June		July		Aug		June		July		Aug	
	SO ₄ ²⁻	H ⁺	SO ₄ ²⁻	H ⁺	SO ₄ ²⁻	H ⁺	mean	max	mean	max	mean	max
N/E	71	17	83	27	83	21	68	104	60	100	61	106
ROX	-	-	88	29	83	19	-	-	67	109	58	117
LAB	-	-	91	23	85	14	52	81	53	85	54	100
TEM*	82	15	78	13	86	12	-	-	-	-	-	-
SOO*	-	-	76	10	79	9	-	-	-	-	-	-
PBY	64	10	100	21	88	14	66	101	64	107	62	111
VAL	-	-	91	33	81	21	-	-	-	-	-	-
FRI*	-	-	-	-	-	-	53	91	54	92	50	97
CAM	-	-	-	-	-	-	63	89	66	96	64	104

*: inner city locations

By calculating the average for each hour of the day during each of the summer months, pictures of the daily concentration patterns for O₃ and SO₄²⁻ aerosol can be assembled (Figure 2). For O₃ the diurnal pattern is well known, with the daily peak occurring in the mid-afternoon and the minimum levels occurring in the morning rush hours. Ozone starts to build up during the daytime hours --after a dip in the morning rush hours-- from background levels (≈20 ppb) up to 50-60 ppb at about 3 pm (EST, local time is 1 h later EST). Because the O₃ and its precursors are transported in the windfield, the time of the daily peak is later at the downwind sites. Likewise, at locations proximal to vehicular arteries, the release of fresh nitric oxide (NO) scavenges O₃. The O₃ levels at **FRI** and **LAB** sites are 10-20% lower than the distal city sites (Table 1).

A diurnal pattern, similar to O₃ was observed for hourly SO₄²⁻ aerosol data. The daily peak occurred in the mid afternoon, simultaneously with the O₃ maximum. The dynamic range for SO₄²⁻ was only ≈1.5 max/min), while for O₃, it was 5-6. The peak sulfate levels were only 50% higher than background levels while peak O₃ was 300% higher than background levels. Similar to the spatial pattern of O₃, relatively lower acidity was found in the inner city locations (Table 1). The acidity observed at **TEM** and **SOO** sites were up to 70% lower than distal city sites.

A monthly summary for 24h HEADS, O₃ and continuous SO₄²⁻ aerosol data with respect to different time intervals is presented in Figure 3. The correlation between hourly SO₄²⁻ aerosol and O₃ were examined for various time intervals, such as **hourly**, **12-16**, **16-20** (EST), **daytime** period and **nighttime** period. The **12-16** interval represents the peak hours for O₃ and SO₄²⁻ aerosol. Our concern about the **16-20** interval is because it is the period of most likely weekday recreation. There are strong correlations between O₃ and sulfate data for **hourly**, **12-16**, **16-20** and **daytime** data with highest correlation occurred during **12-16** (Table 2). Only **nighttime** data were not significantly correlated.

Table 2. Correlation and Regression between O₃ (ppb) vs. SO₄²⁻ aerosol (μg/m³) at N/E site.

	Pearson Corr. Coef.	Slope	Intercept	r ²
hourly	0.36*	1.21	18	0.12
12-16	0.52*	1.26	42	0.27
16-20	0.46*	1.06	28	0.21
daytime	0.49*	1.17	33	0.24
Nighttime	NA(p>0.05)	-	-	-
24 h	0.40*	0.73	24	0.16

*: p < 0.0001

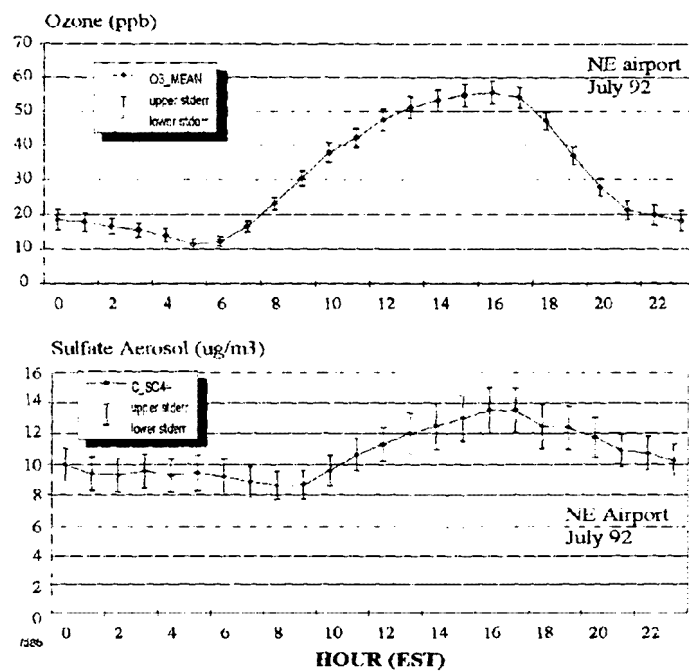


Figure 2. Average hourly ozone and sulfate concentration patterns for the Philadelphia Study 1992.

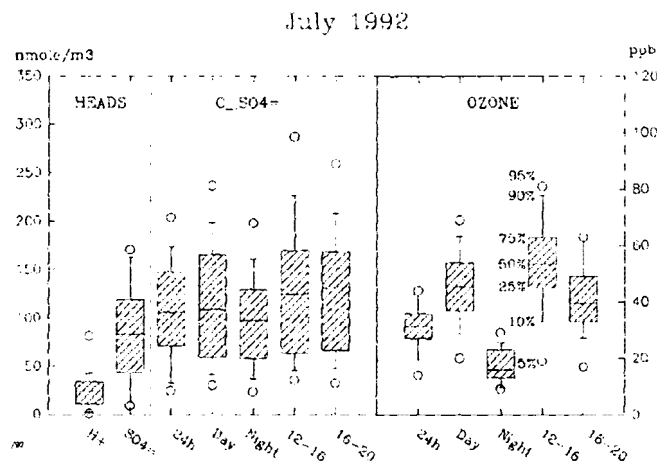


Figure 3 Concentration profile for HEADS, Continuous Sulfate and Ozone data.

A regression analysis was conducted for CSTS SO_4^{2-} (average for 24 hourly values) versus HEA SO_4^{2-} (24-h integrated samples). This indicates an excellent agreement with a slope of 0.96 ± 0.06 , r^2

0.80 and a positive intercept of 34 nmole/m³. The positive intercept is due to the non-volatile sulfate aerosols which HEADS does not analyze collect³. PSA and SO₄²⁻ aerosol data for HEADS were also highly correlated ($p < 0.0001$, $R^2 = 0.82$), and the average ratio of acidity to sulfate was 0.27 ± 0.13 .

Table 3. Correlation analysis among hourly temperature, ozone and sulfate data, 1992

	Hourly data			Daily maximum data	
	Temp	O ₃		Temp	O ₃
O ₃	0.0001*		O ₃	0.0001	
	0.72**			0.62	
Sulfate	0.0001	0.0001	Sulfate	0.0001	0.0001
	0.49	0.36		0.59	0.50

*: Pearson correlation probability

**: r-square

Since O₃ and sulfate are products of photochemical reactions and both demonstrate strong diurnal pattern, we have investigated the relationships among temperature, O₃ and SO₄²⁻ aerosol levels during the summer months study period. Daily average and daily maximum levels were examined for correlation and regression relationships. There are strong correlations among temperature, O₃ and continuous sulfate data for both daily average data and daily maximum data (Table 3). Because O₃ and SO₄²⁻ aerosol levels in the atmosphere came from different origin and photochemical reactions, these high correlations indicate temperature is an independent variable which enhances the co-variance between O₃ and SO₄²⁻ aerosol levels, which positive slopes when pollutant concentrations are plotted against temperature.

DISCUSSIONS

The O₃ concentrations observed at ground level are a combination of physical and chemical reactions. During the daytime, O₃ is generated through photochemical reactions and influx from air aloft, the rate of O₃ formation exceeds the losses, such as chemical reactions or deposition. The levels of O₃ attained depends on the availability of precursor, such as NO_x, and solar radiation as well as the surface level inversion height. The O₃ levels observed at N/E site indicate a 3 times higher than background levels during the daytime period. At night, photochemical reactions cease and the influx from air aloft is enhanced due to a shallower mixing layer after the sun goes down⁵. Sulfate levels follow a similar pattern as O₃. The generation of sulfate not only depends on the levels of its precursor (SO₂), but also on the availability of oxidant, such as O₃ and hydroxyl radical, in the atmosphere to complete its photochemical reactions. Its formation rate is lower than the O₃. Our observation for Philadelphia was that sulfate only increased 40% above its "background" level. At night, sulfate has lower deposition and loss rate than O₃, therefore retains most of its daytime level. This phenomenon was evident in our previous study where continuous 12-h sulfate sampling data showed a significant auto-correlation from daytime samples following nighttime samples⁴. Due to lower depletion at night and more complicated photochemical mechanism, sulfate showed a less apparent diurnal pattern as O₃ does.

The diurnal patterns for O₃ and sulfate aerosols are similar and the peak levels occur in the middle of the day. This similar pattern of concentration profile will have an important impact on human exposure and associated health outcomes. This is especially true for exposure to pollutants which may

induce an synergistic adverse health effects such as O₃ and acid aerosols. In addition, the acid fraction was found higher during the daytime period than nighttime period⁴. It is putative that higher acid fraction may occur during the peak hours of O₃. Therefore, more human exposure assessment should pay attention on short term (2-4 hours) co-exposure to O₃ and acid aerosols

CONCLUSIONS:

There was a consistent diurnal pattern for O₃ among the Philadelphia metropolitan sampling sites; lower peak values were found in the city center. The peak hour was between 12 and 16 (EST). A similar diurnal pattern was observed for hourly SO₄⁼ aerosol data with peak levels occurred simultaneously with O₃ peak levels. The correlation for peak periods between O₃ and SO₄⁼ aerosol was found to be significant. Nevertheless, the peak exposure interval was more narrow for O₃ than SO₄⁼. Since exposure to O₃ is simultaneous with PSA, they may have synergistic adverse health effects. It is reasor for concern about co-exposure to O₃ and acid aerosols during summer air pollution episodes.

ACKNOWLEDGEMENTS

We are grateful to the City of Philadelphia - Air management Laboratory and to the New Jerse Department of Environmental Protection & Energy for their cooperation and assistance. The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Cooperative Agreements to Harvard University (CR-812050) and to EOHSI (CR 819846). It has been subject to the Agency's peer and administrative review, and it has been approve for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Diurnal and Spatial Variation in Fine and Coarse Particle Concentrations in Metropolitan Philadelphia

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Particle mass ($PM_{2.5}$ and PM_{10}) concentrations were measured in metropolitan Philadelphia during the summer of 1992, as part of a larger effort to characterize acid aerosol concentrations within urban environments. Sampling was performed simultaneously at seven sites located within metropolitan Philadelphia and at a rural site approximately 18 miles from the city center. Sites were selected based on their population density and on their relative locations within Philadelphia. Particle sampling at the eight sites was performed on alternate days, with sampling conducted over 24-h periods beginning at 8am. All samples were collected using 10 L/min Harvard Impactors. At one of the metropolitan sites, additional particle mass measurements were made daily using continuous methods.

In this paper, we examine and compare the temporal and spatial variation in fine ($d_p < 2.5 \mu m$) and coarse ($2.5 < d_p < 10 \mu m$) particle mass concentrations. The analysis of temporal variation examines the daily and hourly variation in fine and coarse mass concentrations and their relationship to measured PM_{10} levels. Daily temporal profiles for fine and coarse particle concentrations also were compared for the eight sites, with factors affecting their daily variation discussed. Similarly, factors affecting spatial variation in fine and coarse particle mass concentrations also were identified, with the specific effects of population density, traffic, location, and wind direction addressed. Results from these analyses will help epidemiologists understand how well, or poorly, measurements of fine, coarse, and PM_{10} aerosols collected from a single urban monitoring site are able to characterize daily particle concentrations within an urban area.

Indoor Air Chemistry: Formation of Organic Acids and Aldehydes

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Laying emphasis on the formation of aldehydes and organic acids, the study has examined the gas-phase reactions of ozone with unsaturated VOCs. The formation of formaldehyde and formic acid was observed for all the three selected unsaturated VOCs: styrene, limonene, and 4-vinylcyclohexene. In addition, benzaldehyde was detected in the styrene - ozone - air reaction system, and acetic acid was also found in limonene - ozone - air system. The study has also examined the gas-phase reactions among formaldehyde, ozone, and nitrogen dioxide and found the formation of formic acid. The nitrate radical was suggested to play an important role in converting formaldehyde into formic acid. Experiments for all the reactions were conducted by using a 4.3 m³ Teflon chamber. Since the conditions for the reactions were similar to those for indoor environments, the results from the study can be implicated to real indoor situations and can be employed to support the findings and suggestions from the previous studies: certain aldehydes and organic acids could be generated by indoor chemistry.

OZONE REACTIVE CHEMISTRY ON RESIDENTIAL SURFACES

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ABSTRACT

The heterogeneous chemistry of ozone on interior latex paint was investigated in a tube flow reactor. The emissions of several polar volatile organic compounds (VOCs) including organic acids, aldehydes and ketones were measured while a glass tube coated with latex paint was exposed to clean air and two different concentrations of ozone. Formic and acetic acid were not found to be generated via ozone reactions; however, both were found to offgas from the latex paints. Formaldehyde, acetaldehyde and acetone were found to be produced by ozone reactions. It was found that formaldehyde is produced in sufficient quantities to impact indoor concentrations. Additionally, ozone, organic acids, aldehydes and ketones were measured over an approximately 24 hour period in 4 residences during the winter of 1993 and in 9 residences during the summer of 1993. Environmental variables such as indoor and outdoor temperature and indoor and outdoor relative humidity were recorded. It was found that the VOC emission rate was correlated with both the environmental variables and the ozone removal rate. A combined ozone removal rate and environmental variable model indicated that both these factors are important, suggesting that polar VOCs may be formed by ozone reactions.

INTRODUCTION

VOCs are receiving increasing attention as indoor air pollutants, mostly due to their potential to cause irritation to occupants, (1). Numerous VOCs have been detected in residential environments in concentrations exceeding those found outdoors, indicating that there are indoor sources, (2). Several household products and materials have been identified as sources of VOCs, (3), and VOCs in the ambient environment will enter residences through air infiltration. However, a new source of indoor VOCs is emerging: the production of VOC compounds via the reaction of ozone with both indoor surfaces and other indoor VOCs. Ozone, which is formed as a secondary pollutant in the ambient environment, infiltrates into indoor residences. Some of this ozone is deposited on indoor surfaces or reacts homogeneously to result in lower ozone concentrations indoors compared to outdoors. However, it is additionally been assumed that the deposition was irreversible and that homogeneous reactions with VOCs are of negligible consequence.

Olefins (double-bonded hydrocarbons) are the most likely species to react indoors with ozone as the one-olefin reaction is one of the fastest in the indoor environment. The likely by-products of an ozone-olefin reaction are polar VOCs such as carbonyls (aldehydes and ketones) and organic acids, (4). Weschler *et al.* (5) have found, in a laboratory study, that ozone reacts with constituents of carpet to form formaldehyde, acetaldehyde and other C₅-C₁₀ aldehydes. Zhang *et al.* (6) have measured aldehydes and organic acids as gas-phase reaction products of ozone and several olefin species including 4-methylcyclohexene, styrene and *d*-limonene. Reiss *et al.* (7) have shown, through model calculations, that terpenes, particularly *d*-limonene, are present in sufficient quantities and have fast enough reaction rate constants to contribute significantly to indoor ozone removal. Additionally, Zhang *et al.* (8) have found, in a residential field study of 6 homes in New Jersey, that the indoor ozone concentration is correlated with concentrations of several aldehydes and organic acids.

In this paper, the results of a laboratory study to measure the products of an ozone-latex paint reaction are presented. Also, a method for extrapolating laboratory measurements of heterogeneous reactions to real indoor residential environments is introduced. The results of a pilot-scale residential field study designed to examine indoor ozone chemistry are presented.

MATERIALS AND METHODS

Laboratory Study

The formation of polar VOCs via ozone reactions was measured in a laminar tube flow reactor. Reiss *et al.* (9) gives a detailed description of the apparatus. Basically, a zero-air (*i.e.*, clean air) or zero-air with ozone (generated with a UV Photometric Ozone Calibrator) stream is pumped through the tube and exposed to a glass cylindrical test section that is coated on the inside with latex paint. The test section is 30 cm in length and 2.1 cm in diameter. The flow rate through the test section was 2.5 L/min. Several brands of latex paint were tested. The concentrations of ozone and carbonyls (aldehydes and ketones though C₆) or organic acids, depending on the experiment, were measured before and after the test section. Organic acid concentrations were measured by glass annular denuders coated with potassium hydroxide (KOH) that were placed in-line. After the experiment the denuders were extracted with ultra-pure water, and the extract analyzed by High Performance Liquid Chromatography (HPLC) for formate and acetate ions. Carbonyl concentrations were measured with 2,4-dinitrophenylhydrazine (DNPH) Sep-Pak. The Sep-Paks were extracted with acetonitrile and the hydrazone derivative was measured by HPLC. Ozone concentrations were measured with continuous, chemiluminescent ozone analyzers (Monitor Labs Model 8410).

For a typical experiment, a latex paint coated tube was first exposed to a zero-air stream. Carbonyl experiments lasted for about 3 hours, and organic acid experiments lasted about 18 hours. After the initial zero-air exposure, the tubes were exposed to ozone at about 75-100 ppb. For carbonyls, there was an additional exposure to a higher ozone concentration, 100-150 ppb.

Modeling Ozone Heterogeneous Chemistry

The deposition of pollutants to indoor surfaces is typically modeled by the concept of the deposition velocity, which can be written as follows,

$$K_d = \frac{J^{O_3}}{C} \quad (1)$$

where J^{O_3} is the flux of ozone to the surface and C is the indoor ozone concentration. The deposition velocity can be divided into a boundary layer mass-transport and surface uptake component, where the surface uptake is modeled by the mass accommodation coefficient, (10). The mass accommodation coefficient is defined as the ratio of the number of ozone molecules that deposit on the surface and the total number of ozone molecules that collide with the surface. To model heterogeneous chemistry we have defined a new term, referred to as the VOC formation factor, which is essentially an extension of the mass accommodation coefficient. The VOC formation factor is defined as the ratio of the number of VOC molecules of a particular species that are formed via an ozone reaction and the number of ozone molecules that deposit on the surface. This factor can be determined from the chamber experiments by a simple mass balance. We can extrapolate the chamber experiments by use of the following steady-state relationship,

$$J^{VOC} = \kappa * J^{O_3} \quad (2)$$

where J^{VOC} is the flux of VOC emitting from the surface formed via an ozone reaction and κ is the VOC formation factor.

Description of Field Study

The field study was conducted in two phases, one during the winter and one during the summer. In the winter phase we sampled in 4 residences during February, 1993, and in the summer phase we sampled in 9 residences (including the four winter phase residences) during late May and June of 1993. The residences were all in the greater Boston area and included both apartments and houses. Homes with smokers were excluded, and wood burning fireplaces were not used in any of the residences while sampling occurred. Sampling was done over an approximately twenty four-hour period, and each residence was sampled twice, on consecutive days. Carbonyls were measured with Sep-Paks, and organic acids were measured with KOH denuders. Ozone was measured with sodium nitrite-coated passive monitors. (see ref. 11). The air exchange rate of the residence was measured by the steady-state tracer-gas technique. (see ref. 12).

The following is a summary of the sampling protocol for our study:

Indoor Sampling

For the indoor sampling, there was always one centrally located sampling site. For larger residences (i.e., ones with more than one floor), there was an additional sampling site. The following is a description of the sampling arrangement for each pollutant and environmental variable.

- *Carbonyls* - One co-location (i.e., two measurements at the same location) at the central site. For large residences there was an additional sampling location where a single measurement was made.
- *Organic Acids* - One co-location at the central site. For large residences there was an additional sampling location at which a single measurement was made.
- *Ozone* - One co-location at the central site. Also, there were ozone monitors placed at 2 to 5 other locations in the residence, depending on the size of the residence.
- *Air Exchange Rate* - Tracer-gas collection tubes were placed in 2 locations during the winter, and 2 to 5 locations during the summer when the air exchange rate is higher, resulting in lower collection masses on the tubes.
- *Temperature and Relative Humidity* - Measured at a single, centrally located position.

Outdoor Sampling

For the outdoor sampling, there was a single sampling location that was placed at least a meter away from the residence so that the samples were outside the boundary layer around the residence. At this site, there were co-located Sep-Paks, KOH denuders and ozone monitors.

RESULTS AND DISCUSSION

Laboratory Study Results

The organic acids were found to offgas from the latex paint at significant quantities during the zero-air exposure. For acetic acid the offgasing was dependent on the relative humidity. For example, for one particular brand of latex paint, the acetic acid emission rate was 1 µg/hr for a 10% relative humidity experiment while the emission rate was 60 µg/hr for an 80% relative humidity experiment. When ozone was added, there was no increase in the emission rate, indicating that there is no organic acid formation via ozone reactions.

Several of the carbonyl compounds were found to offgas from the latex paint during the zero-air exposure, including formaldehyde, acetaldehyde and acetone. The formaldehyde offgasing was the highest. None of the higher molecular weight compounds were detected. In several of the experiments, we observed the production of a secondary pollutant from an ozone-latex paint reaction, as evidenced by an increase in the emission rates of these compounds when the latex paint tubes were exposed to ozone. In a few of the experiments, the emission rate is clearly linear with respect to ozone. It is expected that at some unknown ozone concentration the VOC formation will begin to level off asymptotically with respect to ozone deposition due to the saturation of sites where the ozone reaction is occurring. This does not appear to be happening for the experiments reported. Most of the experiments showed formaldehyde production, but a few showed acetaldehyde and acetone production.

Using the model developed above, we can extrapolate the results from this laboratory study to actual indoor air environments. However, to do this we need to make some assumptions about the concentration of ozone, the deposition of ozone and the air exchange rate of the residence. Therefore, we will return to this question after discussion of the field study results.

Field Study Results

The indoor and outdoor concentrations and emission rates were calculated for all of the pollutants. Sisk *et al.* (7) provides a detailed summary of these results. Table 1 shows the indoor concentrations of polar VOCs. Among the carbonyls, 10 of 12 that were measured were detected. Only acrolein and formaldehyde were not detected. All of the compounds were detected in higher concentrations indoors compared to outdoors, indicating that there are indoor sources for these compounds. The concentrations of the carbonyls were similar for the summer and winter. However, the average air exchange rate for the winter was 0.9 hr⁻¹, and for the summer it was 2.3 hr⁻¹. Therefore, the carbonyl emission rate was much higher for the summer. The organic acid concentrations were about twice as high for the summer compared to the winter.

Several statistical tests were conducted to examine this data. First, the inter-correlations between the polar VOCs were calculated using the Spearman correlation coefficient. Most of the compounds were

Table 1. Summary of Polar VOC Concentrations in Field Study

Compound	Winter Conc. (ppb)		Summer Conc. (ppb)	
	Indoor	Outdoor	Indoor	Outdoor
<u>Organic Acids</u>				
Formic Acid	9.8	3.1	17.8	3.9
Acetic Acid	15.5	1.8	28.7	2.0
<u>Carbonyls</u>				
Formaldehyde	11.1	3.1	16.1	2.6
Acetaldehyde	6.4	1.5	5.1	1.1
Acetone	6.7	1.4	6.1	1.7
Propionaldehyde	1.1	0.21	1.9	0.83
Butanone	2.4	1.5	2.9	1.2
Butyraldehyde	0.62	0.26	0.56	0.13
Benzaldehyde	0.70	0.42	0.51	0.08
Isovaleraldehyde	0.35	0.04	0.12	0.01
<i>n</i> -Valeraldehyde	0.96	0.80	1.1	0.09
<i>n</i> -Hexaldehyde	1.4	0.03	2.2	0.16

correlated with one another, indicating that these emission rates are controlled by similar processes. We also tested some models to determine which factors are the most important determinants of the VOC emission rates. Anderson *et al.* (13) have found that formaldehyde emissions from pressed wood products was dependent on the relative humidity of the air above the surface. It is also expected that temperature will affect the emission rates. Additionally, we have hypothesized that these compounds are formed via ozone reactions on surfaces and in the gas-phase. The models were derived from simple mass balance considerations and using the compartmental model approach. The derivation of these models are provided in Reiss *et al.* (7).

Three different models were tested: (1) a VOC emission rate versus environmental variable model, separately considering indoor temperature, indoor relative humidity and outdoor temperature, (2) a VOC emission rate versus ozone removal rate model and (3) a VOC emission rate versus combined environmental variable and ozone removal rate model. These models were tested for each of the polar VOC compounds that were detected. The environmental variable terms in model (1) were statistically significant for most of the compounds, particularly indoor relative humidity and outdoor temperature. The ozone removal rate term was significant in model (2) for most of the compounds. It should be noted that these terms were not significant for the summer or winter data set separately. For model (3), the environmental variable term was more statistically significant compared to the ozone term for most of the compounds, suggesting that the environmental variables are a more important determinant of the polar VOC emission rate. However, two compounds, *n*-valeraldehyde and formic acid, showed a higher significance for the ozone term, suggesting that ozone was a more important contributor to the polar VOC emission rates for these compounds. A calculation was also performed to estimate the fraction of the polar VOC emission rate that can be attributed to ozone reactions based on the regression coefficients of the model. The calculation showed that about 15 to 60 percent, depending on the compound, of the polar VOC emission rate can be attributed to ozone reactions.

Extrapolation of Laboratory Results

We can now use the results of the simultaneous measurements of the carbonyls and ozone from the field study to estimate the impact of the ozone-latex paint reaction on the total emission rate of formaldehyde. In the field study we found the following during the summer phase: (1) indoor

formaldehyde concentration - 16.1 ppb, (2) formaldehyde emission rate - $2.3 \mu\text{g}/\text{m}^3$, (3) outdoor ozone concentration - 26.3 ppb, (4) air exchange rate - 2.6 hr^{-1} , and (5) average volume (V) - 300 m^3 . By examining the floor plans of the residences that were sampled, we estimate that A_s/V to be about 1.0 m^{-1} , where A_s is the surface area of only the latex paint. Additionally, the ozone flux to the surface was modeled by a method outlined by Cano-Ruiz *et al.* (14). This model considers both laminar and turbulent flow scenarios. With the ozone flux to the surface and the VOC formation factor, we can determine the VOC flux from the surface. With the surface area and volume, we can then determine the VOC emission rate. For a high end value of the VOC formation factor, 0.25, the calculated source emission rate of formaldehyde is $0.25 \mu\text{g}/\text{sec}$ for laminar flow and $0.35 \mu\text{g}/\text{sec}$ for turbulent flow, which 10.9% and 15.2%, respectively, of the formaldehyde emission rate measured by Reiss *et al.*, (7). For a low-end value of the VOC formation factor of 0.03, the source emission rate of formaldehyde is $0.029 \mu\text{g}/\text{sec}$ for laminar flow and $0.041 \mu\text{g}/\text{sec}$ for turbulent flow, which is 1.3% and 1.8%, respectively, of the measured formaldehyde emission rate. The acetaldehyde emission rate was also in this range. Figure 1 shows a general plot of the VOC formation factor versus the polar VOC emission rate via ozone reactions, given the assumptions listed above.

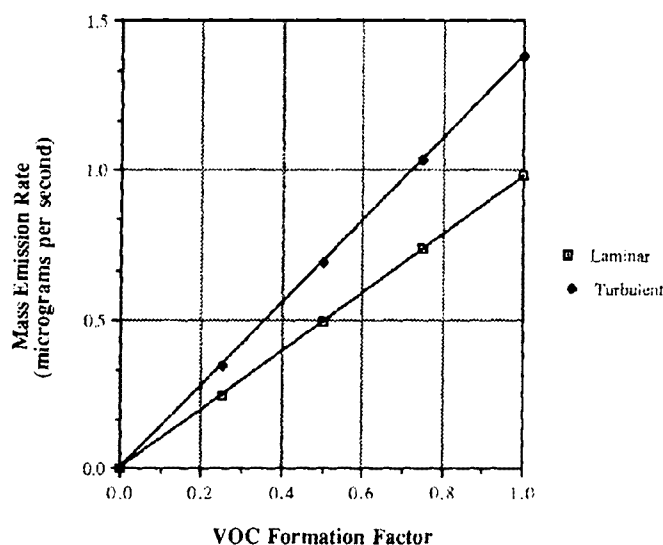


Figure 1. VOC formation factor versus mass emission rate of formaldehyde, given assumptions listed in the text.

CONCLUSIONS

It was shown that ozone reacts heterogeneously with interior latex paint to form polar VOC compounds including formaldehyde, acetaldehyde and acetone. Formaldehyde was formed in sufficient quantities to influence the concentration of indoor formaldehyde significantly. No evidence was found for the formation of organic acids via the ozone-latex paint reaction. A residential field study showed that the polar VOC emission rate (both carbonyls and organic acids) were correlated with environmental variables including temperature and relative humidity and the ozone removal rate. A combined ozone and environmental variable model indicated that indoor ozone chemistry may account for about 15-60% of the polar VOC emission rate, depending on the compound.

ACKNOWLEDGEMENTS

This study was funded by the Center for Indoor Air Research under contract no. 90-31. Support for Richard Reiss was provided by the National Institute of Health training grant number ESO7155. Bob Weker provided advice and technical assistance for the analytical work in this study. Mark Davey also provided valuable assistance in constructing the sampling equipment. We would also like to thank the following individuals for making their homes available for our testing: Denise Belliveau, Michelle Clapp, Mark Davey, Jane Hoppin and Jack Spengler. Dr. Haluk Ozkaynak and Dr. Joseph Harrington provided valuable critiques of the work presented here and made helpful suggestions.

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**CASTNet Air Toxics Monitoring Program (CATMP):
VOC and Carbonyl Data for July, 1993 through March, 1994**

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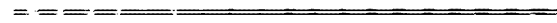
The U.S. EPA has, under the auspices of the CASTNet program (Clean Air Status and Trends Network), initiated the CASTNet Air Toxics Monitoring Program (CATMP). Volatile Organic Compounds (VOC) and carbonyls and metals are sampled for 24-hour periods on a 12-day schedule using TO-14 samplers (SUMMA canisters) and dinitrophenylhydrazine-coated (dmph) sorbent cartridges and high volume particle samplers. Sampling was begun at most sites in July of 1993. The sites are operated by state and local air pollution control programs and all analysis is performed by Environmental Science & Engineering (ESE) in Gainesville, Florida. The network currently supports 15 VOC sites, of which 7 also sample carbonyls. Three sites sample metals only in Pinellas County, Florida. Analytical methods for the network are discussed in two other papers in this symposium (Winslow, 1994; Prentice, 1994). The limits of detection of 0.05 ppb for VOCs allow routine tracking of a wide range of pollutants including several greenhouse gases, transportation pollutants and photochemically-derived compounds. The sites range from major urban areas (Chicago, St. Louis) to a rural village (Waterbury, Vermont). Results of the first three quarters of VOC and carbonyl data collection are summarized in this presentation.

Sources and Factors Influencing Personal and Indoor Exposures to PAHs and PHTHALATES

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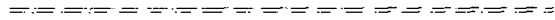
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During the fall of 1990, a large-scale field monitoring program for personal exposure to PM_{10} was conducted in Riverside, California by Research Triangle Institute, Harvard School of Public Health and the Accurex Corporation. The pilot PTEAM (Particle Total Exposure Assessment Methodology) study, co-sponsored by the EPA and the California Air Resources Board, collected personal exposure data on PM_{10} and elemental mass for 175 residents of Riverside. During this study, indoor and outdoor concentrations of PM_{10} , $PM_{2.5}$, and elements were also collected at participants' homes; PAH and phthalate data were collected in a subset of 125 homes. Twelve-hour recall time-activity diaries and questionnaires regarding exposure to ETS and other sources of particles, PAHs and phthalates were also obtained and later used in exposure modeling. Measurements showed that most PAHs and phthalates had high detection rates: 60-100%. Aside from smoking, analysis did not indicate cooking, spraying, house cleaning activities or proximity to busy roadway as possible sources of PAHs or phthalates. Both physical and empirical statistical models were used to estimate the contributions of outdoor sources, cigarette smoking, and other indoor sources. Results from modeling showed that: (1) The physical models fit the PAH data well. Coefficients between model predicted concentrations and observed concentrations averaged about 0.7. (2) Penetration factors for most PAHs were found to be very close to one. (3) The estimated average decay rates for PAHs ranged from 0.4 to 1.6 per hour with sizable variation. (4) Smoking contributed 20-40% of the total concentrations of eight PAHs in homes reporting smoking. (5) Smoking was not estimated to be an indoor source of phthalates. (6) In the entire set of homes, outdoor air contributed more than half the total concentrations of six PAHs, mostly the less volatile ones, and "other" (unidentified) indoor sources contributed more than half of three volatile PAHs.



SESSION 18:

INDOOR AIR POLLUTION



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Gas and Particulate Phase Acids, Organic Compounds and Oxidants in a Sick Room

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ABSTRACT

Employees in a single large room of the administration building at Brigham Young University began experiencing respiratory problems in the spring of 1993. A study of the atmospheric environment in the building was done to see if we could identify any causes for the appearance of this "sick room" problem. The concentrations of fine particulate phase mass, sulfate, nitrate, ammonium ion and acidity were determined using diffusion denuder sampling techniques. The corresponding concentrations of gas phase SO_2 , HNO_3 and HNO_2 were also determined from the denuder sampling results. Concentrations of NO , NO_2 , O_3 and formaldehyde were determined using appropriate Dräger absorption tubes. The concentrations of total volatile organic material was determined using a charcoal sorbent filter. The concentrations of each of these species were determined in the "sick room," at two control locations in the building and in the outdoor environment as a function of time of day for six different days. Temperature and humidity were also monitored in the various study areas. The symptoms experienced by the personnel in the room appear to be associated with slightly elevated temperature and humidity in the study area, a build-up of oxidants and nitrogen oxides associated with changes in air recirculation in the room during the evening, and the generation of emissions during the production of materials for large mailings during the evening.

INTRODUCTION

In April of 1993, employees who work in a large office area in the Abraham Smoot Administration Building (ASB) on Brigham Young University's (BYU) Provo, UT, campus began experiencing health problems. Reported complaints included itching eyes, headaches and scratchy/sore throats. The affected employees reported their symptoms to the health and safety department of the University. That department conducted monitoring in the area to determine if high concentrations of organic compounds and ozone could be causing the health problems the employees were experiencing. These studies revealed nothing that could account for the reported health problems.

In keeping with BYU's continued commitment to employee health and safety a further, more intensive, study was undertaken. This study included the determination of several atmospheric species present in the sick room and at control locations as a function of time during a one-week study using a Briefcase Automated Sampling System (BASS) (1), and the administration of a symptom questionnaire that was to be completed by all employees in each of the sampled areas. The objective of the study was to determine if there were any significant differences between concentrations of the species determined in the sick room, two control rooms (the copy center in the Administration Building or the office of a University Vice President), and ambient air.

Sick building syndrome seems to have become prevalent in the early 1970's and is frequently associated with a sealed office building whose environment is controlled by a heating, ventilation and cooling system (HVAC) (2). The National Research Council has defined sick building syndrome as being characterized by an increased prevalence of certain nonspecific health related symptoms in more than 20 percent of the work force. In addition, general monitoring does not show individual pollutants to be at unsafe levels (3). Studies show that sick building syndrome can usually be attributed to synergistic effects of various contaminants as well as the thermal environment which is dependent on both the air temperature and the radiant

temperature. Radiant temperature is a function of air velocity and humidity (4).

DESCRIPTION OF THE ABRAHAM SMOOT BUILDING

The Abraham Smoot Building is the administration building for BYU. Construction was completed in 1961. There have been no additions or major construction renovations to the original building. The building consists of four floors, one underground. The ASB is an X-shaped building with a total area of 99,182 ft².

The HVAC system consists of a single central unit that serves the entire building. Outside air is drawn down from ground level on the north side of the building to the ventilation system which is contained in the basement. The air is then distributed to the entire building via a series of conduit piping. The minimum ratio of outdoor air to recycled air is 15%. The ratio of ambient to recycled air is a function of ambient temperature. All parts of the building receive their air from the same source. Heating and cooling of building air is controlled separately for each area of the building. During the evening hours, when the building is unoccupied, the rate of air recirculation is cut by a factor of four for energy conservation purposes.

EXPERIMENTAL

Sampling system

All sampling was done using a Briefcase Automated Sampling System, BASS. The sampling system has been previously described in detail (1,5). The air inlet is an 8 mm Teflon line which flows directly to a University Research Glass (URG) (Model 2000-30k/30 P) elutriator to remove particles larger than 2.5 μm . The total air flow is 12 sLpm. The air flow then passes into a Teflon coated aluminum sampling manifold where it enters one of several sampling devices.

The first sampling device measures the concentrations of ozone (O_3), nitrogen dioxide (NO_2), nitrogen oxides (NO_x), carbon monoxide (CO) and formaldehyde utilizing Dräger absorption tubes (1). Air is continuously drawn through each tube during the sampling period at a flow rate of 300 mL/min. The flow rate is controlled using a needle valve as a critical orifice. Flow to each tube was determined at the beginning and end of each sampling period using a bubble flow meter. The concentration of each species was determined by noting the coloration change in each Dräger tube immediately after each sampling session and converting the reading to an average atmospheric concentration from the measured flow rate through each tube and the total sampling time.

The second sampling device was a diffusion denuder sampling system for the collection of gas phase acids, bases and particles. The sampled air stream passed through a set of micro-diffusion denuders (URG model 2000-15B). The first section was coated with a 5% wt NaHCO_3 /5% wt glycerine solution to remove gas phase acids. The second section was coated with a 5% wt oxalic acid/5% wt glycerine solution to collect ammonia. The denuder set was followed by a Teflon filter pack (URG Model 2000-15-ABT) which contained a 25 mm Teflon filter (Gelman Science, Zetfluor P5PJ047) followed by a 25 mm Nylon filter (Gelman Science, Nylasorb 66509). Flow through the system was controlled at 3 L/min with a critical orifice. The flow was determined at the beginning and end of each sampling period using a bubble flow meter. This system is designed to measure the gas phase concentrations of SO_2 , HNO_3 , and HNO_2 in the first diffusion denuder tube and ammonia (NH_3) in the second diffusion denuder tube. The particles collected by the Teflon filter were analyzed to determine fine particulate sulfate and nitrate. The Nylon filter collected any nitric acid lost from the particles during sampling.

The third sampling device was a filter pack (URG Model 2000-15-ABT) containing a 25 mm quartz filter (Pallflex) and a 25 mm charcoal impregnated fiber filter (CIF) (Schleiser & Schuull). The quartz filter collected particles and the charcoal impregnated filter collected

volatile organic compounds (VOC). The quartz filter was analyzed to determine fine particulate carbonaceous material and the charcoal impregnated filter was analyzed to determine total collected VOC (6).

The air quality questionnaire was designed to determine age, sex, appearance of symptoms during work, type of symptoms, and severity of reported symptoms. The questionnaire is identical to that previously used in an National Cancer Institute study of air quality in commercial aircraft passenger cabins (7) except the questions related to cigarette smoking were omitted since BYU is a non-smoking campus. It was to be filled out daily by all employees in each sampled area.

Sample collection

Samples were collected on six days, three times each day, beginning at 8:00am, 12:00pm and 7:00pm. Each sampling period was three hours long. Days one through four were normal working days, Tuesday, Wednesday, Thursday, and Friday. Day five was a Sunday; the building is essentially unoccupied on this day. Day six was the following Monday.

Samples were collected at four different locations:

- 1) The Sick Room studied is on the basement floor at the end of the northeast hall. This room houses the Financial Aid department of BYU. It is a very congested business office, having 40 employees in a 4565 ft² area. Equipment in the room whose emissions might affect air quality includes general office equipment such as computers, printers, and photocopiers. This equipment includes a large, computer-controlled printing facility which is usually operated each night following a work day to output mailings from the Financial Aid office. This room was sampled all six days, all 3 daily sessions.
- 2) The Copy Center is also located on the basement floor, in the middle of the building. It is a small room when compared to the SR location and it is equipped with extra ventilation. At most, two employees occupy the room. This room was sampled days one, two, and three of the study, all 3 daily sampling sessions.
- 3) The vice-president administrator's office is located on the fourth floor in the same relative position as the Financial Aid office. The 280 ft² area is sparsely occupied and has only one computer. This room was sampled days three through six of the study, all three daily sessions.
- 4) Ambient samples were collected from the grating on the air intake system for the building. Ambient samples were collected only in the morning and evening sampling sessions to allow the BASS system the required time to recharge the batteries as power was not available at this location.

Analytical techniques

Samples from the sodium bicarbonate and oxalic acid coated annular denuder sections were recovered by washing with distilled/deionized water and stored at 4°C until analyzed. The Teflon and CIF filters were stored at 4°C until analyzed. Field handled blank samples were obtained for every three samples collected.

The concentrations of SO₂(g) and HNO₃(g) for each experiment were determined from analysis of the base coated denuder section. The NaHCO₃/glycerine coating and collected gases in the denuder annulus were recovered by rinsing with 3 mL of water. The extract solution was kept refrigerated (4°C) until analyzed by ion chromatography (Dionex Model 2000i) for sulfate and nitrate using a Na₂CO₃/NaHCO₃ eluent. The concentrations of ammonia were determined by a similar extraction of the acid coated denuder section and colorimetric determination of

ammonium ion in the extract solution (8). The Teflon filter collected material was extracted by sonication for 20 minutes with 3 mL of water and the resulting solution was analyzed by ion chromatography. Volatile organic compounds collected by the CIF were determined using temperature programmed volatilization (6). The carbon impregnated sorbent filters were analyzed in a stream of N_2 by heating the sample from ambient ($25^\circ C$) to $350^\circ C$ at a nominal rate of $10^\circ C/min$. Organic compounds desorbed from the sorbent filter were catalytically converted to CO_2 and detected by nondispersive infrared spectroscopy. The instrument was calibrated regularly with three CO_2 standards. The gas phase compounds collected by carbon sorbent filters appear to be revolatilized between about 140 and $280^\circ C$.

RESULTS AND DISCUSSION

Air quality

The concentrations of the various determined species for each sampling period are given in Figures 1 and 2. At no time during the study did any sampled species reach concentration levels that exceed acceptable tolerance levels, Table 1.

The concentrations of fine particulate sulfate and $SO_2(g)$, Figure 2, were both dominated by ambient sources and did not tend to be higher in the sick room than in the control rooms. Ambient conditions explain the daily variance, Figure 2. Indoor concentrations were generally less than ambient.

No detectable concentrations of formaldehyde were measured. The detection limit of formaldehyde, 0.04 ppm, is lower than the normal formaldehyde of 0.1ppm in indoor environments (9). The concentrations of ambient O_3 were not unusually high throughout the various sampling periods, Figure 2, indicating there was no extensive photochemical production of pollutants in the ambient air which would adversely impact the building through air brought into the HVAC system (10). The concentrations of ozone in the building were always lower than in the ambient air, but not zero. Also, the concentrations of ozone in the sick room were comparable to those in the administrative office and the copy center. Concentrations of NH_3 were generally higher in the building than in the ambient air, Figure 2. NH_3 is a reflection of room occupancy. The concentrations of ammonia were always highest in the sick room, reflecting the higher occupancy of this room, Figure 2.

NO_2 and NO_x exhibited abnormal diurnal variations on all days when business activity was occurring in the building, e.g. on days one, two, three, and four, Figure 1. NO_x concentrations in both the sick room and the copy center were very high in the morning on these days and then by the afternoon the NO_x concentrations had decreased to near ambient concentrations, Figure 1. A similar pattern, but with a much less pronounced early morning maximum, was seen in the administrative office. This diurnal pattern was completely absent on the last two sampling days, days not preceded by a working day. There was very little difference between the morning and evening concentrations of NO_x on these two days. Days one through four were a Tuesday, Wednesday, Thursday and Friday. Days five and six were a Sunday and Monday. The high morning NO_x concentrations, dependent on the preceding day being a work day, suggest that there was a condition that was unique to the copy center and the sick room but not the rest of the building.

The diurnal pattern seen in the NO_x and NO_2 concentrations in the sick room and the copy center was not present for HNO_3 and particulate nitrate. In general, the concentrations of HNO_3 and particulate nitrate showed little variation from room to room, and overall low concentrations were recorded, Figure 1. However, the concentrations of both of these species were slightly higher indoors than in the ambient samples. This suggests an indoor source for both of these species. This was particularly evident on day two (Wednesday) in the copy center where concentration of HNO_3 was triple the concentrations seen in the other sampling location.

The humidity and temperature in the sick room were both elevated as compared to the other two indoor study areas. The temperature and relative humidity in the copy center and

administrative office averaged $22 \pm 1^\circ\text{C}$ and $43 \pm 5\%$. In contrast, the temperature and relative humidity in the sick room were $26 \pm 1^\circ\text{C}$ and $60 \pm 5\%$. These values border on being unacceptable for a working environment, Table 1.

Air quality questionnaire

No adverse increase in symptoms during work was reported by occupants of the copy center or the administrative office. The number of people completing the questionnaire in the sick room declined each day, from 29 (72.5% of the employees in the office) on the first day of the study to a low of 6 (15% of the employees in the office) on the last day. However, the ratio of employees in the sick room who completed the questionnaire and reported symptom changes while at work was always greater than the 20% standard used to define a sick room, Table 2. The ratio of percent of reporting women to men reporting symptom changes was always about 4:1. The fact that women are more likely to report symptoms than men has been well documented (11,12,13,14). The gender issue in reporting symptoms disappears when the population has hypersensitivity to atmospheric pollutants resulting from allergies, hayfever or asthma (14). Our results from the questionnaire can be considered typical of the expected response from a population residing in a sick room. The three symptoms that were reported to have the greatest change were itching eyes, headache and scratchy/sore throat. The severity of symptom change varied from day to day with headache being the most consistently reported problem.

In the sick room the symptom change was the greatest on day three. Twenty people completed the questionnaire on that day, sixteen women and four men. The average age was 31 years. An increase in symptoms was reported by twelve of the respondents. Forty-five percent of the population stated they had been told they had hay fever. Fifty percent first experienced a symptom increase in the morning while the other fifty percent reported first experiencing symptom increases in the afternoon. There was a negative correlation between peak concentrations of species tested and greatest change in symptoms experienced. On day 3 NH_3 showed peak concentration, but that is the only species that exhibited a high concentration. Day 1 showed the second highest mean symptom change, but again there was a negative correlation between high chemical species concentration and mean symptom change. On day 6 both O_3 and CO showed peak concentration levels in the sick room but the reported mean symptom change on day 6 was the lowest of all sampled days. However, the sample size on day 6 was small, Table 2.

CONCLUSIONS

The uniqueness of this study lies in the fact that only one room in a large building experienced the reported illness symptoms. Analysis of the questionnaire data showed that we were indeed dealing with a sick building syndrome problem (11,12,13,14). The objective of the sampling program was to identify differences between the sick room and the control rooms which might be related to the sick room problem, and then find the possible source or sources of these differences. It has been shown that sick building syndrome is usually not a result of a specific etiologic agent but a combination of factors (12). The only chemical species measured which showed significant differences from normal expected patterns was the unusually high concentrations of NO_x and NO_2 in the morning in both the sick room and the copy center, Figure 1. The abnormal NO_x concentrations probably result from the printing processes in both of these rooms with the associated degassing of NO_x from the ink. This process has been previously associated with sick building syndrome (15). The printing system in the sick room is heavily used at night, after a work day. This, coupled with the decreased ventilation during the night, probably accounts for the unusually high concentrations of NO_x on mornings after the printer has been working all night. This would also account for the lack of high morning NO_x concentrations on the last two days of the study. These two days, Sunday and Monday, were

not associated with computer print runs the preceding night. The presence of elevated NO_x concentrations in association with ozone and volatile organic compounds would be expected to result in the formation of noxious organic species (10). The other difference between the sick room and other control rooms in the study was the elevated temperature and relative humidity present in the sick room. Temperature and humidity have been identified as being factors in sick building syndrome (16).

In summary, the sick room syndrome was probably due to a combination of three factors in the sick room: high NO_x concentrations in the presence of VOC and ozone, high humidity and elevated temperature. Although any one of these factors alone may not cause an uncomfortable working environment, the combined effect is apparently enough to cause the room occupants to become uncomfortable and feel increased illness symptoms. The problem could be alleviated by moving the printer or increasing the HVAC recirculation during the night, lowering the room temperature, and finding and eliminating the source of the increased humidity in the sick room.

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Table 1. Suggested tolerance concentrations for indoor pollutants.

<u>Chemical species</u>	<u>Acceptable concentration</u>	<u>Source*</u>
NO ₂	50 ppb	EPA (17)
CO	9 ppm	NAAQS (17)
CH ₂ O	0.1 ppm	ASHRAE (18)
VOC's	2 mg/m ³	EPA (17)
O ₃	0.05 ppm	ASHRAE (18)
TEMP	20 TO 26° C	ASHRAE (18)
RH	20 TO 70 %	ASHRAE (18)
NH ₃	50 ppm	OSHA (19)

*EPA, Environmental Protection Agency

NAAQS, National Ambient Air Quality Standards

ASHRAE, Modification of American Conference of Governmental Industrial Hygienists

OSHA, Occupational Safety and Health Administration

Table 2. Results of the questionnaire study.

<u>Day*</u>	<u>Total^b</u>	<u>Change^c</u>	<u>Percent^d</u>
1	29	20	69
2	25	16	64
3	20	12	60
4	14	8	57
6	6	2	33

*Day: The day of the study.

^bTotal: The total number of employees who completed the questionnaire. The average room occupancy is 40 employees.

^cChange: The total number of employees reporting an increase in symptoms while at work.

^dPercent: The percent of employees who completed the questionnaire and reported a symptom increase.

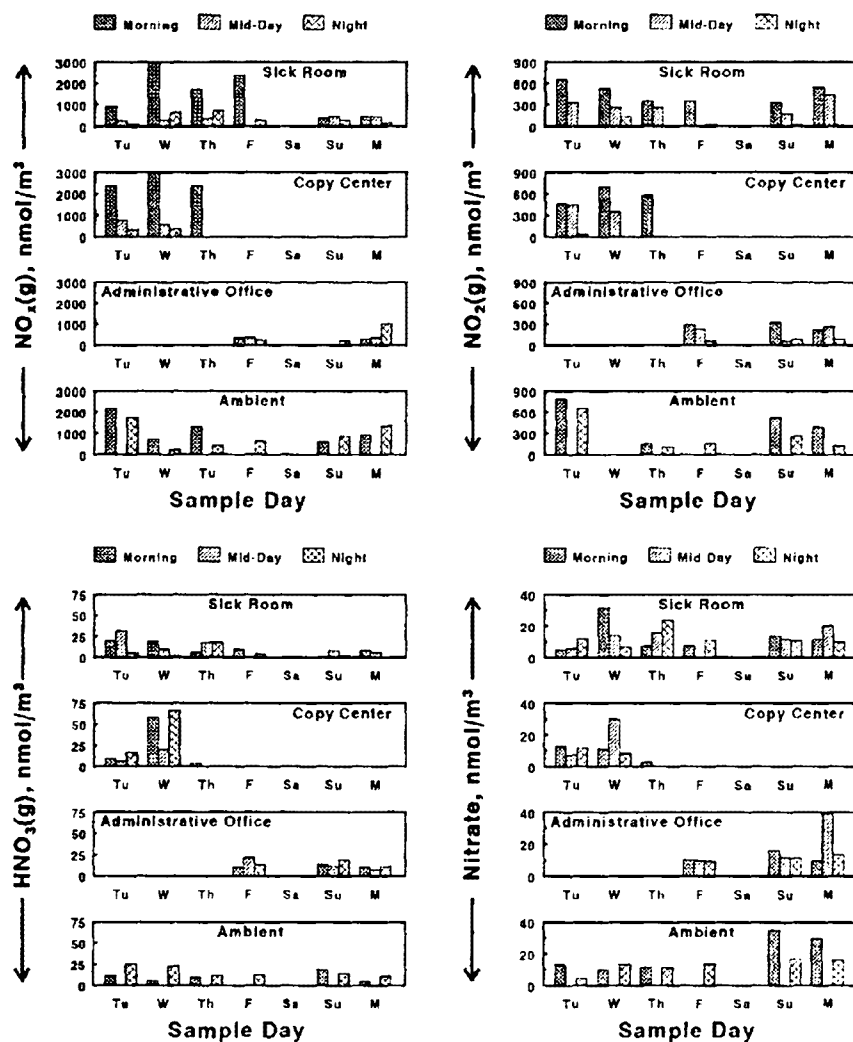


Figure 1. Concentrations of $\text{NO}_x(\text{g})$, $\text{NO}_2(\text{g})$, $\text{HNO}_3(\text{g})$ and particulate nitrate at each sampling location for each sampling period.

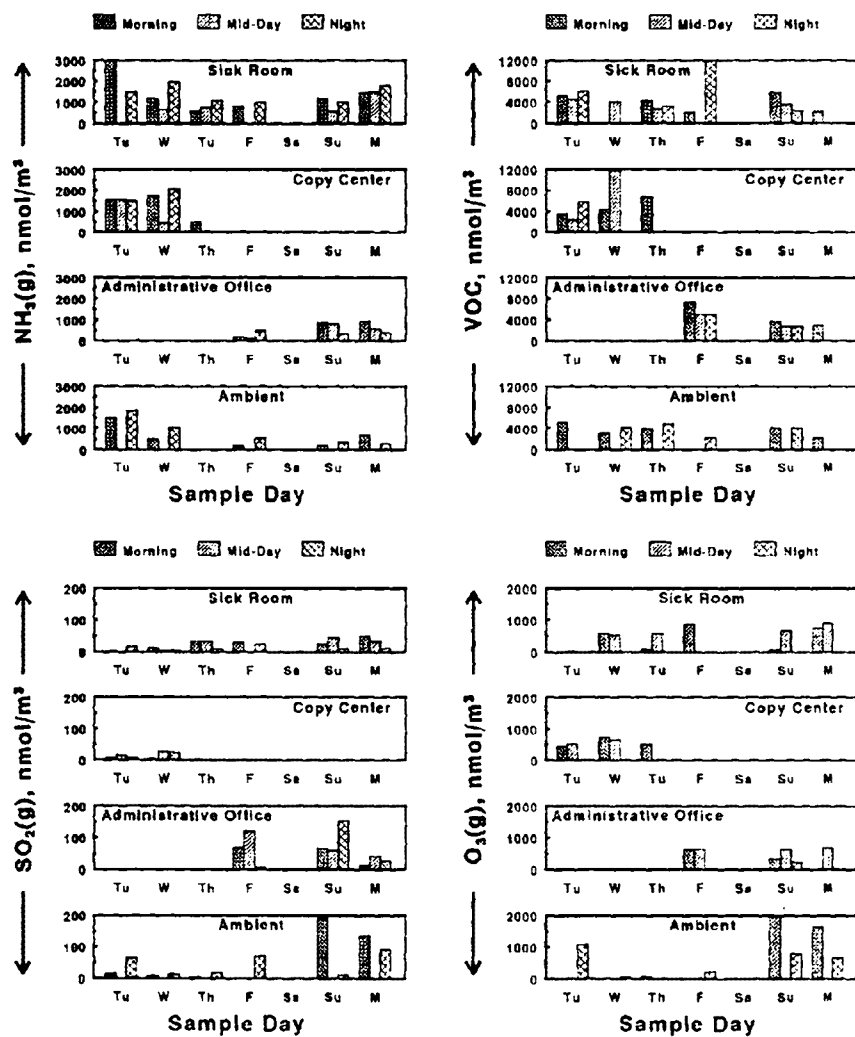


Figure 2. Concentrations of $\text{NH}_3(\text{g})$, VOC, $\text{SO}_2(\text{g})$, and $\text{O}_3(\text{g})$ at each sampling location for each sampling period.

Tracer Gas Measurement of Indoor-Outdoor Air Exchange Rates

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ABSTRACT

Indoor air quality studies often require the determination of the indoor-outdoor air exchange rate. The air exchange rate is defined as the volume of outdoor air that enters the indoor environment in 1 hour divided by the volume of the indoor space. Air exchange rates are usually determined by tracer gas techniques. Researchers at EPA's Air and Energy Engineering Research Laboratory recently completed a study that compared two tracers and three measurement systems: sulfur hexafluoride (SF_6) measured by a photoacoustic infrared detector, SF_6 measured by gas chromatography with an electron capture detector, and carbon monoxide (CO) measured by a non-dispersive infrared detector. Controlled tests, using the tracer gas decay method, were conducted in a small (166L) environmental chamber. Uncontrolled experiments were run in a test house. Data describing the accuracy and precision of each method are presented.

INTRODUCTION

In studies of indoor air quality, a knowledge of the indoor-outdoor air exchange rate is often necessary. The air exchange rate is the rate at which outside air replaces the air in the indoor space and is defined as the volume of outdoor air that enters the indoor environment (typically per hour) divided by the volume of the indoor space. A commonly used method for determining air exchange rates is the tracer decay method. A tracer gas which ideally does not react with the indoor environment is released into the indoor space and mixed with the indoor air. As outdoor air infiltrates the indoor space, the tracer gas is displaced and diluted and its concentration declines according to:

$$C(t) = C_0 e^{-kt} \quad (1)$$

where

$C(t)$ = concentration of tracer gas at time t (ppb)

C_0 = concentration at time zero (ppb)

k = air exchange rate (h^{-1})

t = time (h)

A variety of instrumentation and tracer gases are available for conducting tracer decay testing. Three techniques are examined here: photoacoustic infrared detection of SF_6 , detection of SF_6 by gas chromatography with an electron capture detector (ECD), and CO measured by a non-dispersive

infrared continuous monitor. In this investigation, controlled tests were conducted in a 166L stainless steel test chamber, and an uncontrolled test was conducted in a test house.

METHODS AND RESULTS

Monitoring Techniques

The three measurement systems used include a Thermo-Electron model 48 gas filter correlation CO monitor, a Shimadzu gas chromatograph (GC) with electron capture detector, and a Brüel and Kjær model 1302 multi-gas monitor.

CO Monitor. The Thermo-Electron model 48 gas filter correlation monitor is a continuous emission monitor using infrared (IR) detection. The instrument output is updated every 10 seconds and is connected to a computer running LabTech Notebook for data acquisition. The computer creates 1 minute averages which are written to an ASCII data file. The system is normally run with a 2 minute purge between 1 minute sampling intervals to allow for monitoring of multiple indoor locations sequentially. Although this experiment required only one sampling location, the system was still operated under its standard operational mode. Therefore the sample frequency of the system was one sample every 3 minutes. A multipoint calibration was conducted to ensure linearity. The system was calibrated over a range of CO concentrations of 0 to 254 ppm.

GC/ECD. A Shimadzu GC, equipped with an electron capture detector, was used. Samples were collected by dual sample loops. While carrier gas flows through one loop into the GC, a mass flow controller and pump purge the second with sample air. The GC is connected to a Hewlett Packard integrator and then to a computer running ChromPerfect for data acquisition. Sample frequencies of approximately one sample every 4 minutes allowed resolution of the SF₆ from the air peak. The column used for this analysis was a carbosieve packed column. The GC was operated isothermally at 45°C.

Brüel and Kjær 1302. The model 1302 is a photoacoustic IR gas monitor containing up to five IR filters and a water vapor filter. The water vapor filter is necessary to compensate for the presence of IR absorption by water across most of the IR spectrum. The manufacturer states that the system is linear for at least four orders of magnitude starting at its detection limit of 5 ppb for SF₆. The system was factory calibrated and operated with the Brüel and Kjær 7620 applications software. The software operates the entire system and provides data acquisition. Sample frequency for these experiments was approximately one sample per minute.

Test Chamber Configuration

In order to provide an ideal environment for comparison of the three techniques, controlled testing occurred in a 166L stainless steel environmental test chamber. Zero-grade air was supplied to the chamber at a constant rate using a mass flow controller. Mixing in the chamber was achieved by introducing the air into the chamber through a length of perforated tubing coiled around the bottom of the chamber and by using a small mixing fan near the bottom of the chamber. When exiting from the chamber, the air passed through a sampling manifold which supplied air to each of the monitors simultaneously. Since the pump for the GC could pull more air from the sampling manifold than was supplied by the airflow from the chamber, the flow to the GC was limited by a mass flow controller. Tracers were injected into the chamber via an injection port at the inlet between the mass flow controller and the chamber.

Test Procedure for Chamber Tests

In order to evaluate the three techniques under a variety of conditions, tests were conducted at

air exchange rates of approximately 0.75, 1.30, and 2.00h⁻¹. For each air exchange regime, two tests were conducted. Actual air exchange rates were determined by measuring the flow rate into the chamber and dividing by the chamber volume. Tracers were then injected and the decay followed for 2 hours. In each case the first hour of data was discarded in order to allow ample time for the chamber to become well-mixed.

Data Analysis

Solving for the air exchange rate in equation (1) yields:

$$k = -\ln[C(t)/C_0]/t \quad (2)$$

Experimentally, air exchange rates for tracer decay data are calculated by using the natural log of the concentration data as the dependent variable in a linear regression versus time in hours. Accuracy of the methods is examined by comparison of the calculated air exchange rates versus the measured flow rates. Precision is investigated by examining duplicate tests. Since the photoacoustic monitor and the CO IR monitor both have linear responses over the range of concentrations used in the testing, calibration of these instruments was straightforward. The ECD, however, was quite non-linear. Equation (3) was used to convert the raw data (area counts) into concentrations (in ppb):

$$C = 7.38 + (0.0007964)A + (4.6467 \times 10^{-6})A^2 \quad (3)$$

where

C = concentration

A = area counts

It was noted during data analysis that a different curve fit,

$$C = -\ln(1 - A / 490300) / 0.00149 \quad (4)$$

gave significantly different results in spite of the fact that the two curves are extremely similar. Figure (1) plots the two curves and the calibration points.

Results of Chamber Testing

Table 1 summarizes the results of the six small chamber tests conducted. Results for the GC/ECD are given using both of the calibration curves to demonstrate the variation caused by the slight differences in the curves. Accuracy is defined as $100 - |measured - actual| \times 100 / actual$. Accuracies for each technique are summarized in Table 2. From this data, the average accuracies of the techniques are 95.2% for photoacoustic IR, 96.7% for analysis by ECD, and 96.3% for CO via IR monitor. Precision is indicated by the percent difference between duplicate runs. Since runs 1 and 2 were not true duplicates, they are not comparable in this way. Precision data are summarized in Table 3.

Finally, it is important to examine the results across all runs for each of the three techniques. Using a Student's t-test can determine if the differences between the results of each technique and the actual air exchange rates are due to normal statistical variation or represent true discrepancies. If a series of data points has a t-value less than t(0.05), then the results of the technique may be considered to be equivalent to the actual air exchange rate with variations being attributed to normal statistical error. For this evaluation, all data were normalized to allow equal weighting of data across each of the air exchange regimes examined. The results of the t-test indicate that the air exchange rates determined by each of the three methods are correct within normal statistical variation. However, air exchange rates calculated by the application of equation (4) to the GC/ECD data fail to pass the t-test and therefore show error which cannot be attributed to normal statistical variation.

Uncontrolled Testing in Test House Environment

In addition to the controlled testing previously described, a single uncontrolled test using the three techniques was conducted in a test house located in Cary, NC. The house used is a three bedroom single-story dwelling with central heating/air conditioning. The internal volume of the house is 305 m³. The attached garage has been converted to laboratory space where all the monitors used in this test were located.

The test was conducted by dosing the house with CO and SF₆ through 1/4-inch Teflon lines leading into the air handling system's return air vent. Approximately 27L of CO and 8.6L of SF₆ were released. The heating/air conditioning fan was kept on continuously to guarantee good mixing. Indoor temperature was set for 22°C. Each of the monitoring systems sampled from the house via independent sampling systems. The GC system used a pump which pulled sample from the house directly through the sampling loops. The CO monitor has an internal pump which sampled from a sample stream (since the internal pump was not strong enough to pull from the house). The Brüel and Kjær system has an internal pump which pulled directly from the house. All three systems sampled from the same location in the den of the house. Linear regressions from the resulting data were conducted over 1 hour time periods after an initial 1/2 hour of data was discarded for mixing purposes for each of the methods. The air exchange rates determined by each of the three detectors ranged from 0.50 to 0.52.

CONCLUSION

All three methods investigated yielded results which are statistically equivalent to the actual air exchange rates. Data analysis for the CO analyzer and the photoacoustic IR monitor was straightforward since both those instruments exhibit a very linear response over the range of concentrations used in this testing. The analysis of the ECD data was complicated by the non-linear nature of this particular detector. While it is possible to obtain accurate air exchange rates from each of the systems using the tracer decay method, it is recommended that the detector used have a very linear response over the range of interest in order to avoid possible confusion caused by the difficulty of ensuring an accurate fit to the calibration data generated by a non-linear system. In order to be confident that the calibration curve assigned to a non-linear detector is acceptable for tracer decay determination of air exchange rates, the system must be tested by applying the fit to data from a controlled environment with a known air exchange rate.

Table 1. Measured versus actual air exchange rates.

TEST NUMBER	ACTUAL ACH ⁻¹	SF ₆ VIA PHOTO- ACOUSTIC IR	SF ₆ VIA GC/ECD EQUATION (3)	SF ₆ VIA GC/ECD EQUATION (4)	CO VIA IR
1	0.79	0.85	0.85	0.74	0.86
2	0.74	0.74	0.74	0.64	0.70
3	1.98	2.21	1.88	1.79	1.94
4	1.98	2.16	1.86	1.79	1.93
5	1.27	1.27	1.27	1.09	1.29
6	1.27	1.26	1.28	1.10	1.25

Table 2. Accuracy of Techniques.

TEST NUMBER	SF ₆ VIA PHOTO- ACOUSTIC IR	SF ₆ VIA GC/ECD	CO VIA IR
1	92.4	92.4	91.1
2	100	100	94.6
3	88.4	94.9	98.0
4	90.9	93.9	97.5
5	100	100	98.4
6	99.2	99.2	98.4

Table 3. Percent differences within duplicate runs.

TEST NUMBER	SF ₆ VIA PHOTOACOUSTIC IR MONITOR	SF ₆ VIA GC/ECD	CO VIA IR
3 & 4	2.29	1.07	0.52
5 & 6	0.79	0.78	3.15

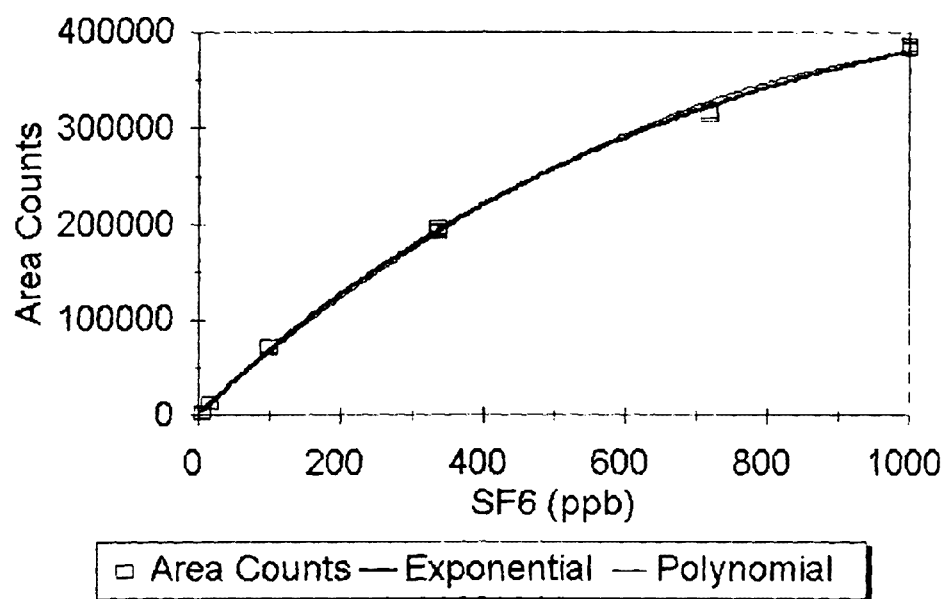


Figure 1 Comparison of calibration curves

Reference

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Measurement of Airborne Particle Counts and Mass in a Healthy Building During a One-Year Cleaning Effectiveness Study

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ABSTRACT

The Research Triangle Institute, under a cooperative agreement with the U.S. EPA's Environmental Criteria and Assessment Office conducted a year-long field study to understand and assess the effectiveness of an improved cleaning program to better indoor air quality. A four-story healthy building was monitored with a Laser Particle Counter (LPC), commonly used in clean rooms, to characterize airborne particle size ranges of >0.5 to $>15\ \mu\text{m}$. Monitoring was also done with a Fine Particle Sampler (FPS) that measures airborne dust mass concentrations which are routinely used to assess dust exposure and potential health effects. LPC and FPS measurements were taken once monthly on each floor for five months, with building housekeeping performed as usual. Professional cleaners then deep cleaned the building which included walls, windows, furniture, light fixtures, bathrooms, and tiled and carpeted floors, after which, an improved cleaning regimen was instituted and monitoring continued for seven months.

While LPC total particle counts correlated well with those outdoors, they were of limited value, providing particle size distributions which did not correlate with total airborne particle mass. Mean total particle count size distributions were similar on the four floors -- decreasing as particle size increased, and they remained relatively constant over the study. On the second floor, LPC large particle counts ($5, 10, 15\ \mu\text{m}$) decreased significantly, while small particles ($0.5, 1\ \mu\text{m}$) increased immediately after cleaning. LPC particle counts may be most useful in preliminary site evaluations or in locating bioaerosol sources. FPS mass particle mass concentrations were low in the building (5 to $11.5\ \mu\text{g}/\text{m}^3$). The second floor, a child care facility which had the greatest activity levels and multiple accesses to an outdoor sand moat, also had the highest concentration of total airborne dust. In comparing the two modes of measurement in a healthy building, FPS total airborne dust mass gave the most meaningful data and showed a 48% improvement with improved cleaning.

INTRODUCTION

The Research Triangle Institute (RTI), under a Cooperative Agreement with the U.S. Environmental Protection Agency's (EPA) Environmental Criteria and Assessment Office conducted a year-long, field study to understand and assess the effectiveness of an improved, cleaning program to better indoor air quality. The building was 20 years old, and had four-stories with a total of 18,000 ft^2 . The multi-use building consisted of day care, offices, and medical laboratories. The building is inset into a hill such that there are ground level entrances on the first, second, and third floors. The building had no history of indoor air complaints, and after an intensive screening at the beginning of the study, it was considered to be a healthy building. The building was monitored with a Laser Particle Counter (LPC), commonly used in clean rooms, to characterize airborne particle size ranges of >0.5 to $>15\ \mu\text{m}$. Monitoring was also done with a Fine Particle Sampler (FPS) that measures airborne dust mass concentrations, which are routinely used to assess dust exposure and potential health effects. The EPA uses airborne particle mass to define their national ambient air quality M_{10} (particles less than $10\ \mu\text{m}$) standard. LPC and FPS measurements were taken monthly on each

floor. For five months, measurements were taken while building housekeeping was performed as usual. Professional cleaners then deep cleaned the building which included walls, windows, furniture, light fixtures, bathrooms, and tiled and carpeted floors. Some airborne particle measurements were taken soon after deep cleaning, after which, an improved cleaning regimen was instituted and monitoring continued monthly for seven months.

METHODS

LPC measurements were taken with a Met-One Model 217 Laser Particle Counter. The unit measures particles $>0.5\mu\text{m}$ on one channel and particles >1 , >5 , >10 , or $>15\mu\text{m}$ simultaneously on another channel. The user must select each particle size $>0.5\mu\text{m}$ separately and take multiple measurements to get particle counts of the other particle sizes. The sample rate was 0.1 cfm, and one-minute samples were taken for each particle size at two or three locations on each of the four floors on a sample day. The unit was placed at different heights from the floor according to activity levels in each location. Sampling heights were 30 cm in day care areas, 90 cm in offices, and 120 cm in halls. Outdoor samples were also taken at ground level on the 1st and 3rd floors, and on the roof at the air intake.

FPS measurements were taken with a URG (Carrboro, NC) Fine Particle Sampler. The unit has an adjustable inlet positioned over a filter which can be set to various particle size cut points. For this study, it was set to collect total airborne particulates. The unit was used to draw air at 28 liters per minute through a $3\mu\text{m}$ polycarbonate filter for 24 hours. Measurements were taken once monthly on each floor of the building in a hallway. The filter was positioned at approximately 1 meter above the floor. The filters were weighed on a Perkin-Elmer Microbalance which was calibrated with NIST traceable weights. Filters were equilibrated at 47% relative humidity prior to weighing. A laboratory control filter was used throughout the study, and field blanks were used as measures of quality control.

RESULTS

The particle size distribution for the second floor as shown in Figure 1 was similar on all floors of the building during the study. As particle size increased, counts decreased for all indoor and outdoor measurements. A comparison of mean total particle counts indoors and outdoors is shown in Figure 2. Outdoor counts correlated well with, and were consistently higher than indoor counts. The second floor showed the most dramatic reduction of airborne particles immediately after cleaning (Figure 1) for all but the smallest particle size range ($0.5\mu\text{m}$) which showed a slight increase. For particles $\geq 1\mu\text{m}$, $\geq 5\mu\text{m}$, and $\geq 10\mu\text{m}$ aerodynamic diameter, the second floor had statistically significantly greater particle counts than the other three floors ($p\leq 0.05$). Particle counts at each sampling location were relatively uniform over time, but there were often large differences between sampling locations on each floor of the building. Mean particle counts were relatively constant on each floor over the course of the study.

Mean total airborne dust mass concentrations for the study as shown in Table 1 were low in the building, ranging from values of $5.0\mu\text{g}/\text{m}^3$ on the 4th floor to $11.5\mu\text{g}/\text{m}^3$ on the 2nd floor. The EPA PM_{10} standard is $50\mu\text{g}/\text{m}^3$ for 24 hour annual average, and $150\mu\text{g}/\text{m}^3$ for individual daily averages. Airborne dust concentrations were 44-51% lower on each floor in the period following deep cleaning than before cleaning, despite wide variations in monthly measurements. The building mean airborne particle concentration during the improved housekeeping period was significantly less ($p\leq 0.05$) than during routine housekeeping. Figure 3 shows the mean monthly airborne dust mass data for each floor during the study.

CONCLUSIONS

Monthly, individual, particle counts and airborne, dust mass did not correlate. This may be due to the very different methods by which the two measurements were made. Particles were counted for very short periods (1 minute sampling) and all floors were monitored on the sampling day, while 24 hour samples were taken on consecutive days for mass determinations. Because air in a building may not be well mixed everywhere, short-term air sampling in various locations may yield samples that represent a range of particle counts in a relatively nonhomogeneous airstream. Airborne dust was collected for 24 hours, effectively integrating many small samples into a larger one. Preferably, particle counts should be taken several times during the period in which dust mass samples are taken and probably should include additional sampling locations.

Overall, counts of particles and mass concentrations of airborne dust were consistently higher on the second floor than on the others. Generally, the lowest particle counts and airborne dust mass levels were on the fourth floor. Higher airborne particle counts and dust masses on the second floor may have been influenced by several variables. First, there was frequent opening of doors to the outdoors along the sand moat play area, and the propping open of second floor hallway doors, which was a common practice during much of the study. This practice may have effectively lowered the air pressure on the second floor, allowing infiltration of outdoor air and particles. This effect would be consistent with higher indoor particle counts observed in telecommunications buildings following shut-down of HVAC fans.¹ Secondly, day care residents (of whom there are 50 on the 2nd floor) and workers also track in soil from the sandy moat, potentially contributing elevated airborne particle loads. Surface contamination, whatever its origin, may become airborne and inhaled by workers or casual passers by.² Also, floors in hospital wards contaminated with large numbers of bacteria have been implicated as reservoirs of hospital infection through the dispersal of the bacteria into the air.³ Entrances to the other floors of the building have concrete aprons or staircases that may reduce the amount of tracked in dirt. In addition, there were greater activity levels on the second floor associated with rooms full of children, indoor sand and water boxes, a small kitchen, and pet animal cages, as opposed to floors with offices and laboratories -- such as the fourth floor having less dense occupancy.

Mean total airborne particle counts remained relatively stable over the entire study, unlike airborne dust mass, which showed a 52% decline after total building cleaning. Particle count data revealed nonhomogeneous local microenvironments, but mean particle counts reflected the fact that building use remained constant over the course of the study. Particle counts may provide better measures of the homogeneity of an indoor environment, and may be a more sensitive measure of variations from the mean in specific locations. Thus, particle counters may be most useful in surveys to detect nonhomogeneities of indoor air, such as searching for sources of biopollutants. Because particle counts yield immediate results and are relatively inexpensive, their greatest advantage may be in obtaining preliminary information for a sampling plan in a complaint situation. Additional research is needed to determine the role of particle counters in screening and/or assessing indoor air quality.

The institution of improved cleaning practices accompanied the general decline in airborne dust mass seen from January - July, 1993. One such practice, the use of damp, disposable dust cloths, may have contributed to this. Cleaning re-disperses dust, and it is generally believed that dry methods stir dust more than wet methods.⁴ Total LPC particle counts were comprised by several orders of magnitude of particles $<0.5 \mu\text{m}$. Most smaller particles probably remained suspended, and only larger particles settled on surfaces that were dusted. Since the mass contributions of larger particles is disproportionate to their numbers, removing larger, heavier settled particles may not affect overall particle counts, while decreasing the mass of suspended particles. LPC airborne mass concentrations provided the most useful data in this study, showing a significant improvement after deep cleaning and improved housekeeping. Airborne mass concentrations are also likely to be the most useful in determining the potential for health effects.

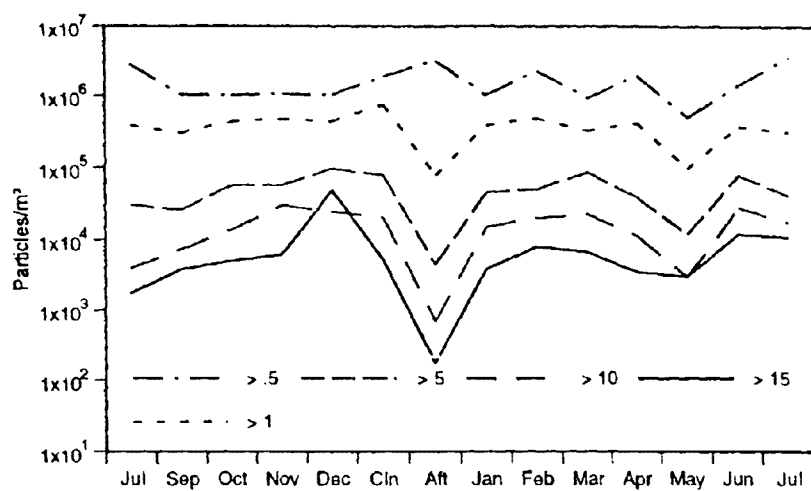


Figure 1. Particle Counts on Second Floor

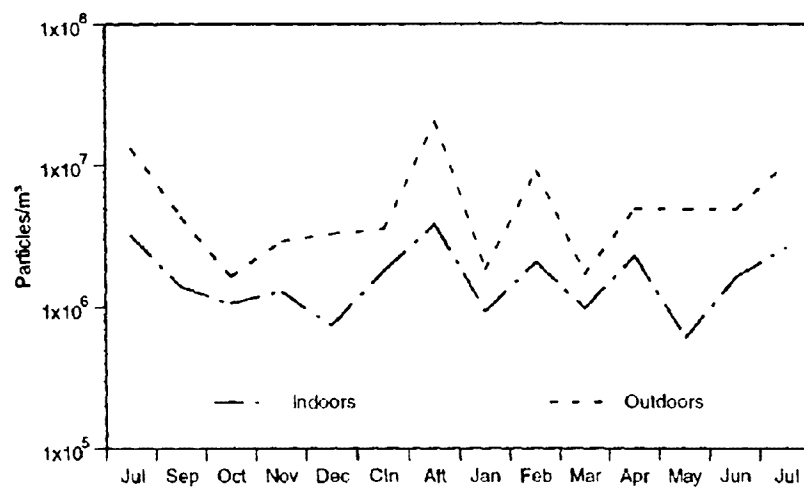


Figure 2. Total Particle Counts - Indoors and Outdoors

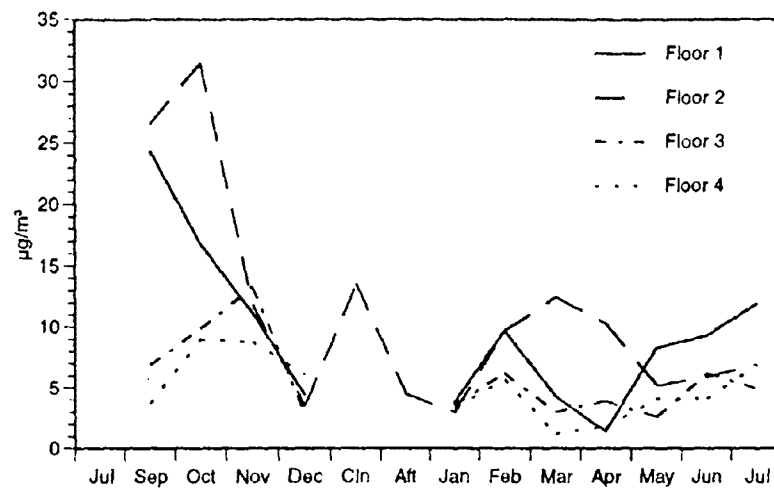


Figure 3. Monthly Airborne Dust Mass

Table 1. Airborne Dust Mass in $\mu\text{g}/\text{m}^3$

Phase	Date	Floor 1	Floor 2	Floor 3	Floor 4	Building Mean
Routine Housekeeping	9/10/92	24.4	26.6	6.9	3.8	15.4
	10/8/92	16.8	31.5	9.9	9.0	16.8
	11/12/92	11.2	11.9	13.3	8.8	11.3
	12/10/92	4.4	3.5	2.8	6.1	4.2
	Mean	14.2	18.4	8.2	6.9	11.9
	Std Dev	8.5	12.9	4.5	2.5	5.7
During Deep Cleaning	12/19/93 (a)	13.6				
After Deep Cleaning	12/23/93 (a)	4.5				
Improved Housekeeping	1/14/93	3.8	3.0	3.6	3.4	3.4
	2/11/93	9.7	9.7	6.2	5.7	7.8
	3/18/93	4.3	12.5	3.0	1.2	5.2
	4/15/93	1.4	10.3	3.9	1.8	4.4
	5/13/93	8.3	5.2	2.6	4.1	5.0
	6/10/93	9.3	5.9	6.2	4.1	6.4
	7/8/93	11.9	6.9	4.9	6.8	7.6
	Mean	6.9	7.6	4.3	3.9	5.7
	Std Dev	3.8	3.3	1.5	2.0	1.6
Year (b)	Mean	9.6	11.5	5.8	5.0	8.0
	Std Dev	6.6	9.3	3.3	2.6	4.6
Change from Routine to Improved Housekeeping		-51%	-58%	-47%	-44%	-52%

a - Measurements were taken on the second floor only during and after cleaning

b - Year-long mean for routine and improved housekeeping only

ACKNOWLEDGEMENT

The research presented in this document was funded by the U.S. Environmental Protection Agency under Cooperative Agreement number CR-815509-02-1 to the Research Triangle Institute.

DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency or the Research Triangle Institute.

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Effects of Activated Charcoal Filtration and Ozonation on Hydrocarbon and Carbonyl Levels of Ambient Air Used in Controlled-Exposure Chamber Studies of Air Pollutant Human Health Effects

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ABSTRACT

Air sampling experiments were done in 1985, 1987, and 1993 at the human exposure chamber facilities of the U.S. EPA Health Effects Research Laboratory in Chapel Hill, NC. Measurements of VOCs by GC-FID and aldehyde measurements by the DNPH silica gel cartridge method were made, comparing levels at the outside air intake to levels in the human controlled-exposure chamber. Ambient air passed through activated-charcoal filters can contain varying residual amounts of water vapor and gaseous pollutants such as hydrocarbons, oxygenates, and other organic and inorganic species. When the charcoal-filtered air stream is exposed to high-intensity radiation to generate ozone for use in human controlled-exposure experiments, there may be formation of compounds other than ozone. In this study, filtration appeared ineffective in removing hydrocarbons; and with ozonation of the airstream, carbonyl compounds increased.

INTRODUCTION

The current National Ambient Air quality Standard (NAAQS) for ozone is based upon data from controlled exposures of experimental animals and human volunteers and from various types of population exposure studies. Controlled exposures of human volunteers in specially designed chambers have provided key data for the health risk assessment contributing heavily to the basis for the current primary, health based ozone standard (1,2). In particular, findings from three controlled-exposure studies (3-5) of human volunteers provided important scientific evidence on human health effects used by the U.S. Environmental Protection Agency in its 1993 decision on the ozone NAAQS (2,6).

Public comments received by EPA during the most recent review (1986 through 1993) of the ozone NAAQS included questions regarding the possible formation of chemically or biologically reactive species during the generation of ozone for human controlled exposures. In brief, the central questions posed concerned the level of nonmethane hydrocarbons in the ambient air stream sent to the ozone generator and the possible formation during ozonation of peroxides or other reactive, irritant pollutants that could elicit respiratory symptomatic or functional responses in human subjects so exposed.

These questions were regarded by EPA as relevant, particularly since the bulk of the evidence for human pulmonary function decrements and respiratory symptoms came from studies in which ozonized ambient air was used for human controlled exposures to ozone. In addition, theoretical considerations indicated that at the wavelength and intensity of the mercury lamp ozone generator oxygenated compounds might indeed be produced, depending upon factors that included the level and kind of hydrocarbons in the air stream passing through the ozone generator. The availability nearby of the U.S. Environmental Protection Agency's human exposure chamber provided an opportunity for exploring these questions. The exposure facility is called the Clinical Laboratory for Exposure Assessment of Noxious Substances, and will hereafter be referred to by its acronym, CLEANS.

STUDY OBJECTIVES

This study had three principal, related objectives:

- 1) To determine the presence or absence in the CLEANS exposure chamber of air contaminants, especially contaminants that could conceivably interfere with the results of controlled exposures to ozone and could potentially produce misleading results.
- 2) To evaluate the effectiveness of the air train purification system in removing organic compounds (e.g., NMOCs, carbonyl compounds) from the ambient air streams ozonated and mixed to supply the exposure chamber.
- 3) To determine the possible production of reactive species such as peroxides during ozonation of the ambient air stream.

EXPERIMENTAL DESIGN AND METHODS

The engineering configuration of the EPA CLEANS facility at Chapel Hill has previously been described (7,8). A simplified schematic of the ambient air train and purification systems is shown in Figure 1. Outside air (1200 cfm) is prefiltered; passed through a bed of activated charcoal (~45 lb of 6- to 12-mesh activated charcoal in a 1-inch-thick bed); dried to about 9% RH by passage through a spray of chilled lithium chloride brine; and then passed through HEPA (high-efficiency particulate) filters. (Lithium chromate is used to keep the dehydrating brine clean.)

The purified air stream is then split into two, with 200 cfm going to the ozone generator and 1000 cfm to a steam rehumidifier. These two streams are recombined, post-ozonation, with 6800 cfm of recirculated air before entering the exposure chamber. The resulting air stream (8000 cfm) exits the chamber, is filtered a second time, and is split again, with 1200 cfm being exhausted through a roof vent and 6800 returning to the chamber air train.

Ozone generation is achieved by irradiation of the purified air stream (200 cfm) with low-pressure mercury lamps. Mercury lamp ozonators produce O_3 by direct photodissociation of O_2 at 185 nm. However, water vapor also absorbs at 185 nm (9, as cited in 8), producing OH radicals; and significant levels of OH radicals are also produced by the reaction of excited O atoms with water. It has been calculated that steady-state levels of OH radicals in the ozonator in the CLEANS air train greatly exceed ambient concentrations (8).

The study reported here was designed to compare indoor and outdoor concentrations of total nonmethane organic compounds, peroxides, and carbonyl compounds, to determine the effectiveness of filtration in removing contaminants from the air stream used to supply the EPA CLEANS human exposure chamber. The study was also designed to compare ozonated and non-ozonated chamber air to determine the effects of ozonation on peroxides, carbonyl compounds, and nonmethane hydrocarbons. To that end, samples of outdoor air and of chamber air were simultaneously taken without the generation of ozone (to determine filtration effects) and then with the generation and equilibration to steady-state chamber levels of pre-selected ozone concentrations (to determine the effects of ozonation). No attempt was made to sample at various points within the air train.

Sampling was conducted on 5 days: 12/17/85, 4/22/87, 6/17/87, 6/23/93, and 12/16/93. At each sampling session, samples were taken simultaneously of air in the chamber and air entering the outside air intake duct. Samples were collected within 6 inches of the intake port outside the building and at central points in the chamber that approximated nose-eye level of human experimental subjects (none present during these sampling experiments). The first paired indoor-outdoor samples were taken with non-ozonated chamber air. Subsequent paired samples were taken at predetermined, equilibrated levels of ozone in the chamber.

Samples were collected into stainless steel spherical canisters, using metal bellows pumps (12/17/85 and 4/22/87), with special low-level sampling equipment (from R. Rasmussen; 6/23/93), or with evacuated stainless steel canisters fitted with calibrated needle valves (6/17/87 and 12/16/93). Sampling lines were 3/16-inch i.d., 2-meter long FEP Teflon.

Samples for NMOC analysis were collected over 10 minutes on 12/17/85 (zero and 400 ppb ozone in chamber) and on 12/16/93 (zero, or 120, or 250 ppb ozone in chamber). On all other sampling days, integrated 1-hour samples were collected. Peroxides were measured by the luminol method of Kok et al. (10). Carbonyl compounds were collected and analyzed using a DNPH-coated silica gel cartridge/HPLC method (11) and, on one sampling day (12/16/93), a DNPH-acetonitrile impinger collection method (12) was also used to verify cartridge measurements of formaldehyde. Sampling times for the carbonyl compounds were a minimum of 20 minutes (longer on the first sampling day, 12/17/85). Nonmethane hydrocarbons were measured by the GC-FID speciation method previously described by Scila et al. (13).

Except for ozone levels, chamber conditions were consistent across sampling days. Chamber air was maintained at 22°C and 40% RH throughout the study. Outdoor conditions varied by season and time of day, as well as with vehicle traffic and activity outside the building. Between the 1987 and 1993 experiments, the air train intake port was moved from the side of the building (2 meters above the ground) to the roof of the one-story building.

RESULTS AND DISCUSSION

As indicated in Figure 2, filtration is not particularly effective. It should be emphasized that, as described earlier, the air train used to supply the exposure chambers not only uses fresh ambient air but also uses recirculated air. This recirculated air, plus the possibility of some breakout from the charcoal bed, probably accounts for the presence in the chamber at zero ozone concentrations of NMOC and carbonyl levels in excess of those seen in ambient intake air.

Concentrations of NMOCs in the chamber in the presence of ozone were in some cases, but not all, lower than those in outdoor air. Where NMOCs were in excess in the chamber over and above outdoor concentrations, the differential was less in ozonated chamber air than in zero ozone chamber air. This is consistent with findings of the Rancho Los Amigos research group in Downey, CA (Ollison, 1985).

Peroxides were increased in chamber air, but did not occur at high levels even at the highest ozone concentrations generated (400 and 500 ppb). For this reason, peroxide concentrations were not measured on the 1993 sampling days, when lower ozone concentrations were used. No detectable hydrogen peroxide was found in chamber air in the absence of ozone. The following levels of hydrogen peroxide and organic peroxides were found at the respective levels of ozone generated: (1) At 250 ppb ozone, 3.4 ppb H_2O_2 and 0.14 ppb organic peroxide; (2) at 400 ppb ozone, 3 ppb and 4 ppb H_2O_2 for two separate samples (organic peroxide not measured); and (3) at 500 ppb ozone, 5 ppb H_2O_2 and 0.8 ppb organic peroxide. In these three separate experiments, no hydrogen peroxide or organic peroxide was detected in outside ambient air samples. In a fourth, <1 ppb H_2O_2 was detected in outside air.

The most notable finding of the study is the production of carbonyl compounds during the generation of ozone. Figure 3 shows changes in carbonyl compound concentrations in chamber air as a function of the ozone concentration. Although specific points within the air train were not sampled, theory supports the production of these carbonyl compounds at the ozone generator, as well as the possible titration of olefins by ozone, with subsequent cleavage and oxidation. Because of the known chamber conditions—lighting, air exchange rates, etc.—the observed increases in carbonyl compounds in the ozonated air stream are postulated to result from reactions in the mercury-lamp ozone generator. Given the lack of close correspondence between NMOC concentrations and carbonyl concentrations it appears (1) that carbonyl production is not carbon-limited, that is, it is not dependent on NMOC concentration under the conditions of this study; and (2) that carbonyl production is highly dependent on the ozone concentration being produced by the ozonator.

As the filtration data show, there was a trend for less removal of carbonyl compounds and light molecular-weight NMOCs by the air train purification system. One might expect from those data that carbonyl concentrations in the chamber would fluctuate randomly if they were the result of intake of ambient air and possible slow buildup from recirculation of ambient air. However, the increase was

consistently related to the level of ozone being generated. This also implies the destruction within the air train of previously formed carbonyl compounds, but not by filtration, as the filtration data indicate. The atmosphere in and near the ozone generator is dynamic and may result in photodegradation of existing compounds while also producing new compounds.

It should be emphasized that the concentrations of carbonyl compounds observed in this study may represent the lower bounds of possible production during ozonation. This is indicated by the finding of Arnts and Tejada (14) that ozone is a negative interference in the DNPH-silica gel cartridge method for collecting and analyzing carbonyl compounds. Note that no ozone denuder/scrubber was used in these experiments; the Arnts and Tejada paper appeared after most of the sampling and analyses had occurred.

CONCLUSIONS AND RECOMMENDATIONS

The ozonation of ambient air to supply the atmosphere for controlled ozone exposures of human volunteers has been shown to result in the disappearance, though inconsistent, of carbon from hydrocarbons in the air stream and a consistent increase in carbonyl compounds, along with the production of an insignificant amount of peroxides. While this study was not extensive enough to permit carbon balance studies or modeling of the kinetics involved, the qualitative trends toward decreased hydrocarbons and increased carbonyls are clear. Whether the carbonyl compounds occur in sufficiently high concentrations to affect any of the results obtained from controlled exposures to ozone over the range of 120 to 500 ppb ozone in CLEANS or in similar exposure facilities is a question to be examined by the health researchers. The occurrence, however, of carbonyl compounds as the result of ozonation of ambient air indicates that careful engineering design and quality control measures should be observed in all human and animal exposure chambers, including an examination of the composition and chemistry of the atmospheres introduced into the exposure chambers.

Options for preventing the formation of unwanted contaminants during generation of ozone atmospheres include the use of a more efficient ozone generator (e.g., silent discharge) and the use of clean tank air or oxygen for ozonation and subsequent mixing with an ambient air stream to supply the exposure chamber with ozonated air. Other steps, such as high-temperature combustion, prior to ozonation, could also be taken for preventing the inadvertent production of carbonyl compounds and even more reactive compounds such as the peroxides.

Finally, it should be pointed out that EPA has built a new controlled-exposure facility and the CLEANS exposure chambers will no longer be used once the new facility is fully operational.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the impetus for this study provided by Dr. Will Ollison, American Petroleum Institute, and helpful discussions with Dr. Ollison. In addition, the authors gratefully acknowledge the timely and capable technical assistance of Dr. Silvestre Tejada, U.S. EPA, for carbonyl analyses, and of Mr. Robert L. Seila, U.S. EPA, and Mrs. Amalia Alexoudis, ManTech Environmental, for sampling assistance. Dr. Timothy R. Gerrity, Chief, Clinical Research Branch, U.S. EPA, and staff of the CLEANS facility are gratefully acknowledged for their helpfulness and cooperation during this study.

DISCLAIMER

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer-review and administrative policy and approved for presentation. Mention of trade names of commercial products does not constitute endorsement or recommendation for use.

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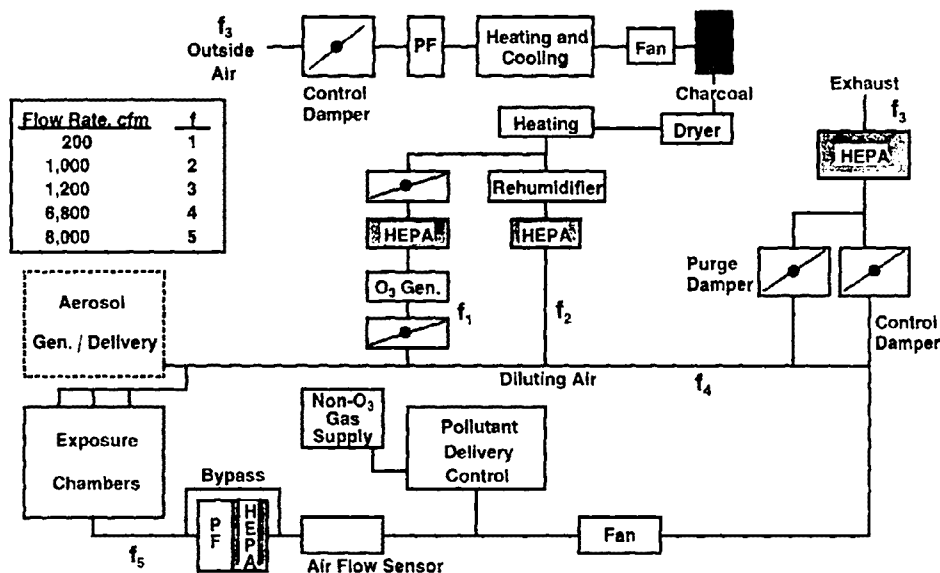


Figure 1. CLEANS air supply system (simplified schematic).

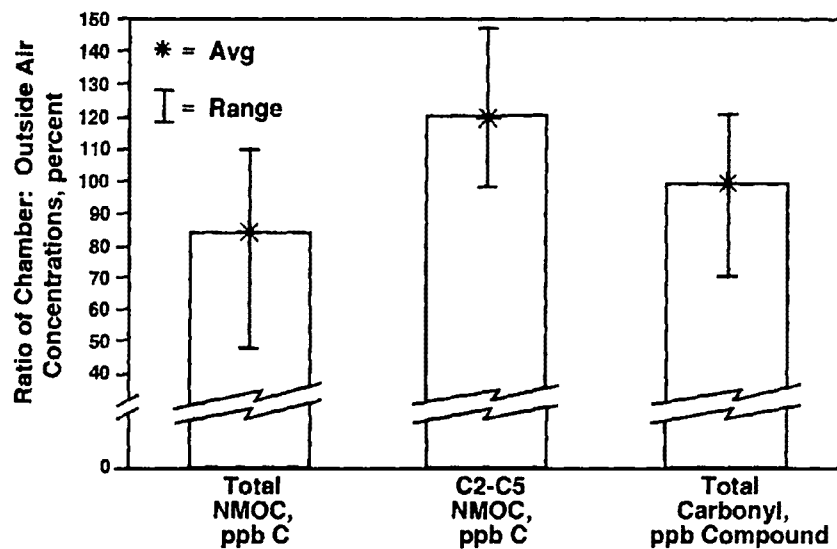


Figure 2. Effects of activated charcoal filtration of ambient and recirculated air on concentrations of total and light NMOCs and carbonyl compounds in a human exposure chamber. Comparison is between outside air samples and chamber air samples that were not ozonated.

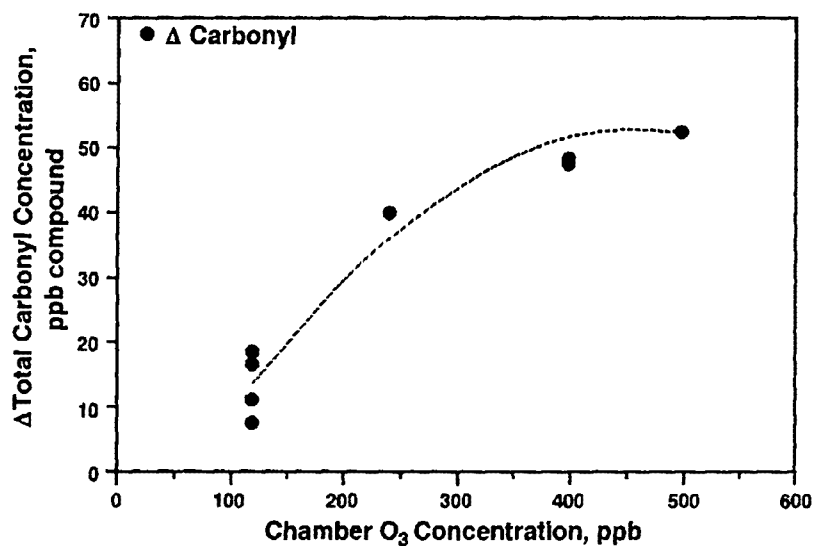


Figure 3. Chamber carbonyl concentration as a function of chamber O₃ concentration, where Δcarbonyl is ([C=O] at [O₃] > 0) - ([C=O] at [O₃] = 0).

THE U.S. EPA/ORD LARGE BUILDINGS STUDY
Results of the Initial Survey of Randomly Selected GSA Buildings

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ABSTRACT

The Atmospheric Research and Exposure Assessment Laboratory (AREAL), Office of Research and Development (ORD), U.S. Environmental Protection Agency (EPA), is initiating a research program to collect fundamental information on the key parameters and factors that influence indoor air quality and comfort in randomly selected General Services Administration (GSA) owned and operated large office buildings. A standardized week-long investigative protocol will be employed in each building a minimum of three times during different seasons over the next 3-5 years to characterize the key physical parameters of the selected GSA buildings and randomly selected test areas; measure key comfort and environmental parameters inside and outside the building; characterize the heating, ventilating, and air conditioning (HVAC) system(s); and collect occupant response data associated with their perceptions of indoor air quality.

An initial set of forty GSA office buildings was selected using a stratified random sampling strategy and a probability proportional to the total number of GSA occupants. The building managers of the selected buildings were contacted and then the buildings visited to verify their eligibility for inclusion in the program. Information on the building and potential test areas was also collected. The selected GSA buildings range in age from two to 80 years old, the size from 3172 m² (34,140 ft²) to 198,775 m² (2,140,000 ft²), and the number of occupants from 46 to 8000. The buildings are highly diverse with respect to design, floor plans, office layout, furnishings, density of workstations, and ventilation systems. Although most of the buildings are mechanically ventilated, some are naturally ventilated including one 33,340 m² building.

This presentation provides a brief overview of the EPA/ORD Large Buildings Study and objectives, including the study design, measurement parameters, and measurement protocol. The initial survey results are presented to show the diversity of the randomly selected GSA study buildings.

DISCLAIMER

The information in this document has been funded wholly or in part by the U.S. Environmental Protection Agency. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

INTRODUCTION

The Atmospheric Research Exposure Assessment Laboratory (AREAL), Office of Research and Development (ORD), U.S. Environmental Protection Agency (EPA), is planning to conduct a series of longitudinal indoor air investigations in selected General Services Administration (GSA) owned and operated buildings located across the U.S. over the next 3-5 years. The study results, when combined with the results of the parallel, but cross-sectional, EPA Buildings Assessment, Survey, and Evaluation (BASE) study, will provide EPA and the indoor air research community with a set of consistently collected, high quality indoor data to evaluate spatial and temporal variability and identify the status and trends for key parameters influencing indoor air quality and occupant perceptions of comfort and health. The primary objectives of the combined EPA projects are to:

- Consistently collect a representative set of key physical, comfort, environmental, and human-response data that contribute to the indoor air quality in large office buildings and other important microenvironments.
- Survey the temporal and spatial variability of those certain parameters known to be associated with indoor air quality and occupant comfort and health.
- Provide high quality data, collected using standardized procedures, to the indoor air research community for assessing the results of their studies and developing new indoor air research hypotheses.
- Identify the critical factors associated with and distinguish complaint and non-complaint buildings.
- Validate new methods and protocols for investigating indoor air quality in large office buildings and other key indoor microenvironments.

DESCRIPTION OF THE PROGRAM

The EPA/ORD Large Buildings Study activities include:

1. An initial set of 40 GSA owned and operated office buildings was selected from the available GSA office buildings. The GSA buildings were first divided into the 10 EPA regions and the greater District of Columbia (Maryland, Virginia, and DC). Initial information was collected to verify that the buildings were office buildings, were available,

and had a sufficient number of occupants to be eligible for the study. The number of buildings to be investigated in each of the 11 areas was established as follows:

- a. A minimum of two buildings would be selected in each area.
- b. The actual number of buildings for each area was then determined using the proportional number of GSA employees in that area compared with the total number of GSA employees in all the available GSA buildings.
- c. The final number of buildings were then rounded to a total of 40 buildings.

Once the number of buildings for each area was established, the buildings to be investigated were randomly selected from the available buildings within that area.

2. Each selected building was visited and characterized in terms of location, physical structure, furnishings, ventilation, occupant activities, and potential indoor pollutant sources.
3. All the potential study areas within each building were defined using the following criteria: a minimum of 25 occupants contained on a maximum of two floors served by a maximum of three air handlers. One primary and two replacement study area(s) were randomly selected. Within the selected study area(s), locations for taking physical and chemical measurements were also identified and randomly selected.
4. A week-long investigation will be performed in the study area(s) to generate data on HVAC operation, environmental pollutants, and comfort factors. All building characterization and monitoring will be performed using standard procedures. Standard measurement and strict quality assurance and quality control (QA/QC) procedures will be used to ensure that high quality and comparable data are consistently collected.
5. Occupants in the study area(s) will be surveyed on perceived indoor air quality and health symptoms using a self-administered questionnaire at the end of the week of field monitoring.
6. Data from each building will be entered into an easily accessible, user- friendly EPA database.

Table 1 summarizes the status of the major program activities. Initial survey visits, the first activity after building selection, have been completed for the first set of 40 GSA buildings. Additional activities associated with the building and HVAC characterization as well as the comfort and environmental monitoring will be performed during a one-week period. These activities will begin with a building walk-through and equipment preparation on Monday and conclude with packing and shipment of equipment and samples on Friday. The occupant questionnaire will be administered to the study area(s) participants on Thursday during the week monitoring is conducted.

Data collection will be performed using standardized protocols and standard operating procedures. The *EPA Large Buildings Studies Integrated Protocol* (dated February 1, 1994) contains specific procedures to be used for the study area(s) selection, monitoring location(s) selection, building and study area characterization, environmental and comfort measurements, HVAC measurements, survey administration, data reduction, and data validation.

In most buildings, environmental and comfort monitoring will be performed in 3-10 locations within a single study area. In a limited number of buildings, a second study area will be studied to assess intra-building variability. Table 2 summarizes the measurement parameters, the number of locations, and the week-long investigation schedule. A minimum of three randomly-selected indoor locations will be established for the collection of integrated environmental samples and the continuous monitoring of selected contaminants and parameters on Wednesday. A series of real time measurements will be made using portable monitors at these three sites and up to seven additional randomly-selected indoor sites during selected times in the morning and afternoon on Wednesday and Thursday. Comparable ambient sample sets will be collected at a site located in close proximity to the outdoor air intake for the test area(s). Duplicate samples will be collected outdoors and at one indoor site.

Selected ventilation measurements (Table 2) will also be made in the test area and in the air handler(s) serving the test area on Tuesday. During the Wednesday and Thursday mobile monitoring periods, selected HVAC supply, return, and outdoor air supply parameters will be measured to characterize the air flows and estimate the amount of outdoor air being supplied to the test area during the monitoring periods.

On Thursday, the EPA Indoor Environmental Quality Questionnaire will be administered to all occupants in the test area(s) to collect information about the occupants' workplace, their health and well-being, workplace conditions, and job characteristics.

The building data will be processed, reviewed, validated, and placed into a standardized format. The validated data will be published in peer-reviewed journal articles and EPA reports and input into a publicly accessible EPA database.

CHARACTERISTICS OF THE BUILDINGS SELECTED FOR THE STUDY

The GSA buildings initially selected and surveyed for the EPA/ORD Large Building Study are located in 23 different states throughout the U.S. and DC, with eight of the forty buildings located in DC. The buildings are located in small urban areas (population 100,000 or less) as well as large metropolitan areas (population >1,000,000). The geographic regions, which represent a wide range of climates, include the Northeast (Massachusetts), Southeast (Tennessee, Florida), Midwest (Iowa, Illinois, Indiana), West (California), Northwest (Oregon), and Southwest (Texas).

The selected GSA buildings range in age from two years to 80 years old. Sixteen of the forty buildings were constructed prior to 1960 and 22 were constructed between 1960 and 1975. Although detailed data were not collected on renovations and modifications to the HVAC system(s)

since construction, it is known that the HVACs have been modified in a number of these buildings. In almost all of the buildings, particularly the older buildings, there have been extensive renovations of the office space since construction.

Many of the buildings in the study are large. The gross square footage of the buildings ranges from 3,172 m² to 198,775 m² (34,140 ft² to 2,140,000 ft²) and 24 of the 40 buildings have a gross floor area greater than 28,000 m² (300,000 ft²). The occupied area of the buildings ranges from 1,645 m² to 112,029 m². Although building managers could not always provide accurate counts of the number of workers in the buildings, the estimated occupancy ranges from 46 to 8000. Based on the information provided for the occupied area and the number of occupants, the area per occupant would range from approximately 9 m² per occupant (100 ft²/occupant) to 56 m² per occupant (600 ft²/occupant) with an average 23 m² per occupant.

The building shape and number of floors varies dramatically for the 40 GSA buildings. The number of floors ranges from one to 33, with the gross square footage per floor ranging from 8,000 to 375,000 ft². Not all buildings had basements, but many had both a basement and subbasement which covered all or part of the building footprint. Basement parking garages were present in a number of buildings. In some cases, the buildings have been converted to office space although designed for a different use. One building was once a hospital, at least two are converted warehouses, and one was a converted ammunition plant. The office layout and the furnishings in these buildings is also highly diverse. Office layouts represented in the buildings include individual offices, bays of interconnected offices, small open spaces with systems furnishings or partitions, an large (whole floor) open spaces with systems furnishings. Open office space, with no partitions or systems furnishings, although rare, was observed at some buildings. The type of office layout, age and style of the furnishings, and amount of renovated space varies substantially between buildings and is related to the agency occupying the office space.

There is a wide diversity of ventilation systems in use at the buildings. Many buildings contain one or more central air handlers with heating and cooling coils and ducted air distribution to supply all, or a large portion, of the building. There are also a number of buildings that have small air handlers that serve individual floors or portions of floors. One 69,800 m² building has 72 air handlers used only to provide outdoor air to the building. There are constant air volume, variable air volume, and economizer systems. Fan coil units are present on the perimeter of a number of buildings. Although steam and hot water are the most common methods for heating, some buildings have electric baseboard heaters on the perimeter. A number of the older buildings have steam radiators and window air conditioners. Not all buildings have air handlers for supplying outdoor air to the office spaces. In one older building, the ventilation system has not been used for the past 10 years. Two buildings have natural ventilation for cooling; one is a 33,334 m² five story building in California and the other is a 4,560 m² building in Alaska.

SUMMARY AND CONCLUSIONS

The EPA/ORD Large Buildings Study will collect data to evaluate spatial and temporal variability and identify the status and trends for key parameters influencing the indoor air quality in GSA owned and operated large office buildings. A week long investigation will be conducted in each building to characterize the physical parameters of the building, one or two randomly-selected test area(s), and the HVAC system(s) servicing the test area(s). Key environmental and comfort parameters will be monitored indoors, outdoors, and in the HVAC systems during the week using both real-time and integrative monitoring techniques. A questionnaire will be administered to the test area occupants to assess their perception of indoor air quality and comfort.

The initial surveys to the initial forty GSA buildings reveal a diversity of the buildings in the study population. The buildings range in age from two to 80 years. The building size ranges from 3172 m² to 198,775 m² (gross floor area), with occupancy ranging from 46 to 8000 employees. A wide range of HVAC system types are represented in the building. The office layouts vary, as does the type and age of the furnishings.

ACKNOWLEDGEMENT

The authors would like to acknowledge Dr. Vivian Mills and the other supporting General Services Administrative professional staff for their contributions and support. Funding for this program is provided through EPA's Indoor Air Research Program.

Table 1. Schedule and Status of Program Activities

Activity	Time
Initial Survey Visit	Completed
Study Area(s) Selection	Completed during initial visit
Selection of Monitoring Locations	Completed. Validate during initial investigation
Building Investigation Activities	
- Study area(s) verification	Monday
- Equipment preparation, set-up, and calibration	Monday - Tuesday
- Building and study area(s) characterization	Monday - Thursday
- Environmental and comfort measurements	Tuesday - Thursday
- HVAC measurements	Monday - Thursday
- Questionnaire Administration	Thursday
- Equipment take down, packing, and shipment	Thursday - Friday

Table 2. Measurement Parameters, Locations, and Schedule

Real-time Monitoring - Mobile Sites (Wed. & Thurs. at 3-10 indoor locations) <ul style="list-style-type: none"> - Temperature - Relative humidity - CO₂ - CO - Respirable particles - Sound level (noise) - Illuminance (light) 	Real-Time Monitoring - Fixed Sites (Continuous Tues. through Thurs. at three indoor and one outdoor location) <ul style="list-style-type: none"> - Temperature (at four heights) - Relative humidity - CO₂ - CO - Sound level (noise) - Illuminance (light)
Integrated Samples (Wed., nine-hour sample) <ul style="list-style-type: none"> - PM_{2.5} - Nicotine - PM₁₀ - Bioaerosols - TSP - Biological Agents - VOCs - Ozone - Aldehydes - Radon 	Exhaust Fans (All exhaust fans in the test area measured on Tuesday and checked for operating conditions on Wed. and Thurs.) <ul style="list-style-type: none"> - Air flow rate
HVAC Air Handler - Supply Air, Return Air, and Outdoor Air (Tues., a.m., Wed. and Thurs., a.m. & p.m.) <ul style="list-style-type: none"> - Air flow rate - Air temperature - Relative humidity - CO₂ - CO 	HVAC - Test Area Supply Diffusers (Tues. p.m. - flowrates only for AHU(s) supply and all supply diffusers in study area; Wed. and Thurs., a.m. and p.m. - selected subset near monitoring locations) <ul style="list-style-type: none"> - Air flow rate - Air temperature - Relative humidity - CO₂ - CO

Large Building Characterization

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Abstract

Buildings are characterized in this project by examining radon concentrations and indoor air quality (IAQ) levels as affected by building ventilation dynamics. IAQ data collection stations (IAQDS), for monitoring and data logging, remote switches (pressure and sail switches), and a weather station were installed. Measurements of indoor radon, carbon dioxide (CO₂), and particle concentrations; temperature; humidity; indoor to outdoor or sub-slab pressure differentials; ambient and sub-slab radon concentrations; and outdoor air intake flow rates were collected. The outdoor air intake was adjusted, and fan cycles were controlled while tracer gas measurements were taken in all zones and IAQDS data are processed. Ventilation, infiltration, mixing rates, radon entry, pressure/temperature convective driving forces, CO₂ generation/decay concentrations, and IAQ levels were defined. These dynamic interacting processes characterize the behavior of this and similar large buildings. The techniques incorporated into the experimental plan are discussed with project rationale. Results and the discussion of those results are beyond the limits of this paper.

Introduction

This paper describes a research study undertaken in support of the Florida Standard for Radon Resistant Construction in Large Footprint Structures (currently under development by the Florida Department of Community Affairs) ¹. The project entails an extensive characterization and parametric assessment study of a single large building with the purpose of assessing the impact of radon entry on design, construction, and operating features of the building, particularly, the mechanical subsystems ^{2,3,4}.

As part of the study, the response of the structure to a range of heating, ventilating, and air-conditioning (HVAC) operating conditions will be continuously monitored with the purpose of determining the optimum HVAC conditions to reduce indoor radon within the envelope of acceptable operation as regards to energy, comfort, and IAQ impacts on the structure.

The Polk County Administration Building located in Bartow, Florida, is a publicly owned building constructed in 1988. The building has 149,000 ft² (14,000 m²) of floor space distributed over five floors, and has a permanent occupancy of roughly 300 county employees and elected officials. HVAC needs are met by 11 air handlers (3 on the first floor and 2 on each of the other four floors). The building is equipped with a variable air volume (VAV) distribution system with plenum return, and each air handler is supplied by a separate outdoor air (OA) intake.

Study Objectives

The building was selected for this study as best representing the research criteria determined in a workshop review process by the Florida Radon Research Program (FRRP). These criteria represent specific information needs identified by the FRRP as important to the development of a definable construction standard for this class of structure. The study has five main objectives:

1. Determine the effect of HVAC operating cycles (including OA level and exhaust ventilation) on radon-relevant parameters of the structure. These parameters include building pressure, ventilation rate, radon concentration, and radon entry rate (assuming a well-mixed building). The results will be determined in the course of a parametric study in which HVAC parameters such as ventilation air will be systematically varied.
2. Evaluate the effect of a larger extent slab on the driving pressure which promotes radon entry. In the course of the study, we will monitor subslab pressure variations with position and HVAC status. (We expect two superimposed effects, one dependent on position and the time derivative of the barometric pressure and the other dependent on the HVAC cycle and possibly outside temperature).
3. Assess the effect of ground floor pressure balance or imbalance on radon entry. If pressures are not found to be unbalanced, we plan to use fire dampers to partially isolate the return of two distant zones on the first floor. A pressure differential of -5 Pa will be targeted between near and far zones, and ventilation rates, and radon concentration and entry will be compared in the depressurized zones.

4. Monitor the transport of air (and radon) between zone and floors. If mixing of air appears slow, we will experiment with first floor injection coupled with build-up monitoring.
5. Assess the effect of building features/faults on response variables. Some of the features and assessment strategies to be used are: elevators (monitor shaft bottom for radon and estimate flow induced by car movement to evaluate a semi-quantitative estimate of radon pumping); stairwells (determine concrete wall isolation of radon entry by monitoring radon as source); ground floor mechanical rooms (assess as entry locations by monitoring pressure differential and radon); and visible slab penetrations (seal and assess effect using either local or whole-building measurements).

Measurements

The IAQ investigation of the Polk County Administration Building involves a series of manual measurements and the use of measurement instrumentation operating continuously and downloading automatically. Manual measurements will be taken as part of both an initial intensive testing phase and a weekly testing series to evaluate HVAC and building performance. For continuous measurements, 13 IAQDS will be used, with internal and remote input sensors. Each IAQDS stores information in an internal microprocessor and transmits this information by modem. In addition to the IAQDS, air exchange rates, weather station data, and ambient radon measurements will be recorded.

The IAQDS measurements include indoor radon concentrations, differential pressures, room temperatures, relative humidities, and carbon dioxide concentrations in several zones. In addition, percentage operation cycle times for selected air handlers, exhaust fans, and elevators are obtained via switches; duct air temperature and relative humidity in selected air handlers are monitored; and a particle counter in a single first floor zone is monitored to provide indicative measurement of indoor particulate levels. The 13 IAQDS are distributed two per floor on the top four floors, with five stations distributed in several zones on the first floor. Further discussion of locations and assignments of the IAQDS (as installed) is beyond the scope of this paper.

Building Selection and Plan Development

The building was located and a survey of radon measurements was taken which indicated elevated radon (in the 4-15 pCi/L range). A draft study proposal was presented to the building owners, and approval was obtained. Plans to the building were obtained and used to guide selection of measurements. Walk-through visits were conducted to confirm locations of continuous samplers, phone and electrical connection availability, and to obtain a survey of pressure differences between zones of the structure. Monitoring equipment was obtained, calibrated, and prepared for installation ^{5,6}.

A) Installation of Continuous Monitoring Systems

A team installed 13 IAQDS sensors and associated interconnecting wires and tubes. A weather station was installed and monitored by a Campbell 21X datalogger.

Building features were inspected and modifications made to some measurement locations in response to on-site conditions.

Several deficiencies in the HVAC installation and operation were noted and reported to the County Facilities Management Staff. The most significant of these included: significant supply duct leakage in the attic, areas above the fifth floor; and a total lack of ventilation (outdoor) air into both second floor air handlers due to obstruction of OA intakes by building framing after installation. Repair of these conditions delayed the HVAC characterization phase.

Walk-through surveys were coordinated for related projects.

B) Characterization of HVAC Systems

In addition to the design survey and survey pressure measurements performed, a certified HVAC test and balance (TAB) company was contracted to verify and spot-check data from earlier balance reports of the system. These measurements include:

Monitoring of total flow and trunk line supply flow rates from all air handlers at full open VAV conditions.

Measurement of supply and outdoor air flow rate at each air handler at four demand flow conditions (nominally 60, 70, 85, and 100% of capacity) and at four positions of all operable outdoor air dampers (full open, closed, and nominally 50 and 75%).

Measurement of exhaust fan flow rates.

C) Installation of Tracer Gas System

Sample lines and a computerized sample injection and gas chromatograph electron capture detector system were installed, checked, and left in continuous operation. The injection cycle (SF_6) will be set at 4 - 8 injections per day depending on observed decay rates. In addition, SF_6 will be injected into OA intakes to measure OA intake rates.

D) Operating Cycles

1: Baseline

With all systems operational, a week of data in the "as found" condition will be obtained, downloaded, and analyzed. Particular attention will be given to the effects of the building setback period.

2: Maximum Outdoor Air

All operable outdoor air dampers will be set to their full open position, and a week of data obtained, downloaded, and analyzed. During this period, the data will be surveyed frequently for indications of cooling system incapacity to meet the added latent heat load (inability to maintain set points, or excessive relative humidity in air zones).

3: Minimum Outdoor Air

Operable outdoor air dampers will be set to a condition of low outdoor air consistent with occupant comfort and IAQ status. The target OA level will be at most 50% of the baseline outdoor air flow rates. Outdoor air levels will be further reduced, to a level corresponding to less than 5 cfm (0.00236 m³/s)/person at full building occupancy. During this period, the data will be surveyed daily, and the outdoor air levels increased if any of the following signs are observed: CO₂ levels above twice the baseline level or 1500 ppm; reported occupant discomfort; or any other indication of compromised IAQ.

After the results of conditions 1-3 are obtained, conditions for the final 3 weeks of study will be finalized. Nominal conditions for these weeks are shown below.

4: Altered First Floor Pressure Balance

During this cycle, the pressure imbalance between first floor zones will be enhanced by partial obstruction of dampered return sleeves through fire zone walls in plenums above ceilings.

5: Modified Setback

Depending on observed time-resolved behavior of pressures, temperatures, and relative humidity during earlier setback periods, an alternate setback cycle will be designed and tested. Likely components will include:

One hour (rather than 30 min) setback periods.

Reductions of exhaust air flow either continuously (by throttling exhaust lines) or intermittently (by cycling fans off with air handler setback).

6: Sealed Penetrations to Soil

In the initial walk-through, several locations were discovered with significant pathways (i.e., several holes greater than 1 in.² [6.45 cm²] in area) to soil. Some of these penetrations are in mechanical rooms or other similarly vulnerable locations. At the beginning of this week, major penetrations will be sealed with a suitable polymeric compound. Mechanical rooms will be monitored for radon concentrations.

Conclusion

The continuous measurement equipment has been installed and the manual measurements described above have been initiated. It is anticipated that the completion of all measurements by the above described procedures will accomplish the project objectives. This presentation of objectives and methods of accomplishing those objectives is part of an on-going research project.

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A Comparison of Sorbent Sample Cartridges for the Collection and Analysis of Volatile Organic Compounds Collected in Large Office Buildings

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The use of sorbent materials for the collection of volatile organic compounds (VOCs) in ambient air has been utilized for decades. Both polymeric (i.e., Tenax) and carbonaceous (i.e., Amborsorb, charcoal) sorbents have been used for the collection of VOCs. Each material has a unique affinity for various volatile compounds and, subsequently, are often selectively employed for the collection of specific classes of chemicals. In an effort to increase the number of VOCs which can be collected and analyzed using a single sample cartridge, draft BASE protocols for the collection and analysis of VOCs using both multi-sorbent sample cartridges have been developed.

The purpose of this study was to compare the performance of Tenax GC and multisorbent cartridges. A sample collection of VOCs on both Tenax and multisorbent sample cartridges was conducted in three large office buildings. Both sample types were analyzed by thermal desorption-gas chromatography/mass spectrometry. Data for instrument calibration, method blanks, method controls, and estimated method quantitation limits are presented. The results of the sample analysis for the co-located cartridges are compared. The agreement between the Tenax and multisorbent methods is discussed.

Although the research described was funded by the U.S. EPA (Contract 68-D2-0131), it has not been subjected to the required peer and administrative review and does not reflect the views of the Agency, and no official endorsement should be inferred.

MANAGING RESIDENTIAL SOURCES OF INDOOR AIR POLLUTION

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ABSTRACT

Sources of indoor air pollutants in residential environments can be managed to reduce occupant exposures. Techniques for managing indoor air pollution sources include: source elimination, substitution, modification, and pretreatment, and altering the amount, location, or time of use. Intelligent source management requires knowledge of the source's emission characteristics, including chemical composition, emission rates, and decay rates. In addition, knowledge of outdoor air exchange rates, heating/air-conditioning duct flow rates, and kitchen/bath exhaust fan flow rates is needed to determine pollutant concentrations. Indoor air quality (IAQ) models use this information and occupant activity patterns to determine instantaneous and/or cumulative individual exposure. This paper describes a number of residential scenarios for various indoor air pollution sources, several air flow conditions, and typical occupant activity patterns. IAQ model predictions of occupant exposures for these scenarios are given for selected source management options.

INTRODUCTION

Indoor air pollution, especially due to volatile organic compounds (VOCs), is primarily caused by emissions from indoor sources. The levels (concentrations) of these pollutants are affected by many factors, including: 1) the emission characteristics of the source (e.g., chemical composition, emission rate, decay rate); 2) the interaction of these emissions with interior surfaces (e.g., sink adsorption/desorption); 3) dilution and flushing by outdoor air exchange (assuming unpolluted outdoor air); and 4) processes designed to remove pollutants (e.g., local ventilation, air cleaners). Occupant exposure to indoor air pollution is a function of the temporal and spatial distribution of the pollutants coupled with individual activity patterns.

The purpose of this paper is to explore options for reducing occupant exposure in residential environments by managing IAQ. The focus is on management of sources, including selecting high, medium, or low emitting sources. This may be accomplished by source substitution, modification, pretreatment, or elimination. Source management also includes selecting the amount used, the time of use, and the location of use. In addition, sources can be used with various air exchange rates and with or without local ventilation. Finally, occupant activity patterns ultimately dictate individual exposures.

EXPOSURE SCENARIOS

An IAQ model has been developed to predict occupant exposure to indoor air pollutant based on source/sink behavior, ventilation parameters, and occupant activity patterns.¹ The model was used to predict occupant exposures for several combinations of sources, ventilation scenarios, and activity patterns.

Residential Environment

A three-room, single-level residential environment was evaluated (see Figure 1). The forced air heating and cooling system has supply registers in the living area, bedroom, and bath; the return grill is in the hall. The bath has a separate exhaust fan.

Sources

Four typical indoor sources with a wide range of emission rates and decay rates were selected. The emissions of interest from these sources are VOCs. The sources, except for the aerosol product, were assumed to have first-order emission rate decay of the form:

$$ER = ER_0 e^{-kt} \quad (1)$$

where, ER = emission rate at time t ($\text{mg}/\text{m}^2 \cdot \text{h}$)
 ER_0 = emission rate at time 0 ($\text{mg}/\text{m}^2 \cdot \text{h}$)
 k = first-order decay rate (h^{-1})
 t = time (h)

Table 1 describes the sources and provides emission rate information.

Sinks

Interior walls, ceilings, and floors were assumed to behave as indoor sinks exhibiting Langmuir sink behavior; i.e., at equilibrium:

$$Ck_s = Mk_d \quad (2)$$

where, C = VOC concentration (mg/m^3)
 k_s = adsorption rate (m/h)
 M = VOC mass in sink (mg/m^2)
 k_d = desorption rate (h^{-1})

For walls, ceilings, and bathroom floors: $k_s = 0.1 \text{ m}/\text{h}$ and $k_d = 0.1 \text{ h}^{-1}$. All other floors are carpeted: $k_s = 0.1 \text{ m}/\text{h}$ and $k_d = 0.008 \text{ h}^{-1}$. (See Reference 2.)

Occupant Activity Patterns

The occupant activity patterns for each source are given in Table 2.

Ventilation and Air Movement Scenarios

Three separate outdoor air exchange rates were assumed: high = 2 ACH (air changes per hour); medium = 0.5 ACH; and low = 0.2 ACH. The IAQ model was configured to distribute the outdoor air proportional to the outside wall area for each room. The outdoor air was assumed to contain no VOCs.

The heating/air conditioning (HAC) fan distributed the air as follows: 350 m^3/h to the living area; 150 m^3/h to the bedroom; and 75 m^3/h to the bath. All the HAC air (575 m^3/h) was recirculated via the hall return. Some air movement was also assumed to occur when the AC fan was off: 70 m^3/h between the living area and hall; 30 m^3/h between the bedroom and hall; and 15 m^3/h between the bath and hall. An exhaust fan with flow of 24 m^3/h was in the bathroom.

EXPOSURE PARAMETERS

Occupant exposures were calculated for three types of health effects: chronic, acute, and irritation/odor. Chronic health effects are due to cumulative **total exposure** which was calculated for each occupant by multiplying the concentration, in milligrams per cubic meter, by the exposure time, in hours. Acute health effects are a function of the **maximum concentration**, in milligrams per cubic meter, to which each occupant is exposed. Irritation and odor responses occur at threshold levels and were evaluated by determining the length of time the occupant is exposed to concentrations exceeding the threshold level. Two

irritation/odor thresholds were used for each source. All sources were assumed to have a high irritation/odor threshold of 3 mg/m³ total VOC. For paints and aerosols, a low irritation/odor threshold of 0.3 mg/m³ total VOC was selected. For carpet, the low irritation/odor threshold was assumed to be 0.01 mg/m³ total VOC, based on an odor threshold of 1 ppb for 4-phenylcyclohexene (4-PC) and assuming two-thirds of the total VOC emission are 4-PC. The low irritation threshold for furniture/particleboard was set at 0.2 mg/m³ total VOC, based on an irritation threshold of 0.1 ppm for formaldehyde and assuming two-thirds of the total VOC emissions are formaldehyde.

PREDICTED OCCUPANT EXPOSURES

IAQ model predictions of occupant exposures over a 30 day period were made for various combinations of source emission rates, ventilation scenarios (general and local), and occupant activity patterns. Figure 2 shows the time history of the VOC concentration in the living area due to emissions from the four sources at medium emission rates, outdoor air exchange rate = 0.5 ACH, the HAC fan on, and the bath exhaust fan off. Note that the total VOC (TVOC) concentrations range from <0.1 to >1000 mg/m³ depending on the source and time. This plot shows the effect of each source individually, not the combined effect of all the sources.

Tables 3 - 6 present the results of IAQ model analyses of various exposure scenarios for the three exposure parameters discussed above. Table 3 show how changing the emission rate affects exposure; Table 4 highlights the effect of occupant activity; Table 5 illustrates the influence of general ventilation (i.e., dilution and flushing with outdoor air); and Table 6 shows the impact of local ventilation (bath fan) and air movement (HAC fan). Both fans were assumed to be *on* or *off* for the complete 30 day period.

DISCUSSION

An examination of Tables 3 - 6 illustrates that the effectiveness of various IAQ management options (e.g., changing emission rates, different occupant activities, and various ventilation scenarios) is dependent on the exposure parameter of interest. For example, reducing the emission rate (Table 3) and increasing the air exchange rate (Table 5) both reduce total exposure and the maximum concentration, but the duration of exposure to odor and irritation thresholds may not change significantly. The results also show how interactions between various factors can affect exposure. For example, Table 4 shows how product users (painter and aerosol user) can have exposure to high maximum concentrations due to locations and times of uses. The strategy of vacating for 1 day during painting can reduce chronic and acute exposure by about 80%. Also, the interaction of local ventilation with HAC systems is shown in Table 6 where the person who does not enter the bath (Full-time 2) is completely isolated from exposure only if the bath fan is *on* and the HAC fan is *off*. These types of interactions make it necessary to examine the effect of all relevant factors before drawing any conclusions regarding the effectiveness of IAQ management vis-a-vis exposure.

CONCLUSIONS

Individual exposures to indoor air pollutants are affected by source emission characteristics, occupancy patterns, and ventilation scenarios. Source management options that alter these parameters can dramatically affect exposures. The effectiveness of source management depends on the type of exposure (i.e., chronic, acute, odor/irritation) reduction desired. Exposure reduction by local ventilation is strongly affected by general ventilation system (HAC) operation.

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Table 1. Sources and emission rate information.

Source	Type	Time of Use	Location	Emission Rate	ER ₀ (mg/m ² ·h)	k (h ⁻¹)
Paint	Fast Decay	8AM-5PM, 1st Day	All Walls (135 m ²)	High	50000	0.5
				Medium	20000	0.5
				Low	2000	0.5
Carpet	Slow Decay	New on 1st Day	All Floors, Except Bath (43 m ²)	High	2	0.004
				Medium	0.2	0.004
				Low	0.02	0.004
Furniture	Constant*	New on 1st Day	All Rooms, Except Hall (10 m ²)	High	5	0
				Medium	0.5	0
				Low	0.05	0
Acrosol	Multiple Use	6AM Every Day	Bath	High	5000 mg/use	---
				Medium	500 mg/use	---
				Low	50 mg/use	---

*The emissions are not truly constant, but for the 30 days of the evaluation period the decay was assumed to be zero.

Table 2. Occupant Activity Patterns.

Occupant	Sources	Time (0 - 24 h/day)	Location
Full-time	Paint, Carpet, Furniture, Aerosol	0 - 6.5	Bedroom
		6.5 - 7	Bath
		7 - 22	Living Area
		22 - 24	Bedroom
Full-time (2)	Aerosol	0 - 7	Bedroom
		7 - 22	Living Area
		22 - 24	Bedroom
Part-time	Paint, Carpet, Furniture, Aerosol (User)	0 - 6	Bedroom
		6 - 6.5	Bath
		6.5 - 7.5	Living Area
		7.5 - 18	Outdoors
		18 - 22	Living Area
		22 - 24	Bedroom
Painter	Paint	8 - 12	Living Area
		12 - 13	Outdoors (Lunch)
		13 - 14	Hall
		14 - 15	Bedroom
		15 - 16	Bath
Vacate Painting Day (Full-time After)	Paint	0 - 24	Outdoors
		24 & after	Living Area

Table 3. Effect of Emission Rate on Occupant Exposure (Full-Time Occupant, Medium Ventilation Rate).

Source	Emission Rate	Total Expos. {(mg/m ³)h}	Max. Conc. (mg/m ³)	Time > Hi I/OT* (h)	Time > Lo I/OT (h)
Paint	High	168,000	14,900	430	720
	Medium	68,400	5,440	312	616
	Low	6,730	598	66	309
Carpet	High	268	0.97	0	727
	Medium	27	0.1	0	623
	Low	2.7	0.01	0	0
Furniture/ Particleboard	High	459	0.65	0	726
	Medium	46	0.07	0	0
	Low	4.6	0.01	0	0
Aerosol	High	1,840	56	106	694
	Medium	184	5.6	11	106
	Low	18	0.56	0	11

*I/OT = Irritation/Odor Threshold

Table 4. Effect of Occupant Activity Patterns on Exposure (Medium Emission Rate, Medium Ventilation Rate).

Source	Occupant	Total Expos. {(mg/m ³)h}	Max. Conc. (mg/m ³)	Time > Hi I/OT (h)	Time > Lo I/OT (h)
Paint	Full-time	68,400	5,440	312	616
	Part-time	34,700	6,000	178	354
	Painter	22,100	8,480	7	7
	Vacate 1 Day	14,200	1,280	296	600
Carpet	Full-time	27	0.1	0	623
	Part-time	15	0.1	0	360
Furniture/ Particleboard	Full-time	46	0.07	0	0
	Part-time	27	0.07	0	0
Aerosol	Full-time	184	5.6	11	106
	Part-time (user)	234	19.9	12	48

Table 5. Effect of General Ventilation on Exposure (Medium Emission Rate, Full-time Occupant).

Source	Ventilation Rate (ACH)	Total Expos. {(mg/m ³)h}	Max. Conc. (mg/m ³)	Time > Hi I/OT (h)	Time > Lo I/OT (h)
Paint	0.2 (low)	222,000	10,700	684	720
	0.5 (medium)	68,400	5,440	312	616
	2 (high)	22,300	2,970	64	310
Carpet	0.2 (low)	84	0.26	0	727
	0.5 (medium)	27	0.1	0	623
	2 (high)	9	0.04	0	333
Furniture/ Particleboard	0.2 (low)	144	0.21	0	499
	0.5 (medium)	46	0.07	0	0
	2 (high)	15	0.02	0	0
Aerosol	0.2 (low)	602	7.3	18	677
	0.5 (medium)	184	5.6	11	106
	2 (high)	49	2.9	0	33

Table 6. Effect of Local Ventilation on Exposure to VOCs from Aerosol Product (Medium Emission Rate, Medium Ventilation Rate).

Bath Fan	HAC Fan	Occupant	Total Expos. {(mg/m ³)h}	Max. Conc. (mg/m ³)	Time > Hi I/OT (h)	Time > Lo I/OT (h)
On	On	Part-time (user)	211	20	12	48
		Full-time 1	144	5	6	93
		Full-time 2	119	1.7	0	93
On	Off	Part-time (user)	221	23	12	15
		Full-time 1	119	12	12	12
		Full-time 2	0	0	0	0
Off	On	Part-time (user)	234	20	12	48
		Full-time 1	184	6	11	106
		Full-time 2	160	2.3	0	106
Off	Off	Part-time (user)	277	27	12	48
		Full-time 1	238	15	11	89
		Full-time 2	100	1	0	89

Figure 1. Residential Environment

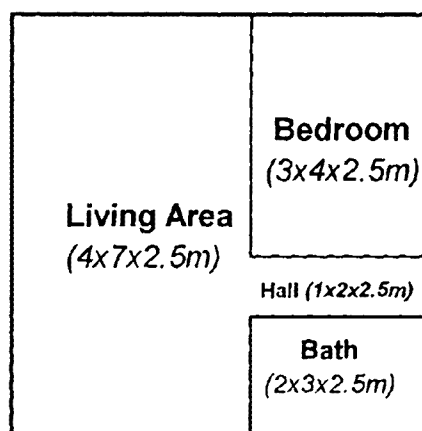
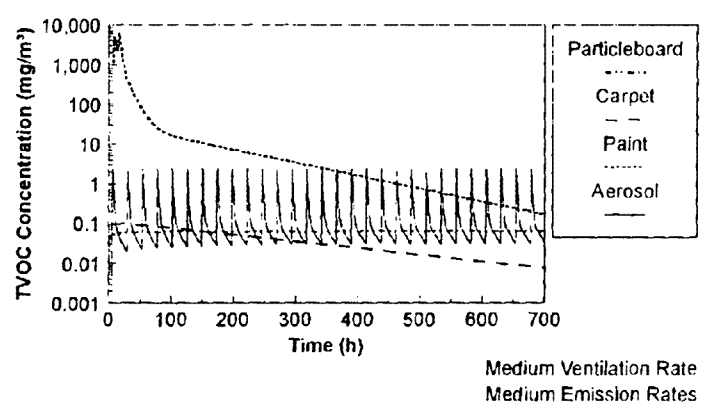


Figure 2. TVOC Concentrations - Living Area



RELATIONSHIP AMONG DRAG SLED, PUF ROLLER, AND HAND PRESS TRANSFER OF PESTICIDE RESIDUES FROM FLOORS

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ABSTRACT

The transfer efficiency of formulated pesticide residues from treated carpets and vinyl flooring was consistently highest by the drag sled, intermediate by the PUF roller, and lowest by human skin. The flooring material and the pesticide application method had major effects on transfer, but the specific active ingredient had no effect. The mean \pm standard deviation of the ratios for 17 data sets were 7.4 ± 2.8 for drag sled/hand press and 3.3 ± 2.1 for PUF roller/hand press. Either mechanical method can be used to estimate dermal transfer of pesticide residues from recently treated floors.

INTRODUCTION

The Dow drag sled (1) and the Southwest Research Institute polyurethane foam (PUF) roller (2) are dislodgeable sampling methods which were recently developed to estimate the transfer of a chemical from a contaminated surface to the skin and which perform well (3). This paper reports the results from two of a series of experiments. The objective was to compare transfers of formulated chlorpyrifos, pyrethrins, and piperonyl butoxide residues from plush carpet (Experiment 6) and from sheet vinyl (Experiment 7) obtained by the drag sled and the PUF roller to collocated transfers obtained by presses of a human hand.

METHODS

Transfer Methods

Relevant characteristics of the methods are compared in Table 1. For the drag sled method, one pass was made over a 1 m \times 7.6 cm strip of flooring by dragging a precleaned dry (4 in.)² denim-weave cloth (supplied by B. Shurdut, Dow Elanco) attached beneath foil under a (3 in.)² plywood block on which an 8-lb weight was mounted to provide a contact pressure of 5,900 Pa through the cloth. For the PUF roller method, one pass was made over a 1 m \times 7.6 cm strip of flooring by rolling a precleaned dry ring of PUF mounted on an aluminum cylinder, with two stainless steel blocks mounted on the instrument frame to provide a constant contact pressure of 8000 Pa through the PUF ring. For the hand press method, a subject made one pass over a cardstock-template-exposed 0.635 m \times 7.6 cm strip of flooring by pressing the soap-and-water-washed palm of one hand for 1 s at a pressure of ca. 1 psi (6,900 Pa) onto each of ten adjoining sections of the strip. The subject wiped transferred residues from his hand using two 2-propanol-moistened gauze sponges, a procedure shown to quantitatively remove chlorpyrifos and pyrethrin I (4).

Experimental Design

The previously-treated plush nylon carpet in the test room was professionally cleaned prior to Experiment 6A and new sheet vinyl flooring was installed in the room before Experiment 7. A licensed pest control applicator treated the test flooring for each experiment according to label directions to control a light infestation of fleas. An aqueous formulation (0.25% chlorpyrifos, 0.25% piperonyl butoxide, and 0.025% pyrethrin I) of Dursban® L.O. (EPA Reg. 62719-55) and Kicker® (EPA Reg.

4816-707AA) was applied from a pressurized tank with a fan broadcast nozzle about 40 cm above the floor at 1 gal/1600 ft² for Experiments 6A and 7. The applicator sprayed Siphotrol® premise spray (0.015% methoprene, 1.0% piperonyl butoxide, and 0.2% pyrethrin I) from the aerosol can using a sweeping motion as a second treatment of the carpet for Experiment 6B. The room was ventilated by opening doors and windows (with a box fan in the doorway) for 20-30 min and by operating the air conditioning for 2 h after application to ensure the pesticide residue was dry before sampling commenced.

For each experiment, adjacent deposition and transfer samples were sequentially collected using two coupons, the PUF roller, the drag sled, and ten adjoining presses (one press in Exp. 6A) of the same hand by each of three human subjects within each of six rectangular blocks of treated flooring. Field blanks of each transfer method were obtained by sampling prior to the application. Field samples were collected from two blocks after label-permitted re-entry (>2 h after application) on the day of application, and from two more blocks on both of the succeeding days. Field spikes of each precleaned transfer medium were performed both before and after the six blocks of field sampling to assess losses during transport, storage, and extraction.

Drag cloths and PUF rings were Soxhlet-extracted with 6% ethyl ether/94% hexane. 2-Propanol-saturated handwipes were shake-extracted with 1:1 ethyl ether:hexane (4). Extracts were analyzed for chlorpyrifos, methoprene, piperonyl butoxide, and pyrethrin I on a Fisons MD 800 operating in selected-ion monitoring mode. Reported data have not been adjusted for field spike recoveries.

RESULTS AND DISCUSSION

Recovery of target analytes in field spikes of the sampling media was essentially quantitative (Table 2). Methoprene, piperonyl butoxide, and pyrethrin I were not detected in any of 42 hand press/2-propanol wipe field blanks. However, chlorpyrifos was found in 41 of 42 hand press/2-propanol wipe field blanks, at mean levels of 0.18 µg and 0.26 µg after single presses onto aluminum foil and carpet, and of 0.23 µg after ten presses along clean cardstock, respectively (Table 3). The absence of chlorpyrifos in 2-propanol-gauze laboratory matrix blanks indicates that the chlorpyrifos was wiped from the subjects' hands, but its source is unclear. Each subject washed his hands with soap and water before performing each hand press. One possibility is transfer from a chlorpyrifos-contaminated object, such as the faucet handle or soap bar, during handwashing. More likely is removal by the more vigorous 2-propanol-wipe of chlorpyrifos in fats and oils deeply embedded in the skin, which were not removed by the soap-and-water wash.

Table 4 presents the data on loading and rate of transfer by the three methods for a typical active ingredient and experiment, piperonyl butoxide in Exp. 6B. A comparison of the transfer rates of the three methods is given in Table 5 by active ingredient within experiment. The transfer rates of every active ingredient from both flooring materials were consistently highest for the drag sled, intermediate for the PUF roller, and lowest (when measurable) for the human hand press. The frequent high variability in transfer observed for some methods and flooring was also observed for deposition coupons; it largely reflects non-uniform deposition during applications, where the professional applicator glanced over his shoulder to avoid stepping on the coupons.

The efficiency of transfer of the three methods relative to surface loading is shown in Table 6. Each method simultaneously transfers all applied active ingredients with virtually the same efficiency from the treated flooring (i.e., percent mean transfer is within a factor of two). In contrast, transfers from sheet vinyl are one to several orders of magnitude greater than transfers from plush carpet. For a given method, transfers after broadcast application were 100- to 300-fold greater from sheet vinyl than from plush carpet. Transfers from plush carpet were 20- to 30-fold greater after aerosol can application than after broadcast application.

Table 6 indicates that the transfer efficiency is about three times higher for the drag sled than for the PUF roller, and about three times higher for the PUF roller than for the hand press, for every active ingredient, flooring, and application method investigated. To obtain a more precise estimate of this relationship, the ratio of the mechanical method transfer mean (n=2) to the simultaneous hand press

transfer mean (n=6) was calculated for the 17 specific sets of pesticide within day within experiment. Both the drag sled/hand press ratio and the PUF roller/hand press ratio were quite stable over the broad range of transfers in these 17 sets. The mean \pm standard deviation of the ratios were 7.4 ± 2.8 for drag sled/hand press and 3.3 ± 2.1 for PUF roller/hand press.

These observations indicate that the PUF roller and the drag sled can both be used to estimate transfers of formulated pesticide residues from flooring to a human hand by press contact. Crude estimates of the transfer to human skin of residues of pesticides recently applied to a floor surface can be obtained from drag sled or PUF roller measurements of the surface, using the mean transfer ratios given above.

ACKNOWLEDGEMENT

This research was funded by the U.S. Environmental Protection Agency (Contract 68-DO-0007) under subcontract from Battelle. This paper has received EPA's peer and administrative review, but no official endorsement should be inferred.

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Table 1. Characteristics of dislodgeable residue and hand press methods

	Drag Sled	PUF Roller	Human Hand Press
Sampling medium	Denim weave cloth	Polyurethane foam (PUF) ring	Skin on palm of hand
Surface of sampling medium	Square (10.2 cm) ²	Curved exterior of ring (8.9 x 7.6 cm)	Palm through template
Contact motion	Drag	Roll	Ten presses (for 1 s)
Pressure through medium	5,900 Pa	8,000 Pa	6,900 Pa
Sampled floor area	7.6 cm x 1.0 m = 760 cm ²	7.6 cm x 1.0 m = 760 cm ²	10 x 7.6 cm x 6.3 cm = 480 cm ²
Number of passes	1	1	1
Sampling speed	7 cm/s	10 cm/s	Each press for 1 s

Table 2. Field spike recoveries (%) from sampling media

Matrix	Analyte	n	Mean	Std. Dev.
Denim drag cloth	Chlorpyrifos	21	113.1	35.3
		18 ^c	100.6 ^a	13.9 ^a
	Methoprene	4	125	24
		2 ^a	108 ^a	17 ^a
	Piperonyl butoxide	5	83	18
	Pyrethrin I	7	95	46
PUF ring	Chlorpyrifos	6 ^a	111 ^a	21 ^a
		24	101.0	21.1
	Methoprene	23 ^c	103.9 ^a	15.9 ^a
		4	112	14
	Piperonyl butoxide	6	90	18
	Pyrethrin I	8	117	25
2-Propanol-moistened SOF-WICK® gauze	Chlorpyrifos	26	85.5	14.9
	Methoprene	4	74	14
	Piperonyl butoxide	8	108	43
	Pyrethrin I	26	114.9	49.1
		24 ^a	102.9 ^a	23.7 ^a

a Apparent outlier(s) excluded

Table 3. Chlorpyrifos (µg/sample) in field and laboratory 2-propanol handwipe^a blanks

No. Subjects	No. Hand Presses ^b	Pressed Surface	No. Blanks	Chlorpyrifos Detected		
				n	Mean	Range
Lab Blanks						
0	0	None	3	0		
Field Blanks						
2	1	Aluminum foil	8	8	0.18	0.10–0.38
3	1	Carpet (48 cm ²)	12	12	0.26	0.14–0.60
3	10 ^c	Cardstock (480 cm ²)	22	21	0.23	0.11–0.88

a Two wipes of hand(s) with 2-propanol-moistened SOF-WICK® gauze.

b Press of palm of one hand onto cleaned surface.

c Ten presses of palm of one hand onto adjacent sections of clean cardstock.

Table 4. Transfer rates (ng/cm²) of piperonyl butoxide from plush carpet in Experiment 6B by drag sled, PUF roller, and human hand presses

Block	Deposition	Drag Sled	PUF Roller	Hand	Ten Hand Presses		
					A	B	C
6-22-93 (Application)							
NE	4,980	167	67	R	12	18	13
NW	5,810	178	75	L	42	39	21
6-23-93							
CE	2,870	160	41	L	26	12	10
CW	2,480	116	48	R	19	17	14
6-24-93							
SE	4,120	107	61	R	17	13	11
SW	4,000	39	53	L	9	5	16
<u>Statistics</u>							
n	6	6	6			18	
Mean, \bar{x}	4,040	127.9	57.6			17.4	
Std. dev., s	1,250	52.1	12.5			9.7	
Coef. of Variation	0.31	0.41	0.22			0.56	

Table 5. Comparison of transfer of fresh dried formulated pesticide residues from flooring by drag sled, PUF roller, and human hand presses^a

Exp.	Flooring	Applied Active Ingredient	Transfer Rate ($\bar{x} \pm s$) ^b , ng/cm ² , Using		
			Drag Sled (n=6)	PUF Roller (n=6)	Ten Hand Presses (n=18)
6A	Plush carpet (used)	Chlorpyrifos	5.6 \pm 3.2	1.8 \pm 1.0	CB ^{d,e}
		Piperonyl butoxide	7.0 \pm 4.0	2.2 \pm 1.1	ND ^{d,e}
		Pyrethrin I	1.0 \pm 0.9	0.2 \pm 0.1	ND ^c
6B	Plush carpet (used)	Chlorpyrifos ^c	9.2 \pm 3.7	2.9 \pm 0.3	1.3 \pm 0.8
		Methoprene	2.5 \pm 0.7	0.8 \pm 0.5	0.3 \pm 0.2
		Piperonyl butoxide	128 \pm 52	58 \pm 12	17 \pm 10
		Pyrethrin I	38 \pm 22	16 \pm 3	ND
7	Sheet vinyl (new)	Chlorpyrifos	1890 \pm 1430	780 \pm 440	250 \pm 200
		Piperonyl butoxide	1660 \pm 990	630 \pm 390	300 \pm 210
		Pyrethrin I	192 \pm 49	116 \pm 68	39 \pm 42

a Transfer by single pass over flooring using dry contact medium

b Mean and standard deviation of transfer rates from 0 to 2 days after application

c Transfer rates from 6 to 8 days after application

d Single hand press

e CB = comparable to field blank; ND = not detected

Table 6. Transfer efficiency^a (%) of fresh dried residues by flooring, active ingredient, and transfer method^b

Exp.	Flooring	Application Method	Active Ingredient	Transfer Efficiency, % ^a		
				Drag Sled	PUF Roller	Ten Hand Presses
6A	Plush carpet (used)	Broadcast	Chlorpyrifos	0.10	0.03	
			Piperonyl butoxide	0.12	0.04	
			Pyrethrin I	0.19	0.04	
6B	Plush carpet (used)	Aerosol can	Methoprene	3.0	1.0	0.4
			Piperonyl butoxide	3.2	1.4	0.4
			Pyrethrin I	3.3	1.4	
7	Sheet vinyl (new)	Broadcast	Chlorpyrifos	24	9.7	3.2
			Piperonyl butoxide	22	8.3	4.0
			Pyrethrin I	16	9.6	3.2

a Transfer efficiency (%) = $100 \times (\text{mean transfer rate, ng/cm}^2) / (\text{mean surface loading, ng/cm}^2)$. Means of transfer rates and surface loadings are for observations from 0 to 2 days after application.

b Transfer by single pass over flooring using dry contact medium.

COMPARISON OF PM_{2.5} AND OPEN-FACE INLETS FOR SAMPLING AEROSOLIZED PESTICIDES ON FILTERED POLYURETHANE FOAM

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ABSTRACT

Ten pairs of air concentrations were obtained using collocated PM_{2.5} and open-face inlets to collect aerosolized formulations of neutral pesticides and acid herbicides in wind tunnel experiments. In sampling the generated aerosol, the PM_{2.5} inlet measured significantly smaller air concentrations of chlorpyrifos, 2,4-D, and mecoprop than the standard open-face inlet. In contrast, both inlets determined similar concentrations of neutral pesticides in ambient air.

INTRODUCTION

In sampling the particles and vapor of an aerosolized pesticide through the standard open-face inlet (1), a filtered polyurethane foam (PUF) trap will collect some airborne particles which are too large to be respired. A portable size-selective impactor inlet for the standard filtered PUF plug enclosed in sturdy plastic housing has recently been developed to sample vapors and particles of dia. 2.5 μ m or less (PM_{2.5}) for personal monitoring. Wind tunnel experiments were performed to determine if this personal PUF sampler with a PM_{2.5} inlet collects a smaller mean pesticide air concentration than the standard PUF sampler with an open-face inlet.

METHODS

Air Sampling Methods

Air samples were collected on precleaned PUF with a quartz fiber prefilter using the standard cartridge with an open-face inlet (1) and the URG-2000-25A cartridge (Figure 1, University Research Glassware, Carrboro, NC) with a PM_{2.5} inlet. Relevant properties of both cartridge assemblies are compared in Table 1. Each cartridge was attached by Tygon® tubing to a DuPont Alpha 1® sampler calibrated at a nominal 3.8 Lpm flow rate, and hung with the inlet facing downward. Air samples were collected for 16 to 30 min to span the release of aerosolized pesticide during an experimental run. PUF plugs were cut and cleaned, Whatman filters were cleaned, and sampling cartridges were assembled and protected as previously described (2). 50 μ L of diluted Dow Corning 704 high temperature silicone oil was placed on the impactor frit of the URG cartridge. Aluminum foil was also wrapped around the URG cartridge and the union connector of the standard cartridge to protect exterior surfaces and avoid possible transfer contamination of the PUF or filter during set-up for extraction.

Wind Tunnel

A simple outdoor wind tunnel was constructed from large cardboard boxes mounted on sawhorses to contain an aerosol generator, an air movement system, and four air sampling systems (Figure 2). The tunnel was oriented parallel to the prevailing wind direction. The fan speed of the box fan was set so

that ambient air traversed the tunnel at 2 to 4 m/s during each experimental run. A burst of aerosolized pesticide formulation was generated by operating a heavy-duty sprayer for 3 s to release a fine spray in a cone pattern from the nozzle every 15 s into the airstream near the tunnel entrance. Two screens were placed across the tunnel between the nozzle and the air samplers to enhance aerosol mixing and diffusion. Initial qualitative tests were performed with fluorescent tracers which demonstrated uniform horizontal dispersion of the aerosolized tracer at the tunnel outlet.

Experimental Design

Ten pairs of air concentrations were obtained using collocated open-face and $PM_{2.5}$ inlets in each of two wind tunnel experiments. Each experiment consisted of a preliminary run, a field blank run, and five replicate field sampling runs. Two inlets of each type were positioned at the opposite corners of a square with 40-cm sides to collect the air samples for each run (Figure 2). The two inlets at the same height were treated as one pair. To prevent possible location bias, the positions of the open-face and $PM_{2.5}$ inlets were alternated on successive runs. The preliminary run verified that the quantity of formulation aerosolized was sufficient to yield detectable sampled air concentrations. The five replicate runs to sample the aerosolized formulation were performed over three days. 100 mL of Zema Fast Acting Spray for Dogs[®] (0.225 % chlorpyrifos, 0.05 % pyrethrins, 0.10 % piperonyl butoxide) in 1.5 L of deionized water was aerosolized in each run of the neutral insecticide experiment. 100 mL of Ortho Weed-B-Gon for Southern Lawns Formula II[®] (10.6 % dimethylamine [DMA] salt of mecoprop, 3.05 % DMA salt of 2,4-D, 1.30 % DMA salt of dicamba) in 1.5 L of deionized water was aerosolized for each run of the acid herbicide experiment. A field spike of the PUF plugs (insecticide experiment) or filters (herbicide experiment) was placed on both types of sampling cartridges, both before and after the five replicates.

Analytical Methods

The PUF and filter from each cartridge were extracted together as a single sample. Samples from the neutral pesticides experiment were Soxhlet-extracted with 6% diethyl ether/94% hexane (3). Samples from the acid herbicides experiment were cold-shake extracted using acidified 1:1 diethyl ether:hexane, and the extracts were esterified with diazomethane (3). Extracts were analyzed for chlorpyrifos, pyrethrin I, and piperonyl butoxide (neutral pesticides experiment) and for the methyl esters of 2,4-D, dicamba, and mecoprop (acid herbicides experiment) on a Fisons MD 800 operating in selected-ion monitoring mode.

Statistical Methods

Reported data have not been adjusted for field spike recoveries. The differences between paired open-face and $PM_{2.5}$ air concentrations were evaluated over all ten pairs by a t-test of the null hypothesis of equal determinations of the pesticide against the one-sided alternative of a smaller determination with the $PM_{2.5}$ inlet at the 0.05 level of significance.

RESULTS AND DISCUSSION

Pyrethrin I and piperonyl butoxide were not detected in the air samples. Reported analytes were efficiently recovered from field spikes of sampling media (Table 2). Field blanks showed that off-gassing of dried residues from prior runs was minor compared to aerosols generated for the field replicates.

The individual measured air concentrations from the ten pairs and their summary statistics are presented for chlorpyrifos and 2,4-D (Table 3). The $PM_{2.5}$ inlet appears to give generally smaller mean air concentrations than the open-face inlet for each measured aerosolized analyte (Table 4). However, the validity of three pairs of measurements from the acid herbicide experiment is uncertain. The levels obtained for 2,4-D, dicamba, and mecoprop in the $PM_{2.5}$ inlet sample of the Replicate 4 upper level pair may underestimate the actual concentrations because the extract went to partial dryness during blow-down. In addition, for all three acid herbicides, the air concentrations from the Replicate 3 upper level

pair exhibit a relationship (open-face \ll $PM_{2.5}$) which differs markedly from the other nine pairs, and is the opposite of the relationship seen in eight other pairs (open-face \gg $PM_{2.5}$). This suggests a possible mix-up during labelling or processing of these two samples or their extracts, despite a lack of supporting evidence. The hypothesized sample mix-up might also have affected the lower pair of Replicate 3. To be conservative, the statistical analysis was performed both including (n=10) and excluding (n=7) the pairs with a questionable acid herbicide measurement (Table 4). Significantly smaller air concentrations of chlorpyrifos, 2,4-D, and mecoprop were sampled with the $PM_{2.5}$ inlet than with the standard open-face inlet in aerosols generated in the wind tunnel experiments. No inference can be drawn from the dicamba measurements.

Pairs of ambient concentrations of neutral pesticides were also obtained with collocated open-face and $PM_{2.5}$ inlets by sampling ambient outdoor air in an urban area for 24 h as described. Both inlets gave very similar air concentrations of the prevalent pesticides, chlorpyrifos and lindane, but the $PM_{2.5}$ determination was usually slightly larger (Table 5). Heptachlor was detected more frequently with the $PM_{2.5}$ inlet, while atrazine and 4,4'-DDT were more frequently detected with the open-face inlet. The open-face and $PM_{2.5}$ inlets appear to trap similar concentrations of neutral pesticides from ambient air.

ACKNOWLEDGEMENT

This research was funded by the U.S. Environmental Protection Agency (Contract 68-DO-0007) under subcontract from Battelle. This paper has received EPA's peer and administrative review, but no official endorsement should be inferred.

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3. Geno, P.W., Camann, D.E., Villalobos, K., Lewis, R.G., "Analytical methods for assessing the exposure of farmers and their families to pesticides," in *Proceedings of the 1993 U.S. EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants*, "VIP-10; Air & Waste Management Association; Pittsburgh, 1993; pp 698-705.

Table 1. Comparison of properties of cartridge assemblies used for sample collection.

Property	Standard Open-face Filtered PUF Cartridge	URG $PM_{2.5}$ Filtered PUF Cartridge
Impactor disc	None	#30 aluminum insert
Particle size collection	All	<2.5 μ m dia.
Filter type	2500 QAT-UP (0.5 μ m)	2500 QAT-UP (0.5 μ m)
Filter size	32 mm	25 mm
PUF plug size	2.5 cm dia. x 7.6 cm	2.5 cm dia. x 7.6 cm
Air sample flow rate	3.8 Lpm	3.8 Lpm

Table 2. Field blank^a amounts and field spike recoveries.

Analyte	Mean (n=4) field blank amount, μg	Spike recovery, % Mean \pm std. dev. (n)
Chlorpyrifos	0.02	89 \pm 8 (4)
2,4-D	0.005	85 \pm 4 (2)
Dicamba	<0.005	88 \pm 4 (2)
Mecoprop	0.02	98 \pm 6 (2)

a Four clean cartridge assemblies operated in the wind tunnel for 20-30 min (3-5 days after a preliminary run using the aerosolized analyte)

Table 3. Comparison of air concentrations from collocated open-face and $\text{PM}_{2.5}$ inlets for chlorpyrifos and 2,4-D.

Rep- licate	Inlet height ^a	Air Concentration, $\mu\text{g}/\text{m}^3$					
		Chlorpyrifos			2,4-D		
		Open- face	$\text{PM}_{2.5}$	Open-face - $\text{PM}_{2.5}$	Open- face	$\text{PM}_{2.5}$	Open-face - $\text{PM}_{2.5}$
1	U	3.6	2.2	1.4	4.8	0.6	4.2
	L	3.8	4.4	-0.6	9.0	0.4	8.6
2	U	2.7	2.0	0.7	2.9	0.9	2.0
	L	6.9	4.3	2.6	15.0	0.7	14.3
3	U	4.8	2.1	2.7	0.6 ^b	7.2 ^b	-6.6 ^d
	L	4.5	1.4	3.1	2.8	0.7	2.1 ^d
4	U	2.2	1.2	1.0	2.0	0.8 ^c	1.2 ^d
	L	6.1	2.8	3.3	6.4	0.4	6.0
5	U	3.8	0.7	3.1	2.5	0.3	2.2
	L	3.3	1.8	1.5	0.40	0.45	-0.05
n		10	10	10	10. (9 ^e)	10. (8 ^e)	10. (7 ^e)
\bar{x}		4.16	2.29	1.87	4.64 (5.09 ^e)	1.23 (0.54 ^e)	3.40 (5.34 ^e)
s		1.46	1.24	1.30	4.51 (4.53 ^e)	2.11 (0.20 ^e)	5.54 (4.88 ^e)

a Samples from same horizontal plane are paired: U = upper level, L = lower level.

b Possible mix-up of samples by inspection of results for all three acidic analytes.

c Possible underestimate, since sample went to partial dryness during extraction.

d Questionable result; see footnotes b and c.

e Excluding questionable results.

Table 4. Summary of tests to determine if PM_{2.5} inlet collects a smaller mean air concentration of aerosolized analytes than a collocated open-face inlet.

Aerosolized Analyte	Air Concentration, µg/m ³ Mean ± Std. Dev. (n)		Is PM _{2.5} Concentration Smaller?			
	Open-face Inlet	PM _{2.5} Inlet	No. Pairs	Mean difference µg/m ³	p-value	Significantly smaller?
Chlorpyrifos	4.2 ± 1.5 (10)	2.3 ± 1.2 (10)	10	1.9	0.001	Yes
2,4-D	4.6 ± 4.5 (10)	1.2 ± 2.1 (10)	10 7 ^b	3.4 5.3	0.04 0.015	Yes Yes
Dicamba	1.8 ± 1.4 (10)	0.7 ± 1.0 (10)	10 7 ^b	1.2 2.0	0.05 0.01	No Yes
Mecoprop	13.8 ± 11.1 (10)	4.0 ± 7.1 (10)	10 7 ^b	9.9 15.7	0.04 0.007	Yes Yes

a One-sided t test at α=0.05.

b Excluding pairs with questionable results.

Table 5. Pesticide concentrations in ambient air (ng/m³) determined by collocated open-face and PM_{2.5} inlets.

Day	Chlorpyrifos		Lindane	
	Open-face	PM _{2.5}	Open-face	PM _{2.5}
1	1.3	1.4	<0.4	1.1
2	1.3	0.8	1.0	1.1
3	0.9	0.7	1.0	1.2
5	1.9	0.8	1.2	1.3
6	0.9	1.3	1.2	1.0
8	0.7	1.3	1.2	<0.04
9	1.2	2.5	1.0	1.3
10	0.9	1.1	1.1	1.3
11	0.8	0.9	1.2	1.4
No. larger measurements	3	6	2	7

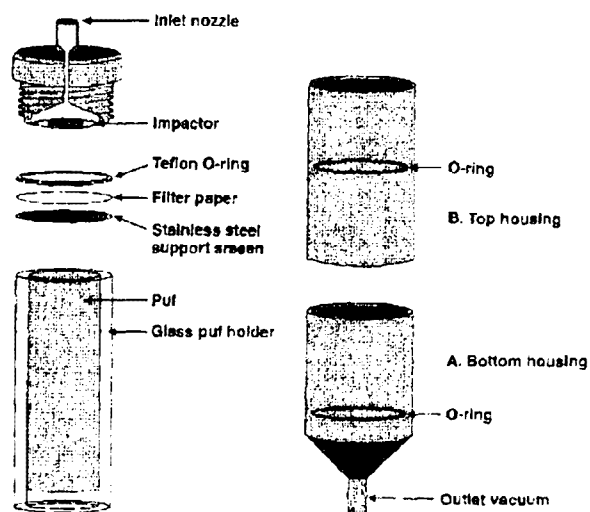


Figure 1. URG-2000-25A, Portable Size - Selective Impactor Inlet with PUF, 4 Lpm, 2.5 μ m cut

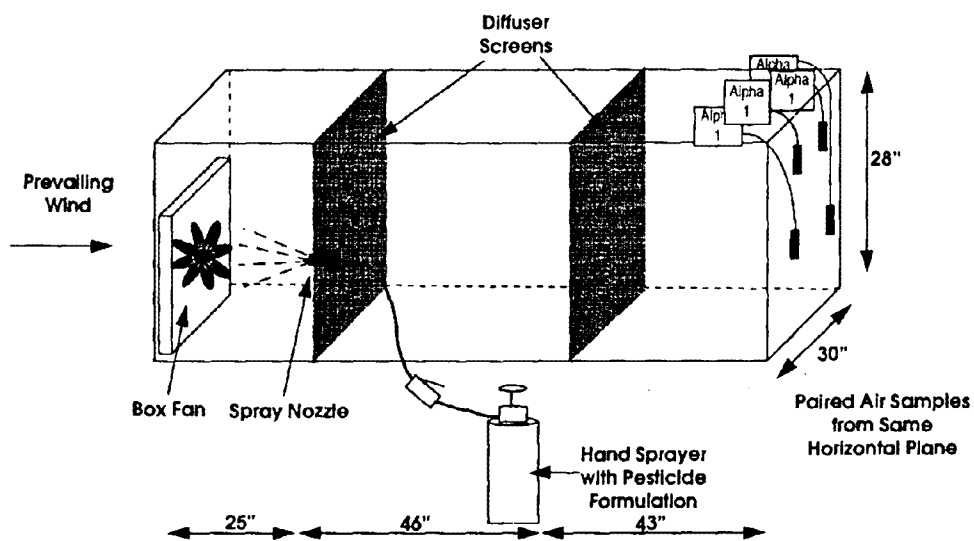


Figure 2. Outdoor wind tunnel system to generate aerosolized pesticide mixture and collect collocated air samples.

SESSION 19:
SOURCES AND FATE OF
ATMOSPHERIC VOCS

**Methods to Determine the Biogenic Contributions
to Ambient Concentrations of Volatile Organic Compounds**

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Vegetative emissions of photochemically reactive volatile organic compounds (VOCs) (e.g., isoprene) are considered important sources of ozone precursors. The U.S. EPA is currently evaluating a number of procedures to obtain reliable biogenic emission inventories. This report describes ambient measurement procedures to collect, process and analyze VOC samples to measure the relative percent of the total VOCs that originates from vegetative emissions. In 1992, VOC were collected in 32L canisters at a downtown location in Atlanta as part of the summer Southern Oxidant Study. These canister samples were to be submitted to the National Institute of Standards and Technology to measure their ^{14}C content. Vegetative (also referred to as biogenic) VOCs are enriched in ^{14}C while emissions from fossil fuels (e.g., gasoline) are practically devoid of this isotope. Thus, the ratio of ^{14}C to ^{12}C in ambient VOC samples can provide a direct determination of the fraction of carbon whose origin is biogenic. To date, the cryogenic procedure being developed at NIST to isolate the total VOC fraction from whole (humid) air effectively separates all VOCs from CO and CH_4 and only the less volatile VOCs, defined by their equilibrium vapor pressure at -80°C , from CO_2 . Separation of the more volatile VOCs from CO_2 remains problematic until the necessary preparative gas chromatographic/combustion technique

is developed. In the mean time, a new pre-cryogenic procedure has been developed to reduce the CO_2 concentration by a factor of 10^4 (e.g., from 360 ppm to 30 ppb) in whole air samples through the use of a LiOH trapping system. These samples would then be submitted to NIST for subsequent cryogenic separation of VOCs from CO and CH_4 , followed by oxidation to CO_2 measurement processing. The identification and quantification of VOC species lost during the CO_2 removal step has been incorporated into the methodology. For example, as part of the procedure an aliquot of whole air sample, prior to removing the CO_2 , is analyzed by identical gas chromatographic (GC) systems, one equipped with a flame ionization detector (FID) and the other a mass selective (MS) detector. The GC/FID analyzer quantifies each of the chromatographic peaks and the GC/MS system identifies each species eluted from the GC column. After the CO_2 has been removed from the whole VOC air sample, it is reanalyzed by the GC/FID and GC/MS analyzers. In this way, losses of VOCs (especially oxygenates) may be quantified and identified. Those species which have been identified as biogenic or biogenic reaction products are incorporated into estimates of the fraction of VOCs that may originate from biogenic sources. The report describes the status of these studies and presents preliminary results of the gas chromatographic analysis and ^{14}C measurements.

Radiocarbon Measurements Of Wintertime Atmospheric Carbon Monoxide in Albuquerque, NM: Contributions Of Residential Wood Combustion

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In the past during winter months, Albuquerque, NM, has occasionally exceeded the $9 \mu\text{L/L}$ (part-per-million by volume, ppmv) - 8 hour National Ambient Air Quality Standard (NAAQS) for carbon monoxide (CO), thereby, requiring action toward attainment. Previous results of CO concentrations and radiocarbon (^{14}C) measurements from a wintertime 1984-1985 study of Albuquerque suggested that, during this time of year, residential wood combustion (RWC) and motor vehicle emissions were the primary sources of ground-level CO concentrations [Einfeld et al. (1988), Klouda et al. (1986) and (1988)].

The major objective of this study was to reevaluate these source contributions in light of the more recent implementation of no-burn days based on the meteorological forecast 24 hours in advance. Whole air samples were collected during the Winter of 1989-1990 in Albuquerque, NM, for CO concentration and ^{14}C measurements. Since resources for this study were limited, a 23-factorial design with limited replication was used to obtain optimal source information given a constraint of 10 ambient samples. The three-factor two-level sampling design included the following: 1) sampling location; residential vs traffic sites, 2) time-of-day; 0630 to 1430 vs 1630 to 0030, and 3) forecasted meteorology; dynamic vs stagnant air mass, to effectively cover time-space. On three occasions, samples were collected for target periods of maximum wood burning, as predicted by the forecast meteorology that suggested times of cold stagnant air which would likely result in temperature inversions with little mixing. Radiocarbon results, assuming that a measured ^{14}CO background component applies, indicated that the contribution of RWC ranged from 0% to 32% for all samples analyzed. For samples collected when conditions were most favorable for high CO but designated as no-burn, the RWC contribution ranged from 0% to 18%. The data suggested that the no-burn strategy has been effective and that further controls on motor vehicles may be necessary especially during unique periods, e.g. over Christmas holiday, when the NAAQS is more likely to be exceeded. Additionally, the relation of fossil CO and benzene was explored in light of a possible reduction in an occupational health and safety standard from 1 ppmv to 0.1 ppmv.

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Progress toward Validating the Separation of Atmospheric Volatile Organic Carbon from Air for ^{14}C Measurements

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It is well known that atmospheric volatile organic compounds (VOCs) from fossil and biomass sources contribute to the production of ozone (O_3) during summer months via photochemical pathways. The degree to which each source participates in the chemical process is important to help design effective strategies to control O_3 levels in urban atmospheres. An accurate measure of source contributions can be obtained from radiocarbon (^{14}C) measurements made directly on the VOC fraction. With the sensitivity of accelerator mass spectrometry $^{14}\text{C}/^{12}\text{C}$ measurements now at 10 μg modern carbon (1 μg blank) and 2% precision (Currie et al., 1994), the ability to obtain quality (interpretable) VOC- ^{14}C measurements relies on other factors: 1) the recovery of VOCs from air, 2) the bounds for bias (chemical and isotopic) due to inefficiencies in the chemical separation process, and 3) minimal chemical and isotopic contamination (blanks).

This report will include more recent steps taken to validate techniques developed at NIST for separating VOCs from either untreated (humid) air (Klouda et al., 1993) or air preprocessed with LiOH (Stevens et al., this proceedings) to remove H_2O and CO_2 . A hydrocarbon (gasoline) reference material, diluted gravimetrically to $\sim 2 \mu\text{mol C/mol}$ with hydrocarbon-free air containing ambient CO_2 concentration, and ambient samples from Atlanta and Houston are used to evaluate recovery and isotopic blank. Results of these experiments will be presented along with a discussion of other chemical and isotopic information necessary for reliable interpretation of atmospheric VOC- ^{14}C measurements.

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Klouda et al. (1993), proceedings of the AWMA Meeting on Measurement of Toxic and Related Air Pollutants.

Stevens et al. (1994), this proceedings of the AWMA Meeting on Measurement of Toxic and Related Air Pollutants.

**Atmospheric Chemistry of Unsaturated Oxygenates:
Alcohols, Aldehydes, Ketones and Esters**

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It has been known for many years that biogenic emissions include unsaturated oxygenates such as alcohols, aldehydes, ketones and esters. Yet, while the atmospheric chemistry of other important biogenic hydrocarbons (isoprene and terpenes) has received much attention, little is known regarding the atmospheric persistence and fate of unsaturated oxygenates. As olefins, unsaturated oxygenates are expected to be oxidized in the atmosphere in pathways initiated by their reactions with ozone and with the hydroxyl radical. These reactions produce carbonyls, carboxylic acids, and, in the presence of oxides of nitrogen, peroxyacyl nitrates. Thus, information on the atmospheric chemistry of unsaturated oxygenates is important in the context of assessing the role and impact of biogenic hydrocarbon emissions.

We have measured ozone reaction rate constants for a number of unsaturated alcohols, esters and carbonyls. Using these rate constants together with structure-reactivity relationships, rate constants have been estimated for the reaction of the hydroxyl radical with the unsaturated biogenic oxygenates of interest. From these kinetic data, estimates could be made of the atmospheric lifetimes for a number of unsaturated alcohols, esters and carbonyls. We have also investigated, in laboratory experiments carried out under conditions that are relevant to the atmosphere, the oxidation of the unsaturated alcohols *cis*-3-hexen-1-ol, 3-buten-1-ol, and allyl alcohol. Two types of experiments have been performed, one involving sunlight irradiations of unsaturated alcohol-NO mixtures and the other involving the reaction of ozone with the unsaturated alcohol in the dark. Carbonyl and peroxyacyl nitrate products of the alcohol-NO reaction in sunlight have been identified and their concentrations measured. Peroxypropionyl nitrate (PPN, $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OONO}_2$) was a major product of *cis*-3-hexen-1-ol and accounted for 14-20% of the initial NO. Atmospheric persistence of unsaturated alcohols and implications for the formation of propanal and PPN from biogenic emissions of *cis*-3-hexen-1-ol will be discussed.

Atmospheric Chemistry and Fate of C2-C5 Peroxyacyl Nitrates

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Peroxyacyl nitrates, $RC(O)OONO_2$ (PANS), are of major importance in atmospheric chemistry. They have also received attention as toxic air contaminants: the several PANS studied so far are eye irritants, mutagenic and phytotoxic. While the simplest compound, PAN ($CH_3C(O)OONO_2$), has been studied in detail, little is known regarding the ambient concentrations, atmospheric persistence and atmospheric fate of higher molecular weight PANS.

In this study, we have investigated twelve saturated and unsaturated aliphatic PANS, $R = CH_3$ (PAN), C_2H_5 , C_3H_7 (2 isomers), C_4H_9 (4 isomers), $CH_2 = CH-$, $CH_2 = C(CH_3)-$, $CH_2 = C(C_2H_5)-$ and $CH_3CH = CH-$. These compounds have been synthesized in the liquid phase, prepared in-situ by sunlight irradiation of NO-carbonyl mixtures (e.g., $CH_2 = C(C_2H_5)C(O)OONO_2$ from NO and 2-ethylacrolein), measured at ppb levels by electron capture gas chromatography, and characterized using a number of chemical and physical diagnostic tests. Thermal decomposition, a major loss process for all PANS in the atmosphere ($RCO_3NO_2 \rightarrow RCO_3 + NO_2$) has been studied at ambient temperature and 1 atm. of air. Other removal processes studied include reactions with OH, and, for the unsaturated PANS, reaction with ozone. These removal processes will be discussed with respect to the persistence of PANS in the atmosphere.

**Comparison of Ambient Ratios of NMHCs and CO to NO_x with
Emission Inventory Values for Atlanta**

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Ratios of NMHCs and CO to NO_x obtained during the 1990 Atlanta Ozone Precursor Study are compared to values predicted by emissions inventories. Ambient data and emissions inventory values for the early morning rush hour are used following methods originally adapted for the Los Angeles Air Shed by Fujita et al. (JAWMA, **42**, pp. 264-276, 1992.) A number of factors which could affect the conclusions of ambient data-emissions inventory reconciliation studies such as the photochemical processing of emissions, transport from background areas and the effectiveness of pollution control devices are discussed. Results from these analyses are qualitatively consistent with other studies from the Los Angeles air basin and the Lake Michigan air quality region, indicating an underprediction of these ratios by the emissions inventories compared to ambient data.

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SESSION 20:

RUSSIAN AIR POLLUTION STUDIES

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**MEASUREMENT OF TOXIC POLLUTANTS IN RUSSIA
CITIES AND THEIR EFFECT ON HUMAN HEALTH**

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ABSTRACT

This paper includes the results of measurements of concentration benz(a)pyrene, benzene, phenol and formaldehyde in Russian cities for 1992. The effect of meteorological conditions is shown. This presentation includes discussion of the effects of annual means concentrations toxic pollutants on the number of cases of adult population of cancer tumours cases for 47 cities of former USSR for period of 1986-1990.

INTRODUCTION

The national network of air pollution (AP) in Russia assess concentrations of not only widespread pollutants, but also many toxic pollutants.

To assess benz(a)pyrene (BP) concentrations, dust is collected on aerosol filters 3 times of day during a month and analysed. Phenol and other pollutant concentrations are assessed by sampling 20 min. Methods to assess concentrations of pollutants are given in Guidance (1991).

To estimate the degree of AP in a city the measured values of pollutant concentrations are compared with air quality criteria - maximum permissible concentrations for Russia (MPC) or WHO standards.

RESULTS OF MEASUREMENTS

The data of the benz(a)pyrene (BP), benzene, phenol and formaldehyde mean concentrations and number of measured stations in Russia for 1992 are given in Table 1. The mean concentration of BP for all cities of Russia is 3 times higher, of benzene 3.6 times higher than WHO standards, of formaldehyde 3 times higher, of phenol 1.1 times higher than MPC. These concentrations for 5 years (1988-1992) are increased in many biggest cities of Russia (Fig.1) (Annual Report, 1993).

It was important to take into consideration the effect of meteorological conditions in spread of benz(a)pyrene. The most unfavourable conditions for spreading pollutants are observed in the Eastern Siberia and particularly in the Trans-Baikal area. In this areas with high air pollution potential the mean concentrations of BP are more than twice as high as in the rest of part of Russia (Fig.2).

The formaldehyde concentrations are higher near high ways in summer month under high solar radiation intensivity. In all biggest cities (more 500 thousand population) the relationship between annual mean formaldehyde concentration and latitude of place is rather clear. Correlation factor equals 0.62.

EFFECT OF AIR POLLUTION ON HUMAN HEALTH

This research has been supported by the Research Support Scheme of the Central European University.

To study the effect of air pollution on human health, the annual mean concentrations of different pollutants have been used for 47 cities for the period of 1986-1990 from Annual Reports (1987, 1988, 1989, 1990, 1991) published by Main Geophysical Observatory.

For statistical analysis there were chosen cities where the data are available for the recent 3 years and where the regular measurement results for each month of the year during 3 years or more are available on benz(a)pyrene or formaldehyde or phenol concentrations since, as is well known, it affects considerably the morbidity with cancer diseases.

From 1982 in the USSR the complex program "ASIS-Health" (ASIS is automated state information system) existed. To carry out the work, the data of this information system kindly provided to me Dr.Yu.A.Abrsimova, and from Protection of environment (1989) are used on the number of cancer tumours cases (NCTC) for the above 47 cities.

The data were not used for the cities located in the area of Chernobyl APP influence where the effect of radiation pollution can prove to be higher than that of chemical air pollution.

An important problem in studying the dependence of human morbidity on air pollution is establishing a complex air pollution index (API) which would characterize the real state of pollution by many pollutants. API has been developed by Bezuglaya and others (1993). It is calculated from the mean concentration of the i -th pollutant (x), the daily mean MPC and the class of danger of each pollutant.

$$J(n) = \sum_{i=1}^n J_i = \sum_{i=1}^n \left(\frac{x}{MPC_i} \right)^{C_i} \quad (1)$$

C_i is coefficient allowing to reduce the degree of air pollution by the i -th pollutant to the degree of air pollution by sulphur dioxide; C_i is equal 1.5, 1.3, 1.0 and 0.9 for 1, 2, 3 and 4 class of danger.

API sums up the above annual mean concentrations of 5 harmful pollutants determining the basic contribution to air pollution level, including benz(a)pyrene, formaldehyde, phenol and others.

As a result of joint statistical analysis of the data on the NCTC and API for 1986-1990 reliable conclusions were drawn on the effect of air pollution on morbidity. The factor of correlation between these values in different years was 0.42-0.69, for the whole period 0.60 ± 0.07 (Table 2).

Table 2 also demonstrates that the coefficient b related with API is stable. In all variants of calculation " b " changed within 0.11-0.13. This points to the fact that the increase of air pollution is followed by the increase of the NCTC. The regression equation has the following form:

$$N = 1.80 + 0.11 J \quad (2)$$

The type of dependence is shown in Fig.3.

The lower limit of the number of cases of morbidity is almost the same for each year. The minimum NCTC increases clearly with API growth. Therefore for each year we selected cases related to the lower limit (41 cases) and from these data the regression equation was calculated. The correlation proved to be very high, $r = 0.934$. In the absence of other harmful effects the NCTC cases caused by air pollution can be estimated from formula

$$N_{n,l} = 0.14 J \quad (3)$$

From this equation one can assume that at $J = 10$ the minimum number of cases of diseases would equal 1.4 per 1000 men and at $J = 20$ it would double.

One can assess the values of API at which one case of cancer would appear. It is equal 7.14. API is a total air pollution by 5 pollutants. Therefore one case of disease is observed when MPC is exceeded on the average for these 5 pollutants by 42% only.

The conclusions were checked against independent material of 27 cities for 1990. The results of checking show that the error of diseases is 29%.

For 17 cities for which necessary information on API and morbidity was available for 5 years there were calculated trends of these values. The decrease in the NCTC was hardly observed (0.6%) when air pollution decreased by 5%. It is evident that the decrease in the number of diseases as a result of reduction in air pollution level does not occur immediately. The consequences of high air pollution in cities would show up as the NCTC from now over many years.

Considerable contribution to the high level of urban air pollution is made by mean BP concentrations. For cities under study the contribution of BP to the total API is 25-70%. It is believed that BP and other carcinogenic pollutants against the background of the general high level of air pollution determine the number of cancer cases. However the probability is high of diseases under the effect of formaldehyde, phenol and other toxic pollutants present in the atmosphere.

Comparison of the USA technique (W.F.Hunt and others, 1985) for the risk assessing and actual data on the NCT cases in Russian cities shows the good agreement. The sum of the risk estimates has been calculated on the basis of the US risk assessment (RA) data (E.Anderson, 1982) and air pollution concentrations for this obtained from the real results of observations from the 47 cities of Russia and the data on malignant tumour cases (N_c) for the above 47 cities. The relationship between the mean US risk assessment (RA) and malignant tumour cases in Russian cities is good (Fig.4).

At high pollution levels one can forecast the increase of probability of up to 5 cases of cancer diseases per 1000 inhabitants from 17% at $API > 10$ to 32% at $API > 20$.

CONCLUSIONS

1. The mean concentrations of toxic pollutants in Russian cities are high and are increased in many biggest cities for 5

year. The most unfavourable conditions for spreading pollutants are observed in the Eastern Siberia with high air pollution potential.

2. Conclusions have been drawn as a result of statistical analysis of data on the number of cancer cases and AP levels for 1986-1990 in 74 cities. The factor of correlation between API and morbidity is 0.60 ± 0.07 . The possibility of estimating the minimum of cases of diseases is shown. The error of estimating the number of cases of diseases is 29%. The contribution of BaP to the total API is 25-70%.

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Table 1. Number of stations (N) and pollutant concentrations (x, ug/m³) and maximum permissible concentrations (MPC) in the Russian cities

Pollutant	N	x	Stand. deviat.	Standard	max	City
BP	327	0.003	0.005	0.001(WHO)	0.086	Bratsk
Benzine	54	90	95	25(WHO)	0.28	Podolsk
Formalde- hyde	248	9	9.7	3(MPC)	28	Lipetsk
Phenol	221	3.3	3.2	3(MPC)	12	Usolve- Sibirskoye

Table 2. Results of statistical analysis of the relationship between cancer tumour cases and API

Year	a	f a	b	i b	r	r ²	n
1986	1.59	1.06	0.11	0.03	0.69	0.48	22
1987	1.47	1.17	0.13	0.03	0.58	0.34	31
1988	1.86	0.98	0.11	0.02	0.65	0.42	39
1989	1.93	1.25	0.11	0.04	0.42	0.18	40
1990	1.58	1.16	0.11	0.02	0.66	0.43	45
For the whole period	1.80	1.11	0.11	0.01	0.60	0.36	180
From averages	1.67	1.00	0.12	0.02	0.62	0.38	41

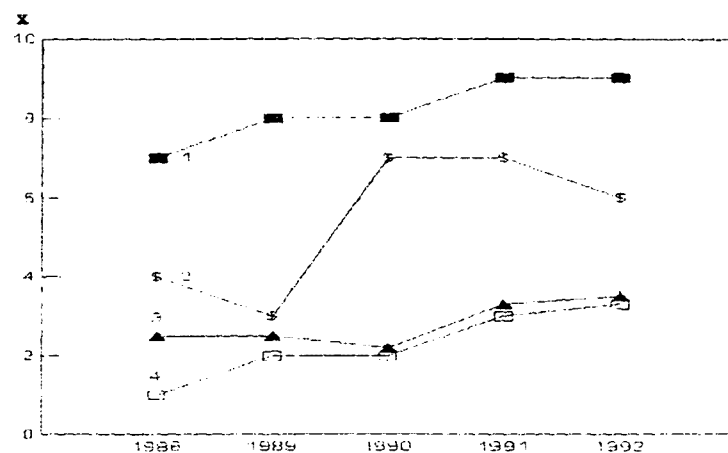


Fig.1. Annual means of phenol concentrations (x , $\mu\text{g}/\text{m}^3$) in some cities: 1 - Krasnodar, 2 - Magnitogorsk, 3 - Novokuznetsk, 4 - Tomsk

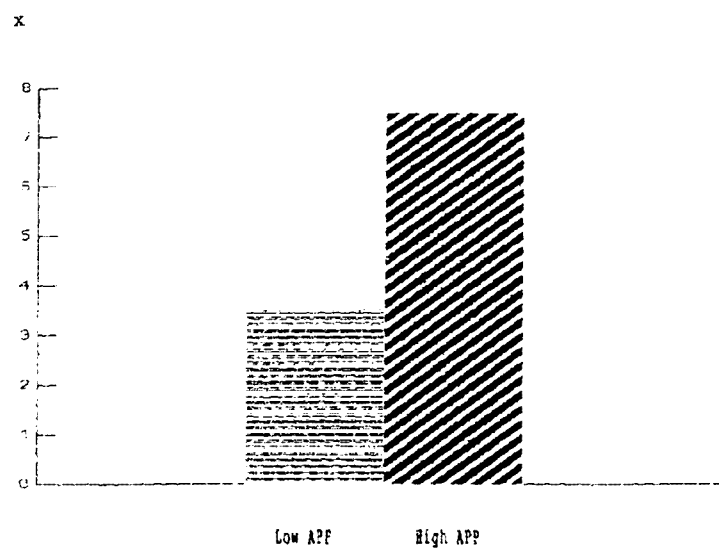


Fig.2. Mean concentrations ($x * 10^3$, $\mu\text{g}/\text{m}^3$) of benzopyrene in groups of cities situated in different zones of meteorological air pollution potential (APP): low APP, high APP

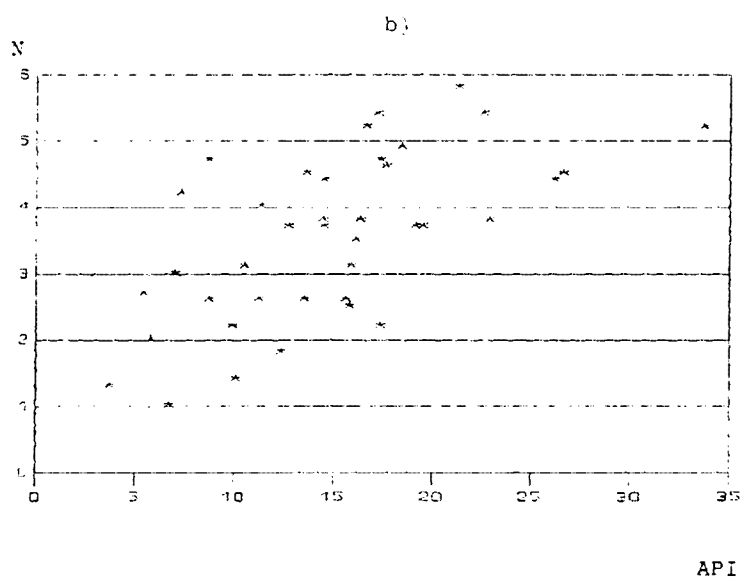
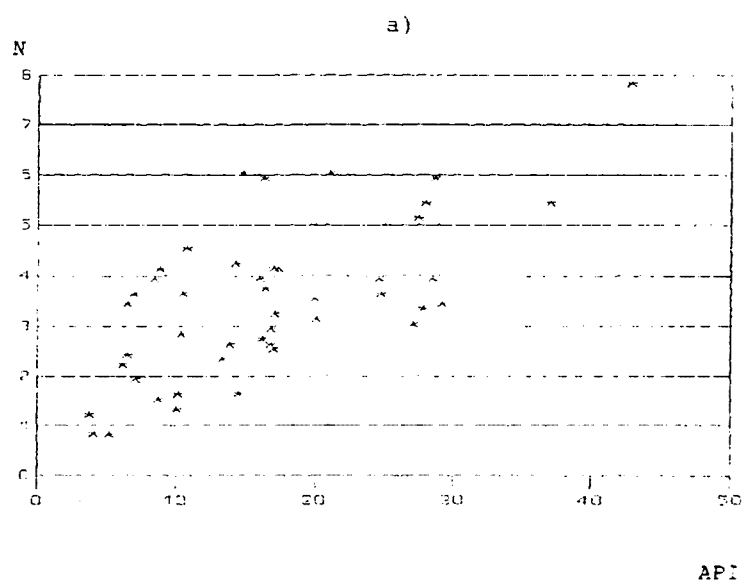


Fig.3. The relationship between the number of cancer tumours cases (N) and API: a) 1990; b) from averages for 1986-1990

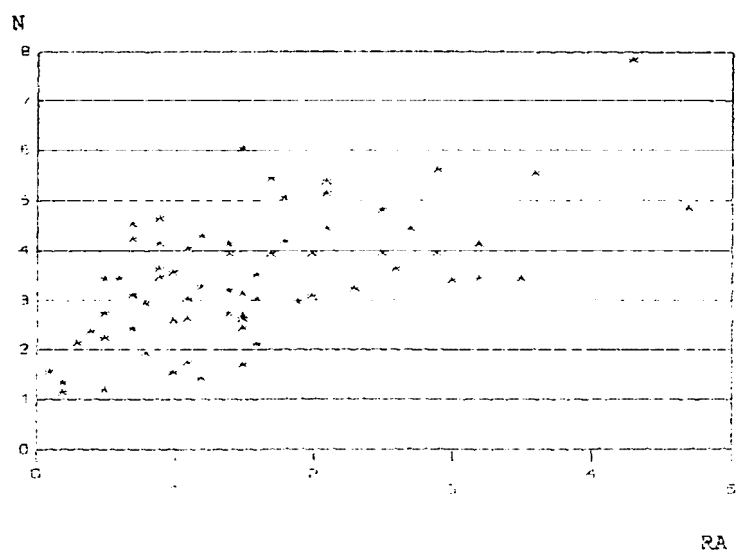


Fig.4. The relationship between the mean US risk assessment (RA) and malignant tumour cases (N) 1988, 1990

EXAMINATION OF ATMOSPHERIC DIFFUSION CALCULATING SCHEMES
UNDER EXPERIMENTAL DATA

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ABSTRACT

Application of atmospheric diffusion models for calculation a pollution level of air is immediately related to satisfying of received data. Evaluation of obtained results by field and regular measurements gives the possibility to postulate that relative differences of values are decreased if averaging period grows. We proceeded the first investigation phase of air pollution diffusion model which are used in studies of background monitoring data analysis and evaluations of environmental pollution from local sources. Basic model formula realizes analytical equation in Gaussian approach with dispersion parameters by Briggs' approximation. Calculating scheme and program were modified according to experiment conditions. The wind-tunnel experimental measurements of diffusion were used for study in the case of floor roughness surface. The comparison shows a good correspondence of results.

INTRODUCTION

A great part of modern investigations of the dangerous pollutant influence are devoted to people's health and natural ecosystem stability. However, the measuring the concentration in real atmosphere is a very laborious and time-consuming task. One of the perspective ways of the estimation and prediction of pollution level is creation and using of dispersion models simulating the processes in the boundary atmospheric layer (BPL).

Unfortunately, theoretic formulas of atmospheric diffusion models and methods of parametrization cannot give a fully adequate picture of real situation. The most of them requires considerable adaptation before being applied to regulatory practice. One of the ways of model examination is a comparison of the model results and the data of field or laboratory experiments.

Generally, there are two model types used in practice for calculation of concentration fields from different sources. One of them is based on analytical solution of semi-empirical turbulence diffusion equations and uses different application forms of diffusion coefficients and mean velocity. Another one is based on the statistic approaches. In this case the estimated pollutant concentration from sources depends on the application of dispersion parameters for Gaussian plume models.

The number of such Gaussian type models were presented in literature [1,2,3]. Now such model schemes are adopted to regular sing in ecological investigation with the aim of determination of long-term industry-made impact on environment in Russia.

The purpose of our study was to examine of atmospheric diffusion calculating schemes based on the Gaussian model according to experimental data. We were interested to know how this calculating

scheme could simulate the concentration from sources of different height and at what distance we could receive closer results by data of natural experiment.

STUDY DETAIL

Experimental Data

The results of the experiment made in the Environmental Sciences Research Laboratory, EPA were used as a data on natural experiment. This research was conducted in meteorological wind tunnel of EPA's Fluid Modeling Facility. In this tunnel a near-equilibrium boundary layer with nominal depth of 1 m was produced. It allowed to provide an equivalence of full-scale boundary layer with a scale ratio of 1250:1. Specific characteristics and results of this experiment were described in [4,5].

The certain stack heights and concentration profiles were chosen to examine diffusion model: for stack height of 80 mm the longitudinal profile of ground level concentration (GLC) and lateral profiles of GLC and on height of 120 mm at distances of 625, 1250 and 2500 mm from the source and vertical profiles at the same distances; for stack height of 160 mm the same are but at the different distances from the source (825, 1650 and 3300 mm) and, in addition, the longitudinal profile at the height of 120 mm.

The results received from experimental data were converted according to real atmosphere using the scale ratio of BPL (1:1250).

Model detail

We investigated the Gaussian diffusion model which are widely applied in practice. It is the most simple scheme for calculation of the plume diffusion from the stack and it needs the small set of input data. At the same time it allows to use different conditions of atmospheric stability by set of dispersion parameters according to Pasquill classes and frequency function of wind velocity and direction. Gaussian models are based on the assumption of normal distribution of the pollutants across the plume. The main equation of used model for the elevated point source is following:

$$C(x, y, z) = \frac{Q}{2U\pi\sigma_y\sigma_z} \exp\left(-\frac{y^2}{2(\sigma_y)^2}\right) \left[\exp\left(-\frac{(z-H)^2}{2(\sigma_z)^2}\right) + \exp\left(-\frac{(z+H)^2}{2(\sigma_z)^2}\right) \right] \quad (1)$$

where C - estimated concentration; Q - source flow rate; U - mean wind velocity; σ_y , σ_z - the dispersion parameters in horizontal and vertical directions; H is the stack height.

This equation was written under the condition that plume axis is directed along the wind velocity vector. We used formulas for dispersion parameters recommended by [1] in this model (Table.1):

$$\sigma_y = \frac{ax}{\sqrt{1+mx}}; \sigma_z = \frac{bx}{\sqrt{1+mx}} \quad (2)$$

Results

The results of the numerical experiments are nondimensional concentrations (as presented in [5]) for chosen longitudinal, lateral and vertical profiles (see below). This data were received for Pasquill stability categories C and D. Relative deviations of estimated concentrations from measured ones were calculated for every profile. Additionally, statistic parameters were obtained for rows of relative deviations: average, mode, median, standard deviation, extremes of values. Data of statistic calculations for source height

of 200 m are presented in Table 1.

Good results of comparison of GLC are received for longitudinal profile estimated under Pasquill stability category D. However, if we compare the convergence of calculated and measured results for longitudinal profile of GLC and at the height of 150 m one of the last case is better.

Fig. 1 shows plots of measured and estimated concentrations for C and D stability types for chosen lateral profiles. Estimated lateral profiles for both stability categories quite exactly draw the shape of measured concentration plots but their numerical values are different. The best accordance of estimated and measured data are observed for lateral concentration profile at the distance of 4125.0 m from the source and at the height of 150 m under stability class D. Generally, measured values agree with estimated on the surface much worth than at heights for lateral profiles. The best results for higher profiles are received for neutral stratification of flow (class D).

For vertical profiles convergence of results is better at heights more than 140-160 m under stability class D for any distance from the source and the best is at the distance more than 2000 m. In our study we received the best correspondence between measurement and estimated concentrations at height. This results are differed from those presented in [1]. As the results of our study we also detected that investigated model simulated diffusion at the middle and far distances better than near the source (Fig.2).

CONCLUSIONS

Investigation of used Gaussian diffusion model has been made for definition of its widely application in practice. The results of this study showed that this model described better the diffusion at height and at middle and far distances from source. Of course, the physical experiment which was made in artificial wind tunnel couldn't represent all diversity of atmospheric conditions. In addition, any model is only idealization of reality and it is necessary to verify model parameters according to local conditions of applications.

One has to use climatic frequency functions of wind velocity and atmospheric stability for model application in ecological studying practice. On this case errors of measured wind values, climatic averages and uncompleted definition of the source feature contribute to the final common error values of concentration. From this point of view it is necessary to make an estimation of model sensitivity to different types of errors.

Presented study shows the influence of calculating scheme of diffusion to the final results only. We plane to make a more complex evaluation of different error influence on results which could be used in ecological expertize.

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Table 1. The set of values for equation (2) according to Pasquill's stability class.

Pasquill's stability class	C	D
a	0.11	0.08
b	0.08	0.06
n	0.0001	0.0001
m	0.0002	0.0015

Table 2. The statistics of relative deviations for different profiles under the Pasquill's stability classes C (upper value) and D.

Profiles	Average	Median	St.dev.	Extremes
Longitudinal, GLC	3.20 0.81	0.48 0.89	42.55 0.13	-103.05; 161.66 0.67; 1.25
Longitudinal, z=150 m	0.62 0.24	0.64 0.23	0.05 0.25	0.53; 0.67 -0.10; 0.65
Lateral, GLC x=2000 m	-0.58 0.89	-2.96 0.88	49.36 0.83	-82.45; 314.85 -0.59; 6.15
Lateral, z=150 m x=2000 m	-0.05 -0.45	0.45 0.0002	1.53 1.35	-8.10; 0.68 -7.12; 0.27
Lateral, GLC x=4000 m	-2.58 0.05	0.10 0.68	9.39 2.11	-60.34; 0.57 -12.91; 0.79
Lateral, z=150 m x=4000 m	-0.60 -1.24	0.26 -0.31	2.75 2.93	-16.29; 0.60 -17.94; 0.06
Vertical, x=1000 m	1.11 -0.49	-0.23 0.76	48.31 0.53	-221.06; 253.71 -0.54; 1.09
Vertical, x=2000 m	0.07 0.32	0.31 0.41	0.67 0.44	-2.09; 0.70 -0.41; 0.90
Vertical, x=4000 m	0.49 0.18	0.52 0.18	0.12 0.36	0.09; 0.64 -0.40; 0.77

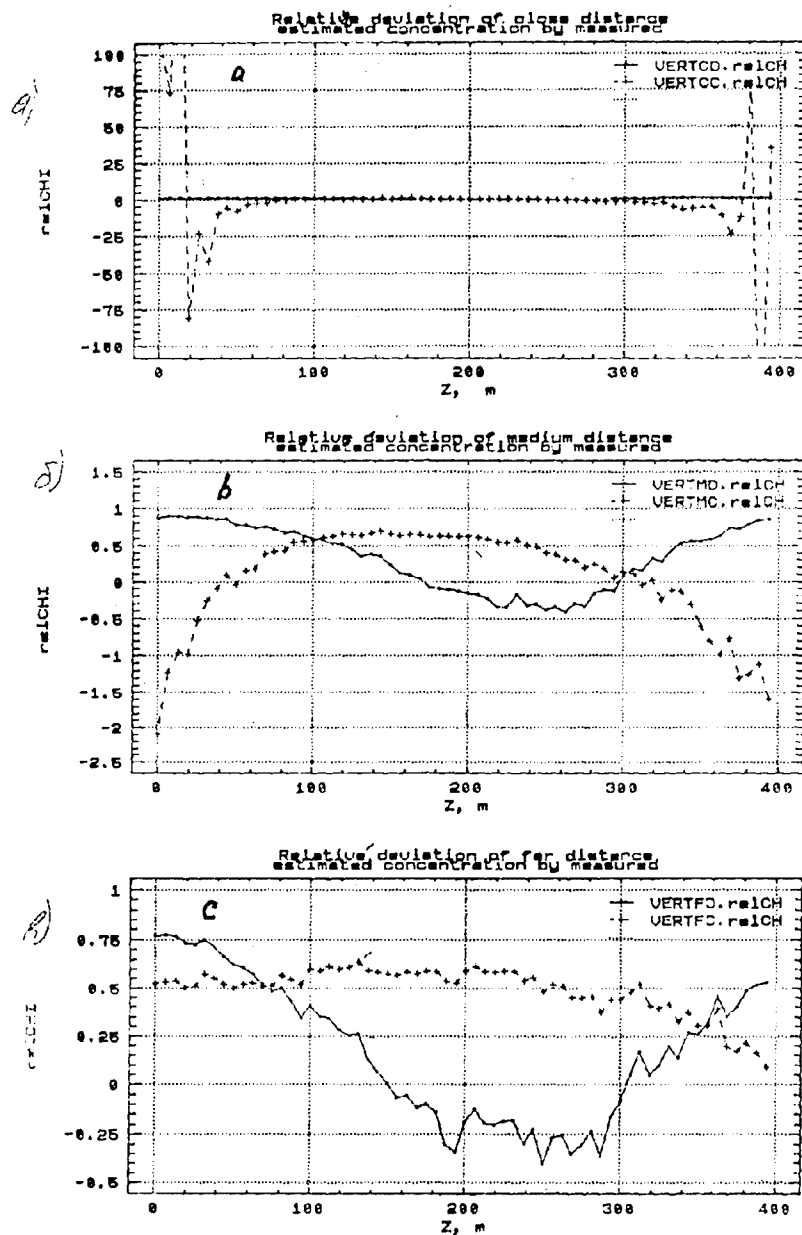


Fig. 2. Vertical profiles of relative deviations of estimated and measured values for C (dashed line) and D (solid line) stability classes for: $x=1000$ m (a), $x=2000$ m (b) and $x=4000$ m (c).

Background Pollution of the Atmosphere: The Multi-Year Observation in Russia

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The observations on the integrated background monitoring program at a network of stations in biosphere reserves embracing a considerable part of the Eurasian continent began late in the seventies in the former USSR. The atmospheric part of the programme envisages daily evaluation of sulfur and nitrogen compounds, ozone, heavy metals (Pb, Cd, Hg, Cu, Zn, etc.), organochloride and polyaromatic compounds. The same compositions of the components are evaluated in precipitation samples.

The spatial distribution of background concentrations for the most of pollutants is irregular: a decrease could be observed eastwards and northwards, and the concentrations are significantly lower in the mountain areas also. This regularity is mostly distinct for pollutants of fuel-power cycle - sulfur and nitrogen dioxides, benzo(a)pyrene, Pb; as for DDT and HCH the regularity is weaker.

The time-related daily and seasonal variations are present. These variations are connected both with power source volumes and atmospheric processes.

Multi-year trends demonstrate that during the last decade the mean annual sulfur dioxide, benzo(a)pyrene and Pb concentrations are 2-4 times lower in the western and central parts of the European territory of Russia and they practically do not change over the southern Russia and Siberia, and the DDT concentrations monotonously decrease with time.

The assessment of the anthropogenic heavy metals contribution (Pb, Cd, As, Cu, V) in background pollution of the atmosphere was obtained with the help of the geochemical relations methods. This value changes from 20-50% for the continental regions up to 70-98% in the western part of the former USSR (more urbanized).

The multi-year statistical data on background pollution of the precipitation and their acidity demonstrate that noted irregularities for the atmosphere in the whole are characteristic for the precipitation, as well.

As it is shown by the multi-year observation data, the background pollution of the atmosphere endure the anthropogenic influence over large-scale territories.

Methods of Studying Sources in the Boundary Atmospheric Layer of the Background Areas

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The data on major sources required for assessment and prediction of ozone variation in the boundary atmospheric layer and their effects on environmental objects. The most important sources of ozone input in the lower atmospheric layers are photochemical reactions and transport from upper atmospheric layers, advection of ozone and its precursors.

The method of the simultaneous measurements of ozone in the chamber volume filling by ambient air and in the outdoor atmosphere was applied to study the effect of photochemical ozone production in the atmosphere of the background areas. The material used as chamber shell was inert with respect to heterogeneous ozone sink and transparent for solar radiation.

The results of carried-out observations indicate of ozone concentration exceeding in chamber from 10 to 100 percent in the Berezinsky reserve area (Belarus) in the daytime (July) caused by its photochemical production in comparison with ozone content level in the outdoor air.

Used technique allows to estimate the upper boundary of ozone content in the air is caused its photochemical sources in the observation area.

The effect of air transport and possible photochemical ozone production on its content level in boundary atmospheric layer was investigated with help of ozone gradient measurements method and meteorological parameters (air temperature, speed and direction of wind). For this purpose was using captive balloon ($v=800 \text{ m}^3$) with the basket containing measuring instruments.

The results of the measurements carried out in the background area of Kurakaya district, their comparison with existing data in world literature on type of vertical ozone distribution in the lower atmospheric layers indicate of dominant effect of ozone convective input in the near surface layer for the upper atmospheric layers during observation period (June - August).

APPLICABILITY OF TRAJECTORY ANALYSIS FOR AIR BACKGROUND
MONITORING NETWORK OPTIMIZATION

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ABSTRACT

At present time four air background monitoring stations working over European part of Russia. A number of pollutants' concentrations in the surface layer of air are measured by these stations constantly. The level of observed concentrations depends on the lifetime of substances in the atmosphere and the anthropogenic emission sources density over the path "source-receptor". The areas whose emission influences to the pollutants' concentrations in the fixed receptor site were estimated with help of a back-trajectory model. The model permits us to calculate five-day back trajectories according to ageostrophical relations between fields of wind and pressure.

The trajectory calculations for Russian background monitoring stations started in July 1989 and since that time are executed everyday. Database of more than 6000 trajectories are collected. All trajectories were classified and statistics of long-range transport were estimated. On the basis of this data, the areas of polluted air parcel's path were determined for each monitoring station for the periods one, three and five days. The areas have a complex shape and are extended backward along the prevailing air transport direction. Additionally there are territories where the areas around different stations intersect each other. In the same time there are a vast territories, pollution transport from which isn't under observation of the existing monitoring network; the considerable parts of the North-East European Russia, Kola peninsula, West Ural are among them. The named regions need additional air pollution monitoring station organized.

INTRODUCTION

The estimation of territory's size which could be representative for air pollution observations in one local site is one of the speculative questions in air background monitoring. This territory will be obviously different in every determine case due to peculiarities of pollutant's emission field, surface roughness, meteorological conditions. It may be suggested that the territory will vary for different pollutants characterized by their lifetime in the atmosphere. And the shorter lifetime of specific pollutant, the more monitoring station are need for air pollution observation over the test region. The task of territory's size determination observed by one stationary air background monitoring station (BMS) may be solved on the base of air parcels trajectories' analysis.

The method of trajectory analysis is well-studied and widespread for investigation of the pollution transport to or from fixed site. But only the few works consider a vast data bases (about 102-103 trajectories), for example the study by J.M. Miller devoting to Arctic trajectories' climatology (Miller, 1981). In Europe and Russia there almost have no investigations of similar nature with long-term trajectory data sets. The appreciable trajectory model was created in Institute of Global Climate and Ecology by Dr. Gromov

(Paramonov, Gromov, 1992). The model permit to calculate back trajectories of air parcels two times a day from or to any place in the Northern Hemisphere. The input data are taken from Moscow Meteorological Center gridded fields for standard pressure levels. Trajectories are calculated for not more than five-day period, considering that the longer its duration, the less trajectory accuracy.

Permanent calculations of five-day back trajectories started for every former USSR air background monitoring station in July 1989. The period of study in this work was taken from the beginning of the calculations up to September 1992. The total quantity of trajectories used in the work adds up to 6200, 61% of which falls within an warm season. The sites of BMS location are presented in Fig.1. For statistical procedure a year was divided into two seasons - cold (October-March) and warm (April-September).

TRAJECTORY ANALYSIS

Climatology of Back Trajectories.

Every trajectory was assigned to a category according to the direction of air flow. The horizon was divided into eight 45-degree sectors by standard meteorological manner. The classificative criteria for the curved trajectories, crossing the sectors' borderline was the trajectory presence in the definite sector more than half of an air parcel's transporting time. The percentage of trajectories' directions are shown in Table 1. The North West and West trajectories' directions prevail for all BMS in both warm and cold seasons. The total average frequency of these directions runs to 50% in warm and 66% in cold season. In the cold season there are scarcely any trajectories from the Eastern directions. In the warm season there are no such common relations and the difference between directions is less than in cold season, especially at Southern BMS.

The averaged speed of the air flows within every 45-degree sectors differ from each other as well as the frequency of trajectories' direction (Tab. 2). Generally, in the cold season air masses moves faster than in warm one. During the whole year the air flows from North-West were the fastest. From October to March averaged in this sector flow speed exceeds 1500 km per day for the three from investigated air monitoring stations. The lowest speed usually occurs when South or East flows are observed. From April to September there are three sectors with the lowest trajectories' speeds: South, South-West and North-East. The ratio between the highest and the lowest averaged speeds may exceed 4-6 times in warm and 7-9 times in cold season. Another regularity one could see from Table 2 is the increasing of averaged flow speed from Southern to Northern BMS both cold and warm seasons.

Besides direction, the speeds of air flows are influenced by the duration of the trajectories. As a rule, the averaged trajectories' speed for a one-day period is higher, then for the three-five-day periods. This fact is connected with the influence of air flows meandering in the sector limits. Only when the trajectory leaves the continent for the ocean, it accelerates due to decreasing friction and the trajectory speed may exceed the initial one. From the other side this phenomenon may have an artificial genesis as a result of formal averaging procedure, when averaged trajectories' length from BMS is less than individual one.

Areal Analysis

To describe the territories, emissions from which influence

observed air pollution levels, contour lines were drawn, which outlined the areas from whom air parcel may reach the BMS for one, three and five days. Generalized outlines around all air monitoring stations situated over European Russia are represented in Fig.1 for warm and cold seasons. As may be seen from this figure the results of the observations for the concentrations of the pollutants with a lifetime more than three days are subjected to emission from almost all Europe: from France to the Ural mountains. The seasonal variations mainly spread to marine territories where there are no emission sources. As to pollutants with life-time of less than one day BMS are subjected to emission from Baltic countries, Ukraine, Kazakhstan and Central part of European Russia in the warm season. In the cold season one need add influence of the emission from Central Europe and Scandinavian countries. During the year emission of pollutants with short life-time from extensive area of European Russia from the left bank of Volga to the Western Urals isn't under observation by existing air background monitoring stations.

The outlines around separate BMS may vary from year to year. Sometimes yearly variation of areas within the outlines may exceed 30% (Fig.2, 1989 and 1990). As it is seen from Fig.2, variation mainly takes place in Eastern parts of contours, information about air pollution from where is interesting for Russia. This region of variability is common to all considered BMS.

Network Optimization

The territories under observation by separate background monitoring stations intersect each other and the longer the life-time of the pollutant, the larger an area of intersection. Thus the area of intersection of at least a couple of BMS inspected territory up to 85-95% for the pollutants with life-time from three to five days. In this case one or two BMS will be enough to monitor the same area which is now under observation by four stations for purposes of long-range pollution transport monitoring. So Oka-Terrace and Astrakhan may be suggested as such stations. As may be seen if one compares Fig.1 and Fig.3, the outlines around four air monitoring stations and around Oka-Terrace BMS are closely allied. The difference takes place only in South part of the one-day contour. If this contour is added to Astrakhan's one the total outline will be similar to the outline surrounding all the four Russian BMS. Taking into account typical distances from BMS to the one-five-day area's boundaries in every sector one may choose a site to put an additional monitoring station to inspect the North-East part of European Russia. The best place for additional BMS may be situated in triangle between cities Syktyvkar, Perm and Vyatka.

CONCLUSIONS

First results in trajectory climatology over European Russia were worked out. This investigation is proceeding now and the new trajectory data sets are added to existing ones. The applicability of using trajectory analysis for background monitoring network optimization has been demonstrated.

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Table 1. The percentage of directions of 5-day back trajectories from Russian air monitoring stations.

Warm season									Cold season								
Year	N	NE	E	SE	S	SW	W	NW	Year	N	NE	E	SE	S	SW	W	NW
Central-Forest BMS																	
89	8	1	3	15	8	10	31	24	89-90	17	7	1	0	2	3	32	38
90	21	12	6	6	5	6	24	21	90-91	11	3	2	3	9	11	29	32
91	17	0	3	13	10	10	27	20	91-92	11	5	0	3	5	10	26	40
92	13	4	5	8	4	15	29	22									
Oka-Terrace BMS																	
89	10	1	0	24	11	6	38	12	89-90	17	1	1	0	1	6	29	45
90	16	11	6	3	6	8	24	22	90-91	18	3	3	5	7	11	23	35
91	13	2	4	16	9	14	20	23	91-92	14	3	0	9	5	9	21	39
92	13	7	8	11	8	11	28	19									
Woronezh BMS																	
91	10	1	10	19	9	11	18	22	90-91	17	2	5	7	12	9	18	30
92	13	7	6	14	8	7	20	25	91-92	17	0	4	7	2	11	17	42
Astrakhan BMS																	
89	12	12	9	10	10	2	13	29	89-90	8	0	0	1	1	4	33	53
90	9	13	3	7	10	4	18	36	90-91	11	6	5	4	5	9	29	32
91	24	6	29	4	2	3	9	26	91-92	19	6	10	6	4	6	15	35
92	26	12	15	11	4	3	8	21									

Table 2. Averaged in 45° sectors trajectories' speed (10^3 km/day).

Warm season									Cold season							
Days	N	NE	E	SE	S	SW	W	NW	N	NE	E	SE	S	SW	W	NW
Central-Forest BMS																
1	0.7	0.2	0.3	0.5	0.7	0.5	0.9	0.8	1.1	0.5	0.4	0.2	0.6	0.6	1.2	1.2
3	0.7	0.3	0.3	0.5	0.4	0.4	0.9	0.9	0.9	0.3	0.3	0.3	0.5	0.8	0.9	1.0
5	0.5	0.2	0.2	0.3	0.3	0.3	0.6	0.9	0.6	0.4	0.2	0.4	0.4	0.5	0.9	>1.5
Oka-Terrace BMS																
1	0.6	0.3	0.3	0.7	0.8	0.6	0.7	0.7	1.0	0.5	0.4	0.2	0.7	0.7	1.0	1.1
3	0.6	0.2	0.3	0.4	0.3	0.4	0.5	0.6	0.8	0.3	0.3	0.4	0.3	0.6	1.0	1.1
5	0.4	0.3	0.4	0.3	0.2	0.3	0.5	0.8	0.5	0.3	0.3	0.3	0.3	0.4	0.7	>1.5
Woronezh BMS																
1	0.6	0.6	0.7	0.7	0.8	0.6	0.6	0.8	0.8	0.3	0.3	0.6	0.6	0.7	0.9	1.1
3	0.5	0.2	0.5	0.5	0.3	0.7	0.7	0.8	0.7	0.3	0.4	0.4	0.3	0.4	0.7	1.1
5	0.5	0.2	0.3	0.3	0.2	0.5	0.5	0.8	0.6	0.2	0.3	0.3	0.2	0.4	0.6	>1.5
Astrakhan BMS																
1	0.6	0.4	0.5	0.6	0.3	0.2	0.6	0.6	0.6	0.3	0.4	0.3	0.3	0.3	1.1	1.1
3	0.4	0.3	0.4	0.4	0.2	0.2	0.3	0.5	0.8	0.2	0.3	0.2	0.2	0.2	0.3	1.1
5	0.4	0.3	0.3	0.2	0.2	0.1	0.3	0.6	0.7	0.3	0.2	0.1	0.1	0.2	0.5	0.9

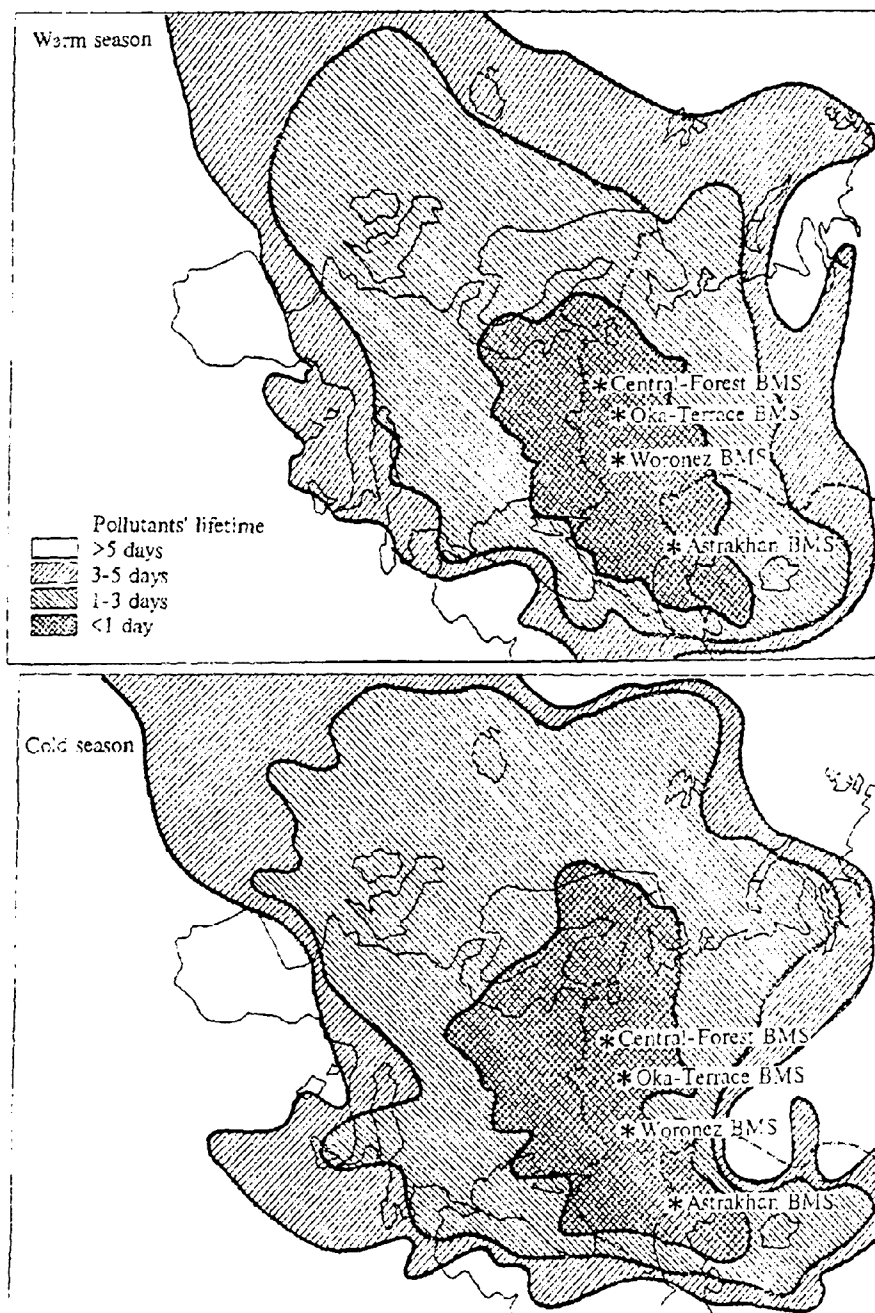


Figure 1. Areas controlled by Russian background monitoring stations for pollutants with different lifetime.

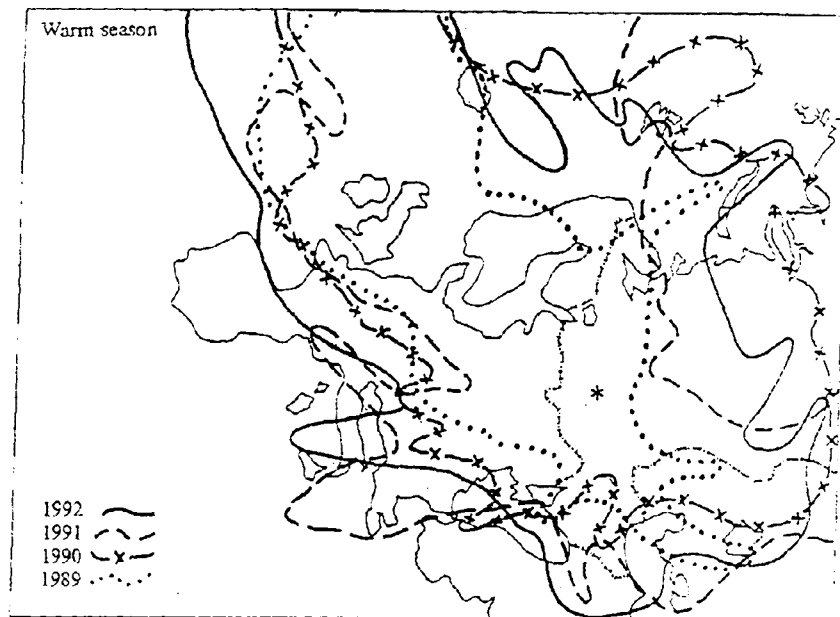


Figure 2. Year variations of the outer boundaries of five-day back trajectories from Oka-Terrace BMS in the warm season from 1989 to 1992.

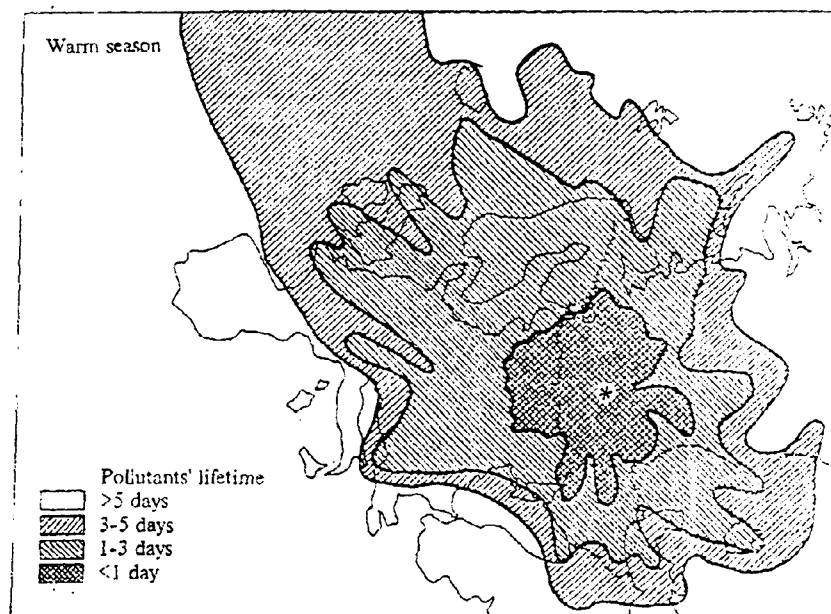


Figure 3. Areas controlled by Oka-Terrace BMS for the pollutants with different lifetime.

LONG-RANGE MODEL FOR ATMOSPHERIC POLLUTION ANALYSIS OF BACKGROUND TERRITORIES

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ABSTRACT

Goals of GEMS station's measurement data analysis appear to evaluate inputs of regional sources into long-term background atmospheric pollution level and to investigate its seasonal or multi-year changes. Lagrangian model is supposed to study atmospheric pollutant transport. It is based on 5-days backward trajectories calculated from ageostrophical wind-pressure relations using meteorological data of Moscow World Meteorological Center. The two-layer barotropic model of BPL included to estimate such parameters as transporting averaged wind, turbulence coefficient and exchange with upper layers. Pollutant advection is simulated as moving of separate "puffs" along trajectory. Lateral diffusion is applied as a Gaussian approach. The vertical diffusion equation is solved numerically taking into account the BPL's results and dry deposition which depends on seasonal features. Time-depending decrease of concentrations by first order chemical reactions is used when transformation of pollutants exists. Wet deposition is simulated by the same manner when cloudiness or precipitation takes place. The results are concentrations and depositions in each point for a chosen time interval. The model had been tested on analytical evaluations of long-range environmental background concentration of sulphur dioxide over former USSR' European territory.

INTRODUCTION

Mathematical modelling of air pollution transport is one of the most perspective methods in the field of geographical and geophysical investigations in ecology. It allows to create a basis for forecasting in the natural environmental pollution and for analysis of influence of accepting economic decisions.

The task of long-range transport modelling is to determine a changes of pollutant concentrations and output flux intensity from atmosphere under the influence of emission, diffusion, transformation, deposition and washout.

Generally, regional-continental air pollution models must be comprehensive the number of requirements without dependance on model construction:

1. to accept a lot of emitting sources;
2. to follow a pollutant moving for hundreds or thousands kilometers while taking into account a temporal atmospheric flow instability;
3. to use spatial and time-depending averaging manners of measurement and emission data;
4. to include a processes of chemical transformation and removing of pollutants from the atmosphere.

Any different types, forms and variants appear inside common model structure realizing the modeler' theoretical approaches and compromise decisions in satisfaction of requirements on accuracy,

fullness, spatial accuracy, available input information and computer calculation effectiveness.

The operational models for estimating of transboundary pollution flux had been constructed in both Meteorological Synthetic Centres of EMEP [1,2]. Another method of mathematical solution was demonstrated by Frahm and Cristensen [3]. A statistical approach to long-term modelling was used by A.Venkatram [4].

Our way of model creation is determined by practical goals of its applications: to use model in regional-scale analyzing and forecasting of atmospheric pollution, to evaluate download pollutant flows, to investigate a possible "source-receptor" relationships and to reach calculating efficiency.

MODEL DETAIL

The physical approximation principles of the suggested model are the following:

1. Trace matter moves in changing wind field which could be estimated from data on geopotential analysis. The transport paths can be determined according to air parcel trajectories within lower troposphere.

2. Source's plume is approximated by set of moving independent portions of emission ("puff") which are injected at one moment. The cloud amount is equal to emitted mass from continuous source for limited time interval.

3. The influences of deposition, transformation and washout are determined as a "living-time" functions and described by set of parameters depended on meteorological and geographical conditions.

4. The pollutant concentration and deposition on the earth surface are calculated for receptor point from which a backward trajectory have been restored.

5. The value of concentration is estimated as a sum of ones produced by trajectory's crossing area sources for one trajectory time period.

The suggested model is classified as Lagrangian receptor oriented. This approach allows to divide advection and diffusion processes during the solving of atmospheric substance balance equation. General suppose of this way is: a smaller diffusion processes place on large scale transport of pollutant masses by atmospheric flows.

The realization of the above principles went along the way of creating the block aggregated software package. The later gives a possibility to write programs of different parts step-by-step or to improve it without touching others.

Independent vertical moving velocity of trace gases and aerosols can be neglected for long range transport movements. The differential equation of local concentration change is solved according to coordinate system restored in centre of laterally moving puffs from each source fixed on trajectory and applying to diffusion, source intensity (Q) and sinks due to washout (W), dry deposition and chemical transformation (R) processes:

$$\frac{\partial c}{\partial t} = K_L A_L c + \frac{\partial}{\partial z} K_z \frac{\partial c}{\partial z} + Q + R - W \quad (1),$$

A_L - two dimensional Laplacian, K_L and K_z - lateral and vertical turbulent diffusion coefficients.

The equation solution is found under the suppose that local

concentration change is the result of separate influences:

$$C(x, y, z, t) = \sum_n Q_n \rho_1(x, y, z, t_n) \rho_2(z, t_n) \rho_3(t_n) \rho_4(t_n) \quad (2),$$

ρ - functions of spreading (1, z) and removing (x, y); t_n - the time of puff moving from source N to receptor point along the trajectory.

The basis of puff travel determination is sub-model of 5-days backward trajectory calculation according to ageostrophical relations of wind and pressure fields [5]. Estimations of trajectory point coordinates are proceeded with 1 hour step using real aerological and meteorological data analyzed and received from Moscow World Meteorological Center. The calculating algorithm allows to correct wind fields between terms of analyzed data reception.

The two-layer barotropic model of boundary planetary layer (BPL) [6] is included as counting block. The BPL parameters are determined by synoptic processes and are calculated from analyzed meteorological data. Such parameters as averaged wind at pollutant transport layer, turbulence coefficient profile and speed of exchange with upper troposphere layers are estimated with help of BPL model.

The boundary conditions for solving of lateral diffusion equation is the pollutant absence toward the longest distances. Under the assumptions on semi-uniform lateral turbulent diffusion and relationship of lateral dispersion parameter (σ) and turbulent diffusion coefficient the corresponded function is following:

$$\rho_2(x, y, t) = \frac{1}{2\pi\sigma^2} \exp\left(-\frac{R^2}{2\sigma^2}\right) \quad (3),$$

- R - distance from puff centre to point (x, y).

Parametrizing formula of (σ) is used as suggested in [7] according to measurements during the periods of long-range transport studies. This parametrization approach is strongly valid for flat territory only.

Vertical diffusion equation is solved numerically by taking into account the BPL model results and following boundary conditions: dry deposition of pollutant on the surface as a function depended on seasonal variations and upward transboundary flow at the top. The later is proportional to the upward wind component calculated from BPL model. The temporal and spatial variation of diffusional and depositing parameters need to be taken into account under long-term and long-range modelling. The BPL model is used in order to include its influence. In addition, the quality evaluations of role played by surface type, insolation, seasonal and local meteorological conditions show: the parametrization of large-scale surface differences and seasonal deposition velocity variation is necessary in the first [8]. Using the large-scale averaged data on surface roughness and calculated value of dynamic velocity parameter we assumed that dry deposition velocity can be as following:

$$V_d(h) = V_d(z_i) \left[1 - \frac{V_d(z_i)}{2u_*} \ln \frac{h}{z_i} \right]^{-1} \quad (4),$$

z_i equal to 1 meter where the most of data was obtained, h - height of constant vertical flow layer, α - Karman constant. Internal year variation is defined by set of seasonal values.

The transport layer was divided into different thickness sublayers. Using the varying vertical step does complicate the calculating procedures and need more counting time. However, as reported in [8] including the additional levels into lower part of

BPL allows for a decrease in pollutant mass disbalance.

The Crank-Nikolson algorithm was used for numeric integrating of finite-difference equation. The time step was limited by following condition:

$$\delta t \leq \min [2(\delta x)^2 / K_x] \quad (5).$$

The investigation of numerical solution features under influences of turbulent diffusion coefficient profile and dry deposition was carried out. We found more intensive vertical spreading than according to analytical solution [1] (Fig.1). It seems to be more adequate because of uniform diffusion condition is rarer. The including of dry deposition leads to closer results. The moving toward uniform distribution appears to accompany movement away from the source.

The exponential decrease of concentrations by first order chemical reactions is used when transformation of nonconservative pollutants is estimated. We had tried to include the processes of wet deposition by rainfall. It is simulated by the same manner when cloudiness or precipitation takes place at the transport layer if it is defined from meteorological analysis. The seasonal changes of emission was taken into account.

The results of calculations are vertical profiles of pollutant concentrations, wet and dry deposition sums in the receptor point during fixed time period:

$$\begin{aligned} q_d &= c(x, y, z, t) V_d \delta t \\ q_w &= [1 - \exp(-\Lambda_w \delta t)] \int_0^H c(x, y, z, t) dz \end{aligned} \quad (6)$$

The following order of calculations established for each receptor point during single time interval of trajectory analysis (for region the procedure is repeated for each chosen point during same time interval):

1. The 5-days backward trajectory line is restored. The turbulent diffusion coefficient, BPL height and related parameters is determined in trajectory points;
 2. The set of emission sources is found by searches after each time travel period (for example, after 3 hours) in vicinity of trajectory points;
 3. The heavy cloudiness or rainfall existing is analyzed along the trajectory;
 4. The values of lateral and vertical diffusion, chemical transformation (if needed) and wet deposition are calculated;
 5. The concentration and deposition are counted for receptor point as a sum of particular values from each source.
- Averaging of calculated values is produced after accumulation of data for a longer time period.

The model will be used for analytical evaluations of long-range environmental background pollution over former USSR European territory. We tested its applicability on calculation in conditions of stable west flows over Europe during summer (July) and winter (January) seasons without wet removal. Meteorological information was obtained from base of Moscow World Meteorological Center as regular net fields. The distribution of emission was chosen as a square grid cell net of sulphur uptake. The modelling results for summer situation is shown on Fig.2.

We compared calculated values of sulphur dioxide with measured on background monitoring station over European part of former USSR in same conditions (according to trajectory analysis). This data are in Table 1. The exceeded calculated values may be explained by enormous influence of nearest sources and, hence, not enough good acceptance of emission data. Moreover, we cannot include here a washout processes due to lack of data.

CONCLUSION

Presented model was created for analysis of background atmospheric pollution according to long-range transport. It includes the main processes which exist in lower troposphere and change the pollutant concentration. It is obvious that this model is not as perfect as a number of others. We shall improve it by using better parametrization, good initial and input data acceptance.

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Table 1. Statistical parameters of measured concentration and calculated values for background monitoring station during west large-scale flows.

Parameters (mkg/m ³)	Background station			
	Berezina	Oka-Terrace	Preila	Central-Forest
Average (6)	0.99	0.91	2.97	1.06
Stand. dev.	1.14	0.74	2.58	1.09
Maximum	3.2	3.4	10.9	4.28
Coef. variat.	114.8	81.8	86.6	103.1
Calculated	50.	95.	10.	8.

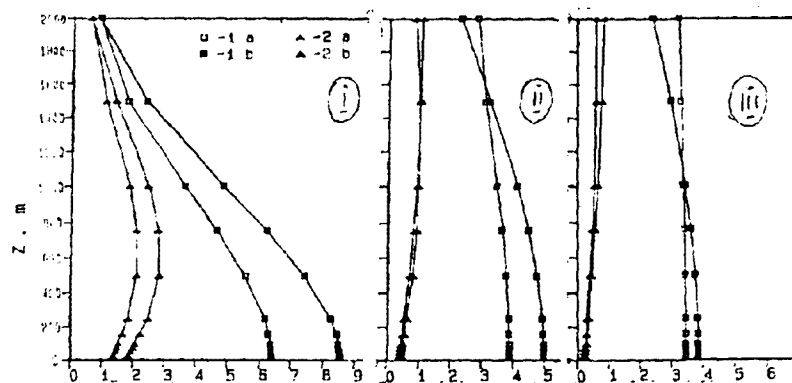


Fig.1. Vertical spreading function profiles after 24 (I), 72 (II) and 120 hours (III) without dry deposition (1) and with $V_d = 1$ cm/sec (2): a) numeric solution; b) analytical solution [1]

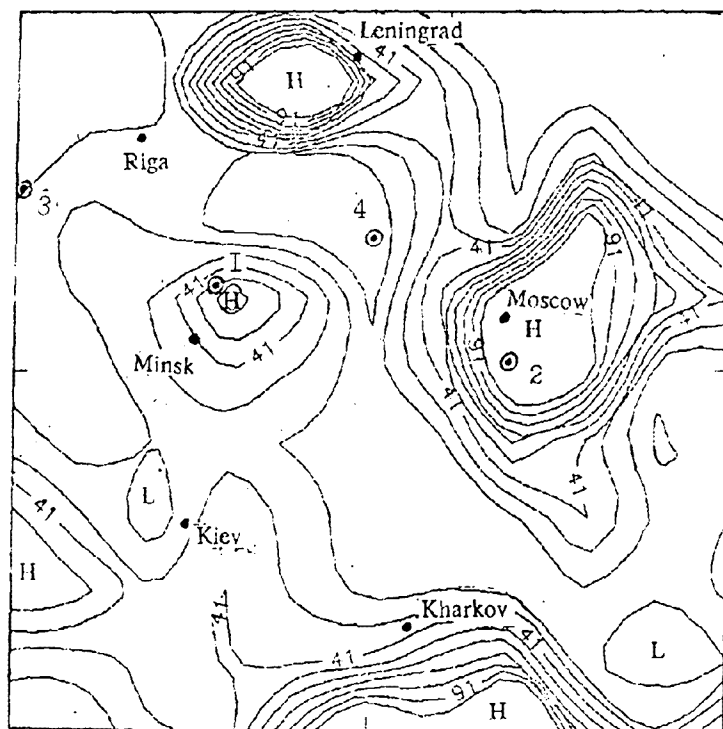


Fig.2. Field of calculated sulphur dioxide concentrations over European part of FSU due to summer west flow (measurement sites in reserves: 1 - Berezina, 2 - Oka-Terrace, 3 - Preila, 4 - Central Forest).

SESSION 21:
ENVIRONMENTAL TOBACCO SMOKE

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REAL-TIME MONITORING OF POLYCYCLIC AROMATIC HYDROCARBONS AND RESPIRABLE SUSPENDED PARTICLES FROM ENVIRONMENTAL TOBACCO SMOKE IN A HOME

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ABSTRACT

Real-time measurement of polycyclic aromatic hydrocarbons (PAH) on fine particles was evaluated in a home with environmental tobacco smoke (ETS) as a source. The PAS 1000i PAH monitor (EcoChem Technologies, Inc., West Hills, CA) is based on photoelectric ionization of surface PAH, loss of the photoelectrons, and subsequent measurement of the remaining positively charged particles in a filter electrometer. Cigarettes were smoked in the living room of a small house, with the time series of PAH concentrations logged with high time resolution using a Langan DataBear L15 data logger. Respirable suspended particles (RSP) were monitored using the Model 8510 Piezobalance (TSI, Inc., St. Paul, Mn), which measures fine particle concentrations with 2 min averaging periods. Comparison of PAH and RSP concentrations from these experiments suggests: (1) the PAH concentrations for the two types of cigarettes -- a regular Marlboro filter cigarette and a University of Kentucky reference cigarette No. 2R1 -- were similar, but the RSP concentrations were different; (2) concentrations from the real-time PAH monitor were linearly related to RSP concentrations; (3) the slopes of the regression lines between PAH and RSP differed for the two types of cigarettes. The real-time PAH monitor appears to be a useful tool for evaluating mathematical models to predict the concentration time series in indoor microenvironments.

INTRODUCTION

Measurement approaches that rely on collection devices (for example, pumps and filters) often give averages as long as 12 hours or more. Development of mathematical models of human exposure to pollutants in indoor settings requires monitoring instruments that have rapid time responses (usually less than two minutes), or "real-time" instruments. Real-time measurements are needed because human activities (for example, smoking a cigarette, burning toast, using a chemical spray) often occur for a few minutes or less. For example, indoor air quality models such as the Sequential Cigarette Exposure Model (SCEM; Ott, Langan, and Switzer, 1992) compute the time series of indoor pollutant concentrations for smoking activities with a time resolution of 10 seconds. Although real-time measurement methods do not exist for many pollutants, a real-time monitoring instrument has been introduced for polycyclic aromatic hydrocarbons, the PAS 1000i PAH monitor (EcoChem Technologies, Inc., West Hills, California). This paper explores the application of this new monitor to a practical problem: measuring the concentration time series generated by ETS in a home.

Polycyclic Aromatic Hydrocarbon (PAH) Monitor

The PAS 1000i PAH monitor operates using the principle of photoelectric ionization of surface PAH, loss of the photoelectrons, and subsequent measurement of the remaining positively charged particles in a filter electrometer. Bartscher and Schmidt-Ott (1984) presented the first results on the response of a photoelectric aerosol sensor (PAS) showing qualitatively that, with the combination of a

relatively large irradiation unit and a sensitive electrometer, an instantaneous detection of PAH is possible. Niessner (1986) examined the response characteristics of the sensor to different PAH to determine if there is a preference in charge due to the molecular structure of the PAH. Observing the normalized concentration of charged particles at different particle sizes, he found a quantitative linear relationship between the surface area and the photoelectric activity. The correlation coefficient between the PAH amount (at the surface) and photoelectric activity was above $r = 0.998$ ($n = 8$ measurements), indicating that the sensor signal reflects the amount of PAH present. He concluded that the PAS methodology allowed for continuous, sensitive (under ng/m^3) *in situ*-monitoring of four- and higher-ring PAH. As long as the PAH are enriched in sub-monolayers, which is usually the case in combustion situations, the method yielded quantitative information on the amount of adsorbed PAH. Niessner and Walendzik (1989) examined the response of the PAS monitor to cigarette smoke. They found that the PAS results correlated well ($r = 0.94$, $n = 20$) with benzo(a)pyrene (BaP) concentration, which was determined independently by *in situ* synchronous fluorimetry on TLC plates. The absolute lower detection limit was about 50 pg.

Wilson *et al.* (in press) compared readings from the commercially available PAS 1000i monitor (EcoChem Technologies, Inc., West Hills, California) with 12 integrated measurements of PAH collected by a pump-driven sampler in homes and offices with smokers. The collection device included an annular denuder to remove vapor-phase PAH, a 2.5 μm impactor to remove coarse particles, and an XAD-2 resin cartridge to collect any PAH vaporized from the particles on the filter during sampling. The integrated monitors operated over an 8-h period with a sampling volume of 20 L/min, and the filter and resin were extracted with dichloromethane, with the extract analyzed by gas chromatography/mass spectrometry (GC/MS). Comparison of the PAS 1000i with the integrated samples showed that the results were highly correlated ($R^2 = 0.985$). They found the instrument easy to operate, rugged for use in field settings, stable, and reliable. It had a low limit of detection (around $10 \text{ ng}/\text{m}^3$) and was highly sensitive to variations in concentrations in indoor settings. They recommended replacement of the electrostatic precipitator (ESP) with a straight stainless steel tube, since the ESP is not needed for indoor and ambient aerosols. The PAS 1000i used in the present study was modified in this manner, and a newer model, the PAS 1002i, is now available from the manufacturer.

Respirable Suspended Particle (RSP) Monitor

The piezobalance originally was developed to monitor RSP levels in occupied buildings in Japan, because Japanese law requires measurement of RSP levels several times each day in stores, offices, apartments, and other buildings. The theory, performance characteristics, size selectivity, and history of its design are found in papers by Olin, Sem, and Christenson (1970), Olin and Sem (1971), Carpenter and Brechley (1972), Daley (1974), Daley and Lundgren (1975). Sem, Tsurubayashi, and Homma (1977) found, over the range of 50–5,500 $\mu\text{g}/\text{m}^3$, that readings from 11 piezobalances were generally within $\pm 10\%$ and always within $\pm 15\%$. The TSI Model 8510 piezobalance is a portable instrument designed for measuring the mass concentration of fine particles with a 3.5 μm cutpoint.

METHODOLOGY

Real-time concentration readings from the PAS 1000i PAH monitor with the ESP removed were compared with successive 2-minute average concentrations from two Model 8510 piezobalances in the living room of a home. Two different types of cigarettes were smoked: a regular Marlboro filter cigarette (Experiment A) and a University of Kentucky research cigarette reference No. 2R1 (Experiment B). The instruments were collocated on a stand 0.5 m above the floor of the living room but were not connected to a common intake port; the intake ports were within 0.5 m of each other. In each experiment, two cigarettes of the same type were smoked sequentially one after another. The time series of concentrations from the two piezobalances were recorded manually every 2 minutes from the

instrument's digital display, while the concentrations from the PAH monitor were recorded electronically at 10-second intervals using a Langan L15 DataBear data logger (Langan Products, Inc., San Francisco, California). The DataBear data logger was attached to a Macintosh IIsx personal computer that displays the concentrations on its color monitor in real time. At the end of the experiments, the data generated by the PAH monitor were downloaded into the Macintosh computer.

The home -- a single-story, two-bedroom, one-bathroom structure -- was 606 ft² (56.3 m²) with a volume of 139 m³. The area of the living room was 151 ft² (4.28 m²), and its volume was 35.7 m³. During the experiments, the adjoining door to the kitchen was open 2"; the adjoining door to the bedroom was open 2"; and the front door of the home, which opens into the living room, was closed. One window in the living room was closed and the other was opened 6" to give a higher than usual ventilation rate for wintertime to enable the experiments to be completed within a reasonable time.

RESULTS

Comparing the two piezobalances with each other for the Marlboro cigarette in Experiment A (Figure 1, top) shows that the resulting regression line has a slope of nearly unity (RSP2/RSP1 slope = 1.12) with $R^2 = 0.86$ ($n = 49$), indicating that readings from the two piezobalances are correlated with each other and have little bias. A similar regression of the PAH readings versus one piezobalance (Figure 1, bottom) shows a high correlation ($R^2 = 0.88$, $n = 50$), but the PAH/RSP slope = 0.0138. This result indicates that the PAH readings are correlated with the RSP readings and that the PAH concentrations for the Marlboro filter cigarette are about 1.38% of the RSP concentrations.

For the Kentucky 2R1 cigarette (Figure 2, top), Experiment B also shows good agreement between the two piezobalances (RSP2/RSP1 = 1.11) and a high correlation ($R^2 = 0.88$; $n = 38$). Two outlier data points above 700 $\mu\text{g}/\text{m}^3$ have been excluded from the regression, because random outliers often occur during the "source-on" period in chamber experiments (Furtaw, 1994). Occasional deviations between the two piezobalances are not surprising for two-minute averages, since the instruments are next to each other but are not connected to a common sampling intake. The regression analysis of the PAH readings versus both piezobalances (Figure 2, bottom) shows a moderate correlation ($R^2 = 0.66$; $n = 32$), and the PAH/RSP slope = 0.006. Thus, for the Kentucky 2R1 research cigarettes, the PAH readings are moderately correlated with the RSP readings, and the observed PAH concentrations are about 0.6% of the RSP concentrations.

The much lower value of the PAH/RSP ratio for the Kentucky 2R1 research cigarettes than for the Marlboro cigarettes is consistent with the relative slopes of the regression lines, which have a ratio of $0.0138/0.006 = 2.3$. Comparison of the source strengths from the two types of cigarettes indicated that both types emitted about the same amount of PAH, but that the RSP emission was about 2.3 times higher for the research cigarette than for the Marlboro filter cigarette.

CONCLUSIONS

This study indicates that a real-time PAH monitor using a photoelectric aerosol sensor (PAS) can generate concentration time series that are useful for measuring effective air exchange rates and validating indoor air quality models. In experiments with cigarette smoke as a source, the PAH monitor showed a high correlation with RSP concentrations measured using a piezobalance. The similarity in PAH levels measured by the PAS but the difference in RSP concentrations for two types of cigarettes (a Marlboro filter versus a Kentucky Research 2R1) indicate that the PAH monitor is measuring a particular subspecies of the particles, as it should be, and is not just responding to changes in the mass concentration. The broad sensitivity range of the PAH monitor spanned three orders of magnitude, and its ruggedness and reliability suggest it is well suited for exposure model development.

and validation experiments in homes and other locations. Because the instrument is relatively small and can be adapted for battery operation, it can also be used in motor vehicle exposure field studies.

DISCLAIMER AND ACKNOWLEDGEMENT

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. This research was supported in part by the Tobacco Related Disease Research Program (Grant No. 2RT0274) of the University of California.

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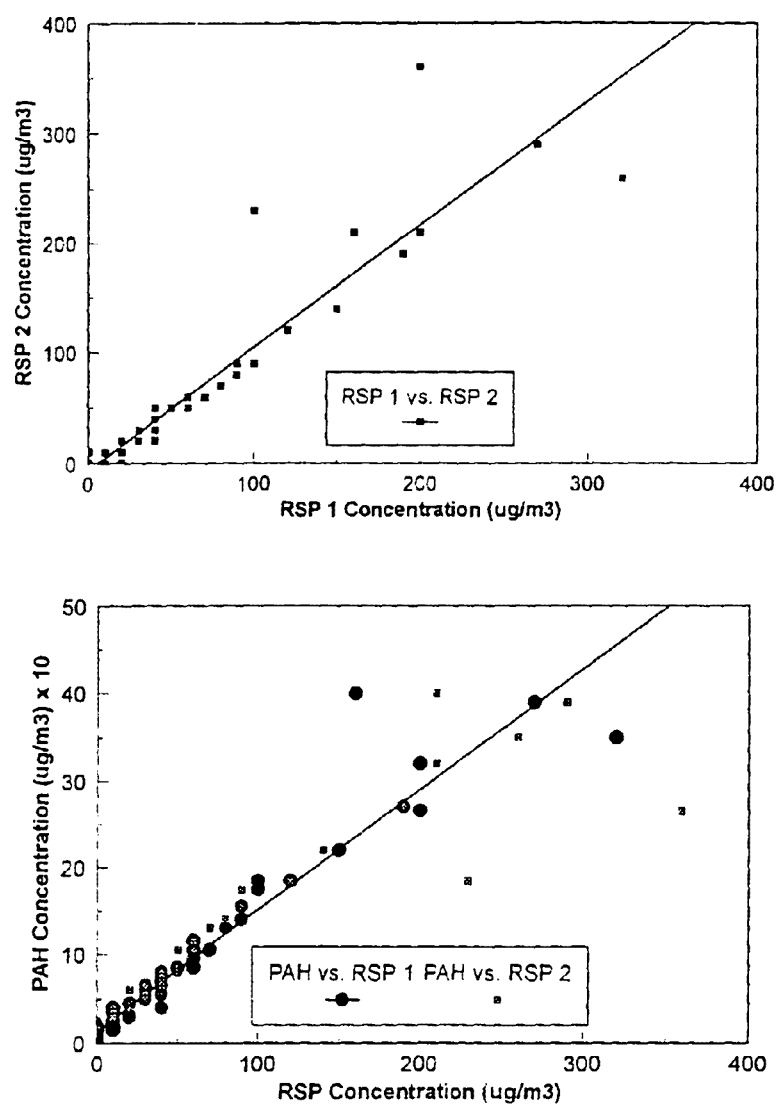


Figure 1. Comparison of two piezobalances (RSP 1 and RSP 2) and comparison of PAH and one piezobalance for the Marlboro filter cigarettes (Experiment A).

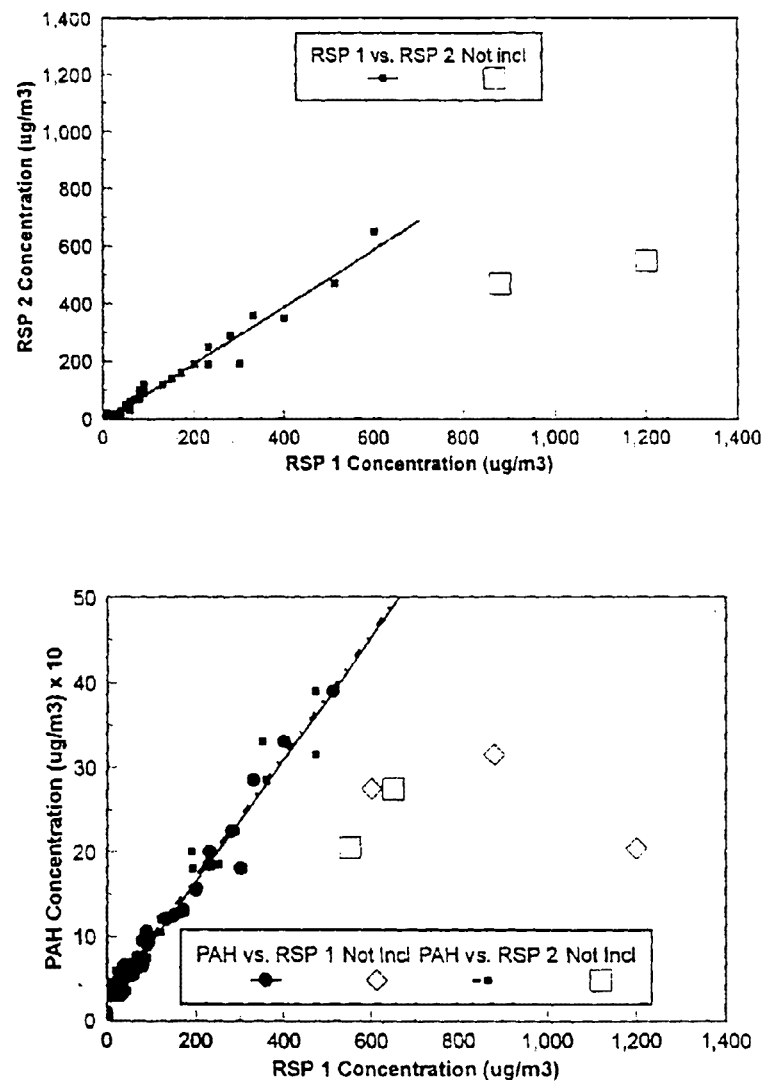


Figure 2. Comparison of two piezobalances (RSP 1 and RSP 2) and comparison of and one piezobalance for the Kentucky Research 2R1 cigarettes (Experiment

Measurement of Environmental Tobacco Smoke

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ABSTRACT.

A review of some measurements of environmental tobacco smoke (ETS) is summarized. After several definitions, ETS is briefly discussed and measurements of exposure to ETS are reviewed. Benzene in smoking is discussed, including the quotation: "Smoking is by far the largest anthropogenic source of background exposure to benzene." Proxies, surrogates, tracers, and markers as indicators of ETS in both personal and indoor space monitoring are treated.

INTRODUCTION.

Smoke from cigarettes, cigars, and pipes is one of the most prevalent sources of pollution of air of particular concern indoors in the workplace, in the home, in restaurants, in public buildings, in buses, on trains, etc. Pollutants from cigarette smoking are by far the most prevalent of smoking pollutants. In this paper we shall summarize a review (1) of some measurements of environmental tobacco smoke.

DEFINITIONS

Environmental Tobacco Smoke.

Environmental tobacco smoke (ETS) is tobacco smoke in the environment, to which smokers and nonsmokers (also referred to as involuntary smokers and passive smokers) are exposed.

Mainstream Smoke.

Mainstream smoke (MS) is the complex mixture that exits from the mouthpiece of a burning cigarette and is drawn through the tobacco into the smoker's mouth when a puff is inhaled by the smoker.

Sidestream Smoke.

Sidestream smoke (SS) is the smoke emitted by the burning tobacco between puffs (2).

ETS originates at the lighted tip of the cigarette, and exposure is greatest in the proximity of the smoker (2). ETS exists in two phases: 1) the vapor phase; 2) the particulate phase. It is the only source of nicotine in the environment (3). It can be a substantial contributor to the level of indoor pollution concentrations of:

- 1) benzene
- 2) acrolein
- 3) N-nitrosamine
- 4) carbon monoxide
- 5) respirable particles.

Sidestream smoke contains greater amounts (than mainstream smoke)

f:

- 1) nicotine
- 2) benzene
- 3) carbon monoxide
- 4) N-nitrosamine
- 5) ammonia
- 6) 2-naphthylamine
- 7) 4-aminobiphenyl
- 8) benz(a)anthracene
- 9) benz(o)pyrene.

Sidestream smoke contains more free nicotine in the vapor phase than does mainstream smoke.

MEASUREMENT OF EXPOSURE TO ETS

Use of Diffusion Denuder Samplers.

Eatough et al. (4) used diffusion denuder samplers to collect gas-phase acids and bases separately from particle-phase acids and bases present in ETS. ETS was sampled from a 10-m³ unventilated chamber in the initial experiment; a 30-m³ unventilated chamber was constructed and used for all subsequent chamber experiments. The environmental chambers consisted of Teflon bags with Teflon sampling manifolds at the bottom of the bag.

A cylindrical and/or annular diffusion denuder (with 0.8M benzenesulfonic acid solution) was used to sample the atmosphere in the environmental chamber for 1 to 4 hours. In some experiments, a total hydrocarbon analyzer was used to monitor changes in gas phase organic compounds.

The results indicated that the following gas-phase compounds may be unique to ETS in an indoor environment and may be suitable tracers of tobacco smoke:

- 1) nicotine
- 2) 3-ethenylpyridine
- 3) myosmine
- 4) nitrous acid
- 5) pyridine.

EFFECTS OF TWENTY-SIX ACTIVITIES.

In a controlled study, Wallace et al. (5) determined the effects of each of 26 activities on personal exposure, indoor air concentrations, and exhaled breath for volatile organic chemicals. Two of the activities were:

- 1) tobacco smoking
- 2) passive smoking.

The breath levels of benzene and styrene in cigarette smokers' breath were found to be about 5 to 10 times the level for nonsmokers or pipe and cigar smokers.

The major source of exposure to benzene and styrene is mainstream tobacco smoke (6). Indoor levels of these two compounds in the cigarette smokers' homes were slightly elevated.

The measurements of exhaled breath were useful in detecting exposures from smoking that otherwise would not have been detected.

BENZENE IN SMOKING.

Benzene is produced in the largest volume of any chemical that has been causally linked to cancer in humans (7,8). In addition, it is a by-product of various combustion processes including the

combustion of cigarettes. Approximately 8.5 billion kg of benzene is emitted annually in the U.S. alone (9).

We quote now from a review of toxicology (10):

"Benzene is widely regarded as the most dangerous hydrocarbon used in industry today. It is rapidly absorbed upon ingestion, inhalation, or skin contamination and has a particular affinity for nerve tissue.....Because of its toxic potential, benzene has been banned as an ingredient in products intended for use in the home."

The Total Exposure Assessment Methodology (TEAM) studies (8) found that benzene levels averaged 2 times higher in air people breathe (personal air) than concentrations in outdoor air. Exposure to benzene concentrations indoors was found to be greater than exposure to the benzene level near gasoline stations in most cases (9). "Smoking is by far the largest anthropogenic source of background exposure to benzene" (7).

It has been reported that smokers had benzene levels in expired air 2 to 10 times higher than those of nonsmokers (11). Also, nonsmokers who lived with smokers or came in contact with smokers had elevated levels of benzene in their breaths (11). About 3 times more benzene is taken in daily by average smokers (20 cigarettes per day) from smoking than from their exposure to background benzene contamination.

NICOTINE

Intercomparison of Sampling Techniques for Nicotine in Indoor Environments.

An intercomparison of sampling techniques for nicotine in indoor environments was made by Caka et al. (12). The sampling systems studied used filter packs, annular denuders, sorbent beds, and passive samplers. The intercomparison evaluated the precision and equivalency of each of the techniques. Determinations were made of both airborne gaseous nicotine and particulate-phase nicotine.

The four laboratories participating in the study were: 1) a group from Brigham Young U.; a group from Harvard U.; a group from the R.J. Reynolds Company; and a group from the University of Massachusetts Medical School and Yale U. The sampling techniques were: an annular diffusion denuder; a filter pack sampling system; 2 passive sampling devices; a Tenax semi-real-time sampler; a miniannular denuder; a Millipore cassette; an XAD-IV sampler; a stainless steel diffusion sampler; and an active sampler.

Determinations of total nicotine using the various sampling systems were generally in good agreement. There was agreement among samplers for determination of nicotine in the gas phase. The precision of particulate-phase nicotine data was poor. Loss of particulate-phase nicotine to the gas phase occurred in a filter pack sampling system, and nicotine was lost from particles.

PROXIES, SURROGATES, TRACERS, AND MARKERS.

A number of proxy, or surrogate, constituents have been investigated in a number of studies as indicators of environmental tobacco smoke in both personal and indoor space monitoring. They have also been referred to as markers or tracers. No single marker has quantified accurately the exposure to each of the constituents of smoke over the wide range of environmental settings in which smoking occurs (2).

Markers should be chosen because of their accuracy in estimating exposure and because of their relevance for the health outcome of

interest (2). An ideal marker should be unique (or nearly unique) to tobacco smoke, should be a constituent of tobacco that is present in sufficient quantity that it can be measured even at low levels of ETS, and should stand in constant ratio across brands of cigarettes to other tobacco smoke constituents or contaminants of interest (3).

Nicotine appears to be a promising tracer for ETS because of its specificity for tobacco and its presence in relatively high concentrations in tobacco smoke (2). At a practical level, the technology for measuring nicotine levels is available and accurate. Nicotine volatilizes during dilution of sidestream smoke, so that it occurs almost exclusively in the vapor phase (2). Almost all of the nicotine shifts from the particulate phase in mainstream smoke and sidestream smoke to the vapor phase in ETS (3). Tobacco is the only source of nicotine, so the Nicotiana alkaloid is a specific indicator for tobacco smoke pollution (3).

Identification of a Group of Potential Tracers of ETS.

The objective of a study by Benner et al. (13) was the detailed chemical characterization of both the gas-phase and the particulate-phase constituents of environmental tobacco smoke in order to identify a group of potential tracers that would meet the National Academy of Sciences recommended criteria:

- 1) uniqueness
- 2) ease of measurement
- 3) similarity in emission rates for different tobaccos
- 4) consistent ratios to ETS compounds of interest.

The characterization of particulate-phase ETS was described and recommendations were made of several potential tracers which were identified.

Based on the experimental results, the following particulate-phase components of ETS were proposed as possible tracers:

- 1) nicotine and related compounds
- 2) solanesol
- 3) sterols and sterenes.

Other Potential Tracers and Markers.

Ogden and Maiolo (14) concluded from their experiments that of all the potential tracers that had been suggested for quantifying ETS particulate concentrations in indoor environments, solanesol appeared to be the best candidate; although more work needed to be done before solanesol could be used as a routine tracer of ETS.

Chuang et al. (15) found in a field study that there were good correlations between nicotine and quinoline and between nicotine and isoquinoline. They recommended that quinoline and isoquinoline, instead of nicotine, be used as ETS markers.

CONCLUSIONS.

Environmental tobacco smoke (ETS) exists in the vapor phase and the particulate phase. It is the only source of nicotine in the environment and is a substantial contributor to the level of indoor pollution concentrations of benzene, carbon monoxide, and other compounds.

The major source of exposure to benzene and styrene is mainstream smoke. The breath levels of benzene in cigarette smokers' breath were about 5 to 10 times the level for nonsmokers or pipe and cigar smokers. Nonsmokers who lived with smokers or came in contact with smokers had elevated levels of benzene in their breaths. Average

smokers (20 cigarettes per day) take in about three times more benzene daily from smoking than from their exposure to background benzene contamination. Again, "Smoking is by far the largest anthropogenic source of background exposure to benzene."

A number of proxy, or surrogate, constituents have been measured in a number of studies as indicators of environmental tobacco smoke in both personal and indoor space monitoring. Nicotine appears to be a promising tracer of ETS because of its specificity for tobacco and its presence in relatively high concentrations in tobacco smoke. Nicotine and related compounds, solanesol, and sterols and sterenes have been proposed as possible tracers. Quinoline and isoquinoline have been recommended as ETS markers, rather than nicotine.

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A Comparison of Smoking and Non-Smoking Areas
Private Homes and Bingo Halls

by

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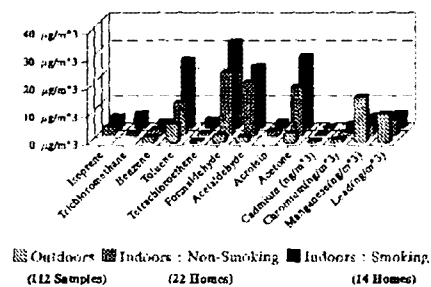
During the past 3 years, personal exposure studies were carried out in Windsor and Hamilton as part of the "Cities of the Nineties" program by the Ontario Ministry of Environment and Energy. During these studies, airborne concentrations of 56 carbonyls and other volatile organic compounds (VOCs) and 8 selected airborne trace metals were measured. Since people usually spend less than 10% of their time outdoors and the main objective of these studies was to obtain personal exposure profiles, these studies examined the personal and general air quality in a variety of microenvironments including different homes, offices, m/hotels, vehicles, garages and a variety of communal places such as several bingo halls, a cafeteria, a retirement home, a swimming pool and a gymnasium. Samples were also gathered during the volunteers' commuting to and from work.

When and where ever possible, personal air sampling was the preferred method of sampling with the samplers being carried by the volunteers during their regular day. When this was not feasible nor practical, sampling was carried out in the major microenvironments in which the volunteers lived, travelled and worked. For each volunteer, a 24-hour "snapshot" personal air quality profile was compiled and together with their time activity diary for these 24 hours, an exposure profile was computed.

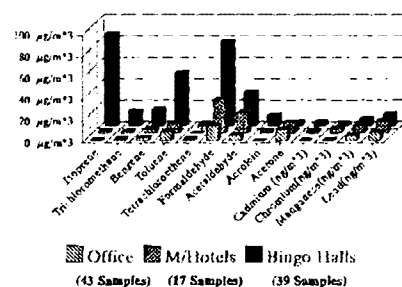
Depending upon the compound class, the air was sampled at flow rates ranging from 5 millilitres to 25 litres per minute and all samples were either acquired within the volunteers' "breathing zone" or at a height of 1.5 metres in their microenvironments. Throughout the study, concurrent outdoor sampling was conducted at the volunteers' homes and if possible, at their offices. For determining volatile organic compound concentrations in air, three-stage adsorption cartridge samples were used and these were subsequently analyzed by thermal desorption and cryo-focusing at the head of a column of a GC/FID-MSD (gas chromatograph fitted with flame ionization and mass selective detectors) system. For the carbonyls, the sampling and analytical method involved the derivitization with DNPH (2,4-dinitrophenyl hydrazine) followed by HPLC separation and detection of the hydrazone products. For the trace metals, exposed Whatman 41 filters were digested in a weak (5%) nitric acid and the extract was then analyzed by ICP-MS (inductively coupled plasma - mass spectrometry).

Environmental tobacco smoke (ETS) is an important source of many of these compounds and has been identified as the major, if not the leading cause of many indoor air quality problems. During these studies, a questionnaire was given to each of the volunteers and the answers allowed a correlation with smoking. Although our studies dealt with only a small portion of the more than 4,700 identified ETS components, the results indicated that isoprene would be an excellent marker or indicator for general air quality in these microenvironments. This feature was highlighted during our investigations of bingo halls: a place that allows potentially large exposures to ETS and a place where patrons can spend many hours each day, several days a week. Differences between smoking and non-smoking areas were more evident in the bingo halls than in the other settings and isoprene was clearly seen in all situations as a primary gaseous component of ETS.

Windsor Personal Air Quality Study Median Concentrations (at Home)



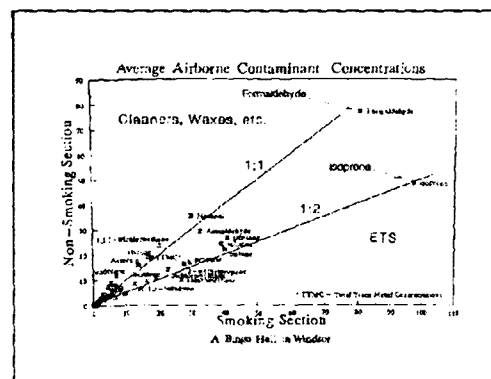
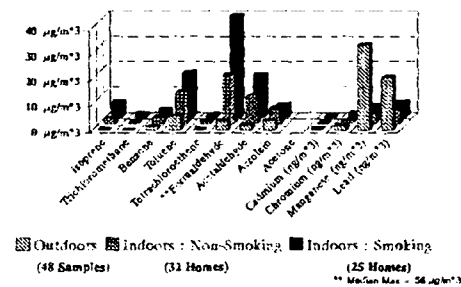
Windsor Personal Air Quality Study Median Concentrations (Indoors)



For the Windsor study, the volunteers were all involved with either the academia, the government or other environmental agencies. For Hamilton, the volunteers were randomly selected. In both studies, the volunteers usually had 1 week notice before samples were taken. The volunteers tended to make their homes more presentable during sampling times and this was very obvious from the Windsor results as the isoprene concentrations in the "Smoking" and "Non-Smoking" homes were similar. In Hamilton, there were definitive differences in the isoprene, formaldehyde and acetaldehyde concentrations; all major constituents of ETS.

During one 24-hour period, 1 carbonyl, 1 trace metal and 7 VOC samples were acquired in the smoking section and 1 carbonyl, 1 trace metal and 4 VOC samples were acquired in the non-smoking section of a very large ($\approx 17,000$ square feet) bingo hall in Windsor. This bingo hall accommodated ≈ 400 people regularly and from the data, isoprene was shown to be a very good air quality indicator for ETS.

Hamilton Personal Air Quality Study Median Concentrations (at Home)



Median Concentration Values: Windsor and Hamilton Personal Exposure Studies

Airborne Compounds	Hamilton at Home			Windsor at Home			Windsor - Indoors		
	Out	HNS	HSk	Out	HNS	HSk	Ofc	M/H	Bgo
Isoprene	0.3	2.0	5.9	-	3.0	4.4	0.9	2.6	86.3
Trichloromethane	0.1	0.6	1.1	-	1.0	5.4	1.2	1.9	14.4
Benzene	1.4	2.5	3.1	2.0	2.5	2.6	2.8	4.3	16.2
Toluene	5.6	12.5	17.5	6.9	11.9	25.0	8.4	9.5	50.2
Tetrachloroethene	0.3	1.0	0.9	0.9	0.6	3.3	1.4	0.7	2.6
Formaldehyde	3.7	19.2	56.0	2.9	22.8	31.4	14.1	31.8	79.0
Acetaldehyde	2.2	11.1	16.8	2.0	19.4	22.5	5.5	19.5	31.5
Acrolein	3.9	6.3	5.0	-	1.7	2.3	0.3	2.7	10.2
Acetone	-	-	-	3.4	17.7	26.0	10.6	10.2	4.0
Cadmium	0.7	0.4	0.3	0.6	0.4	0.3	0.4	2.5	4.1
Chromium	1.7	1.3	1.7	1.3	1.3	1.7	0.8	4.5	2.6
Manganese	33.6	4.0	4.6	16.7	4.0	4.6	4.7	7.7	7.2
Lead	20.9	5.6	5.7	10.6	5.6	5.7	7.6	11.7	11.6
Number of Samples/Homes									
VOCs	48	32	25	112	22	14	43	17	39
Carbonyls	11	6	5	49	22	12	18	3	4
Trace Metals	31	15	15	46	22	15	17	3	4
Concentration Units: Volatile Organics and Carbonyl - $\mu\text{g}/\text{m}^3$; Trace Metals - ng/m^3 "-" insufficient data (compound detected in fewer than 20% of the samples) Out - Outdoors; HNS - Indoors Home, Non-Smoking; HSk - Indoors Home, Smoking Ofc - Office; M/H - Motels and Hotels; Bgo - Bingo Halls									

The outdoor samples were acquired either at the volunteers' homes or near their offices. For the indoor samples, the average concentrations for the various airborne compounds for each home were computed.

The Windsor information will be available in greater detail during the summer of 1994 when the Ontario Ministry of Environment and Energy will be releasing the following 9 reports on the Windsor Air Quality Study: *Executive Summary*, *Emission Inventory*, *Ambient Fixed Network Monitoring*, *Specialized Mobile Air Monitoring*, *Personal Exposure Survey*, *Soil and Garden Produce*, *Mathematical Modelling and Source Apportionment*, *Health Effects Assessment* and the *Plain Language Summary*.

SESSION 22:
ANALYSIS OF POLAR
VOLATILE ORGANIC COMPOUNDS

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GC-MS Analysis of the Exhaled Breath Matrix

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The organic components of the exhaled breath matrix are considered a non-invasive "window" into the blood gases. These compounds reflect normal biogenic function, direct exposure to pollutants, and metabolites of such exposure. Given appropriate analysis and interpretation of the data, the organic fingerprint of the exhaled breath can become an important exposure and health assessment tool. Standard gas chromatography-mass spectrometry (GC-MS) methods for measurement of volatile organic compounds in ambient air are not well suited to the breath matrix due to the high carbon dioxide and moisture content and the wide variety and concentration ranges of potential analytes. This paper presents a set of three complementary analytical methods for GC-MS analysis specifically designed for measuring CO_2 and VOCs in the exhaled breath matrix. Example chromatograms and the performance of the methods will be discussed.

**Deactivating SUMMA Canisters for Collection and Analysis of
Polar Volatile Organic Compounds in Air**

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SUMMA canisters are commonly used as the collection medium for whole air samples for the measurement of a variety of volatile organic compounds (VOCs). The interior electropolished surface is inert for most non-polar compounds even at trace levels, however, certain polar species (PVOCs) exhibit reduced recoveries after storage. A surface deactivation process, referred to as Silcosteel, has been developed wherein the interior of the canister is coated with a thin layer of fused silica. In addition to the silica layer, a variety of chemical deactivations can be used to increase the inertness of the surface for specific classes of VOCs. Canisters with the standard electropolished interior surfaces were tested and compared to those treated with the Silcosteel process and various deactivation layers. This paper presents an explanation of the process and the results of the comparisons with particular emphasis on the storage stability and minimum detectable limits for PVOCs.

**CLEANLINESS OF COMMON AIR SAMPLING SORBENTS
FOR APPLICATION TO PHENOLIC COMPOUNDS MEASUREMENT
USING SUPERCRITICAL FLUID EXTRACTION**

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ABSTRACT

The trace-level measurement of phenolic compounds in the ambient air is complicated by the acidic and polar nature of the compounds especially during recovery from the sampling medium. Recently, supercritical fluid extraction (SFE) has been proposed as an alternative extraction method to Soxhlet extraction or thermal desorption to achieve more efficient recoveries. For such methodology to become practical, the candidate sorbents must first be tested for stability and cleanliness under SFE conditions. This paper describes exploratory research results of background contamination tests and cleanup properties of some common air sampling sorbent media with respect to future application to phenolic compounds monitoring.

INTRODUCTION

SFE offers the following advantages over more traditional extraction methods such as Soxhlet: 1) less expensive in terms of solvent purchase and disposal, 2) less harmful to the environment, 3) less time consuming in sample preparation, and 4) equivalent or better recoveries to traditional methods. It is for these and other desirable characteristics that SFE has become an increasingly popular alternative to other extraction techniques.¹⁻⁵ It is also makes an attractive alternative means of cleaning and extracting sorbents used in air monitoring.

This work describes preliminary results of clean up properties and contaminants in these sorbents. Also investigated were the effects of storage and exposure to ozone^{6,7}.

EXPERIMENTAL PROCEDURE

Sorbents

The sorbents used in this work were Tenax-GC, Tenax-GR (Alltech Assoc., Inc., Deerfield, IL), XAD-2, and Carboxen 563 (Supelco, Bellefonte, PA). For SFE extractions the following amounts of each sorbent were used: Tenax-GC, 0.2g; Tenax-GR, 0.4g; XAD-2, 0.4g; Carboxen 563, 0.6g. For Soxhlet extractions the following amounts of sorbent were used: Tenax-GC, 0.6g; Tenax-GR, 1.0g; XAD-2, 2.0g; Carboxen 563, 1.0g.

SFE conditions

Extractions were performed using a system that included two Isco pumps (models 260D and 100D), a Lee Scientific oven (model 501), stainless steel tubing, and deactivated fused silica restrictors (Polymicro Technologies, Phoenix, AZ). A sample of each sorbent was placed in a

clean 1 mL stainless steel extraction cartridge and extracted using 5% methanol (MeOH)/carbon dioxide (CO₂) (v/v) at 50° C and 6000 psi. Each sorbent was statically extracted for 30 minutes then dynamically for 0.5 -1.5 hours with collection of extracted material over 30 minute intervals during this time. Flowrates of the supercritical fluid were approximately 1 mL/min. Collection was in vials containing 2-3 mL of methylene chloride (MeCl₂). These solutions were then reduced to a final volume of approximately 1 mL with a N₂ flow.

Soxhlet conditions

Sorbent samples were weighed and placed in cleaned cellulose extraction thimbles. The thimbles were then loaded in the Soxhlet extractors and the extractors were charged with 200 mL of extraction solvent. 5% ether/hexane (v/v) was used for the Tenax-GC and Tenax-GR sorbents and MeCl₂ was used for XAD-2 and Carboxen 563. The Soxhlet extractors were then allowed to run for 16-18 hours; after which the solvent was rotary evaporated down to 3-4 mL and then transferred to an evaporation vial for final reduction to 1 mL with a N₂ flow.

Analysis by GC/MS

Once the samples were blown down to 1 mL, an internal standard of 4,4'-dibromo-1,1'-biphenyl was added at a concentration of 1 ng/μL. A 1-μL aliquot was then injected into a Hewlett-Packard GC/MS (HP5890/HP5971A, respectively) equipped with an XTI-5 column (Restek, Bellefonte, PA, 30 m, 0.25-mm i.d., 0.25-μm d.f., catalog # 12223).

Temporal and chemical stability

Once the sorbents were cleaned, the SFE cartridges were sealed and allowed to remain sealed for 4 weeks. This was done to determine if the sorbents remained clean once they were extracted. At the end of this 4-week period the sorbents were once again extracted by SFE as in the original clean up extraction above and the extract analyzed.

Chemical stability was investigated by exposing the sorbents to ozone and extracting them using SFE as above. The ozone exposure was 115 ppb for 18.5 hours at a flowrate of 1.3 L/min. with a relative humidity of 48-52% for the Tenax-GC and Tenax-GR. For the XAD-2 and Carboxen 563, ozone exposure was 115 ppb for 16.0 hours at 1.5 L/min. with a relative humidity of 40-50%. Again, the extracts were analyzed by GC/MS as above.

RESULTS

Initial "Clean-up" Extractions

As expected, analysis of the SFE and Soxhlet extracts from Tenax-GC, Tenax-GR, and Carboxen 563 revealed significant amounts of impurities in the first sequential extracts. However, the third sequential SFE extracts and the second sequential Soxhlet extracts showed no detectable impurity except a consistent phthalate ester component. This compound was found in all sorbents at varying levels but was greatly reduced with each subsequent extraction. It should be noted that it was much easier and quicker to reach this level of "cleanliness" using SFE (1.5-2 hours) than Soxhlet extraction (16-18 hours).

Analysis of the XAD-2 extracts revealed that this particular lot was surprisingly clean given past experience with XAD-2. Previously, XAD-2 was repeatedly extracted but still retained significant amounts of impurities. The impurities detected were the phthalate ester as

in the other sorbents and an acid ester. The acid ester was only observed in the Soxhlet extract. Subsequent extractions reduced the amount of these compounds in each extract.

During these initial clean-up extractions, it was noted that the hexane/ether mixture added significantly to the background signal. Therefore, higher purity hexane was purchased and the problem was eliminated.

The following observations were made after comparing the chromatograms of the sequential SFE and Soxhlet extracts for the various sorbents.

Tenax-GC

- There were four primary contaminants associated with this sorbent. Two were common to both the SFE and Soxhlet extracts and of the other two, one was found in each.

Tenax-GR

- There were ten primary contaminants and they were components of both the SFE and Soxhlet extracts at about the same relative levels.

XAD-2

- There were only two primary contaminants and one was associated with the SFE extract and the other was associated with the Soxhlet extract.

Carboxen 563

- There were nine primary contaminants and only one was associated with the SFE extract. The other eight were associated with the Soxhlet extract.

Temporal and Ozone Stability

Comments below pertain to chromatograms obtained from analysis of SFE extracts of sorbent sealed for 4 weeks then extracted (●) and sorbent exposed to ozone then extracted (○).

Tenax-GC

- Comparison of the third sequential extract before sealing and the first extraction after being sealed revealed that there was no residual contaminants except for the ever present phthalate ester mentioned above. Also, after a second extraction this peak also became negligible.
- Exposure to ozone did produce artifacts from the degradation of the Tenax-GC which could be problematic if ambient measurements of compounds such as benzaldehyde and acetophenone were being performed.

Tenax-GR

- Comparison of the third sequential extract before sealing and the first extraction after being sealed revealed that there was no residual contaminants except the phthalate ester. Again this was removed completely after the second extraction.

- Only two artifacts were formed from exposure to ozone and at levels lower than for Tenax-GC and did not include benzaldehyde nor acetophenone.

XAD-2 and Carboxen 563

- Comparison of the extracts before and after sealing showed no change in the sorbent.
- No effect on the sorbents was noted and no artifacts were extracted.

CONCLUSIONS

The following conclusions can be drawn from this preliminary study:

- ◇ Since the two extraction methods can extract different components from the sorbents, whichever method is used for clean up should also be used for the extraction of the sample collected on the sorbent.
- ◇ Tenax-GR is preferable to Tenax-GC because of its greater stability in O₃.
- ◇ XAD-2 and Carboxen 563 may be preferable to either Tenax type because of their ease of cleaning and stability in O₃. Comparison of their collection and recovery efficiencies to those of Tenax GC and GR will help determine this.
- ◇ For preparation of small amounts of sorbents such as sorbent cartridges, SFE would be preferable to Soxhlet extraction in terms of time and handling ease. A cartridge could be filled, cleaned, used, extracted, and possibly reused, all without having to remove and handle the sorbent thus minimizing the chance of contamination and sample loss.

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract No. 68-DO-0106 to ManTech Environmental Technology, Inc. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Collection of Ambient Air Phenols Using an Anion Exchange Membrane

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We have previously demonstrated the feasibility of collecting vapor phase ambient air phenols by reversible chemical reaction with a solid sorbent. This sorbent, similar to XAD-2, consists of a styrene divinylbenzene polymeric backbone with chemically bound quaternary amine functional groups and exchangeable anion. The smallest mesh size used (200-400 mesh, 37-75 μm diameter) provided the highest collection efficiency for diverse phenols at sampling rates of 100 mL/min. Detection limits were about 1 ppbv ($\sim 7 \mu\text{g}/\text{m}^3$).

We report here enhanced detection limits for ambient phenols using an anion exchange membrane that allows high collection efficiency at 10 L/min sampling rate. The membrane consists of 5 μm particles of the anion exchange resin enmeshed in a Teflon microfibril matrix. This membrane is similar to "Empore" membranes, with the addition of the anion exchange capacity. Sampling is accomplished using a 10.5 cm (diameter) membrane and a General Metal Works PS-1 sampler. A Teflon-coated glass fiber filter, spiked with deuterated phenols, and placed ahead of the membrane, is used to deliver these surrogate recovery standards to the membrane during the sampling. Following sampling, membranes are shaken gently in an acidified mixture of methanol and dichloromethane. The extract is derivatized with BSTFA and analyzed using either GC/FID or EI GC/MS. Analytical methodology allows detection at the 0.02 ppbv level for 12 hrs of sampling ($\sim 0.1 \mu\text{g}/\text{m}^3$).

**Controlled Desorption Trap (CDT): A Water Management Technique
for Quantitative Analysis of Polar VOCs in Ambient Air**

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Compendium Method TO-14 details the analysis of Volatile Organic Compounds (VOCs) in ambient air using cryogenic preconcentration for sample enrichment. These trace level organics require preconcentration of volumes greater than 50ml to provide a sufficient sample mass to an analytical detector.

When working with high humidity sample volumes of 50ml and greater, water management becomes critical. Compendium Method TO-14 specifies the Nafion[®] semi-permeable membrane to reduce water vapor in the sample stream during cryogenic concentration. The same mechanism responsible for this effective dehydration of the sample compromises recoveries of polar species. Consequently, alternate water management techniques are necessary when polar compounds are analyzed.

The CDT is effective as a water management techniques since it allows volatile organics, collected on a primary cryotrap, to vaporize at a temperature that limits the partial pressure of water vapor. Temperature control of the cryotrap and the total volume of the desorption gas are essential parameters in optimizing CDT. A secondary cryotrapping step is necessary to refocus the slowly desorbed sample prior to injection to a GC or GC/MS.

The analytical system consists of the Grasby/Nutech 3550A Cryogenic Concentrator, the 354A Cryofocusing Accessory and the HP 5971 GC/MS. Some of the classes of compounds investigated using this application include alcohols, ketones and ethers.

The effectiveness of the CDT will be compared with analyses using (a) no water management and (b) the Nafion dryer.

A Comparison of Concentration Techniques for the Analysis of Polar Compounds in Canister Samples

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The analysis of Polar Volatile Organic Compounds (PVOCs) in ambient air by GC/MS requires sample preconcentration to achieve 0.1 ppb detection limits. Necessary sample volumes can exceed 300 cc resulting in the co-collection of approximately 3-6 μ l of water, depending on the humidity of the sample. This much water will degrade column performance and will cause signal attenuation in benchtop mass spectrometers making quantification of target analytes difficult. Although most of the water vapor can be eliminated by passing the sample through a Nafion Dryer, such an approach usually results in loss of the polar VOC fraction in the sample due to passive and/or active interaction with the dryer.

Two 3-Stage preconcentration techniques have been previously reported which allow both polar and non-polar VOCs to be quantified by eliminating most of the water before injection into a GC/MS. These techniques, namely Automated 2-Dimensional Chromatography (A2DC) and Microscale Purge & Trap (MP&T), both eliminate water and CO₂ in the sample before GC/MS injection to improve detection limits and quantitation accuracy.

A concentration system utilizing yet a third water management technique called Cold Trap Dehydration (CTD) will be presented. Using this technique, water can be substantially eliminated without loss of polar VOCs of interest. CO₂ is also eliminated before GC/MS injection resulting in superior chromatographic performance and a more consistent GC/MS response for the extremely light VOCs. The preconcentrator uses the same hardware trapping configuration for Cold Trap Dehydration as it does for Automated 2-Dimensional Chromatography and Microscale Purge & Trap, and can select any one of the three applications under software control. To determine which approach is best for TO14 and CAAA Title III compounds, all three water management procedures will be examined and compared. Data will be presented showing detection limits and %RSD's from the analysis of PVOCs in canisters using the 3-stage Entech 2000/2016CM Automated preconcentration system and an HP 5972 GC/MS.

SESSION 23:
SEMI-VOLATILE ORGANIC COMPOUNDS

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**Method Validation Program for the Long Duration Sampling of
PCDDs/PCDFs in Ambient Air**

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A method validation program was completed to assess the technical viability of extended, long duration sampling periods (15- and 30-day) for the collection of PCDDs/PCDFs in ambient air in lieu of the 48-hour sampling periods typically employed. This long duration approach, if successful, would provide measurements data more representative of average ambient PCDDs/PCDFs levels on an annual basis, and hence provide enhanced support of the 1.0 pg/m³ annual ambient standard for PCDDs/PCDFs (expressed as 1987 EPA toxic equivalents) required by Connecticut regulation.

The method validation program utilized nine collocated "PUF" samplers which were operated for 15-day and 30-day periods during each of two seasonal monitoring campaigns (winter and summer). Each "PUF" sampler was outfitted with a Teflon coated glass fiber filter and polyurethane foam (PUF) cartridge for the collection of particulate-associated and vapor phase PCDDs/PCDFs, respectively.

Samples were analyzed using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) based on EPA Method 8290. Each "PUF" cartridge consisted of two foam halves; the top half PUF and filter were analyzed as a single sample separately from the bottom half PUF section. This approach provided an assessment of analyte breakthrough using the sampling system for large sample volumes of approximately 4,000 m³ and 8,000 m³ for the 15-day and 30-day sampling periods, respectively.

Effect of Combustion Temperature on the Atmospheric Stability of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans

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Atmospheric emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs and PCDFs) are likely to increase in the future due to an increase in municipal and hazardous waste incineration. There is little information regarding the atmospheric stability of PCDDs and PCDFs. In this study PCDDs and PCDFs were generated from the combustion of a mixture of pentachlorophenol, polyvinyl chloride pipe shavings, and wood chips treated with pentachlorophenol. These emissions were injected into outdoor Teflon film chambers and aged in sunlight under typical atmospheric conditions. Incineration experiments were conducted using "low temperature" combustion (400-470°C range) and "high temperature" combustion (670-800°C range). Concentrations of PCDDs and PCDFs were determined over time by collecting both particulate and vapor phase samples. These compounds were found to exist primarily in the particulate phase. Based on previous results with polybrominated dioxins and furans, we expect particulate phase PCDDs and PCDFs to slowly degrade over periods of hours in the "low temperature" experiments. However, in "high temperature" experiments, we expect particulate phase PCDD and PCDF emissions to be stable. Differences in the morphology and chemical composition of the combustion particles generated can explain the differences in the Atmospheric stability of particle associated organics produced from the "low temperature" and "high temperature" experiments. Previous results show that incinerators operating near 450°C can generate particulate phase brominated dioxins and furans and PAH emissions with atmospheric half-lives of 1-2 hours. These observations also indicate that the corresponding emissions from incinerators operating near 800°C will have much longer half-lives, allowing for the possibility of long distance transport. If the same observations are made for PCDDs and PCDFs, this dependence on combustion temperature must be considered when evaluating the potential exposure to toxic organic compounds emitted from waste incinerators.

Modeling the Mass Transfer of Semi-Volatile Organics in Combustion Aerosols

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The atmospheric transport and fate of airborne organic compounds are highly dependent upon which phase or phases (i.e., gas or particle or gas/particle) the compound exists. Semi-volatile organics partition into both gas and particle phases and this partitioning is a function of the compound's vapor pressure, the amount of available surface area, and the ambient temperature. Over the last 10 years, efforts to predict atmospheric semi-volatile partitioning have been primarily based on equilibrium theory (June 1977; Pankow 1987, 1991, 1992; Bidelman 1986, 1988). However, recent discoveries in this area suggest that full partitioning equilibrium may rarely be achieved in the atmosphere. Therefore dynamic mass transfer models, rather than equilibrium models, may be better suited to predict semi-volatile partitioning.

Recently Rounds and Pankow (ES&T 1990, 1993) developed a radial pore-diffusion model to simulate the mass transfer of semi-volatile organics in and out of combustion aerosols. Preliminary results from their model and other recent discoveries suggest that many types of combustion aerosols may be coated with a liquid organic layer and that diffusion of semi-volatile organics through this layer impedes rapid mass transfer of these compounds. Therefore a radial diffusion model was developed to describe the mass transfer of semi-volatile organics into and out of combustion aerosols. The model combustion aerosol consists of a solid carbon core that is surrounded by a viscous, liquid-like, organic layer. Diffusion takes place only within the organic layer and is controlled by mass transfer at the particle surface. Modeling of semi-volatiles requires the tuning of two separate parameters: a diffusion coefficient and a surface mass transfer coefficient. Preliminary testing of the model on the uptake of deuterated pyrene by diesel exhaust aerosol at 25°C suggests that diffusion coefficients for PAH are on the order of 10^{-15} cm²/sec and that surface mass transfer coefficients for pyrene are on the order of 10^{-9} cm/sec.

**Experimental Observations of Non-Equilibrium Gas-Particle
Partitioning of PAHS in an Outdoor Smog Chamber**

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To study non-equilibrium gas-particle partitioning of various PAHs, three specially designed smog chamber experiments were conducted (October 1993, January 1994, and February 1994). Automobile diesel exhaust was injected for five minutes into a 190 m³ Teflon film chamber and allowed to age during the night at temperatures below 15 degrees Celsius. A large denuder system was utilized during the injection period in order to remove PAH vapors from the injection stream. Thus, PAH-laden particles were observed to off-gas in the near absence of vapor phase PAHs during the initial stages of the 8-hour experiments. The large denuder was designed as a parallel plate system, made of activated charcoal impregnated filters. It was characterized to remove greater than 90% of PAH vapors from the diesel injection system. During the experiments, air samples were collected in the chamber at twenty-minute intervals for the first two hours, and hourly thereafter. The sampling system consisted of an XAD-4 coated annular denuder, followed by a quartz-fiber filter, which is then followed by a second annular denuder. Sample extracts were analyzed on Hewlett-Packard GC/MS. Results from these experiments are compared to output from a radial diffusion computer model, detailed in another paper ("Modeling the Mass Transfer of Semi-Volatile Organics in Combustion Aerosols" by Jay R. Odum and Richard M. Kamens).

Use of the Phenanthrene to Benzo(e)pyrene Ambient Air Ratio as an Indicator for the Source of Polycyclic Aromatic Hydrocarbons

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ABSTRACT

Polycyclic Aromatic Hydrocarbons (PAH) are emitted by many industrial, domestic and natural sources. In 1990, the principal sources of PAH for the Province of Quebec were primary aluminum smelters (858 t), residential heating with wood (162 t), forest fires (148 t) and transportation (33 t). A sampling program was developed to measure PAH levels in ambient air at different locations influenced by these sources. The highest concentrations of PAH in ambient air (470 ng/m³ geometric mean) were measured near primary aluminum smelters using Horizontal Stud Söderberg technology. Areas influenced by wood heating (157 ng/m³ winter geometric mean) and transportation (80 ng/m³ geometric mean) had lower total PAH concentrations. Ratios of ambient air concentration for phenanthrene/benzo(e)pyrene were lower in samples collected in the surroundings of the primary aluminum smelters (7-14), whereas high ratios were observed for residential heating with wood and transportation (20-45). The use of this ratio was found to be a good indicator for PAH originating from primary aluminum smelters.

INTRODUCTION

In 1989, Environment Canada began a sampling program to characterize the ambient air levels of polycyclic aromatic hydrocarbons (PAH) and to use the data obtained to assess their toxicity, as defined by the *Canadian Environmental Protection Act (CEPA)*. This program was done in parallel with an estimate of their releases to the Canadian environment. During the summer of 1991, many forest fires occurred in the Province of Quebec, including some that were of concern for the population living near the shore of the St. Lawrence River estuary in the city of Baie Comeau. In addition to the danger fires represent, concerns regarding the impact of those fires on air quality were expressed. Polycyclic aromatic hydrocarbons were measured, in cooperation with the Quebec Ministry of the environment and wildlife (MEF) and the city of Baie Comeau. High levels of PAH were measured but could not be attributed to forest fires (Naturani, 1991). In order to confirm this, additional sampling was undertaken during winter when forest fires had ceased. Again, high PAH values were measured. In order to identify the origin of PAH, ratios between compounds can be looked at (Daisey *et al.*, 1986; Lavalin, 1988). We examined different ratios for the locations at which we sampled. The areas surveyed were

influenced by activities from industrial sources (mainly aluminum smelters using different electrolysis technologies), residential wood heating, forest fires, and traffic.

EXPERIMENTAL

Ambient air sampling was carried out using a General Metal Works model GMWL-2000 II High Volume Air Sampling System, modified as per Environment Canada specifications [e.g. addition of Polyurethane foam (PUF) cannister and dry gas meter] (Dann, 1987). Cleaned teflon-impregnated glass fiber filters (Pallflex Emfab Teflon Coated Glass Fibre TX40H120WW; 8 x 10 in.) and cylindrical polyurethane foam (9 x 15 cm) were used to collect PAH in two particulate and gaseous phases.

The samples were collected at different locations and seasons every 6th day over a 24-h period, in accordance with the National Air Pollution Sampling Network (NAPS). Samples were sent to laboratory in a cooler at 4° C and stored at -20° C until analysis. Filters and PUF were spiked with seven (7) deuterated compounds [D_8 -naphthalene; D_{10} -Acenaphthene; D_{10} -Anthracene; D_{10} -Pyrene; D_{12} -Benz(a)anthracene; D_{12} -Benzo(a)pyrene; D_{12} -Benzo(ghi)perylene] before soxhlet extraction for 18-h with benzene and cyclohexane respectively. Extracts were passed through a 20-cm silica gel clean-up column and analysed with a Hewlett Packard model HP-5971 MSD GC-MS in Selected Ion Monitoring (SIM) mode, a SPB-5 (Supelco) fused silica capillary column (30 m x 0.32 mm i.d.) and temperature programming (80° C to 300° C). Quantification was done using an internal standard (D_{10} -Fluoranthene) (Novalab, 1992).

RESULTS

Table 1 presents geometric means (g.m.) of the different PAH measured in ambient air in the Province of Quebec. Highest concentrations of total PAH were measured in Jonquiere (457 ng/m³, g.m.) and Shawinigan (263 ng/m³, g.m.), where aluminum smelters using the Horizontal Stud Söderberg (HSS) process are located. Baie Comeau, near which forest fires occurred during the summer of 1991, had the third highest geometric mean (165 ng/m³). There is also an aluminum complex in Baie Comeau using the Vertical Stud Söderberg (VSS; 2/3 of its production capacity) and Pre-baked (PB; 1/3 of its production capacity) processes. Based on stack sampling and measurements of fugitive emission, the estimated PAH emissions for these processes (HSS, VSS and PB) are 2.05, 0.23 and 0.0013 kg/tonne of aluminum produced (I.G.L., 1993). In a residential area of Montreal (R.D.P.), total PAH concentration in ambient air was found to be 102 ng/m³ (g.m.), whereas in Sept-Iles, the concentration was found to be 69 ng/m³ (g.m.). These two areas are known to be impacted by residential wood heating. These values were in the same range as those measured at a station located 100 m off two major highways, in Montreal (D & D; 79 ng/m³ g.m.).

The measurement made by Environment Canada in Jonquiere showed high ambient air PAH concentrations were measured when the sampling station was downwind of the aluminum smelter for most of the day (Lavalin, 1992; Germain and Bisson, 1992). It was found that ratios of the different compounds with respect to benzo(e)pyrene [B(e)P] were

of the same order of magnitude for the samples collected at the roof vents of the aluminum smelter (Houle, 1986) located in Jonquiere and for the daily ambient air results when total PAH were elevated ($> 1000 \text{ ng/m}^3$). The phenanthrene/B(e)P ratios were 2.7 ($n = 3$) and 6.2 ($n = 45$) respectively. Similar ratios were observed at stations near aluminum smelters in Shawinigan (4.8; $n = 14$) and Baie Comeau (8.0; $n = 7$) when total PAH were greater than 1000 ng/m^3 .

In residential areas of Montreal (R.D.P.) and Sept-Iles, influenced by residential wood heating, the phenanthrene/B(e)P ratio calculated with the mean concentrations are greater (21.2 and 45.1 respectively) than those observed in areas influenced by aluminum smelters. A similar ratio (41.7) is also observed for the data obtained from the Montreal station (D & D) representing heavy traffic.

In Baie Comeau, the results from individual samples seem to indicate that high total PAH levels in ambient air were measured when the sampling station was downwind of the aluminum smelter whereas lower levels were more associated with wood combustion (either residential or forest fires).

Two other ratios were examined: fluoranthene to pyrene and fluorene to pyrene. Based on the ratios calculated with the geometric mean of those compounds, fluorene/pyrene ratios calculated for areas influenced by aluminum smelters ranged from 0.1 to 0.5, whereas they ranged from 1.1 to 1.4 in those areas where transportation and wood burning are predominant. The fluoranthene/pyrene ratios did not show large differences, ranging from 1.3 to 1.6 (stations near aluminum smelters) and from 1.0 to 1.3 (transportation and wood burning).

CONCLUSION

The levels of PAH in ambient air are strongly dependent on the source of emissions. The use of the phenanthrene/B(e)P ratio can be used to indicate if PAH measured in ambient air originate from an aluminum smelter, but they can not be used to discriminate between residential wood burning or traffic. The fluorene/pyrene ratio may represent another alternative for identifying the origin of PAH. In both cases, collection of air samples must be done with filter and PUF, in order to retain phenanthrene, fluorene, fluoranthene and pyrene which are present mainly in the gaseous phase.

ACKNOWLEDGEMENTS

This work would not have been possible without the participation of a number of people, including personal from MEF, and field operators. Special thanks are due to Tom Dann from Environment Canada, for his valuable contribution in the project.

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Table 1. PAH geometric mean concentrations (ng/m³) for different locations in Quebec (Canada).

	Jon- quiere	Shawi- nigan	Bale Comeau	Beau- harnois	Later- riere	Cap- Madeleine	Montreal (D & D)	Montreal (RDP)	Sept Iles
Number of samples	121	62	39	30	7	16	21	31	24
Sampling period	89-93	89-93	91-93	91-93	1991	89-90	1991	89-90	90-91
Acenaphthylene	2.9	2.4	0.5	0.8	0.1	8.9	3.1	7.8	2.6
Acenaphthene	8.7	3.8	6.3	2	0.1	0.6	1.5	2.1	0.6
Fluorene	11.2	4.1	5.7	3.6	0.1	14.4	6.2	9.3	5.4
Phenanthrene	104.7	52.5	47.9	26.3	0.4	51.3	30.2	30.9	23.4
Anthracene	4.3	5.1	4.1	2.2	0.1	3.6	2.6	4.4	4.0
Fluoranthene	74.1	41.7	24.0	15.1	0.2	9.8	6.2	9.8	6.5
Pyrene	51.3	31.6	15.1	10.2	0.1	10	5.5	7.6	4.8
Benzo(a)Fluorene	8.7	5.0	1.9	1.4	0.1	1.9	0.9	1.7	1.4
Benzo(b)fluorene	2.7	1.8	1.1	0.8	0.0	0.4	0.3	0.7	0.5
Benzo(ghi)fluoranthene	3.2	2.1	1.0	0.8	0.0	1.4	0.8	1.0	0.7
Benz(a)anthracene	7.2	3.2	1.7	1.0	0.0	0.7	0.4	1.1	0.7
Chrysene	24.6	12.6	7.6	5.9	0.1	4.2	1.2	2.5	1.3
7,12-Dimethylbenzanthracene	0	0	0	0	0	0	0	0	0
Benzo(b+k)fluoranthene	34.7	15.8	8.5	6.9	0.1	4.1	1.7	3.5	1.4
Benzo(e)pyrene	14.8	6.6	3.3	2.9	0.1	2.3	0.7	1.5	0.5
Benzo(a)pyrene	5.1	2.0	1.7	0.6	0	0.3	0.4	0.8	0.4
Perylene	1.4	0.5	0.7	0.1	0	0.1	0.3	0.8	0.1
3-Methylcholanthrene	0	0	0	0	0	0	0	0	0
Indeno(1,2,3-cd)pyrene	5.7	2.7	1.1	0.9	0.1	1.5	0.4	1.3	0.4
Dibenz(a,h)anthracene	1.8	0.6	0.3	0.2	0	0.6	0.3	0.6	0.1
Benzo(b)chrysene	1.1	0.1	0.1	0.0	0	0.3	0	0.3	0.1
Benzo(ghi)perylene	5.7	3.0	1.5	1.1	0.1	2.0	0.8	1.2	0.3
Anthanthrene	0.6	0.1	0.1	0.1	0	0	0.4	0.6	0.1
Coronene	1.6	0.4	0.0	0.4	0	1.0	0.8	0.7	0.3
Dibenzo(a,i)pyrene	0	0	0	0	0	0	0	0	0
Total PAH	457	263	166	105	13	162	79	102	69

Table 2. Summary of ratios calculated with geometric mean of ambient air PAH results.

	Phe/BeP¹	Fluot/Pyr²	Fluo/Pyr³
Jonquiere	7.1	1.5	0.2
Shawinigan	7.8	1.3	0.1
Baie-Comeau	14.5	1.6	0.4
Beauharnois	9.1	1.5	0.4
Laterriere	4.7	1.6	0.5
Cap-Madeleine	21.9	1.0	1.4
Montreal (D&D)	41.7	1.1	1.1
Montreal (RDP)	21.2	1.3	1.2
Sept-Iles	45.1	1.3	1.1

1: Phenanthrene/Benzo(e)pyrene

2: Fluoranthene/Pyrene

3: Fluorene/Pyrene

**Polycyclic Aromatic Hydrocarbons in House Dust
and Track-In Soil in an Eight-Home Study**

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The analytical method to determine polycyclic aromatic hydrocarbons (PAH) in house dust and soil samples was validated. The method consists of sonication with 10 mL of hexane (C6) for two 30-minute extractions, and analysis of the C6 extract by gas chromatography/mass spectrometry (GC/MS). An eight-home pilot field study was conducted in Columbus Ohio before and after the 1992/1993 heating season to obtain concentration profiles of PAH in house dust and track-in soil, and to determine whether track-in of outdoor soil residues is an important source of PAH in house dust. A total of 19 PAH, ranging from 2-ring naphthalene to 7-ring coronene, was monitored. The sum of the concentrations of all target PAH in the house dust samples evaluated in this study ranged from 41 to 580 ppm and from 25 to 310 ppm in the samples collected during October 1992 and April 1993. Higher concentrations were observed in entryway soil samples and the sums of the concentrations of target PAH ranged from 68 to 4000 ppm and 58 to 5500 ppm in samples collected before (October 1992) and after (April 1993) the winter heating season, respectively. The sum of the concentrations of PAH in the pathway soil samples varied from 3.0 to 1200 ppm in samples collected before the heating season. The sum of the concentrations of PAH ranged from 0.58 to 610 ppm and from 0.63 to 63 ppm in pathway soil and foundation soil samples collected after the heating season, respectively. The concentrations of most 4- to 6-ring PAH, the sum of all target PAH, and the sum of PAH that are probable carcinogens in house dust correlated well with the corresponding levels in the entryway soil. However, there was no correlation between the PAH concentrations in house dust, and in pathway soil, nor was any relationship found between house dust and foundation soil.

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SESSION 24:
GENERAL PAPERS

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Future Research Directions for the Great Waters Program

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The 1990 Report to Congress contained Section 112(m), requiring the assessment of the deposition of air pollutants to the Great Lakes, Lake Champlain, Chesapeake Bay and coastal waters. This program, called the Great Waters program, is required to have a report to Congress in three years and every two years thereafter. The first Report to Congress is to be released this spring (paper by Amy Vasu is describing the report).

With the completion of the first Great Waters report and the ensuing discussions within the Agency, it is now appropriate to assess the future needs and direction of the program. We know now where we stand in terms of the state of the knowledge, and what kinds of efforts are needed to provide a comprehensive picture of atmospheric deposition of toxics to aquatic ecosystems. Given that the problem is a vastly complex one, and that research in this area is extremely expensive, the Agency must now determine where efforts are best spent to collect the most important information to meet the mandate of Section 112(m) of the Clean Air Act.

The Agency is working on a program strategy to target those most-effective efforts. This paper will describe the strategy and the rationale for its design.

**Scientific Findings and Regulatory Recommendations of the
1993 Great Waters Report to Congress**

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As a requirement of Section 112(m) of the 1990 Clean Air Act, the Environmental Protection Agency (EPA) must submit a report to Congress on the deposition of air pollutants to the Great Lakes, Lake Champlain, Chesapeake Bay, and coastal waters (i.e., "the Great Waters") by November 15, 1993 and every two years thereafter. The 1993 report to Congress includes scientific findings on the following: (1) human health and environmental effects associated with deposited air pollutants, (2) atmospheric loadings of pollutants to the Great Waters, and (3) sources of the pollutants being deposited to the Great Waters. Findings of the report indicate that significant adverse effects on human health and wildlife have been caused by exposure, especially through fish consumption, to persistent chemicals that bioaccumulate. Atmospheric deposition is shown to be a major contributor of mercury, PCBs, and other persistent chemicals that bioaccumulate. Emissions from local as well as distant sources may contribute to pollutant loadings to water bodies. The scientific findings provide support for the regulatory recommendations of the report. These recommendations include taking actions under the Clean Air Act (e.g., early completion of emission standards for sources of Great Waters pollutants) and under other Federal authorities (e.g., the Federal Insecticide, Fungicide, and Rodenticide Act), and continuing research efforts in areas where critical data gaps exist.

Laser-Induced Photofragmentation/Photoionization Spectrometric Detection of NO, NO₂, HNO₃ and CH₃NO₂ Under Atmospheric Conditions

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ABSTRACT

Laser-induced photofragmentation/photoionization (PF/PI) spectrometry has been explored as a technique for measuring trace levels of nitrogen oxides under sub-atmospheric conditions. The technique employs tunable radiation near 226 nm to perform the photofragmentation and subsequent photoionization of NO fragments generated in the probe region, and a miniature pair of electrodes for nonselective (total) ion detection. Optimum signal-to-noise conditions were determined and the results demonstrate the feasibility of nonselective detection of the NO⁺ ions. Limits of detection are 1 ppbv, 22 ppbv, 5 ppbv and 220 ppbv for NO, NO₂, HNO₃ and CH₃NO₂, respectively.

INTRODUCTION

Current measurement methods for nitrogen oxide species consist of chemiluminescence spectrometry, absorption spectrometry and a variety of filter and denuder collection techniques (1). For measurements requiring very high sensitivities (pptv), photofragmentation/laser-induced fluorescence (PF/LIF) techniques have been developed that allow near real time monitoring of NO, NO₂ and HNO₃ at pptv levels (2-4). Despite the analytical capabilities of the PF/LIF approaches, the techniques are considerably more complex than conventional approaches and are therefore impractical for routine applications.

Since 1979, laser-induced ionization has been recognized as a potentially powerful method for trace determinations of atmospheric species (5,6). However undesirable aspects of laser-induced ionization measurements, including relatively high laser intensities and sometimes persistent nonresonant background ionization signals, have inhibited the development of the method.

Photofragmentation methods are especially effective for monitoring oxides of nitrogen since most of the compounds share a common functionality, NO₂, which is readily removed by absorption of ultraviolet radiation ($\lambda < 250$ nm). Species that have been determined by photofragmentation approaches include HNO₃ (by OH LIF) (2), NO₂ (by NO LIF) (4) and various nitroorganics (by NO ionization) (7-10). Previously we demonstrated that a photofragmentation/photoionization (PF/PI) approach is feasible when the samples are present in a molecular beam and a time-of-flight mass spectrometer is used for ion detection (7). The selectivity of the PF/PI approach when using 226 nm radiation was evidenced by virtually exclusive ionization of NO relative to any other species. The analytical selectivity was such that nonselective ion detection was proposed as a simplification to the method.

In the current approach, nitric oxide (NO) is detected directly by a 1+1 resonance-enhanced multiphoton ionization (REMPI) process via the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition at 226 nm. Other nitrogen oxides are detected using a photofragmentation/photoionization (PF/PI) approach where the laser is first used to fragment the parent molecule and then probe the resulting fragments. Nitrogen dioxide (NO₂), nitric acid (HNO₃) and other nitrocompounds all share the NO₂ functionality which is efficiently fragmented at 226 nm. Following fragmentation, the NO₂ or NO₃ fragments absorb another photon at 226 nm and predissociate to produce NO, which is detected by the REMPI process described above. Due to the high efficiency of the individual fragmentation processes and the photoionization at 226 nm, the PF/PI approach can easily be accomplished with only modest pulse

energies (on the order of μJ).

We have investigated the analytical utility of PF/PI detection of atmospheric nitrogen oxides at near ambient conditions. Studies have been performed to determine the optimum conditions for PF/PI measurements and to evaluate analytical figures of merit for NO, NO₂, HNO₃, and CH₃NO₂. Measurements have been performed up to atmospheric pressure employing total ion detection. Results of the PF/PI studies are compared to similar PF/LIF approaches to illustrate the relative merits of the methods.

EXPERIMENTAL

An excimer-pumped dye laser system with frequency doubling (Lumonics, HYPER EX-400, HYPER DYE-300 and HYPER TRAK-1000) was used to provide up to 100 μJ pulses at 226 nm. The laser output was directed using prisms to the photolysis/ionization sampling cell. Focusing of the laser was accomplished using a 250 mm lens external to the cell. The photolysis cell consisted of a six arm stainless steel cross with arm diameters of 4 cm. Quartz windows mounted on the cell provided optical access to the center of the cell where two planar electrodes served as ion/electron detectors. The electrodes, laboratory constructed from stainless steel sheets, were each approximately 1.5 cm² in area and were separated by 0.63 cm. Electrical contact to the electrodes (used for biasing and for signal collection) was accomplished through a plate mounted to one of the arms on the cell. Collection voltages ranged from 0 to 800 V.

Samples were prepared by serial dilution of standard gases (NO, NO₂ in air or N₂) or were sampled as trace species at their room temperature vapor pressures (HNO₃, CH₃NO₂) in buffer gases (air, N₂). Samples were flowed through the photolysis cell to prevent build-up of photolysis products. Sample flows were nominally 500 cc/min. The photolysis cell volume was estimated to be 350 cc.

Signals from the detection electrodes were amplified using a current amplifier (Keithley 427, gain 10⁶ V/A, time constant 0.01 ms) and then sampled by a boxcar averager. The signals were also viewed in real-time on a digital oscilloscope. The output of the boxcar was acquired by a personal computer for storage and subsequent data analysis. Analytical sensitivity determinations were performed using a boxcar gate of 15 μs with 100 shot averaging at 10 Hz laser repetition rate.

RESULTS

In previous studies of the PF/PI approach at low pressure, selective ionization of the NO fragment was observed at 226 nm for a wide variety of compounds (7). The high selectivity observed in that study suggested extension of the PF/PI method to higher pressures with nonselective ion detection, since mass selective detection was apparently unnecessary at reduced pressures. In the present studies, fragment ionization spectra were recorded at near atmospheric pressure conditions with nonselective ion detection. The excitation spectra for NO and NO₂ exhibit numerous rotational lines belonging to the A² Σ^- -X² Π band of NO. Ionization spectra for NO generated from HNO₃ and CH₃NO₂ also show similar features confirming the production of NO fragments. It is noteworthy that there is sufficient spectral resolution to distinguish individual rotational lines of NO, which is an important criterion for the PF/PI technique to be useful at near atmospheric pressures. As there is no mass selectivity in the ion detection step, the selectivity of the method depends directly on optical selectivity provided by the laser. The current results indicate that the use of low laser pulse energies enables sensitive and selective detection of ambient nitrogen oxides with a minimum of nonresonant background ionization signals at 226 nm.

To determine the optimum experimental conditions for the PF/PI technique as applied to ambient measurements, parametric studies of the signal-to-noise ratio (SNR) as functions of the measurement cell pressure and voltage were performed. A plot of the SNR as a function of the measurement cell pressure shows a maximum in the near 100 torr indicating an optimum pressure

region for analytical measurements. Over the pressure range studied (10-760 torr, constant mixing ratio), the measured noise is relatively stable and the SNR is dominated by changes in the signal magnitude. At higher pressures, the signal is suppressed by quenching. At lower pressures, the observed signals are reduced by sample dilution.

A similar study of the SNR as a function of the detection electrode voltage was performed. Plots of the data for NO and NO₂ (at a constant mixing ratio) are characterized by a saturation curve which indicates that the SNR reaches a maximum value above 400 V. The saturation behavior suggests that at 400 V the electrode voltage is sufficient to collect all available ions/electrons produced within the electrode spacing before they are lost to attachment and/or recombination processes (5). It is worth noting that the optimum conditions determined in the present study are characteristic of the experimental parameters employed and it is therefore likely that different optimum conditions will be realized for different electrode spacings, different focal characteristics of the laser, etc.

In previous studies of the PF/PI approach applied at low pressure, limits of detection (LODs) ranged from 8 ppbv for NO and 240 ppbv for NO₂ to ppmv for larger nitroaromatics (7). In the present study, LODs of 1 ppbv for NO, 22 ppbv for NO₂, 5 ppbv for HNO₃, and 220 ppbv for CH₃NO₂ (signal-to-noise of 3) have been obtained at the optimized experimental conditions (100 torr and 400 V). From the results of the current study, there appears to be an order of magnitude improvement in the LODs over the low pressure results (7), although improvements in sensitivity should be weighed against potential losses in selectivity. Alternatively, the simplicity of nonselective ion detection and freedom from high vacuum apparatus are also important advantages in favor of the current PF/PI technique.

It is worthwhile to compare the results of the current study with those obtained using similar PF/LIF approaches. The best LODs (signal-to-noise of 3) reported for NO, NO₂, HNO₃, and CH₃NO₂ using PF/LIF techniques are 5 pptv (3), 15 pptv (4), 30 pptv (2) and 2 ppbv (11), respectively. Both one and two-color excitation PF/LIF approaches have been employed with emphasis placed on the two-color approaches for NO and NO₂ in recent years (3,4). For NO and NO₂, it has been observed that the one-color excitation PF/LIF is approximately one order of magnitude less sensitive than the two-color approach, primarily due to the "white" fluorescence background which is a limiting noise in the one-color approach. For comparison, the PF/PI technique (as employed in the current studies) employs a single laser as both the photolysis and ionization source and is not susceptible to laser scatter and/or "white" fluorescence noises.

A direct comparison of the results of this study employing PF/PI with those employing LIF indicates that the two methods are similar in performance. In the case of NO, the most appropriate comparison of the PF/PI and LIF methods is with the one-color LIF measurements of NO at 226 nm, as the PF/PI technique only uses a single laser source. The LOD for NO is 1 ppbv for PF/PI (10 sec integration) and 50 pptv for one-color LIF (1 min integration) (12). These sensitivities (LODs) are nearly within an order of magnitude and are likely to be even closer for similar integration times. In the case of NO₂, the PF/LIF result is approximately 3 orders of magnitude lower than the PF/PI result, however, the PF/LIF measurement makes use of three lasers, one as a laser photolytic converter and two for the two-color excited LIF measurement.

Tropospheric nitric acid levels have been measured using an ArF excited PL/LIF approach (2). Papenbrock and Stuhl have reported an LOD of 30 pptv which compares with 5 ppbv observed using the PF/PI approach. It should be noted, however, that the ultimate sensitivity of the PF/LIF method was evaluated using an integration period of 1 hour (compared to 10 s for PF/PI), which implies that similar integration periods would lead to more similar sensitivities.

As the PF/PI sensitivity for HNO₃ is higher relative to that of NO₂, it is of interest to speculate on the fragmentation/ionization mechanism for HNO₃ at 226 nm. If it is assumed that the production of NO from HNO₃ occurs exclusively by way of NO₂ fragmentation followed by NO₂ redissociation, the sensitivity for HNO₃ should not be higher than for NO₂. As the sensitivity is in fact higher, this suggests that another PF/PI mechanism is operative for this compound. In recent

studies of the 193 nm photolysis of HONO , Kenner et al. have determined that the production of OH(A) fragments proceeds by way of an intermediate species rather than direct photolysis (13). Based on energy and spin conservation requirements, they have concluded that the intermediate is triplet HONO.

From studies of the photodissociation of HNO_3 at 248 nm, Schiffman and coworkers have suggested two possible mechanisms by which HNO_3 is fragmented to produce NO, one of which produces NO directly from the parent, the other through the HONO intermediate (14). They contend that both of these pathways are possible at wavelengths less than 250 nm. These proposed mechanisms suggest that the high sensitivity of HONO may be due to the direct photolytic production of NO or the production and subsequent photolysis of the HONO intermediate rather than NO_2 . The different PF/PI sensitivities for HNO_3 and NO_2 can therefore be rationalized by different rovibrational distributions of NO(X) resulting from the photolysis of HNO_3 or HONO versus the predissociation of NO_2 at 226 nm, respectively.

The PF/PI technique has been demonstrated in this study using a variety of odd nitrogen compounds including NO, NO_2 , HNO_3 and CH_3NO_2 . Although it is obviously well suited to measuring NO_x ($\text{NO} + \text{NO}_2$), it may also be a potentially effective way to measure total odd nitrogen, NO_y . Current methods for measuring NO_y emphasize the use of standard chemiluminescence technology in combination with catalytic reduction of odd nitrogen to NO using Au or Mo catalysts. The techniques are sensitive but can suffer significant interferences from non-odd nitrogen compounds leading to erroneously high measurements (1,15). The PF/PI technique is highly selective and will not suffer interferences from those same compounds.

One of the most abundant atmospheric nitrogen oxide compounds is N_2O and it was of interest as to whether it could be detected using the PF/PI approach. As the tropospheric levels of N_2O are generally higher than NO_x , sensitivity to this compound would represent a significant interference for determinations of odd nitrogen compounds. Although fairly high concentrations of N_2O were sampled (>500 ppmv), no detectable NO^+ ion signals were observed. Based on the known spectroscopy of N_2O in this wavelength region, it is not surprising that ion signals were not observed. According to Herzberg (16), and Sponer and Bonner (17), absorption in this region is dominated by predissociation of the molecule to N_2 and O. Lack of sensitivity to this compound at high concentrations indicates that N_2O will not interfere with PF/PI measurements of NO_x and/or NO_y at typical tropospheric levels.

The PF/PI method possesses important analytical features that are well-suited to atmospheric monitoring applications. The present technique is sensitive, as evidenced by the low ppbv LODs demonstrated. By virtue of the low laser pulse energies employed and the high spectral resolution of the dye laser output, the technique possesses excellent selectivity for NO, NO_2 and NO_2 functionalities with minimal nonresonant background ionizations. Furthermore, by using a single laser tuned to 226 nm and a simple photolysis cell with total ion collection, the PF/PI apparatus is easily implemented since it does not require multiple lasers or stringent geometric considerations which are necessary when optical detection approaches are used (e.g. LIF). By employing a 10 sec integration time, the PF/PI technique is able to detect low ppbv levels in virtual real-time and thus is competitive with other conventional methods used for NO_x monitoring applications.

CONCLUSIONS

We have demonstrated a PF/PI approach used to determine trace levels of nitrogen oxide compounds. The technique employs a laser operating at 226 nm that selectively excites and ionizes NO molecules by a 1+1 REMPI process via the $\text{A}^2\Sigma^+ \leftarrow \text{X}^2\Pi$ band. The laser is simultaneously used to fragment larger odd nitrogen species, which at 226 nm results in the production of NO photofragments that can be detected by the same REMPI process. Thus, one laser can accomplish simultaneous detection of NO, NO_2 , HNO_3 and other nitrogen oxide species. Presently the LODs extend to the low ppbv for NO, NO_2 and HNO_3 with sub-ppbv LODs anticipated. The technique is

well-suited to NO_x determinations and has excellent potential for measuring NO_y. Although the technique is sensitive to a wide range of nitrogen oxides, it is insensitive to N₂O.

Acknowledgements: Support from the ARL/NRC Postdoctoral Research Associateship Program (JBS and GWL), the Independent Laboratory Initiated Research (ILIR) Award (RCS) and the PIF/OSD Capital Investment Program (RCS) is gratefully acknowledged.

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Measurement of the Effects of Moisture Distribution
on the Transport Properties of Radon and Other
Soil Contaminants in EPA's Soil Chamber

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ABSTRACT

Measurements of both diffusive and advective transport of SF_6 used as a tracer in EPA's soil chamber are reported. These studies involve measurements of the times-of-flight of a tracer gas along different paths in the soil to determine the uniformity of the soil and the moisture distribution. It is observed that values of permeability computed from the measurement of total flow are not consistent with permeabilities determined from the time-of-flight measurements. The reason for this discrepancy is not understood.

INTRODUCTION

Significant health risks are associated with radon and other soil-gas-borne contaminants that enter the indoor environment. In an effort to develop better methods to reduce these risks, EPA is studying the physical mechanisms by which soil gas contaminants migrate through the soil and enter buildings. It is widely accepted that advective flow is the dominant mechanism by which radon and other soil gas contaminants enter buildings. Consequently, it is important to understand how the properties of soils influence these processes. The present measurements were performed in EPA's soil chamber. While radon distribution in the soil has been measured and reported in the past, the current measurements use a tracer gas in order to look at specific properties of the soil. Both diffusive and advective transport of SF_6 was studied to investigate the effects of moisture distribution

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

on the transport rates. SF_6 , used as a tracer, served as a surrogate for a contaminant gas and was used to evaluate the degree of uniformity of the transport properties of the soil. These measurements are important because both the diffusion coefficient and the permeability for gaseous migration in soils depend strongly on the distribution of moisture in the soil.

EQUIPMENT AND EXPERIMENTAL DESIGN

The soil chamber has dimensions of 2 x 2 x 4 m, with 4 m being the length. The chamber, described elsewhere, (1,2) was designed to simulate an infinitely long cylindrical cavity buried 1 m below the surface of the soil. The cylinder attempts to simulate the infinite geometry by using guard ends to isolate the measurements in the central region of the soil from the edge effects introduced by the chamber walls at the ends of the cylinder. The finite dimensions in the direction transverse to the axis of the cylinder can be accounted for by imposing the appropriate boundary conditions (3). Twenty-three recirculating probes for collecting gas samples as well as for measuring temperature and pressure are distributed in the central plane 2 m high and 4 m long. These probes are arranged in rows at five different depths in the soil. All the measurements and calculations discussed here relate to this measurement plane. Four vertical moisture measurement tubes are offset from the measurement plane. A Troxler's Sentry 200-AP unit is used to measure moisture over the entire depth of the soil. The approach is to inject SF_6 into the probes, one at a time, and measure the time required for it to be advectively transported to the central collection tube. A fixed volume (about 10 cm^3) of SF_6 was injected into a probe followed by an injection of sufficient air to flush the SF_6 from the probe. The arrival of the SF_6 was detected by a Miran Infrared detector. A Miran 203 Specific Vapor Analyzer and sometimes an additional Miran 1A-CVF were used. The time was determined by the arrival of the peak of the pulse. By comparing the times-of-flight for symmetrically located points, the uniformity of the transport properties of the soil can be judged. These data will also test the validity of mathematical models (4).

ADVECTIVE FLOW

A mathematical expression for the time-of-flight of an air parcel along a flow streamline using the geometry of the soil chamber was presented by Mosley (4):

$$t = \frac{\mu h^3}{16kP_c\sqrt{h^2-b^2}} \ln \left(\frac{h+\sqrt{h^2-b^2}}{h-\sqrt{h^2-b^2}} \right) \left(\frac{(\xi^2+1)^2}{\xi^3} \right) (2\xi + (\xi^2-1) \left\{ -\frac{\pi}{2} + \cos^{-1} \left(\frac{2\xi}{\xi^2+1} \right) \right\}) \quad (1)$$

where t is the time-of-flight along a streamline (min), μ is the dynamic viscosity of the soil gas ($\text{kg m}^{-1} \text{s}^{-1}$), h is the depth of the cylinder in the soil (m), k is the soil permeability (m^2), P_c is the applied pressure (Pa), b is the radius of the cylinder (m), and ξ is the distance (in multiples of h) horizontally from the cylinder

to where the streamline intersects the surface of the soil. This expression applies when the diffusion is negligible in comparison to advective flow. The approach for the experiment is to inject a puff of SF_6 at numerous points within the measurement plane and measure the time required for its arrival at the central collection tube of the chamber. These measured times will be used to test the validity of equation (1). The intent was to flow at a sufficiently high rate that the contributions from diffusion could be ignored. These measurements were performed at 19 of the 23 probes. The measured times are given in Table 1. Equation (1) consistently overpredicts the times-of-flight by a factor of 3 - 4 when using a value of permeability that correctly predicts the total flow rate.

Since the absolute values of times predicted by equation (1) do not agree with the measurements, ratios of measured times are compared for pairs of probes that are symmetrically located relative to the collection tube. It is reasoned that air parcels travelling from symmetrically located probes will traverse comparable distances in soils with similar moisture contents. Therefore, the times should be comparable. For a more quantitative analysis, a very simple model is considered. If the probe were considered a cylindrical source with small radius located in an infinite uniform medium, the velocity resulting from an applied pressure would be (5)

$$v = \frac{kP_c}{2\pi\mu} r^{-1} \quad (2)$$

where v is the velocity (m s^{-1}) and r is the radius of the cylinder (m). The time-of-flight along a flow line would then be given by integrating the reciprocal of the velocity

$$t = \int \frac{dr}{v} = \frac{2\pi\mu}{P_c} \frac{r^2}{k} \quad (3)$$

For the pairs described above, the ratios of the times vary like the squares of the ratios of the distances. These ratios along with their percent differences are shown in Table 2. The percent differences are all within the expected errors of measurement. This result suggests that the permeability and moisture distribution are largely independent of horizontal position. Suppose we now plot all the measured times as a function of the square of the distance between the injection point and the collection point. These results are shown in Fig. 1. While these data are quite scattered, it can be seen that they tend to separate into two groups. Probes at the bottom of the chamber where the moisture is high tend to lie along a straight line near the upper edge of the data, while much of the remaining data tend to lie on a lower line with smaller slope. This result should not be surprising since the permeability is known to vary with moisture content. Fig. 2 shows an empirical fit of the same data to a

product of distance squared and a power of the moisture content at the injection probe. It was found that an exponent of 0.75 provided the best fit. The coefficient of determination, R^2 , is 0.98, indicating a relatively good fit. The regression slope (1342.7) yields an estimate for the permeability of $9.62 \times 10^{-11} \text{ m}^2$. This value of k is three times larger than was inferred ($3.17 \times 10^{-11} \text{ m}^2$) by earlier measurements of total flow and also by measurements with point permeability probes (1). In fact, if this were the correct value of permeability, equation (1) would give a much better prediction. The moisture dependence represented in Fig. 3 could be interpreted as the reciprocal of an effective permeability averaged over the migration path.

DIFFUSIVE FLOW

The inability of equation (1) to predict the migration times, naturally leads to the question of whether diffusion was really negligible. After considering that diffusion might not be negligible after all, diffusion measurements were performed for 14 of the previous 19 probes. These measurements were performed in a manner similar to the advective measurements except no flow was induced. A puff of SF_6 was injected into each probe, and the time required to arrive at the central tube was measured. Once again suppose that the probe represents a point source in a plane. The solution for the diffusion problem is given by Crank (6) as

$$C(x, t) = \frac{A}{t} \exp\left(-\frac{x^2}{4Dt}\right) \quad (4)$$

where A is a measure of the amount of gas injected, and D is the moisture dependent diffusion coefficient. The Miran detector will see the passing puff as a pulse with a peak. The time required for the arrival of the peak can be computed by differentiating equation (4), equating the derivative to zero, and solving for the time corresponding to the maximum in the concentration curve. This process yields

$$t_{\text{max}} = \frac{x^2}{4D} \quad (5)$$

where t_{max} represents the time at which the peak of the pulse arrives at the collection tube (min). Motivated by a model by Rogers and Nielson (7) for the dependence of diffusion coefficient on soil moisture, Fig. 3 plots the diffusion times as a function of $r^2 \exp(3s + 6s')$. The coefficient of determination, R^2 , for the regression curve is (0.99). Since these data represent probes from all regions of the measurement plane, they not only show good agreement with the Rogers and Nielson model, but also suggest that the soil and the moisture distribution within the soil are fairly uniform in the horizontal direction. Using the slope (425.8) of the regression curve in Fig. 3, the effective diffusion coefficient is computed to be $9.1 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ near the surface of the soil and

$4.48 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ near the lower row of probes. These values can be compared with previously measured values of 1.2×10^{-6} and $8.8 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ (8).

DISCUSSION AND CONCLUSIONS

While the measurements of the diffusion rate of SF_6 seem in reasonable agreement with other measurements and with an accepted model for its dependence on moisture, the time-of-flight measurements associated with advective flow seem to imply a larger permeability ($9.6 \times 10^{-11} \text{ m}^2$) than is required to describe the total rate of flow ($3.17 \times 10^{-11} \text{ m}^2$). The reason for this discrepancy is not presently known. Diffusion taking three times as long as advective flow might suggest that diffusion is negligible, but this conclusion is not certain. It is possible that the time-of-flight depends more sensitively on the shape of the streamlines than does the integrated flow. Neither equation (1) nor equation (3) accounts rigorously for the shape of the streamlines for the boundary conditions associated with the soil chamber. A rigorous calculation in this case will require a numerical solution to both the velocity and the integrated time.

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Table 1 Time measurements for diffusion and convection.

Probe #	x (m)	y (m)	Radial distance (m)	Diff time (min)	Convec time (min)
1	-1.543	0.435	1.621	1321	541.5
2	-0.511	0.435	0.713	a	a
3	-1.031	0.935	1.031	750	256.5
4	-1.543	1.462	1.631	2611	1468
5	-0.511	1.463	0.735	a	a
6	-0.264	0.277	0.367	173	46
7	-0.257	0.935	0.257	a	23
8	0.007	0.435	0.498	279	78
9	0.260	0.935	0.260	a	26
10	0.262	0.677	0.366	169	45
11	0.513	0.435	0.713	a	a
12	-0.251	1.182	0.353	183	54
13	0.013	1.562	0.629	576	376.5
14	0.261	1.191	0.367	210	56
15	0.518	1.465	0.743	a	a
16	0.999	0.945	0.999	752	261
17	1.259	0.400	1.356	905	406
18	1.763	0.695	1.779	2050	730
19	1.761	0.435	1.830	a	699.5
20	1.284	1.462	1.368	2438	1107
21	1.769	1.462	1.847	a	1656
22	1.770	1.207	1.791	a	1009
23	1.764	0.900	1.764	2100	764

a - Measurements were not performed.

Table 2 Comparison of ratios of time and distance squared for symmetrically located pairs of probes.

i	Probe pair j	(t_i/t_j)	$(r_i/r_j)^2$	% diff
1	17	1.334	1.429	7
1	19	0.774	0.784	1
6	10	1.011	1.005	0.6
7	9	0.868	0.971	11
12	14	0.9732	0.9257	5
4	20	1.326	1.422	7
4	21	0.882	0.7799	12

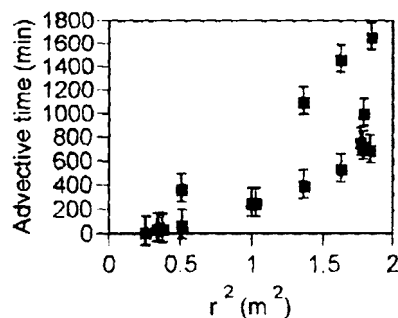


Fig. 1 Plot of time vs distance squared.

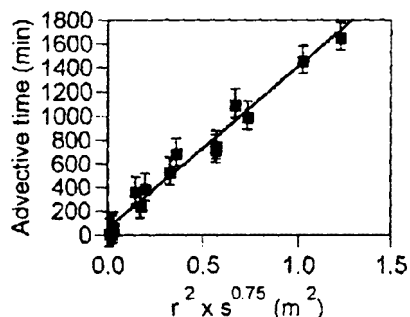


Fig. 2 Plot of time vs the product of distance squared and moisture to 0.75 power.

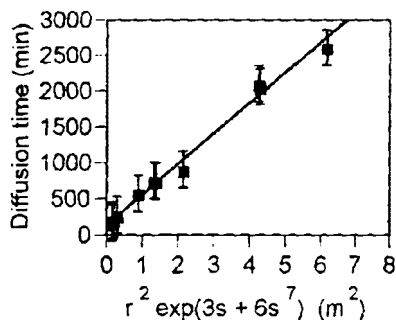


Fig. 3 Plot of time vs the product of distance squared and the exponential factor in the Roger's model.

Comparison of Soil Permeability Measurements Using
Probes of Different Sizes and Geometries

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ABSTRACT

The traditional method of measuring soil permeability to air movement uses localized probes of varying size and geometry to collect and measure the total flow passing through the probe over a range of applied pressures. The permeability is typically extracted from the measured flow/pressure relationship using a derived solution to an idealized geometry that frequently does not match the reality of the probe. This study compares side-by-side measurements of soil permeability for a number of probes with different geometries and relative sizes. A comparison of results is discussed in terms of appropriate shape factors based on geometrical differences. Attention is focused on the limit in which the traditional approximations for short cylindrical probes break down. It is suggested that the product of length and shape factor in expressing flow for a very short cylindrical probe is better approximated by an equivalent sphere with nearly equal surface area.

INTRODUCTION

In order to measure the permeability of soil to air flow, it is necessary to insert some type of instrumentation into the soil. Most *in situ* measurements involve inserting some type of cylindrical tube with gas entry orifices into the soil and measuring the rate of gas flow resulting from a given applied pressure. Probes vary from tubes with an open end to closed tubes

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with a short section having numerous holes in the side for gas entry. While both cylindrical and spherical geometries have been used to represent the conditions for these measurements, few details have been published on the assumptions used or the analyses performed to evaluate these measurements. Researchers at Lawrence Berkeley Laboratory (LBL) (1-3) have provided some details about the analysis of their probes. EPA's soil chamber contains 23 small cylindrical probes made of fritted brass. While these probes were designed primarily for collecting samples of soil gas for measuring radon concentration, tracer gas concentration, or other soil contaminants, they will also be used for local permeability measurements. The need to develop geometrical shape factors for analyzing the data from these probes prompted the current studies.

DEVELOPMENT OF EQUATIONS

Probes used for measurements can be simulated by the idealization of a simple geometry for which mathematical solutions are obtained. We will discuss cases of both cylinders and spheres. First consider a cylinder buried in a semi-infinite block of soil with a specified pressure difference relative to the air at the soil surface. The approach will be to express the pressure/flow relationship in terms of a geometrical shape factor that can be computed from mathematical solutions for advective flow in a porous medium. This relationship for cylinders can be expressed as

$$Q = S_c L \frac{k}{\mu} \Delta P \quad (1)$$

where Q is the flow rate ($\text{m}^3 \text{s}^{-1}$), S_c is the geometrical shape factor (dimensionless), L is the length of the cylinder (m), k is the soil permeability to air flow (m^2), μ is the dynamic viscosity of the soil gas ($\text{kg m}^{-1} \text{s}^{-1}$), and ΔP is the applied pressure (Pa). An expression for S_c , obtained from Hahne and Grigull (4), is given by

$$S_c = \frac{2\pi}{\ln\left(\frac{L}{r} \sqrt{1 + \left(\frac{L}{4h}\right)^2} - \frac{L}{4h}\right)} \quad (2)$$

where r is the cylinder radius (m), and h is the depth of the cylinder below the surface of the soil (m). This approximation is valid when $h \geq 2.5r$ and $L \gg r$. While these conditions are easily met, the standard probes used for *in situ* permeability measurements frequently violate the second condition. The length of the perforated section is usually not large compared to the probe radius. It is readily seen that equation (2) becomes invalid as L approaches r (the sign becomes negative). The short probes in the soil chamber approach this limit and consequently gives rise to the present concern relating to short probes. Because equation (2) does not apply in the limit of short cylindrical probes, it is

believed that the short probes can be better approximated by appropriately chosen equivalent spheres. Spheres have been chosen as an alternative representation for short cylinders because mathematical solutions are available for spheres buried in a semi-infinite medium (1), and because of the similarity between equations (1) and (3).

The relationship for spherical geometry is given by

$$Q = S_s r \frac{k}{\mu} \Delta P \quad (3)$$

where S_s is the shape factor for spherical geometry (dimensionless), and r is the radius of the sphere (m). The shape factor is given by (1)

$$S_s = \frac{8\pi\sqrt{1-(r/h)^2}}{1-r/h\sqrt{1-(r/h)^2}} \quad (4)$$

A comparison of equations (1) and (3) indicates that the two geometries would be equivalent if $LS_c = rS_s$. Intuitively, one would expect this condition to apply most readily when the surface areas of the sphere and cylinder are nearly equal.

MEASUREMENTS

In order to investigate the influence of the shape factor of the probe on measured permeability, a number of spherical and cylindrical probes of various sizes have been studied. The dimensions of the cylinders are listed in Table 1, while the dimensions of the spheres are given in Table 2. These studies were performed by placing the probes in soil contained in a large barrel. The permeability of the soil was varied by adding water to the soil. The moisture profile in the soil was measured using a Troxler Sentry 200-AP soil moisture monitor. While the expressions for the shape factors given above do not apply rigorously for these studies because of the finite volume of soil, they are reasonable approximations and provide good relative comparisons of the different geometries. It is the relative comparison that is stressed in this presentation.

Each probe was constructed to have a highly porous surface to ensure no significant pressure drop associated with penetration through the surface of the probe. The spherical probes were constructed from wire mesh, while some cylinders were made of wire mesh and some were constructed from commercial well points. To eliminate uncertainty introduced by pressure drop in the flow lines, two lines were installed in each probe: one was used to measure the flow, while the other was used to measure the static pressure in the probe. The roles of these two lines were interchanged to confirm that there was no difference in the results.

Measurements of pressure and flow rate are illustrated for four cylinders in Fig. 1. Similar curves for four spheres are shown in Fig. 2. As indicated in equations (1) and (3), the slopes of the regression curves in these two figures contain both the permeability of the soil and the geometrical shape factor. The slopes of the regression curves of Figs. 1 and 2 are shown in Table 1. The slopes of the regression curves in Fig. 2, corresponding to spheres, are plotted as a function of $(rS)^{-1}$ in Fig. 3. A similar plot for the curves in Fig. 1, corresponding to cylinders, are shown in Fig. 4. According to equations (1) and (3), these data could be combined to give a single composite curve which is shown without the outlier data in Fig. 5. The slopes of the regression curves in Fig. 5 yield values for permeability of 3.70×10^{-11} and 2.76×10^{-11} m², corresponding to the dry and wet conditions, respectively. To determine the reasonableness of this apparent change in permeability, we first consider the manner in which the moisture was added to the soil. The first set of measurements was performed after the soil had been packed dry with no compaction other than hand patting. The soil was then flooded with water from the bottom of the barrel until it was fully saturated. The water was then allowed to drain out the bottom of the barrel. Previous observations with this soil indicate that the density increases by at least 10% through this process. The porosity can be assumed to decrease by about the same amount. In addition to having decreased porosity, the soil also retains a significant amount of water that fills additional pores, resulting in further reduction of the permeability. A quantitative estimate of the change in permeability can be obtained from a model due to Rogers and Nielson (5). According to this model, the ratio of soil permeabilities in the two different states would be

$$\frac{k_1}{k_2} = \frac{\epsilon_1^2}{\epsilon_2^2} \exp(-12[m_1^4 - m_2^4]) \quad (5)$$

where subscript 1 denotes the dry state, subscript 2 denotes the wet state, ϵ is the porosity of the soil, and m is the fraction of moisture saturation. In the dry state there was no measurable moisture, while after wetting the measured moisture was about $m_2 = 0.30$. If we assume $\epsilon_1/\epsilon_2 = 1.1$, equation (5) yields a value of 1.33 for the ratio of permeabilities. This value compares very favorably with the ratio of 1.34 for the permeabilities given above.

One of the primary points of this paper is that equation (2) is an approximation which breaks down when the length of the cylinder is not large compared to its radius. Cylinders represented by C5 and C6 in Table 1 are examples for which equation (2) is inadequate. These cylinders are not represented in Fig. 4. However, if $S_c L$ in equation (1) is replaced by $S_c r$ with $r = \sqrt{I_c L/2}$, the results can be plotted on the composite curve in Fig. 5. Points representing both C5 and C6 are denoted by stars in Fig. 5. Note that the two points on each curve are represented by two stars

very close together. As can be seen from Table 1, C5 computed from equation (1) would lie on the negative horizontal axis and both values for C6 would have been significantly above the upper curve. Using the idea of an equivalent sphere clearly gives a much better representation for these short cylinders.

CONCLUSIONS

Since equation (2) is an approximation, it clearly breaks down when the cylinder becomes sufficiently short. This has been demonstrated in the cases of cylinders C5 and C6. It was shown that an adequate substitute for the shape factor can be developed using an equivalent sphere of comparable surface area. A more rigorous relationship between the surface areas of equivalent cylinders and spheres could be developed on an empirical basis.

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Table 1. Characteristics of cylindrical probes

ID	CYLINDERS				DRY	WET
	r (m)	L (m)	L/r	(LS) ⁻¹ (m ⁻¹)	$\langle \frac{\Delta P}{Q} \rangle (10^5)$ (Pa m ³ s)	$\langle \frac{\Delta P}{Q} \rangle (10^5)$ (Pa m ³ s)
C1	0.0166	0.330	19.8	1.16	7.31	9.49
C2	0.0117	0.254	21.7	1.66	10.4	13.4
C3	0.0166	0.0508	3.05	3.20	22.4	30.9
C4	0.0117	0.0556	4.76	4.18	23.5	32.2
C5	0.0442	0.0476	1.08	-0.117	13.4	17.0
C6	0.0348	0.0584	1.68	1.32	13.4	17.4

Table 2. Characteristics of spherical probes

ID	r (m)	SPHERES		WET $\langle \frac{\Delta P}{Q} \rangle (10^5)$ (Pa m ³ s)
		$\langle rS \rangle^{-1}$ (m ⁻¹)	DRY	
			$\langle \frac{\Delta P}{Q} \rangle (10^5)$ (Pa m ³ s)	
S1	0.0372	1.84	11.4	15.1
S2	0.0299	2.36	13.9	18.4
S3	0.0211	3.48	15.6	20.2
S4	0.0187	3.98	21.0	26.6

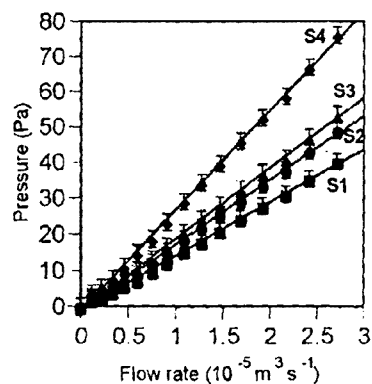


Fig. 2 Pressure vs flow for spherical probes.

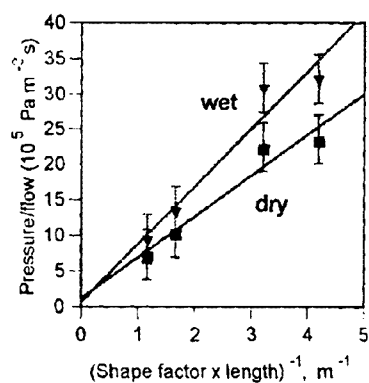


Fig. 4 Plot of the regression slopes from Fig. 1 vs the reciprocal of LS.

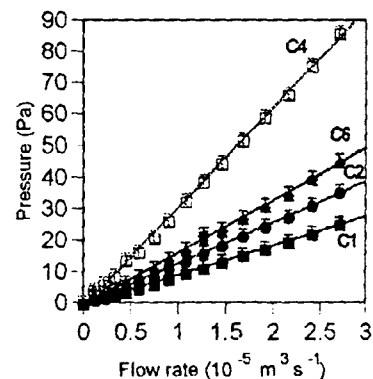


Fig. 1 Pressure vs flow for cylindrical probes.

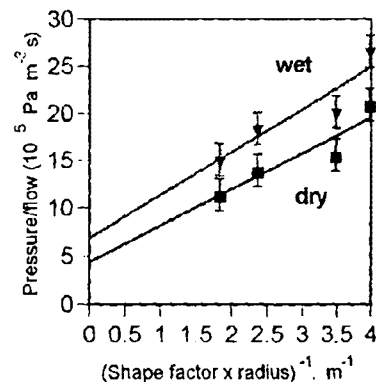


Fig. 3 Plot of the regression slopes from Fig. 2 vs the reciprocal of rS.

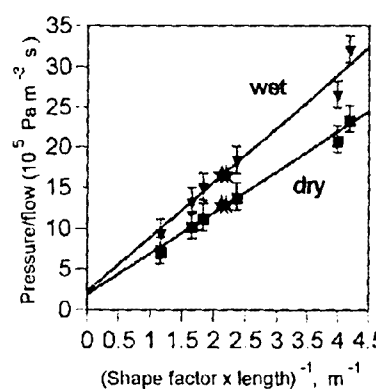


Fig. 5 Composite plot of the slopes from Fig. 1 and 2 vs the reciprocal of LS or rS.

Test Methods for Evaluating Reformulated Fuels

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The U.S. Environmental Protection Agency (EPA) introduced regulations in the 1989 Clean Air Act Amendment governing the reformulation of gasoline and diesel fuels to improve air quality. These statutes drove the need for a fast and accurate method for analyzing product composition, especially aromatic and oxygenate content. The current method, gas chromatography, is slow, expensive, non portable, and requires a trained chemist to perform the analysis. The new mid-infrared spectroscopic method uses light to identify and quantify the different components in fuels. Each individual fuel component absorbs a specific wavelength of light depending on the molecule's unique chemical structure. The quantity of light absorbed is proportional to the concentration of that fuel component in the mixture. The mid-infrared instrument has significant advantages; it is easy to use, rugged, portable, fully automated and cost effective. It can be used to measure multiple oxygenate or aromatic components in unknown fuel mixtures. Regulatory agencies have begun using this method in field compliance testing; petroleum refiners and marketers use it to monitor compliance, product quality and blending accuracy.

Peculiarity of Toxic Metals Emission Measurements at Wastewater Treatment Plants

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Toxic metals emission can have a profound effect on the results of a facility's health risk assessment, because of the extremely high unit cancer risks or hazard index values of many metals.

The testing of metals emission at Publicly Owned Treatment Works (POTWs) offer significant challenges due to the specifics of emissions from wastewater treatment processes. Among these specifics are low concentrations of compounds of interest, high air flow rates, and the fact that most of the metals considered as toxics may be present in the plant's influent wastewater. It often makes the results of the testing very difficult for proper evaluation.

CSDOC conducted extensive air- and liquid-phase source testing to characterize toxic metals emission from the treatment processes at our two large wastewater treatment plants. The presented paper describes the methods of sampling used, results of the testing and their affect on the facilities' health risk assessments. A significant part of the paper is devoted to a discussion concerning the sources of uncertainties in testing results, including the effect of metals concentration in ambient air. Methods for the handling and evaluation of results below the detection limit is also discussed.

An Assessment of Low Emission Sewer Systems for Industry

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The U.S. EPA is currently developing air emission standards to control the emissions of hazardous air pollutants (HAPs) from industrial wastewater sources. These new emission standards will require maximum achievable control technology (MACT) which represents the most stringent level of control that is practically achieved. A variety of emission control techniques are capable of meeting MACT criteria, therefore, these standards provide some flexibility in selecting a strategy to reduce HAP emissions from wastewater sources.

Emission control techniques that allow facilities to maximize the use of existing capital equipment in sewer and pretreatment systems may offer a more cost effective approach in complying with MACT standards. Water seals and covers can be installed on existing sewer and pretreatment systems and are capable of achieving MACT emission control standards. The purpose of this assessment was to:

- 1) identify emission suppression techniques that minimize the release of volatile organic HAPs and other organic pollutants from industrial sewers and pretreatment systems;
- 2) characterize the applicability, design criteria, and technical issues associated with the use of each suppression technique identified; and
- 3) relate the significance of these emission suppression techniques to current and future federal air emission standards for wastewater sources.

The assessment indicated that industrial facilities are currently using a variety of techniques for minimizing emissions from sewer and pretreatment systems. In addition, safety concerns have been expressed with the use of emission suppression techniques. Some techniques allow volatile organic emissions to accumulate within an enclosed space and create potential fire or explosion hazards. These hazards are minimized when current safety practices and safeguards are implemented and maintained.

Common suppression techniques applied to sewer systems include: installing above ground hard pipe sewers; installing water seals on process drains and sewer ventilation pipes; creating surcharged sewer lines; and creating negative pressure sewer

lines. An increasing trend of using above ground hard pipe sewers at facilities was noted. This technique is favored because it allows the development of an integrated environmental strategy to comply with multimedia standards.

Common suppression techniques applied to pretreatment systems include: using purge gases for fixed roof structures; installing floating roofs for storage tanks and oil-water separators; and installing floating membranes for large surface impoundments. No trends of favoring the use of any one emission suppression technique were observed for pretreatment systems.

Based on this assessment, sufficient information on individual control techniques is available. However, little guidance is available for selecting and applying alternative emission control techniques to reduce air emissions from an entire sewer and pretreatment system.

An Odor Control Study at Bissell Point Wastewater Treatment Plant

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ABSTRACT

The Metropolitan St. Louis Sewer District's Bissell Point Treatment Plant has been in operation since 1970. Odor complaints from the vicinity of the plant have occurred yearly, primarily from June to September. The purpose of this study was to identify the sources of odors, determine the odor-causing constituents and their emission rates, and recommend a phased plan that leads to the abatement of objectionable odors from the Bissell Point Treatment Plant. In addition, the recommended plan addresses Missouri Department of Natural Resource's (MoDNR) rules relating to odor emission, U.S. EPA's pending Hazardous Air Pollutant standards, and MoDNR's pending plan on achieving VOC reductions mandated by the Clean Air Act Amendments of 1990.

INTRODUCTION

The Metropolitan St. Louis Sewer District's Bissell Point Treatment Plant currently receives an average of 111 mgd of wastewater from a 57,000 acre service area covering the northern and eastern parts of the City of St. Louis, and portions of North St. Louis County. Over half of the treatment plant's influent BOD₅ and TSS loadings result from industrial sources.

The number of odor complaints has increased since the new secondary treatment facilities began to be brought on-line in October 1992. Two significant odor episodes occurred on December 14, 1992 and February 4, 1993, resulting in over 100 odor complaints. These episodes were apparently related to the operation of the new trickling filters.

The Bissell Point Treatment Plant is a secondary treatment facility located adjacent to the Mississippi River on East Grand Avenue. Land use around the facility is primarily industrial and commercial. The closest residential areas are located 0.3 miles west of the treatment plant's fence line.

Wastewater and residuals treatment at the Bissell Point plant consists of the following operations: Influent Screening, Influent Pumping, Grit Removal, Comminution, Preaeration, Primary Settling, Primary Effluent Pumping, Trickling Filters, Aeration, Final Settling, Secondary Sludge Thickening, Sludge Dewatering, Sludge Incineration, and Ash Handling.

ODOR AND VOC/HAP SOURCES AND EMISSION RATES

A variety of historical information relative to odor and VOC emissions at the Bissell Point Treatment Plant was researched including:

- Odor complaint records from 1983 to 1993
- Qualitative odor sampling data from June 1982
- Gas and liquid-phase hydrogen sulfide (H₂S) sampling data from Summer 1985
- Plant Influent VOC analysis from September 12, 1985
- Liquid-phase H₂S sampling data from 1990
- QUAD scrubber performance test data from Summer 1993

A file of odor complaint records spanning the years 1983 to 1993 was reviewed. All complaints are registered between the months of June and August, with the exception of the major odor episodes on December 14, 1992 and February 4, 1993. In a few instances, descriptive information regarding the odor was recorded; "septic", "sewage", "sour", and "burnt" smells were noted. Many of the complaints are from a residential neighborhood located southwest of the plant. During the December 14, 1992 episode, most complaints were from locations within 1 mile to the north and west of the plant.

Sampling Plan and Methods

A summary of the sampling plan is presented in Table 1. Odor sampling was conducted on September 15 and again on September 21, 1993. These days were chosen for the dry weather conditions, relatively warm wastewater and ambient air temperatures, and river stage low enough to have only a minimal impact on the influent wastewater characteristics.

On each day, two samples were collected at each location (with four grab samples and one 24-hour composite of the treatment plant influent being the exception). At the preparatory and primary treatment facilities, samples were collected between the hours of 8:00 a.m. and 10:30 a.m., and again between the hours of 2:30 p.m. and 5:00 p.m. Samples at other locations were collected in late morning, and again in the late afternoon or early evening hours.

Several different sampling techniques were used, depending on the nature of the odor emission source, and are described in the following paragraphs.

Air Samples from Building Spaces. Samples of air from building spaces, or the headspace above water surfaces, were collected by use of an integrated sampler; see Figure 1. A vacuum pump was used to pull a vacuum in the sampler, thereby causing the Tedlar® sample collection bag to expand and fill with air drawn from the odor source through Teflon® tubing. The bag, thus conditioned, was then deflated, and a second sample collected in the bag over a period of approximately 1 to 2 minutes. The bag was then sealed and transported to the laboratory for analysis within a 24-hour period. Sulfur-bearing compounds were identified through Gas Chromatography/Flame Photometric Detection (GC/FPD) using modified CARB Method 16. Certain samples, as defined in the sampling plan, were also analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) to identify and quantify the 20 largest peaks, using modified EPA Method TO-14. Ammonia was measured on site using Sensidyne® tubes.

Air Samples from Liquid Surfaces. Samples from sources characterized as emissions from a water surface were taken by use of a Summa® passivated AISI Type 304 stainless steel flux chamber; see Figure 1. Compressed zero air was fed through Teflon® tubing and swept through the flux chamber at a measured rate for a period long enough to reach equilibrium. A sample of the off gas was then collected in a Tedlar® bag via Teflon® tubing from the flux chamber. The bag, thus conditioned, was then deflated, and a second sample collected in the bag. The bag was then sealed and transported to the laboratory for analysis within a 24-hour period, as defined above.

Wastewater Samples. Samples of influent and effluent wastewater streams were collected in 40-ml glass vials with Teflon® caps, cooled to 4°C, and transported to the laboratory for analysis. Liquid samples were analyzed for VOC/HAP purgeables by EPA Method 624.

Sampling Results

Ten (10) sulfur compounds and twenty-two (22) VOC/HAP compounds were detected at significant levels; see Table 1. In addition to the specific VOCs listed, various higher molecular weight (9 to 12 carbon) branched alkanes and alkyl benzenes were identified in the emissions from various treatment processes.

Ammonia never exceeded 0.3 ppm, and was most often at concentrations of less than 0.1 ppr. Ammonia does not appear to be a significant odor contributor at the Bissell Point plant.

A high concentration of carbonyl sulfide (COS) was detected in the incinerator stack gas. The compound has an odor similar to hydrogen sulfide (rotten eggs) at concentrations above 1 ppm. At concentrations below 1 ppm, COS smells like "gunpowder, fireworks, carbamate, and burnt rubber"¹

Emission Rates

Table 2 contains the calculated emission rates for the morning and afternoon of September 15, 1993. Table 3 contains the same information but for the morning and afternoon of September 21, 1993. The emission rates are listed by sampling locations (sources) and individual compounds. As the tables show, the first five compounds have the highest emission rates and contribute to odors at a variety of sources. The most significant odor causing compounds appear to be hydrogen sulfide, dimethyl sulfide, and methyl mercaptan. Carbonyl sulfide appears to be a significant odor-caus-

compound primarily at the incinerator stack.

Non-sulfur odorous compounds, such as ammonia and various volatile organics (e.g., toluene, acetone, methylene chloride), were detected in the off gas from various treatment units. However, these compounds were detected at relatively low concentrations.

At 10:30 a.m. on September 21, a hauled-in waste was received at the plant that contained large quantities of dimethyl sulfoxide. Under certain conditions, the dimethyl sulfoxide degrades and forms dimethyl sulfide. As the September 21 afternoon data shows, the dimethyl sulfide emission rate as measured at the inlet to the QUAD scrubbers was 219.2 lb/day. Higher than normal releases of dimethyl sulfide were also noted at the primary settling tanks and aeration tanks. It is likely that the severe odor episodes of December 14, 1992 and February 4, 1993 resulted from similar releases of dimethyl sulfide as a result of hauled-in wastes.

Comparison of emission rates from various sources was achieved by normalizing the emission rate data in terms of odor units per second. An odor unit is defined as 1 cubic meter of air at the threshold concentration. Thus, a concentration of 1 odor unit per cubic meter is the level at which you can just smell an odorous compound. To convert the mass emission rates (lb/day) for each odorous gas to emission rates in odor units per second, the following conversion was made (Equation 1):

$$\frac{lb}{\text{OdorUnit}} = 1 \text{ m}^3 \cdot X \cdot Y \cdot \frac{1}{10^6} \quad (1)$$

To determine the number of pounds per odor unit, the following calculation was made (Equation 2):

$$\frac{\text{OdorUnits}}{\text{second}} = \frac{lb}{\text{day}} \cdot \frac{\text{day}}{86,400 \text{ sec}} \cdot \frac{lb}{\text{OdorUnit}} \quad (2)$$

where

X = Odor threshold of compound in ppm, v/v

Y = Odorous gas density, lb/m³

The total emission rate in odor units per second (last column of Tables 2 and 3) for each source is the sum of the individual emission rates for each odorous compound in odor units per second. Although this technique may not account for the synergistic or antagonistic effects of combinations of odorous compounds, it was considered to be conservative for this study.

Baseline Odor Dispersion Modeling

Emission rates of odorous compounds were not sufficient by themselves to assess the significance of the odor sources. The manner in which these emissions are dispersed between the sources and receptors must also be considered. For this study, a computerized odor dispersion model was used to determine how the odors from each source impact the community. This allowed each of the odor sources to be categorized as either a major, moderate, or minor odor source. In addition, the dispersion model was used as a basis for evaluating various odor control scenarios.

Isopleth Map for a Worst-Case Odor Emission Scenario. Figure 2 shows odor concentration isopleths for worst-case emission rates from a day when special waste was hauled in at the Bissell Point Treatment Plant (with fence line) and the surrounding area. In this scenario, the entire receptor grid (3 miles by 3 miles) is covered with an objectionable odor since the 1 odor unit/cubic meter isopleth is beyond the boundary of the grid. To avoid obfuscation of the isopleth data as a result of cluttering, the highest odor concentration shown on this map is 74 odor units/cubic meter. More isopleth maps are presented later which reflect the results of implementing various control strategies that should bring the plant into compliance with applicable odor regulations.

Ranking of the Odor Sources

To determine the relative contribution of each source to the total odor burden, a culpability analysis was performed. Based on the results of this modeling, each odor source was ranked as either "major" (contribution $\geq 30\%$), "moderate" ($10\% < \text{contribution} < 30\%$), and "minor" (contribution $\leq 10\%$). The following odor source ranking was established:

Major

- Primary Settling Tank Weirs
- Trickling Filters

Moderate

- Grit Tank Weirs
- Precacration Tanks
- Sludge Bldg. Ventilation Air
- Incinerator Stack
- Ash Settling Basin

Minor

- Influent Pump Station
- Grit Tanks (water surface)
- Grit Building
- Comminutor Building
- Primary Settling Tanks
- Trickling Filter Pump Station
- Aeration Basins
- Final Settling Tanks
- Sludge Wells Ventilation Air
- Thickener Building Ventilation Air

VOC/HAP Emissions

One of the objectives of this project was to assess the plant's status relative to Volatile Organic Compound (VOC) and Hazardous Air Pollutant (HAP) emissions. A combination of modeling and air sampling was used to determine the VOC/HAP emission rates.

For estimating the emissions from wastewater treatment processes, the Bay Area Sewage Toxic Emissions (BASTE v3.0) model was used. BASTE is a general fate model, and estimates various pathway losses (e.g., volatilization, sorption, and biodegradation) for 26 VOCs. Sverdrup has extended the applicability of BASTE by adding several more VOCs that were detected at Bissell Point. The model allows for analysis of complex treatment configurations including split flows, recycle streams, and biological processes.

Table 4 is a summary of VOC/HAP emission rates. For each compound, the emissions estimate by BASTE for wastewater treatment processes are listed, along with the emissions measured from the sludge processing operations. The total of the wastewater and sludge emissions for each compound are listed in the third column of numbers; the fourth column denotes those compounds that are classified HAPs. The data indicate a total of 23.3 tons of volatile organics emitted per year, with the majority emissions coming from the wastewater treatment processes. It should be noted that limited VOC/HAP air sampling data from the wastewater treatment processes collected during this study indicate that the BASTE model predictions are conservative.

EVALUATION OF ALTERNATIVE ODOR CONTROL SCENARIOS

The degree of control necessary is defined in the Missouri Department of Natural Resources (MoDNR) odor control regulation for the St. Louis Metropolitan Region (10CSR 10-5.160) which requires that²:

No person shall emit odorous matter that will cause an objectionable odor (in this study > 1 odor unit/cubic meter):

- on or adjacent to residential, recreational, institutional, retail sales, hotel or educational premises
- on or adjacent to industrial premises when air containing such odorous matter is diluted with twenty or more volumes of odor-free air (for this study, the odor concentration at an adjacent industrial site may therefore be 20 odor units/cubic meter); or
- on or adjacent to premises other than those described above when air containing such odorous matter is diluted with four or more volumes of odor-free air (for this study, the odor concentration at such sites may therefore be 4 odor units/cubic meter).

In addition, the City of St. Louis (where the Bissell Point plant is located) has an odor control regulation that differs slightly from the MoDNR rule³. In the City regulation, the 1 odor unit/cubic meter limit applies to property zoned as residential. The four-to-one dilution applies to commercially zoned

property, and a 19-to-1 dilution applies to premises zoned for industrial use. The City's regulation defines an odor as objectionable if 50 percent or more of a panel of at least 5 persons can perceive the odor in a properly diluted sample.

To meet the above regulatory requirements, alternative odor control scenarios were developed to control the major and moderate odor sources identified in this study. Control of minor sources would only be considered if the alternatives for control of odors from major and moderate sources were insufficient to resolve the odor problem at the plant. The odor control scenarios were then evaluated/modeled to determine the degree of control necessary to bring the plant into compliance with the odor regulations.

The baseline odor control scenario assumes current conditions, i.e., wastewater loadings and odor emissions will remain at present levels, dimethyl sulfoxide hauled-in waste will no longer be fed upstream of the primary settling tanks, trickling filters will be covered and ventilation air scrubbed, and incinerator afterburner controls will be used.

In a stepwise fashion, each odor control option was modeled and the isopleth maps were compared with the regulatory odor concentration requirements to determine compliance. Figure 3 shows that with all currently planned controls in place, odor regulation compliance is achieved on the nearest industrial site with an odor concentration of less than 20 odor units per cubic meter, but at the nearest residential, retail, and hotel sites, odor concentrations are between 4 and 7 odor units per cubic meter. Thus, additional controls are necessary to comply with the odor regulations.

As determined in the odor source ranking, the primary tank weirs are the largest uncontrolled odor source and contributor to off-site receptors. Using the estimated emission rate from the primary weirs with controls, the dispersion model was run again, resulting in a odor concentration isopleth map (Figure 4). With the addition of primary weir controls, the plant still produces odor concentrations greater than 1 odor unit/cubic meter at the residential, hotel, gas station, and restaurant sites and thus, additional controls are necessary.

The remaining control options address the odor sources ranked as moderate sources. Figure 5 shows that the resulting odor concentrations at the restaurant, hotel, gas station, and residential receptors are 1.0 odor unit/cubic meter with the addition of grit weir, preaeration, and sludge building controls. A summary of the plant's compliance status with the odor regulations under various odor control scenarios is presented in Table 5.

RECOMMENDED ODOR CONTROL PLAN

The following recommendations were selected for the first phase of odor control at the Bissell Wastewater Treatment Plant:

- Implement controls at each of the two major odor sources identified in this study (trickling filters and primary settling tank weirs)
- Implement partial controls at several of the moderate odor sources (grit tanks, preaeration tanks, and incinerator stack), where such controls have small implementation costs.
- Develop and implement an effective hauled-in waste strategy, especially for wastes containing dimethyl sulfoxide.
- Continue good O & M practices by cleaning out-of-service tanks as soon as possible and removing sludge and scum from the primary settling tanks on a regular basis.

Odor Control at Major Odor Sources

Trickling Filters. The trickling filters were identified as the most significant odor source at the treatment plant. At the present time, covers are being added that should allow for the containment and collection of the majority of odors for treatment in the existing QUAD scrubbers. The odor concentrations in the feed to the scrubbers varies depending on season, weather conditions (dry or wet weather), and the nature of hauled-in waste being received at the plant on any particular day. Control of the sodium hypochlorite (NaOCl) feed to the scrubbers is being enhanced to handle a wide range of odorous trickling filter off-gas.

Primary Settling Tanks. The primary settling tank weirs were identified as the second most significant odor source at the treatment plant. It was recommended that the weir area of the primary settling tanks be covered, odorous air be collected from the covered area at a rate equivalent to about one air change per hour, and that the collected air be treated for odor removal. Based on the concentrations of odorous compounds expected in the off gas from the weir area, there are three types of control systems that could be used for odorous air treatment. These are a packed bed scrubber, a mist-type scrubber, and a biofilter. All three systems can be designed to provide equivalent performance, and are expected to have similar capital costs. Advantages and disadvantages of each type of system for this particular application are listed in Table 6.

Based on a comparison of the options, the biofilter appears to be ideally suited to this application and was consequently recommended.

Impact of Recommended Scheme on VOC Emissions

The recommended odor control approach will have a further benefit in reducing the emissions of Volatile Organic Compounds and Hazardous Air Pollutants from the Bissell Point treatment plant. Reductions in emissions can be expected at the grit basins, preaeration basins, primary settling tanks, and incinerator. VOC removals of 90 percent were assumed for the biofilter and incinerator afterburners. A VOC removal of only 10 percent was assumed for the trickling filter scrubbers, based on test results from this study. Table 7 shows the effect of recommended odor controls on plant VOC emissions.

CONCLUSION

Hydrogen sulfide, dimethyl sulfide, and methyl mercaptan appeared to be the most significant odor causing compounds emitted from the plant. Carbonyl sulfide was released in significant amount from the incinerator stack.

Using dispersion modeling, odor sources were ranked as major (contribution to modeling receptor grid $\geq 30\%$), moderate ($10\% < \text{contribution to receptors} < 30\%$), minor (contribution to receptors $< 10\%$). Two major odor sources were identified: 1) primary settling tank weirs; and 2) trickling filter. Based on this ranking, several odor control scenarios were developed and evaluated. With the implementation of all controls, the model predicted that the plant would meet the odor regulation.

A phased odor control implementation plan was developed for the Bissell Point plant. With the implementation of all odor control recommendations, VOC/HAP emission reductions from the plant were estimated to be 20%.

REFERENCES

1. Polgar, L.G.; Duffee, R.A. "Odor Characteristics of Mixtures of Sulfur Compounds Emit from the Viscose Process", at the 68th Annual Meeting of the Air Pollution Control Association, Boston, Massachusetts, paper #75-55.2, 13 pages.
2. MoDNR 10 CSR 10-5.160 Control of Odors in the Ambient Air.
3. St. Louis City Ordinance 59.270 Section 20 Control of Odors in the Ambient Air.

Table 1. Sulfur and VOC/HAP compounds detected at the Bissell Point Treatment Plant.

<u>Detected Sulfur Compounds</u>			
	hydrogen sulfide	dimethyl disulfide	
	carbonyl sulfide	thiophene	
	methyl mercaptan	3-methyl thiophene	
	dimethyl sulfide	isobutyl mercaptan	
	carbon disulfide	ethyl methyl sulfide	
<u>Detected VOC/HAP Compounds</u>			
acetone	dichlorobenzene	methylene chloride	trichloroethene
benzene	ethanol	styrene	trichlorofluoromethane
carbon disulfide	ethyl methyl benzene	tetrachloroethene	trimethylbenzene
carbonyl sulfide	ethylbenzene	tetrahydrofuran	m & p-xylenes
chlorobenzene	isopropanol	toluene	o-xylene
chloroform	methyl ethyl ketone	trichloroethane	

Mean

[illegible][illegible]

Note: Percentages for ordered categories are in parentheses. ND = Not Determined. NS = Not Significant.

Table 2. Diesel Fuel Treatment Plant odor compound emission rates for September 22, 1993

[illegible][illegible][illegible]

NOTE: Asterisks indicate the following significance levels: * = 0.05, ** = 0.01, *** = 0.001.

Table 4. Bissell Point Treatment Plant VOC/HAP emission rates.

Compound	Emission Rate, tons/year			HAP
	Wastewater Treatment	Sludge Treatment	Total	
Acetone	0.93	0.45	1.38	--
Benzene	0.12	0.06	0.18	0.18
Carbon disulfide	0.63	0.14	0.77	0.77
Carbonyl sulfide	0.00	2.18	2.18	2.18
Chlorobenzene	0.08	<0.01	0.08	0.08
Chloroform	0.81	<0.01	0.81	0.81
Dichlorobenzene	0.15	0.01	0.16	0.16
Dimethyl sulfide	<0.01	0.31	0.31	--
Dimethyl disulfide	<0.01	<0.01	<0.01	--
Ethanol	1.79	0.02	1.81	--
Ethyl methyl benzene	1.72	0.05	1.77	--
Ethylbenzene	0.12	0.01	0.13	0.13
Isopropanol	0.28	0.00	0.28	--
Methyl ethyl ketone	0.46	0.04	0.50	0.50
Methyl mercaptan	<0.01	0.37	0.37	--
Methylene chloride	3.24	0.03	3.27	3.27
Styrene	0.02	0.04	0.06	0.06
Tetrachloroethene	0.44	0.03	0.47	0.47
Tetrahydrofuran	0.03	0.00	0.03	--
Toluene	4.79	0.54	5.33	5.33
Trichloroethane	0.00	0.03	0.03	0.03
Trichloroethene	0.11	<0.01	0.11	0.11
Trichlorofluoromethane	0.00	0.02	0.02	--
Trimethylbenzene	2.43	0.05	2.48	--
Xylenes	0.65	0.08	0.73	0.73
Total	18.80	4.46	23.26	14.81

Table 5. Compliance status with St. Louis City odor regulation.

Control Options	Receptor Type		
	Industrial	Commercial	Residential
Eliminate Special Waste			
Flicking Filter Covers	Yes	No	No
Incinerator Afterburners			
Primary Weir Controls	Yes	No	No
Int Weir Controls	Yes	No*	No*
Aeration Controls	Yes	Yes**	No*
Sludge Bldg. Controls	Yes	Yes**	Yes**

* = in compliance with the current odor regulations for the St. Louis Metropolitan Region

-- out of compliance with the current odor regulations for the St. Louis Metropolitan Region

dicted value is out of compliance, but because of the model's margin of error, the actual value could be in compliance

dicted value is in compliance, but because of the model's margin of error, the actual value could be out of compliance

Table 6. Comparison of odor removal technologies for the primary settling tank weirs.

<u>Odor Control Technology</u>	<u>Advantages</u>	<u>Disadvantages</u>
Packed Bed Scrubber	<ul style="list-style-type: none"> • Handles variations in odor concentrations well • Moderately efficient at VOC removal • Small size 	<ul style="list-style-type: none"> • High chemical costs • Maintenance of chemical feed systems • Maintenance of bed (fouling) • Maintenance of water distribution system (plugging) • Chemical carryover • Higher ΔP (fan operating costs)
Mist-type Scrubber	<ul style="list-style-type: none"> • Relatively small size • Low ΔP (fan operating costs) • No bed maintenance 	<ul style="list-style-type: none"> • Moderately high chemical costs • Less responsive to variations in odor concentration • Less efficient at VOC removal • Chemical feed system maintenance • Nozzle maintenance • Compressed air system • Chemical carryover
Biofilter	<ul style="list-style-type: none"> • Fairly responsive to changes in odor concentrations • High VOC removal • Minimal chemical feed costs • Minimal chemical feed systems to maintain • No chemical carryover 	<ul style="list-style-type: none"> • Periodic bed replacement • Moisture and pH control requirements • Larger space requirements • Higher ΔP (fan operating costs) • No controllable process parameters • Potential cold-weather performance deterioration

Table 7. Effect of recommended odor controls on plant VOC emissions.

<u>Source</u>	<u>Uncontrolled VOC Emission Rate (tpy)</u>	<u>Controlled VOC Emission Rate (tpy)</u>
Grit Tanks	2.53	1.61
Preaeration/Influent Channel	2.05	0.49
Primary Settling Tanks	1.16	0.68
Trickling Filters	11.68	12.55
Incinerators	3.03	0.30
All Others	2.80	2.93
Total	23.26	18.56

Integrated Sampler



Flux Chamber

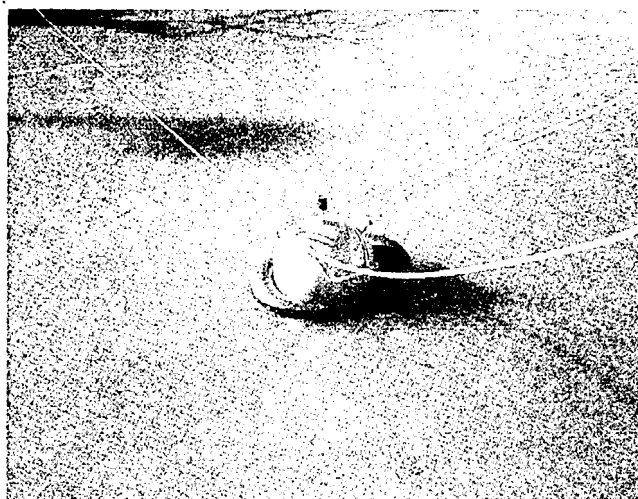


Figure 1. Photograph of the Integrated Sampler and the Flux Chamber.

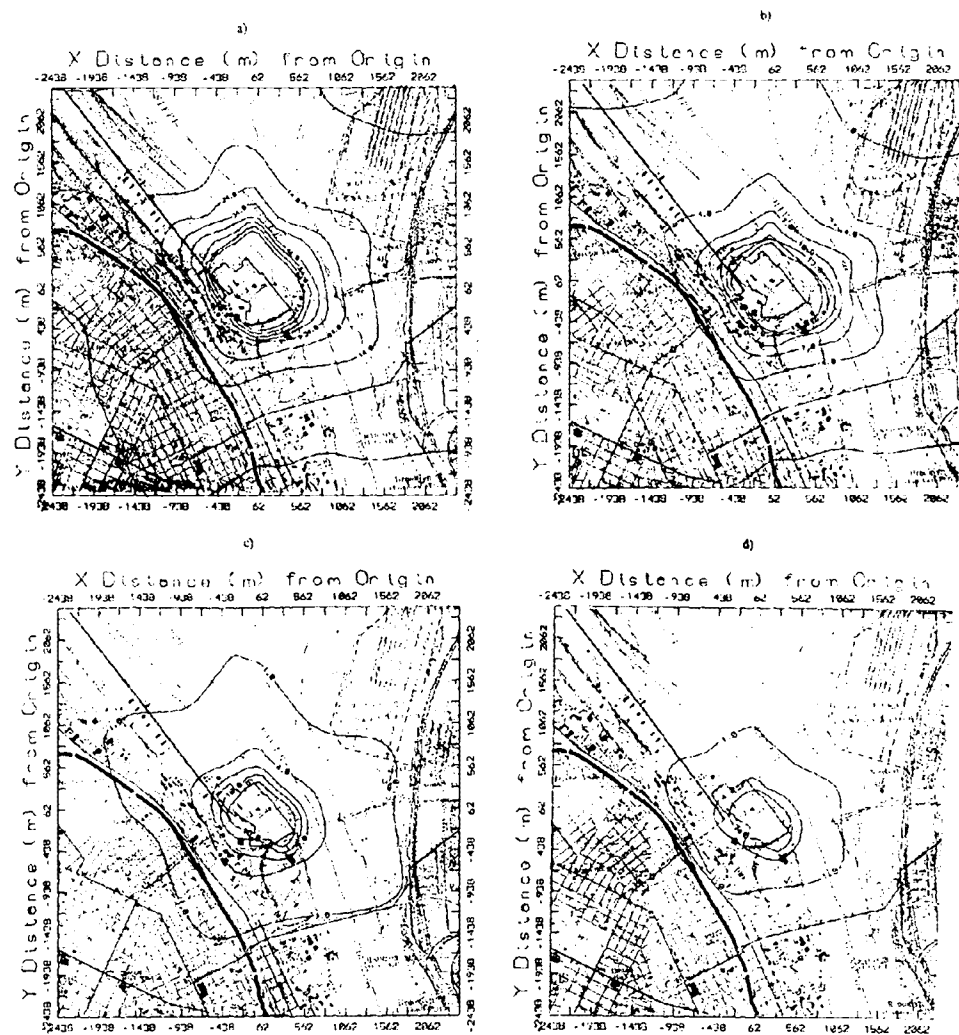


Figure 2. Bissett Point and vicinity odor isopleth maps a) with special hauled-in waste; b) with all currently planned odor controls implemented; c) with all currently planned and primary weir odor controls; and d) with all currently planned and recommended odor controls implemented.

POSTER SESSION

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Air Pollution Monitoring in the Republic of Latvia

by

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First investigations of the air pollution in Latvia were started by the Hydrometeorological Agency in 1968 in Riga. The surveys and preliminary results, information available on the pollution sources, knowledge of climatic and meteorological peculiarities of the Republic's regions formed the basis for the foundation of a national air pollution observation service in 1972.

Currently the system of observations covers 9 cities (20 posts) with emissions of maximum concentrations from industrial sources and roads (Fig.1, 2, 3), as well as recreation zones.

The list of substances to be under observations is specified taking into account the amount and composition of emissions into the atmosphere. Simultaneously with the air samplings, meteorological variables (wind direction and speed, humidity and temperature of the air, atmospheric phenomena) are measured at the posts.

The most wide-spread admixtures encompass solid substances, sulphur dioxide, nitrogen dioxide, carbon oxide, phenol, formaldehyde, ammonia, aromatic hydrocarbons, hydrogen chloride, hydrogen sulphide and metals (zinc, cadmium, lead, copper).

Samplings are made by aspiration of some volume of the air through an absorber filled with liquid or solid absorbent, which collects a substance, or through an aerosol filter, which traps particles the air contains. For the laboratory analyses, physico-chemical methods are used: photocolourimetry, atomic absorption, spectrophotometry, gas chromatography. The annual data base averages about 70,000 units.

Key principles of observations made in the Republic are:

- regularity of observations
- complexity of observations
- unity of sampling and analysis methods.

The Latvian national service is in the opinion that the hydrometeorological service is responsible for both, environmental pollution and hydrometeorological observations that provides for integrated monitoring. The service has the only real systematic and standard observational network in the Republic.

This enables the observational network to serve the main targets in the air pollution monitoring:

- assessment of pollution levels;
- determination of the tendencies in the pollution level under the influence of human activities and meteorological conditions;
- possibility to produce short-and long-term forecasts of variations in the air quality;
- possibility to warn concerned organizations of sudden changes in the air pollution level;
- comparison of the air pollution levels over different regions of the Republic.

The long-term compatible observational data series allowed to determine characteristics of the air pollution to be taken into consideration in building objects of national economy, general planning of towns and settlements to minimize impact on the atmospheric air.

To get more information on the air pollution, to further investigations of regional pollution in order to support socio-economical sector in our Republic, and to warn of the transfer of pollutants from accidental emissions, episodic and under-plume surveys are carried out in addition to standard observations.

The data of observations show, that formaldehyde, nitrogen dioxide, phenol and ammonia highly contribute to the air pollution over the Republic's towns.

Notwithstanding a decreasing tendency recorded in the emissions, a marked reduction has not been observed in the air pollution with particulated matter, sulphur dioxide, carbon oxide and nitrogen dioxide.

To estimate the air pollution level, indirect methods are also run, including precipitation chemical composition and snow pollutant content determinations.

Precipitation chemical composition is analyzed to measure contributions of local emitting sources and admixtures transfer with the air masses.

In 1989 precipitation quality monitoring network was established in the Republic, and in 1981 snow cover observations began (Fig.4). The samples taken are analyzed to measure Ca^{+2} , K^{+} , Na^{+} , NH_4 , SO_4^{2-} , Cl^{-} , NO_3 , pH, specific electric conductivity. Monitoring of precipitation and atmospheric chemical compositions is carried out at the station for transboundary pollutants transfer observations at Rucava. The program of works follows the EMEP recommendations. Methods for chemical analyses have been worked out at the Norwegian Institute for Air Research (NILU).

Atmospheric aerosols (sulphate, ammonium, nitrate) sampled annually number 150-200. Samples of atmospheric precipitation (sulphate, pH, sodium, calcium) amount to 100-150 and of atmospheric air (sulphate dioxide, nitrogen dioxide) - 150-200 units/year.

Since 1992 air samples have been taken to measure volatile organic compounds (VOC), and since 1993 ketone and aldehyde measurements made. Chemical analyses have been carried out by NILU.

With respect to pollution assessments at the EMEP stations, density data of fallouts of nitrogen and sulphur compounds are the most significant (Fig.5).

Within the EMEP programme, an International Meteorological Synthesizing Centre (MSC-V) makes model based calculations of transboundary transfer, fallouts and concentrations of harmful substances in Latvia. In turn, the Republic provides for MSC-V annual data on harmful substances emissions.

In 1992-1993 Latvia prepared and submitted information to join GAW WMO.

Prospects in the development of the atmospheric pollution observation service envisage establishing control over ozone concentrations and greenhouse gases (carbon dioxide, methane, nitrous oxide, chlorofluorocarbons).

Such observations must be accompanied by the activities of the Latvian Environmental Protection Committee directed towards keeping of National Cadastre of anthropogenic emissions from the sources, drawing up, carrying-out and up-dating of a national programme, that contains measures to mitigate implications of climate change by solving the issues of anthropogenic impact and promoting adaptation to climate change.

The National service of the air pollution observations is now facing objective difficulties of formation:

- in order to meet the public wish to have one "supermarket" to serve the demands for a more wide ecological information, and the necessity to systemize current and past information on observations, creation of a national data bank is an essential aspect in the work to be carried out; at the same time there is serious shortage of computers and data processing software;

- in view of the importance of observation and research products, public interest in ecology, and of an increasing demand for various consultations for decision - making in economic activities, running of approved scientific methods for the assessment and verification of the results available before their publication is of great importance. That's why training of Latvian specialists is necessary to up-grade scientific potential.

In order to put to effect WMO strategy and policy, as well as the main tasks of the Service and possibilities to take part in the world-wide climate and nature-protective activities, one of the greatest difficulties is linked with a low technical level of monitoring:

- lack of modern instruments and sampling equipment (automated included);
- lack of modern methods for the determination and analysis of harmful substances to be used in routine work and in emergency situations;
- lack of modern scientific criteria of harmful and extremely dangerous levels of the air pollution.

These are the main directions in the development of the Latvian air pollution monitoring system on the basis of modern international achievements.

FIG.1. AIR POLLUTION OBSERVATIONS OVER THE REPUBLIC OF LATVIA

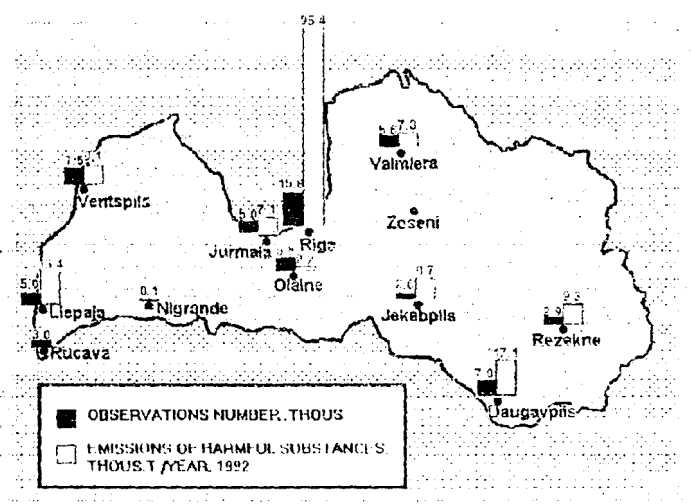


FIG.2. DENSITY OF HARMFUL SUBSTANCES EMISSIONS, 1992

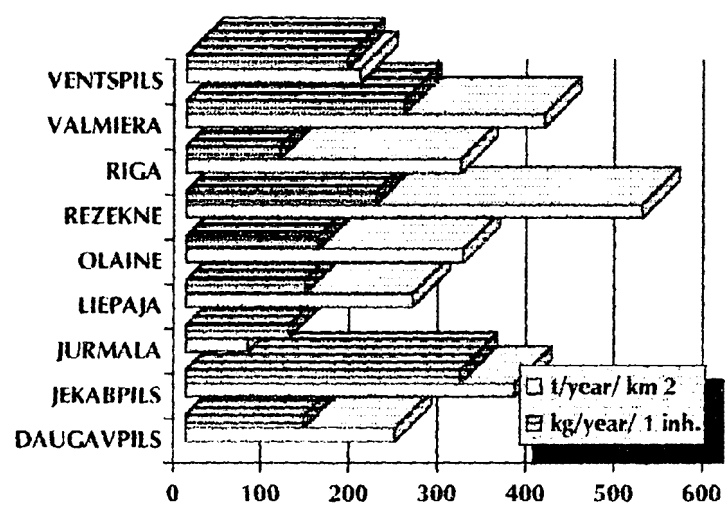


FIG.3. HARMFUL SUBSTANCES EMISSIONS INTO THE ATMOSPHERE, 1992

(% OF THE TOTAL)

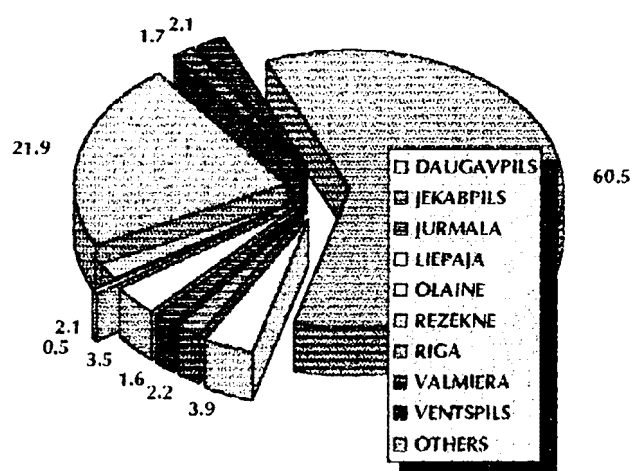


FIG.4. PRECIPITATION POLLUTION OBSERVATION NETWORK

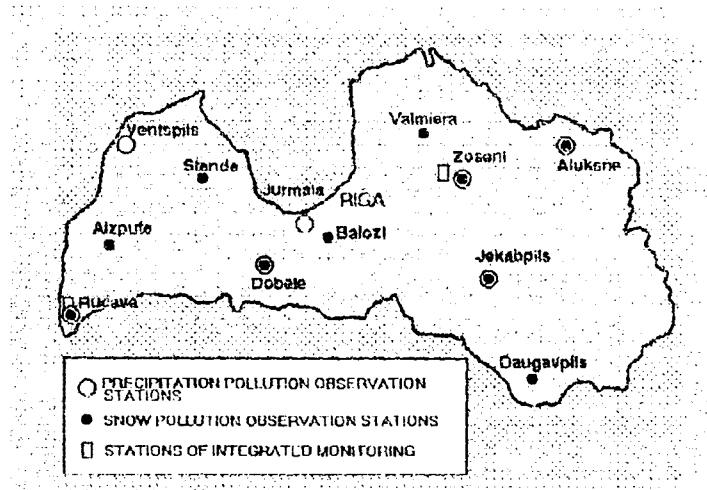
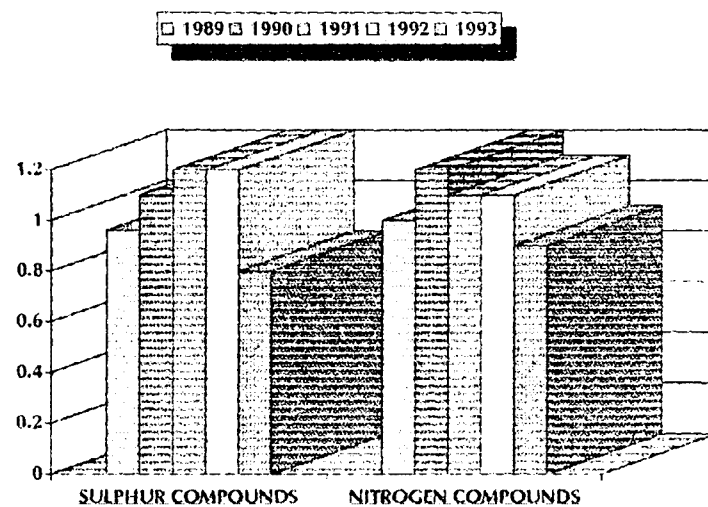


FIG.5. FALLOUTS DENSITY (g/m^2), STATION RUCAVA



**Evaluation of the Effects of Humidity on the Transfer of
C2-C10 Hydrocarbons from Cylinders**

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We prepare complex mixtures of VOCs in 1.5 liter high pressure cylinders. These cylinders are used as proficiency test samples. Audit materials of this type are usually prepared in humidified SUMMATM polished canisters. We compared the recovery of high molecular weight compounds in humidified canisters and high pressure 1.5 liter cylinders. A high pressure 1.5 liter cylinder containing C2-C10 hydrocarbons at the 5 ppbv level was prepared by diluting a master cylinder containing these compounds at the 50 ppbv level. The contents of this small cylinder were used to prepare a humidified SUMMA polished canister. The relative humidity of the canister was approximately 50 percent and the final pressure was about 45 psia. Both the 1.5 liter cylinder and the canister were analyzed and compared to a calibration curve prepared using the master cylinder. Recoveries for high molecular weight compounds in the humidified canister were greater, and closer to the theoretical values than in the 1.5 liter cylinder used to prepare the canister. This may happen because the contents were properly delivered from the small cylinder to the canister but that humidity was needed to deliver the higher molecular weight compounds to the detector.

The information in this abstract has been funded wholly by the U.S. EPA. It has been subjected to Agency review and approved for submission to the A&WMA.

Compound Break-through Comparison on Different Trapping Materials

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ABSTRACT

Many air analysis techniques require concentrating volatile organic compounds from a sample stream onto a trap for subsequent detection. The aim is to convert a large sample volume at low concentration to a small injection volume at higher concentration. Small injection volumes are more suitable for analytical techniques such as GC/MS. Sample concentration accomplishes two important functions for analysis. It concentrates the sample to introduce a sufficient mass of analytes to available detectors and reduces the volume to one which can be managed by the analytical system. In whole air analysis this is accomplished during the analytical procedure using some type of trap. The trapping technique must therefore retain the compounds throughout the concentration event without significant loss due to migration of analytes through the trap. As regulatory limits for toxic compound exposure are lowered, the ability to trap larger sample volumes in analysis has increased importance.

Sample concentration has been performed using adsorbent and cryogenic trapping for many years. When a targeted compound migrates completely through the trap prior to the completion of the concentration period it is referred to as break-through. The purpose here is to examine break-through as a function of sample volume for a number of compounds representative of current demands. Data presented will help define limiting factors and provide comparative information for various traps.

INTRODUCTION

Lowering detection limits and obtaining both consistent and accurate results for a growing number of compounds are some of the challenges facing the analytical chemist in ambient air analysis. Trapping a larger volume of sample is one approach to this problem. The ideal trap will hold compounds of multiple characteristics over the entire sampling period, trap 100% of the sample target compounds, release 100% of the sample compounds without altering them and itself be unchanged in effectiveness after multiple uses. In reality the effectiveness of a trap is often limited to a specific compound group, subject to break-through of compounds, effected by humidity and concentration of the sample and effected by rate and volume of sample introduction. This study focuses on break-through characteristics as a function of volume for several traps. The compound set chosen is meant to represent a variety of compounds characteristic in ambient air analysis. The study does not evaluate the effects of humidity, temperature, or combined trapping techniques. Other relevant literature is sparse or prepared many years ago with other applications as the focus. Some studies have focused on field collection of source level samples.

BODY

Three different types of adsorbent traps and the cryotrap were evaluated for recoveries of four representative compounds. The cryotrap is a well known and widely utilized trapping technique in the air analysis field. It consists of fifteen and one half inches of eighth inch diameter Nickel tubing. The middle four and one half inches are filled with non-silanized glass beads (60/80 mesh) obstructed at either end with glass wool (Figure 1). The tubing is coiled around a heater which is then wrapped in

tape. The thermocouple is placed for optimum temperature readout of the trap and wrapped in place. This is then encased in a chamber which provides cooling space for the liquid nitrogen.

For consistency, each trap was configured identically and the amount by weight of each adsorbent was measured. This was accomplished by weighing the Nickel tubing before and after introduction of the sorbent. The gram weight of the sorbent used is recorded on Figure 1. Each trap was checked after packing to assure that a 50ml/min flow was achievable. Data was collected using a Nutech model 8533 configured with an HP5890II/5971 GC/MS (Figure 2).

Benzene, chloroform, and acetone gas standards were made by injecting a calculated volume of neat standard into three separate static dilution bottles. The standard concentration in the static dilution bottles was calculated to introduce 100ng of each compound in a 200ul injection volume of gas. The standards were stored at X degrees until usage. Prior to analysis the standards were heated in an oven to 45C then removed and allowed to equilibrate to room temperature.

Ethane was purchased at a 10.1 ppm concentration and was introduced by loop injection technique. Using a 5.5ml volume loop in the loop pathway of the 8533, 68ng of ethane were introduced to the trap. This technique did not allow for a direct injection therefore all recoveries were based on the initial 12.5ml He volume injection. The two traps that managed to trap ethane showed consistent results and it can be extrapolated that the traps held the entire 68ng of ethane with no break-through on the initial and subsequent injections.

For each trap a direct injection was acquired in order to establish an expected response. Direct injections were made through injection port 2 of the 8533 by-passing the trap. A cryofocuser was used to focus the standard on the head of the column prior to injection. The GC was programmed to optimize detection for each compound specifically.

After establishing the expected response, the remaining injections were made through injection port 1 onto the trap. Each injection was followed by a given volume of helium introduced through a mass flow controller at 50ml/min. After the given volume was collected, the trap was desorbed and refocused on the head of the column by the cryofocuser. The desorption time for each trap was optimized to allow all of the introduced compound to be released. Desorption temperatures used were those recommended by the manufacturer.

Each compound was individually introduced to the four traps to evaluate the trap performance. To understand the responses we will look briefly at the functional theories of each trap. The premise by which the cryotrap works is somewhat different than that of the adsorbents. As the kinetic energy of the molecules is minimized due to temperature, weak Van der Wa's forces are formed with the surface area of the glass beads. Upon heating compounds revolatilize and continue to pass through the trap leaving no residue behind and leaving the trap fully intact for the next usage.

While the efficiency of adsorbent traps can be enhanced by using a cooling mechanism, the adsorbent itself functions to retain the compound on the trap. Various adsorbents are more or less effective depending on the properties of the compounds and the adsorbent itself. Sorbent materials are classified by mesh size, indicating the particle size. A mesh size of 60/80 means that a screen with 60 wires per inch contains holes big enough for all sorbent particles to pass through and an 80 wires per inch screen is too small for the sorbent particles to pass through. Sorbents are often characterized by their pore size and surface area. Each sorbent has a structure that contains openings into which compounds, if not bigger than the pore size can move into. The greater surface area available for compounds to interact with the sorbent, the greater the likelihood that the compound will form a weak bond and be retained on the sorbent material. This may serve as an effective trapping mechanism so long as all the compound can be removed. Some compounds may form bonds that are harder to break than others. The stronger the interaction between the sorbent and the compound, the more energy input needed to remove the compound. Carbon based sorbents such as carbon molecular sieve have a higher desorption temperature because they hold tightly to compounds.

Sorbents are commonly known to release "artifacts". Artifacts can be compounds left over from previous sample runs that have not been removed during desorption or reconditioning of the trap.

Residual compounds can interact with sample matrix compounds held in close proximity by the sorbent structure or with the sorbent material itself. High desorption temperatures encourage these interactions. Other artifacts are by-products from repeatedly heating the sorbent and can increase as the trap ages.

The flow can be restricted by sorbents with small particle size because of decreased air space in the trap. Tunneling is another flow problem that can sometimes occur with sorbent materials and reduce the trap efficiency. This happens when the sample stream follows a route through the sorbent particles rather than flowing evenly through the entire trap. Using a narrow diameter tubing as well as consistently packing the trap can reduce the chances of this type of problem.

The graphitized carbon blacks of Carbpak™ B are designed for trapping C4-C8 compounds as well as large molecules such as polychlorinated biphenyls. The entire surface of the adsorbent particles (60/80 mesh) are available for interactions by dispersion or London forces. The large surface area (820 m²/g) and small pore size of Carbosieve™ S-III, a beaded carbon molecular sieve, make it particularly well suited for trapping small molecules such as the C2 hydrocarbons. Carbpak™ and Carbosieve™ adsorbents typically need higher desorption temperatures than Tenax®,. Tenax-TA® is a synthetic porous polymeric material used for trapping semi-volatile and volatile organic compounds.

The volatile compounds chosen in this study represent some of the most common compound sets analyzed for today. Ethane is a very light hydrocarbon found on the ozone precursor list and one of the most challenging to capture. A common organic solvent, acetone, represents the polar compounds. Chloroform is a halogenated hydrocarbon found on the TO-14 compound list. The aromatic hydrocarbon benzene is one of the BTEX compounds. Typical ambient samples range from less than 0.2 ppbv as high as 100 ppbv. The majority however fall between 0.2 and 20 ppbv. Assuming a 2 ppbv ambient air sample is to be analyzed, a five hundred milliliter volume collected on a trap would introduce 3.2 ng benzene, 4.9 ng chloroform, 1.2 ng ethane, and 2.4 ng acetone on the trap.

CONCLUSIONS

Reviewing the data we find that the cryotrap performed optimally for all challenge compounds (Graph/Table 1). This is so because the trap does not depend primarily on the characteristics and interactions of the sorbent and compound, but on the temperature. The trap has a minimal desorption time and temperature to retrieve all compounds. There is no concern for carryover or artifacts from the cryotrap.

Carbpak™ B trap showed consistent results for benzene up to two liters. Acetone began to break-through after 500 ml and chloroform recoveries were at 86 % at 100 ml and continued to drop until 1000 ml where they stabilized at 27% recovery of compound from the trap (Graph/Table 2). It is not surprising that ethane was not retained by the trap at all since it is designed for heavier hydrocarbons.

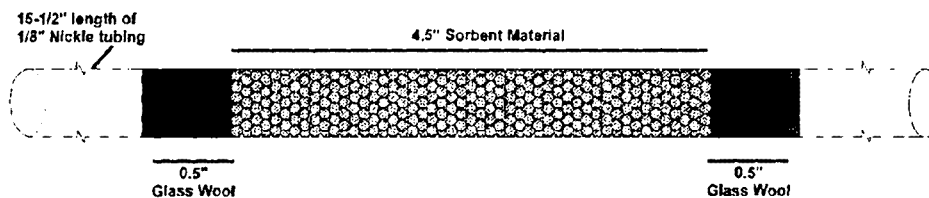
Carbosieve™ S-III trapped both ethane and benzene very effectively. Acetone responses were consistently at 70% and could not be improved by longer desorption time or raising the desorption temperature (Graph/Table 3). Chloroform had unexpectedly low recoveries. This may be a reflection of compound decomposition rather than break-through.

Tenax® is the final sorbent evaluated in this study (Graph/Table 4). Tenax® showed break-through on all challenge compounds in this study. Ethane, being the lightest was not trapped at all. Acetone and chloroform recoveries were good for a 100 ml volume sample. Benzene recoveries were good to a volume of 1250 ml after which some break-through occurred. Tenax® is frequently used in combination with other sorbents because of its low break-through volumes for compounds.

This study succeeded in characterizing the performance of some currently available sorbents as trapping materials for sample concentration prior to analysis. For the purposes of this study, the cryotrap was able to perform for all compounds up to a two liter sample volume. Other studies could develop the sorbent trap by using lower temperatures for trapping and by combining sorbent materials. Analysis interested in a specific compound set may use this information to determine an appropriate sorbent material or trapping technique in analysis.

FIGURE 1

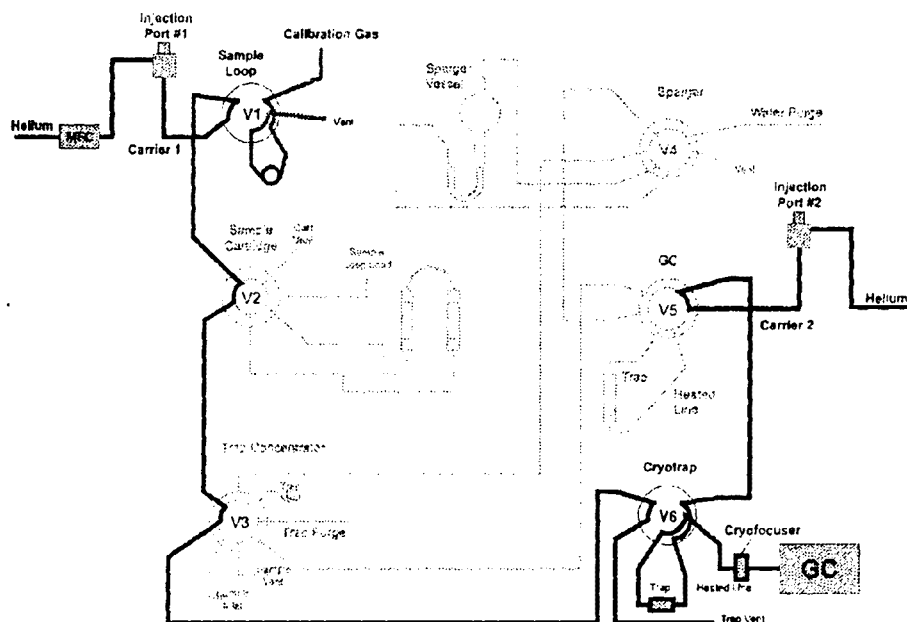
DIAGRAM OF TRAP



Tenax-TA® - 115 mg
 Carbowax B - 151 mg
 Carbosieve S-II - 320 mg

Model 8533 Universal Sample Concentrator

FIGURE 2



GRAPH 1:

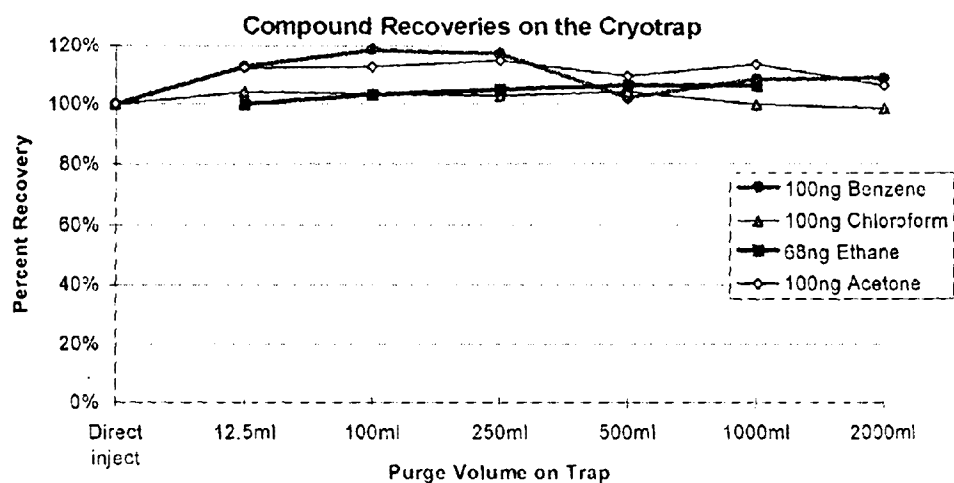


TABLE 1:

Area Response								
	Direct inject	Helium Purge volume of trap						
		12.5ml	50ml	100ml	250ml	500ml	1000ml	2000ml
Benzene	12639754	14262944	14479649	15000692	14843571	12908761	13751994	13809701
Chloroform	12506773	13010209	---	12945829	12860750	13067450	12603626	12347471
Ethane	---	5257084	---	5426092	5525382	5601048	5605982	---
Acetone	12045060	14439334	---	14500688	14795222	14104519	14647264	13700608

Percent Recovery								
	Direct inject	Helium Purge volume of trap						
		12.5ml	50ml	100ml	250ml	500ml	1000ml	2000ml
Benzene	100%	113%	110%	113%	117%	102%	108%	109%
Chloroform	100%	104%	---	104%	103%	104%	100%	99%
Ethane	---	100%	---	103%	105%	107%	107%	---
Acetone	100%	112%	---	113%	115%	110%	114%	107%

GRAPH 2:

Compound Recoveries on Carbopak B

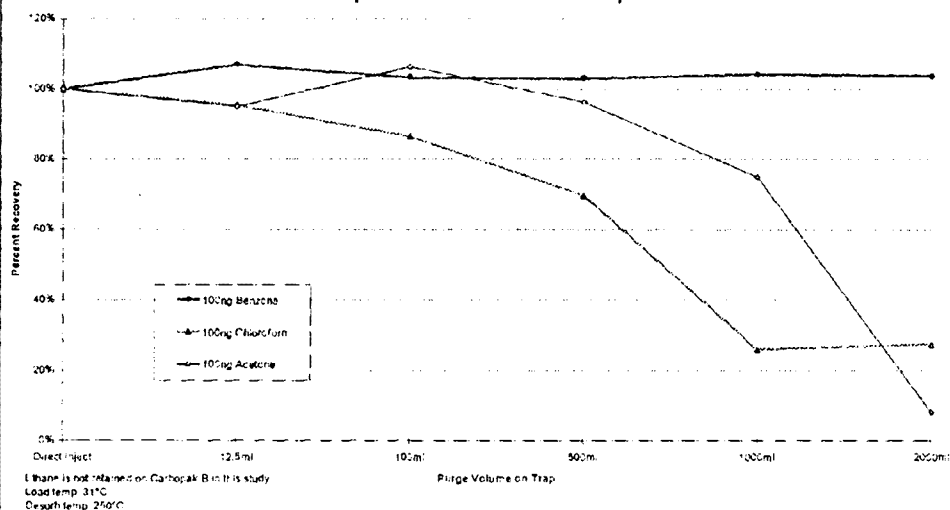


TABLE 2:

Area Response

	Direct inject	Helium Purge volume of trap					
		12.5ml	100ml	250ml	500ml	1000ml	2000ml
Benzene	11840443	12440776	12021514	---	11991914	12124808	12071391
Chloroform	10016079	9553547	8618574	7689273	6979318	2613251	2751416
Acetone	9990033	5474206	10615236	10277481	9624587	7475362	814079

Percent Recovery

	Direct inject	Helium Purge volume of trap					
		12.5ml	100ml	250ml	500ml	1000ml	2000ml
Benzene	100%	107%	103%	---	103%	104%	104%
Chloroform	100%	95%	86%	77%	70%	26%	27%
Acetone	100%	95%	106%	103%	96%	75%	8%

Ethane is not retained on Carbopak B in this study.
Load temp: 31°C
Desorb temp: 250°C

GRAPH 3:

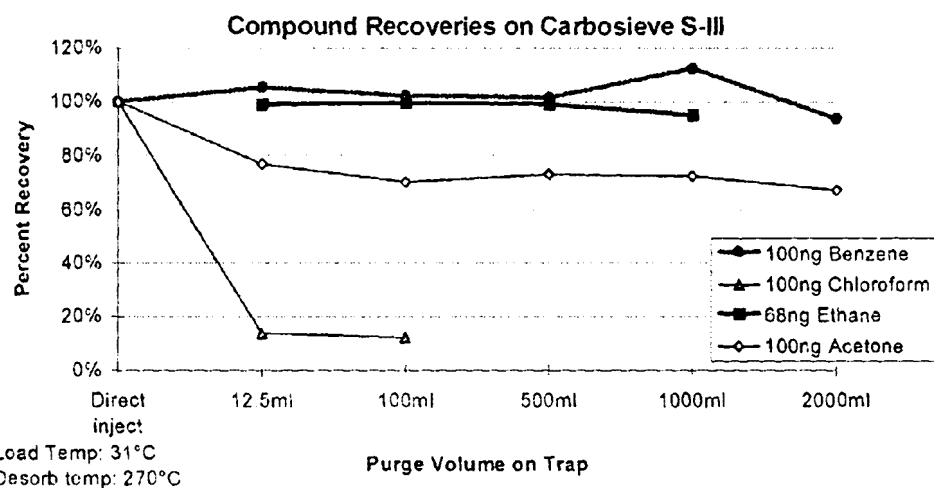


TABLE 3:

Area Response							
	Direct inject	Helium Purge volume of trap					
		12.5ml	100ml	250ml	500ml	1000ml	2000ml
Benzene	11066244	11654439	11331743	---	11241662	12452737	10350312
Chloroform	9775740	135024	1199245	---	---	---	---
Ethane	---	5476993	5543287	5490975	5422631	5107889	---
Acetone	10967105	8425549	7707658	8007399	8021018	7947109	7365128

Percent Recovery							
	Direct inject	Helium Purge volume of trap					
		12.5ml	100ml	250ml	500ml	1000ml	2000ml
Benzene	100%	105%	102%	---	101%	112%	93%
Chloroform	100%	14%	12%	---	---	---	---
Ethane	---	100%	99%	100%	99%	95%	---
Acetone	100%	77%	70%	73%	73%	72%	67%

Load temp: 31°C
Desorb temp: 270°C

GRAPH 4:

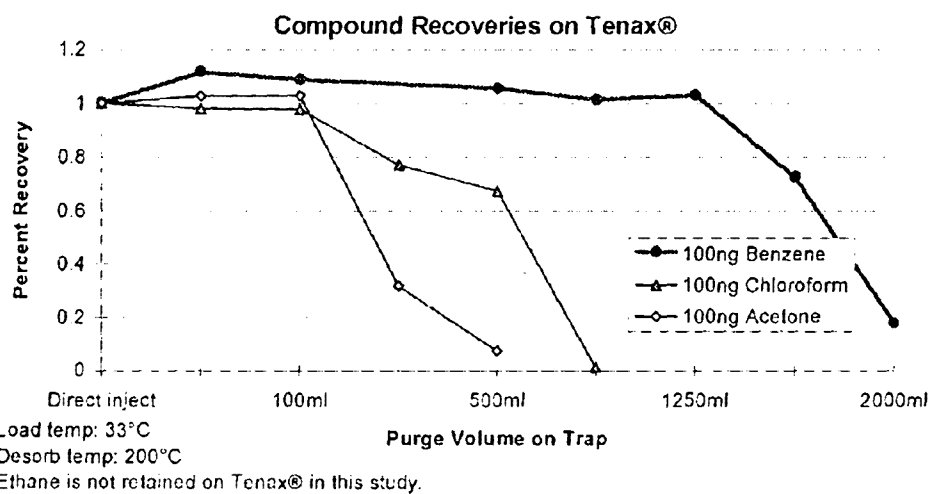


TABLE 4:

Area Response									
	Direct inject	Helium Purge volume of trap							
		12.5ml	100ml	250ml	500ml	1000ml	1250ml	1500ml	2000ml
Benzene	11606389	12949758	12618491	--	12231503	11753788	11954798	8438332	2099638
Chloroform	10606489	10390862	10365305	8187682	7168078	131139	--	--	--
Acetone	10496429	10682373	10702249	3306628	781457	--	--	--	--

Percent Recovery									
	Direct inject	Helium Purge volume of trap							
		12.5ml	100ml	250ml	500ml	1000ml	1250ml	1500ml	2000ml
Benzene	100%	112%	100%	--	106%	101%	103%	73%	18%
Chloroform	100%	98%	98%	77%	68%	1%	--	--	--
Acetone	100%	103%	103%	32%	8%	--	--	--	--

**Evaluation of Modifications to the Tekmar™ 5010 for the
Analysis of Indoor Air Pollutants on Multisorbent Tubes**

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Solid sorbents, such as Tenax™, may be used for the collection of complex chemical pollutants. The pollutants are desorbed from the tenax at the head of a GC column and analyzed by various detectors. Tenax and other sorbents may be packed into tubes of various sizes and shapes. Because we provide quality assurance support to a wide variety of projects, our equipment must be adaptable to many sample types. The Tekmar™ 5010 automatic desorber has furnace sizes capable of desorbing seven inch tubes of 5/8 inch and 1/4 inch diameter. Desorbing other, multisorbent bed tubes that are eight inches long requires a modification to the furnace cap. We have designed and built a replacement cap for the 1/4 inch furnace that allows the Tekmar 5010 to desorb the eight inch multisorbent bed tubes. The modification is simple enough to be performed by small machine shops. This modification increases the flexibility of existing equipment. Details of the modifications are provided along with an evaluation of its performance.

The information in this abstract has been funded wholly by the U.S. EPA. It has been subjected to Agency review and approved for submission to the A&WMA.

**Evaluation of Storage Conditions for Indoor Air Pollutants on
Solid Sorbents in UHP Helium Purged Mylar™ Packs**

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Solid sorbents, such as Tenax™, may be used for the collection of complex chemical pollutants. The pollutants are desorbed from the tenax at the head of a GC column and analyzed by various detectors. Many laboratories pack Tenax into glass tubes of various sizes and shapes. Shipping and storage of both clean and used Tenax cartridges are problematical due to the fragility of the glass tubes. This laboratory provides audit materials for a wide variety of projects, and an optimum shipping and storage system will maintain sample integrity and protect against breakage. Sealing cartridges in a Mylar™ package purged and slightly pressurized with ultra high purity helium provides an inert environment, and helps to maintain sample integrity. The sealed package also provides a protective bubble-like environment perfect for shipping. The preparation method is described and the results of stability studies reported for important indoor air pollutants when compared to traditional storage methods.

The information in this abstract has been funded wholly by the U.S. EPA. It has been subjected to Agency review and approved for submission to the A&WMA.

**Environmental and Occupational Exposures to PAH in the Czech Republic:
Personal Exposure Monitoring Coupled with HPLC/Time-Programmed Fluorescence Detection**

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ABSTRACT

The US Environmental Protection Agency has collaborated with health researchers in the Czech Republic to determine polynuclear aromatic hydrocarbon (PAH) exposures for populations in highly polluted environments and in various occupations. These investigations used personal exposure monitors (PEMs) that were developed to allow separate and simultaneous collection of fine particles, vapor phase nicotine and vapor phase organics. Samples were extracted and analyzed for 16 priority PAHs by optimized HPLC coupled with time-programmed fluorescence detection. Nicotine analysis was performed using capillary gas chromatography with nitrogen-phosphorous detection. Personal exposure monitoring periods of up to 24 continuous hours were conducted for: 1) Teplice and Prachatice policemen, who spent a major portion of their day outdoors; 2) open-pit coal miners; 3) health researchers working in a laboratory; and 4) coke oven workers. Total particle-bound PAHs ranged from 1.5 $\mu\text{g}/\text{m}^3$ for the health researchers to 52 $\mu\text{g}/\text{m}^3$ for the topside coke oven workers. Vapor phase PAH concentrations also varied greatly depending on occupation and ranged from 0.6 $\mu\text{g}/\text{m}^3$ for city policemen to 261 $\mu\text{g}/\text{m}^3$ for the coke oven workers. Carcinogenic PAHs, which were predominantly found associated with particulate matter (>90%), typically included benzo(a)anthracene, chrysene, and benzo(a)pyrene.

INTRODUCTION

The Northern Bohemia area of the Czech Republic has been heavily polluted from sources associated with the industrial and residential uses of high-sulfur brown coal¹. This coal, found in abundance in the region, is used in coal-fired power plants, chemical processing sites and for business and residential heating. Fossil fuel contribution from mobile sources as well as pollution from coal and other emissions have resulted in Czech Republic concerns over possible human exposures to hazardous agents such as PAHs. Czech scientists associated with the Teplice District Institute of Hygiene have been working with the US Environmental Protection Agency in efforts to quantify personal exposure to PAHs in the Teplice District of Northern Bohemia². This site, centrally located in an area of heavy coal mining and utilization offered opportunities to evaluate personal sampling methodologies and investigate the relationship between PAH exposures and selected occupations.

STUDY DESIGN

Four occupational groups were personally evaluated for PAH exposures. Groups consisted of: 1) Teplice coal miners, 2) Teplice and Prachatice policemen, 3) Teplice health researchers, and 4) Ostrava coke oven battery workers. Coal miners monitored were involved in open pit mining of the high sulfur brown coal. Their main duties involved mechanical repair of large, outdoor, conveyor belts that moved excavated coal from extraction points to transportation and storage sites. A noted feature of these open pit mines were in-ground coal fires which continually burn. The combustion emissions from these point sources fill and often envelope the open pits (bowls) and therefore inversion-like episodes occur. A group of Teplice policemen were involved in the study. These were largely involved in foot patrol of the central business district (CBD) of the town of Teplice. It was postulated that monitored individuals would be exposed to coal combustion emission products associated with heavy industrialization and residential heating along with mobile source emissions from automobiles and buses. Emission control devices on most automobiles and buses, upon visual observation, did not appear to retard pollutant emission. Prachatice policemen, who live in a relatively pristine area of Southern Bohemia were also monitored as a control group where PAH concentrations were presumed to be near background levels. Health researchers associated with the Teplice District Institute of Hygiene were monitored for PAH exposures. These individuals were involved in laboratory research as well as project management and were generally indoors. They were postulated as being exposed to urban air similar to that encountered by the Teplice policemen but at levels reduced by the modifying effects of being indoors.

The fourth occupational group monitored did not reside in the Teplice mining district. These were coke oven battery workers from a site in Ostrava. This group was selected due to known PAH exposure among coke oven workers and as a means to evaluate the samplers ability to collect PAHs under high concentration conditions. Larry car drivers (outdoor-topside workers), pushing machine helpers (outdoor-lower level workers), and quench car drivers (outdoor-ground level workers) were monitored. Larry car drivers are highly exposed individuals involved in dispensing coal charges into open and venting oven portals. Combustion emissions, constantly being released by the 24 hour/day coking process results in a thick fog of coal combustion emissions at the top of the coke oven battery. Pushing machine workers are involved in forcing the processed coke from the furnace using a large mechanical ram. This is conducted at the base of the oven (side) where point sources, and the emission plumes, are considerably less than atop the coke ovens. Quench car drivers are involved in transportation of coke extruded by the pushing machine to quench stations where cooling and particulate suppression procedures are conducted. This operation is generally conducted at ground level using motorized carts or conveyor assemblies.

PAHs, collected using battery powered personal exposure monitors (PEMs), would be collected and extracted for analysis. Sample collection would consist of periods from 8-24 continuous hours with simultaneous capture of both particle and vapor phase PAHs. Vapor phase nicotine, resulting from environmental tobacco smoke (ETS), would be collected to investigate cigarette smoke contribution to total PAH levels. Dichloromethane extraction would be utilized to extract PAHs from collected respirable particulate matter (RSP) and macroreticular resin (XAD-2). Solvent exchanged extracts would then be analyzed using high performance liquid chromatography equipped with a PAH specific analytical column as well as time-programmable fluorescence detection. Vapor phase nicotine, collected as a stoichiometrically bound reaction product with sodium bisulfate, would be extracted and then analyzed using capillary gas chromatography with nitrogen-phosphorous detection.

MATERIALS AND METHODS

Personal exposure monitors (PEMs) consisted of an inert, modular designed inlet, impactor, filter pack, and resin chamber assembly connected to a lightweight sampling pump. Detail about this device has previously been reported^{2,3}. In brief, a Teflon coated aluminum inlet was utilized to collect particulate matter and focus particles $>2.5 \mu\text{m}$ onto a coated impactor surface to remove it from the

sample to be analyzed. The RSP stream was then forced into a three-stage Teflon filter pack. The first filter stage, consisting of a 2.5 cm Teflon impregnated glass fiber filter (TIGF), was used to collect particle phase PAHs. The second and third stages contained identically prepared sodium bisulfate TIGF filters used in vapor phase nicotine collection. The mechanism by which nicotine is collected in this manner along with extraction and analysis procedure using this technique has been reported^{2,4}. Vapor phase PAHs, pulled into the filter pack but not collected at this point, pass through a 2.5 gram bed of styrene-divinyl benzene (XAD-2) where retention occurred.

PEMs were individually issued to each respondent after sampling rate calibration was performed. At the end of each collection period, PEMs were recovered, final sampling rate determined, and filter and XAD-2 samples recovered. A sampling log was utilized to document the effort as well as note any irregularities. Filter samples, PAH and nicotine separately, were transferred into light protected borosilicate vials equipped with Teflon lined closures while XAD-2 units were sealed using Teflon screw caps designed specifically to seal the PEM's resin chambers. All collected samples were returned to the Health Effects Research Laboratory (US EPA, RTP, NC) for extraction and analysis.

PAHs collected upon TIGF filters were extracted using three (sequential) 7 ml portions of dichloromethane (DCM) added to the vials containing each filter. Each extraction period consisted of 10 minutes of sonication at 25°C. Extract from each attempt was ultimately pooled, filtered through a 0.45 μm Teflon, and volume reduced to 10 ml using nitrogen evaporation. Vapor phase PAHs collected upon the XAD-2 resin were extracted using 25 ml of DCM. This was performed by "eluting" DCM through the actual resin chamber used to collect the sample. The resin chamber (made from Teflon) was designed to accommodate just such a procedure. This flow-through extraction technique minimizes possible XAD-2 contamination from laboratory and field artifacts by not having to remove the resin from the collection device to permit solvent extraction and analyte recovery. Extract from each resin chamber was individually captured into borosilicate tubes, filtered through 0.45 μm Teflon, and solvent normalized to 10 ml using nitrogen evaporation. Portions of the filter and XAD-2 extracts were then solvent exchanged into 100% acetonitrile to accommodate reverse phase HPLC analysis of the PAHs. Nicotine, collected using the sodium bisulfate treated filters, was recovered using procedures referenced earlier. Bound nicotine was released from the sodium bisulfate using sequential treatments of 5% ethanol followed by basification (10N NaOH). The resulting nicotine free base was then extracted into an organic layer of ammoniated n-heptane. Portions of this phase for each nicotine sample were individually transferred into autosampler vials for capillary gas chromatography.

PAH analysis using time-programmed fluorescence analysis was conducted using procedures discussed in depth elsewhere^{2,4}. This procedure involves use of a PAH-specific reverse phase HPLC column to optimize resolution between the 16 Priority PAHs. These PAHs are listed in Table I. Time-programmed fluorescence analysis is a technique that utilizes the optimum individual (or group) excitation and emission wavelengths for the PAH of interest. This technique has been found, in our hands, to be almost 3 orders of magnitude more sensitive than capillary GC-flame ionization detection. Because optimized detection is utilized, interferences from species of non-interest present in the extract are greatly minimized.

RESULTS

A comparison of particle phase and vapor phase PAHs collected for the Teplice District respondents is presented in Figure 1. These graphs reveal that vapor phase PAHs (like naphthalene, phenanthrene, anthracene, etc) account for the majority of the total PAHs detected in the Teplice district. This was true for all of the Teplice occupations monitored. The Teplice miners were exposed to the highest overall levels observed with some individuals exposed to as much as 10.3 $\mu\text{g}/\text{m}^3$ of total PAH with less than 0.5 $\mu\text{g}/\text{m}^3$ of this accounted for by particle phase PAH. While the numbers of individuals sampled were too small to allow a statistical comparison between the groups ($n=3$), patterns were observable. The Teplice health researchers were determined to be the least exposed. This was not unexpected due to the amount of time these individuals spent indoors daily. It was also expected that the Teplice policemen, monitored in January, would have exposures greater than the heal

institute workers but less than the miners. Note that when these same policemen were monitored in March, at the end of the winter inversions, PAH concentrations fell 2-3 fold. We have observed this phenomenon in other studies at this site. Prachatice policemen, presumed to have little PAH exposure due to the lack of heavy industrialization in Southern Bohemia, were found to have the highest level detected ($10.9 \mu\text{g}/\text{m}^3$ of total PAH). Vapor phase PAHs dominated this result. Investigation of this site revealed that while little industrialization is present in Prachatice, there is a high occurrence of residential heating using coal in this mountainous town. This source is believed responsible for the majority of PAH exposure.

Carcinogenic PAHs were predominantly observed to be collected in the particle phase. This is detailed also in Figure 1. Carcinogenic PAH exposures follow the same ranking as that observed for total PAH (Teplice miners > Teplice policemen > Teplice health researchers). Species such as benzo(a)anthracene, chrysene, and benzo(a)pyrene were observed in the highest concentrations of the particle phase carcinogens. Teplice miners were determined to be exposed to levels ranging from 90-340 ng/m^3 . Note that carcinogenic levels detected for the Teplice policemen fell to those of the Prachatice policemen control group during a March retest at the end of winter inversions.

Coke oven workers, an occupational group known to have an epidemiologically investigated rate of cancer, were exposed to as much as 30 fold higher PAH concentrations than the Teplice citizens (Figure 2). Lorry car workers (like respondent #10) performing an 8 hour shift atop the coke oven battery, had monitored levels of over 300 $\mu\text{g}/\text{m}^3$ total PAH. Patterns between the various worker assignments typify the examples included here (24 total workers were monitored at the site). Topside workers, like the lorry car drivers, are exposed to much higher levels than workers whose jobs are performed on the side or ground level of the coke oven plant (pushing machine or quench car workers). This is mainly due to the way in which coal is processed into coke and the point source emissions that result. The PEM utilized to collect PAHs (and the high particulate matter levels observed at the plant) had no detectable problems with filter overloading or vapor phase breakthrough of the XAD-2 resin at the concentrations encountered.

Nicotine, as a marker of environmental tobacco smoke (ETS), was monitored for all of the Teplice study groups to determine the level of PAH contribution from this source. ETS was not observed to heavily influence any measurement of PAH (Figure 3). Nicotine concentrations, noted by the + symbols and solid lines in the figure, did not appear to follow any pattern of observed PAH level for monitored respondents. This result probably indicates that PAH contribution from ETS sources are inconsequential to those from the other sources in this study (like coal combustion or mobile sources) when a highly polluted environment is monitored.

CONCLUSION

The PEM system utilized was determined to successfully monitor particle and vapor phase PAHs as well as vapor phase nicotine. Collection periods of 8-24 hours were utilized at both high as well as low analyte concentrations. Vapor phase PAHs were observed to be in much higher concentrations than the particle phase PAHs with most carcinogens collected upon filters. Coke oven workers were determined to be highly exposed with respect to the Teplice citizens. Teplice citizens, working in outdoor situations, are more likely to be exposed as compared to those working indoors.

ACKNOWLEDGMENTS

This work was supported by US EPA contract# 68D-300096 with Integrated Laboratory Systems.

DISCLAIMER

This report, nor data presented therein, does not necessarily reflect EPA policy.

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Table 1. Priority PAH quantified using HPLC

1. Naphthalene	9. Benzo(a)anthracene
2. Acenaphthylene	10. Chrysene
3. Acenaphthene	11. Benzo(b)fluoranthene
4. Fluorene	12. Benzo(k)fluoranthene
5. Phenanthrene	13. Benzo(a)pyrene
6. Anthracene	14. Dibenzo(a,h)anthracene
7. Fluoranthene	15. Benzo(g,h,i)perylene
8. Pyrene	16. Indeno(1,2,3-cd)pyrene

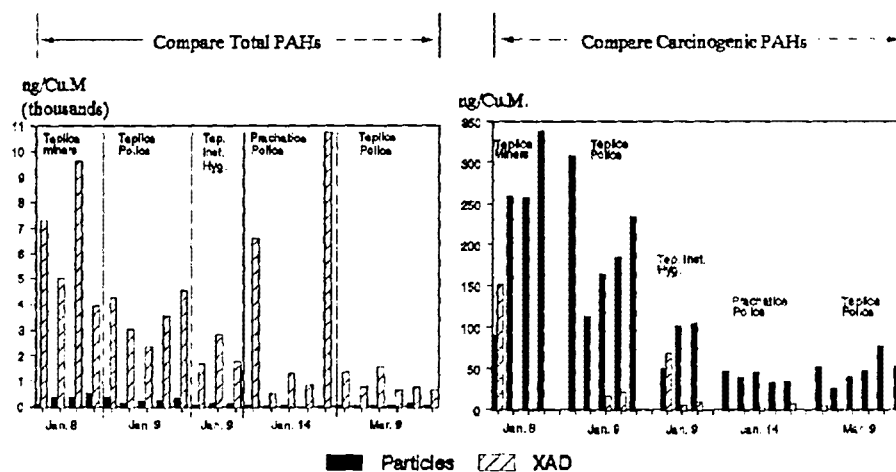


Figure 1. Personal sampler: particle filter compared to XAD for PAH.

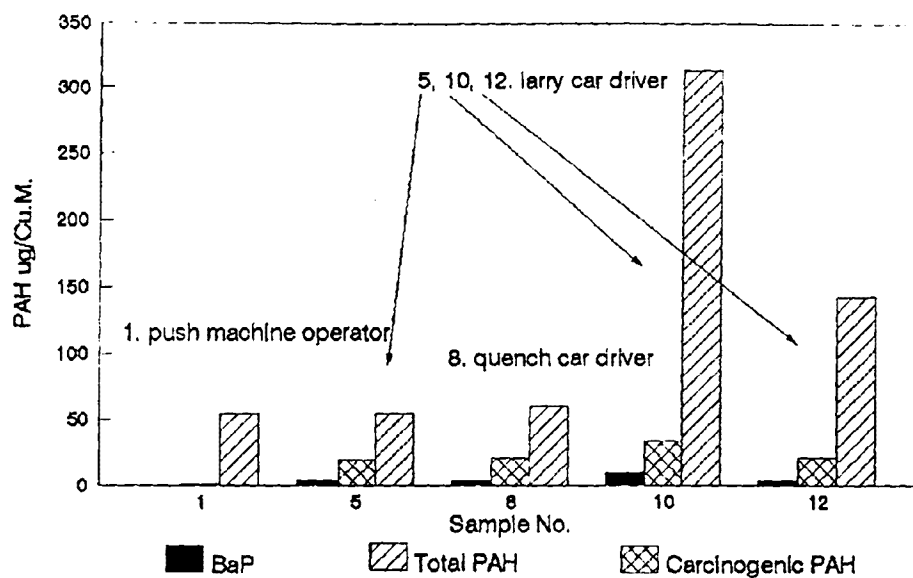


Figure 2. Personal monitoring of coke oven workers for PAH exposures.

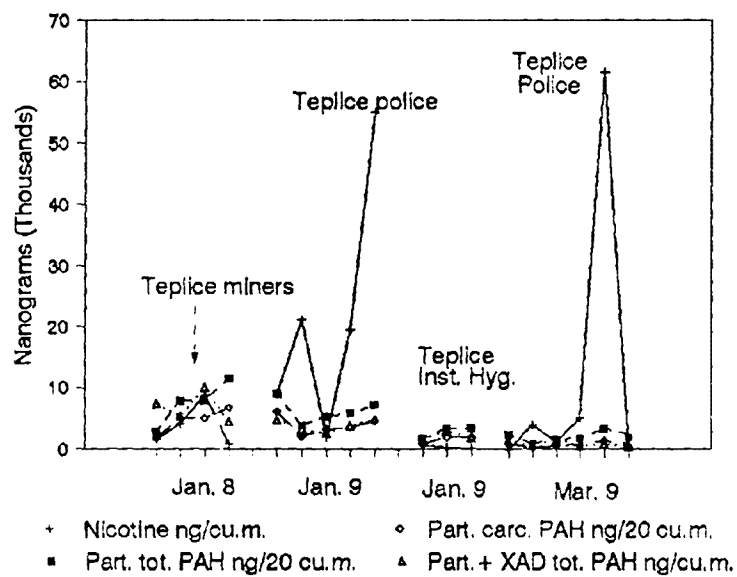


Figure 3. Personal sampler comparison of nicotine and PAH

**Evaluation of the Transfer Efficiency of High Molecular Weight
Hydrocarbons Using Various Types of Regulators**

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We prepare complex mixtures of VOCs in 1.5 liter high pressure cylinders. These cylinders are used as proficiency test samples. We also provide a regulator with those samples supplied to participants in the PAMS network. Different regulator types from various suppliers were evaluated for cleanliness, recovery efficiency and our ability to reclean them for use with compounds in the parts per billion range. All regulators were alternately attached to the same cylinder containing UHP nitrogen. For each regulator, about 500 millimeters of nitrogen that had passed through it were cold trapped and analyzed by GC/MS. The number of chromatographic peaks and total area was recorded. All regulators were then made dirty by attaching to a 20 ppmv source of VOCs and purging the regulator. The regulators were then cleaned by purging with UHP nitrogen. This nitrogen was analyzed as before and the number of peaks and area was noted. All cylinders were attached to a source of 50 ppbv C2-C10 hydrocarbons and evaluated for relative recovery. Low dead volume, highly polished, single stage regulators proved to be the regulator of choice for our purposes.

The information in this abstract has been funded wholly by the U.S. EPA. It has been subjected to Agency review and approved for submission to the A&WMA.

Simplified Preparation of TO14 and Title III Air Toxic Standards Using a Windows Software Package and Dynamic Dilution Schemes

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The preparation of Air Toxic standards in the laboratory can be performed using several methods. These include injection of purge and trap standards, static dilution from pure compounds, and dynamic dilution from NIST traceable standards. Static dilution and dynamic dilution are the preferred choices as they keep high methanol concentrations from being introduced into the TO14 SUMMA passivated sample containers (methanol is a TITLE III target compound). Using static and dynamic dilution, standards can be created accurately with the flexibility to add new compounds to a laboratory's list of target analytes at a very low cost.

Using static and dynamic dilution in the laboratory to prepare standards containing 40 to 80 target analytes requires performing complex, time consuming calculations. To simplify manually performed calculations, corrections for room temperatures and barometric pressures are sometimes ignored, which can add to the error in performing these calculations. In addition, mass flow controllers are assumed to be correct rather than trying to manually determine and implement correction factors for each flow channel using multipoint calibrations.

A software package running under Windows has been developed that makes calculating dilution parameters for even complex mixtures fast and simple. Compound parameters such as name, molecular weight, boiling point, and density are saved in a data base for later access. Gas and liquid mixtures can be easily defined and saved as an inventory item, with preparation screens that calculate appropriate transfer volumes of each analyte. These mixtures can be utilized by both the static and dynamic dilution analysis windows to calculate proper flow rates and injection volumes for obtaining requested concentrations. A particularly useful approach for making accurate polar VOC standards will be presented.

Results from the August 1993 DOAS Evaluation in Baytown, Texas

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An EPA-sponsored field study to further evaluate DOAS technology took place in Baytown, Texas in August, 1993. The goals of the study were to evaluate calibration and audit procedures and to further evaluate DOAS performance in an area with potentially high pollution levels. The gases being measured were ozone, nitrogen dioxide, and sulfur dioxide. Two separate DOAS systems were operated simultaneously using nearly identical air paths. Two sets of conventional point measurement monitors were operated at the site to provide EPA-approved reference concentration measurements. Hourly-average concentration measurements were recorded from all measurement systems. Intercomparisons of the various data sets have been carried out. Excellent agreement between the two DOAS systems and between the two point measurement systems was seen. The agreement between the DOAS and point measurement systems varied from excellent to poor, depending upon the gas being measured. The quality of the correlations between the two fundamentally different techniques was dependent upon the homogeneity of the air mass. When nearby sources were present, the pollutant plume at the monitoring site was narrow enough to differentially affect the two types of monitors. Thus the different techniques measured different concentrations and the data correlations were degraded.

Effects of Using Nafion® Dryer on Hydrocarbons Analyzed from Canisters by Modified EPA Method TO-14

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ABSTRACT

Hydrocarbons in the range of C₂ to C₁₂ were analyzed from SUMMA-polished stainless steel canisters by cryogenic preconcentration, desorption with boiling water and high-resolution capillary-column gas chromatography with flame ionization detection. Eight samples taken inside a highway tunnel were analyzed with and without a Nafion® dryer (Perma Pure Products, Inc.). The membrane successfully removed water and polar species like methanol and ethanol, however, it also removed a significant amount of the olefins and aromatics and lowered the total measured ppbC by 10-15%. The paraffins seemed to be less influenced by the membrane. Several other peaks were noted to appear when using the membrane. We therefore do not recommend using this type of water-removing device when performing sepiciated hydrocarbon analyses.

INTRODUCTION

Water removal membranes are used extensively prior to cryogenic preconcentration in the analysis of hydrocarbons by EPA Method TO-14 (US EPA, 1988¹), which recommends the use of such devices and states that there is "no substantial loss of targeted VOCs..." when using such devices. However, there has been little discussion in the literature of the effects of these devices when analyzing for total non-methane hydrocarbons (TNMHC) (Cochran 1987²; Coutant and Keigley 1988³; Pieil, et al. 1987⁴). We report here on some preliminary work assessing the effects of the Nafion® dryer (Perma Pure Products, Inc.) conducted as part of a larger study.

EXPERIMENTAL METHODS

Sample Collection

Samples were collected as part of a study to measure on-road vehicle emissions (Pierson, et al. 1994⁵). The samples reported on here were collected in the Tuscarora Mountain Tunnel on the Pennsylvania Turnpike in south-central Pennsylvania. During this study eleven sampling periods of one hour were conducted to determine emission rates from on-road motor vehicles. By selecting various times of day and days of the week, a range of fleet composition (and thus exhaust species profiles) were obtained. In this study the fleet composition ranged from 20 to 94% light-duty spark-ignition vehicles with the remainder of the fleet consisting primarily of heavy-duty diesel trucks. For the lighter hydrocarbons (those generally analyzed out of canisters) there was little difference between the light- and heavy-duty vehicles (Sagebiel, et al. 1994⁶; Zielinska, et al. 1994⁷). There was considerable atmospheric moisture during the sampling periods with an average relative humidity of 85%, thus we were concerned that the moisture would influence the analysis.

Whole air samples were collected in SUMMA-passivated canisters by means of an active pumpex sampling system designed to fill the canister to about one atmosphere above ambient pressure at the end of the sampling period. For more details on the collection and methods of the tunnel study, see Pierson et al. 1994⁵ and Zielinska, et al. 1994⁷.

Sample Analysis

The samples presented in this paper were analyzed twice: once with the Nafion® dryer and once without. In either case the methods of analysis was identical except for the dryer. The method employed is a modified EPA method TO-14, the details of which are given in Zielinska, et al. 1994⁷. Briefly, sample aliquot was transferred by use of a vacuum system to a freeze-out loop made from chromatographic-grade stainless steel tubing packed with 60/80 mesh deactivated glass beads. The loc

was cooled by immersion in liquid oxygen. The trap was then flash-heated with hot water and via a rotary valve switched to transfer the condensed NMHC into the gas chromatograph for analysis. The chromatographic column used was a 60 m long J&W DB-1 fused silica capillary column with a 0.32 mm inside diameter and 1 μ m phase thickness. To help the chromatographic system deal with the extra moisture, an approximately 1 m long section of 0.53 mm id deactivated fused silica tubing was used as a pre-column. The larger diameter prevented an ice plug from blocking the column. The oven temperature program was: -50° C for 2 min., to 220° C at 6° C per min. The GC/FID response was calibrated in ppbC, using NIST Standard Reference Material (SRM) 1805 (254 ppb of benzene in nitrogen). Since this column did not provide complete separation of the C2 and C3 hydrocarbons a second chromatographic run on a J&W GS-Q column was used to obtain values for these light hydrocarbons. Since the GS-Q is unaffected by water, no attempt was made to remove water prior to this analysis. Thus the results presented here are for the C4 and above compounds only.

RESULTS AND DISCUSSION

The Nafion® dryer has been reported previously (Cochran 1987²; Coutant and Keigley 1988³; Pieil, et al. 1987⁴) to be effective at removing water and other polar compounds without adversely affecting the major components in the sample. However, in the present study we were quantifying approximately 160 hydrocarbons species, many of which were present in small quantities. The TNMHC quantities in these samples ranged from approximately 100 to over 400 ppbC (Table 1), which are among the lowest concentrations seen in highway tunnel measurement, and is even lower than would typically be seen in ambient air measurement in urban areas. As a result, a larger volume of air had to be transferred to the freeze-out loop and subsequently a larger amount of atmospheric moisture. This extra moisture presented a problem and resulted in the loss of resolution for some compounds. However, after assessing the effect of the Nafion® dryer we decided not to use it for the tunnel project.

The effect of the Nafion® dryer on the major groups of hydrocarbons is presented in Table 1. The paraffins were generally less affected than were the other groups. The non-HC grouping consists of oxygenated, chlorinated, and other compounds found in the sample. These are generally strongly removed by the dryer, as is expected. One sample (EPR9) suffered significant losses from all three groups of compounds. This is an unusual case and may not be representative of the effect of the dryer.

Some selected compounds from sample EPL1 are presented in Table 2. These are grouped the same as Table 1, and are in order of highest concentration to lowest. Again, the paraffins are influenced very little, while some of the olefinic species are influenced very strongly. Among the aromatics, it appears that those with higher molecular weight are affected more than lower molecular weight compounds. It is apparent that the effect of the dryer is different for different compounds and that some compounds are very strongly affected.

As it can be seen from Table 1, the Nafion® dryer also lowered the TNMHC concentration by 10-20%. While this may not be a large amount, it is significant, and since there are alternative methods to using a dryer, we recommend that an assessment be made of the effect of the dryer before it is employed for analysis of speciated hydrocarbons in air.

CONCLUSIONS

We have presented here some preliminary results on the assessment of the effects of a Nafion® dryer on the non-methane hydrocarbons determined by a modified EPA Method TO-14. Based on these findings, we do not recommend the use of this or similar drying membranes for speciated hydrocarbon determination.

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Table 1. Results of analyses with and without the Nafion[®] dryer. Values are ppbC for each group and total non-methane hydrocarbon (TNMHC).

Totals	Without	With	% Drop
EPL1			
Paraffins	39.78	41.07	-3%
Olefins	27.35	11.65	57%
Aromatics	27.47	26.35	4%
TNMHC	94.6	79.07	16%
Other non-HC	88.03	36.23	59%
EPL2			
Paraffins	181.04	160.12	12%
Olefins	51.57	33.53	35%
Aromatics	137.75	121.06	12%
TNMHC	370.36	314.71	15%
Other non-HC	163.41	57.08	65%
EPL3			
Paraffins	53.19	40.19	24%
Olefins	18.94	15.03	21%
Aromatics	39.48	32.77	17%
TNMHC	111.61	87.99	21%
Other non-HC	124.43	48.19	61%
EPL4			
Paraffins	212.51	196.07	8%
Olefins	66.28	49.55	25%
Aromatics	184.44	164.26	11%
TNMHC	463.23	409.88	12%
Other non-HC	137.57	48.46	65%
EPL5			
Paraffins	149.32	134.57	10%
Olefins	38.91	25.55	34%
Aromatics	126.21	115.88	8%
TNMHC	314.44	276.00	12%
Other non-HC	62.56	34.97	44%
EPR1			
Paraffins	54.36	43.94	19%
Olefins	13.60	11.06	19%
Aromatics	33.51	29.46	12%
TNMHC	101.47	84.46	17%
Other non-HC	62.5	16.48	74%
EPR9			
Paraffins	324.53	173.68	46%
Olefins	97.47	43.63	55%
Aromatics	279.68	157.86	44%
TNMHC	701.68	375.17	47%
Other non-HC	186.00	25.67	86%
EPR10			
Paraffins	109.23	79.34	27%
Olefins	32.84	17.48	47%
Aromatics	84.17	65.88	22%
TNMHC	226.24	162.70	28%
Other non-HC	60.36	18.59	69%

NOTES:

% Drop = (without Nafion[®] - with Nafion[®])/Without Nafion[®]

"Other non-HC" category is a grouping of oxygenated, chlorinated and other compounds found in these samples. Since these were not individually calibrated for, the results are relative only.

Table 2. Effect of Nafion dryer on selected compounds from EPL1. Note the significantly larger drop for the olefins over the other groups.

	Without	With	% Drop
Paraffins			
Isopentane	4.28	4.37	-2%
2-MePentane	2.69	2.37	12%
n-Butane	2.42	2.33	4%
n-Hexane	2.38	2.13	11%
n-Pentane	2.08	1.91	8%
Olefins			
2-Me-2-Butene	7.55	0.31	96%
2-Me-1-Pentene	3.94	0.81	79%
1Butene+iButylene	3.93	3.32	16%
4-Me-1-Pentene	1.65	1.69	-2%
1,3-Butadiene	1.52	1.20	21%
Cyclohexene	1.47	0.34	77%
t-2-Pentene	0.47	0.35	26%
2-Me-1-Butene	0.37	0.20	46%
Aromatics			
Benzene	4.63	4.38	5%
Toluene	7.56	6.83	10%
EtBenzene	1.07	0.99	7%
m/p-Xylene	4.07	3.93	3%
Styrene	0.80	0.74	8%
o-Xylene	2.25	2.04	9%
nPropBenzene	0.45	0.39	13%

Statistical Distributions of Airborne PCB and Pesticide Concentrations Measured at Regional Sites on the Great Lakes.

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ABSTRACT

The purpose of this paper is to report results of testing measured concentrations of total PCBs and ten chlorinated pesticides in air and precipitation in the Great Lakes area for goodness-of-fit to the lognormal distribution. Samples were collected at sites on Lakes Superior, Michigan, Erie, and Ontario in 1991-1993. With very few exceptions, distributions of concentrations in the gas and particle phases and in precipitation were not significantly different from lognormal.

INTRODUCTION

Concentrations of total PCBs and ten chlorinated pesticides have been measured in air and precipitation over periods of 20-33 months at four regionally-representative locations in the bi-national Integrated Atmospheric Deposition Network (IADN) on the Great Lakes. The purpose of the measurements is to provide information needed to estimate atmospheric deposition of toxic materials to the lakes. It is useful to know whether the measured concentrations conform to standard statistical distributions, both to describe pollutant concentrations in air or in precipitation, as well as to guide summarization and future uses of such data.

The lognormal distribution has frequently been found to describe the distribution of common criteria air pollutants (1). However, relatively few measurements have been made of such non-criteria pollutants as PCBs and chlorinated pesticides, and their dominant distributional model is not well established.

The purpose of this paper is to report results of testing the observed distributions for goodness of fit to the standard lognormal distribution.

METHODS

Sampling sites are shown in Figure 1. Data used in this paper were derived from samples collected at sites located at Eagle Harbor, Michigan, on Lake Superior; at Sleeping Bear Dunes National Lakeshore, on Lake Michigan; at Sturgeon Point on Lake Erie; and at Point Petre, Ontario, on Lake Ontario. Canadian scientists also collect samples on Burnt Island in Lake Huron, but data from that site are not examined here. Twenty-four hour samples of airborne particles and vapor were collected at 12-day intervals on glass fiber filters and vapor traps of polyurethane foam (PUF) or XAD-2 resin, using modified high volume samplers. Twenty-eight day precipitation samples were collected using wet-only samplers with stainless steel sampling surfaces and a heated enclosure containing an XAD-2 absorption column. The XAD and PUF sorbents and the glass fiber filters were Soxhlet-extracted for 24 hours with 1:1 hexane/acetone, concentrated by rotary evaporation, and then cleaned and fractionated by column chromatography with silica gel. Fractions eluting from the

silica column were analyzed for 103 PCB congeners and ten pesticides using GC/ECD (2, 3). Logarithms of the measured concentrations in air and precipitation were tested for normality by the Lilliefors variation of the nonparametric Kolmogorov-Smirnov test using SYSTAT statistical software.

RESULTS

Results of the tests of goodness-of-fit to a lognormal distribution are given in Table 1. Very few distributions were found to be statistically different from the lognormal distribution at the 1% or 5% levels. In at least one case (gas-phase HCB at the Sleeping Bear site; see Figure 2), a single questionable data point appears to have been the cause of the significant probability.

Figure 2 shows distributions of four selected compounds plotted as blank-corrected concentrations on a \log_{10} scale vs. percentile on a probability scale. Lognormally-distributed concentrations will appear as a straight line on such a plot. The lowest concentrations shown may have percentile values of 10-30%, or even higher. This was the result of blank subtraction reducing the net concentrations of many samples to zero, which cannot be plotted on a log scale. These plots also show the limit of detection (LOD), which is defined as the mean matrix-specific field blank (over all sites) plus three standard deviations.

It is clear from the distribution plots that, consistent with the statistical goodness-of-fit tests, the concentrations of most compounds display a close approximation to straight lines in the gas-phase, the particle-phase, and in precipitation. The upper and lower tails of the distributions show occasional deviations from straight lines. Upper-tail deviations may signal strong local sources, as in the case of gamma-HCH (Lindane) at the Sleeping Bear site (Figure 2), where occasional use in local orchards is suspected. Co-elution interferences are another possibility. Deviations at the lower tails are more frequent, and are probably related to the vagaries of the blank correction procedure at low concentrations.

While a detailed comparison of concentrations between sites and between gas, particle, and precipitation phases is beyond the scope of this paper, it is worthwhile to point out some obvious features. For most of the compounds analyzed in this work, including those shown in Figure 2, gas-phase concentrations exceed those of the particle phase, sometimes substantially. Gas-particle partitioning is known to be a function of the vapor pressure of the compound.

Variations in concentration between sampling sites are also apparent. Typically, the Sturgeon Point (Lake Erie) and Point Petre (Lake Ontario) sites experience the higher concentrations. Some compounds demonstrate that they are well-mixed in the atmosphere by showing little variation between sampling sites, particularly in the gas phase; HCB is a good example (Figure 2).

CONCLUSIONS

Gas-phase, particle-phase, and precipitation concentrations of field-blank-corrected total PCBs and the ten pesticides examined in this paper were found to be not statistically different from the lognormal distribution in nearly every case at four Great Lakes sampling sites.

ACKNOWLEDGEMENTS

This paper would not have been possible without the diligent efforts of all those who collected the samples in the field, sometimes under adverse conditions, and those who analyzed them in the laboratory. Sherman Bauer provided timely computer help. This work was supported by the U.S. Environmental Protection Agency (EPA), Great Lakes National Program Office, under Contract No. GL995476-01-1.

DISCLAIMER

This paper has not been subjected to EPA policy review and should not be construed to represent the policies of the agency. Mention of any product name does not constitute endorsement.

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Table 1. Probabilities given by the Lillicfors variation of the nonparametric Kolmogorov-Smirnov test that concentrations of airborne toxic organic compounds are lognormally-distributed. Values in bold face indicate instances where the hypothesis may be rejected at the 1% significance level, or better, based on a Bonferroni-adjusted critical probability of $0.01/44 = 0.00023$ for 44 comparisons. The corresponding critical probability for 5% significance is 0.00114. Probabilities are not given for $N < 10$.

a) Gas phase.

Compound	Eagle Harbor		Pt. Petre		Sleeping Bear		Sturgeon Pt.		No. significant at:	
	N	Prob	N	Prob	N	Prob	N	Prob	1%	5%
alpha-Chlordane	34	0.38745	33	0.67741	37	0.13609	38	0.56710	0	0
gamma-Chlordane	34	0.17086	33	0.54109	37	0.00309	38	0.90097	0	0
DDD	49	0.07481	49	0.80145	46	0.47444	51	0.28694	0	0
DDE	72	0.04480	59	0.76009	54	0.39466	52	0.93699	0	0
DDT	52	0.30595	67	0.19071	54	0.36634	54	0.21648	0	0
Dieldrin	74	0.77336	72	0.21752	56	0.54467	18	0.10328	0	0
HCB	73	1.00000	60	0.00136	55	0.00000	51	0.24681	1	1
alpha-HCH	84	1.00000	80	0.99444	57	0.34531	59	0.18584	0	0
gamma-HCH	84	0.00648	80	0.05912	56	0.00046	59	0.00434	0	1
trans-Nonachlor	34	0.10899	32	0.80774	36	0.17317	38	0.33968	0	0
Total PCBs	78	0.17912	78	0.01352	55	0.06992	54	0.93863	0	0
Totals									1	2

b) Particle phase.

Compound	Eagle Harbor		Pt. Petre		Sleeping Bear		Sturgeon Pt.		No. significant at:	
	N	Prob	N	Prob	N	Prob	N	Prob	1%	5%
alpha-Chlordane	6	0.21111	5	---	5	---	7	---	0	0
gamma-Chlordane	18	0.00022	13	0.34872	12	0.43474	14	0.47063	1	1
DDD	11	1.00000	5	---	5	---	11	0.36180	0	0
DDE	22	0.20316	20	0.04092	16	0.30222	17	0.83685	0	0
DDT	19	0.80166	25	0.55681	11	0.95210	17	0.10187	0	0
Dieldrin	14	0.57388	14	0.48382	13	1.00000	12	1.00000	0	0
HCB	24	0.00751	18	0.16842	14	0.82408	17	0.22970	0	0
alpha-HCH	18	1.00000	14	0.82046	10	0.06632	10	0.47319	0	0
gamma-HCH	19	0.76274	21	0.33913	11	1.00000	14	0.18308	0	0
trans-Nonachlor	20	0.91907	12	0.98615	10	1.00000	12	1.00000	0	0
Total PCBs	26	0.00740	25	0.63075	13	0.07375	17	0.92447	0	0
Totals									1	1

c) Precipitation.

Compound	Eagle Harbor		Pt. Petre		Sleeping Bear		Sturgeon Pt.		No. significant at:	
	N	Prob	N	Prob	N	Prob	N	Prob	1%	5%
alpha-Chlordane	17	0.51924	6	---	12	1.00000	9	---	0	0
gamma-Chlordane	17	0.28085	14	0.62704	15	0.72697	16	0.09071	0	0
DDD	5	---	8	---	6	---	10	0.88816	0	0
DDE	28	0.32772	26	0.24768	17	0.07842	25	1.00000	0	0
DDT	19	0.47176	23	0.12388	20	1.00000	20	0.99457	0	0
Dieldrin	29	1.00000	28	0.58466	18	0.52451	24	0.58326	0	0
HCB	32	0.93477	28	0.57274	22	0.52539	24	0.01840	0	0
alpha-HCH	28	0.24376	30	0.24458	18	0.19583	22	0.53775	0	0
gamma-HCH	27	0.69745	27	0.98416	17	0.14638	18	0.88656	0	0
trans-Nonachlor	14	0.89574	13	0.18950	12	0.86128	10	0.22915	0	0
Total PCBs	37	1.00000	32	0.59908	22	0.21214	25	0.71791	0	0
Totals									0	0

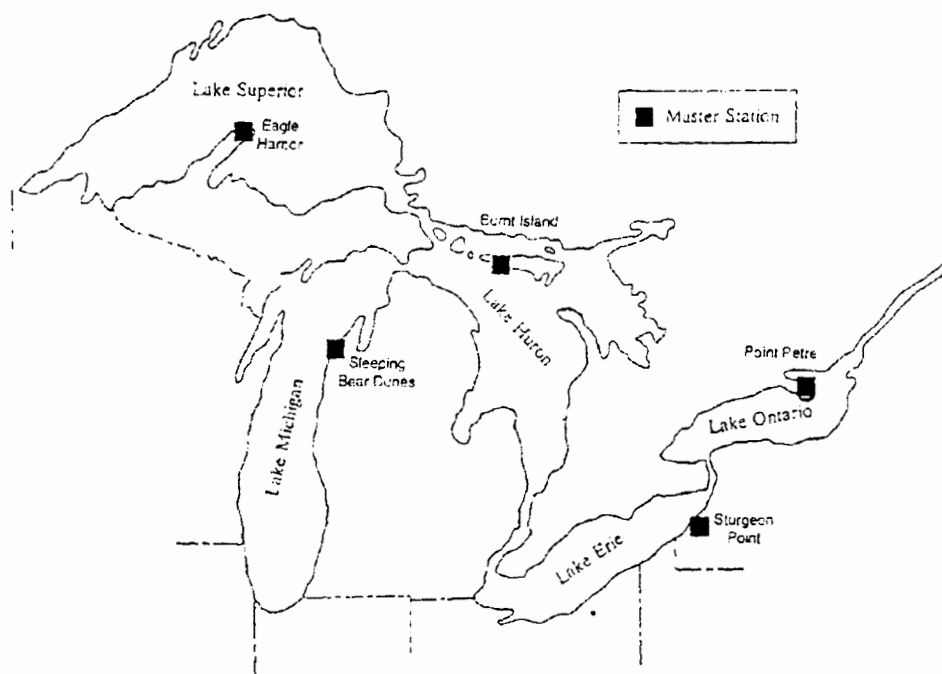


Figure 1. IADN sampling site locations.

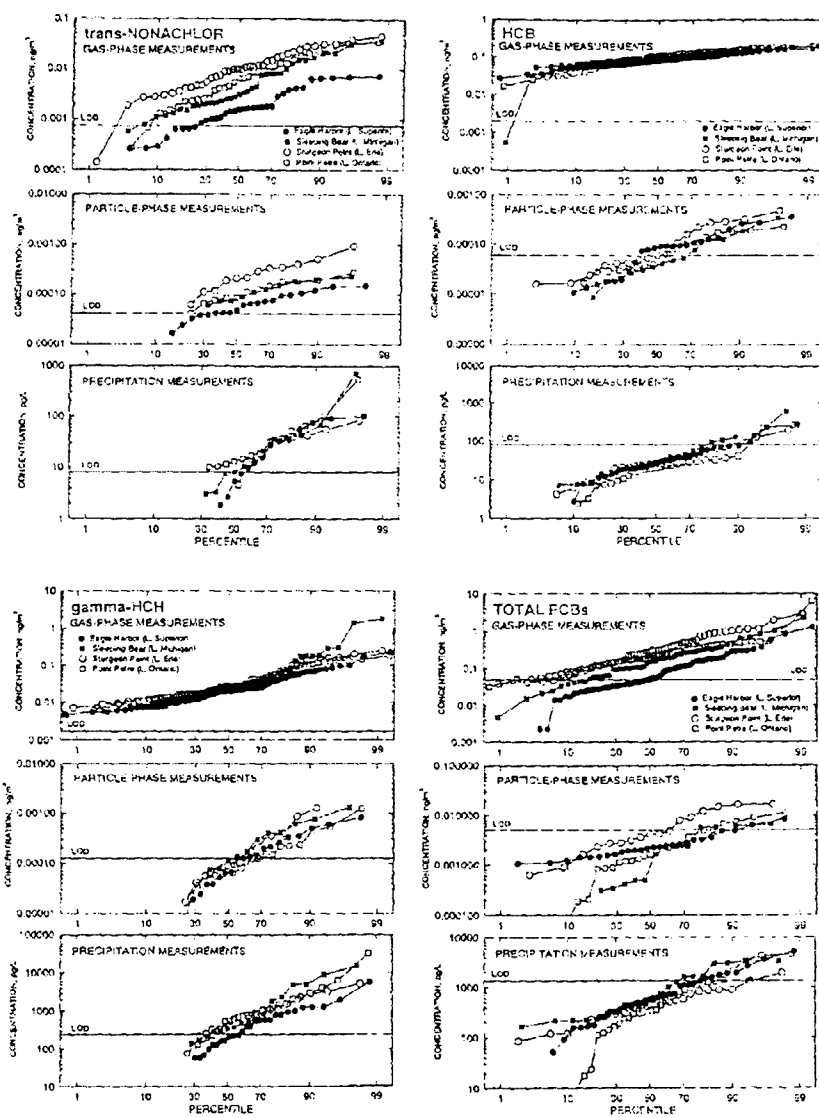


Figure 2. Observed distributions of concentrations of total PCBs and three of ten pesticides measured at four sites on the Great Lakes.

Stability of Reduced Sulphur Compounds in Whole Air Samplers

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ABSTRACT

Reduced sulphur compounds can cause odour nuisance problems associated with kraft mill and sewage treatment operations. Accurate and reliable determination of reduced sulphur compounds is often required, but it is a challenging task due to the reactivity of reduced sulphur species and consequent difficulties in collection and storage of air samples. Several whole air samplers were evaluated for storage of reduced sulphur compounds at concentrations of 100 ppb (Tedlar bag only), 1 ppm and 100 ppm. Severe losses of H_2S and mercaptans were found in samples collected in electro-polished stainless steel canisters, although these canisters have been proven suitable for many volatile organic compounds. The losses of more volatile species were less severe than less volatile ones in Teflon vials, and glass and silanized glass bottles with Teflon-lined septum caps. In general, COS, CS_2 , CH_3SCH_3 , and CH_3SSCH_3 were more stable than H_2S and mercaptans, and the reduced sulphur compounds were more stable in the Tedlar bag than in other sample containers.

INTRODUCTION

Reduced sulphur compounds are important constituents in the sulphur cycle between hydrosphere, lithosphere, biosphere and atmosphere.¹ Certain reduced sulphur compounds, such as hydrogen sulphide (H_2S), methyl mercaptan (CH_3SH or MeSH) and ethyl mercaptan ($\text{C}_2\text{H}_5\text{SH}$ or EtSH), dimethyl sulphide (CH_3SCH_3 or DMS) and dimethyl disulphide (CH_3SSCH_3 or DMDS), can cause odour nuisance problems normally associated with emissions from kraft mill and sewage treatment operations.² Therefore, measurements of reduced sulphur compounds in air are necessary for studies on sulphur chemistry and the environment, and are specifically required for certain cases of air quality assessments.³ However, accurate and reliable determination of reduced sulphur compounds is a challenging task, mainly due to the reactivity of reduced sulphur species and consequent difficulties in collection and storage of air samples containing these compounds.

A number of analytical methods (references 2, 3 and as cited in reference 4) have been applied for determination of reduced sulphur compounds in air. On-site direct measurement provides the most reliable results, and is suitable for process monitoring. However, the method is limited by field conditions and requirement for skilled field personnel capable of operating the on-site analyzers. It is also expensive or not feasible for large scale environmental studies, especially those conducted in remote areas or requiring simultaneous multi-location monitoring. Field sampling followed by laboratory analysis of samples collected from different sites affords the possibility of a full scale environmental impact assessment, but may suffer from poorer data quality caused by degradation of instable sulphur species during sample storage.

Several whole air samplers were evaluated for storage of reduced sulphur compounds at concentrations of 100 ppm, 1 ppm and 100 ppb in air. Initial test results are reported in this paper.

EXPERIMENTAL SECTION

Supplies and Instrumentation

Sample Containers. The whole air samplers evaluated included 10-L Tedlar[®] bags (with stainless steel inlet and septum ports) from SKC Inc., Eighty Four, PA (referred as Tedlar bag), 2.8-L Summa[®] canisters from Scientific Instrumentation Specialists, Moscow, ID (SIS canister), a 1.7-L electro-polished canister from KBU Environmental Technologies Inc., Hamilton, ON (KBU canister), and 0.85-L electro-polished canisters from Biospherics Research Corp., Hillsboro, OR (BRC canister). Other containers, including 30-mL Teflon vials (Oak Ridge FEP Centrifuge tubes, Nalge Company, Rochester, NY) with ETFE (Tefzel, i.e. ethylene-tetrafluoroethylene) sealing cap assembly, and 60-mL (2 oz) amber screw cap glass bottles with Teflon-lined septa (Supelco, Inc., Bellefonte, PA), were also tested. Some glass bottles were used without further treatment while others were deactivated with Supelco Sylon-CT solution (5% dimethyldichlorosilane in toluene). All sample containers had never been used.

Chemicals and gases. The reduced sulphur gas standards were prepared from a gas mixture (101 ± 2 ppm H_2S , 106 ± 2 ppm COS, 104 ± 2 ppm MeSH, 84.0 ± 1.7 ppm EtSH, and 110 ± 2 ppm CS_2 in N_2) from Matheson Gas Products Canada, Whitby, ON, and DMS (99+) and DMDS (99%), both from Aldrich Chemical Company, Inc., Milwaukee, WI. Ultra high purity helium used as the carrier gas, "zero gas" hydrogen and air used for the flame photometric detector (FPD), and the ultra dry air used for preparation of gas standards, were all from Linde Division, Union Carbide Canada Limited, Toronto, ON.

Analytical Instrumentation. An Hewlett Packard (Palo Alto, CA) HP5890 Gas Chromatograph (GC) equipped with an FPD and a 75 m x 0.53 mm x 3.0 μm DB-624 column (J&W Scientific, Folsom, CA) and an HP5890 Series II Plus GC equipped with an HP 5972 mass selective detector (MSD) and a 60 m x 0.32 mm x 1.8 μm DB-624 column were used for sample analysis. Gas samples were injected with a Hamilton #1725 (0.25-mL) gastight syringe (Reno, NE). Complete GC resolution of the 7 test compounds was achieved with a temperature program as follows: 40°C for 1 min, 5°C/min to 80°C and 25°C/min to 200°C. The helium flow rates for the megabore and capillary columns were ca. 10 mL/min and 1 mL/min, respectively. The chromatograms obtained with the GC/MSD and GC/FPD are shown in Figure 1.

Procedures

All sample containers, with the exception of the Tedlar bags, were evacuated to -100 kPa with a vacuum pump (PN. 7411-70, Canadawide Scientific Ltd., Toronto, ON). New canisters came from manufacturers/suppliers under vacuum and were evacuated again in our laboratory without other treatment procedures. Previous experience in our laboratory indicated that conditioning of canisters with moisturized air resulted in severe losses of H_2S and mercaptans. After thorough flushing of the regulator, the 100-ppm gas standard (H_2S , COS, MeSH, EtSH and CS_2) was used to fill a Tedlar bag spiked with 3 μL of DMS and 3.7 μL of DMDS to prepare a standard containing the 7 sulphur compounds at ca. 100 ppm. One SIS canister was filled with the gas standard from the 100 ppm Tedlar bag to atmospheric pressure, and slightly pressurized by adding 500 mL of the same gas standard to the canister using a 50-mL gas tight glass syringe (B-D Multifit). One Teflon vial was filled with 60 mL of the 100-ppm bag standard.

Appropriate volumes of the 100-ppm bag standard were injected into other sample containers, which were then filled with air to prepare gas standards at ca. 1 ppm. The canisters (SIS, KBU, and BRC) were filled with air to 20 psi; the glass bottle, silanized glass bottle, and Teflon vial were filled with air to double volumes of their nominal capacities; the Tedlar bag was filled to volume (10 L). A 100-ppb standard in the Tedlar bag was prepared with proper dilution of the 100-ppm Tedlar bag standard.

The gas standards were analyzed within 15 minutes of preparation and during the following days using the GC/FPD and GC/MSD. The analytical relative standard deviations were 15% and 10% for the GC/FPD and GC/MSD, respectively. To assess the sample stability, the analytical results of the 1-ppm and 100-ppm samples were compared, respectively, with the results of the 1-ppm and 100-ppm Tedlar bag standards, whose initial values upon preparation were assigned as 100 in Tables 1, 2 and 3.

RESULTS AND DISCUSSION

Non-Conventional Sample Containers

The silanized or non-silanized glass bottles and Teflon vials used in this study were not containers regularly used for air sampling. They were made of different materials and the physical and chemical properties of their inner surfaces differed from those of the conventional air samplers. They were therefore tested for comparison with the commonly used air sample containers. Compared to canisters whose metal inner surfaces, though deactivated, might act as a catalyst for the reactive reduced sulphur species, the glass and Teflon surfaces might provide the possibility of reducing sample losses during storage. However, the test results did not suggest apparent advantages of using these containers for sampling reduced sulphur compounds in air.

In general, the losses of H_2S and COS were less severe than the other 5 compounds in these non-conventional sampler containers. Within 24 hours, the concentrations of MeSH, EtSH, DMS, CS_2 and DMDS in the glass bottle and Teflon vials were reduced to less than 25% of the original values, with the exception of MeSH in the glass bottle. The silanized glass bottle was better than the other three containers for MeSH, EtSH and DMS. The magnitudes of decrease were similar for samples at 1 ppm and 100 ppm levels in Teflon vials. Concentrations of MeSH, EtSH, DMS, CS_2 and DMDS in all these containers further decreased with time, most to less than 1% after 12 days of storage (Table I). It appeared that the stability of the test compounds were related to their volatility.

Canisters

The storage stabilities of reduced sulphur compounds in canisters were apparently different and also varied with different canisters (Table 2). It was obvious that the stability of the test compounds in canisters were more dependent on their reactivity rather than volatility.

SIS Canister. At 1 ppm level, at least 70% of H_2S , MeSH and EtSH vanished once prepared in the SIS canister and the concentrations of these compounds further decreased with time to less than 5%. No significant losses were observed for other four compounds. At 100 ppm, all 7 compounds were relatively stable.

BRC Canister. H_2S , MeSH and EtSH practically disappeared upon introduction into the BRC canisters. The concentrations of the other four compounds decreased with time.

KBU Canister. This sampler appeared to be even worse than the BRC canister. In addition to H_2S , MeSH and EtSH, DMS was also eliminated upon entering the canister.

Tedlar Bag

It was observed that when reduced sulphur compounds at 100 ppb were prepared in the bag, losses up to 30% occurred. By comparison with the COS response, it was certain that losses of 10% occurred for H₂S when the 1-ppm bag was prepared and it is why the initial value for H₂S is listed as 90 in Table 3. The losses throughout the storage period of the 1-ppm bag were not significant for most compounds. The storage losses of the less volatile compounds were slightly greater than the more volatile ones (except H₂S), suggesting the losses were likely due to surface adsorption. This was similar to the observation with glass bottles and Teflon vials. Losses of the 100-ppb sample were 5% to 40% more severe than the 1-ppm one, while the losses of 100-ppm sample were not obvious during the test period.

CONCLUSIONS

Although the Tedlar bag also suffered from sample losses, it was the most favourable device for whole air sampling of reduced sulphur compounds.

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Table 1. Stabilities of reduced sulphur compounds in non-conventional air samplers

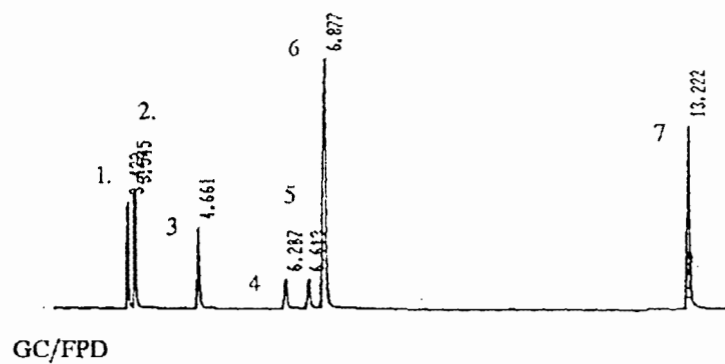
	H ₂ S	COS	MeSH	EtSH	DMS	CS ₂	DMDS
Silanized glass (1 ppm)							
Within 15 minutes	107	87	97	90	101	110	93
1 day	91	93	95	93	54	30	5
2 days	90	100	90	83	30	15	1
12 days	30	50	10	<1	<1	<1	<1
Glass bottle (1 ppm)							
Within 15 minutes	91	110	106	78	87	79	91
1 day	95	89	70	25	24	20	1
2 days	85	84	50	17	14	7	<1
12 days	20	30	<1	<1	<1	<1	<1
Teflon vial (1 ppm)							
Within 15 minutes	96	79	90	87	77	109	67
1 day	73	56	15	15	8	2	5
2 days	60	43	6	5	3	1	1
12 days	50	6	3	<1	<1	<1	<1
Teflon vial (100 ppm)							
within 15 minutes	111	91	104	103	91	87	93
1 day	77	72	16	16	10	12	10
2 days	67	54	13	12	13	5	5
12 days	50	6	<1	<1	<1	<1	<1

Table 2. Stabilities of reduced sulphur compounds in canisters

	H ₂ S	COS	MeSH	EtSH	DMS	CS ₂	DMDS
SIS canister (100 ppm)							
Within 15 minutes	95	107	99	93	103	89	92
1 day	96	85	87	89	84	84	83
2 days	103	81	74	62	78	62	61
12 days	98	78	64	68	71	77	84
SIS canister (1 ppm)							
Within 15 minutes	28	95	30	30	97	93	102
1 day	17	86	23	15	105	95	97
2 days	2	76	6	7	125	111	121
12 days	<1	64	3	2	82	85	87
BRC canister (1 ppm)							
Within 15 minutes	14	98	9	19	80	95	89
1 day	4	86	3	7	81	82	109
2 days	<1	67	1	2	83	82	88
12 days	<1	70	<1	<1	75	67	73
KBÜ canister (1 ppm)							
within 15 minutes	13	93	1	7	12	92	95
1 day	<1	86	<1	<1	<1	81	70
2 days	<1	67	<1	<1	<1	94	93
12 days	<1	70	<1	<1	<1	65	82

Table 3. Stabilities of reduced sulphur compounds in Tedlar bag

	H ₂ S	COS	MeSH	EtSH	DMS	CS ₂	DMDS
100 ppm							
Within 15 minutes	100	100	100	100	100	100	100
1 day	96	91	93	96	105	94	122
2 days	90	101	115	113	101	103	116
12 days	97	102	90	85	83	83	116
1 ppm							
Within 15 minutes	90	100	100	100	100	100	100
1 day	81	91	87	94	92	91	81
2 days	70	83	84	96	88	89	83
12 days	57	101	79	86	86	78	43
100 ppb							
Within 15 minutes	70	89	83	81	85	78	71
1 day	53	91	61	55	79	67	57
2 days	40	73	59	71	64	61	66
12 days	33	86	66	70	81	72	49



1. Hydrogen sulphide
2. Carbonyl sulphide
3. Methyl mercaptan
4. Ethyl mercaptan
5. Dimethyl sulphide
6. Carbon disulphide
7. Dimethyl disulphide

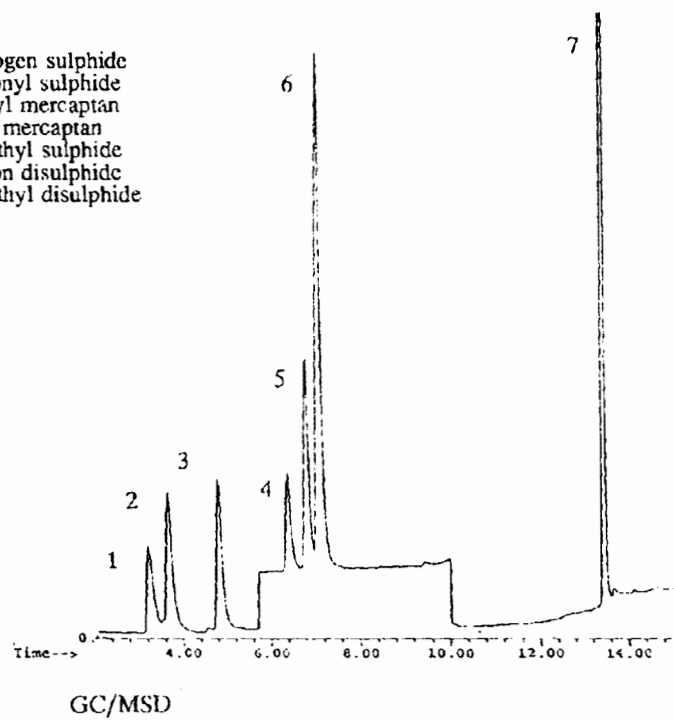


Figure 1. GC/FPD and GC/MSD chromatograms of 7 reduced sulphur compounds

A New Vapor and Gas Test Atmosphere Generator with Broad Concentration and Flow Output Capabilities

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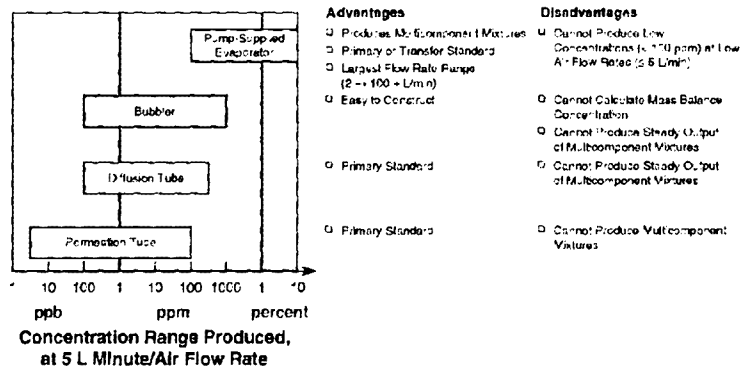
Abstract

This poster describes a dynamic flow vapor generator that can produce vapor test atmospheres of both pure compounds or mixtures with concentrations ranging from parts per billion (ppb) to percent, within the limiting constraint of the saturated vapor pressure(s). Test atmosphere flow rates can be varied from 2 L/min to over 100 L/min. The generator consists of a pump-supplied liquid evaporator coupled to a unique output control section. The output control section allows either all or a fraction of the generator vapor output to be mixed with the dilution air supply. Metering of a fraction of the generator vapor output is accomplished with a mass flow controller that requires only 0.05 atm pressure to actuate to its full scale flow. With a simple modification, the generator can also prepare gas test atmospheres.

Introduction

Laboratories that analyze ambient air directly or perform environmental chamber studies need to be able to prepare a wide range of volatile organic compound (VOC) atmospheres for calibration or test. Multiple vapor generation methods are frequently required.

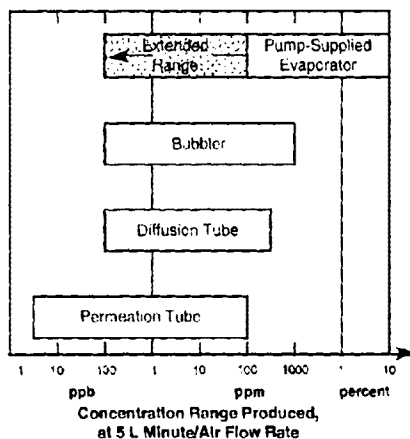
Vapor Generation Methods



We have developed a simple, reliable apparatus to safely split the output of dynamic vapor generators, and extend the lowest stable output concentration by three orders of magnitude.

Although the apparatus design is generic, and able to be coupled to most vapor generators, first applications have been with the "j-tube" liquid evaporator for use in inhalation exposure chambers.

Vapor Generation Methods



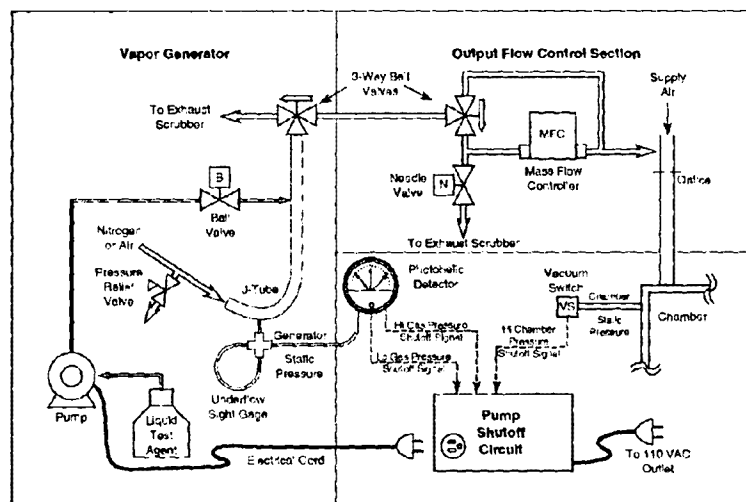
Materials and Methods

The Generation System Consists of Three Subsystems:

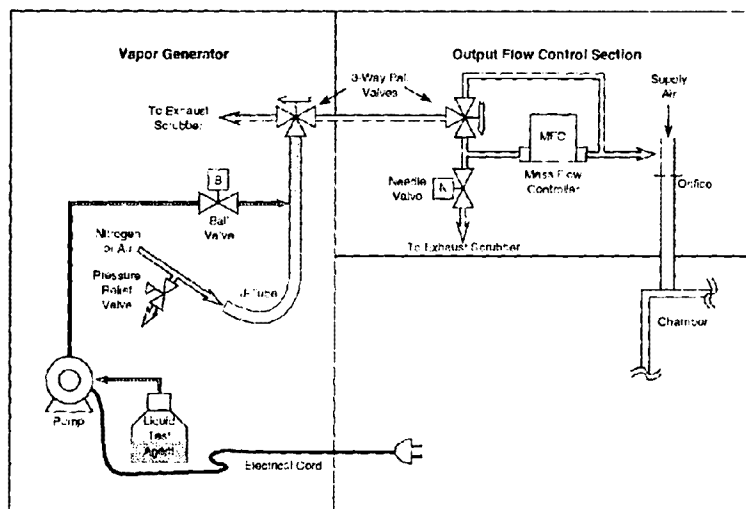
- ❑ J-Tube Countercurrent Evaporative Vapor Generator
- ❑ Output Flow Control Section
- ❑ Safety System (metering pump shutoff)

■ Schematic of Generation System

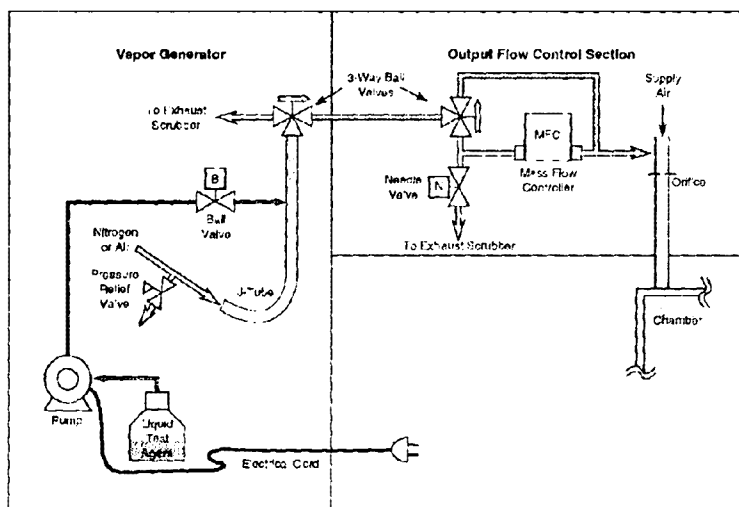
Note: Generator and output control section temperature controlled by a heating tape and variac. Generator and output flow control section are all constructed of stainless steel.



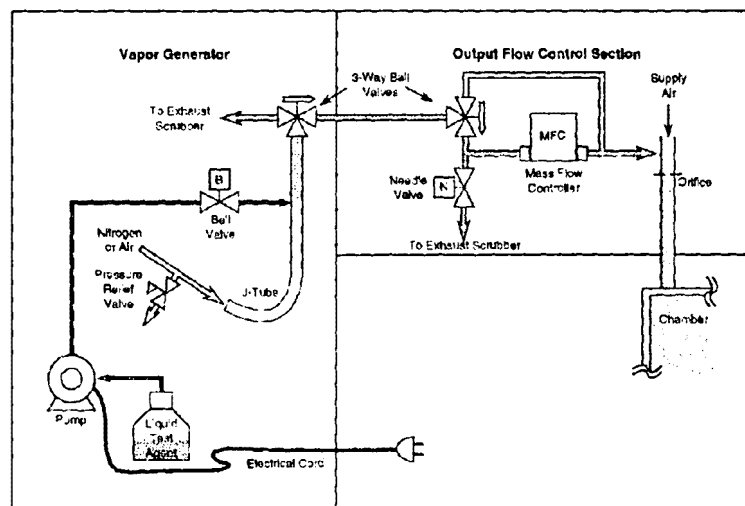
- The generation system may be operated in three independent modes, to allow none, all, or part of the vapor output to be directed to the chamber.
- **Mode #1, Bypass.** No vapor flow to chamber.
Bypass mode allows generator output to be quickly routed into and away from the environmental chamber main air flow. It is used during startup and shutdown, to keep chamber concentration rise and fall curves as sharp as possible.



- **Mode #2, Total Flow.** All vapor flow goes to chamber.
Total flow mode is used for VOC feed rates of $> 5 \text{ mg/min}$ to the chamber air supply (5 mg/min into 5 L/min total gas flow gives 100-600 parts-per-million (ppm) for most VOCs).



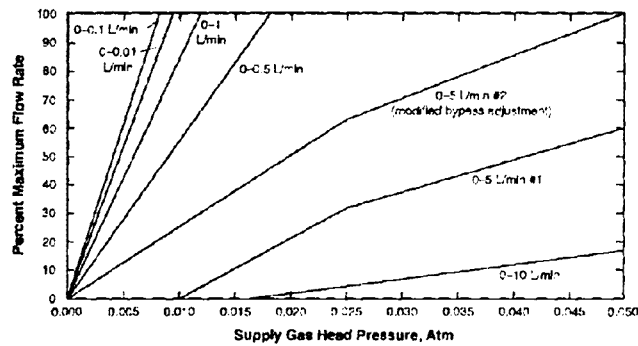
- Mode #3, Split Flow:** Part of vapor flow goes to chamber.
 Split Flow is used for VOC load rates of 5 ng/min to 5 mg/min to the chamber air supply (5 ng/min into 5 L/min total gas flow gives 100–500 parts-per-billion [ppb] for most VOCs). Excess VOC flow rate is very small (0.3 g/hr) and easily scrubbed using small charcoal filter units.



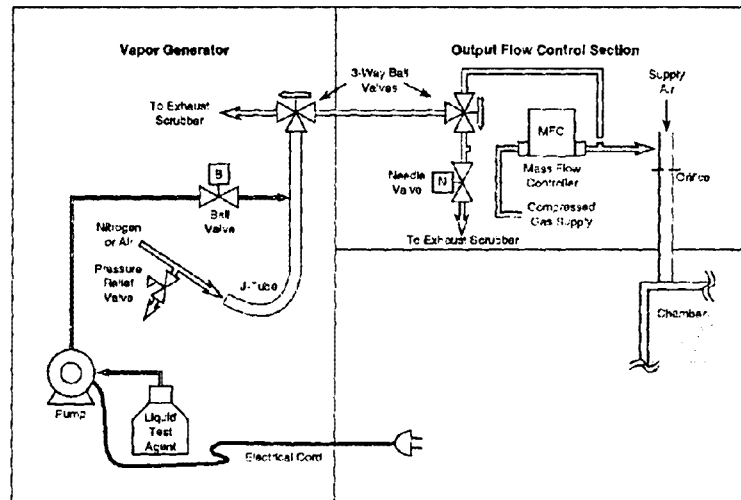
- The choice between operating in Total Flow or Split Flow modes depends upon the liquid flow rate needed to produce the desired concentration. At flow rates of less than 5 mg/min, uneven evaporation may lead to oscillations in the measured vapor concentrations, and operation in Total Flow mode may not be practical. In this case, the liquid flow rate and generator temperature should be increased to a level that gives an even evaporation rate, a new generator concentration should be calculated, and the portion of the total generator output required to give the desired chamber concentration should be determined. After an initial warm-up period in Bypass mode, Split Flow operation is begun, using the following steps:
 - Close the internal solenoid of the mass flow controller.
 - Adjust the mass flow controller setpoint to the desired setting.
 - Open the output control section needle valve fully.
 - Turn the output control section 3-way ball valve to direct the generator output to Split Flow operation mode.
 - Turn the generator output 3-way ball valve to direct vapor flow from the Bypass mode to the Split Flow mode.
 - Pressurize the generator to 0.05 atm pressure by adjustment of the needle valve.
 - Open the mass flow controller internal solenoid valve to begin vapor flow to the environmental chamber.
- There are several advantages of splitting generator output flow using a mass flow controller, as compared to rotameters or other devices:
 - Flow rates are not affected by changes in supply gas temperature and pressure.
 - Precise, automated control of desired flow rate.
 - Mass flow controller may be heated to 70 °C.

- Very low head pressures are required to achieve full-scale flows, so vapor condensation is not a problem.

**Percent Maximum Flow Rate Versus Supply Gas Head Pressure
for TYLAN FC 280 Mass Flow Controllers**
(all are unmodified stock, except 0-5 L/min #2)



- By a simple modification of the output flow control section, gas test agent atmospheres can also be prepared:
Mode #4, Gas Metering. Compressed gas sources metered to chamber.
Cylinders are plumbed to mass flow controller inlet; the remainder of the generation system is unused in this operation mode.



Results and Discussion

- There are currently 11 copies of this generation system design operating in 4 laboratories.
- The oldest has been in service since 1990.
- They have been used to prepare test atmospheres of the following chemicals:
 - Vapor
 - *n*-Butanol
 - *n*-Butyl Acetate
 - Carbon Disulfide
 - Chloroform
 - Methanol
 - Methyl *t*-Butyl Ether
 - Mixtures of Dimethyl Succinate, Dimethyl Glutarate, and Dimethyl Adipate
 - Mixtures of Chloroform and Trichloroethylene
 - Toluene
 - Trichloroethylene
 - *m*-Xylene
 - Gas
 - Phosphine
- Vapor concentrations produced ranged from ppb to percent, in chambers varying in size from 1.7 to 422 L. Concentration output has proven to be stable and reliable in each mode of operation.
- For all studies, calculated concentrations were based on gravimetric calibrations of generator and output control section gas flows, and either wet test or dry gas meter calibration of chamber air flow rates.
- Measured concentrations were made with independently calibrated infrared spectrophotometers or gas chromatographs.
- Agreement between calculated and measured concentrations was within 10% for almost every run; larger errors were traced to altered chamber air flow rates caused by shifted orifice plate calibrations or chamber leaks.

Conclusions

- Generation system operation is simple and straightforward in all modes.
- Output flow control system is applicable to extending lowest stable concentrations of other dynamic generators.
- Small size of system allows construction of portable systems.
- Agreement between calculated and measured concentrations shows promise for development as a calibrator for air monitoring instrumentation.

Acknowledgments

We would like to thank Will Doyes, Phil Bushnell, and Ken Hudnell for allowing the development of the output control section apparatus during construction of their inhalation exposure facilities; John Bobrowski, Paul Killough, and Earl Puckett for construction of containment hoods and j-tubes; Mark H. Guchi for sharing a stainless steel j-tube design; George Hudson for design and construction of electromechanical safety circuits.

This work was performed under contract 68-D2-0056. Contents do not necessarily reflect the views and policy of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

**Air Monitoring at Alert in the High Arctic: Results of
One Year of Monitoring of Organochlorine Compounds and PAH**

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In January 1992, an air toxics sampler was set up at Alert, on Northern Ellesmere Island in the Canadian Arctic (82.5° N, 62.3° W) as part of an arctic air toxics monitoring and assessment program. Since then, three more sites were added to the network: Tagish, Yukon Territory near Whitehorse, Dunai Island in the former Soviet Union, and Cape Dorset on Baffin Island. Organochlorines (OCs) and PAHs were sampled weekly to determine the types, concentrations and vapour-particle relationships. High volume samplers with a 10 micrometre size selective inlet were used with a collection cartridge consisting of glass fibre filter(s) for particulates followed by two 20 cm diameter 5 cm thick polyurethane foam plugs for vapours, with a weekly sample volume of approximately 11,000 m³. Samples were analyzed by gas chromatography using electron capture detection and confirmation by GC/MS.

This paper will focus on selected compounds for 1992 at Alert: a volatile OC hexachlorobenzene, a semi-volatile OC DDT, and the PAHs pyrene, benzo(c) and benzo(a) pyrene. We will present annual average concentrations as well as weekly integrated values to look for potential seasonal variation through temporal profiles and their distribution between the particle and gas phases.

**Laboratory Preparation of DNPH Derivatives of Carbonyl Compounds on
Sep-Pak[®] Cartridges for Quality Assurance Purposes**

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ABSTRACT

Aldehydes and ketones are receiving increased attention both as hazardous substances and as promoters in the photochemical formation of ozone in the atmosphere (1). They enter the atmosphere in the exhaust of motor vehicles and other equipment using hydrocarbon and alcohol fuels. Formaldehyde, the most prevalent aldehyde, is widely used as a preservative, a textile treatment agent, and an intermediate in the manufacture of urea-formaldehyde and phenol-formaldehyde resins. Figure 1 (1,2) shows formaldehyde concentration ranges for several types of environments. Waters Sep-Pak[®] DNPH-Silica cartridges are convenient, reproducible sampling devices for quantifying aldehydes and ketones in gases, including air. These cartridges trap the compounds by reacting them with the DNPH, 2,4 Dinitrophenylhydrazine, on the cartridge (see Figure 2) to form stable hydrazone derivatives. Derivatives are later eluted and analyzed by HPLC. Cartridges spiked in the laboratory are used for quality assurance and instrument performance verification.

INTRODUCTION

Our laboratory prepares derivatized carbonyl compounds on Sep-Pak[®] DNPH-Silica cartridges at requestor specified concentrations and combinations for a variety of projects. This is accomplished by direct application of aliquots of stock solutions onto the cartridges. Levels are usually no greater than 75% of the DNPH loading on the cartridge and are within established limits (3,4,5). Procedures for spiking cartridges and preliminary analyses results are summarized in this report.

EXPERIMENTAL

The solutions used to spike cartridges are quantitatively prepared by a successive dilution technique using acetonitrile and 100 ml volumetric flasks. Using a syringe needle, both polyethylene filters (See Figure 3) in the cartridge are pierced and calculated volumes of these solutions, in microliters, are then injected onto the top of the DNPH-Silica bed. The DNPH-carbonyl derivatives are eluted using acetonitrile and the extracts analyzed by HPLC.

RESULTS

Figure 4 compares micrograms spiked for formaldehyde, acetaldehyde, and acetone to the concentrations found when a group of the cartridges were extracted and analyzed. From this graph the relationship appears to be linear for the 3 compounds examined. As more data becomes

available more extensive curve fitting may be carried out. Figure 5 shows a graphic representation of the % difference between spiked concentrations and HPLC analysis values for each cartridge. With the exception of acetone, the majority of the values fall within our current control limits of $\pm 25\%$.

Contamination due to unintentional exposure of cartridges to aldehyde and ketone sources can be a problem. Laboratory air often holds high concentrations of acetone, in particular. This problem may be alleviated by removing acetone sources from the spiking area and/or modifying overall usage of acetone in the laboratory when cartridges are being spiked. If not properly cleaned, glassware and syringes hold the potential for contamination. Labeling inks, adhesives, and packaging containers are also possible sources of contamination. In some instances, acetonitrile may contain traces of aldehydes and ketones, especially acetone. 10ug/L of an aldehyde or ketone in acetonitrile adds 0.1 ug DNPH derivative per cartridge to background values. If it is unacceptable for a particular application, the supplier should be contacted and/or the acetonitrile purified (6). Figure 6 shows micrograms found but not spiked for a group of cartridges.

ACKNOWLEDGMENTS

The author acknowledges all those persons involved in the independent analyses of the cartridges whose data was used in this report.

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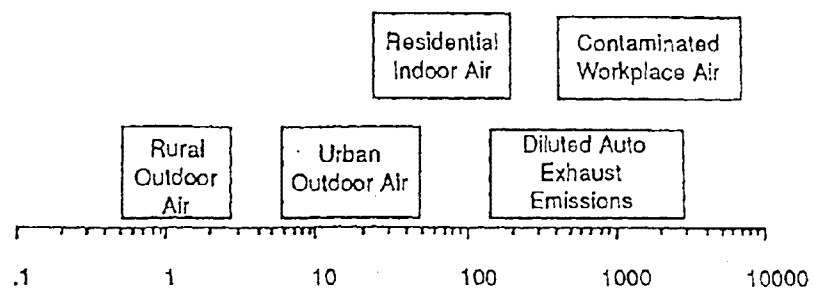


Figure 1. Ranges of Formaldehyde Concentrations, PPBV.

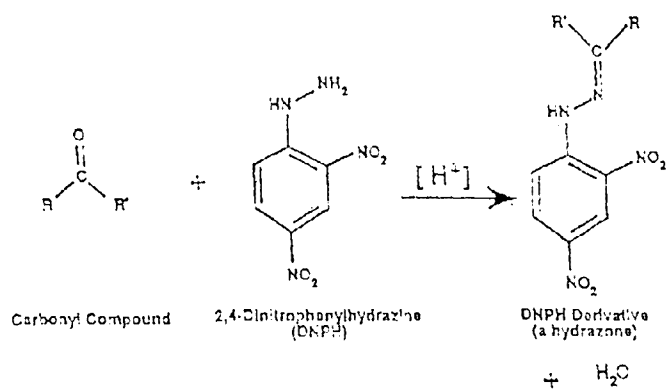


Figure 2. Derivatization Equation.

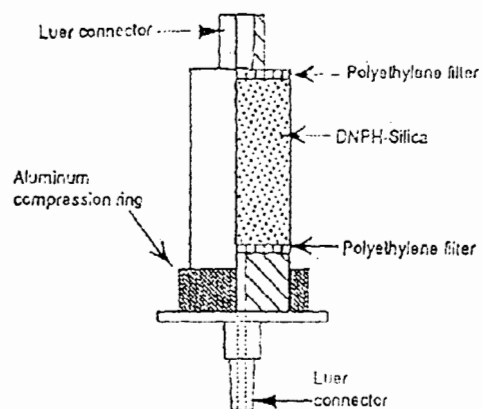
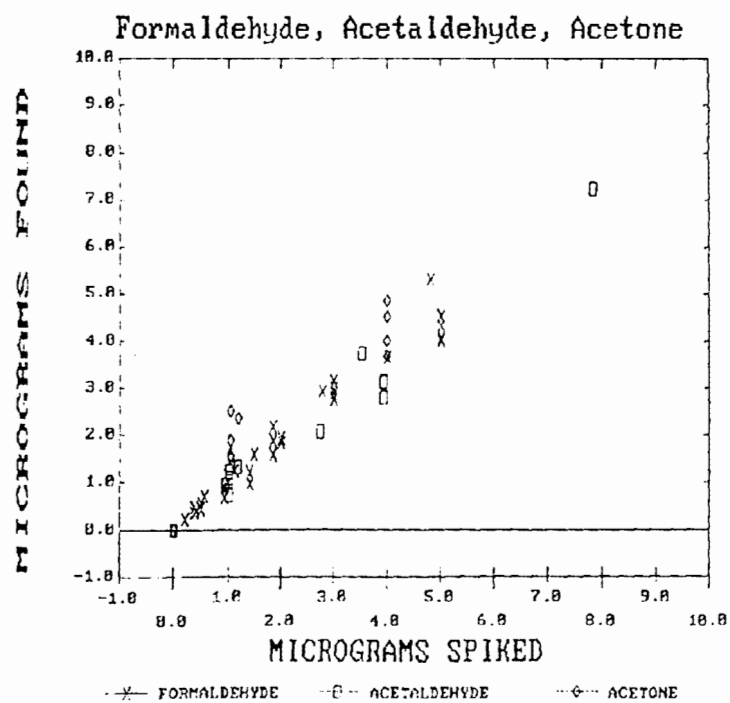


Figure 3. Cutaway View of Sep-Pak[®] DNPH-Silica Cartridges



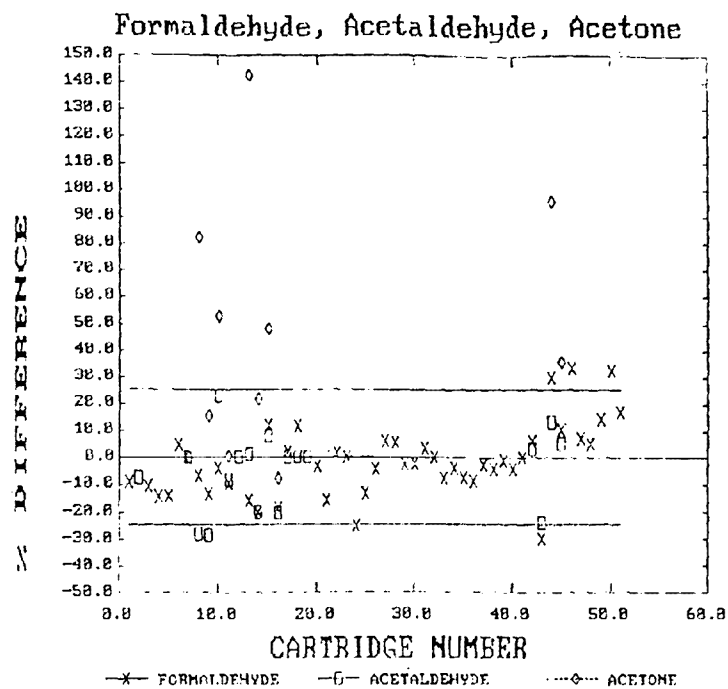


Figure 5. % Differences Between Calculated Spiked Concentrations and Analysis Values.

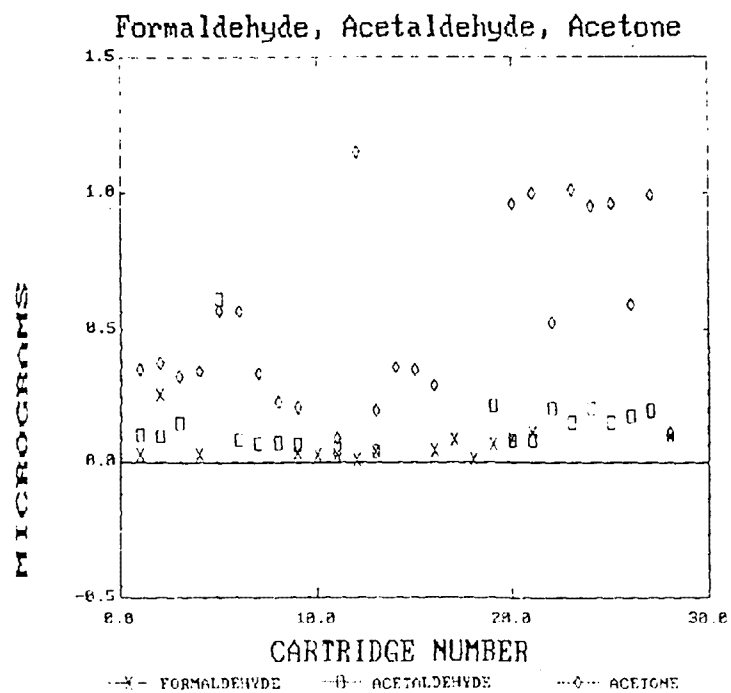


Figure 6. Micrograms Found but not Spiked.

Experimental Studies of an Ethanol-Air Flow Subjected to UV Light

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The photolytic destruction of ethanol in air streams illuminated with high purity quartz low-pressure mercury lamps was investigated. A gas tight composite 316 stainless steel and acrylic reactor loop was constructed which allowed for doping ambient air with ethanol, and circulating it past the lamps. Ethanol concentration measurements were recorded when only one 40 watt lamp was illuminated, and again when three 40 watt lamps were illuminated. It was determined that by increasing the actinic flux from 40 watts to 120 watts the overall rate constant for ethanol increased from $8.25\text{E-}5\text{ s}^{-1}$ to $1.06\text{E-}3\text{ s}^{-1}$ when corrected for wall loss. Organic chemical intermediates were formed by this process, and depended upon the actinic flux and the residence time in the reactor loop. Finally, it was determined the 7.2mW/CFM of 185 nm radiation increased the kinetic rate constant by over two orders of magnitude.

Determination of Test Methods for Interior Architectural Coatings

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Numerous building and consumer products used in indoor environments emit VOCs. The U.S. EPA has undertaken a project to analyze VOC emissions from various types of indoor products to determine which types of products result in the greatest overall exposures to pollutants indoors. Critical to this project are appropriate techniques to evaluate emissions of total and specific VOCs from these sources. During 1992, the Research Triangle Institute (RTI) evaluated seven methods for determining the VOC emissions from interior architectural coatings – specifically interior alkyd and latex paints. Current work has involved a more detailed evaluation of three of the seven methods with the final result being the development of test methods for the determination of volatile and semi-volatile organic compounds and aldehydes from interior latex and alkyd paints.

The methods evaluated during this study were bulk product analysis by direct injection onto a GC/MS, emissions testing using 52 L small stainless steel chambers and ASTM standard methods for total volatiles and water content. Twelve interior paints made by two major paint manufacturers were chosen for testing. The paints represented three gloss types (flat, semi-gloss, and gloss) and six color groups. This paper discusses the analytical test methods and results.

Although the research described was funded by the U.S. EPA (Contract No. 68-D2-0131), it has not been subjected to the required peer review and does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

An Improved DNPH Cartridge Aldehyde Sampler for 3-Day Unattended Sampling

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Title I of the 1990 Clean Air Act Amendment requires monitoring of all compounds suspected of contributing to ozone formation in urban atmospheres. Included in the list of suspected agents are aldehydes and ketones, with formaldehyde being of particular interest due to its toxicity and normally higher concentrations. Monitoring of the aldehydes and ketones during high ozone periods will be performed by collecting eight 3-hour samples daily, seven days a week using samplers operating unattended. The aldehydes and ketones will be sampled by passing ambient air through Dinitrophenylhydrazine (DNPH) cartridges allowing later recovery and analysis in a laboratory.

A new aldehyde/ketone sampler is presented that conforms to the requirements and QA/QC set forth by Federal, State, and Local monitoring agencies. The 32-position sampler allows up to 4 days of unattended sampling if spikes and duplicates are not utilized. To improve QA, 3-days of sampling can be scheduled allowing one duplicate and one spike to be obtained every 24 hours in addition to the eight ambient air samples. Two sampler positions left unused can then be analyzed as field blanks. To provide for the simultaneous collection of samples and spikes or duplicates, two 2000 sccm electron mass flow controllers are used to control the 1 l/min required flow rates. An onboard microcomputer both controls the MFC's and records their actual flow rates for later downloading to a Windows based software package for reporting. Programming and data retrieval can be performed using a local PC system running under Windows™ or by a remote system using a modem. Provisions are made for continuously adding a surrogate standard for added quality assurance for both field sampling and laboratory extraction and analysis. An ozone scrubber is utilized which reduces sample losses on the cartridge due to oxidation of the carbonyl-DNPH complex. Default sampling protocols are provided, although a flexible Windows based editor allows considerable user modification to the sample collection scheme. Field data and software will be presented showing precision and practical advantages.

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