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U. S. Environmental Protection Agency

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has the responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise and Radiation, the Office of Pesticides and Toxic Substances and the Office of Solid Waste and Emergency Response.

This symposium is part of a continuing effort to explore recent advances in pollutant monitoring of ambient air and stationary sources. It serves as a forum for exchange of ideas and scientific information. In response to the Agency regulatory needs, this symposium focused on acid deposition, personal exposure and toxic substances. This publication is intended to assist those researchers interested in furthering the science of air monitoring.

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INTRODUCTION

The fourth annual national symposium sponsored by EPA'e Environmental Monitoring Systems Laboratory was held May 8-10, 1984 in Raleigh, North Carolina. In seven sessions over three days, papers and discussions focused on state-of-the-art systems for monitoring source emissions, ambient air, acid deposition, hazardous emissions and personal monitoring. The sessions were categorized as follows:

SESSION I	Particulate Pollutants
SESSION II	Personal Monitoring
SESSION III	Hazardous Waste Monitoring
SESSION IV	Organic Pollutants
SESSION V	Analysis of Complex Chemical Data
SESSION VI	Acid Deposition
SESSION VII	General and Source Oriented Monitoring

The papers are in the same order as presented by the speakers. Several papers are omitted because the speakers did not submit them in time for the agency's peer review.

PM-10 INSTRUMENTS: A MANUFACTURER'S PERSPECTIVE

By: Michael L. Smith, Andersen Samplers, Inc.

Andersen Samplers, Inc. and its subsidiaries, General Metal Works (GMW) and Sierra-Andersen (S-A), have been manufacturing and marketing size specific particulate samplers since the mid-1970's. The U. S. Environmental Protection Agency recently proposed revisions to the National Ambient Air Quality Standard (NAAQS) for particulate matter [1] which would base the primary, health-related standard on only those particles smaller than 10 micrometers aerodynamic diameter (PM-10).

Both GMW and S-A manufacture and market a complete line of PM-10 instruments, including Medium Flow Samplers, Dichotomous Samplers and Size Selective High Volume Samplers. Although the instruments sold by each company are designed to measure the same particulate pollutants, the collection mechanisms are different. The GMW instruments are based upon cyclonic collection whereas the S-A instruments are based upon impaction.

Each of the three types of instruments have specific features which give them certain advantages in certain applications. Both the Medium Flow and the Dichotomous Samplers utilize high vacuum pumps and therefore can use Teflon membrane filters to collect the PM-10 particles. The use of Teflon filters allows subsequent chemical analysis using x-ray flourescent analysis. The Dichotomous operates at a low flowrate (16.7 lpm) but separates "fine" mode particles smaller than 2.5 micrometers from "coarse" mode particles in the range of 2.5 to 10 micrometers. The Medium Flow Sampler operates at 4 CFM and collects all PM-10 particles on one 102 mm filter.

Because of the separation of coarse and fine mode particles, the Dichotomous Sampler provides the most information in areas where difficult compliance strategies are required. An automated version of the Dichotomous Sampler which allows up to 15 samples without operator intervention provides a method to sample "episode" events and to study short term (e.g., day versus night) fluctuations or cycles. The Medium Flow Sampler collects larger samples and provides the basis for developing compliance strategies for noncompliance areas. The Medium Flow Sampler is easier to use than the Dichotomous Sampler.

For routine monitoring stations, the Size Selective High Volume Sampler will probably be the instrument of choice because the operating procedures are similar to the current TSP High Volume Sampler and it is easy to use. Existing TSP Hi-Vols can be easily converted to PM-10 Hi-Vols by adding a size selective inlet, a flow controller, a flow recorder and a filter paper cartridge. Glass fiber filters will not be allowed because of artifact formation, and the quartz filters require a filter paper cartridge because they are more fragile.

The proposed Federal Reference Mothod (FRM) performance specifications for PM-10 Samplers are shown in Table 1 and the "sampling effectiveness" (penetration) curves for the GMW and S-A Size Selective High Volume Samplers are shown in Figure 1. Both inlets exhibit sharp sampling effectiveness curves which meet the FRM performance specifications. The cutpoint of the S-A Model 321-A Two Stage SSI is closer to the 10 micrometer cutpoint desired by EPA (10 micrometers versus 9.0 micrometers for the GMW Model 9000 inlet). Table 2 summarizes the cutpoints of the two inlets at windspeeds of 2, 8 and 24 km/h.

As part of the FRM performance specifications, candidate samplers must collect within ±10% of the mass that an "Ideal Sampler" would collect if both sampled a hypothetical ambient mass distribution. A summary of the performance of the GMW and S-A inlets compared to the "Ideal Sampler" is shown in Table 3. For the hypothetical mass distribution specified in the FRM, the S-A Model 321-A would read 0.4% low whereas the GMW Model 9000 would read 3.6% low.

There has been some question as to whether the hypothetical ambient mass distribution specified in the FRM is truly representative. The FRM distribution is representative of urban environments with relatively high fine particle concentrations, but may not be representative of rural or fugitive emissions distributions. As a further test of the PM-10 samplers, we have compared their expected performance to the "Ideal Sampler" for the three additional hypothetical ambient mass distributions shown in Figure 2. Table 4 summarizes the variances of the S-A and GMW samplers from the "Ideal Sampler" for each different mass distribution. Even for the Case III distribution (fugitive emission, high large-particle concentration),

the S-A Model 321-A would read 0.7% high while the GMW Model 9000 would read 4.5% low.

SUMMARY AND CONCLUSION

Commercial PM-10 instruments are now available which meet or exceed all of the proposed Federal Reference Method performance specifications. These inlets have been tested in the wind tunnel and in collocated field inter-comparison studies. PM-10 concentrations measured with different commercial instruments should all be well within ±10% of the concentration that an "Ideal Sampler" would be expected to measure.

REFERENCES

1. Federal Register, Vol. 49, No. 55, pages 10408-10462, March 20, 1984.

TABLE 1: PERFORMANCE SPECIFICATIONS
PM-10 SAMPLERS

Parameter	Units	Specifications
Sampling Effectiveness		
A. Liquid Particles	%	Within ±10% of "Ideal Sampler"
B. Solid Particles	%	≤5% higher than results for liquid particles for 20μm particles
Cutpoint (50%)	μm	10± 1 μm D_A
Reproducibility	%	≤15% coefficient of variation for 3 collocated samplers
Flow Rate Stability	%	Within ±10% of initial flow rate for 24-hour sampling period

TABLE 2: CUTPOINTS OF PM-10 INLETS
FOR THE HI-VOL SAMPLER

Sampler	Cutpoint, μm		
	Wind Speed, km/h		
	2 km/h	8 km/h	24 km/h
Sierra-Andersen Model 321 A (2 Stage)	9.7	10.0	9.6
General Metal Works Model 9000	9.1	8.9	9.0
Suggested Allowable EPA Range of Cutpoint Sizes[1]	9.0-11.0	9.0-11.0	9.0-11.0

[1]F.R. 49: No. 55: 10408-10462, March 20, 1984

TABLE 3: COMPARISON WITH "IDEAL SAMPLER"

Sampler	Expected Mass ($\mu g/M^3$) (at 8 km/h)	Relative Error Compared to "Ideal Sampler"
S-A 321 A (2 Stage)	52.1	-0.4%
GMW - 9000	50.4	-3.6%
"Ideal Sampler"	52.3	. . .

TABLE 4: COLLECTED MASS COMPARISONS

Size Distribution	Expected Mass Collected By 321-A Two Stage SSI $\mu g/m^3$	Wedding Hi-Vol Inlet $\mu g/m^3$	Ideal Sampler $\mu g/m^3$
Case I:			
Total Aerosol Concentration 27.2 $\mu g/m^3$	16.4	15.8	16.6
Variance from Ideal	-1.2%	-4.8%	. . .
Case II:			
Total Aerosol Concentration 71.5 $\mu g/m^3$	46.1	44.8	46.1
Variance from Ideal	0%	-2.8%	. . .
Case III:			
Total Aerosol Concentration 179.9 $\mu g/m^3$	74.5	70.7	74.0
Variance from Ideal	+0.7%	-4.5%	. . .

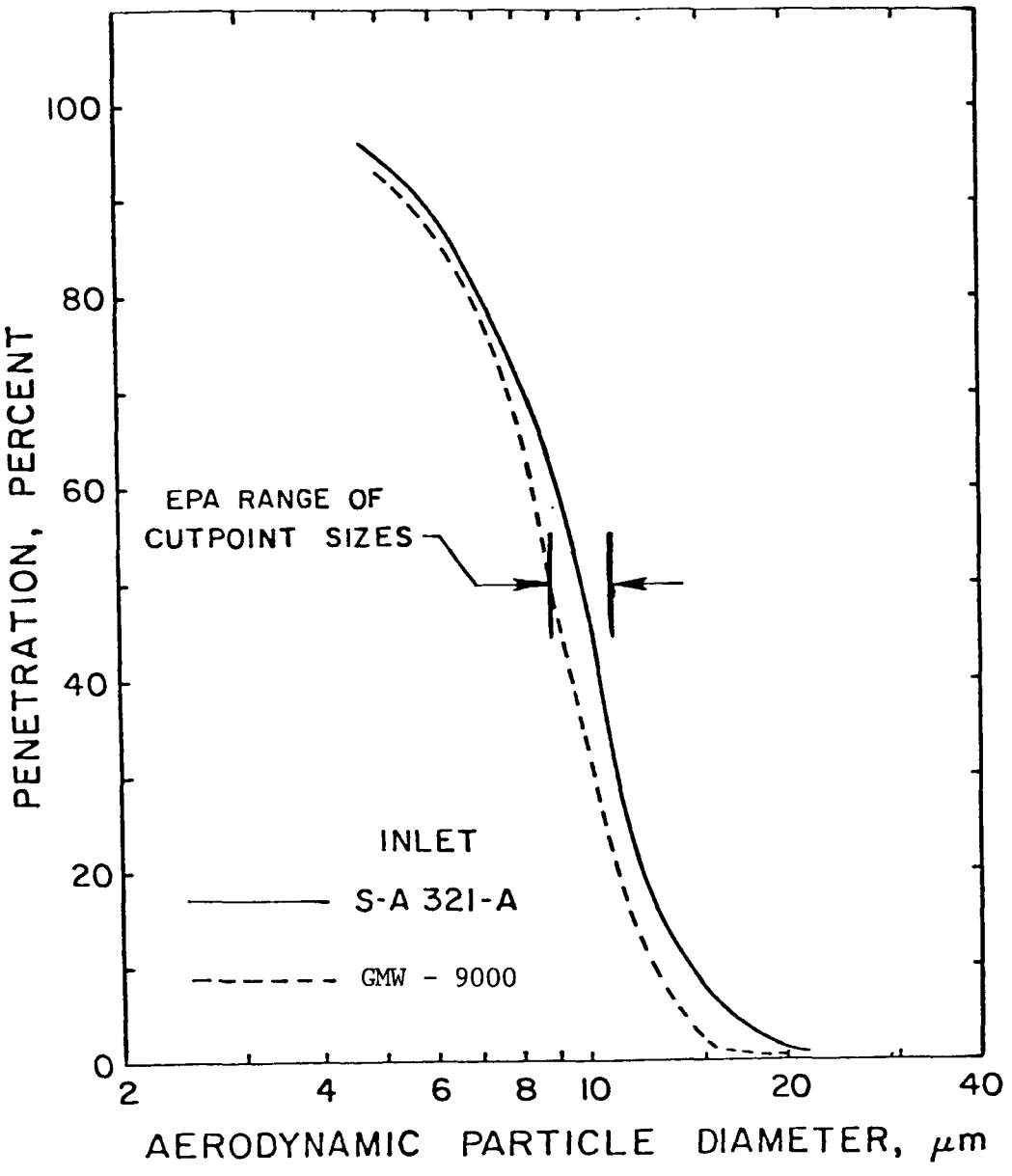

Figure 1: Aerosol Sampling Characteristics of PM-10 Inlets for the Hi-Vol Sampler. Wind Speed = 8 km/h. Flow Rate = 1.13 m^3/min.

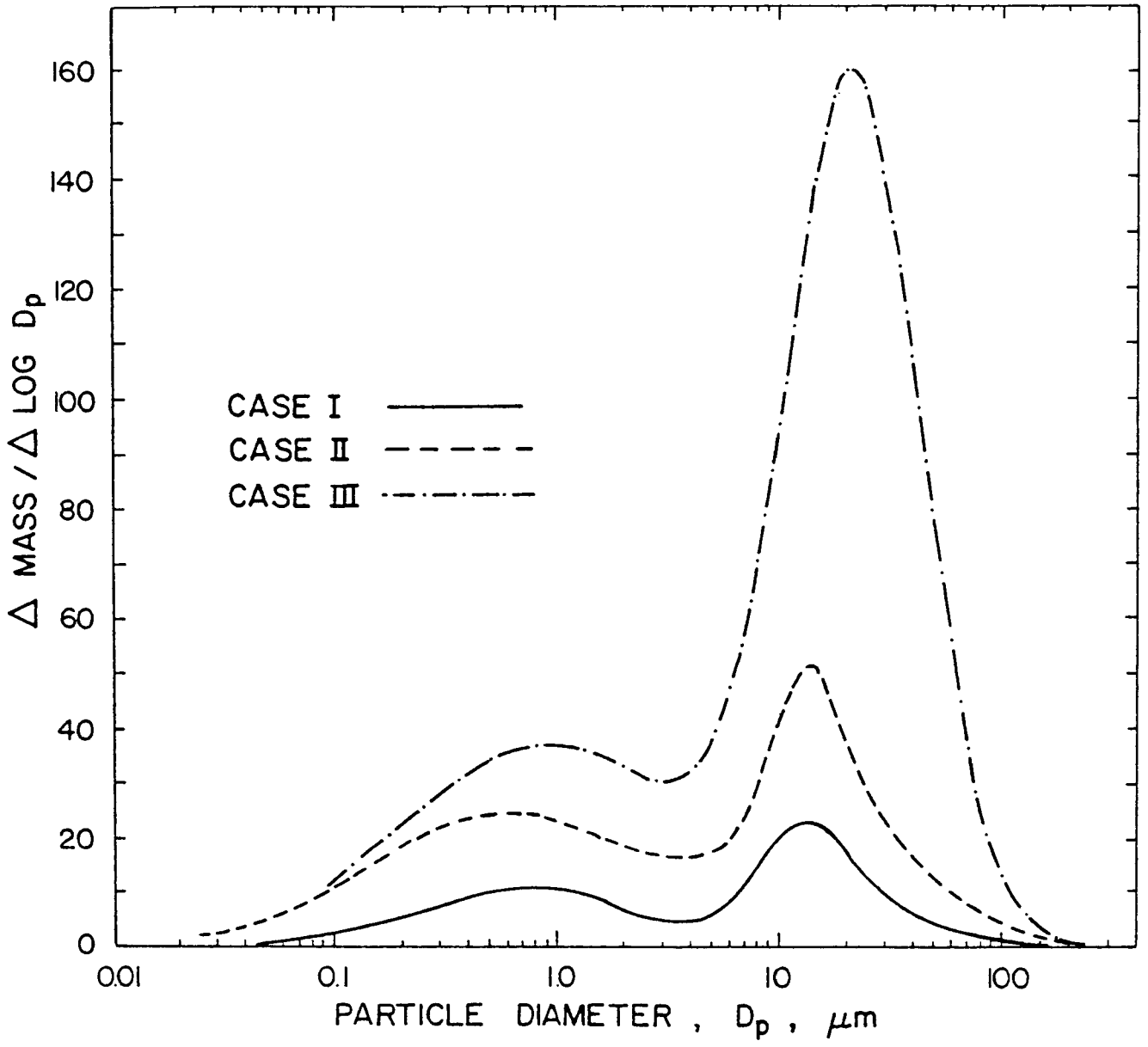

FIGURE 2: Three Hypothetical Ambient Mass Distributions

GENERATION AND USE OF LARGE, SOLID CALIBRATION AEROSOLS

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The calibration of four, large-particle impactors developed at the University of Florida required the development of a technique for the generation of large calibration aerosols. Slight modifications to a vibrating orifice aerosol generator (Model 3050, TSI Inc., St. Paul, Minn.) enabled the successful generation of solid ammonium fluorescein particles up to 70 um aerodynamic diameter. When generated under the proper test conditions, the particles were found to be spherical and of uniform size.

The developed generation procedure does not involve the somewhat awkward inversion of the aerosol generator. The dilution flowrate of the generator, however, is inadequate to suspend generated droplets larger than about 65 um. As a result, large droplets will normally settle out and be lost before having sufficient time to dry to the desired particle size. The successful generation of large particles, therefore, requires the use of liquid solutions of high volume concentrations. This allows production of droplets of suspendable size which dry to form particles of the desired diameter. By dissolving fluorescein powder in aqueous ammonia, volume concentrations as high as 30% were produced. Although the use of high volume concentration solutions requires more patience to start and maintain the liquid jet through the orifice, the overall generation process is considered to be more convenient than inversion of the generator.

The generation of particles larger than 20 um requires careful optimization of the operating parameters of the aerosol generator including orifice diameter, liquid feedrate, vibrational frequency, and dilution flowrate. Guidelines for the proper selection of these parameters are outlined. The results of the impactor calibrations using the described aerosol generation technique are briefly discussed.

A SIZE CLASSIFYING ISOKINETIC AEROSOL SAMPLER DESIGNED FOR APPLICATION AT REMOTE SITES

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Research quality aerosol monitoring projects require an aerosol filter sampling device with the following characteristics:

- Measurement of inhalable (0 to 10 or 15 μm) and fine (0 to 2.5 μm) size-classified particulate matter, with acceptable sampling effectiveness.
- Simultaneous sampling on two different substrates, one amenable to elemental and the other amenable to carbon analysis.
- Sequential sampling, without operator intervention, at greater than 75 l/min flow rates to obtain continous samples over 4- to 24-hour sample durations with sufficient deposits for chemical analysis.
- Simple and reliable field and laboratory operation at an affordable price.

A Size Classifying Isokinetic Sequential Aerosol Sampler (SCISAS) combines the best features of the SURE/ERAQS (Mueller and Hidy et al., 1983) sequential filter sampler and the WRAQS (Allard et al., 1982) and Henry (1977) isokinetic sampling manifolds to meet these requirements.

Ambient air is continuously drawn at a rate of 1100 l/min into a ten inch diameter PVC stack through a 10 or 15 μm McFarland size-selective inlet (SSI). Particles are then drawn from this stack, at a velocity close to that flowing through the main stack to sample 0 to 10 or 15 μm particles on two different filter media. Each of the two 0 to 2.5 μm aerosol samples is withdrawn from the main stack at a flow rate of 113 l/min through a single two-inch internal diameter tube which leads to a cyclone for exclusion of particles larger than 2.5 μm diameter. The outlet of the cyclone leads to a simple rectangular supply manifold into which six 47 mm Nuclepore filter holders are mounted. A general view of the SCISAS is shown in Figure 1.

The basic configuration of the SCISAS includes fourteen two-inch internal diameter supply tubes clustered inside the main ten-inch stack. The flow rate of approximately 80 l/min within each inhalable particle two-inch supply tube was chosen empirically to provide very nearly isokinetic matching between the average velocities in these tubes and that in the main stack with 1100 l/min flow. An alternative design draws the 0 to 10 or 15 μm sample at isokinetic velocities through a four inch diameter tube into a 46" long sampling plenum. Filters along the side of the plenum draw the sample from it.

The following particle loss mechanisms were theoretically evaluated and predicted to be negligible (less than 1%):

- Electrostatic capture in the main PVC stack.
- Turbulent diffusion in the main stack and two inch sampling tubes.
- Brownian diffusion losses.
- Inertial impaction losses in the two inch tubes.

Sedimentation losses in the inhalable particle sampling tubes are calculated to be a maximum of 7% for 15 μm particles. The maximum bias in the 0 to 10 or 15 μm mass estimation is much less than 5%.

In ten tests of a 15 μm cut-point SCISAS prototype, aerosol mass concentrations measured in Reno, NV, ranged from 6 $\mu g/m^3$ to 32 $\mu g/m^3$; the maximum difference between any two of the four SCISAS 0 to 15 μm particle sampling tubes operated simultaneously in each of these tests was 4%. More typically, any two sampling tubes agreed to better than 3%. At the same sampling site, three comparisons of the SCISAS prototype to a collocated hivol outfitted with an identical 15 μm size selective inlet were conducted. Ratios of the mass concentrations measured by the SCISAS, to those measured by the hivol/SSI, were 0.98, 0.95, and 0.96 for these three preliminary tests.

Further tests of the SCISAS are now scheduled and will include extensive comparisons with other sampling devices. Other tests include 1) measurement of passive deposition inside the SCISAS sampling tubes, 2) measurements of re-entrainment of large particles inside the SCISAS, 3) evaluation of virtual impaction into non-operating sampling tubes in the SCISAS tube cluster, 4) quantitative evaluation of the effects of non-isokinetic mismatches at the entrance to the tube cluster, 5) and measurement of the effects of flow rate variations in the main stack and SSI. Velocities inside the main stack at the approach to the tube cluster will be mapped with a hot-wire anemometer. A theoretical evaluation of the possible effects of aerosol particle deliquesence or shrinking, due to heat transfer in the SCISAS, will also be performed.

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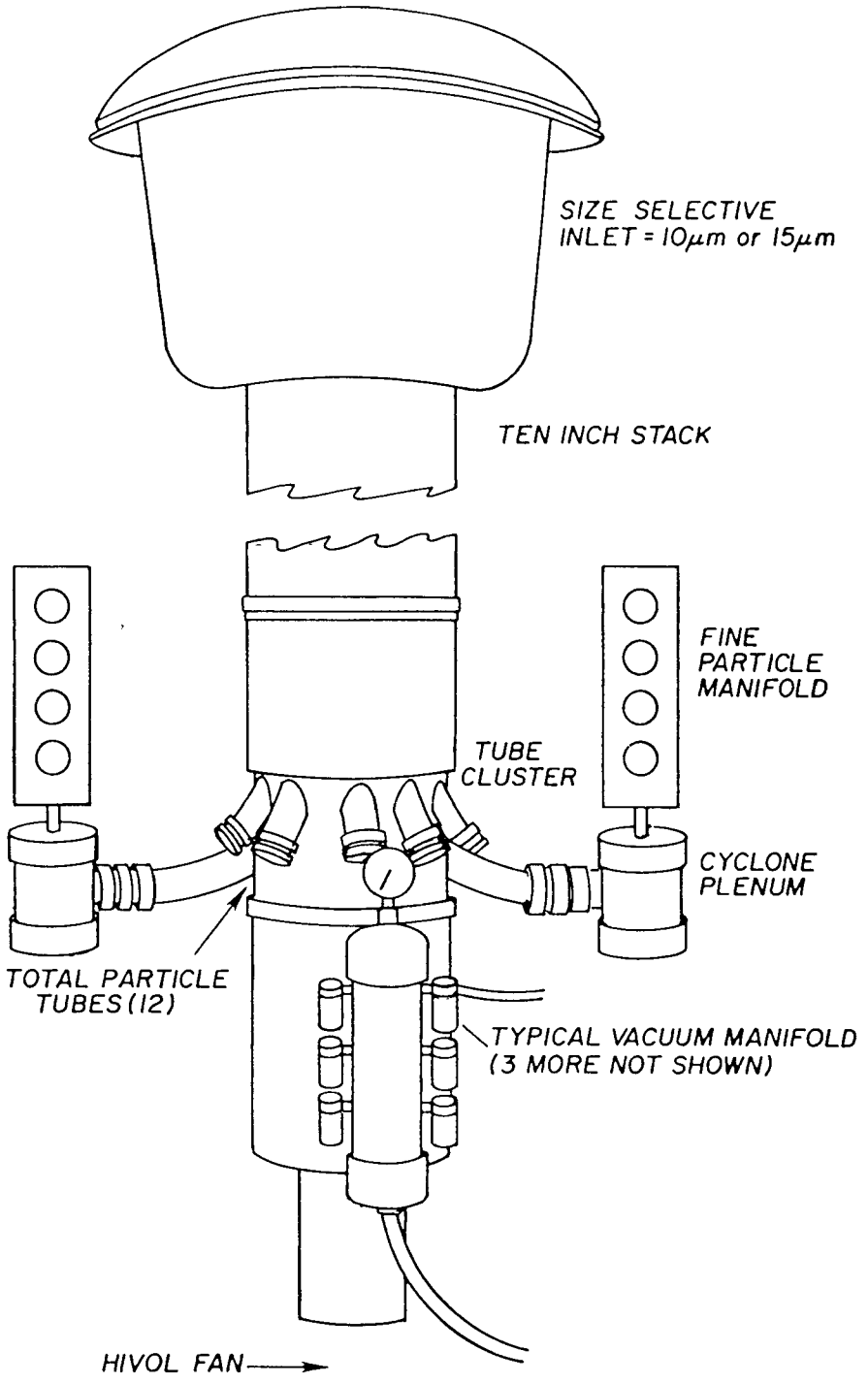

FIGURE 1: General view of SCISAS, not showing Nuclepore filter holders, three of four vacuum manifolds, four suction pumps, connecting tubing and stand.

PARTICLE AND SUBSTRATE LOSSES DURING SHIPMENT OF TEFLON AND QUARTZ FILTERS

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ABSTRACT

A special study was conducted to evaluate particle and filter substrate losses resulting from routine handling of particulate samples collected on quartz and teflon filters. Filters were weighed at pre-determined stages of the filter handling process to estimate changes in mass corresponding to the various filter handling operations. Control filters, both field blanks and sampled filters, were used to estimate passive artifact formation and particulate matter volatilization. The remaining filters were shipped to the laboratory for observation and returned for final weighing. Changes in shipped filter mass could be contributed to both a loss of large particles during shipment and a loss of particulate matter from volatilization. A comparison of control filter weight changes with shipped filter weight changes would provide an estimate of the overriding mechanism responsible for any observed particle and substrate losses following sample collection.

The data presented in this report suggest no significant weight loss from routine high volume sampling of particulate matter using quartz filter media, as long as the final filter weights are performed without archiving or shipping the filter to the laboratory. A reduction in filter mass was observed after the shipment of total suspended particulate quartz filters to the laboratory. Particulate matter loss from volatilization was also noted with the high volume samples collected in Phoenix, Az. No significant weight change was observed in the routine handling of dichotomous teflon filters.

This is an abstract for proposed publication and does not necessarily reflect EPA policy.

INTRODUCTION

The Environmental Protection Agency recently conducted a field evaluation of commercially available nominal 10 micrometer (10μm) inlets for particulate samplers.[1] Total suspended particulate (TSP) and 10μm size selective inlet (SSI) high volume samplers as well as 10μm dichotomous samplers were operated in four cities using established Inhalable Particulate Network (IPN) operating procedures.[2] TSP and SSI samples were collected using 8" x 10" quartz filters. Dichotomous samples were collected using 37 mm teflon filters media identical to those employed in the IPN.

A special filter evaluation study was conducted at two of the four cities, Phoenix, AZ and St. Louis, MO. The purpose of this special study was to evaluate various aspects of the filter handling operation in order to estimate the magnitude of particle and filter substrate losses from quartz and teflon filters during the particulate matter (PM) measurement process. The initial consideration was to determine the magnitude of particle and substrate losses resulting from the folding of quartz high volume sampler filters. Commercially available quartz filters have a tensile strength equal to about 25-40% of the tensile strength cited for glass fiber filters.[3] When folded, quartz filters have a greater tendency to crack and fray along the crease. Glass fiber filters typically do not crack or fray when folded. Monitoring both particulate-loaded and blank quartz filter weights before and after folding would provide information to assess the combined particle and substrate losses resulting from the folding process. The second aspect to be considered was the loss of particulate matter resulting from the shipment of sampled filters to the laboratory for final weighing. Filter weights were monitored both before and after shipment to document mass losses resulting from shipment. Loss of PM mass during filter shipment is thought to be a large particle phenomenon; i.e., with increased large particle concentration, PM loss resulting from shipment is expected to increase. Compared to St. Louis, Phoenix's particle size distribution data indicates a significantly larger coarse particle fraction. Therefore, the Phoenix samples would be expected to be more adversely affected by large particle losses during shipment than the St. Louis samples.

The third aspect to be evaluated in this study was PM losses resulting from volatilization over long periods of time.[4] For a typical PM monitoring network, a lapse of up to 30 days occurs from the date the sample is collected in the field to the date the gross weight is obtained in the laboratory. This study data would provide a means to estimate particulate mass loss resulting from volatilization. Estimating passive artifact formation on quartz filters was the last aspect considered. Sulfate and nitrate artifact formation on glass fiber filters, routinely used in PM monitoring networks such as the IPN, has been documented.[5] Unlike glass fiber filters which have a pH of ca. 9.5, quartz filters have a pH of ca. 7.0. Consequently, passive sulfate and nitrate artifact formation on the quartz filters used in this study should be minimal.

The results from this study are considered to be "best case". Extra precautions were taken by the field operators in both the handling of samples in the field and the operation of the samplers in accordance with the manufacturer's specifications. In addition, the study quality assurance protocol, especially with regards to acceptable weighing procedures, was strictly enforced. Most important, both TSP and SSI sampling was conducted using filter cassettes, minimizing filter handling in the field and reducing the potential for voided filters.

EXPERIMENTAL

Five sampling days were scheduled in both Phoenix, AZ and St. Louis, MO to conduct the special study. Figure 1 diagrams the high volume filter handling process. Prior to sampling, groups of quartz and teflon filters were placed opened in racks inside the mobile weighing laboratory with controlled chamber conditions of 40±3% relative humidity and 20±2° Centigrade. Following 24 hours of conditioning, filter tare weights were recorded. Quartz filters were then loaded into filter cassettes, with lids, while the teflon filters were first placed in Lexan jigs and then into petri dishes. On each sampling day, two TSP and four SSI high volume samplers were operated. Four dichotomous samplers were also operated for each 24-hour sampling period. Additionally, on each sampling day, two quartz filter field blanks and two teflon filter field blanks were identified. These field blanks, quartz filters loaded in cassettes with lids and teflon filters in Lexan jigs inside petri dishes, were removed from the conditioning chamber and placed in the sampling environment during the 24-hour sample period.

At the completion of the sampling period, each filter was then returned to the controlled conditioning chamber. Filters were removed from the cassettes and Lexan jigs and placed opened in the conditioning chamber racks for 24 hours. The gross weight was then recorded for each filter. After weighing, one TSP filter sample, one SSI filter sample, one quartz filter blank, one dichotomous fine sample, one dichotomous coarse sample and one blank teflon filter were designated as controls and returned to the conditioning shelf. The remaining TSP, three SSI and one blank quartz filters were individually folded, placed in separate cardboard supports and enclosed inside manilla envelopes. These folded quartz filters were immediately removed from the envelopes and reweighed to obtain a weight after folding. After reweighing, the filters were returned to their appropriate cardboard supports and envelopes. After weighing, the three coarse, three fine and one blank dichotomous samples were reloaded into their Lexan jigs and placed in their petri dishes. The folded quartz filters and dichotomous filters were then mailed to the laboratory using Jiffy® bags, with three or four samples per bag.

Upon receipt of the filters at the laboratory, each filter was visually inspected for obvious PM loss, cracks, tears or any other unusual physical change. Following this visual inspection, the filters were repackaged and mailed back to the sampling site. Upon arrival at the sampling site, the filters were opened and returned to the conditioning shelf for 24 hours. After reconditioning, the shipped and corresponding control samples were again weighed and final weights obtained. For both Phoenix and St. Louis, the final filter weighing occurred within 30 days after sample collection.

The resulting mass data was summarized and analyzed using standard statistical tests for both paired and non-paired data[6] at the 5% significance level as described below:

For paired data

$$\text{Calculated T Statistic} \quad T = \bar{d} \; / \; (\sigma_d \; / \sqrt{n})$$

where $\bar{d}$ = mean difference between pairs

σ_d = standard deviation of the mean difference

n = number of pairs

Paired Test Interval $t_{n-1,1-\alpha/2} \pm T$

For non-paired data

$$\bar{d}_1 - \bar{d}_2 \pm (t_{n_1 + n_2 - 2, 1-\alpha/2})\ (S_p)\ \left(\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}\right)$$

where $\bar{d}_1 - \bar{d}_2$ = difference between population means

n_1, n_2 = number of observations for groups 1 and 2

$$S_p^2 = \frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}{(n_1 + n_2 - 2)}$$

s_1^2, s_2^2 = variance for groups 1 and 2

For paired data sets, if the test interval, calculated test statistic (T) plus or minus the tabulated Student-t ($t_{n-1,1-\alpha/2}$) value contains zero, then the two sets of data being compared are determined to be indistinquishable. For non-paired data sets, if the test interval defined above includes zero, then the two sets of non-paired data are considered to be indistinquishable. Otherwise, the two data sets are considered distinquishable, i.e., the difference in the two sets are statistically signficant. In instances where the statistical analysis of the data indicate the two data sets to be distinquishable, but the magnitude of the real difference between the two data sets is determined to fall within the experimental error associated with the weighing process, the difference is determined to be marginal and not of practical significance.

Three paired statistical comparisons were performed on the shipped quartz filter weight data for each of the three sample types (TSP, SSI and blank) for each sampling city. First, the 24-hour weights were statistically compared to the corresponding folded filter weights to determine mass loss resulting from folding. Secondly, the folded filter weights were compared to the 30-day weights to estimate the combined losses resulting from PM volatilization and shipment of the filters to the laboratory. Finally, the 24-hour weights were compared to the 30-day weights and a total mass loss since sample collection was calculated. Likewise, the 24-hour control filter weights were compared to the corresponding 30-day weights. As these filters were neither shipped nor folded, any significant loss in mass could be attributed to volatilization. Any significant gain in filter weight observed with the

control filters would be attributed to passive artifact formation. Using the non-paired test statistic, the average weight loss for each shipped filter type was then compared to the average weight loss for the corresponding control filter type to determine if any statistical difference in filter mass observed with the shipped filters was also observed with the control filters. The results of both paired and non-paired statistical tests were then used to determine whether the filter folding process, shipment of the filter or volatilization was the overriding mechanism contributing to any observed weight change.

The dichotomous filter weight data was statistically tested following the same procedures outlined above for the quartz high volume samples with one exception. The shipped dichotomous filters were only weighed at two intervals, 24 hours following sample collection and at the 30-day interval. Therefore, only one paired comparison of the shipped dichotomous sample data was conducted for each city.

RESULTS AND DISCUSSION

When received at the laboratory, the shipped filters were opened and examined for tears, cracks, loss of large particles or any other usual physical change. More that 80% of the shipped TSP and SSI samples received from both Phoenix and St. Louis were cracked and/or frayed along the folded crease. However, less than 10% of the shipped blank filters experienced cracking along the crease. No explanation can be given at this time regarding why the sampled filters cracked and the blank filters did not crack upon folding and shipping. Examination of the St. Louis dichotomous filters revealed no obvious physical changes in the filters. The Phoenix coarse dichotomous filters, however, did show some loss of large particles both to the Lexan jig and the petri dish. No particle loss or other physical change was noted with the Phoenix fine dichotomous samples.

Table 1 summarizes the results of the paired t-test statistics performed on the Phoenix and St. Louis quartz high volume filter weights. For all three sample types (TSP, SSI and blank samples), at both cities, comparisons of the 24-hour filter weights to the corresponding folded filter weights yielded no significant difference in mass. This implies that neither particulate matter nor filter substrate material was lost as a result of the folding process. A statistically significant loss in filter mass was observed for the Phoenix TSP (12.7 μg/m3), Phoenix SSI (4.7 μg/m3) and St. Louis TSP

(4.6 μg/m3) samples shipped to the laboratory. This statistical test suggests that this change in filter mass is directly attributed to both a large particle loss during shipment and to a loss of PM due to volatilization. The shipped St. Louis SSI filter weight change, although statistically significant, was considered marginal as the average SSI filter mass loss falls within the experimental error established for the filter weighing process. An analysis of the shipped blank quartz filter data shows no significant weight change. This suggests that the blank quartz filters used in this special study neither loss substrate due to folding or shipping nor did they undergo significant passive artifact formation. For both St. Louis and Phoenix shipped quartz filters, the overall mass change observed in the 24-hour versus 30-day comparisons corresponded to the summation of the mass change calculated for both the 24-hour versus folded comparison and the folded versus the 30-day comparison. The control quartz high volume sample data reveals that the Phoenix control TSP and SSI filters experienced a significant loss in filter mass equivalent to ca. 3 μg/m3, over the 30-day period. Since the control filters were neither folded nor shipped, this mass loss is thought to correspond to volatilization. The St. Louis control quartz filter data, as well as the blank quartz filter data, indicate no significant mass change over the 30-day period and therefore no loss of PM due to volatilization. The overall differences in the St. Louis particle size distribution, the chemical constituency of the particles and the 24-hour mass loadings as compared to Phoenix are considered the primary reasons for this observation.

Using standard statistics for non-paired data, the overall weight change for each shipped sample type was compared with the weight change for the corresponding control sample type. Testing the Phoenix shipped TSP filters against the Phoenix control TSP filters yielded a significant difference in weight loss. Recalling the earlier paired filter comparisons, this indicates that the observed weight change for the shipped Phoenix TSP filters represents the combined effects of shipment and volatilization. A similar comparison of the Phoenix SSI shipped and controlled filters yielded no statistically significant difference in observed shipped SSI weight loss. Therefore, the shipped Phoenix SSI sample weight loss is solely attributable to volatilization and not large particle loss during shipment. The St. Louis shipped versus controlled TSP filter data suggests that the observed weight changes results solely from large particle losses occurring during shipment of the sample to the laboratory.

Table 2 summarizes the analysis results for the dichotomous filter data. A significant loss in filter mass was noted with the shipped Phoenix fine and coarse dichotomous samples. As was noted previously for the shipped quartz filters, this data indicates a loss of large particles during shipment as well as a loss of PM due to volatilization. No other significant changes in shipped filter mass was observed for either the Phoenix or St. Louis shipped dichotomous filters. The control dichotomous sample statistics show no distinquishable differences between the 24-hour and 30-day weights and indicates that volatilization did not significantly affect the collected dichotomous samples. Therefore, the mass loss observed with the shipped Phoenix dichotomous samples is contributed to a loss of large particles during shipment. Since the Phoenix size distribution contains an extremely large coarse fraction, the loss in filter mass seen in the shipped Phoenix dichotomous filters is attributed to this abnormal large particle loading. Although significant for Phoenix or any other arid environment heavily laden loaded with coarse particles, a loss in filter mass resulting from shipping dichotomous filters to the laboratory is considered unlikely for most routine sampling sites.

CONCLUSIONS

Folding quartz high volume filters does not significantly affect filter mass. Both Phoenix and St. Louis shipped TSP samples experienced large particle losses equivalent to approximately 5% of the filter mass loading as a result of shipping the filter to the laboratory. Based on the blank quartz filter data, no filter substrate material was lost nor did passive artifact formation significantly affect the mass determinations. The Phoenix TSP and SSI sample data showed significant weight loss corresponding to volatization. Except in areas with extremely high coarse particle loadings, you would not expect particle loss from shipping dichotomous filters to the laboratory.

This special study suggests that quartz filters can be used in routine PM monitoring. However, this was a "best case" study. Field operators and laboratory personnel exercised caution in the handling of these quartz filters. The sampling equipment was routinely monitored to insure compliance with the manufacturer's specifications. And most important, filter cassettes were used for high volume sampling, minimizing the handling of quartz filters in the field. Additionally, cracked or frayed quartz filters were not voided but were considered as acceptable samples in this study.

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TABLE 1. Results of Statistical Analysis on Quartz Filter Weights

COMPARISON	PHOENIX			ST. LOUIS		
	TSP	SSI	BLANK	TSP	SSI	BLANK
Shipped Filter 24-Hour versus Folded Weight	Indist	Marg	Indist	Indist	Marg	Indist
Shipped Filter Folded versus 30-Day Weight	Dist	Dist	Indist	Dist	Marg	Indist
Shipped Filter 24- Hour versus 30- Day Weight	Dist	Dist	Indist	Dist	Marg	Indist
Control Filter 24-Hour versus 30-Day Weight	Dist	Dist	Indist	Indist	Indist	Indist
Shipped versus Control Filter 30-Day Weight Loss	Dist	Indist	Indist	Dist	Indist	Indist

TABLE 2. Results of Statistical Analysis on Teflon Filter Weights

	PHOENIX			ST. LOUIS		
COMPARISON	FINE	COARSE	BLANK	FINE	COARSE	BLANK
Shipped Filter 24-Hour versus 30-Day Weight	Dist	Dist	Indist	Marg	Indist	Indist
Control Filter 24-Hour versus 30-Day Weight	Indist	Indist	Indist	Indist	Marg	Indist
Shipped versus Control Filter 30-Day Weight Loss	Indist	Indist	Indist	Marg	Indist	Indist

Dist indicates a significant difference between paired data

Indist indicates no significant difference between paired data

Marg indicates that although a statistical difference is noted, that the real difference is within the experimental error associated with the weighing process

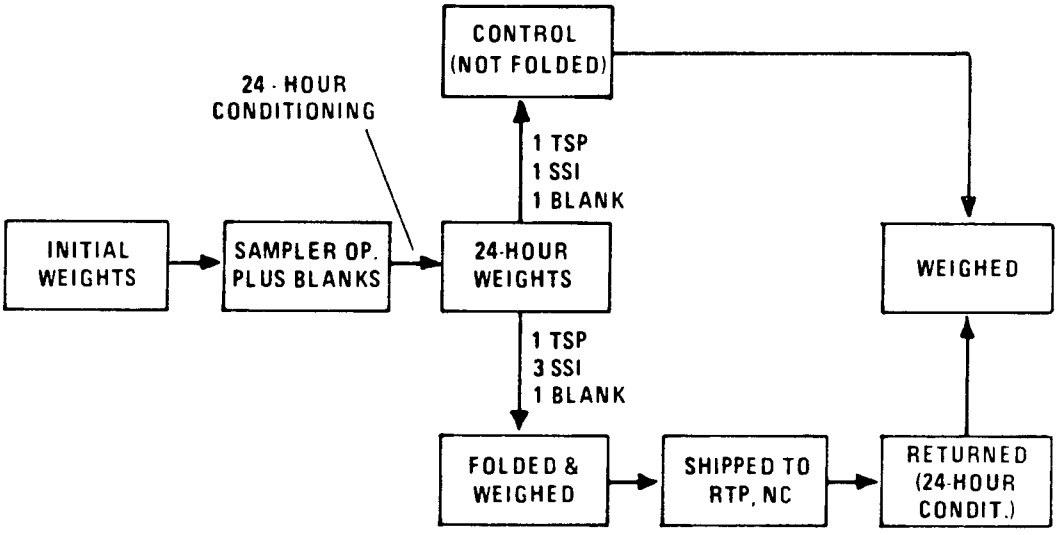

Figure 1. High Volume Sample Handling Diagram.

POLLUTANT LOSSES IN DICHOTOMOUS SAMPLERS

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INTRODUCTION

Ontario Hydro (OH) voluntarily initiated a sulfate aerosol monitoring program in 1975/1/ in response to concerns over health effects. The monitoring network underwent several changes since its inception. In 1981, the sampler used for sulfate aerosol sampling was changed. Dichotomous samplers replaced hi-vol and RAC low-vol air samplers, to take advantage of improved knowledge and methodologies in the study of sulfate aerosol. At the same time, a shift in emphasis from sulfate aerosol to acid precipitation required that other acidic pollutants, such as nitric acid, nitrate and sulfur dioxide, be monitored also. To accomplish this the dichotomous sampler, originally developed for aerosol sampling, was modified slightly to allow collection of these other pollutants.

A comparison with the Ontario Ministry of the Environment (OME) Acidic Precipitation in Ontario Study (APIOS) event network and the Atmospheric Environment Service (AES) of Environment Canada Air and Precipitation Monitoring Network (APN) was undertaken in 1981. The comparison, undertaken at the APIOS monitoring site at Dorset, Ontario, indicated that the OH results for total nitrate and sulfur dioxide were lower than those obtained by OME and AES/2/.

In order to explore the differences observed in the Dorset comparison, two additional studies were undertaken: i) a laboratory investigation to determine whether gaseous nitric acid losses occur in the dichotomous sampler and ii) a second field comparison of a dichotomous sampler, a Teflon-coated dichotomous sampler and an OME/AES-type sampling system under meteorological conditions similar to those encountered in the Dorset comparison. In this paper, the highlights of these more recent studies are presented. Some interpretation of the results is also provided.

LABORATORY STUDY

A modified dichotomous sampler, similar to the ones used in the OH network, was tested in the laboratory. The sampler is composed of three components: 1) inlet head, 2) inlet tube and 3) virtual impactor. The inlet head was placed in a 0.022 m^3 Teflon chamber into which a nitric acid containing atmosphere was introduced. A reference filter cassette, attached to the Teflon chamber, was used to sample the test atmosphere.

Four sampling configurations were examined: these are noted in Figure 1. A total of thirty-six 24-h samples were collected, with at least six 24-h samples for each experimental arrangement. The filter cassettes used in the laboratory tests consisted of a Teflon filter to remove particulates and a single nylon filter which was then extracted and analysed for nitrate using automated colourimetry. The ratio, (C+F)/REF, total (coarse + fine) nitric acid sampled by the dichotomous sampler to that collected on the reference filter were determined and are shown in Figure 1.

The (C+F)/REF results for the complete sampler configuration indicated that gaseous nitric acid is lost to the interior of the dichotomous sampler. The addition of a Teflon liner to the inlet tube reduced the nitric acid loss. Each sampler component was found to contribute significantly to the loss of nitric acid, with the virtual impactor appearing to be the largest sink.

FIELD COMPARISON

An OME/AES-type sampler (1), a modified dichotomous sampler (2), and a Teflon-coated modified dichotomous sampler (3) were compared. The following sampler pairings were made: Pair A - 1 versus 2; Pair B - 1 versus 3 and Pair C - 2 versus 3.

The OME/AES-type sampling system consisted of a multi-stage filter cassette mounted in a Teflon holder, a protective polyethylene cone, a flow controller, a Gast pumping system and a supporting stand. The filter cassette was held in the inverted polyethylene cone 2 meters above ground level. The sampling flow rate was identical to that of the modified dichotomous sampler, 16.7 L/min. The dichotomous samplers collected air at 2 meters also. The dichotomous sampler had an upper cut-off of 15 μm diameter. The OME/AES-type sampler has been estimated to collect particles smaller than about 30 μm, under laminar atmospheric flow conditions.

Identical filter cassettes were used with all samplers. Each multi-stage filter cassette consisted of a 37-mm diameter, 1 μm pore-size Teflon filter for sulfate, nonvolatile nitrate and ammonium aerosol collection; followed by a 37-mm diameter, 1.1 μm pore-size nylon filter for gaseous nitric acid and volatile nitrate collection; and terminated with a 37-mm diameter, potassium carbonate-impregnated Whatman 41 cellulose filter for sulfur dioxide collection. A total of 25 concurrent 24-h samples were collected with the three samplers.

The filters were extracted and analysed for sulfate, nitrate, ammonium and sulfur dioxide by continuous flow analysis (automated colourimetry). The results were evaluated statistically with scattergrams, the nonparametric sign test and least squares linear regression. The nonvolatile nitrate, volatile nitrate and sulfur dioxide scattergrams are shown in Figure 2. The sign test and linear least squares results are presented in Table I.

An examination of Figure 2 and Table I indicates that sulfate, nonvolatile nitrate and ammonium aerosol and sulfur dioxide concentrations measured with the two dichotomous samplers were statistically equivalent. Volatile nitrate concentrations measured with the Teflon-coated dichotomous sampler were larger than those measured with the uncoated dichotomous sampler. This is consistent with the laboratory results. The OME/AES-type sampler was found to collect more nonvolatile nitrate and volatile nitrate (total nitrate) than either of the dichotomous samplers. These nitrate concentration differences are attributed to the additional coarse particulate nitrate sampled by the OME/AES-type sampler and to the partial volatilization of this material/3,4/.

As a comparison, sulfate and ammonium aerosol, both predominantly associated with submicron particles/5/, were sampled in a statistically equal fashion by all three samplers. If nitrate aerosol were predominantly associated with submicron particles then the three samplers would have collected nitrate aerosol in a statistically equal fashion. The loss of nitrate aerosol through volatilization would have been comparable in all samplers, as the flow rates were equal. However, the OME/AES-type sampler collected more nonvolatile nitrate. The difference likely results from the additional coarse aerosol that appears to be sampled by the OME/AES-type sampler.

Sulfur dioxide concentrations measured with the OME/AES-type sampler and the Teflon-coated dichotomous sampler were statistically equivalent. A similar result was expected for volatile nitrate. However, the results were clouded by artifact volatile nitrate from the partial volatilization of the additional coarse nitrate aerosol collected by the OME/AES-type sampler.

These results, combined with the Dorset comparison, suggest that the large nonvolatile and volatile nitrate and sulfur dioxide concentration differences found at Dorset resulted from the following: (a) a small contribution from the inlet height difference (<10%), (b) losses to the aluminum inner walls of the dichotomous sampler, (c) occasional losses to moisture trapped on the OH

filter during the Dorset study, (d) nitric acid artifact contributions during sampling, (e) quality control variations in the preparation of the potassium carbonate-impregnated filters, (f) differences in sample flow rates and (g) the different particle size ranges sampled.

ACKNOWLEDGEMENT

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MASS DISTRIBUTION OF LARGE AMBIENT AEROSOLS AND THEIR EFFECT ON PM-10 MEASUREMENT METHODS

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EXTENDED ABSTRACT

Introduction

A mobile aerosol size classifying sampling system for the collection of very large (100 μm diameter) particles was designed and constructed by Lundgren and Rovell-Rixx at the University of Florida.[1] An analysis van was outfitted to accompany the sampling trailer. A specially designed air sampling inlet was fitted to a very high flowrate (~40 m^3/min) sampler, which greatly reduced the large particle sampling errors due to inertial effects, as described by Lundgren and Paulus.[2] In a 10 km/hr wind, the design criteria predicted a less than 20% error for sampling 100 μm particles. Test results indicated that the sampling error was within this design limit.

Ambient aerosol mass distribution were measured in five cities across the U.S. and compared with data collected using several conventional ambient aerosol samplers and size selective inlet (SSI) samplers. The five cities sampled were Birmingham, Alabama (an industrial area); Research Triangle Park, North Carolina (a background site); Philadelphia, Pennsylvania (metropolitan site); Phoenix, Arizona (high fugitive dust area); and Riverside, California (photochemical aerosol site). These cities provided a variety of sampling conditions and aerosol compositions. The actual location selected in each city was at an EPA Inhalable Particulate (IP) Network station where a history of data for the high-volume air sampler, size selective inlet sampler and the dichotomous sampler were available.

Present ambient air quality standards for particulate matter are based on measurements made by the EPA reference method (High-Volume Method).[3] Weight gain by the sampler filter media, divided by the volume of air sampled, is defined as total suspended particulate matter, or TSP. Health effect studies have correlated this measurement with adverse health effects. However, it is generally accepted that some of the particulate mass collected by this reference method sampler is too large to cause health effects. This has resulted in proposed changes to the primary air quality standard and method of measurement. If new standards are to be set and the method of measurement changed it is necessary to determine the relationship between the present reference method (High Volume Method) measurements and a size selective reference method measurement.

Equipment

Large particle size-distribution data were obtained using the mobile aerosol-sampling system, called the Wide Range Aerosol Classifier (WRAC). A schematic diagram of the WRAC is shown in Figure 1. The large (60cm) diameter aerosol inlet tube leads to a cluster of five individual sampler units, each of which operates at an actual sampling rate of 1.56 m^3/min (55 acfm). The center sampler collects what is considered to be a total aerosol mass sample onto a standard 20.3 by 25.4 cm (8" by 10") glass or quartz fiber filter

media. Four other samplers, placed at 90° intervals around the center sampler, are single stage, rectangular slot impactors. These single stage impactors collect size fractionated samples of the large ambient particles onto grease coated impaction plates. Remaining particles are collected by a standard filter which follows each single stage impactor. Each impactor has a different particle collection efficiency. The particle cutoff diameter (for 50% collection efficiency) for Impactors 1, 2, 3, and 4, are 47, 34, 18.5 & 9.3 μm, respectively. These impactor nozzles were carefully calibrated at the University of Minnesota, Particle Technology Laboratory and the University of Florida to determine their exact cutpoints, as described by Vanderpool.[4]

Particle size-fractionating samplers were operated simultaneously with the WRAC at each site. These samplers included instruments typically found at an Inhalable Particulate (IP) network site such as: high-volume air sampler (HIVOL), a 15 μm type size selective inlet sampler (SSI), and dichotomous sampler (Dicot). These instruments were normally located at the site and were operated by the WRAC sampling team during the special sampling. At each site was at least one high-volume ambient cascade impactor was also used. Most of these samplers were run with a duplicate unit at one or more location to check for repeatability of results.

Results

At each site, samples collected under similar conditions were averaged to determine a representative distribution.

Aerosol Mass Fraction and Particle Size Collected by the High-Volume Sampler

The total atmospheric aerosol mass fraction and particle size collected by the standard High-Volume Sampler (Hi-Vol) can be inferred by comparison with the aerosol mass and size distribution measurements made using the Wide Range Aerosol Classifier (WRAC).

The grand distribution for all 41 usable WRAC runs produce a total aerosol concentration of 134.0 $\mu g/m^3$ with 91.0% of the aerosol mass < 34 μm diameter. Most single city average distribution and the 41 day grand distribution average suggests that the standard High-Volume Sampler collected all particles less than ~ 30 μm diameter (on the average). Calibration data of McFarland, Ortiz and Rodes[5] also suggests a Hi-Vol sampler 50% cut size of about 30 μm. These data were also presented in an article by Watson, Chow, Shah and Pace[6] which discusses the Hi-Vol aerosol collection.

Atmospheric Aerosol Large Particle Mass Distribution

Plots of the total large particle grand average distribution and various city average distributions suggest that the large particle distribution is approximately log-normal. These data also suggests a minimum value between the large and small particle mass modes at about 3 μm (aerodynamic diameter). If one assumes the large particle mass mode is log-normal and that there is a minimum point at 3 μm, several features of the distribution can be determined. A best fitting curve was drawn through the actual mass measurement data plotted as a cumulative distribution curve on log-normal probability paper. Several of these curves were then drawn as histograms in Figure 2.

Discussion

There has been much discussion recently about incorporating an upper size limit for the regulation of particulate matter. A size limit of 10 μm has been suggested. The WRAC measurements reveals that the fraction of particulate matter in ambient air associated with particles less than 10 μm diameter can vary between about 50% and 90% for single run percentages (for Birmingham and Riverside respectively). The average distribution data for the high concentration days in Birmingham and Riverside suggest that a 10 μm size selective sampler would collect 68% and 89% respectively, of what the standard High Volume Air Sampler would collect. An average distribution for all 41 test days from 5 cities suggest the 10 μm sampler would collect 74% of that collected by the Hi-Vol.

Ambient aerosol distributions display a large particle mass mode under a variety of situations. The situations include: relatively clean areas like Research Triangle Park, areas with high small-particle concentrations like Riverside, areas with high large-particle concentrations like Phoenix, and areas with high concentrations of large and small particles like Birmingham. Each of these areas will be affected differently with the implementation of a new health-related particulate matter standard. This will relieve certain areas which have historically been in a non-attainment status because of the presence of a high mass fraction of large particles.

Acknowledgment

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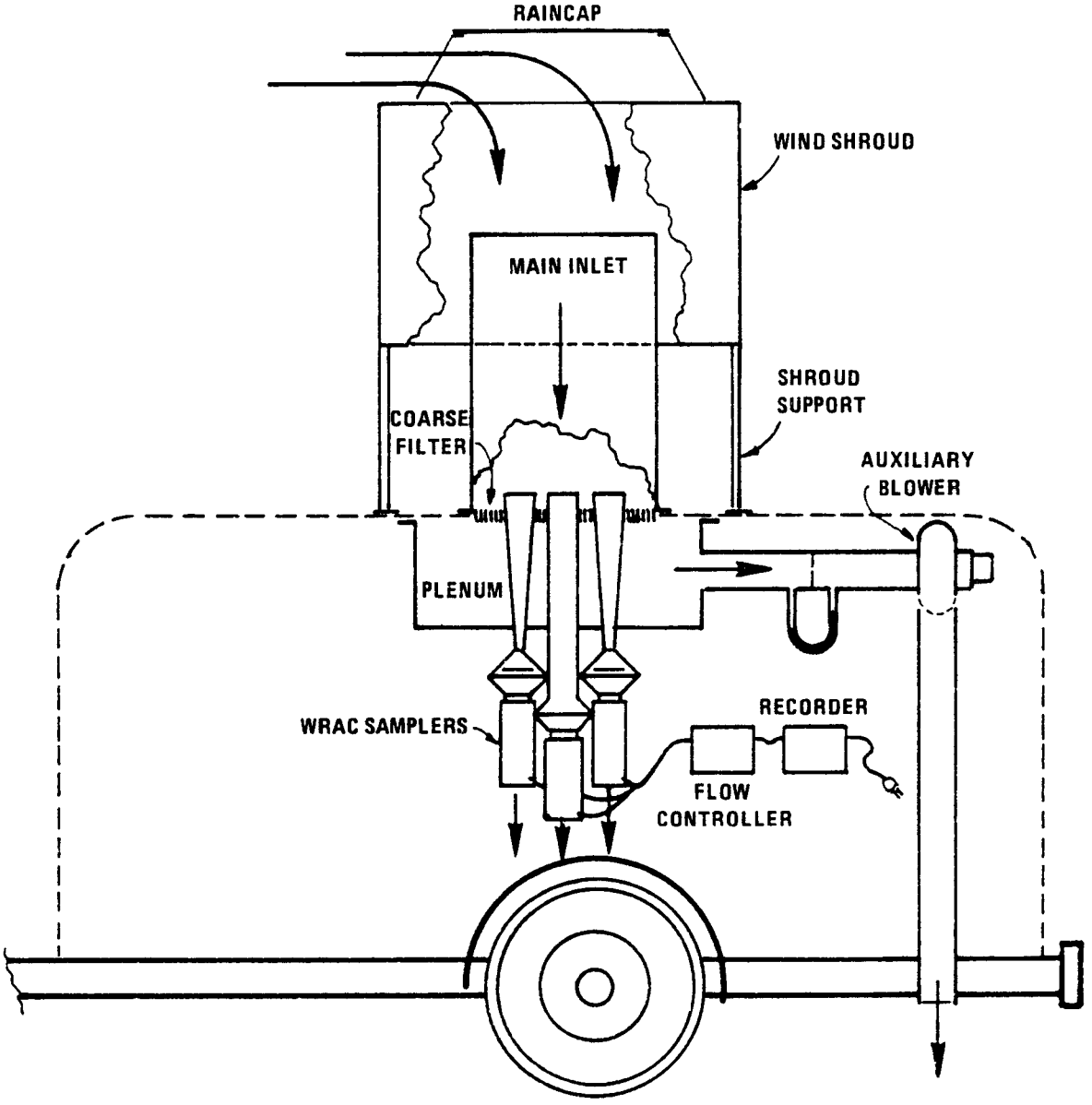

Figure 1. Schematic diagram of mobile sampling system.

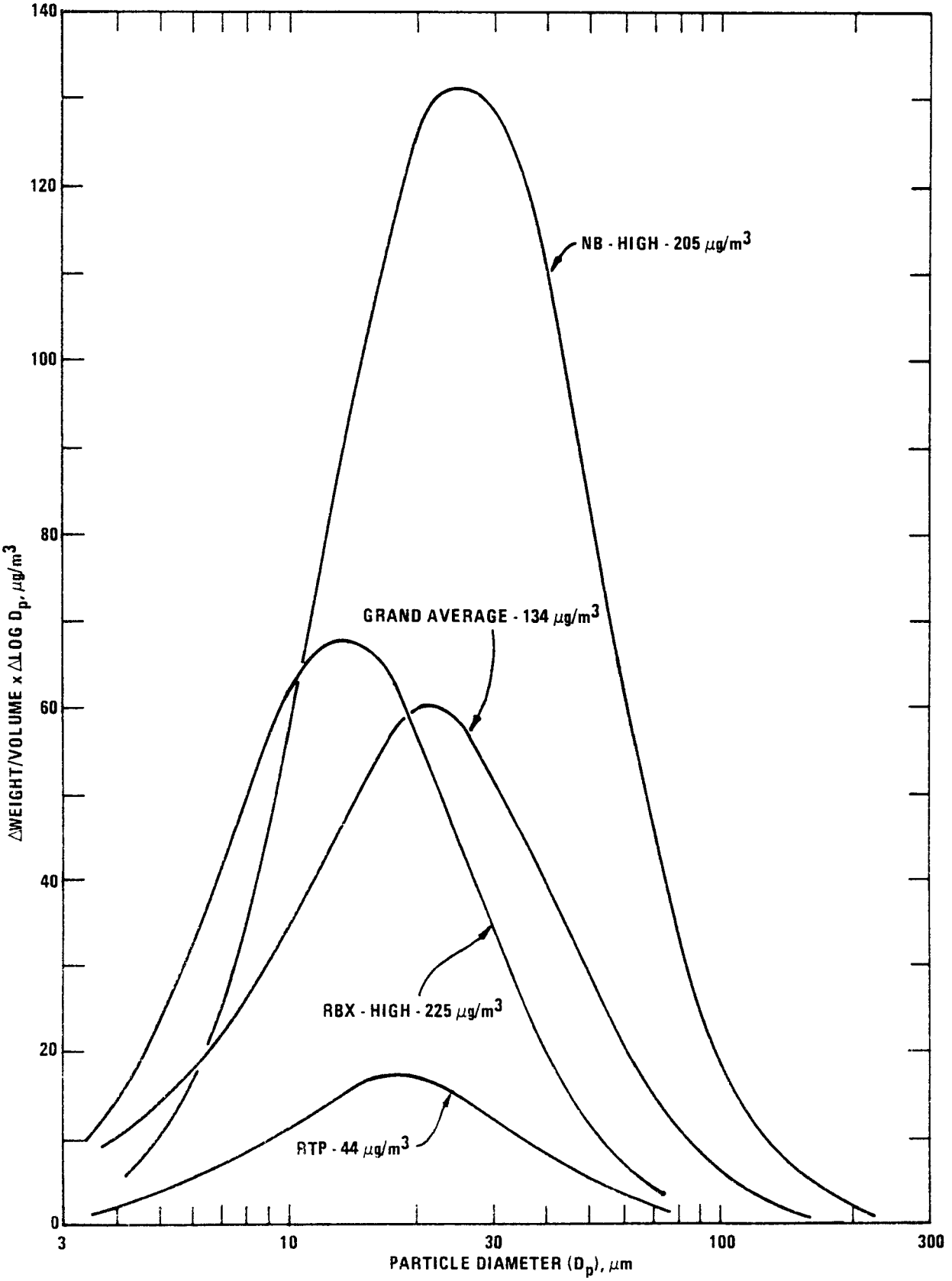

Figure 2. Large particle mode distributions.

ROTARY IMPACTOR FOR COARSE PARTICLE MEASUREMENT - MASS AND CHEMICAL ANALYSIS

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ABSTRACT

A unique combination of an effective sampler and analysis of individual particles has been used in studying large particle (> 5 μm) at a rural site in Eastern United States. The sampler is a modified "high volume" rotary inertial impactor, which consists of four collectors of different widths, rotating at high speed and collecting particles by impaction. The collector surfaces were mylar films coated with apiezon to ensure retention. After sampling, the collection surfaces were weighted to obtain the mass-size distribution. A section of the mylar sample was transferred to a scanning electron microscope to study in detail the morphology and elemental content of individual particles.

The following features characterize the impactor: (a) Particles 6 to 100 are collected effectively on four stages. Stages A, B, C and D -- collect particles larger than 6 μm, 11 μm, 20 μm, and 29 μm, respectively. (b) The sampler operates at high velocities, therefore sampling a "large volume" of air -- a necessary requirement because of the low concentration of large particles; (c) Due to the special collection technique, no losses "to the walls" or "bouncing off" are expected. To insure a high degree of retention the collector faces were coated with a thin film of apiezon; (d) No problems associated with isokinetic sampling at variable wind speed are expected, since the collectors operate at velocities considerably higher than the average wind speed, and the instrument has a wind vane to point it into the wind; (e) The various stages allow the collection of particles over restricted ranges of the

size distribution without interference from particles outside of the range. This eliminates errors in counting and x-ray analysis of individual particles due to the excessive covering of the collector surfaces by numerous small particles.

Samples were taken during the month of August 1983 in a rural site in western Maryland as part of the Deep Creek Lake (DCL) Experiment. The objective of the DCL study was to collect air quality data base and source signatures to determine the impact of primary emissions and secondary pollutants from combustion sources on a remote site. The sampling site is located in a rural area surrounded by over fifteen coal-fired power plants which are big enough (> 1000 MW) and close enough (50 to 300 km) to have a significant impact on the site.

For the electron microscopy analysis, the mylar films were observed in an optical microscopy to verify a homogeneous collection of particles on the collector surface. The analysis includes particle size, shape and special surface features, and elemental content of the particle.

Out of the samples collected at the DCL site, two samples which were chosen for SEM analysis representing two different atmospheric conditions -- low versus high wind speed. Both samples were representative of midday summertime conditions.

Information on a few hundred individual coarse particle has been obtained, including their heterogeneity and surface properties. Based on the elemental content and mosphology, particles were assigned to several category groups such as clay minerals, quartz, calcite, gypsum, coal and oil fly ash, biological (pollen, spores, plant debris) particles, and special particles -- mostly of anthropogenic sources with high metal content -- rich in Fe, Pb, Zn.

The main results are summarized as follows:

(a) In the rural area studied here the aerosol mass distribution peaks in the 10 to 20 μm range with fairly significant mass in the 20 to 60 μm. During windy conditions mass concentration is higher for most parts of the size range, but not in the below 10 μm range. The wind speed may have two effects on aerosol concentration: higher wind speeds cause resuspension of particles, while low wind speeds are associated with less dispersion and higher concentration of the smaller size fraction.

(b) Electron microscopy analysis of individual large particles revealed the overwhelming presence of natural contributions in the whole range, namely minerals (clay minerals, calcite and quartz -- about 50 percent), and biological particles such as pollen and spores.

(c) Contribution of anthropogenic sources to large particles was limited to a few percents and mainly to particles smaller than 10 μm. Most of these were fly ash transported from coal-fired power plants situated 50 to 300 km upwind of the sampling site.

(d) Pollen particles represent a large fraction of the large particles collected at the DCL site. Different types have been observed even on the calm day indicating a fairly long residence time in the air. The pollens contained large amounts of sulfur, either as small sulfate particles deposited on the pollen surfaces, or as absorption of SO_2 through the wet surfaces.

(e) Mineral particles were found to be enriched in sulfate. As with the pollen the sulfate may have accumulated on the particle surfaces while being airborne. The sulfate was found to be associated with calcite and clay minerals in significant amounts, about 1.5 to 3 percent of the particle mass, or an average of 0.02 g $SO_4^=$. g^{-1} solid.

INDIVIDUAL MICROMETER-SIZE AEROSOL COMPOUNDS

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ABSTRACT

A quantitative method for the analysis of individual micrometer-size dry and wet aerosols is developed. It is based on mineralogical and microchemical analysis. An aerosol compound is analyzed for crystallography by petrographic microscopy, and for anions and cations by electron microscopy. Analysis of the anions NO_3^- and SO_4^{--} is based on their microchemical reactions with nitron and $BaCl_2$, respectively. The microchemical analysis is identified by transmission electron microscopy and the anion Cl and cations such as Ca, Mg, K and Na are determined with a scanning electron microscope interfaced with an X-ray energy spectrometer. The methods were tested in several locations: (a) At the Boulder Atmospheric Observatory, a 300 m tower located in a rural area, during chinook conditions and within clouds. (b) At Tel-Aviv University, during air pollution and Sharav conditions. (c) At Masada, Dead Sea, 10 cm above sea level, during winter conditions. The aerosols are classified as mineral, soot containing, water containing and electrolite (mixed dry and wet aerosols).

INTRODUCTION

The study of individual micrometer-size aerosols provides a great deal of new information on the characteristics of aerosols, which otherwise cannot be obtained. The aerosols in the atmosphere are not stable; they change during transport due to chemical reactions within the particles and of particles with gases, coagulation of particles and alterations of relative humidity (Hänel and Zankl, 1979; Mamane et al., 1980). These changes can be noticed by analysis of individual aerosols from different sources.

There are several sources of aerosols, which can be grouped in two categories: (1) Natural (soil-derived aerosols, sea-spray aerosols, volcanic-derived aerosols and organic particles) and (2) Anthropogenic. The basic aerosol components have been classically defined as water-soluble particles, dust like particles, oceanic particles, soot particles and ash particles (WCP, 1983).

In our work we classify the aerosols into four types: mineral and dust like particles, soot particles, electrolite particles and mixed particles. The electrolite particles are sea salt particles generated at the sea surface by the action of the wind: such particles are halite (NaCl), sylvite (KCl), carnallite ($K\ MgCl_2.6H_2O$) and those containing sulfate and nitrate. The mixed particles consist of several compounds and are water containing, such as soot coated with $H_2\ SO_4$ and dust like particles coated with electrolites.

METHODS AND ANALYSIS

Aerosols were collected on electron microscope (EM) grids, on plain glass and on blue gelatine, that were mounted on three stages of a four-stage Casella impactor. The aerosols were collected for chemical and mineralogical analysis by microchemical spot test (Mamane and Pueschel, 1980), X-ray energy dispersion analyzer, electron microprobe analyzer and petrographic microscope (Ganor et al., 1982).

GEOGRAPHIC LOCATION AND METEOROLOGY

The methods were tested in several locations: (1) At the Boulder Atmospheric Observatory (BAO), USA. The BAO is a 300 m tower located in a rural area 20 km east of Boulder and 25 km north of Denver. Aerosol samples were collected at 10, 22, 50, 100, 150, 200, 250 and 300 m levels on the tower (Ganor and Van Valin, 1982). (2) In Israel, at three places: (a) Tel-Aviv University (TAU), a residential area in north Tel-Aviv, on the roof of a 15 m building, located 2 km from the Mediterranean Sea; (b) Tel-Aviv Marina shore (TAM), 0.5 m above sea level; and (c) Masada shore (DSM), 10 cm above the Dead Sea level.

The aerosols were collected during different meteorological conditions: at BAO, during chinook conditions and within a cloud; at Tel-Aviv, in winter, during air pollution and Saharan dust storms; at Masada shore, in winter.

RESULTS

PARTICLE MORPHOLOGY

A treated an a non-treated marked screen were observed by a petrographic microscope, a transmission electron microscope (TEM) and a scanning electron microscope (SEM) for shape, size distribution and chemical composition.

Figures 1-3 are photomicrographs of particles collected at TAU on a dusty day-November 19, 1983. Figure 1 is a petrographic photomicrograph of Saharan particles on a nontreated screen. The particles were identified as quartz, calcite, dolomite, feldspar, clay minerals, fossile fragments and oil soot. Figure 2 is an SEM photomicrograph of the same sample on a non treated screen. The particles were analyzed for their elements with an X-ray energy analyzer. The major elements found in the particles were Al, Si and Ca. Figure 3 is an SEM photomicrograph of the same sample on a treated $BaCl_2$ screen. The figure shows that the particles are mixed sulfates. The circular spots indicate the presence of sulfates. Most of the Saharan particles are coated with a thin layer of sulfate. In the figure there are three particles, identified as (a) clay, (b) textularia fossil fragment and (c) calcium carbonate aggreate.

Reaction spots of individual droplets were tested in the laboratory on blue gelatine, $BaCl_2$ and nitron pre-coated screens for shape, size distribution and microchemical composition by a petrographic microscope and a scanning transmission electron microscope (STEM). Later, the methods were tested at TAM and TAU.

Figures 4 and 5 are typical photomicrographs of aerosols collected on February 21, 1994, at TAM and on October 24, 1983, at TAU. Figure 4a is a

typical TEM photomicrograph of sea drops collected at TAM on February 21, 1984. The reaction spots indicate the impaction of the drops onto a $BaCl_2$ pre-coated EM screen. Figure 4b is an SEM photomicrograph of the sample shown in Figure 4a. The cubic particles inside the reaction spot are salt particles, containing Mg, Na, S, Cl, K and Ca. The use of the TEM and SEM with an X-ray energy analyzer in this case gives us more information, which otherwise cannot be obtained. Figure 5 is a typical photomicrograph of air pollution particles collected onto gelatine pre-coated glass at TAU on October 24, 1983. Some of the rounded particles show drop replicas, and are therefore identified as water-containing particles.

The size distribution of particles collected on stages 3 and 4 of the Casella impactor is shown in Figure 6 ($0.8 < r < 10$ μm). The spectrum of particle size was found to be a straight line, when plotted as log (dN/dlogr) vs. log r, with a slope of -4. dN is particle number (cm^{-3}) per logarithmic size interval, and r is particle radius.

At the Dead Sea valley, aerosols can be found that were transported from different sources: the Mediterranean Sea, the Sahara desert, the surrounding mountains and the Dead Sea. Prevailing meteorology indicated that most of the particles were minerals transported from the surrounding desert. Using the reaction spot technique for individual aerosols, we found out that only one-third of the aerosols were minerals and about two-thirds were Dead Sea particles. Figure 7 is a typical photomicrograph of Dead Sea aerosols collected 10 cm above the Sea. The microchemical spot test indicates the impaction of dry particles and drops onto a pre-coated $BaCl_2$ and nitron screen.

At BAU, sulfate, nitrate and cloud droplets were analyzed and identified with the same test. Figure 8 is an SEM photomicrograph of cloud droplets

collected on a pre-coated carbon screen. The particles inside the drop are NaCl crystals.

Figure 9 shows typical TEM and SEM photomicrographs of nitrate, and the X-ray energy dispersion spectrum (XEDS). The nitrate, identified by the fingerlike microreaction, contains Al, Si, Ca and a trace of K and Fe.

PARTICLE COMPOUNDS

The particles, which have been tested in several locations, were classified as dust like and minerals, soot containing, water containing, droplets, nitrate and sulfate. Tables 1-3 summarize the microchemical analyses: Table 1, the frequency of elements present in the aerosol particles, in percentage collected at BAO, TAU and DSM; Table 2, the percentage of the elements contained in the particles at TAU, TAM and DSM; and Table 3, the percentage of aerosol compounds at BAO, TAM, TAU and Dead Sea, based on sulfate and nitrate identification using the $BaCl_2$ and nitron techniques, by petrographic microscopy and by SEM-XEDS.

SUMMARY

The size spectra of cloud droplets and aerosols and of the aerosol compounds were measured using multi-microchemical techniques, in different meteorological conditions. The techniques provided an assessment of water-containing aerosols, and most particles were identified as electrolite aerosols. It was also found that because of the high relative humidity at TAU the electrolite particles became water-containing droplets. Simultaneously, various techniques were used to obtain relevant data on individual aerosol

compounds. For instance, it was found out that a considerable portion of particles contain dust like nuclei, as in the Dead Sea droplets. On a polluted day at TAU, about 42% of the micrometer-size particles were found to be electrolites. 25%, soot; and 33%, dust like particles. The mixed sulfate and nitrate particles were probably formed through a heterogeneous nucleation of SO_2 and NO_2 on the surface of insoluble dust like particles.

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Table 1. PERCENTAGE OF PARTICLES CONTAINING THE ELEMENT AT VARIOUS LOCATIONS.

	BAO		TAU	DSMTAU
Height (m)	300		15	0.115
Diameter (μm)	0.5-4.00.4-20	0.5-5.0	0.5-5.0	
No. of aerosols	200	100	100	100
Conditions	Polluted	Polluted	Winter	Dusty
Element		Percentage		
Na	27	43	5	24
Mg	12	37	28	24
Al	35	75	37	73
Si	65	93	58	89
P	5	0	4	7
S	66	81	60	63
Cl	13	50	13	61
K	28	75	37	59
Ca	35	88	61	73
Ti	3	67	3	9
Fe	31	63	38	70
Zn	4	0	1	3
Pb	0	25	0	3
V	0	18	0	1
Se	0	12	0	0
Br	0	6	0	0

Table 2. PERCENTAGE OF THE ELEMENTS CONTAINED IN THE PARTICLES AT VARIOUS LOCATIONS

	TAU	TAM	TAM	DSM
Date	23 Jan 84	21 Feb 84	19 Nov 82	21 Dec 83
Height (m)	15	0.5	1	0.1
Conditions	Polluted	Bright	Dusty	Bright
Element		Percentage		
Na	3	31	1	
Mg	1	4	1	7
Al	6	1	9	8
Si	19	1	36	23
S	28	6	2	15
Cl	5	55	2	19
K	5	1	10	3
Ca	24	1	30	22
Ti	1	...	2	...
Fe	4	...	7	3
Pb	2	...	...	...
V	1	...	...	...
Se	1	...	...	...
Br	...	...	...	...

Table 3. PERCENTAGE OF AEROSOL COMPOUNDS AT VARIOUS LOCATIONS

	BAO	BAO	TAU	TAM	TAM	DSM
Height (m)	300	300	15	1	0.5	0.1
Date	16 Apr 81	27 Jul 81	24 Oct 83	19 Nov 82	21 Feb 84	21 Dec 83
Conditions	Chinook	Within Cloud	Polluted	Dusty	Bright	Bright
Percentage						
Nitrate	...	26	6	...	...	...
Sulfate	95	1	36	10	...	...
Dust-like	5	...	33	88 *	14	32
Droplets	...	73 #	...	...	86 **	68 ##
Water Containing	...	...	34	...	...	...
Soot containing	...	...	25	2	...	...

42% of the minerals contain sulfate.
* The droplets contained Na, Al, Si, S, Cl, Ca, Fe.
** The droplets contained Na Cl and elements as Mg, S, K, Ca.
The droplets contained Mg, Al, Si, S, Cl, K, Ca, Fe.

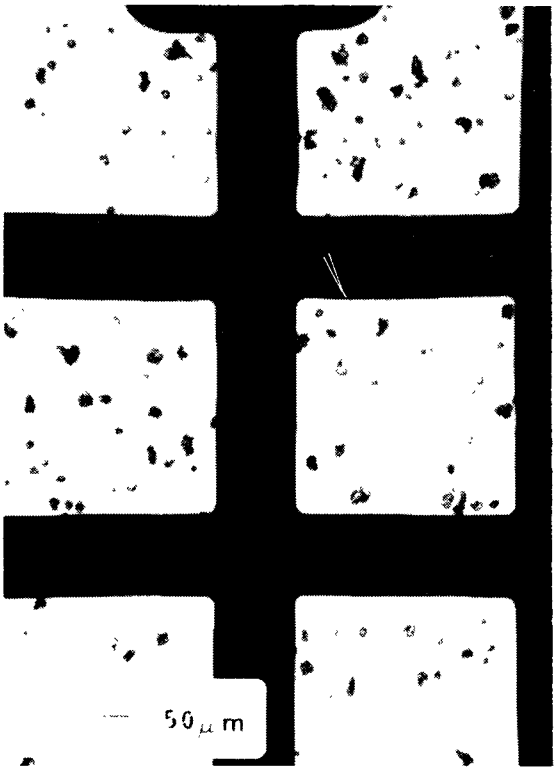

Fig. 1 - Petrographic microscope photograph of Saharan particles on a non-treated EM screen

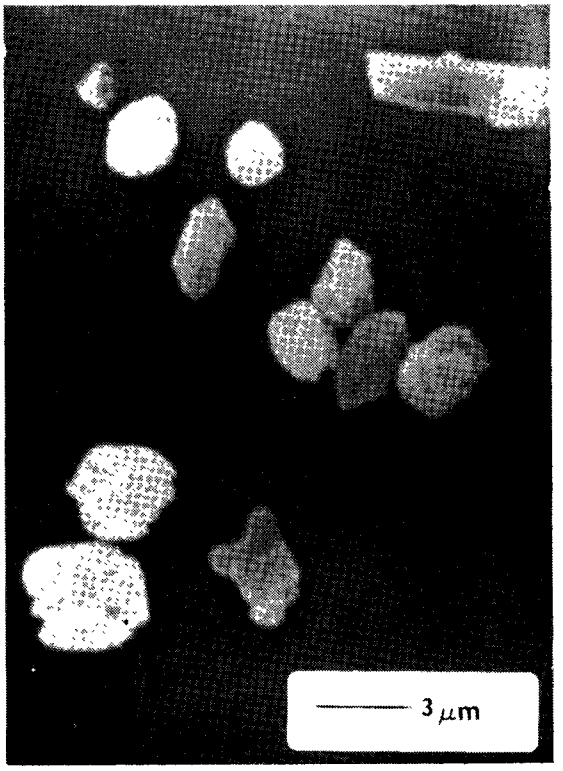

Fig. 2 - Typical non-treated screen SEM photomicrograph of Saharan particles shown in Fig. 1

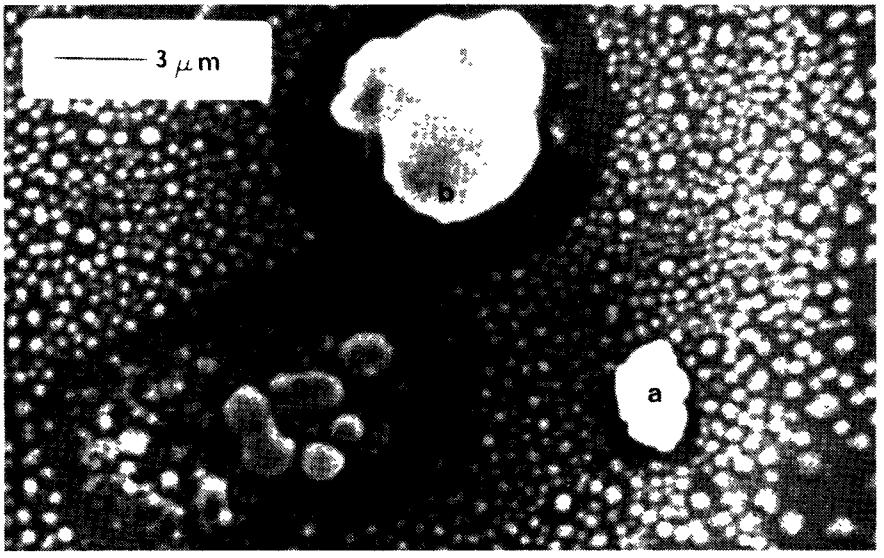

Fig. 3 - Photomicrograph of the $BaCl_2$ treated sample shown in Fig. 2. The circular reaction spots indicate the presence of sulfates. (a) clay, (b) textularia fossil fragment, and (c) calcium carbonate aggregate.

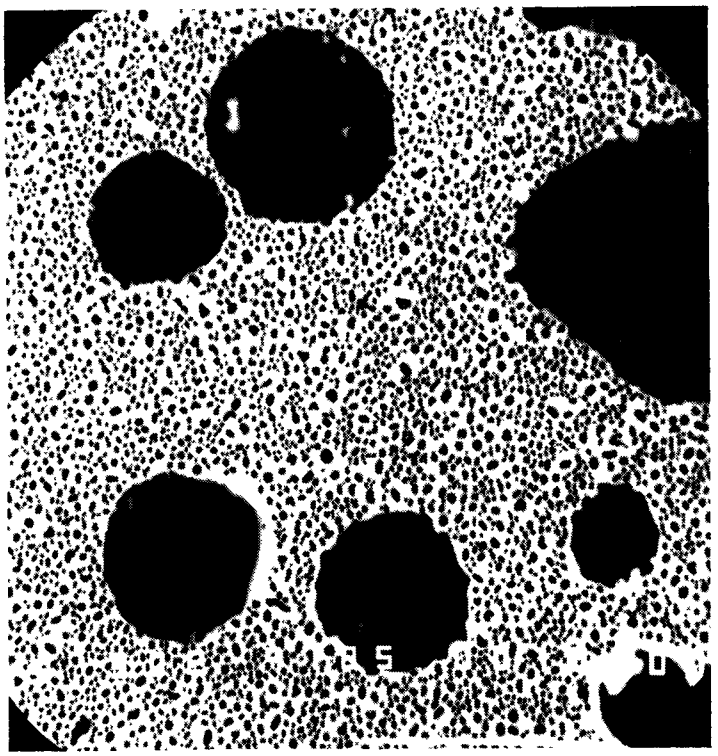

Fig. 4a - TEM photomicrograph of the pre-coated $BaCl_2$ Mediterranean drops collected at TAM

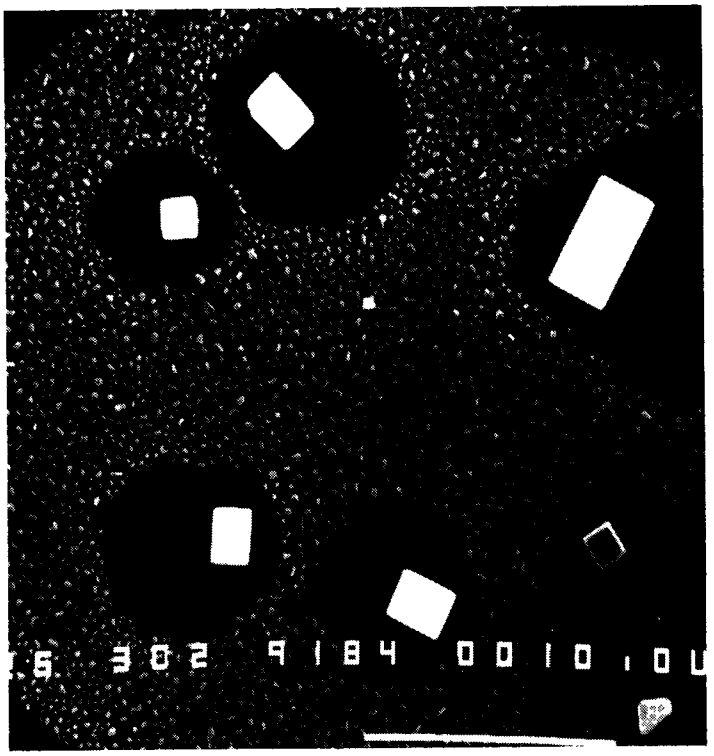

Fig. 4b - SEM photomicrograph of the drops shown in Fig. 4a. The cubic particles in reaction are salt particles, containing Mg, Na, S, Cl, and Ca.

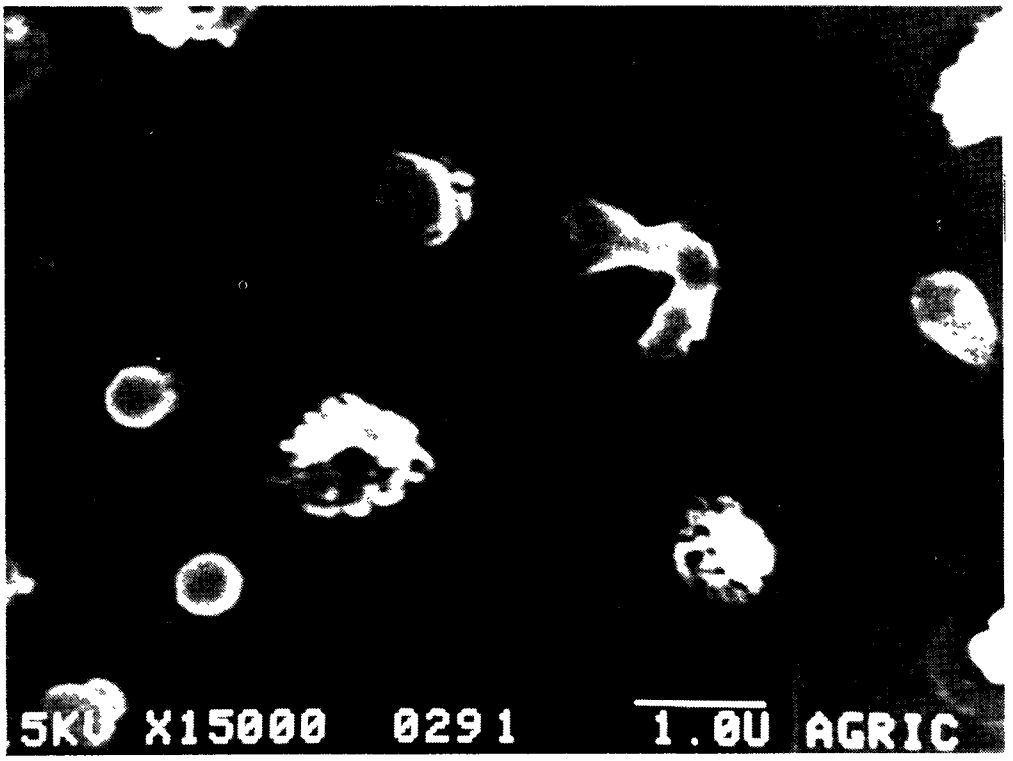

Fig. 5 - SEM microphotograph of particles collected onto gelatine at TAU during a polluted day - October 24, 1983. The circular replica indicate the presence of water.

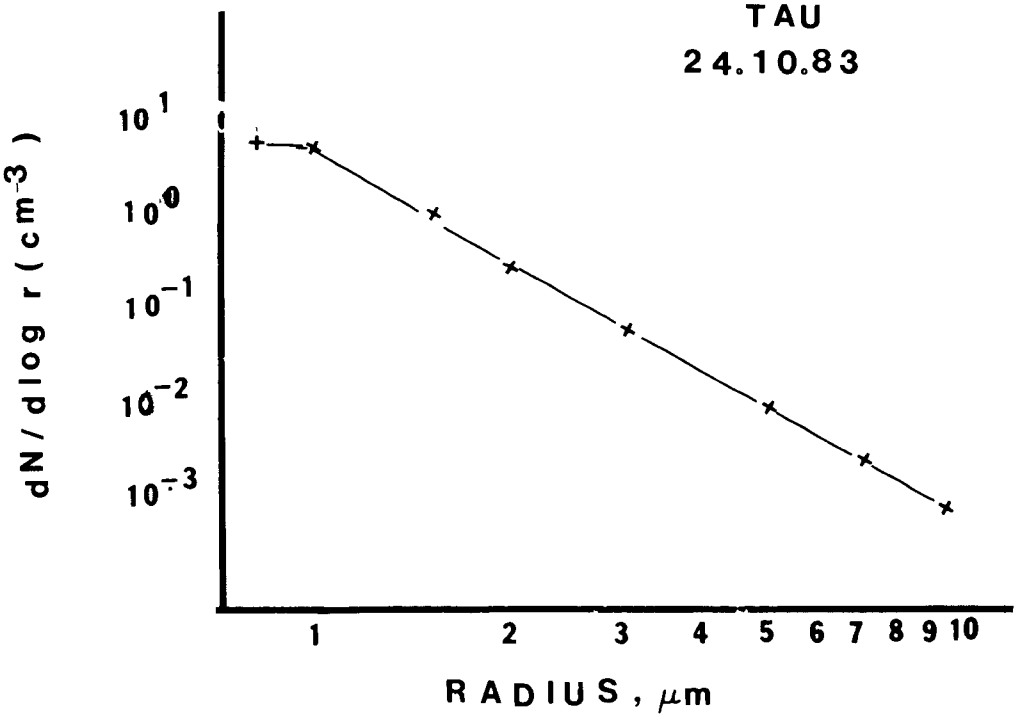

Fig. 6 - Particle size distribution of the sample collected at TAU on October 24, 1983

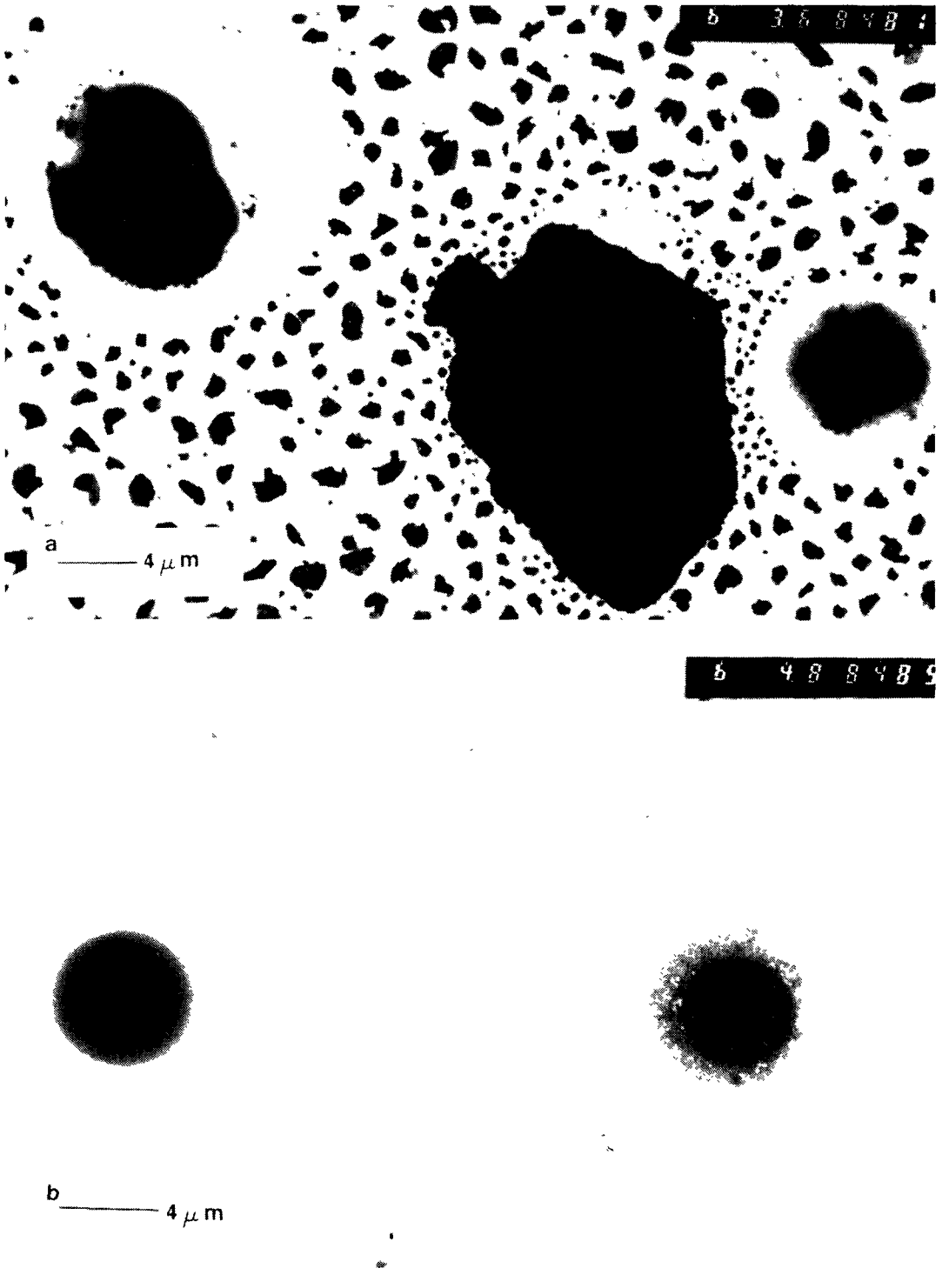

Fig. 7 - Typical TEM microphotograph of Dead Sea aerosols collected on pre-coated (a) $BaCl_2$ and (b) nitron. The circular reaction spots on the $BaCl_2$ indicate the presence of drops. The circular spot reaction on the pre-coated nitron shows the presence of drops.

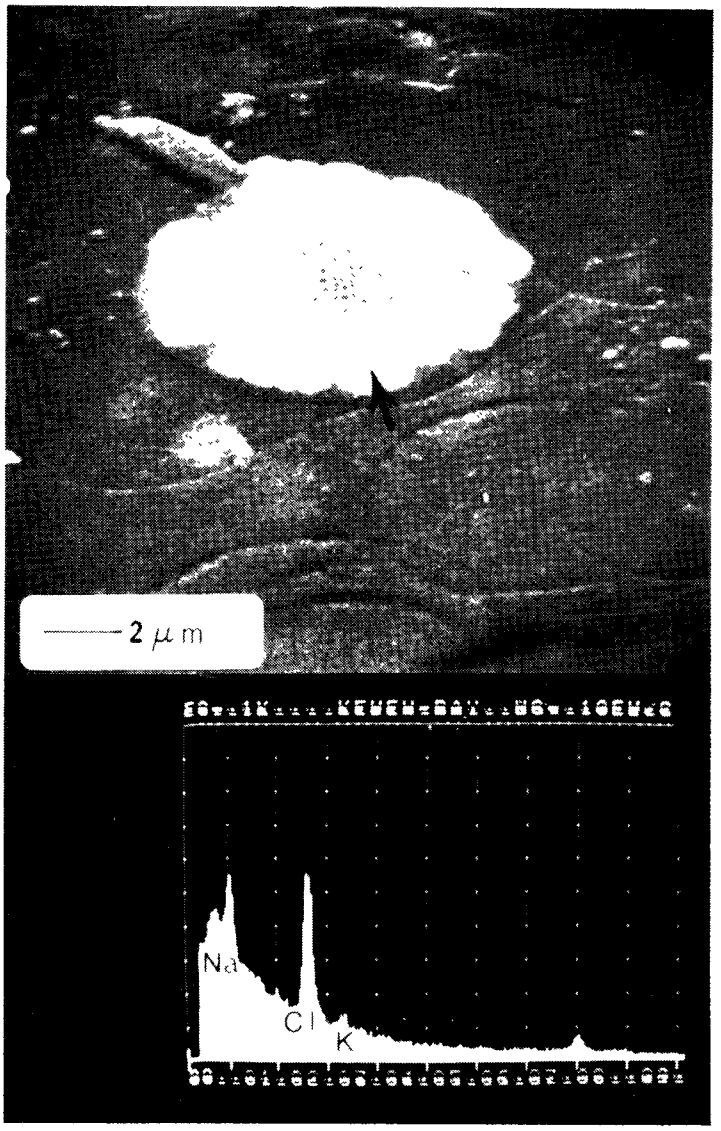

Fig. 8 - SEM photomicrograph of cloud droplets collected onto pre-coated carbon screen at BAO. The particles inside the drops are NaCl crystals.

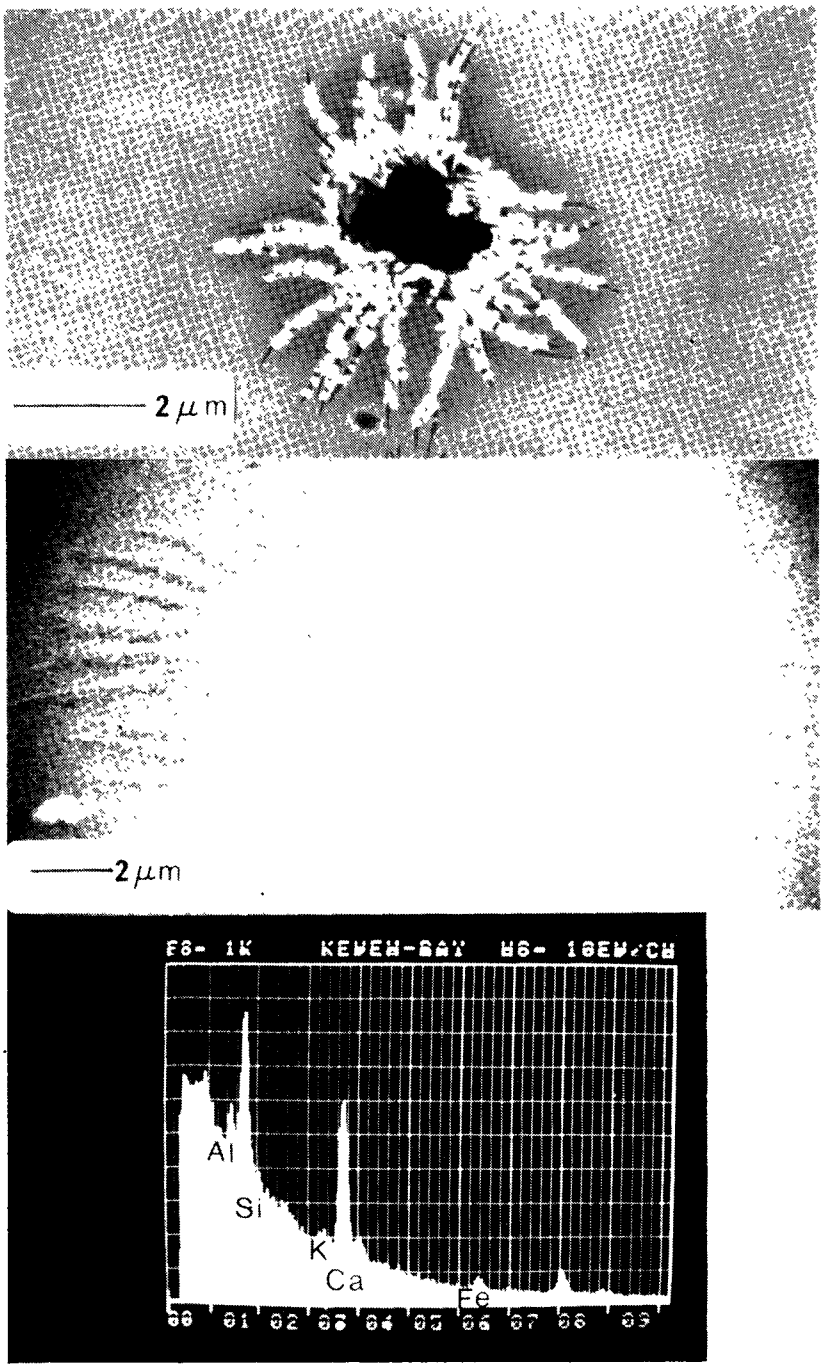

Fig. 9 - TEM and SEM with X-ray energy spectra of nitrate collected at BAO. The nitrate is identified by the finger-like micro-reaction. It is mixed with Al, Si, Ca, K, and Fe.

HUMAN EXPOSURE ASSESSMENT: A NEW METHODOLOGY FOR DETERMINING THE RISK OF ENVIRONMENTAL POLLUTION TO PUBLIC HEALTH

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INTRODUCTION

Determining the risk of environmental pollution to public health requires a knowledge of five fundamental components: (1) the sources of pollutants, (2) the transport of these pollutants from sources to humans, (3) the distribution of exposures of humans to these pollutants, (4) the doses received by people who are thereby exposed, and (5) the adverse health effects resulting from these doses. These five components may be viewed as links in a chain -- from source to effect -- comprising the full risk model (Figure 1):

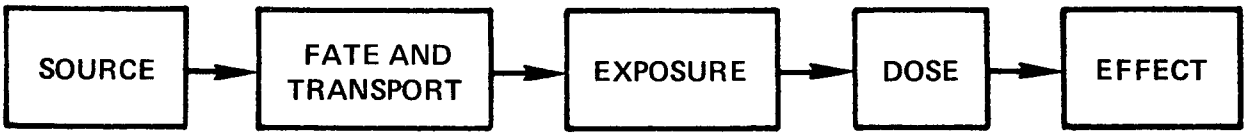

Figure 1. Major components of conceptual risk model relating the sources of environmental pollution to the ultimate effects of pollutants on the population.

Despite the importance of each of the five components for estimating the public health risk associated with environmental pollution, our scientific knowledge about each component is not balanced. Usually, environmental pollution comes to the attention of public officials because pollutant sources, such as a smoke stack plumes or leaking toxic waste drums, provide obvious evidence of a disturbing environmental condition. Thus, a great deal is known about the sources of pollution, and source abatement and control has received considerable research attention. Once a source of environmental pollution is known and identified, interest often focuses on the manner in which the pollutant moves through the environment -- its fate and transport -- ultimately becoming assimilated by ecosystems or transported to humans. As with the source component of this risk model, the fate and transport component

likewise has received considerable research attention. The field of meteorology has developed a great number of atmospheric dispersion models, and other fields have developed models for the movement of pollutants through streams, soil, and the food chain[1].

As with the first two components, the last component -- the effects of pollutants on humans -- also has received considerable research attention. Numerous studies have been undertaken relating various exposures and doses to identifiable effects on animals and humans, as can be seen in any of the published air quality criteria documents[2,3]. However, our knowledge of two important components of the risk model -- exposure and dose -- is very limited for most pollutants. Accurate exposure data unfortunately are lacking for most of the air pollutants that EPA regulates.

The environmental risk model is serial in structure: the output of each component serves as the input to the next component. Thus, the absence of valid information on any component seriously impairs our ability to assess public health risk, and the absence of human exposure data has serious implications for regulatory policies. If, for example, human exposures to a criteria air pollutant were found to be negligible, then the public health risk of the pollutant may be exaggerated, and concern about controlling this pollutant could be reduced. Conversely, if human exposures to a pollutant were found to be higher than previously suspected, then additional control actions might be warranted. In all cases, the important information needed is the frequency distribution of exposures of the population.

APPROACHES FOR DETERMINING EXPOSURES

Two alternative conceptual approaches have been proposed for obtaining information on the frequency distribution of exposures of the population to environmental pollutants:[4,5]

Approach A. An obvious solution, called the "direct approach" by Duan[5], is to measure the concentration at the boundary of the person by monitoring the air he breathes, the water he drinks, and the food he eats. Several recent field studies have implemented this conceptual approach. The Total Exposure Assessment Methodology (TEAM) study measured

the concentration of an important class of chemicals, volatile organic compounds (VOC's), in the air, drinking water, and breath of respondents using personal monitoring techniques[6-9]. In order to generalize to a larger population than the number actually surveyed, a multi-stage statistical sampling design was used. In Elizabeth and Bayonne, New Jersey, 365 respondents carried a Tenax portable personal exposure monitor, and the levels of VOC's in their breath and drinking water also were determined. A major finding was that personal exposures (and indoor levels) were much greater than outdoor exposures for at least 11 important carcinogens[8,9].

More recently, the Denver-Washington, DC, carbon monoxide (CO) human exposure field survey was carried out[10]. Because CO is associated only with air pollutant exposures, it was not necessary to monitor food or drinking water. A specially designed personal exposure monitor for CO was developed which could measure and record concentrations with a time resolution of one minute of less[11]. An interviewer delivered the monitor to each respondent and picked it up 24 hours later. Each respondent carried the monitor with them while engaging in their normal daily activities. By interpreting their diaries listing the times that each activity began, it was possible to obtain 712 24-hour exposure profiles in Washington, DC, and 450 48-hour profiles in Denver, CO. Although these data currently are being analyzed, many new findings are emerging[12-14].

Approach B. An alternative approach, called the "indirect approach" by Duan[5], is to measure and fully characterize pollutant concentrations in the locations (called "microenvironments") people normally visit. Then, by combining this information with data from activity pattern and time budget studies, it is possible to compute an estimated exposure profile for each person. This approach initially was suggested by Fugas[15] and is discussed by Duan[5]. Computer models such as SHAPE[16] and NEM[17] have been developed for combining the activity data with the microenvironmental concentration data, but human exposure activity modeling is in its infancy and needs further development and field testing.

SUMMARY AND CONCLUSIONS

A new methodology, human exposure assessment, is emerging for determining the frequency distribution of exposures of the population to environmental pollutants. Two approaches, direct measurement and indirect estimation through models, have been developed. Several field studies have been undertaken demonstrating the feasibility of the direct approach, yielding a wealth of new exposure data and many important new findings. The indirect approach has not been fully developed and needs further work, but it, too, may yield much important exposure information. Initial studies have dealt with volatile organics and CO, and the same methodology now needs to be extended to NO_2, inhaled particles, and other important pollutants.

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RESULTS OF THE CARBON MONOXIDE STUDY IN WASHINGTON, D.C., AND DENVER, COLORADO, IN THE WINTER OF 1982-83

Introduction

During the winter of 1982-83, the U. S. Environmental Protection Agency conducted a large-scale urban field study to develop and test methodologies for determining, with known accuracy, the exposures to carbon monoxide (CO) of the population of a city. The primary study objective was to develop and evaluate a methodology for measuring the distribution of CO exposures of a representative population of an urban area. Two urban areas were chosen for study; Denver, Colorado, and Washington, D.C. These areas were selected because they differ in elevation, relative CO levels based on historical fixed site data, diversity of land use characteristics and commuter patterns. Approximate dates of field monitoring were November 1, 1982, through February 28, 1983.

Participants in the study were chosen using a 3-stage design. Approximately 3200 households in Denver and 5800 households in Washington, D.C., were screened by telephoning a representative random sample of the population. During the screening process, respondents were asked about their smoking habits, commute times, and other factors which might influence CO exposures. Data from the screener survey made it possible to subsequently create a stratified random sample of individuals with particular characteristics of interest. For example, only non-smokers were selected in the final sample, and persons who commuted long distances were more heavily sampled than were those who commuted short distances.

The exposure measurements were made with a specially designed personal exposure monitors (PEM) with a built-in data logger. The data logger was developed to provide an integrated value expressed in ppm-minutes which was determined by change of activity pattern or automatically on the clock-hour. The clock-hour values were necessary for comparing PEM results with the fixed site results. The interviewer visited the respondent and left a calibrated PEM with instructions for its use and a diary. The respondent carried the PEM recording each change of location and activity in the diary and depressing the data logging button when they changed activity. A questionnaire also was administered to obtain detailed information about the respondent's home, workplace and commute habits. Details of the survey are presented by Whitemore, et al.[1] Other details are reported in the final reports by Johnson[2] and Hartwell.[3]

Study Results

1. Quality Assurance

(a) Precision of PEM Values

The assessment of PEM precision was determined by having a member of the project field staff carry two or more randomly assigned monitors for a 24-hour period. The monitors were exposed to typical sampling conditions of changing temperature, humidity, elevation, etc., as well as to the vibrations and physical shocks inherent in transporting the instruments. In Washington, the mean relative of the standard deviation of the measurement pairs was 30.6%. In Denver, where the average concentrations were higher, the mean relative standard deviation was 14.2%.

Accuracy

Two independent audits of the PEM's were conducted by the Quality Assurance Division, Environmental Monitoring Systems Labor atory, EPA. The first audit was conducted at the start of the project and the second near the end of the study. Results of both audits indicated that the audited PEM's were within ±10% of the audit gases in both cities.

2. Fixed Site Concentrations

One goal of these studies was to compare exposure results obtained from fixed monitors with directly measured personal exposure for CO. It should be noted that the National Ambient Air Quality Standard (NAAQS) levels for CO are 35 ppm for 1-hour concentrations and 9 ppm for 8-hour concentrations. During the study period the 35 ppm level for 1 hour was never reached in Washington, but it was exceeded in Denver on one day (12/16/82) at one site (<1%). The 8-hour level was exceeded at two Washington sites - one site had one exceedance and the other site had five exceedances (0.5% site-days). The 8-hour level was exceeded at 11 Denver sites (8.7% site-days).

3. Personal Exposures

The field study yielded 712 24-hour exposure profiles in Washington and 900 24-hour exposure profiles (450 persons @ 2 days each) in Denver. The 8-hour maximum results in Denver were approximately twice as high as the levels found in Washington. (The fixed site CO concentrations at Denver were also about twice that observed in Washington.) The Denver personal exposure distribution indicates 10.7% of the 8-hour maximum daily CO exposures were above 9 ppm. This compares to 3.9% above 9 ppm observed in Denver at the fixed sites.

Other results include:

(a) The distribution obtained from the concentrations measured at a combination of fixed site monitors can generally provide a reasonable measure of exposure to CO for the study population over the distribution except for the upper 10 percent of exposure.

(b) Personal CO exposures were higher in microenvironments associated with motor vehicles, such as while commuting.

(c) Personal CO exposures were also higher for persons in high-exposure occupations, e.g., truck drivers, construction workers and garage/service station workers.

(d) In Denver, indoor concentrations were higher than corresponding fixed site concentrations during the time period 0900-1600 hours.

(e) In Denver, the first day and the second day personal exposure profiles are approximately equivalent for workdays.

Summary

From these studies we can conclude that the methodology exists for conducting exposure studies for CO for an urban area. The studies have provided an extensive data base from which statistical comparisons can be performed between population subgroups, between fixed site concentrations and personal exposure, and between indoor and outdoor concentrations. In addition, factors associated with exposures can be estimated and modeled. It is clear that an extension of this concept to other pollutants and other areas over differing time periods (for temporal resolution) is warranted.

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A REVIEW OF INDOOR AIR QUALITY RESEARCH AT OAK RIDGE NATIONAL LABORATORY*

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* Research sponsored by the Tennessee Valley Authority under Interagency Agreement IAG-40-1406-83 with the Martin Marietta Energy Systems, Inc. under Contract DE-AC05-840R21400 with the U.S. Department of Energy.

A REVIEW OF INDOOR AIR QUALITY RESEARCH AT OAK RIDGE NATIONAL LABORATORY

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INTRODUCTION

Indoor air pollutants are increasingly recognized as important contributors to the total public exposure to pollutants. Radon, formaldehyde, volatile organic compounds, combustion gases, and particulates are among the more important indoor air pollutants. Indoor levels may in fact be comparable to or greater than levels that have caused concern outdoors. Sources identified as contributing to reduced indoor air quality include construction products, consumer products, combustion appliances, and lifestyle habits. When the potential for elevated concentrations is considered in conjunction with the fact that many people spend a large fraction of their time indoors, the need to understand better the indoor component of the population's total exposure is evident. In addition to assessing the direct impact of indoor air quality, there is a need to determine the impact of indoor exposures on conclusions drawn about outdoor air quality. Much health effects information is based on the assumption that outdoor air quality is the dominant determinant of observed health effects. A better assessment of pollutant exposures from indoor air relative to outdoor air is necessary to test this assumption.

For approximately five years, Oak Ridge National Laboratory has had an active indoor air quality research program. Areas of activity include instrumentation and methods development, source characterization, field studies, modeling, remedial measures, and impact assessment. This paper will briefly review the following components of our research: (1) measurement developments, (2) source characterization, and (3) field studies.

MEASUREMENT DEVELOPMENTS

There is a need for relatively low-cost, easy-to-use monitoring instrumentation that is sensitive enough to meet the requirements for measuring indoor air quality. Much of the available industrial hygiene instrumentation is not suitable for monitoring indoor air quality. Similarly, much of the equipment used in assessing outdoor air quality is either too large, noisy, or expensive for practical use in indoor air quality research. Methods to address this need

have been developed as part of our research program.

Both active and passive methods have been developed for formaldehyde monitoring. A pumped molecular sieve sampling technique was developed and reported by Matthews, T. G., and T. C. Howell, 1982a. This procedure addresses the problem of water vapor collection and presents a procedure that allows low-level formaldehyde monitoring even with relatively high humidities. The method uses a simple water rinse desorption followed by pararosaniline colorimetric analysis. For a 30-L sample taken at 1-2 L/min a detection limit of about 25 ppb is achieved. A second improvement in active formaldehyde monitoring involved modifications to a commercially available CEA-555 formaldehyde monitor (Matthews, T. G., 1982b). Using the reported protocol, this instrument has monitored formaldehyde vapor as low as 10 ppb in a controlled laboratory environment.

Passive formaldehyde monitoring techniques have also been developed. A dimethylsilicone membrane sampler containing water sorbent is exposed for a 24-h period and analyzed using the pararosaniline procedure (Matthews, T. G., et al., 1982c). The detection limit for this method is about 25 ppb. This sampler was used extensively in our field studies.

A surface monitor has been developed to measure the formaldehyde flux rate from a solid material such as pressed-wood products or a wall insulated with urea-formaldehyde foam insulation. The formaldehyde surface emission monitor (FSEM) is a device approximately 20 cm in diameter which holds a layer of molecular sieve parallel to the emitting surface and provides a means to measure the emission rate nondestructively (Matthews, T. G., et al., 1984). For a 2-h measurement period, a detection limit of about 0.025 mg/cm^2-h is achieved.

Although not developed specifically for indoor air quality monitoring, recent advancements in screening methodology for PNAs by room temperature phosphorescence and synchronous luminescence by Vo-Dinh, T., 1983, offer a low-cost means of screening indoor air sample extracts for PNA content. This approach was found to be particularly useful in evaluating indoor air quality in homes with wood stoves (Vo-Dinh, T., et al., 1984a). Another attractive device that is currently being further evaluated for indoor air quality monitoring is the passive PNA dosimeter developed by Vo-Dinh, T., 1984b. The monitor is a diffusion device using a heavy-atom-treated filter paper as the sorbent and room temperature phosphorescence as the analytical method. The unit is particularly attractive in that it does not require sample treatment after exposure and is placed directly into a spectrometer for readout.

SOURCE CHARACTERIZATION

Our activities in source characterization have emphasized resin-containing materials that emit formaldehyde. Laboratory measurements have been conducted using both small chambers and the surface emission monitor. Current activities also include experiments in a room-sized environmental chamber.

An early example of formaldehyde source characterization involved the measurement of emission rates from simulated wall panels containing urea-formaldehyde foam insulation (UFFI) (Hawthorne, A. R., and R. B. Gammage, 1982). The results of this work indicated that UFFI could be a significant source of formaldehyde and that the levels measured in the laboratory were similar to levels observed in homes with recently installed UFFI.

Characterization of formaldehyde release rates from fiberglass insulation has recently been completed (Matthews, T. G., et al., 1983). These results indicate that formaldehyde release from fiberglass insulation is expected to produce a minimal impact on indoor air quality.

The most extensive source characterization activity involves a continuing study of the formaldehyde emission characteristics of pressed-wood products. This work includes the measurement of emission rates of pressed-wood materials from a product survey (measured at standard environmental conditions), measurement of emission decay rates, emission rate dependence on environmental conditions, and a study of permeation barriers and potential sinks such as gypsum wallboard.

FIELD STUDIES

Field studies of indoor air quality in occupied residences are an important component of our research activities. The major study that we have conducted involved 40 homes in the Oak Ridge/Knoxville area of East Tennessee (Hawthorne, A. R., et al., 1984). This study measured the levels of formaldehyde, volatile organics, particulates, and combustion gases during a one-day visit to each house. Formaldehyde concentrations were also monitored once a month with a 24-h passive sampler for about nine months. Radon levels were measured in all 40 homes using passive track etch monitors exposed for three months. Hourly readings of radon were obtained in a subset of the homes for periods of up to a week. Air exchange rates and meteorological data were obtained during the one-day visits. Air leakage was also measured in a subset of the houses using a blower door (Gammage, R. B., et al., 1984).

A continuing investigation of volatile organic compounds in a subset of the 40 homes is currently underway. Compounds more volatile than toluene are being emphasized using a mixed sorbent bed collection tube and high-resolution gas chromatography. A portable photoionization gas chromatograph is also being used to locate sources.

A preliminary study to measure combustion gases produced from the operation of unvented gas space heaters was conducted this spring in six houses. Levels of carbon oxides, nitrogen oxides, and oxygen depletion were monitored. Air exchange rate measurements were also performed.

Monitoring of radon and radon daughter levels in 60 homes in the Tennessee valley is planned to begin this summer. Quarterly measurements will be conducted to evaluate the variability of radon in both basements and living areas of the homes. Air exchange rates will also be determined.

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PASSIVE SAMPLING DEVICES WITH REVERSIBLE ADSORPTION: MECHANICS OF SAMPLING

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INTRODUCTION

Most commercially available passive sampling devices employ activated carbon as the sorbent. With such devices, the sorption process is not thermally reversible, and solvent desorption must be used to recover the sample. Consequently, the use of these devices to sample ambient concentrations (0.1-10ppbv) of volatile organic compounds (VOC) can impose severe restrictions on the analytical techniques (1). On the other hand, passive devices using reversible adsorption offer several advantages specifically suited to sampling of ambient concentrations of VOC's. These include:

1. Independence from solvent contamination
2. Increased sensitivity because of the availability of the whole sample for analysis

and 3. more rapid sample turnaround

However, the sampling behavior of these devices differs from the ideal case normally assumed for activated carbon, and failure to recognize the differences can lead to biases in sampling and interpretation.

This paper discusses the mechanics of sampling with reversible adsorption, and presents a simple model for calculating sampling rates. This model provides guidelines for proper design and application of passive monitors employing reversible adsorption, and the performance of the EPA personal exposure monitor (PEM) is used to illustrate the consequences of proper and improper application of the fundamental principles.

SAMPLING MECHANICS

There are currently two designs of PEMs that use reversible adsorption. Both of these use Tenax^{R}GC, and their major difference in the thickness of

the sorbent bed. The EPA PEM is a large face area system having a thin bed, while the device developed by Brown (2) is a thick-bed system. The fundamental mechanics of sorption are the same for both devices, but the thin bed system is subject to simplifications that more readily obviate the significance of key physical parameters. For the thin bed system, the time averaged sampling rate can be written as

$$R = R_o\left(\frac{1 - e^{kt}}{kt}\right) \qquad (1)$$

where R_o is the sampling rate at zero time and is given by $R_o = DA/\ell$. (D is the gas phase diffusion coefficient of the sorbate, A is the effective area of the diffusion barrier, and ℓ is the effective length of the diffusion path.) k is the ratio of R_o to the bed capacity, WV_b; where W is the weight of sorbent and V_b is the GC retention volume for the sorbate. Equation 1 indicates that for sorbates having relatively low retention volumes, the sampling rates will be strongly dependent on sampling time, but this effect can be offset to some extent by design of the device to yield lower values of R_o.

EXPERIMENTAL RESULTS

The thin bed model was evaluated through exposure of the EPA PEM to various mixtures of VOC's in the Battelle dosimeter test facility. Concentrations were in the range of 1-10 ppbv, and exposure times were varies from 15 minutes to 24 hours. Figure 1 shows a comparison of experimentally determined one hour average sampling rates with values predicted by Equation 1 for 17 common VOC's. Agreement is good for all but 3 compounds. For acrylonitrile, literature values of the retention volume vary widely and good agreement could be obtained by choosing a retention volume near the upper limit of those cited in the literature.

Figure 2 shows examples of long term behavior typical of compounds having high and low retention volumes, with the curves having been calculated using Equation 1. In general, we found excellent agreement between Equation 1 and measured sampling rates for sampling times between 15 minutes and 24 hours, and for compounds having retention volumes ranging from 0.5 L/g (trichlorotrifluoroethane) to over 2000L/g (o-xylene).

An alternative illustration of the applicability of Equation 1 can be gained by using the experimentally measured sampling rates to calculate apparent retention volumes. Table 1 shows calculated retention volumes for 4 VOC's in comparison with literature values for the same compounds.

CONCLUSIONS

Passive monitors utilizing reversible adsorption can be used for monitoring of ambient concentrations of VOC's, but strict attention must be paid to device design and bed capacity to avoid severely time sensitive sampling rates. The thin bed model, which assumes that all of the bed capacity is available, is applicable to the EPA PEM. However, with thick bed systems only a small volume of sorbent near the face of the device will be utilized and sampling rates can be even more time sensitive than illustrated with the EPA PEM, depending on the face area to volume ratio. With thick bed systems, the thin bed model is not applicable, and one must resort to a more complex treatment involving a series solution to the problem.

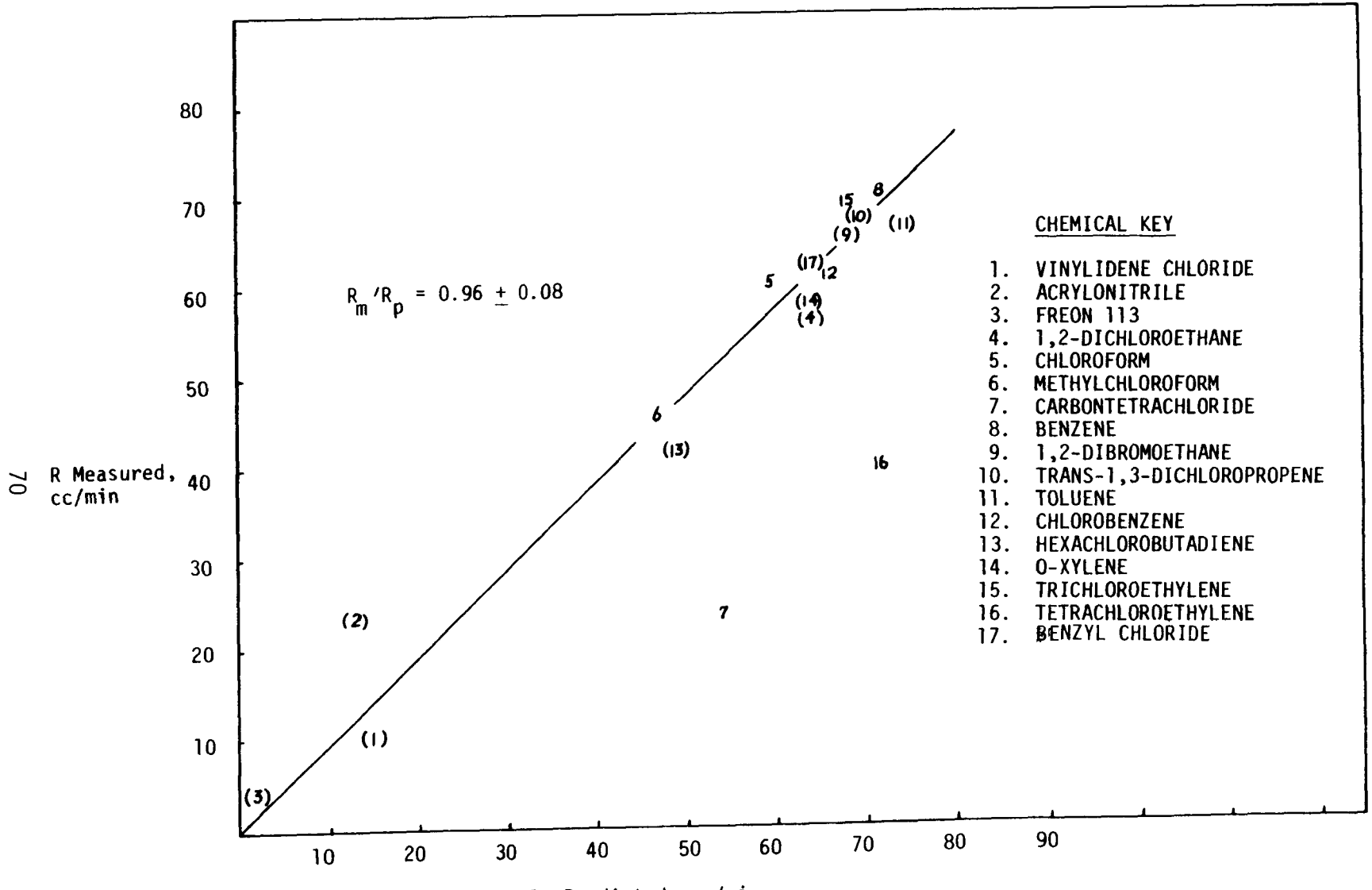

FIGURE 1. ONE HOUR SAMPLING RATES

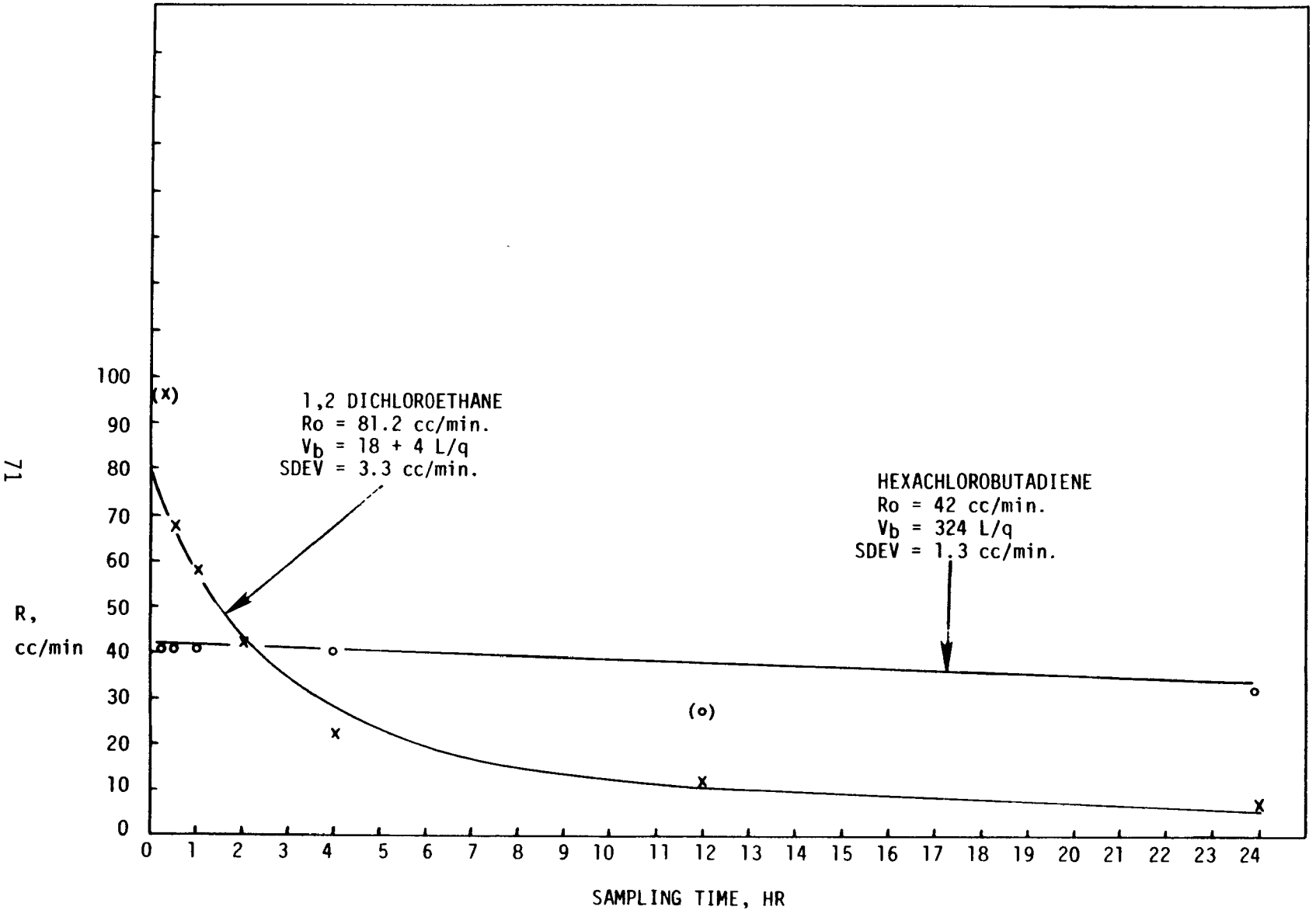

FIGURE 2. RESPONSE WITH HIGH AND LOW RETENTION VOLUMES

TABLE 1. RETENTION VOLUMES

Chemical	V_b(cal),L/g	V_b(Lit),L/g
Acrylonitrile	4.9 ± 0.8	0.3 - 7.0
Vinylidene Chloride	1.5 ± 0.1	2 - 6
Freon 113	0.5 ± 0.08	0.23 - 0.47
1,2-Dichloro-ethane	18 + 4	24.4

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PORTABLE INSTRUMENT FOR THE DETECTION AND IDENTIFICATION OF AIR POLLUTANTS

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INTRODUCTION

A portable instrument for detecting, identifying, and monitoring chemical hazards is described by Stetter et al. (1984a, 1984b). The instrument was developed at Argonne National Laboratory for the purpose of alerting U.S. Coast Guard personnel to the presence of hazardous vapors during cleanup of chemical spills or during inspection of chemical shipments. Instruments of the same type may be used as personal monitors for employees in hazardous waste cleanup operations and in various industrial environments, especially in the chemical, pharmaceutical, petroleum, mining, and metallurgical industries. They may also serve as inexpensive substitutes for, or supplements to, the instrumentation now used to monitor hazardous emissions from smokestacks and other stationary sources.

MAIN FEATURES OF THE PROTOTYPE INSTRUMENT

The recently completed prototype instrument, which uses the array shown in Fig. 1, comprises four electrochemical sensors that respond to toxic gases and two heated noble-metal filaments that cause many compounds to be partially pyrolyzed or oxidized in air (Stetter, Zaromb, and Findlay, 1984). The four sensors can be rapidly switched to one of several operating modes. In practice, four modes and four sensors yield 16 measured parameters, that is, 16 independent data channels.

The prototype instrument fits into a camera bag (Fig. 1), weighs about 15 pounds, and can operate for at least four hours on self-contained rechargeable batteries. The user interface consists of five keys and a 32-character display. The user selects detection, identification, or calibration modes by pressing the appropriate keys. Extensive training of personnel is avoided by having the instrument provide menus of choices for each operating mode desired.

The menus are controlled by a microprocessor that has 12 kilobytes of memory and extensive self-test capabilities.

When monitoring for the presence of any unknown air contaminant, the sensor array is connected directly to a sampling probe. A signal from any of the sensors indicates the presence of a possibly hazardous species near the probe intake. To identify the detected species, the user first draws a sample through the probe intake into a sampling bag. The collected sample is then passed through the sensor array, with the sensors being switched into four differently selective modes at appropriate intervals. The response of each sensor at the end of each interval is recorded in one of 16 independent data channels. The relative magnitudes of these response signals provide the information needed to identify the particular species giving rise to the observed signals. Once the microprocessor identifies a compound based on the recorded data, it then sets the sensor array for maximum sensitivity to that compound in the monitoring mode. The microprocessor can also set the alarm level to correspond to an appropriate fraction of the short-term exposure limit or immediately-dangerous-to-life-and-health concentration of the identified compound.

Of some 30 different compounds tested with the array shown in Fig. 1, each yielded a distinctive response pattern, as illustrated by the histograms of Figs. 2 and 3. These histograms, as well as the response versus concentration plots of Fig. 4, obtained as described in Stetter et al. (1984a), show how specificity and quantitative determinations derive from the measured values. To demonstrate the differences in response patterns, a "fingerprint index" can be derived from each histogram by:

1. Assigning a two-digit index (01 through 16) to each of the channels 1-16;
2. Listing the indices of the strongest channels in order of decreasing channel strength; and
3. If the signal in one of the three strongest channels is negative, drawing a bar over the corresponding channel index (Stetter et al., 1984b).

Thus, for carbon tetrachloride and tetrachloroethylene, the fingerprint indices become $\overline{02}03\overline{07}$ and $07\overline{06}\overline{02}$, respectively (cf. Fig. 2). Figure 4 shows the proportionality of the signals in the strongest channels to the concentrations of four different compounds.

Table 1 lists 19 of the tested compounds that are of concern to the U.S. Environmental Protection Agency (Federal Register, 1980). All but one of the fingerprint indices listed in the second column of Table 1 can be seen to differ from each other. The one exception is the identical fingerprint index (070603) for chloroform and pyridine. However, it is clear from Fig. 3 that the histograms of these two compounds differ substantially in the ratios of the normalized responses in the three strongest channels -- 1.00:0.51:0.18 for chloroform as compared with 1.00:0.77:0.17 for pyridine. Moreover, if our fingerprinting procedure is extended to the five (instead of three) strongest channels, then the new indices for chloroform and pyridine become 070603 0205 and 070603 0208, respectively. Thus, these two compounds are also distinguishable from each other with the array used.

The last two columns in Table 1 list the ELD (estimated lowest detectable) concentrations determined as twice the noise levels (Stetter et al., 1984b) and the TWA (time-weighted average) threshold limit values of the 19 compounds. In 16 out of 19 cases, the ELD concentrations fall below the TWA values. Only three nitrogen-containing compounds (hydrazine, methylhydrazine, and nitrobenzene) present detection problems below the TWA threshold levels with the sensor-filament array used in this work. Since this particular array did not include some of the most sensitive sensors, such as those used in the parts-per-billion-level hydrazine detector (Rogers et al., 1980), we expect that low-level detection should usually be achievable with arrays tailored to the compounds of interest.

FUTURE DIRECTIONS

The numbers of differently selective sensors, S, and their differently selective sensing modes, M, can be varied to yield P = MS independent parameters. The number P required to perform a specified task depends on the number N of different compounds that may be encountered in a given environment and also on the number A of significant components that may be encountered at one time, in accordance with the following inequality (Zaromb and Stetter, 1984):

$$2^P - 1 \geq \sum_{I=1}^{A} \frac{N!}{(N-I)!I!}$$

Thus, P = 16 can serve to identify a maximum of N = 74 different species in mixtures containing up to three different air contaminants or a maximum of N = 30

different species in mixtures of up to four different contaminants. Alternatively, P = 24 (obtainable with S = 4 and M = 6 or S = 6 and M = 4) may serve to identify up to 100 different species in mixtures of up to four contaminants or up to 30 species in mixtures of up to eight contaminants. A computer algorithm developed for estimating measurement errors can be used to evaluate the appropriateness of any given sensor array and selected operating modes for identifying and monitoring any group of compounds that may be encountered in a given environment.

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TABLE 1. SUMMARY OF TEST RESULTS FOR 19 COMPOUNDS OF CONCERN TO THE U.S. ENVIRONMENTAL PROTECTION AGENCY

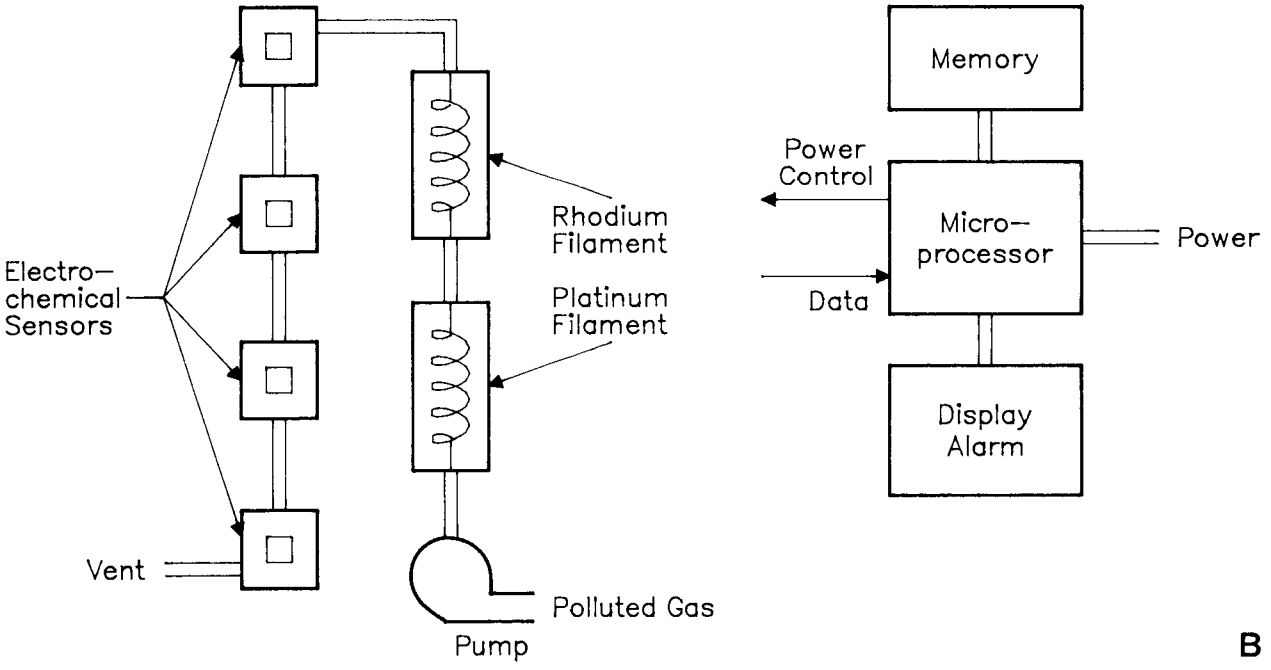
Compound	Fingerprint Index*	ELD Concentration# (ppm)	TWA## (ppm)
Simple Hydrocarbon Ring Compounds			
Cyclohexane	020706	0.4	300
Benzene	070611	2.5±1.5	10
Toluene	150706	3±2	100
Carbon-Oxygen Compounds			
Carbon monoxide	161314	2±1	50
Formaldehyde	120910	0.1	1
Chlorinated Aliphatics			
Carbon tetrachloride	020307	0.1	5
Chloroform	070603	1	10
Tetrachloroethylene	070602	4	50
Nitrogen Compounds			
Hydrogen cyanide	091011	0.4	10
Hydrazine	040302	0.1	0.1
Methylhydrazine	080712	0.8	0.2
1,1-Dimethylhydrazine	120811	0.2	0.5
Pyridine	070603	0.2	5
Acrylonitrile	060705	0.1	2
Nitrobenzene	041110	10	1
Nitric oxide	070609	0.1	25
Nitrogen dioxide	050607	0.15±0.05	3
Sulfur Compounds			
Hydrogen sulfide	080512	0.1	10
Sulfur dioxide	121011	0.2	2

*See text.

#Estimated lowest detectable concentration.

##Time-weighted average threshold exposure level (American Institute of Government Industrial Hygienists, 1983).

A



B

Figure 1. Prototype Instrument for Detection, Identification, and Monitoring of Chemical Hazards: A. Photograph and B. Basic Components.

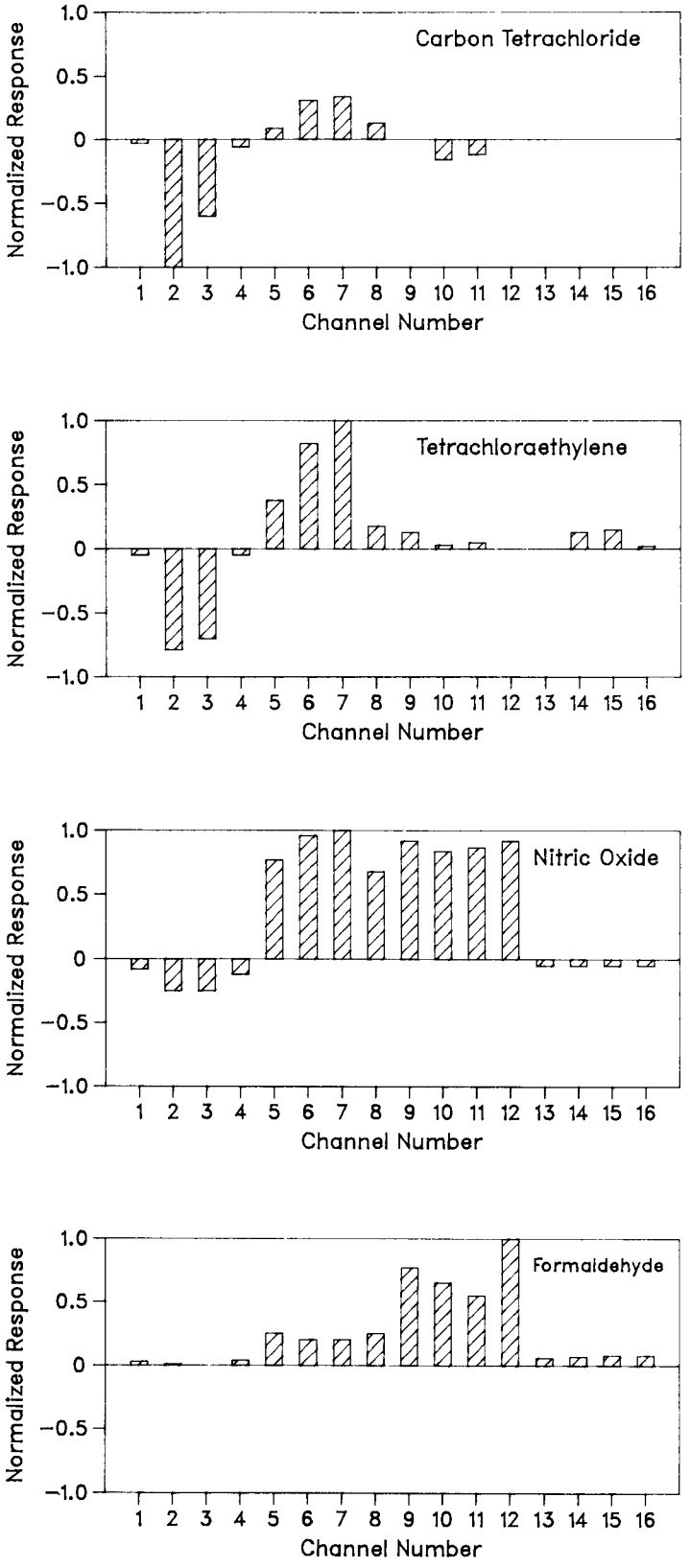


Figure 2. Histograms of the Normalized Responses in Each of the 16 Channels to Four Different Hazardous Compounds.

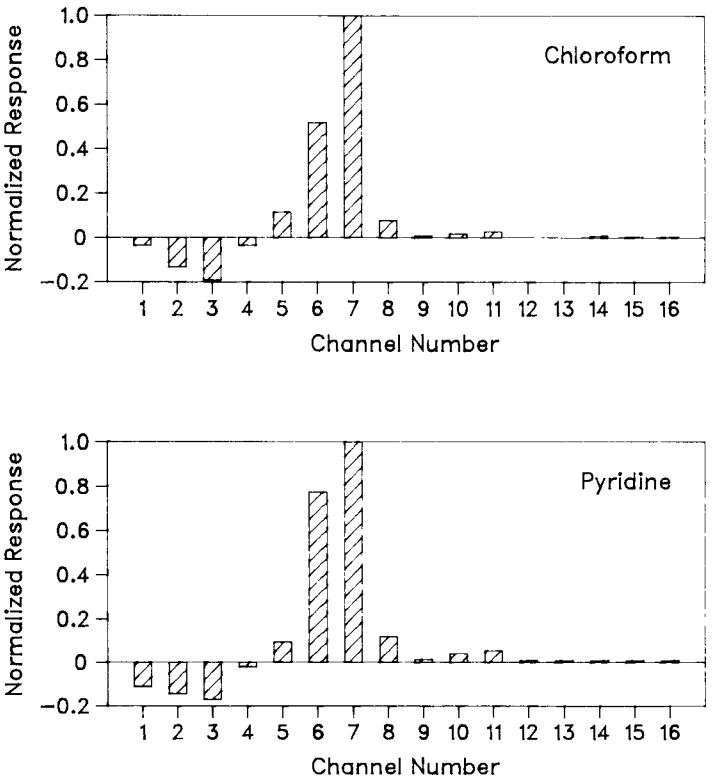
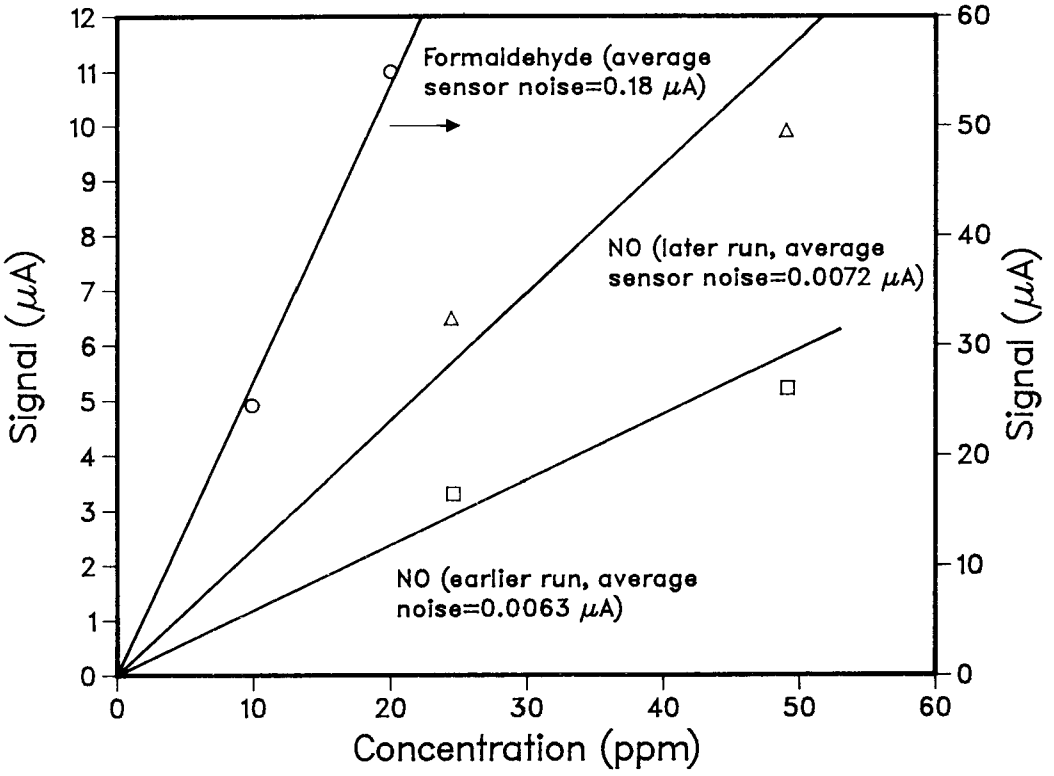


Figure 3. Comparison of the Histograms for Chloroform and Pyridine.



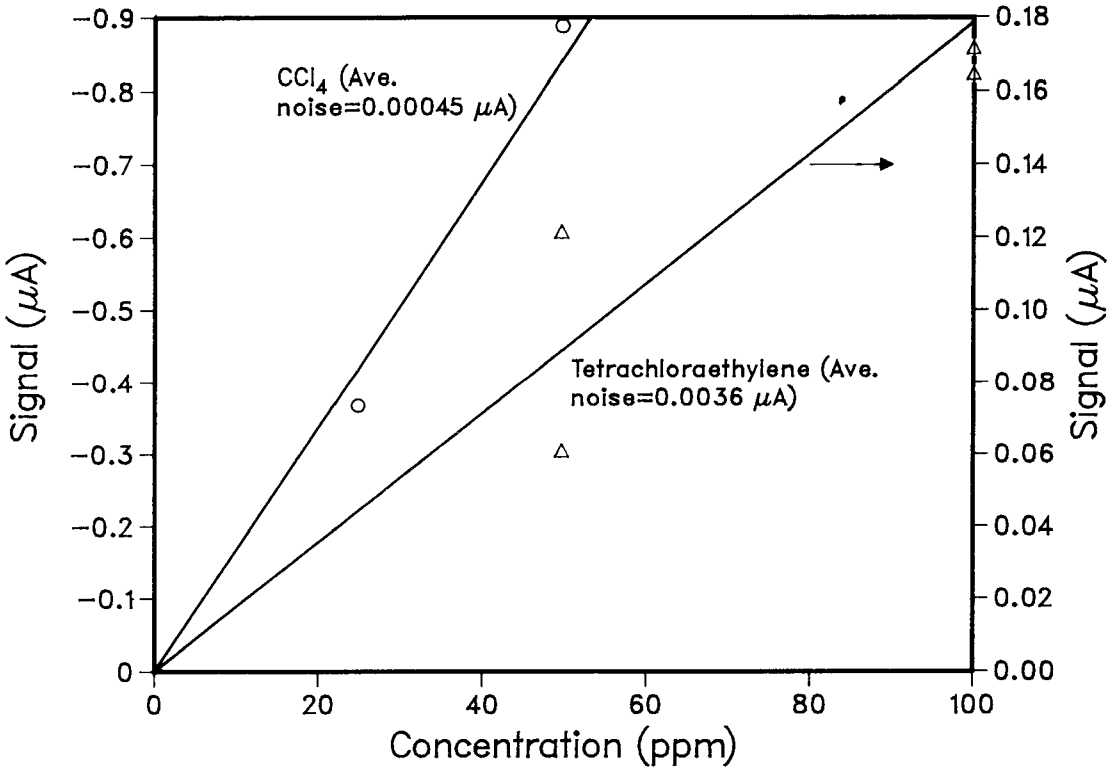


Figure 4. Proportionality of the Response Signals in the Strongest Channels to the Concentration in Air of the Sampled Compounds.

Problems and Pitfalls of Trace Ambient Organic Vapor Sampling at Uncontrolled Hazardous Waste Sites

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Vectors of pollutant migration from uncontrolled hazardous waste sites have been under investigation by regulatory agencies for many years. The current data base has largely been limited to direct impact upon surface and ground water via leachate discharge and ground water infiltration. Leachate sampling and characterization protocols are well established. Subsequently, current engineering practices are adequate to address and mitigate environmental impact from leachate streams. Potential ground water impacts from uncontrolled hazardous waste sites present a more complex problem to environmental scientists than the leachate route. Earlier ground water investigations in the previous decade, though ambitious, fell short of accurately defining ground water flow networks. Refinement of analytical techniques and mathematical modeling approaches in the late 1970's demanded a more sophisticated approach to field techniques and monitoring network design. Subsequent refinement of environmental measurement system design and collection procedures are approaching a convergence with state-of-the-art analytical and modeling protocols.

The airborne route of contaminant migration, though always a concern, has not received comparable attention as other more defined routes, i.e. ground and surface waters. Both liquids & gases, in their natural physical state, take on the shape of their container. In the biosphere, leachate & surface waters take on the shape of their stream channel or local ground water basin. The

atmosphere, however, is relatively dimensionless. Water is of much greater relative density than air, and is constricted by it's container; minimizing dilution effects relative to air. In the past, regulatory agencies have placed their emphasis on point source air emissions due to high concentrations emitted and ability to control said point sources. Efforts to control these point sources have largely been concerned with potential health effects to impacted individuals & communities.

In New Jersey Department of Environmental Protection - (NJDEP) Hazardous Site Mitigation Administration's (HSMA) efforts to perform environmental evaluations and risk assessments at uncontrolled hazardous waste sites, it has become clear to these investigators that non-point source emissions from the subject sites were being largely ignored by federal and state regulatory agencies. These investigators believe organic vapor and particulate emissions from uncontrolled hazardous waste sites represents a significant pathway for offsite migration of contaminants. In order to provide toxicologists with the data necessary to perform a risk assessment, emissions must be qualified and quantified. In order to develop the data base, a literature search was conducted, revealing inadequacies & difficulties in sampling network design and a wide divergence of analytical methodologies. It became apparent that these problems that were encountered were not unlike those faced by investigators performing water quality studies in the early 1970's. In many ways, the problems faced by investigators attempting to design comprehensive sampling and analytical plans to delineate airborne pollution migration from non-point sources are complexed by the relative instability of the air matrix in relation to the water matrix, with regard to diluation effects, variability of direction, and speed of transport.

Design

In attempts to approximate environmental conditions in the air matrix the investigator must correlate the physical nature of the environment with the design of the monitoring network. One of the most critical physical considerations is the availability of adequate meterological data such as air temperature, wind speed, wind direction, humidity and barometric pressure. Though these metrological data may be readily available at regional airports or meterological stations, these conditions may be indicative of the region but lack site · specificity. On site conditions, such as landfill elevations considerably above grade, can significantly disrupt "normal" meterological conditions. Localized anthropogenic disturbences of natural geomorphology can lead to very localized atmospheric conditions both effecting the site as a whole or causing a broad heterogeniety of meterological conditions within the site.

The design of an environmental sampling network must take into consideration not only the regional, but also localized physical conditions outlined above. In order to adequately design a monitoring network, such that mathematical modeling of site conditions & contaminant transport can be addressed, accurate meterological data must be available for each sampling station for the duration of the program. Only by such a strategy can localized site conditions be defined.

Design & implementation of the actual sampling network is dependent upon accurate definition of regional and localized effects catalogued above. These conditions will bear significantly upon selection of sampling locations. Major problems in selection of sampling locations are the number of sampling stations required to adequately define the site situation and selection of a true

statistical background. Selection of a background location is extremely critical in order to determine if ambient site concentrations are significantly different than background concentrations. Establishment of variability of background concentrations is required to statistically evaluate background vs. site concentrations.

The lack of a standardized data base from uncontrolled hazardous waste site emissions causes difficulties in design of a adequate monitoring network with respect to suspected contaminants & concentrations. Uncontrolled hazardous waste sites are characterized by a broad heterogeniety of compounds disposed as well as uneven distribution throughout the site. These facts must be considered in selection of the analytical scheme as well as number & location of sampling stations.

Classically, air quality standards have been directed toward occupational exposures. The relationship of these air quality standards to data derived from ambient air monitoring is nebulous. The paucity of ambient air quality standards drastically effects sampling network design since the design should be dependent upon compounds & concentrations of contaminents which are known to adversely effect the environment or public health. In light of the absence of well defined action levels, it becomes unclear to the investigator the goal or targets of his program.

Sampling

As mentioned earlier, much of the focus of ambient air evaluation has been focused upon industrial or occupational exposure. Subsequently, much of the sampling equipment available to the investigator is limited in it's usefulness.

Specifically, most sampling pumps are designed to monitor eight hour exposures. NJDEP-HSMA's investigations were more concerned with long term chronic exposure. Based on a literature review, no standard sampling periods were established. In order to calculate daily exposures and to minimize man-power considerations, a twenty-four hour sampling period at low flow velocities (10-15 ml/min.) was chosen. This immediately presented a problem, as to the best of our knowledge, no such pump was readily commerciable available. For this study, only volatile organic constituents were considered, due to budgetary & logistical constraints. The sampling device that was chosen was fibricated, consisting of a battery powered Gillian - 10020 pump which draws 10-15 ml/minute of air through a collection trap packed with Tenax - GC. Laboratory calibrated rotameters are adjusted in the field to assure that the proper flow rates were achieved. To prevent airborne particulates from entering the traps, a glass fiber filter is placed before each trap. These filters were impregnated with sodium thiosulfate to avoid any oxidation of the Tenax - GC and to minimize the formation of artifacts.

In conclusion, sampling efforts of trace ambient organic vapors at uncontrolled hazardous waste sites was hindered by the lack of standard procedures and readily available commercial samplers, making data representativeness & comparibility among investigations poor.

Analytical

There are a wide variety of analtyical methods for specific pollutants as well as scanning procedures for chemically related pollutants. None of these analytical methodologies is all inclusive. Many of these methodologies include their own specific sample collection technique. If an investigator chooses to

examine a wide variety of contaminents in ambient air, he is faced with the possiblity of having to use several different sampling apparatus to collect samples as the specific method requires. It is obvious that this can be quite cumbersome & require a high degree of labor to maintain the sampling network. In an attempt to maximize the information gained & minimize the physical effort and money, involved; investigations should be narrowed in scope. This analytical targeting of compounds could be selected by toxicity, mode of transport or pervasiveness in the environment. Analytical targeting can be accomplished by either fine tuning sample collection methodologies to cover a broad spectrum of compounds or adapting current analytical techniques to enhance the detection of specific chemical species. From a regulatory standpoint, standard analytical methods must be employed that are legally defensible and scientifically valid. All of the HSMA sites carry the potential of litigation therefore all analytical methods performed must be of demonstrated quality.

A rigid well defined Quality Assurance/Quality Control program must be established to consistantly demonstrate the validity, representativeness, and comparibility of the data generated from standardized analytical and field methodologies. At present the type & frequency of Quality Control procedures vary greatly. Therefore, Standard Procedures such as duplicate/replicate analysis, blank methodologies, and field practices must be established. The problem of establishment of background for an ambient air study is a case in point. The background can change day by day if not hour by hour, therefore, without measuring the variability of your background sample, data interperation can be complicated. All background data should at a minimum be replicated by collecting and analysing at least two background samples from the same station collected in the same manner. Utilizing more than one sampling station for background calculations can lead to errors caused by pseudoreplication.

Selection of background location and a knowledge of regional ambient concentration of the compounds of interest are the most critical factors in obtaining useful data. It becomes evident that design of the sampling network determines the usefulness of the data to be used in environmental evaluations.

Evaluation

The problems & pitfalls of trace ambient orgaic vapor sampling at uncontrolled hazardous waste sites outlined throughout this paper provides the investigator with a multitude of complexities in the evaluation of data generated from this study. In the process of fine tuning & standardizing the environmental measurement system the information gained will be of superior quality. This increase in data quality does not, however, lead to an immediate corresponding increase in the amount of information gained by the study. The evaluation of these data as they relate to public health, environmental impact and environmental fate of trace ambient contaminants eminating from non-point sources such as uncontrolled hazardous waste sites thrusts the investigator into areas of environmental evaluation and risk assessment not previously addressed at the same level of sophistification as other vectors of pollution migration. The lack of trace ambient air standards creates problems toxicological assessents of potential health effects. Improperly designed sampling and analytical strategies may overlook high, short term exposures, potentially due to specialized or localized meterological conditions that would not be accounted for in mathematical modeling for risk assessment. One area of promise recently commercially available to the investigator is real time, real world, multi point analysis of ambient air. Advantages of a real time, analytical system include large number of analyses over a short period of time which will yield information about the variability of the contaminent load in the atmosphere as

well as allowing for the correction of any apparent analytical problems can take place almost immediately without lose of valuable data. Such a system, used in conjunction with an ambient monitoring network should prove more effective than either methodology used separately.

The problems presented in this paper provide a substantial challenge to the environmental scientist, but are not insurmountable. Accurate & definative characterization of trace ambient organic vapors emitted from non-point sources is currently limited to only an evaluation process. Point source emissions, once a source of gross environmental pollution have been significantly reduced due to regulatory & technical advances. Non-point sources, such as uncontrolled hazardous waste sites, still pose a threat to the environment and public health & will require greatly increased efforts and state-of-the-art technologies to evaluate & mitigate.

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NEW CONTINUOUS MONITORING SYSTEMS FOR MEASUREMENT OF HAZARDOUS POLLUTANTS

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Over the past few years, the HNU PI-101 photoionizer has been one of the primary instruments used for hazardous waste site entry program by the FIT and TAT environmental response teams (1). The PI-101 is used for preliminary screening of the area including the extent of the problem. The 101 can also be used to determine where barrels are located and/or where problematic barrels are stored (underground) by simply breaking the ground with the heel or shovel and looking for an increase in hydrocarbon concentration with the analyzer. The PI-101 can also be used during Phase II to check soil samples or water samples which are collected and stored for subsequent laboratory analysis. One gas chromatograph which can be used for analysis in the field is our Model 301P, a gas chromatograph which will operate on batteries in the field and provides complete GC capabilities in the laboratory with temperatures to 300°C and packed/capillary capability.

Once in the laboratory, the PI-101 can be used as a qualitative tool (2,3) to screen (via headspace) samples and ensure the integrity prior to GC-MS or other analysis. Of course a simpler, less costly, and more useful sample screening technique involves using GC - PID/FID for analysis.

Several years ago, a technique was described (7) that utilized the difference in response ratios for organic compounds on a photoionization detector (PID/10.2 eV) and a flame ionization detector (FID) as a means for hydrocarbon identification.

Typical ratios calculated by: PID attenuation x peak height/FID attenuation x peak height were as follows:

Type of Hydrocarbon	PID/FID Ratio
Saturated	10 or less
Unsaturated	10 - 25
Aromatic	>25

The HNU Gas Chromatographs (GC 301 or GC 421) were designed to incorporate an integral PID, (non-destructive detector) with an FID or another detector in series.

The PID response (10.2) eV was found to be a function of the electronic structure (pi vs sigma electrons) of the solute; as a consequence, it provided

a discriminative response. This characteristic (discriminative response) can be turned into a very powerful qualitative tool, by comparing (ratioing) the PID signal to that of another detector. The preferred detector for comparison was one which had a homogeneous response (i.e., the FID has a homogeneous response in the sense that its response for organic molecules depends mainly on the number of carbon atoms in the molecule). In this way, general classes of compounds could be identified, since the FID response provides the normalizing factor. We have been able to differentiate the presence of aromatic, unsaturated, and small molecular weight chlorinated compounds in a hazardous waste dump site by calculating the PID/FID ratios (5). The compounds present in each group can be further clarified by using retention indices. Retention indices (RI) can be very useful to aid solute identification from the quantitative and qualitative point of view. Quantitatively it provides structural information. (i.e. two adjacent homologs in a series differ by 100 units). Several of the unknown compounds in the dump site were "identified" by matching up its retention index. In Table IV we have detailed an instrument selection guide.

If a hazardous waste site is particularly problematic e.g., very large (clean up cost >$1 M), it is quite possible that Phase III will be reduced (Table I and II), and some types of continuous monitoring equipment will be necessary for Air Quality Monitoring.

We have developed a very powerful and flexible series of analyzer systems for continuous monitoring measurement of pollutants. The first is a dedicated microprocessor controlled chromatograph (501) for fixed installations of specific pollutants (up to 10); the other (301) is a small transportable system which is also microprocessor controlled but can be utilized for a variety of analyses.

The microprocessor controlled environmental chromatograph, the HNU Model 501, which utilizes the high sensitivity Photoionization Detector (PID) or Far UV Absorbance Detector (FUV) (6) for inorganics or hydrocarbons monitoring at percentage or sub-ppm levels. The Model 501 consists of four sections, the oven which contains the columns and PID, the fluidics bay (hardware and valves need to inject the sample), the electronics bay where all the electronics (including microprocessor) for the system are located and the multipoint sequencer capable of sampling up to ten points (7,8).

The Z-80 microprocessor controls all functions of the Model 501 under direction of the operating system in ROM. This includes temperature control, valve control, diagnostic tests, as well as data collection and manipulation. As a result, the Model 501 is designed for unattended operation 24 hours a day. Automated calibration with a known level of a hydrocarbon occurs every eight hours as part of the program.

The chromatographic system used consists of a precolumn, an analytical column and a detector (PID or FUV). The precolumn is used to remove compounds more strongly retained from the air sample during injection. All materials trapped on the precolumn after injection are back flushed to vent during the remainder of the analytical cycle. The analytical column separates the components for quantitation using the PID or FUV.

The use of a properly chosen precolumn as part of the chromatographic system allows the development of a specific analyzer.

The Model 301 system weighs about 30 pounds and consists of two packages; the chromatographic oven, valving, detector, analog electronics; the microprocessor controller/programmer which can be used for temperature control, valve timing, and data reduction. The detectors on this system can be any one or two of the following: PID, FUV, or flame ionization (FID). Virtually any possible combination of contaminants can be analyzed with these detectors. A very flexible automatic analyzer can be constructed with the 301 components.

In conclusion, we have shown that HNU Systems has a variety of instruments which can be utilized for preliminary site entry, screening, analysis and/or continuous monitoring of hazardous waste sites.

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Fig. 1

Tasks for Hazardous Waste Site Evaluation

PHASE I
- Preliminary Field Screening
- Site Evaluation
- Location of Drums

PHASE II
- Sample Collection
  (soil, water, air, hazardous waste)
- Sample Screening
- Analysis and Identification

PHASE III
- Continuous Monitoring
- TLV Data
- Drilling
- "Air Quality Monitoring"

Table I

What Type of Instrumentation is Needed

Table II

PHASE I
- Initial Survey - Field
- Portable instruments for initial survey to measure hydrocarbons and inorganics
  Examples:
  HNU PI-101 Battery operated photoionization based analyzer
  HNU GC-301 P Battery operated gas chromatograph

PHASE II
- Screening - Field or Laboratory
  Example: **HNU PI 101** - Headspace
- Identification & Analysis
  Example: **GC - MS (?)**
  Alternative: **GC - PID/(?)** other detective

PHASE III
- Continuous Monitoring/Air Quality Monitoring - Field
  Example: **GC 301 Automatic EC 501/511**

Hazardous Waste Instrument Selection Guide

	PI-101	GC 301	GC 421	EC 501	EC 511
Skill Level of Operator	low	high	high	low†	high
Portability	yes	yes (301 P)	no	no	no
Ability to Operate in a Van	——	yes	yes	yes	yes
Lab. Screening (gas samples)	yes	yes	yes	yes	yes
Liquid Samples	no‡	yes	yes	no‡	no‡
Capillary Capability	no	yes	yes	no	no
Auto Sampler	no	no	yes	no	no

†Only if 501 is not used with 511
‡Only headspace

Table III

REAGENT IMPREGNATED FILM BADGES FOR PASSIVE POLLUTANT SAMPLING

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INTRODUCTION

Silicone polymer films have previously been used as diffusion barriers placed over reagent substrates for the passive collection of pollutants from the atmosphere (Reiszner and West, 1973; Nelms, 1976). In the present application the collection device is the polymer film itself, in which a reagent or trapping site, has been dissolved and homogeneously dispersed. Prior to this experimental work, a mathematical diffusion model was developed to predict the response of such a device to a given pollutant dose (Rubin, 1980). The model predicted a much improved sensitivity over comparable polymer diffusion barrier sensors and a response which varies as the square root of pollutant dose. Prior to this effort, experimental verification of the model has been lacking.

Briefly, we sought to design and evaluate a personal sampler for ozone using a reagent, 10,10-Dimethyl-9,9'-Biacridylidene (DBA) dissolved homogeneously in a gas-permeable, silicone-polycarbonate copolymer film badge (General Electric, 1978). This system was chosen because the simplicity and rapidity of the O_3-DBA reaction provided an ideal means for testing the behaviour of this general kind of sensor and for model validation. DBA has a reactive double bond that is expected to undergo ozonolysis at a diffusion controlled rate (Kearns, 1969; Turro, 1970). The rate constant of the reaction between ozone and DBA was determined to be $5.2 \pm 0.6 \times 10^9$ M^{-1} sec^{-1}.

The disappearance of DBA upon ozonolysis can be monitored spectrophotometrically at 430 nm. Unlike other reagents for ozone determination (Pryor ;and Collard, 1978; Hodgeson and Surgi, 1984), this reagent is specific for ozone. Interferences from NO_2 and SO_2 are less than 1%. Currently, there is no inexpensive, convenient personal monitor for ambient concentrations of ozone, no experimental evidence supporting Rubin's mathematical models, nor is there an experimental measurement of the permeability of ozone in silicone.

EXPERIMENTAL

Twenty-six independent exposures using ozone concentrations from 0.036 to 1.29 ppm ranging over times of 15 to 400 minutes were run. Each data point (see figure 1) is the average of three independent readings. Various concentrations of ozone were generated by photolysis of air or oxygen by a mercury arc lamp housed in a retractable sleeve. The flow rate was maintained at 12 l/min (.63 M.P.H.) by bearing flow meters. The ozone concentration, corrected for temperature and pressure, was continuously monitored by a Dasibi Model 1008-AH ozone photometer.

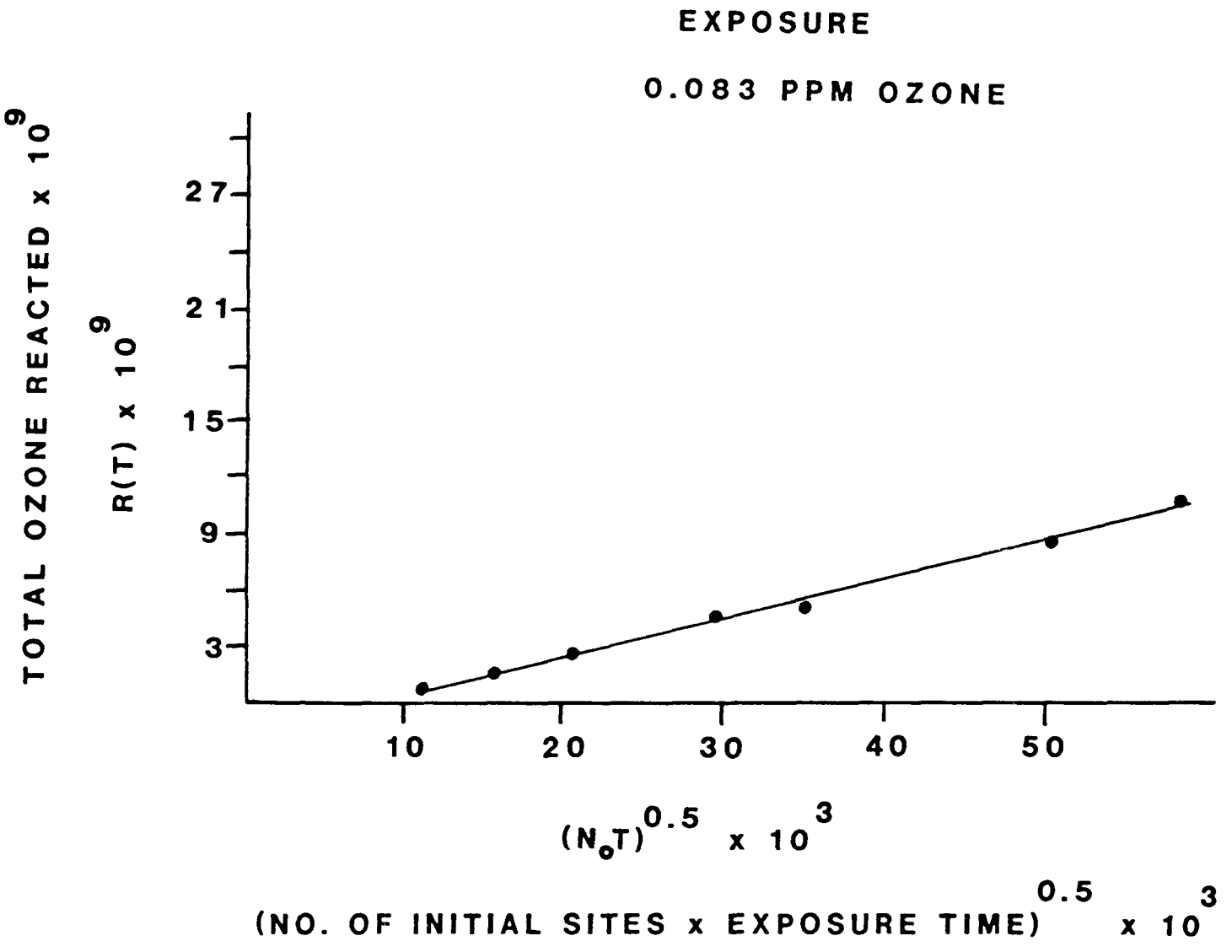
RESULTS AND DISCUSSION

Rubin (1980) has solved Ficks laws of diffusion to obtain two equations which can be interfaced to relate the amount of reagent (DBA) depleted to the dose (atm-min) of ozone:

$$R(t) = (2SP_oDTN_o)^{1/2} \qquad (1)$$

R(t) = total amount of gas per unit area which has reacted up to time

FIGURE 1


EXPOSURE
0.083 PPM OZONE
TOTAL OZONE REACTED x 10^9
R(T) x 10^9
27
21
15
9
3
10
20
30
40
50
(N_oT)^0.5 x 10^3
(NO. OF INITIAL SITES x EXPOSURE TIME)^0.5 x 10^3

t, moles cm^{-2}

S = solubility coefficient of gas in membrane, moles cm^{-3} atm^{-1}.

P_o = partial pressure of gas, atm.

D = diffusion coefficient of gas in membrane, cm^2 min^{-1}

T = time, min

N_o = initial concentration of trapping sites, moles cm^{-3}

$(SD)_b$ = permeability at a given thickness, b.

P(t) = the instantaneous partial pressure at a time t, (atm).

Since the average partial pressure of pollutant, P_o, is simply the time averaged instantaneous partial pressure:

$$P_o = \frac{1}{T} \int_0^T P(t)dt.$$

Thus the following expression can be written:

$$R(t) = \left[2SDN_o \int_0^T P(t)dt\right]^{1/2} \qquad (2)$$

$$\frac{[\ R(t)\ ]^2}{2SDN_o} = \int_0^T P(t)dt$$

The quantity of gas reacted, R(t), is directly proportional to the sensor response as measured by the decrease in absorbance at 430 nm. The proportionality constant includes the molar absorptivity of DBA and the film

thickness, both of which have been determined experimentally. Thus the response of the sensor should be proportional to the square root of the time-averaged dose. Furthermore an experimental determination of the proportionality constant yields a measurement of the pollutant permeability in the polymer film.

The following quantities have been determined experimentally:

$(2SD)_b = 62.3 \pm 5.8 \times 10^{-8}$ (Note: Units given by above expressions)

$N_o = (A_i/_b)\ 8.59 \times 10^{-8}$

$R(t) = (\Delta A)\ 8.59 \times 10^{-8}$

where: $8.59 \times 10^{-8} = \dfrac{(\text{density of membrane 213, } 1.156\ g/cm^3)}{\left[\begin{matrix}\text{molar absorptivity} \\ \text{of DBA, } 34800\ cm^{-1}\end{matrix}\right]\left[\begin{matrix}\text{molecular weight} \\ \text{of DBA, } 386.5\ g/mole\end{matrix}\right]}$

ΔA = initial absorbance, A_i - final absorbance, A_f

Membrane thickness (b) = $36.5 \pm 1.3 \times 10^{-4}$cm

Substituting these values into the above equation yields:

$$\frac{(\Delta A)^2}{1990\ A_i} = \int_0^T P(t)dt \qquad (3)$$

By the use of this expression, the integrated dose may be determined directly from the measured response. A unique advantage of this device is that the proportionality constant given here remains constant as long as the film thickness is controlled. The uncertainty limits given above for membrane thickness reflect the degree of control which has been attained for film

thickness.

The results of one typical run are shown in Figure 1. In this figure the y-axis is proportional to the square root of the dose. All the runs performed showed the same linear relationship. Thus the unique dose-response relationship predicted by the Rubin model has been verified. For each run the doses may be calculated from equation (3) and compared to the actual doses as determined from the measurement of O_3 concentration and time. The results of one such typical comparison are shown below:

A_i	ΔA	Calculated Dose: $\int_0^T P(t)dt$ (atm x min) x 10^6	Actual Dose (atm x min) x 10^6	% Error
.370	.031	1.26	1.11	14
.300	.040	2.71	2.85	4.9
.360	.056	4.31	4.68	7.9
.430	.092	11.0	10.6	3.8
.339	.120	20.1	24.6	18
.400	.140	27.4	32.8	16
.468	.208	47.4	45.0	5.3

Average of % Error = 10%

Average Deviation = 5%

Since reagent is depleted from the silicone portion of the copolymer 300 times faster than the polycarbonate portion (Hwang et al, 1974a). it is also possible to calculate the intrinsic permeability of ozone in siloxane. A plot of $(2SD)_b^{1/2}$ against b, extrapolated to zero thickness, yields a y-intercept which is taken as the intrinsic permeability. A comparison of the experimentally derived intrinsic permeability to that predicted by modeling the permeability of ozone in siloxane (General Electric, 1978; Lange, 1952) is given below.

A) Experimental - Extrapolation to Zero Thickness:

$$(SD)_{b=0} = 153 \pm 20 \times 10^{-9} \frac{(cm^3 \text{ gas}) (\text{cm thick})}{(\text{sec}) (cm^2 \text{ polymer}) (\text{cm Hg}, \Delta P)}$$

B) Model: Boiling Point of Gas, Molecular Diameter of Ozone

$$S = 1.18 \times 10^{-2} \frac{(cm^3 \text{ gas})}{(cm^3 \text{ polymer}) (\text{cm Hg}, \Delta P)}$$

$$D = 13 \times 10^{-6} \frac{(cm^2)}{(\text{sec})}$$

$$SD = 150 \pm 25 \times 10^{-9} \frac{(cm^3 \text{ gas}) (\text{cm thick})}{(\text{sec}) (cm^2 \text{ polymer}) (\text{cm Hg}, \Delta P)}$$

Although the use of this approach to determine the intrinsic permeablity of ozone in siloxane is novel, such an approach is not entirely without precedent. Hwang et al. (1971, 1974b) has investigated permeabilities of carbon dioxide, oxygen and water through acetyl cellulose acetate membranes and discovered the following relationship. A plot of $(b)^{-1}$ against $(SD)^{-1}$ can be extrapolated to a y-intercept which is equal to the reciprocal of the intrinsic permeability.

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A CRYOGENIC PRECONCENTRATION-DIRECT FLAME IONIZATION METHOD FOR MEASURING AMBIENT NMOC

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INTRODUCTION AND APPLICABILITY

A variety of photochemical dispersion models have been developed to describe the quantitative relationships between ambient concentrations of precursor organic compounds and subsequent downwind concentrations of ozone.[1] An important application of such models is to determine the degree of control of such organic compounds that is necessary in a particular area to achieve compliance with applicable ambient air quality standards for ozone.[1,2] For this purpose, the models require input of data on ambient concentrations of nonmethane organic compounds (NMOC).

The more elaborate theoretical models generally require detailed organic species data.[2] Such species data must be obtained by analysis of air samples with a sophisticated, multicomponent gas chromatographic (GC) analysis system.[2,3] Simpler empirical models such as the Empirical Kinetic Modeling Approach (EKMA)[1] require only total NMOC concentration data, specifically the average total NMOC concentrations from 6 a.m. to 9 a.m. daily.[2]

Commercial, continuous NMOC analyzers have been used to obtain urban NMOC concentrations,[2] but these methods have proved to be only marginally adequate[4] because of limitations from variability, zero and span drift, lack of sensitivity, non-uniform response characteristics, and the indirect nature of the measurement. Moreover, these methods are clearly inadequate for determining the low, upwind NMOC concentrations needed when transport of precursors into an area is to be considered in the EKMA application.[4,5]

NMOC GC species measurements can be used by summing the various components to obtain a total NMOC concentration.[2] These measurements are much more accurate than continuous NMOC analyzer data, but species data are not needed for EKMA, and the procedure is therefore unnecessarily expensive and complex.

The cryogenic Preconcentration-Direct Flame Ionization (PDFID) method can be used to obtain the requisite upwind, as well as urban, NMOC measurements.[6,7,8] This method is based on a simplification of the GC speciation technique. It combines the cryogenic concentration technique used in the GC method for high sensitivity with the simple flame ionization detector (FID) for total NMOC measurements without the complex GC columns necessary for species separation. And because of the use of helium carrier gas, the FID has less response variation to various organic compounds than a conventional NMOC analyzer with air carrier or direct sample injection into the FID.

This method can be used either for direct, in situ ambient measurements or for analysis of integrated samples contained in metal canisters. Making direct measurements at the monitoring site avoids the potential sample loss or contamination problems possible with the use of canisters. However, the analyst must be present during the 6 to 9 a.m. period, and repeated measurements (approximately six per hour) must be taken to obtain the 6 to 9 a.m. average NMOC concentration. A separate analytical system and analyst is needed for each monitoring site. (Further development of the method may allow for automatic operation for on-line semi-continuous analysis in the future.)

The use of sample canisters allows the collection of integrated air samples over the 6 to 9 a.m. period by automated samplers at unattended monitoring sites. One centralized system can then analyze the samples from several sites. Degradation or contamination of the air samples by the canister could be a potential problem, but tests indicate that the use of properly fabricated, treated, and cleaned stainless steel canisters, as described in the procedure, is practical and adds relatively little additional variability to the method.[8]

PRINCIPLE

An air sample is taken either directly from the ambient air at the monitoring site, where the analytical system is located, or from a sample canister filled previously at a remote monitoring site. A fixed-volume portion of the sample is drawn at a low flow rate through a glass beaded trap cooled to approximately -186° C. This temperature is such that all organic compounds in the sample other than methane are collected (either via condensation or adsorption) in the trap, while methane, nitrogen, oxygen, etc., pass through. The system is dynamically calibrated so that the volume of sample passing through the trap

does not have to be quantitatively measured, but must be precisely repeatable between the calibration and analytical phases.

After the fixed volume air sample has been drawn through the trap, the helium carrier gas is diverted to pass through the trap in a direction opposite to that of the sample flow and into a flame ionization detector (FID). When the residual air and methane have been cleared from the trap and the FID baseline becomes steady, the cryogen is removed and the temperature of the trap is raised to approximately 90° C. The organic compounds collected in the trap revolatilize and are carried into the FID, resulting in a response peak or peaks from the FID. The area of the peak or peaks is integrated, and the integrated value is translated to concentration units via a previously obtained calibration curve relating integrated areas with known concentrations of propane.

The cryogenic trap simultaneously concentrates the nonmethane organic compounds while separating and removing the methane from air samples. Thus the technique is direct reading for NMOC and, because of the concentration step, is more sensitive than conventional NMOC analyzers. Quantitative trapping has been shown for most compounds tested.[6] A complete description of the method, including the collection of integrated air samples in stainless steel canisters, is provided in Reference 8. Figure 1 is a schematic diagram of the analytical system.

PRECISION AND ACCURACY

The overall precision estimate for the method, including the effect of collecting and storing the ambient samples in stainless steel canisters, has been found to be 4.5%.[9]

Because of the number and variety of organic compounds included in the NMOC measurement, determination of absolute accuracy is not practical. Based on comparison with manual GC speciation analysis--regarded as the best available for measurement of organic compounds--the proportional bias was determined to be +5.7%, with a negligible fixed bias.[9] Although the 5.7% bias was statistically significant, no correction factor is proposed for the method because this bias is modest, and the speciation techique is not an absolute standard.

Experimental tests indicate some degree of FID baseline shift from water vapor in ambient samples, which could result in positive bias, variability, or both. These problems can be adequately minimized by careful selection of the integration termination point and appropriate baseline corrections.[9]

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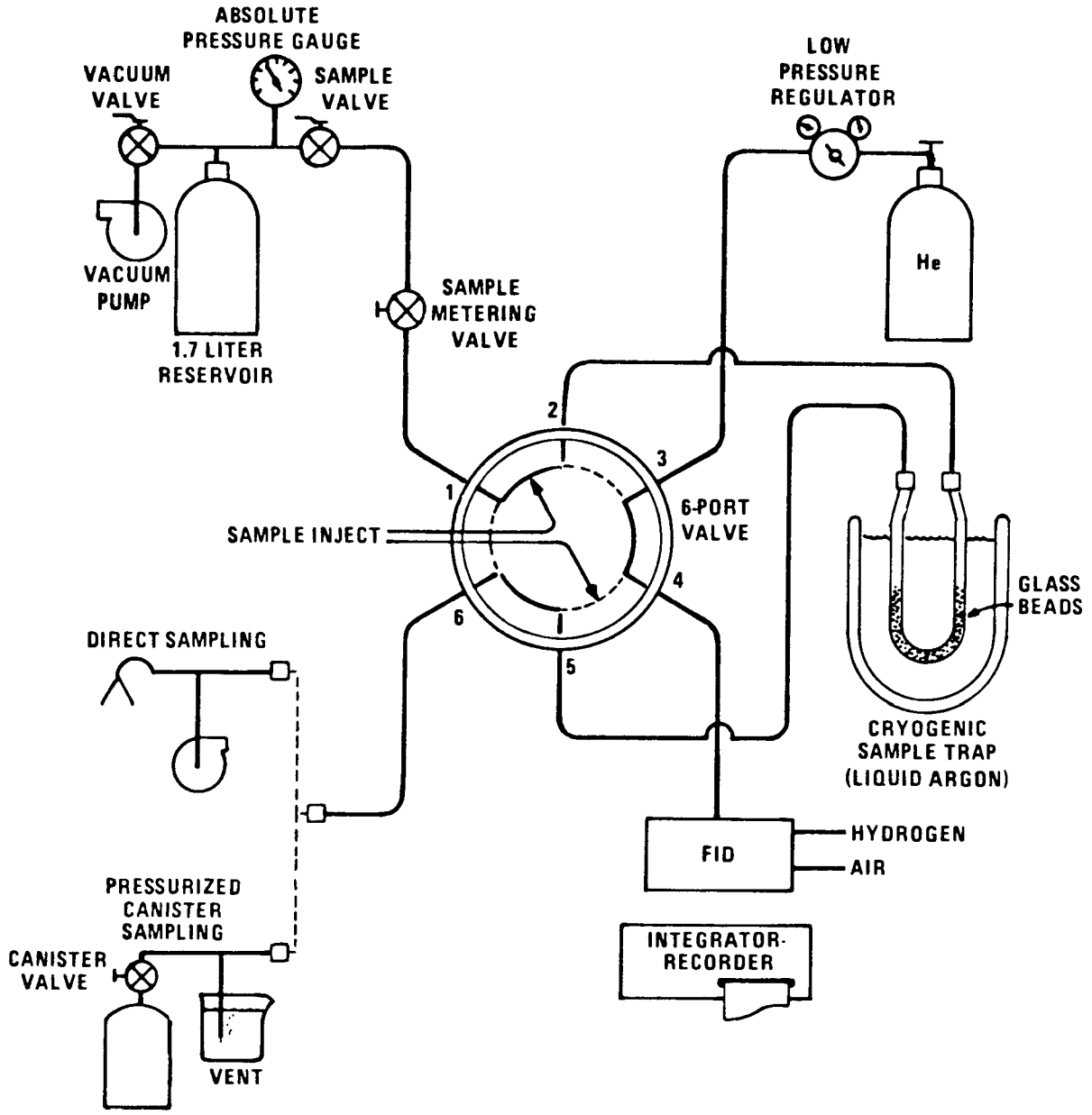

Figure 1. Schematic of analysis system showing two sampling modes.

MOBILE AIR MONITORING BY MS/MS - A STUDY OF THE TAGA® 6000 SYSTEM

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In this paper we report on a series of experiments undertaken to evaluate a mobile Tandem Quadrupole Spectrometer System (the TAGA® 6000) in performing qualitative and quantitative real-time air analysis. The work was a cooperative venture between SCIEX® and the Environmental Monitoring Systems Laboratory, Environmental Protection Agency at Research Triange Park. A mobile TAGA® 6000 located at RTP was used to analyze both synthetic gas mixtures and ambient air in an industrial environment. The results of the tests were intended to indicate to both SCIEX® and EPA what the current strengths and weaknesses of the system are, to show what areas require further development in order to strengthen the capabilities, and to suggest how such a system can best be used as part of an overall approach to air monitoring.

OBJECTIVES

A series of controlled experiments was undertaken in order to evaluate a) the ability to identify unknown organics at ppm and ppb levels in a mixture; b) the ability to rapidly measure the concentrations in a mixture with sufficient accuracy for a field program; c) the possible presence of matrix effects; d) ease of operation of the system and data manipulation and interpretation facilities and e) the reliability of the system in a mobile mode.

During the two week program the TAGA® 6000 was used to analyze seven prepared gas cylinder mixtures. Two of the cylinders were mixtures of compounds selected from a target list of 32, and were prepared and certified by an outside supplier under the direction of EPA. The actual components and concentrations in each were unknown to SCIEX®. Two of the cylinders were uncertified mixtures also supplied to EPA, but with the components completely unknown to SCIEX® (i.e. not necessarily selected from the target list). The other three cylinders were two component mixtures with differing relative concentrations designed to show whether matrix or interference effects were present.

EXPERIMENTAL PROCEDURES

The challenge mixtures were analyzed using both an APCI (Atmospheric Pressure Chemical Ionization) and a more conventional CI (with a discharge ionization process) source. The APCI source is very sensitive to polar compounds; the CI source, using charge transfer from N_2^+, O_2^+ and NO^+, is sensitive towards the chlorinated hydrocarbons and aromatics. Both sources are designed to allow air to be sampled directly into the source (with no pre-separation or concentration) so that analysis is performed continuously in real-time.

The cylinder mixtures were admitted either directly into the sources or by diluting with clean bottled air. Compounds were identified by first performing scans with a single mass spectrometer (Q1) to reveal the parent ions from the source. Each parent ion noted in the spectrum was then collisionally dissociated to produce a daughter ion spectrum and then compared (using computer-match procedures) with standard CAD library spectra. Where library spectra existed, identification was thus accomplished in a few seconds. Where no library spectrum existed, CAD spectra were manually interpreted to identify the compound. Quantitation was performed using a headspace injection technique to produce a five point calibration curve. This technique requires that the vapor pressure of the compound be known, and takes about 5 minutes per compound to perform.

RESULTS AND DISCUSSION

The two certified cylinders were seven component mixtures; the components in each were identical, but the levels were approximately twenty times lower in one cylinder than the other. The components in each were correctly identified by MS/MS, and the concentrations measured in a separate experiment. The other two multicomponent mixtures consisted of 16 and 7 components respectively. In total, among the four cylinders, 13 compounds were correctly and unambiguously identified, 7 were identified as either one or both of a pair, 1 was incorrectly identified and 2 were missed. Table 1 summarizes the results of the qualitative experiments.

The compounds which were identified as either/or could not be resolved because each pair of compounds forms the same parent ion in the source (for example, methylene chloride forms $(M-H)^+$ and chloroform forms $(M-Cl)^+$, both at m/z 83). Appearance potentials of these ions are such that it is difficult

TABLE 1. SUMMARY OF QUALITATIVE CYLINDER ANALYSES

Compounds Present in Mixture	Identification by MS/MS
Benzene	Benzene
Toluene	Toluene
Chlorobenzene	Chlorobenzene
Carbon Tetrachloride	Carbon Tetrachloride
Trichloroethylene	Trichloroethylene
Tetrachloroethylene	Tetrachloroethylene
Acrylonitrile	Acrylonitrile
Pyridine	Pyridine
Xylene	Xylene
Benzyl Chloride	Benzyl Chloride
Dibromoethane	Dibromoethane
Hexachlorobutadiene	Hexachlorobutadiene
Vinyl Chloride	Vinyl Chloride or Dichloroethene
Dichloroethane	Dichloroethane or Vinyl Chloride
Methylene Chloride	Methylene Chloride or Chloroform
Chloroform	Chloroform or Methylene Chloride
Vinylidene Chloride	Vinylidene Chloride or Methylene Chloride
Methyl Chloroform	Methyl Chloroform or Vinylidene Chloride
Ethylene Oxide	Ethylene Oxide or Acetaldehyde
Dichloropropene (cis-1,3 and trans 1,3)	Allyl Chloride
Propane	Not Identified
Trichloro-trifluoroethane	Not Identified

TABLE 2. SUMMARY OF QUANTITATIVE CYLINDER ANALYSES

	Cylinder 9558		Cylinder 11745	
Compound	SCIEX®(ppm)	Manufacturer Certified (ppm)	SCIEX®(ppb)	Certified (ppm)
Vinyl Choride	1.05	0.904	Detected but not quantitated	19.1
Benzene	1.68	1.28	23	17.7
Toluene	1.03	0.894	20	14.4
Chlorobenzene	1.07	0.862	23	18.0
Carbon Tetrachloride	0.63	0.737	17	19.8
Trichloroethylene	0.78	0.66	23	16
Tetrachloroethylene	0.56	0.52	20	15.7

to generate characteristic molecular ions under any ionization condition. Since identical parent ions are formed in the source, CAD spectra are also identical. Some preseparation will likely be required in order to resolve these ambiguities in identification. Evidence existed in the parent ion spectra for the presence of propane and trichloro-trifluoroethane, but this was only observed after their presence was known. Dichloropropene was mis-identified initially as allyl chloride; later experiments revealed that these two compounds also form the same ions in the source, and so cannot be resolved in real-time.

The results of the quantitative experiments are summarized in Table 2. The average deviation from the manufacturers certified values was 17% in the ppm cylinder and 36% in the ppb cylinder. Both of these are based on the primary calibration technique using introduction of headspace vapor. The ppb cylinder was also calibrated by using the other cylinders as a standard; this procedure gave better agreement, yielding an average deviation from the manufacturer of only 13%. The matrix experiments, in which benzene and toluene were present in mixtures at ratios of approximately 1:10, 1:1 and 10:1, revealed that each component could be quantitatively measured in the presence of the other. However with the APCI source, reagent ion depletion resulted in matrix effects above a concentration of about 500 ppb. No matrix effects were noted with the CI source at concentrations of up to 10 ppm.

SUMMARY

The mobile MS/MS system proved capable of identifying unknown components in a mixture at the ppm and ppb level in real-time, using computer library search procedures. Some problems were encountered in resolving pairs of compounds which form the same ion in the CI source; a fast preseparation technique will likely be required where unambiguous identification is necessary. Quantitation could be performed in-situ, with sufficient accuracy for a real-time field monitoring program. More effort needs to be devoted to increasing the CAD library size, and to characterizing single MS spectra of environmentally interesting compounds so that their possible presence can be recognized in a mixture.

ACKNOWLEDGEMENTS

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DEVELOPMENT OF SURFACE-ENHANCED RAMAN SPECTROSCOPY FOR MONITORING TOXIC ORGANIC POLLUTANTS*

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ABSTRACT

Raman spectroscopy has proved its usefulness as a practical tool for organic analysis.[1,2] One limitation of this spectroscopic technique, however, is its low sensitivity due to the small Raman cross section, which often requires the use of powerful and costly laser sources for excitation. Recently a renewed interest has developed in Raman spectroscopy as a result of observations indicating enhancement in the Raman scattering efficiency by factors of 10^3 to 10^6 when a compound of interest is adsorbed onto special metal surfaces.[3] These spectacular enhancement factors for the weak conventional Raman scattering process help overcome the normally low sensitivity of Raman spectroscopy. This new Raman technique, known as surface-enhanced Raman spectroscopy (SERS), could open new horizons for trace organic analysis.

This paper presents the analytical usefulness of a novel technique based on SERS for monitoring toxic organic pollutants. A new method for preparing SERS-active substrate using submicron silver-coated spheres deposited on filter paper substrates is described in detail. The analytical advantages and limitations of the technique are discussed. Figure 1 shows a typical SERS signal of 3.6 ng benzoic acid on a SERS active cellulosic surface having 910 Å spheres coated with 2000 Å film of silver. The detection limits for several organic compounds such as carbazole, 1-aminopyrene, 1-nitropyrene, and benzoic acid are at the nanogram and subnanogram levels.[4] The results of this study indicate that SERS shows great promise as a useful analytical tool for monitoring various important air pollutants, such as the nitro-polyaromatic species, that cannot be detected by other spectroscopic techniques.

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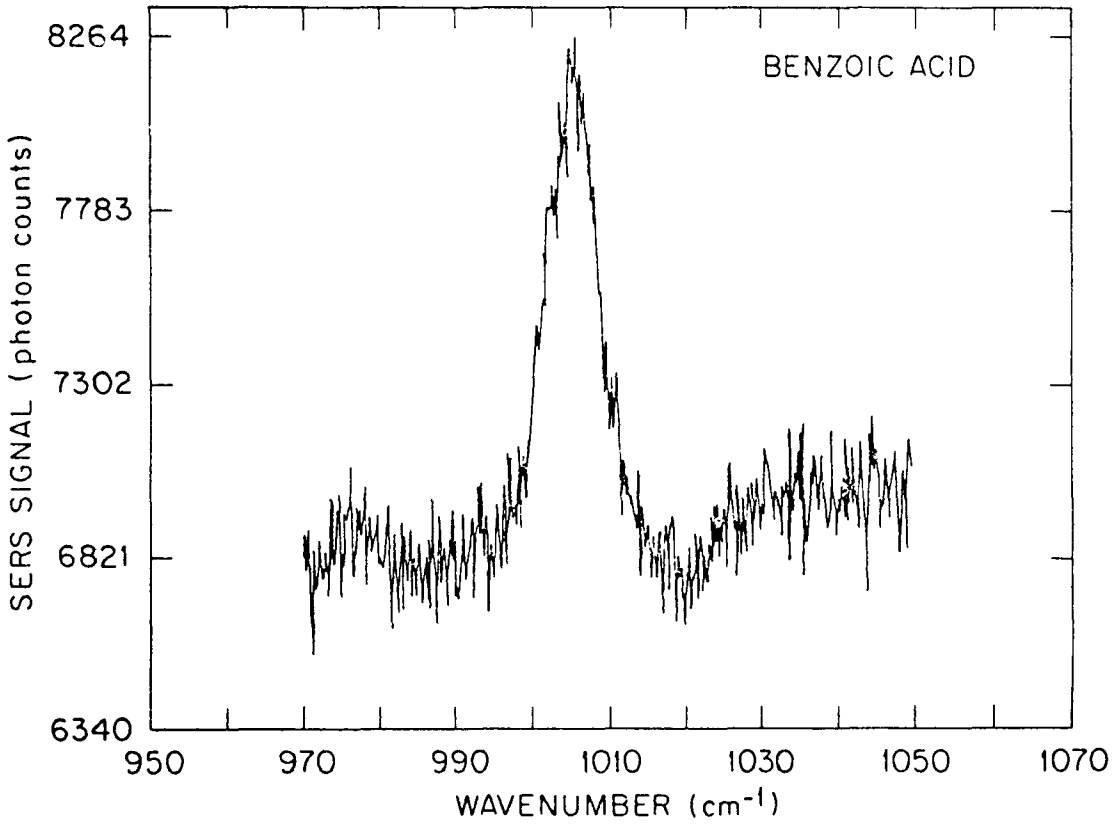

Figure 1. Surface-Enhanced Raman Signal of 3.6 ng of Benzoic Acid. (Laser excitation wavelength = 632 nm)

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THERMAL DESORPTION TECHNIQUES FOR THE GAS CHROMATOGRAPHIC ANALYSIS OF PARTICULATE MATTER

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INTRODUCTION

Simple screening techniques for polycyclic aromatic hydrocarbons (PAHs) can facilitate the characterization of ambient air quality by providing a quick routine means of identifying those particulate samples which should be subjected to a rigorous detailed compositional analysis. Lengthy and laborious solvent extraction and fractionation procedures commonly employed in analyses for PAHs may be circumvented by thermal desorption of PAH directly from particulate samples. Studies reported by other investigators indicate that PAHs can be effectively extracted from particulate matter by sublimation at both atmospheric pressure and at reduced pressure.[1-7] Vacuum-sublimation has been used to reduce extraction time, improve extraction yields, and avoid thermal degradation.[1,4,5] In this study a vacuum-sublimation system was designed and constructed for direct analysis of volatilized PAHs with a capillary gas chromatograph. Early results obtained with test mixtures are reported.

EXPERIMENTAL

Analyses were performed with a Varian Model 3700 gas chromatograph (GC) equipped with a Durabond, DB-5, fused silica capillary column (30m x 0.32mm x 0.1μ film thickness) and an HNU photoionization detector (PID) (Model 52-02, 9.5 eV lamp). The sample injector of the GC was removed and the GC column was extended from the oven through the injector heating block to a connecting union on an external sample oven (Figure 1). The sample trap (borosilicate glass tubing) was connected to the carrier gas line and the end of the capillary column by means of stainless steel tube fittings using graphite or 40% graphite/vespel ferrules. The exit end of the column emerged from the oven through an auxiliary injector heating block and was inserted directly into the

ionization chamber of the detector (Figure 2). The vacuum-sublimation system is shown in Figure 3. The particulate sample is loaded into a borosilicate glass tube (6.4 mm O.D. x 11 cm), which is connected to the sample trap (3.2 mm O.D. x 11 cm) by means of a tube fitting using 40% graphite/vespel ferrules. The tube fitting is bored through so that the arm of the trap can be extended into the sample tube.

Sample tubes and sample traps were cleaned before use with a 20 min helium purge at 260°C. PAHs were vacuum-sublimed for a period of 30 min at 260-280°C and 0.04 to 0.05 Torr. The sample trap containing the extracted material was transferred to the external oven of the GC and purged with carrier gas (helium) at room temperature before analysis. The extracted material was then volatilized at 260°C and concentrated on the cooled section of the external GC column (28-30°C). After 10 min at 260°C the oven cover was removed. After 2 min more, the external column was rapidly heated to 260°C and the temperature programmed analysis was begun at a carrier flow rate of 6 ml/min. The column was held initially at 55°C for 10 min, then raised to 225°C at 10°C/min, and held at the final temperature for 30 min. Measurements were made with a photoionization detector to minimize chromatographic interferences from non-aromatic species co-desorbed with the PAHs.

RESULTS AND DISCUSSION

Standard reference material (SRM) 1647 from the National Bureau of Standards (NBS) was used to test the transfer of PAHs from the sample trap to the GC column. A 30 µl sample which had been diluted 10:1 was injected onto the glass wool plug of the trap and evaporated to dryness at room temperature with a stream of helium. All of the PAHs, ranging in volatility from acenaphthylene to benzo(g,h,i)perylene, were successfully transferred to the GC column and eluted within 35 min.

A previously desorbed urban dust sample (SRM 1649 from the NBS) was spiked with a 5-component PAH solution, dried, and then extracted by thermal purging and by vacuum-sublimation. In both cases 4 of the components, phenanthrene, fluoranthene, benz(a)anthracene, and benzo(a)pyrene were desorbed with approximately 90% or greater efficiency. However, the least volatile component, benzo(g,h,i) perylene was not desorbed sufficiently to be detected (Figure 4).

Vacuum sublimations conducted with virgin SRM 1649 produced chromatograms dominated by a strong envelope of material peaking at an elution time of 28.0 min and containing a strong peak at 22.9 min (Figure 5a). The presence of most PAH compounds was rather obscure although the test sample contained 25-70 ng of several PAHs. Weak peaks were found at elution times consistent with those for phenanthrene and benz(a)anthracene. Fluoranthene plus pyrene and benzo(a)pyrene were overlapped by the strong peaks at 22.9 and 28.0 min, respectively. A repeat sublimation test with the spent SRM 1649 sample indicated that the major portion of desorbable compounds detectable by the PID can be extracted in a reasonable time (Figure 5b). However, the PAHs of interest constitute only a minor portion of these compounds. Similar results were obtained with a 60 min thermal purge of SRM 1649 at 280°C and 100 ml/min, although the extraction was somewhat less efficient.

CONCLUSIONS

Although PAHs deposited from solution on borosilicate glass sample holders may be readily volatilized for analysis by capillary column gas chromatography, urban dust samples are much more resistant to volatilization of adsorbed PAHs. At low PAH concentrations and in the absence of a sufficiently selective detector or a clean-up step the presence of desorbed PAHs is obscured by other co-desorbed species. A multidimensional gas chromatograph with a mass selective detector would offer improved selectivity for PAHs thermally desorbed from urban particulate matter. A more selective PID (8.3 eV lamp) may also be helpful.

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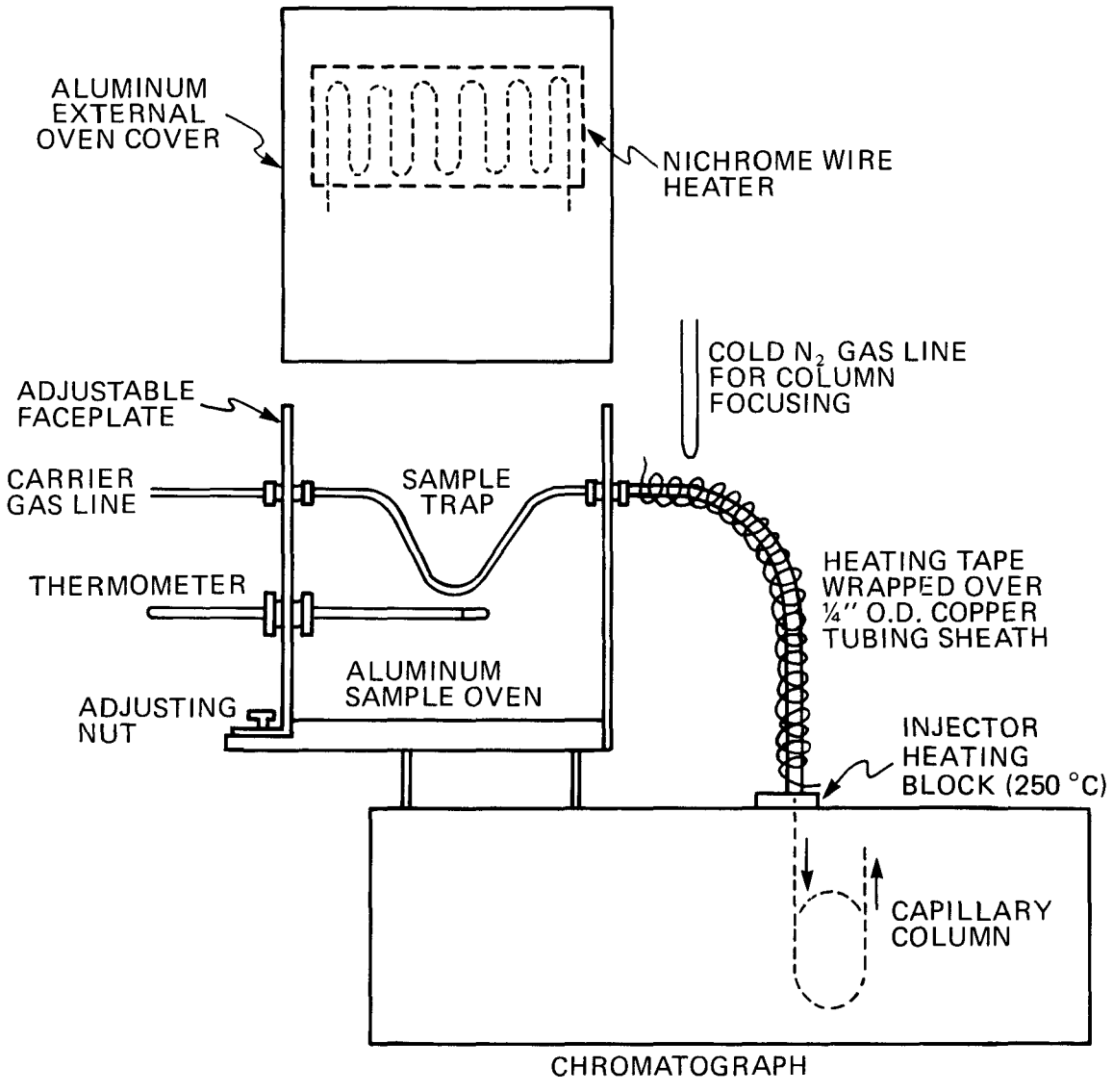

Figure 1. Sample Injection System

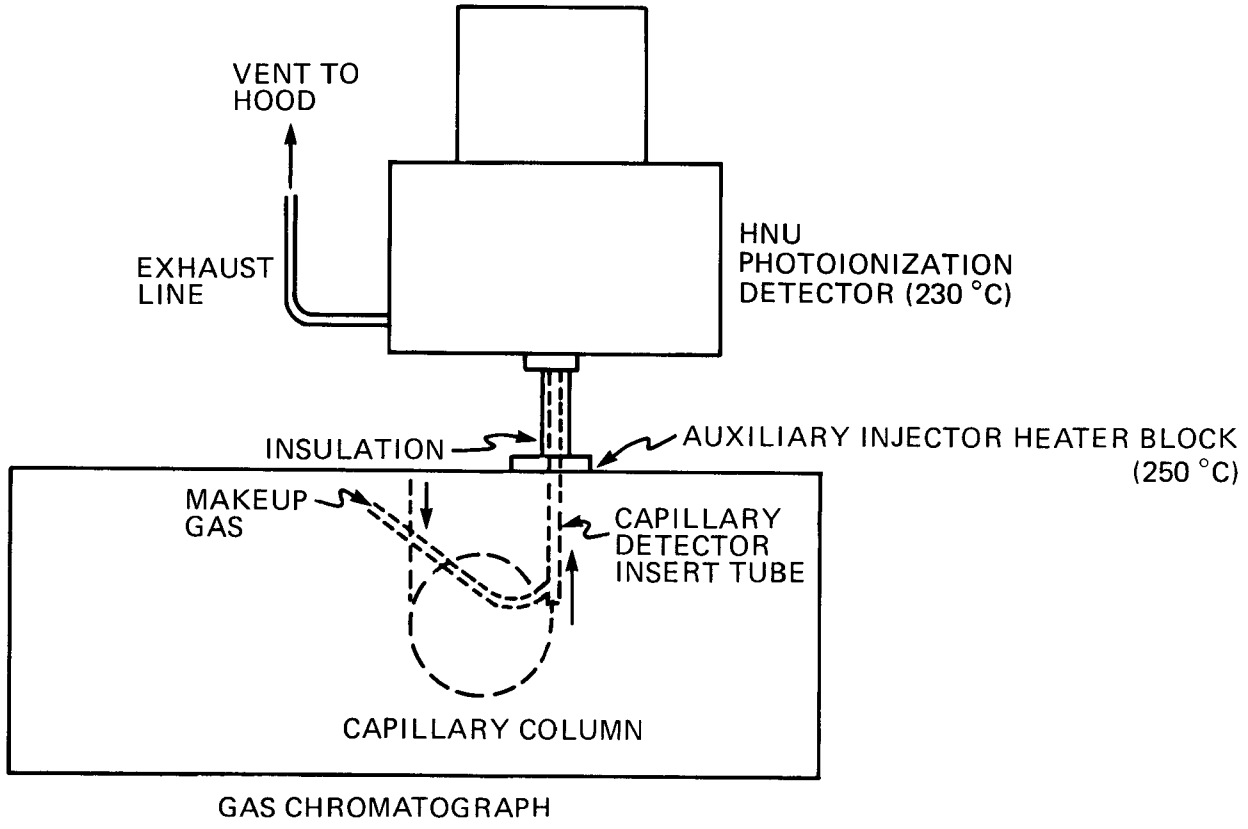

Figure 2. Detection System Configuration

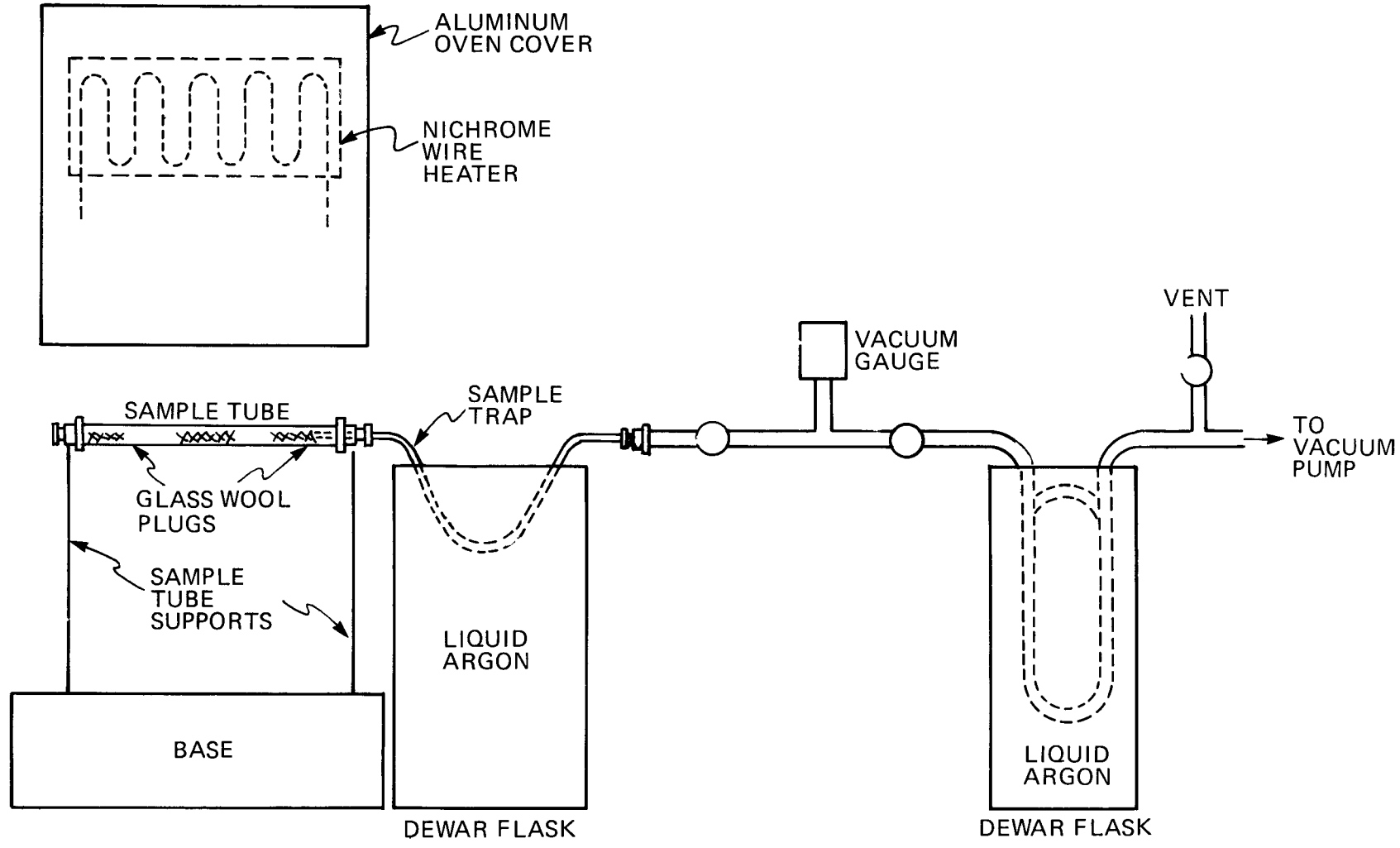

Figure 3. Vacuum-Sublimation System

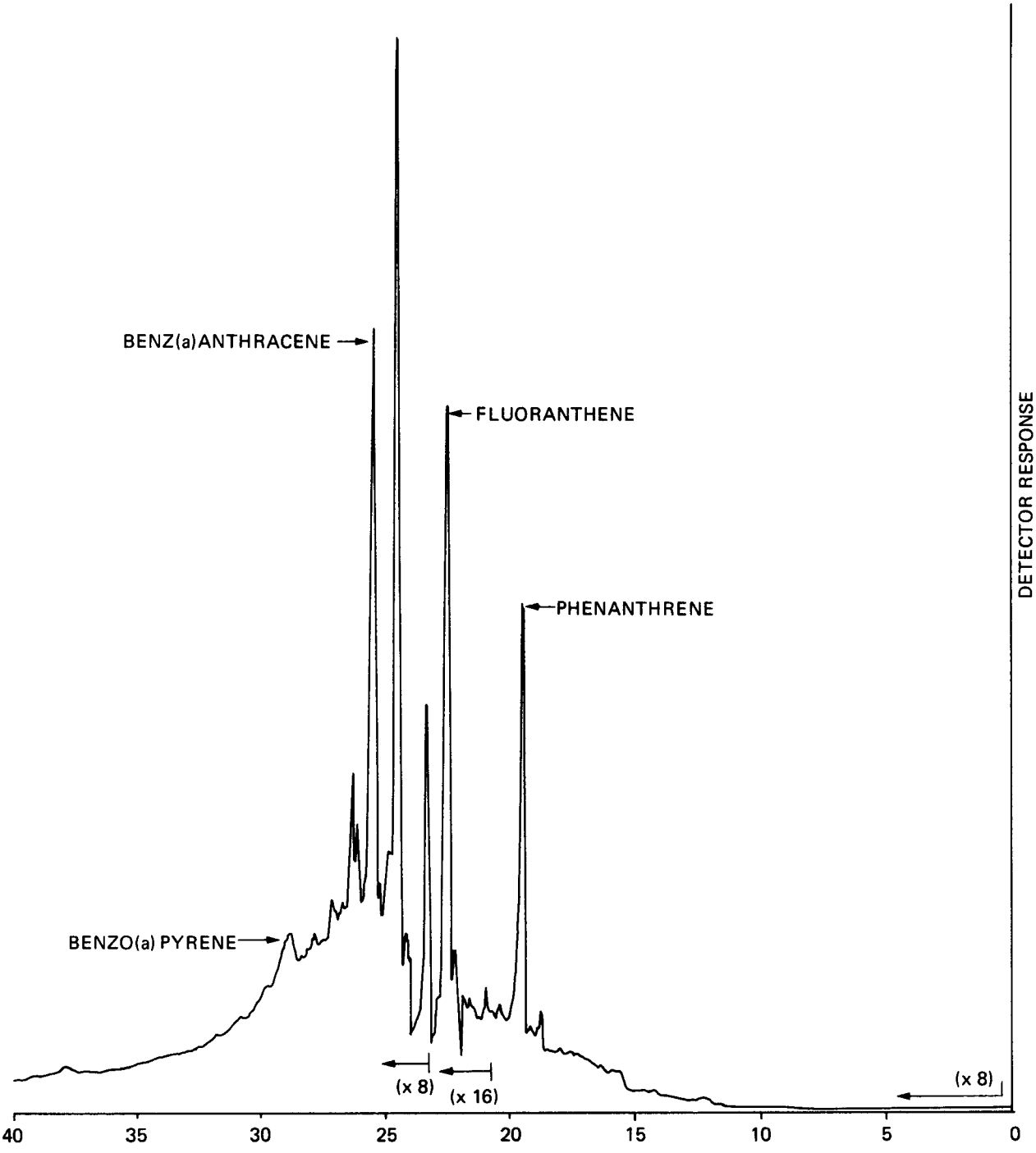

Figure 4. Chromatogram of Vacuum-Sublimed Material from Spiked SRM 1649.

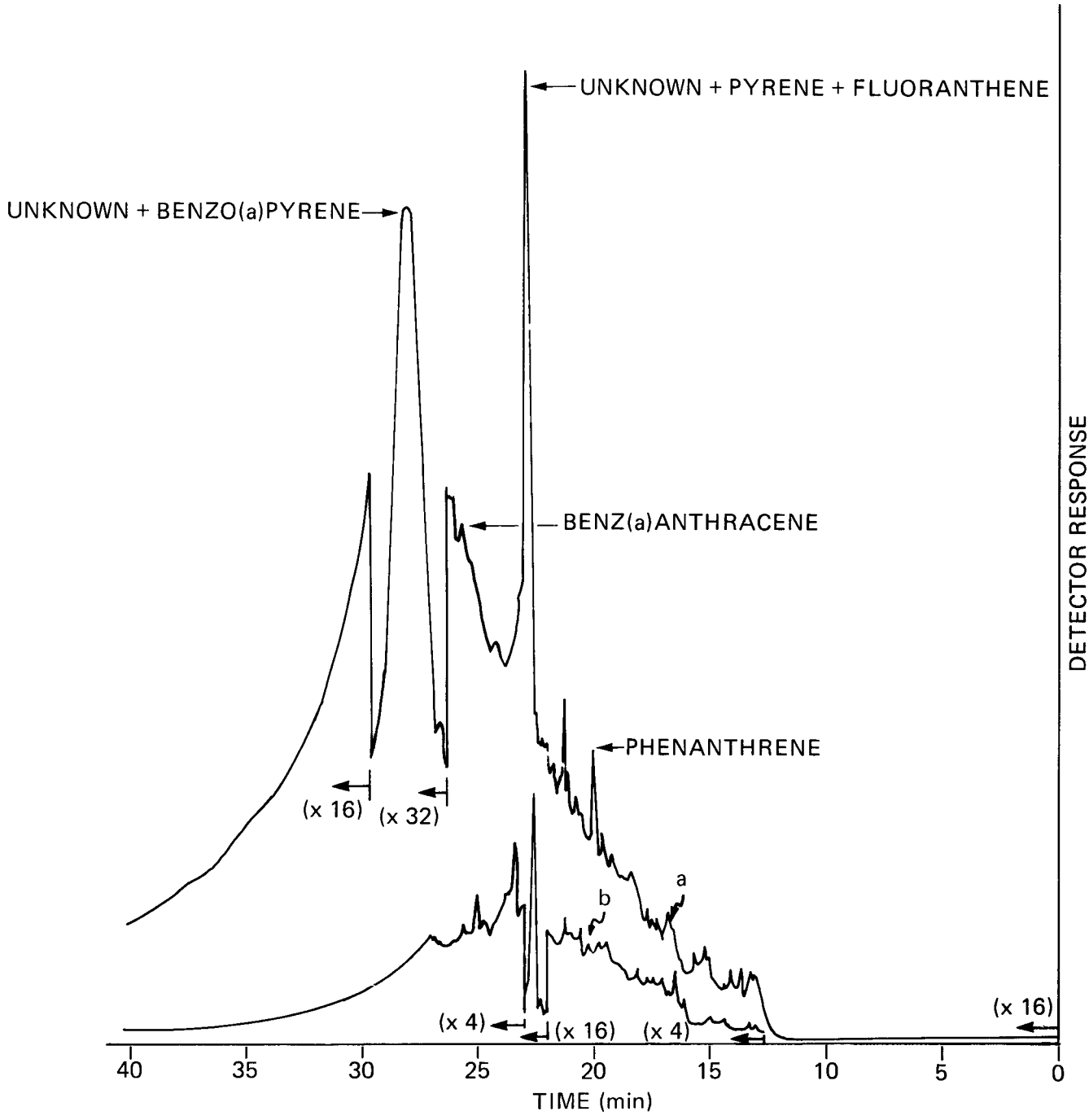

Figure 5. (a) Chromatogram of Vacuum-Sublimed Material from Virgin SRM 1649.
(b) Chromatogram of Vacuum-Sublimed Residual Material from SRM 1649.

A REVIEW OF MULTIVARIATE RECEPTOR MODELS

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The objective of receptor modeling is to deduce information regarding the origins of observed concentrations of ambient species from those measured concentrations. This approach is in contrast to source or dispersion modeling that predict the ambient concentrations from emission source data and the meteorology of the region. In general receptor modeling has focussed on the identification of and apportionment of aerosol mass to particulate emission sources.

Several previous articles have reviewed the development and implementation of these models upto several years ago (Cooper and Watson, 1980; Gordon, 1980). Prior work has primarily been empirical explorations of the application of these approaches to specific urban air quality problems. Recently, there has been the beginnings of some more fundamental studies examining the basic mathematical methods being used and the ways in which the limts of these methods can be rigorously defined.

The fundamental assumption of receptor models has been that a mass balance can be applied; that is, the amount of any particular observed species is a sum of contributions from the independent sources of that species. For example, the total lead concentration observed in a parcel of air can be considered to be the sum of the lead in that parcel from motor vehicles burning leaded gasoline plus smelter emissions plus refuse incinerators, etc.

$$Pb_t = Pb_{motor} + Pb_{refuse} + Pb_{smelter} + \cdots$$

Total aerosol mass would represent a similar mass balance. However, the airborne lead is not the only species in motor-vehicle-generated particles. Thus, Pb_{motor} can be considered to be the product of the concentration of lead in the particles, $a_{Pb,motor}$ times the mass of motor vehicle particles in the sampled air parcel, f_{motor}

$$Pb_{motor} = a_{Pb,motor} f_{motor}$$

Generalizing this approach to multiple variables measured in multiple samples yields

$$x_{ij} = \sum_{k=1}^{p} a_{ik} f_{kj} \qquad i=1,m;\ j=1,n$$

where x_{ij} is the amount of the ith species measured in the jth sample, a_{ik} is the concentration of species i in material from source k at the receptor site, and f_{kj} is the amount of mass contributed to sample j by source k.

There are two commonly used multivariate methods to solve for the desired parameters; multiple linear regression and factor analysis. In the multiple linear regression approach, commonly called the Chemical Mass Balance method, it is assumed that the number of sources, p, and their compositions, a_{ik}'s, are known. The mass contributions, f_{kj}'s, are then calculated as the regression parameters. It is usually assumed that the compositions do not change from source to receptor and source-measured values are employed. Efforts have been made to examine reactions of polynuclear aromatic hydrocarbons using first order reaction kinetics (Duval and Friedlander, 1972). These methods have been widely applied to the study of a variety of air quality problems with particularly good results in the Portland Aerosol Characterization Study (Core et al., 1983) and in Washington, D.C. (Kowalczyck et al., 1983).

The other approach is factor analysis (Hopke, 1981). In this method only the ambient data is employed and the analysis is used to deduce the number of identifiable sources, their composition, ahd the mass contributions. These methods have been primarily applied to data from St. Louis, MO (Alpert and Hopke, 1981; Liu et al., 1982; Severin et al., 1983) where results have appeared to be quite good.

Both approaches have limitations that are only now being studied at a more fundamental level. Inherent in the regression approach are problems in correctly calculating the mass contributions when two or more of the sources have similar compositions even when those compositions are perfectly known. In real situations where there are fluctuating compositions measured with sampling and analytical errors additional problems arise. In many cases in the literature, the number of sources reported to be resolved accurately is considerably overestimated and the results are much more uncertain than they are reported to be (Henry, 1983).

A similar problem exists for the factor analysis in that it also will not be able to separately identify sources of similar composition. However, it can be used to find appropriate linear combinations of the sources that can be accurately fit. Furthermore, factor analysis is driven by variations in the system that can come from both varying source emission rates and from meteorology. If the latter dominates, two sources with quite different composition may be found to be inseparable by factor analysis. However, factor analysis is not unlikely to overestimate the resolvable number of sources nor overlook an unsuspected source. Thus, a combination of these methods is the best current approach to obtain results upon which air quality management decisions can be confidently made.

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A METHOD TO SPECIFY MEASUREMENTS FOR RECEPTOR MODELS

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INTRODUCTION

Numerous chemical measurements have become available in recent years which can be used in receptor models to differentiate between and to quantify the contributions of source emissions to ambient pollutant concentrations. Instrumental neutron activation analysis, x-ray fluorescence, ion chromatography, and step-wise thermal combustion have been used individually and in combinations to supply chemical concentration input data to receptor models for a large number of samples. X-ray diffraction, computer automated microscopy, mass spectrometry, electron capture and flame ionization gas chromatography, and isotopic enrichment analysis have recently been proposed as analytical methods which would provide more characterization of pollutant sources. Since these analytical methods can be very expensive, and since most receptor model studies are performed on a fixed budget, some objective procedure of selecting the observables to be used in the models, and the measurement methods required to obtain values for those observables, needs to be applied at the study design stage. This paper proposes such a procedure. The paper's objectives are to 1) describe a receptor model measurement specification methodology, 2) to illustrate the methodology, and 3) to provide measurement uncertainty specifications for a specific application of the mass balance receptor model.

MEASUREMENT DEFINITION

A measurement posesses the following attributes (Watson et al., 1983): 1) an observable specification, 2) a value, 3) a lower quantifiable limit, 4) precision, 5) accuracy, and 6) validity. The model imposes certain requirements on the tolerances assigned to each of these attributes. Measurement methods must then be selected such that they meet or exceed these tolerances. The most important questions regarding measurements used in receptor models are:

- Does a proposed observable differentiate between sources?
- How many observables or measurements of the same observables are required?
- How low must each detection limit be?
- What precision must each measurement have?

MEASUREMENT SPECIFICATION PROCEDURE

The following steps can be followed to provide a quantitative answer to these questions.

1. List all p likely sources and expected contributions.

2. Obtain likely emissions compositions for all quantifiable species.

3. Set the true contributions (S_j) and true compositions (a_{ij}) at expected values.

4. Generate n true concentrations using a model which physically represents the situation under study. The linear model

$$\bar{C}_i = \sum_{j=1}^{\bar{p}} \bar{a}_{ij} \bar{S}_j, \quad i=1, \bar{n} \tag{1}$$

5. Simulate the measurement process to obtain measured values (C_{ik} and a_{ijk}) k=1 to m times (Watson, 1979) using random numbers (ε_{ik} and ε_{ijk}) drawn from a normal distribution of mean zero and unity standard deviation, and measurement uncertainties σ_{C_i} and $\sigma_{a_{ij}}$.

$$C_{ik} = \bar{C}_i + \varepsilon_{ik} \sigma_{C_i} \tag{2}$$

$$a_{ij} = \bar{a}_{ij} + \varepsilon_{ijk} \sigma_{aij} \tag{3}$$

6. Apply the receptor model to answer the questions.

   - To determine whether or not a new observable differentiates between sources, apply the model to simulated data sets with and without the observable.
   - To determine the number of different observables or measurements, apply the model to selected subsets of the simulated data.
   - To determine required detection limits (D_i) vary the ratio of C_i/D_i.
   - To determine required precisions, vary σ_{C_i} and $\sigma_{a_{ij}}$.

7. Compare the distributions of model-calculated source contributions (S_{jk}) and their uncertainties ($\sigma_{S_{jk}}$) to the true source contributions (S_j).

APPLICATION

To illustrate this methodology, it is applied to the mass balance receptor model using the effective variance least squares solution (Watson et al., 1984). A desert environment is likely to receive ambient particulate contributions from secondary nitrate, secondary sulfate, soil, burning, and motor vehicle sources. Typical compositions of these sources have been drawn from Watson (1979). The chemical species included are organic carbon, elemental carbon, NH_4^+, NO_3^-, $SO_4^=$, Al, Si, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, and Pb. In this application of the procedure, the measurement precision requirements are evaluated, so σ_{C_i} and $\sigma_{a_{ij}}$ are set to 10%, 20%, and 30% of their respective values.

The results of this application appear in Table 1. These results indicate that measurement methods must have precision less than 20% in order to assure model calculations which are within a factor of two of reality and to have the majority of the calculated source contributions fall within one calculated standard deviation of the true contributions. More detailed observations about Table 1 are presented in Watson et al. (1984).

FUTURE STUDIES

This method can be applied to factor analysis and linear regression receptor models in order to determine the value of measurement methods to the modeling process. Future research plans include these applications along with creation of a model/measurement evaluation computer package which can be used to design future receptor modeling studies in an optimal manner.

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TABLE 1. Averages, Standard Deviations and Ranges of Source Contributions and Their Uncertainties as a Function of Uncertainty Level. (Units are $\mu g/m^3$)

Source Type	Parameter	Uncertainty Level 0%	10%	20%	30%
1. NH_4NO_3	Average S_j	0.50	0.50	0.51	0.54
	Range of S_j	---	.29 - .71	.26 - 1.0	.03 - 1.5
	Std. Dev S_j	---	0.081	0.18	0.30
	Average σ_{S_j}	---	0.080	0.17	0.31
	Std. Dev σ_{S_j}	---	0.013	0.06	0.22
	Range of σ_{S_j}	---	.06 - .11	.09 - .32	.11 - 1.2
2. $(NH_4)_2SO_4$	Average S_j	4.50	4.41	4.34	4.28
	Range of S_j	---	3.4 - 6.0	2.5 - 8.0	1.6 - 10.7
	Std. Dev S_j	---	0.51	1.02	1.56
	Average σ_{S_j}	---	0.46	0.92	1.41
	Std. Dev σ_{S_j}	---	0.05	0.22	.60
	Range of σ_{S_j}	---	.37 - .64	.64 - 1.9	.9 - 4.4
3. Soil	Average S_j	2.80	2.92	3.09	3.36
	Range of S_j	---	1.7 - 3.6	.90 - 4.9	.2 - 8.1
	Std. Dev S_j	---	0.42	0.87	1.46
	Average σ_{S_j}	---	0.43	0.91	1.53
	Std. Dev σ_{S_j}	---	0.05	0.26	0.88
	Range of σ_{S_j}	---	.31 - .59	.52 - 1.9	.68 - 6.4
4. Burning	Average S_j	3.10	3.24	3.13	3.12
	Range of S_j	---	2.4 - 4.0	1.7 - 5.0	.9 - 6.1
	Std. Dev S_j	---	0.41	0.79	1.20
	Average σ_{S_j}	---	0.39	0.81	1.26
	Std. Dev σ_{S_j}	---	0.04	0.15	0.37
	Range of σ_{S_j}	---	.34 - .48	.58 - 1.2	.8 - 2.2
5. Motor Vehicle	Average S_j	0.80	0.80	0.79	0.79
	Range of S_j	---	.64 - 1.0	.50 - 1.3	.38 - 1.5
	Std. Dev S_j	---	0.083	0.17	0.26
	Average σ_{S_j}	---	0.082	0.17	0.26
	Std. Dev σ_{S_j}	---	0.010	0.04	0.11
	Range of σ_{S_j}	---	.064 - .110	.10 - .31	.13 - .64

THE APPLICATION OF SIMCA PATTERN RECOGNITION TO COMPLEX CHEMICAL DATA

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Introduction

A number of analytical techniques are used in air quality monitoring depending on the nature of the agents being monitored. For low molecular volatile organic chemicals such as hydrocarbons, aliphatic halides, etc., the method of choice is gas chromatography/mass spectroscopy (GC/MS). Figure 1 is an illustration of an output from GC/MS analysis of a complex mixture. The output consist of two parts, the gas chromatogram and the mass spectrum. The GC data are 2-dimensional in concentration VS. retention time. The mass spectrum is 3-dimensional with ion intensity as a function of retention time and mass (m/e). The GC data contains information regarding the number of components in the sample and their concentration. The mass spectral data, if in terms of relative ion intensities, contains information which can be used to identify the chemical species present. By applying methods of classification or pattern recognition to such data it is possible to classify and identify the components present. It is this aspect of the data analytic problem that will be discussed in this report.

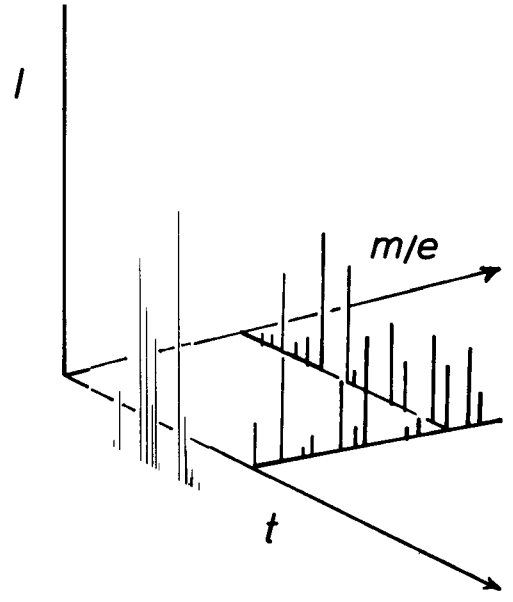

Figure 1. Output from a GC/MS analysis of a complex mixture.

Historical

Before a discussion of the specific methods of data analysis is presented, it is worthwhile to review the levels of information which can be obtained from the application of classification methods to GC/MS data (Albano, et al., 1978). There are two major objectives of such an analysis: 1) classification and 2) quantification. With these two objectives in mind, three levels of information can be obtained from the data analytic method. At the first or lowest level, classification is into one or the other of a group of well defined classes.

At the next level it would be possible, considering the example above, to classify a compound into one or the other of the defined classes, with the possibility that the sample may be neither. At the highest level of classification, it is the objective to quantify the amount of a classified compound. This level includes, in addition to a classification step, a calibration step.

A number of pattern recognition methods are available. These methods have differing potential with regard to the above mentioned levels of classification so at is necessary to know in advance the desired level of classification. The methods commonly used are:

1. the hyperplane or class discrimination methods such as the linear learning machine (LLM) and linear discriminant analysis (LDA),

2. distance based methods such as the k-nearest neighbor (KNN) and

3. the class modeling methods such as SIMCA.

All methods of pattern recognition operate at the first level. However, LLM and LDA operate only at this level. KNN and SIMCA both operate at the second level while SIMCA can operate at level three.

Theory of SIMCA Pattern Recognition

The objective of methods of classification is to identify objects, in this case low molecular weight volatile organics. For the purpose of this report, the identification will be based on information obtained in the mass spectra of the compounds. From information obtained on compounds similar to those whose identity is to be determined, rules are developed which allow the unknowns to be classified. The compounds of known class assignment are the training sets while those compounds of unknown classification are the test set compounds.

In order to apply mathematical methods to the data in the

analysis, the mass spectra for each compound is represented as an object vector as in Figure 2. The elements of the vector are ion intensities at each mass in the interval observed for the classes. The object vectors are tabulated in matrix form in which the elements of the matrix are ion intensities, with $\underline{k}$ the compound index and $\underline{i}$ the mass index.

$$X = (I_0 I_1 I_2 \ldots I_k \ldots I_p)$$

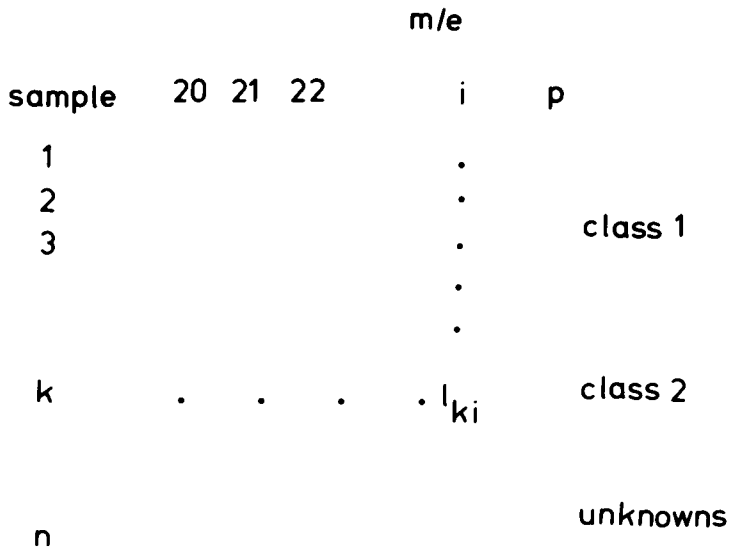

Figure 2. Object vector and matrix employed in SIMCA analysis.

If the compounds in the classes (training sets) are similar, the data for each class can be modeled by a principal components model in few terms (Wold, 1976). This is shown in equation 1

$$I_{ki} = I_i + \sum_{a=0}^{A} t_{ka}\, b_{ai} + e_{ki} \qquad 1)$$

where I is the mean of ion, $\underline{i}$, A is the number of product terms or principal components in the model and e_{ki} is the residual of the observed and predicted ion intensities. The product terms, which model the systematic variation in the data, are composed of the loading term, b_a and the principal component, t_k. For A=0 the class is represented by a point in space (class members are identical); for A=1 the class data structure is approximated by a line and for $A \geq 2$ the class is approximated by a plane or hyperplane.

Classification of the unknowns is based on information in the residuals, e_{ki}, for the test compounds. From the fit of the training set data to their respective class models, a residual

standard deviation (RSD) for each object and for each class can be calculated. From the fit of the unknowns to the class models, a classification result can then be obtained. Since the RSD is approximately F-distributed a confidence interval for the classification result can be established.

A geometric interpretation of the SIMCA classification result is shown in Figure 3. Here the result is shown in 3-dimensions for convenience while in reality the data space is much higher in dimensionality.

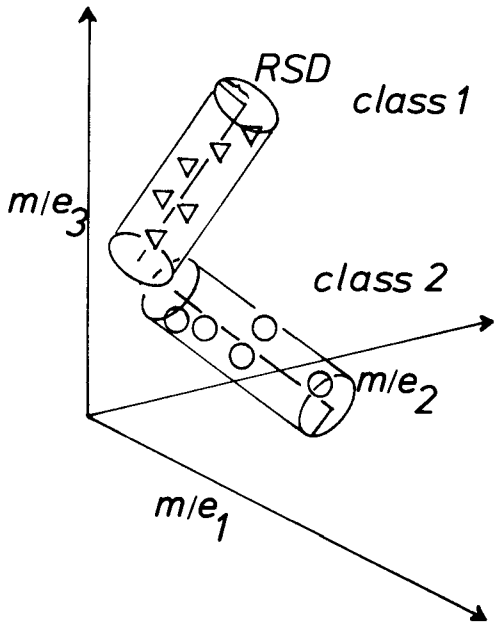

Figure 3. A 3-dimensional representation of a SIMCA classification.

In this example, the classes are represented by a line. The projection of the objects onto the line gives the relative position of each compound in the class structure. This is important if classification is desired at the third level. The RSD about the line defines a volume element in space and classification is based on where the unknown falls with respect to the defined classes.

The class modeling philosophy has a number of advantages when considered in terms of the levels of pattern recognition as discussed earlier. If the possibility exists that a compound is a member of none of the defined classes it will be observed as an outlier to the defined classes. This result is not possible with the methods of LLM or LDA. Another advantage of this approach is that if other information, such as health effects data, are available for the members of the defined classes, correlation methods can be used to relate levels of these effects to chemical structure.

Pretreatment of Data

In order to enhance the various types of information in mass spectral data, the spectral data can be scaled or transformed. This is especially critical with mass spectral data since in normalized form it may not be appropriate for classification purposes. Mass spectra are interpreted by attempting to identify fragmentation patterns within the spectrum of a compound. These patterns result from the loss of a common fragment(s) to give sequences of peaks that are related or correlated. This is illustrated in Figure 4 in which ion of mass i results from the fragmentation of ion $i+j$ by loss of fragment j.

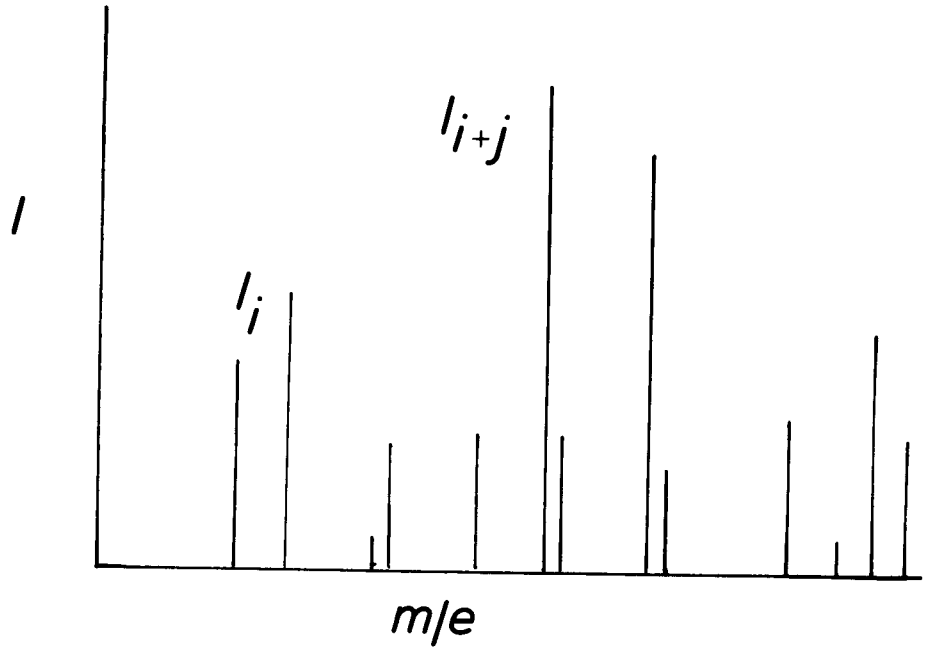

Figure 4. Example of fragmentation patterns within mass spectrum.

The molecular weight of compounds which contain a common functional group will vary depending on the masses of the residual molecular fragments attached to the functional group. The loss of a common fragment j within the series can occur in each spectrum to varying extents, but will be shifted to different masses i. Classification should be based on the relative extent of this fragmentation and this information can be amplified by applying the autocorrelation transform (Wold, et al., 1984) to the normalized mass spectrum. The autocorrelation transform is given in equation 2 (Box, Hunter and Hunter, 1978).

$$r_j = \frac{\sum (I_{i+j} - \bar{I})(I_i - \bar{I})}{\sum (I_j - \bar{I})^2} \qquad 2)$$

I_i and I_{i+j} are the intensities of the respective ions i and i+j and I is the spectral mean. r_j is called the autocorrelation coefficient for lag j. Its range is $-1 \quad r_j \quad 1$ and measures the correlation between ions in the MS which result from loss of the common fragment j.

The MS of 1,2-dichlorobutane and its autocorrelation transform are given in Figure 5. Very pronounced autocorrelations are observed between ions 2, 36 and 38 mass units apart. These result from loss of fragments which contain the isotopes ^{35}Cl and ^{37}Cl and from the loss of HCl containing these isotopes.

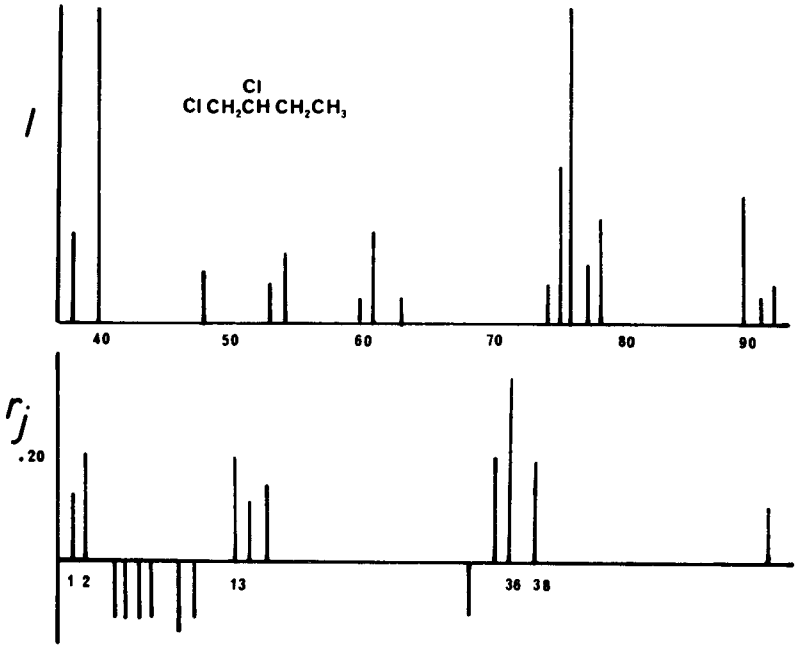

Figure 5. MS of 1,2-dichlorobutane (top) and its autocorrelation transform (bottom).

Application of SIMCA to MS Data

In order to illustrate the utility of SIMCA to classification of volatile organic compounds, the MS of 9 dichlorobutanes and 8 chloromethyl butenes were obtained from the Finnigan catalogue of mass spectra. These two classes of halogenated compounds were used as training sets. The data matrix consisted of relative ion intensities in the interval 39 to 118 m/e with each spectrum consisting of the 16 most intense ions.

Each spectrum was transformed to the autocorrelation spectrum and SIMCA was applied to both types of data for the purpose of comparison. The data for each class were modeled by a 2-component (A=2 in equation 1) model. This is equivalent to fitting the data to a plane. This is somewhat arbitrary but is done in this case as to give the analyst a view of the structure of the classes. By generating principal components plots of the data, the approximate structure of the data can be observed.

Figure 6 is such a plot of the classes when the MS data are modeled. When compared to the results of applying SIMCA to the autocorrelation transformed spectra (Figure 7) it appears that the two classes overlap with very little structure in the dichlorobutanes from either treatment. A more revealing method of displaying the results is the Cooman's plot (Wold, et al., 1984). This plot is obtained by fitting all of the compounds to the class 1 and class 2 models, respectively, and calculating the distance of each compound to each class model. When these class distances are plotted from the analysis of the MS data (Figure 8) and the autocorrelation transformed data (Figure 9) it is seen that the latter result in a much better description of the chloromethyl butenes while the dichlorobutanes are not well described by either method. It is possible, then, to classify the class 2 compounds with a high level of certainty and that the classification results from the autocorrelation data are much better.

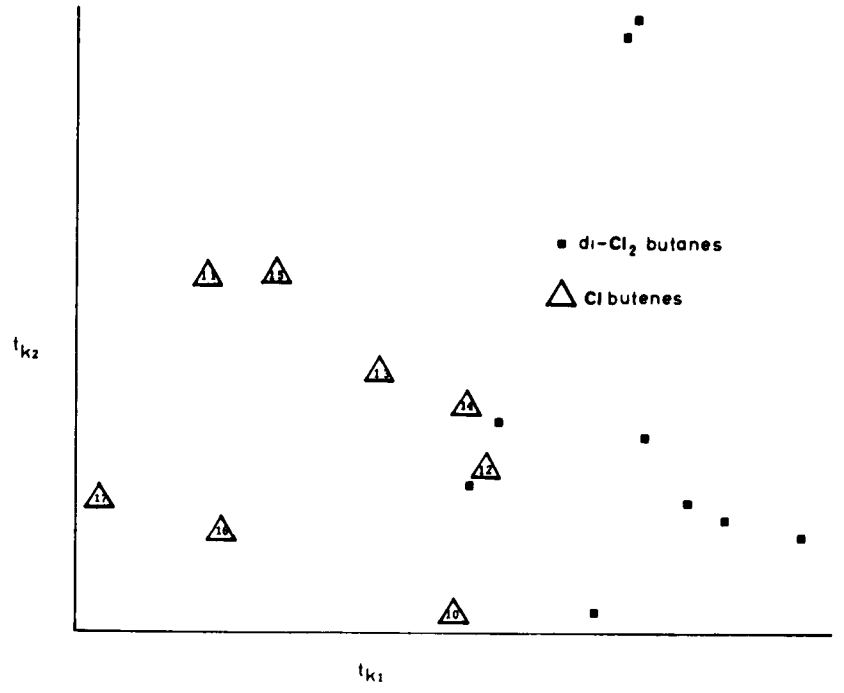

Figure 6. Principal components plot of the classes when the MS data are modeled.

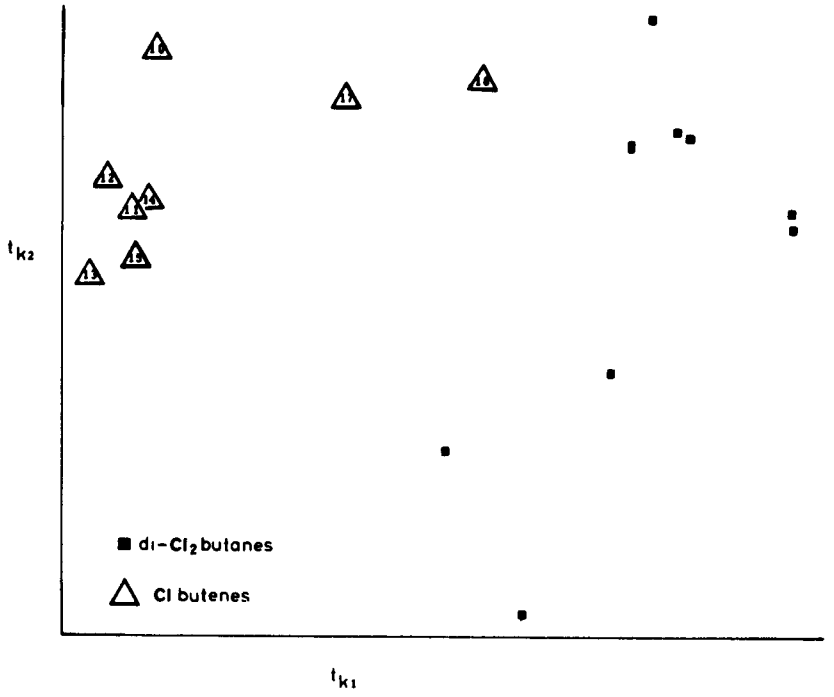

Figure 7. Principal components plot of autocorrelation transformed MS data.

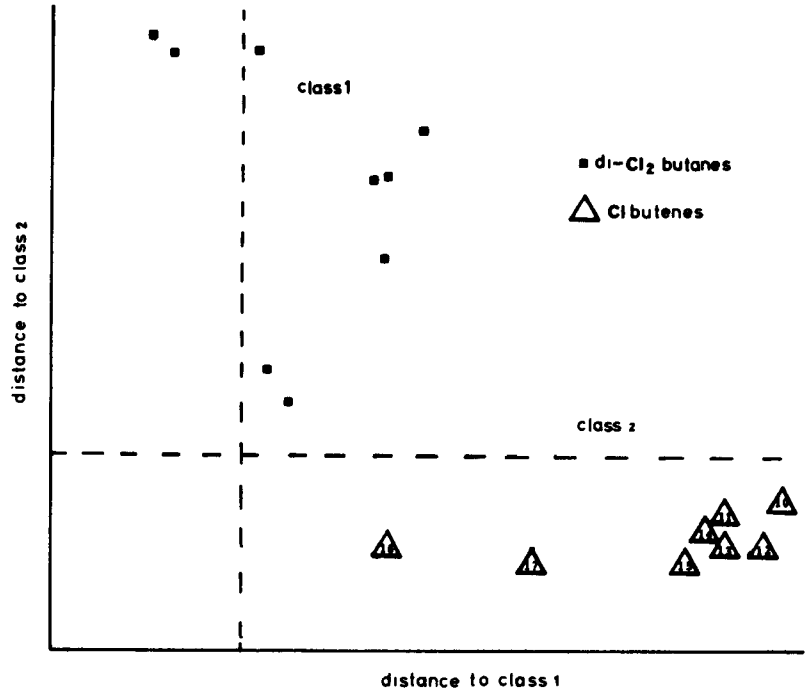

Figure 8. Cooman's plot of the SIMCA analyzed MS data.

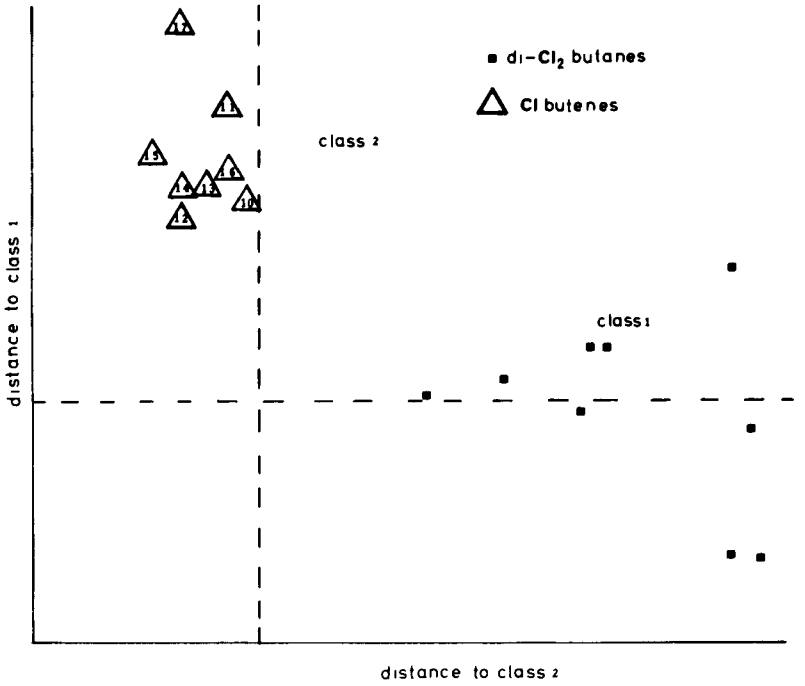

Figure 9. Cooman's plot of the SIMCA analyzed autocorrelation transformed MS data.

Acknowledgements.

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DESCRIPTION OF A CONTINUOUS SULFURIC ACID/SULFATE MONITOR

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ABSTRACT

A flame photometric/thermal speciation system for continuous measurement of ambient total sulfate, sulfuric acid, and two other sulfate fractions is described. The instrumentation is suitable for long-term ground-based installations, and has a limit of detection for sulfate as sulfuric acid of 2 $\mu g/m^3$ for an integrated sample period of one hour.

An example of episodic ambient data from the system is presented. These data are compared to water soluble sulfate data from a co-located dichotomous sampler, and particle scattering extinction coefficient (b_{sp}) data from an integrating nepholometer.

Limitations of the thermal speciation technique with regard to the measurement of total strong acidity of sulfates are discussed.

Presented at the Fourth Annual National Symposium on Recent Advances in Pollutant Monitoring of Ambient Air and Stationary Sources in Raleigh, North Carolina, May 1984.

I. Introduction

Acid Aerosols

There is growing evidence that atmospheric aerosols in the lower troposphere at times can be acidic. Unfortunately, the measurements have been neither extensive nor systematic. The temporal variation and the geographic extent of acid aerosol events have not been documented. While nitrous, hydrochloric, or organic gases can lead to acidified particles by absorption or condensation, sulfur gases are believed to be the dominant source of acid species in the atmosphere.

Health Evidence

Some studies of human populations have linked sulfur dioxide and ambient particulate sulfates to increased respiratory diseases, but have been unable to identify the specific pollutants responsible. It remains to be established which species of sulfates are physiochemically important, since they can occur within a variety of metal cations as well as with the more common ammonium and hydrogen ions. As has been illustrated in a recent review of the toxic effects on pulmonary macrophages, these sulfate species have widely varying effects. Of the variety of sulfate species that exist in the atmosphere, the strong acid sulfates (ammonium bisulfate and hydrogen sulfide) residing in the submicron size range are more likely to induce responses in the human respiratory tract. Evidence exists for alterations in epithelial secretory cells in the lower bronchial airways in rabbits exposed to 250 $\mu g/m^3$ sulfuric acid after relatively short duration exposures (8h/d, 5d/w, 1m). In his work, Lippman points out that these studies provide further support for the role of acid sulfate species in the pathogenesis of chronic bronchitis via effects on the mucociliary clearance system.

As a component of Harvard's Air Pollution Health Study, we have developed an operational monitoring system for real-time sulfate/sulfuric acid aerosol measurements. This system will be deployed in each of the six cities participating in the Harvard Air Pollution Health Study in order to more fully characterize the nature of sulfate particulate exposure. Peak, hourly, and daily concentrations of sulfate particle and sulfuric acid fractions will be incorporated into our aerometric database for the analysis of daily pulmonary function data, or to more fully understand the similarities or differences among our cities.

As we assemble additional units, we will characterize the nature of atmospheric aerosol acidity throughout the year in each city. A plan being considered involves the use of the continuous sulfate monitor to trigger a dichotomous particle sampler during 'episodic' conditions. The particulate filter samples would be used to characterize the elemental composition (by XRF) or ion composition of aerosols, including total strong acid (H^+).

Instrument Description

Based on work done by Dr. Roger Tanner at Brookhaven National Laboratories and earlier cooperative work with Dr. Rudy Husar and Geoff Cobourn at Washington University, we at HSPH have developed a low temperature volatilization flame photometric detection (FPD) method for continuous measurement of ambient sulfate aerosol suitable for long-term ground based field operations. This method allows for some discrimination of the acidic component of the aerosol due to the higher rate of volatilization of the H_2SO_4 species at lower temperature, as well as those sulfates that are stable at 300 ° C (Sulfates of calcium, sodium, lead, zinc, iron, and copper).

The FPD method has been used routinely to measure total gaseous sulfur in ambient air by excluding particles with a membrane filter. The sulfur is detected in a hydrogen flame which results in an optical emission (fluorescence) from the electronically excited sulfur dimer (S_2*). To determine particulate sulfur, a lead oxide (PbO) coated tube is used as a diffusion denuder to remove gaseous sulfur species. Under appropriate conditions of laminar flow, the particles, with much higher momentum, pass through the denuder tube, while the sulfur-containing gas

molecules collide and react with the walls and remain deposited on them. SF_6 doped hydrogen is used to improve the FPD's sensitivity and stability and reduce interferences.

II. Thermal Analysis

Thermal analysis allows discrimination between the different sulfate species. With this technique, the ambient air is heated initially to about $\sim$120 ° C. At this point most of the H_2SO_4 (sulfuric acid) is vaporized. The vaporized material is subsequently scrubbed by the denuder. Consequently, if a decrease is observed in the FPD signal when the temperature is elevated to 120 ° C, the size of this decrease may be correlated with the amount of H_2SO_4 in the ambient air sample. The next step is to heat the sample air to about 300 ° C. At this point the NH_4HSO_4 (ammonium bisulfate) and $(NH_4)_2SO_4$ (ammonium sulfate) in the particles is completely vaporized. Again, the amount of the sum of these two species can be correlated with the change in the FPD signal. Any non-volatile sulfur particulate [i.e., Na_2SO_4 (sodium sulfate) from marine air masses] which is present will give a residual FPD signal. Interference by any potential non-denuded gaseous sulfur species and changes in the FPD's zero will be accounted for by determining the analyzer's baseline signal with particle-free air.

The cycle of measurements (12 min./cycle) is controlled by a timer that is synchronized with the data acquisition system, and includes: 1) ambient temperature; 2) 120 ° C; 3) 300 ° C; 4) Instrument Baseline. See Section V for a detailed example of the thermal analysis technique.

The temperature for the second part of the cycle ($\sim$120 ° C) is chosen to maximize the fraction of H_2SO_4 that is volatilized without any significant loss of $(NH_4)_2SO_4$. With the apparatus we are currently using, about 5% of the H_2SO_4 remains unvolatilized at the temperature that $\sim$1% of the $(NH_4)_2SO_4$ is lost. The Limits of Detection for the system using SF_6 doped hydrogen are presented in Table I. The system's flow diagram can be found in Figure 1.

III. Limitations

It is important to note that this method generally underestimates the total amount of strong acidity of ambient sulfate containing particles because both ammonium bisulfate (NH_4HSO_4) and ammonium sulfate [$(NH_4)_2SO_4$] vaporize at about the same temperature. The NH_4HSO_4 is almost as strong an acid as H_2SO_4, whereas $(NH_4)_2SO_4$ is a relatively weak acid.

If and when there are occasions in which there are aerosol particles that are only pure H_2SO_4, and others that are only pure $(NH_4)_2SO_4$, the TA-FPD method will give a good quantitative determination of total strong acidity. In general, however, we expect that whenever *any* H_2SO_4 is present in ambient air, there is also some NH_4HSO_4 present. Under these conditions the TA-FPD method will underestimate the amount of total strong acidity. The overall situation is even more complicated since: 1) individual aerosol particles generally have a mixture which includes sulfate, ammonium, and hydrogen ions; and 2) different aerosol particles within the same sample of ambient air may have varying amounts of each of these three ions.

IV. Calibration

The FPD method requires a calibration to determine the relation between the aerosol sulfate concentration and the size of the emission signal as measured by the flame photometer. Dynamically generated SO_2/air mixtures between 2 and 15 ppb are used as the principle means of calibrating the flame photometer. A portable aerosol generator is used in situ to determine the system's response to H_2SO_4 and $(NH_4)_2SO_4$ at different temperatures. A diagram of the aerosol generator can be found in Figure 2. In addition, we have semi-continuous calibration by measuring the water soluble sulfate of simultaneous samples (4 to 24-hour collection period) from membrane filters. This method will compare the time-integrated FPD signal for total sulfate with chemically determined water-soluble sulfate data. Figures 3 and 4 show the relationship between

the FPD sulfate and a dichotomous sampler and integrating nephelometer.

V. Explanation of Continuous Sulfate Data Reduction

Figure 5 is an example of the system's output during an episode in St. Louis, Missouri on December 20, 1983, showing both the Meloy analyzer's output and the temperature of the sample heater tube. Four values are taken from the particulate sulfate analyzer every 12 minute measurement cycle. Point #1 represents the analyzer's output when the sample air has not been heated. Point #2 is the output then the sample air is heated to ~120 °C to volatilize most of the H_2SO_4. Point #3 is the output when the sample air is heated to 300 °C to volatilize H_2SO_4, ammonium sulfate and ammonium bisulfate. Point #4 is the output when the sample air has been filtered to remove all particles (instrument baseline).

The first step in reducing the data is to calculate sulfate concentrations for the first three points, using Point #4 as the baseline. In this example, data are reduced as follows:

$$\mu g/m^3 SO_4^{-2} = \frac{3.93\ \mu g/m^3\ SO_4^{-2}}{ppb\ \ SO_2} \times 3.06\ (\text{net chart div} \times \frac{.05V}{\text{chart div}})^{0.929}\ ppb\ \ SO_2$$

The scaling factor of 3.06 and the exponent of 0.929 are derived from the most recent calibration of the analyzer's net voltage output against multiple SO_2 concentration inputs. The first point is total sulfate in $\mu g/m^3$. The third point is sulfate that does not volatilize at 300 °C (sodium sulfate, etc.) in $\mu g/m^3$. To calculate sulfate as sulfuric acid, subtract the sulfate reading for Point #2 from Point #1 and multiply that result by 1.08 (a factor that corrects for the fraction of sulfuric acid that is not volatilized at the mid-point temperature, determined by in-situ testing for this specific unit). To calculate sulfate as ammonium sulfate plus ammonium bisulfate (this system cannot distinguish between these two species of sulfate), subtract the non-volatile sulfate and sulfate as sulfuric acid from the total sulfate.

For this example,

Point #1 = 52.0 $\mu g/m^3$ Total Sulfate
Point #3 = 2.7 $\mu g/m^3$ Non-Volatile Sulfate
Point #2 = 14.2 $\mu g/m^3$ Sulfate, so:
Sulfate as sulfuric acid = (52.0 - 14.2) x 1.08 = 40.8 $\mu g/m^3$
Sulfate as ammonium sulfate
plus ammonium bisulfate = 52.0 - 40.8 - 2.7 = 8.5 $\mu g/m^3$

The signals from the sulfate analyzer are sampled by a data logger and stored on a cassette tape. The tape and strip charts are changed after 7 days and returned to HSPH for validation, processing, and Quality Assurance checks. Figure 6 is a plot of sulfate and particle scattering extinction coefficient data from St. Louis for December 16 to December 23, 1983.

Acknowledgments

The cooperation and help of Dr. Roger Tanner (Brookhaven National Laboratories) continues to be invaluable. We are also indebted to Andrew English for our original prototype development, which he began at HSPH in 1981; to Anthony Majahad, Stephen Bertolino, and Craig Norberg of the HSPH staff for assistance in construction, development, and operation of this system; to Steve Fick and John Chao for data processing efforts; and to Allison Maskell for typing and editorial assistance. This work is funded by grants from the National Institute of Environmental Health Sciences (ESP-1108), and the Electric Power Research Institute (RP-1001).

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TABLE I

HSPH Continuous Sulfate TA FPD System
Limits of Detection
with SF_6 Doped Hydrogen

	L.O.D. in $\mu g/m^3$ Average Period		
SULFATE	1 Hour	4 Hours	24 Hours
TOTAL	1	0.5	0.5
As Sulfuric Acid	2	1	0.5
As Ammonium Sulfate Plus Bi-Sulfate	3	1.5	0.7
That Does Not Volatilize at 300^0 C	1	0.5	0.5

NOTES:

1) L.O.D. is defined as twice the short term peak to peak noise of the system.

2) A concentration of five times the L.O.D. is necessary to insure data precision of 10%.

FLOW DIAGRAM FOR HSPH CONTINUOUS SULFATE SYSTEM

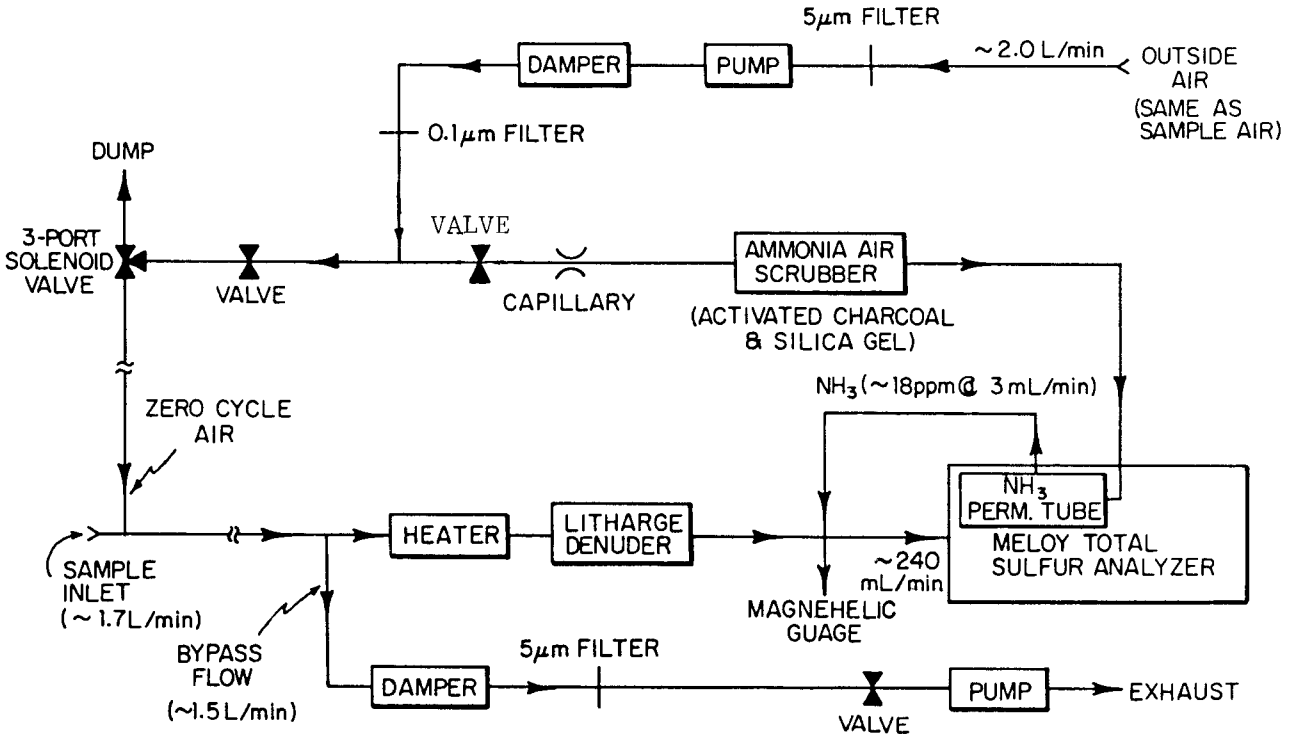


FIGURE 1

HSPH AEROSOL GENERATOR

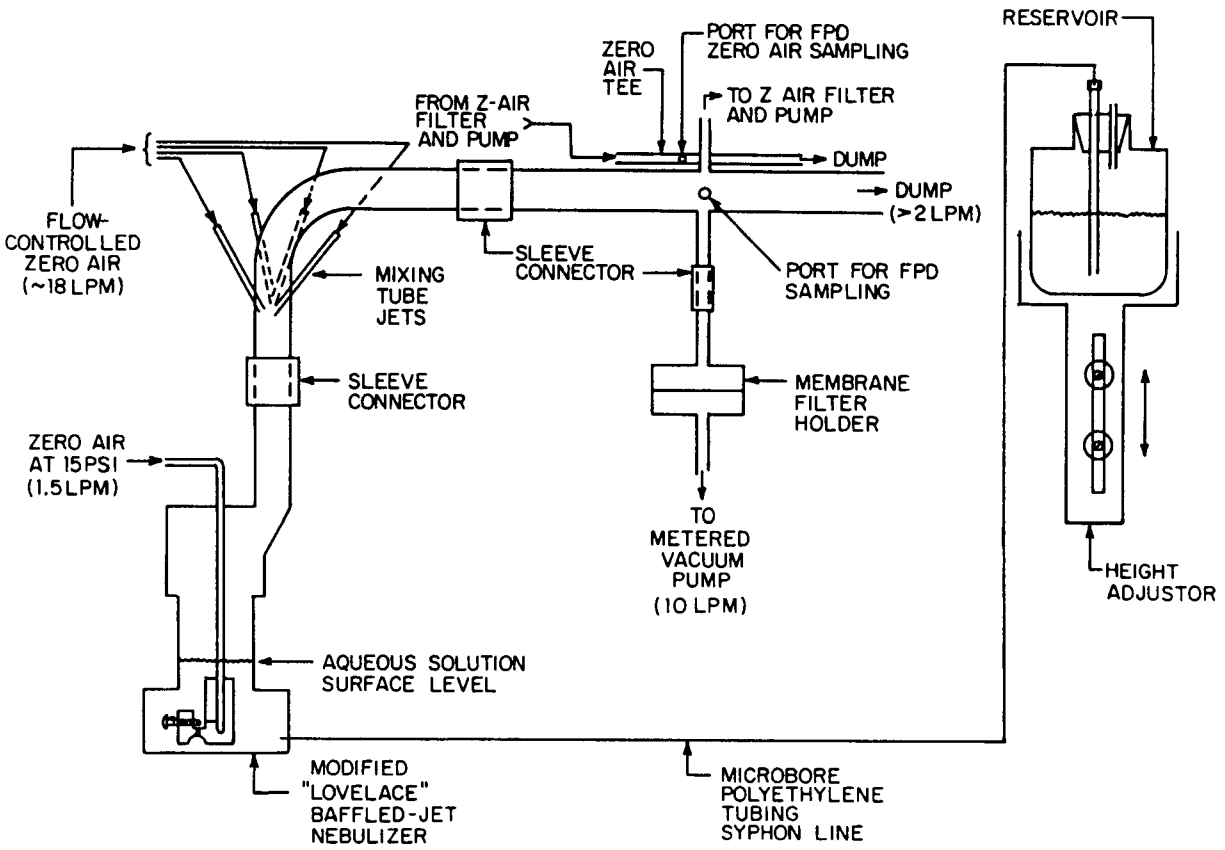


FIGURE 2

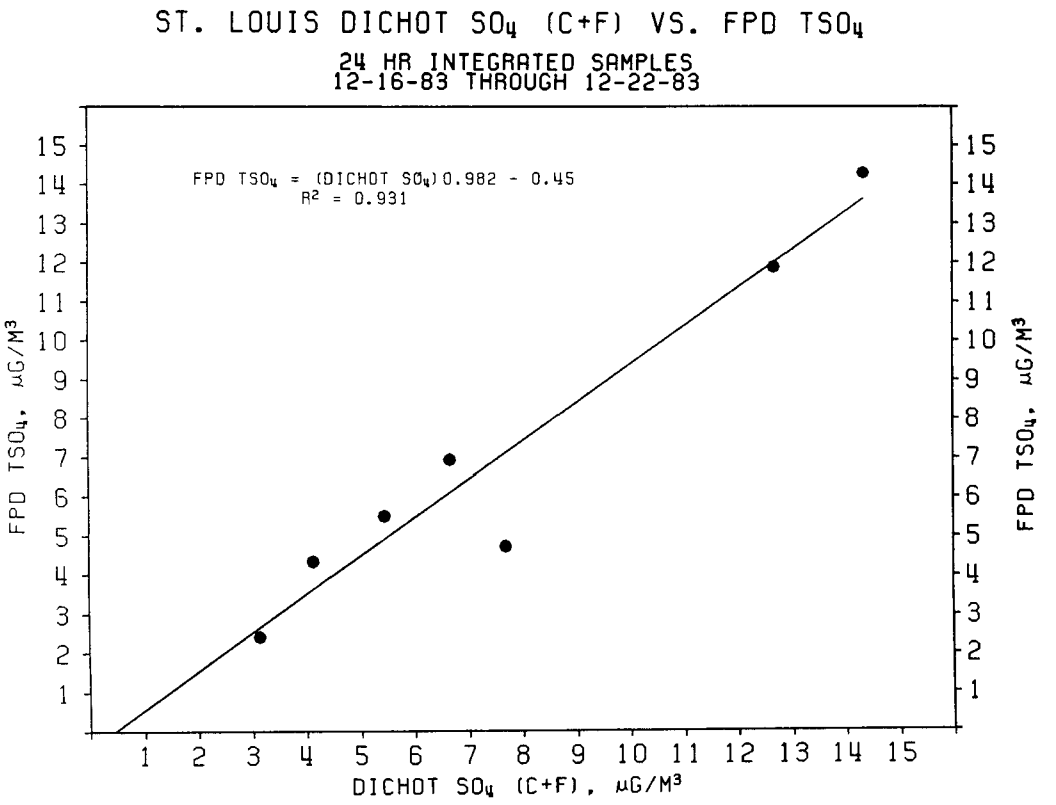


FIGURE 3

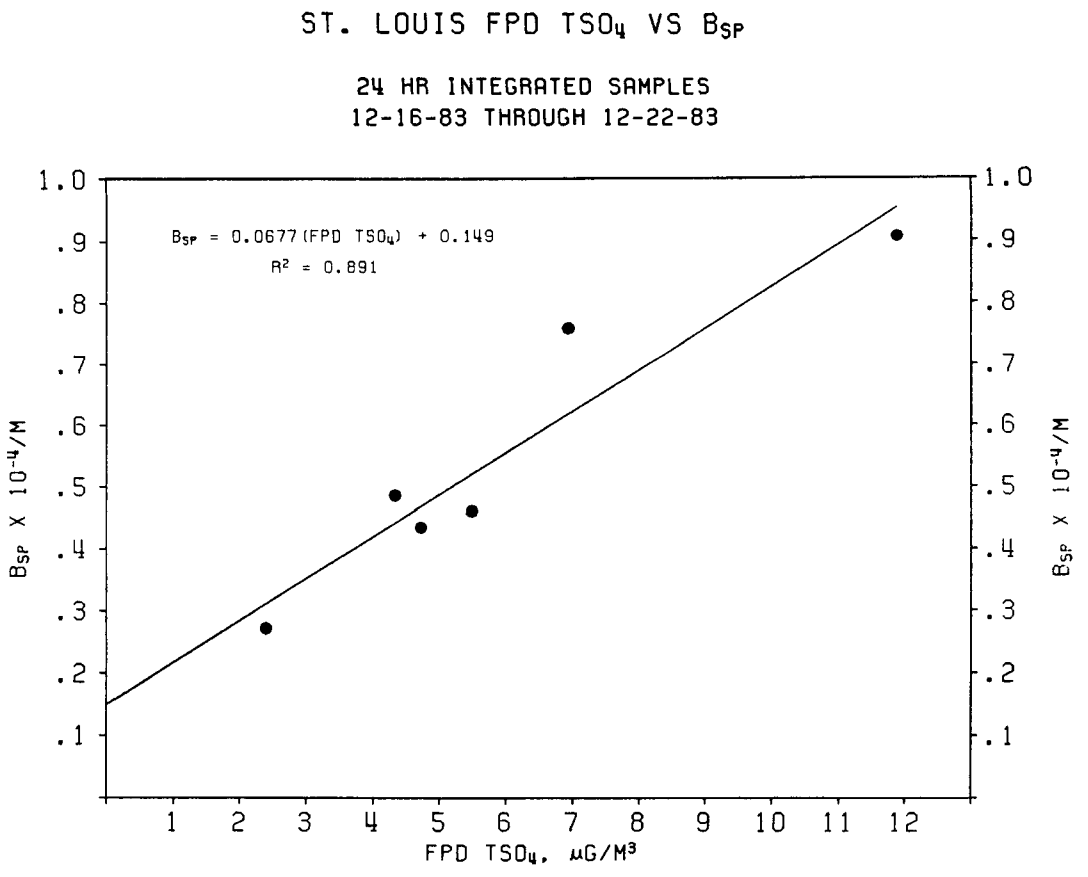


FIGURE 4

EXAMPLE OF SULFATE DATA REDUCTION

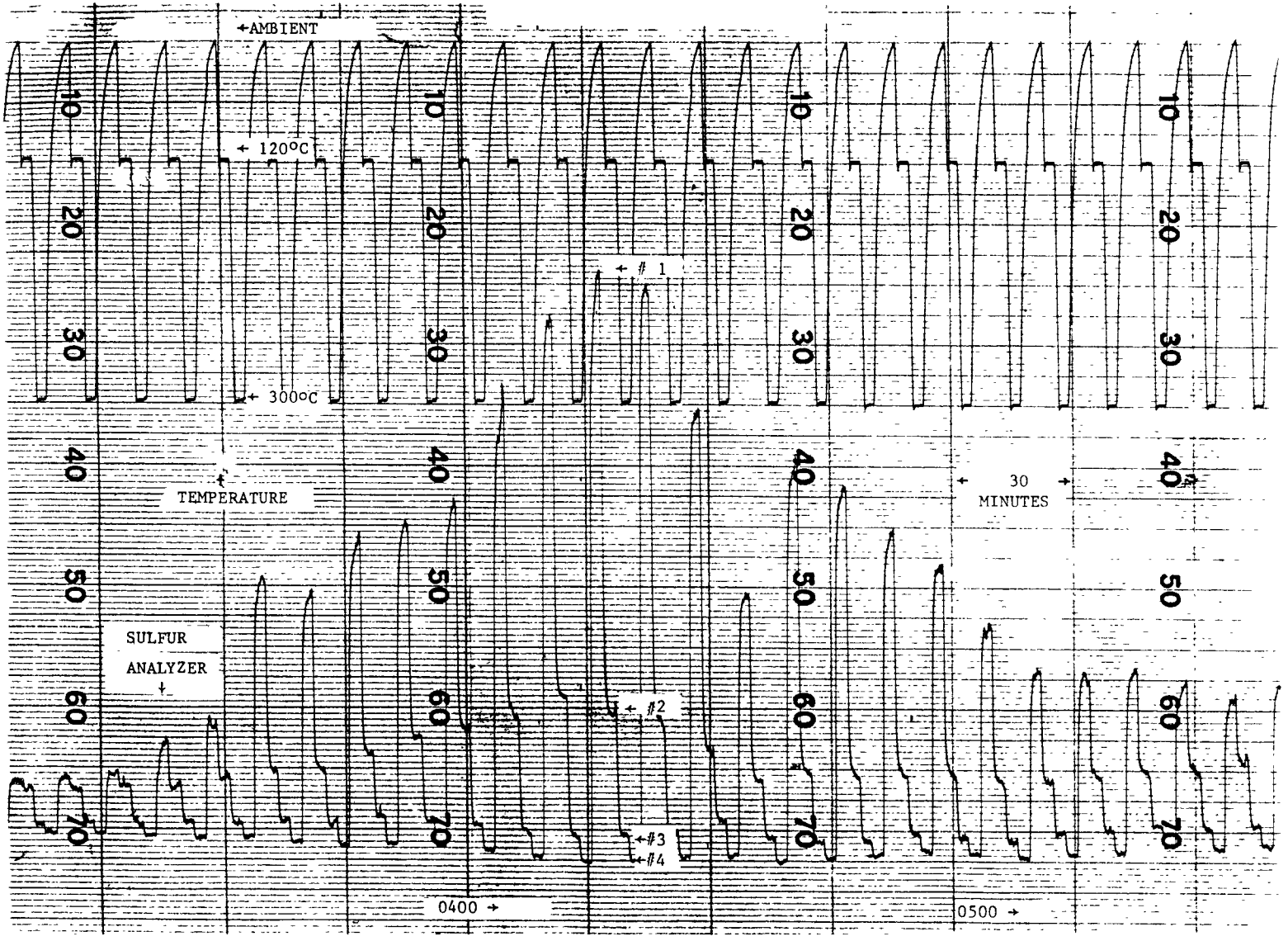
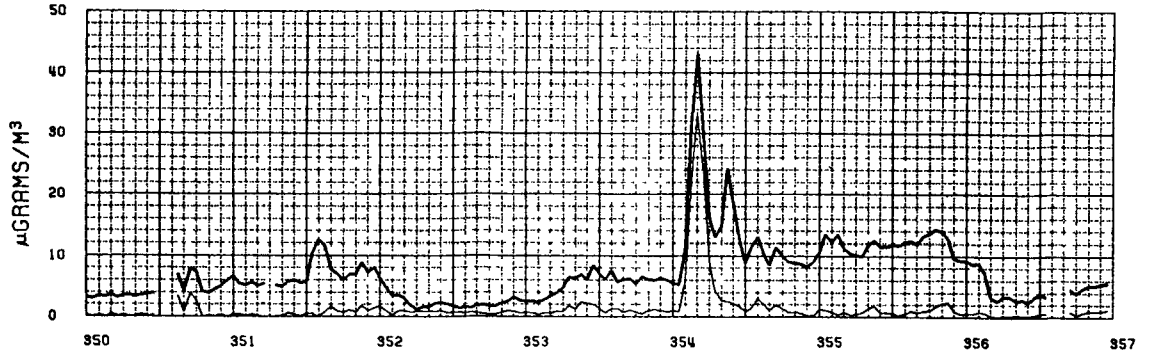


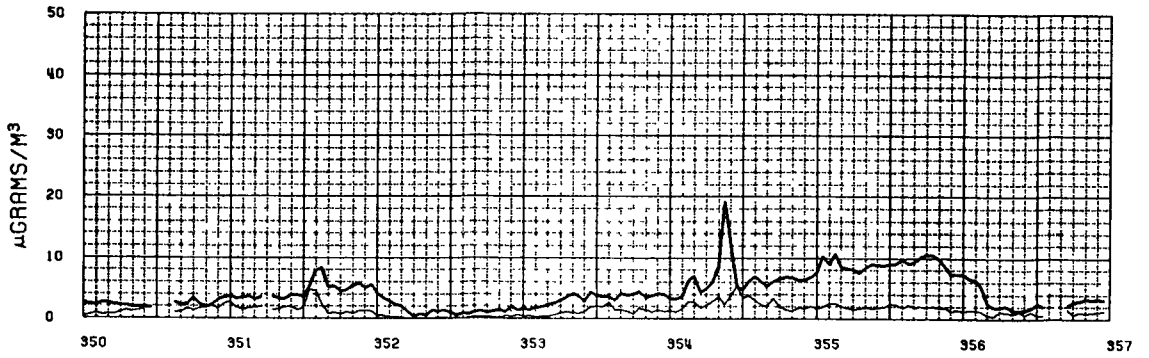
FIGURE 5

ST. LOUIS (ONE-HOUR AVERAGE VALUES)

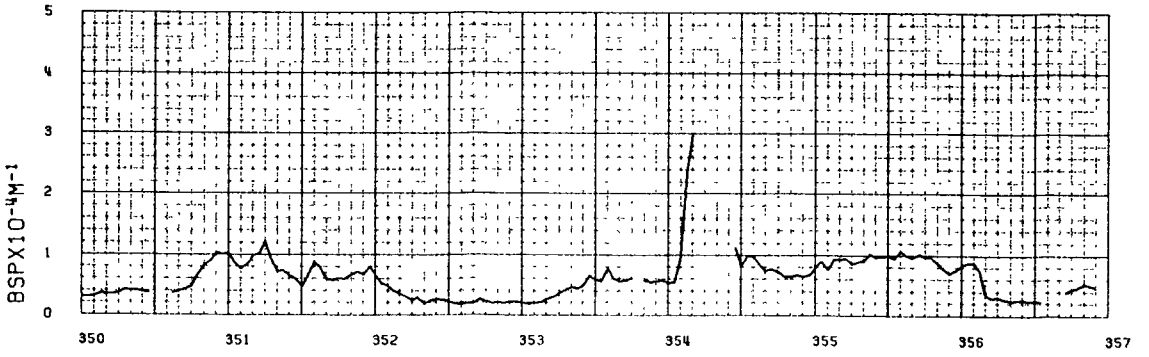
DATA ARE REPORTED AT BEGINNING OF AVG. PERIOD
FROM 350:00:00 (12/16/83) TO 357:00:00 (12/23/83)



TOTAL SULFATE, SULFATE AS SULFURIC ACID



SULFATE AS AMMONIUM SULFATE+BISULFATE SULFATES THAT DO NOT VOLATILIZE AT 300 DEG C



PARTICLE SCATTERING EXTINCTION COEFFICIENT

FIGURE 6

AUTOMATED SAMPLING AND ANALYSIS OF FLUE GASES FROM PLASMA PYROLIZER

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1.0 INTRODUCTION

A Canadian company, Plasma Research, Inc., of Kingston, Ontario, is currently constructing a plasma torch incinerator for the purpose of disposing of toxic waste chemicals on a commercial scale. Hazardous materials, such as PCBs, when subject to the intense, electrically-produced plasma of the facility, are expected to undergo a thorough chemical degradation to form innocuous products such as CO_2 and water, or other products which can be readily neutralized and released safely into the environment.

The breakdown process occurring in the plasma is highly complex and not completely understood. It is possible that highly reactive molecular fragments (free radicals, atoms, ions) produced in the plasma might recombine in a cooler region of the torch to form environmentally undesirable products. At the same time, many of the hazardous chemicals to be destroyed are very stable. For these reasons, it is essential that the gaseous products vented to the atmosphere from the exhaust stack of the facility be closely monitored to ensure proper operation of the incinerator.

The Unsteady Aerodynamics Laboratory (UAL), following a request from the company, has undertaken to assist in the development of a trace gas analysis system suitable for monitoring the concentration levels in the flue stack of the plasma torch. In this paper a design of the monitoring system is outlined, and some preliminary work is described on the collection and analysis of PCBs, 2,3,7,8-tetrachlorodibenzodioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF).

2.0 DESIGN CONSIDERATIONS

2.1 Requirements

Among the prerequisites for a suitable analyzer in the plasma torch scenario are the following:

(1) high sensitivity, to allow the detection of ppt-concentration levels;

(2) qualitative reliability, or specificity, to ensure unambiguous identification of the target compounds;

(3) quantitative accuracy, to meet environmental control standards;
(4) versatility, to cover a broad range of vapours and gases;
(5) computer-based, for unattended analysis as well as for possible feedback control of incinerator operation;
(6) economical, in terms of capital outlay and operating cost.

2.2 Gas Chromatography/ECD/TFD/FID

The detection levels mentioned in (1) dictate the use of a preconcentration technique. Preconcentration of a large air sample results unavoidably in the collection of many vapours and gases in addition to those of interest and, therefore, suggests the use of a separation technique, e.g. gas chromatography (GC), to permit sensing of the target chemicals. The GC sensor could take the form of a class-specific detector, such as the electron-capture (ECD), thermionic flame (TFD), or flame ionization (FID) detector. However, although highly responsive to certain types of compunds, these detectors may lack the specificity and versatility to meet the requirements of (2) and (4).

2.3 Gas Chromatography/MS

A more universal and positive detection technique can be achieved by the use of a mass spectrometer (MS) as the GC sensor. Compact, simplified MS systems have recently become available for use in capillary GC. As analytical instrumentation this equipment has similar specifications to those of more sophisticated mass spectrometers while being lower priced and is *a priori* the preferred choice of GC detector over the ECD, TFD and FID with respect to fulfilling the above prerequisites, especially items (2) and (4).

2.4 Preconcentration

The method of trace vapour preconcentration developed previously at UAL is considered to be adaptable to the present case. In that approach, air to be tested is drawn through an adsorbent-packed tube which collects or preconcentrates the vapours of interest; after sampling, the vapours trapped in the tube are thermally desorbed and transferred by a carrier stream to a second, smaller adsorber tube from which they are subsequently desorbed and injected into the GC column.

The two-stage adsorber concept has been used with success to quantify ppt

levels of airborne vapours, including organophosphorus and carbamate insecticides, chlorophenoxy and chlorobenzoic acid herbicides, as well as organonitrate explosives (1-5). It has recently been extended for use with capillary-column GC, and tested in headspace sampling of high-molecular weight hydrocarbons and fenitrothion (6).

As currently implemented, the technique was designed to permit the (detachable) first-stage adsorber to be used for sampling at remote locations, then returned and manually reinstalled in the analyzer unit. To render the technique suitable for automated sampling and analysis, as required for the type of fixed-installation monitoring of the plasma incinerator products, some modification in instrumentation is required.

3.0 EXPERIMENTAL

3.1 Capillary-column GC Analysis

Two GC instruments have been utilized, a Varian 4600/Vista 401 and an HP 5790A, each fitted for capillary column operation.

The varian GC was equipped with an adsorber tube injector port, illustrated in Fig. 1, as well as a regular septum inlet. The column used in this instrument was 30 m x 032 mm I.D. SPB-5 fused silica. The column oven was temperature programmed as follows: initial temperature 80°, hold 10 min; 80° to 150° at 20°/min; 150° to 260° at 4°/min, hold 2 min. Helium carrier gas flow velocity was 39 cm/sec. Under these conditions good separation of the individual PCBs in Aroclors 1242, 1254 and 1260 and of 2,3,7,8-TCDD and 2,3,7,8-TCDF was achieved in approximately 30 min. Both FID and ECD were used in the PCB analysis. The sensitivity of the FID allowed the analysis of microgram quantities of the Aroclors, while with the ECD sub-nanogram samples were analyzed.

The HP 5790A GC was fitted with a 12.5 m x 0.2 mm cross-linked dimethyl silicone WCOT fused silica column. The column oven was operated with the same temperature programme as the Varian GC. Helium carrier gas velocity was 20 cm/sec. Under these conditions chromatograms were similar to those obtained with the Varian GC. Splitless injection mode was used to inject samples. The GC was coupled with an HP 5970A Mass Selective Detector. The detector was operated in the Peakfinder programme to identify the peaks and in the Selective Ion Monitor programme to determine trace quantities of analytes.

The GCs were calibrated by means of standard solutions of the Aroclors in

iso-octane having concentrations ranging from 10^{-8} to 10^{-10} g/μL. The concentration of TCDD and TCDF standard solutions was 10^{-9} g/μL. Calibrations were made both through direct liquid injection and, in the case of the Varian instrument, through deposition of the solution in the adsorber tube followed by the appropriate desorption/injection procedure.

3.2 Adsorber Tube Sampling

Pyrex adsorber tubes were 7.5 cm x 6.3 mm O.D. containing a 1 cm column of Tenax GC 45/60 mesh adsorbent. Tenax has been reported to be superior to polyurethane foam, XAD-2 resin and Florisil as a sorbent for collecting PCBs in air sampling (7). The thermal stability, hydrophobic properties and high retention capacity of Tenax make it suitable for trapping PCBs and dioxins from large sample volumes of moisture-laden air, and subsequent recovery of the target vapours through thermal desorption.

The breakthrough volume of the sorbent plug was estimated by placing a backup adsorber in series with the first and sampling a spiked air stream; the presence of PCB vapours in the backup adsorber for a measured volume of air sample signifies breakthrough from the first tube.

3.3 PCB Vapour Source

A continuous stream of PCB vapours in air was generated by passage of a low flow of N_2 through a U-tube containing glass beads wet with Aroclors 1254 and 1260. This vapour stream was mixed with a larger flow of air (8) to achieve a controlled dilution ratio of the equilibrium vapour pressure of the PCBs in the test stream. With the U-tube thermostated at 0°C and a dilution ratio of 1/500, PCB concentrations of the order of 100 ng/m^3 were obtained.

In sampling the test stream, adsorbers were maintained at room temperature, or heated to 80°C to simulate the plasma stack temperatures. At room temperature (22°C) it is estimated that less than 5% of the total Arochlors in 30 L of air sampled at 0.5 L/min. escaped the first adsorber; when kept at 80°C, the first adsorber trapped over 90% of the PCBs from a 20 L volume. Chromatograms from some of these tests are shown in Fig. 2, obtained with the Varian GC/ECD.

In Fig. 2 differences between the vapour and liquid signatures are evident, and attest to the fact that the partial pressure of a particular component in the vapour phase may far exceed the mole fraction in solution.

Using the ECD, the smallest mass of Aroclor mixture that can be measured with S/N $\geq$ 5 is about 0.5 ng. With the MSD operated in the Selected Ion Monitoring (SIM) mode and the electron multiplier voltage set at 1600V, the smallest quantity of Aroclor that can be measured is about 1 ng. Assuming a breakthrough volume in sampling of not less than 20 L, the minimum detectable concentration of PCBs measurable with the adsorber tubes is about 25-50 ng/m^3. By way of comparison, in a recent survey the atmospheric PCB background level in the province of Ontario was found to range from 0.01 to 1.4 ng/m^3, averaging about 0.20 ng/m^3.

The sampling system proposed in monitoring the plasma flue gases is based on a first-stage adsorbent bed of comparable dimensions to that tested above.

4.0 SAMPLER CONFIGURATION

A module has been designed and fabricated which interfaces with the Hewlett Packard 5790A/5970A MSD system, and is presently being tested.

The module is essentially an auxiliary oven supporting the first and second-stage adsorbers, and housing two six-port switching valves and associated plumbing. Connection from the second adsorber to the GC is made through heated capillary tubing. The air sampling line is a length of heated stainless steel tubing, 6.3 mm O.D., which is provided with an injection port for calibration/test purposes, and with a (replaceable) filter to remove particulates from the air sample. Care has been taken to avoid cold spots in all vapour transfer lines. A schematic view of the sampler configuration is given in Fig. 3.

The twin-valve design shown is sufficiently flexible to allow for purging of Ads 1 before transfer of the PCB vapours to Ads 2, by operating the valves independently. Valve actuators, adsorber heaters and the air pump are microprocessor-controlled.

5.0 CONCLUDING REMARKS

From the initial study carried out to date it is felt that a viable monitoring system based on the sampler configuration and GC/MS approach outlined in this report is feasible.

In principle, the proposed system is useful for any vapour or gas that is amenable to GC analysis. The preconcentrator component of the system, involving the two-adsorber concept, is of proven efficacy in trace vapour detection, and

can, moreover, be tailored to the gases of interest through selection of suitable adsorbent packings. At the same time, the MS detector provides complete versatility of detection.

6.0 ACKNOWLEDGEMENT

The authors thank Dr. André Lawrence of this laboratory for his valuable assistance in the initial stage of the work.

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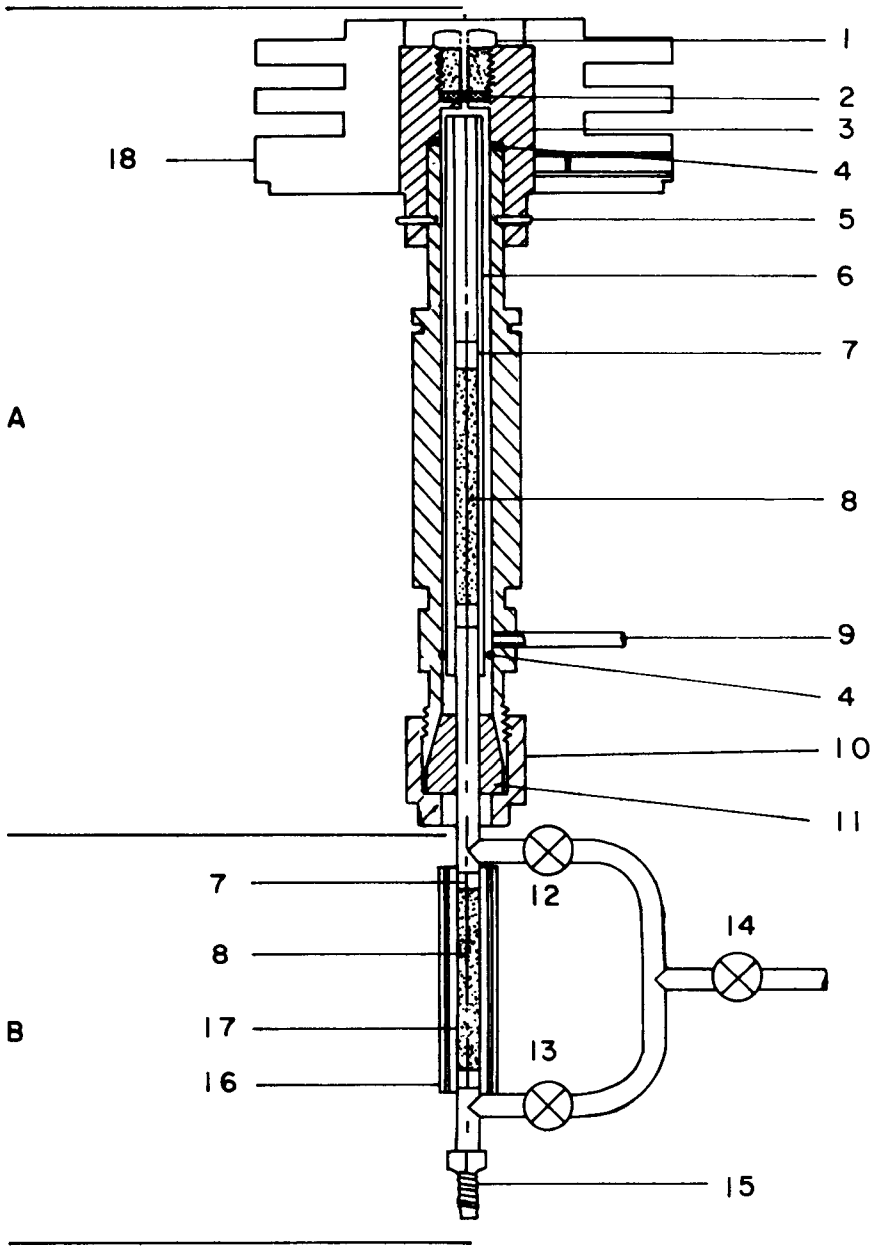

1 – SEPTUM RETAINING NUT
2 – SEPTUM
3 – INJECTOR CAP
4 – SILICONE RUBBER O-RING
5 – BAYONET COUPLING
6 – FIRST ADSORBER GLASS TUBE
7 – GLASS WOOL PLUG
8 – SOLID SORBENT
9 – CARRIER GAS (He) INLET
10 – 1/4 INCH SWAGELOK NUT
11 – GRAPHITE FILLED VESPEL REDUCING FERRULE (1/4 TO 1/8 INCH)
12 – SOLENOID VALVE
13 – SOLENOID VALVE
14 – SPLIT VALVE
15 – 1/16 SWAGELOK FITTING WHERE THE CAPILLARY COLUMN IS ATTACHED
16 – STAINLESS STEEL TUBES HOUSING CARTRIDGE HEATERS AND PLATINUM TEMPERATURE SENSOR
17 – SECOND ADSORBER NICKEL TUBE
18 – BAKELITE INSULATOR

FIG. 1: DUAL TRAP

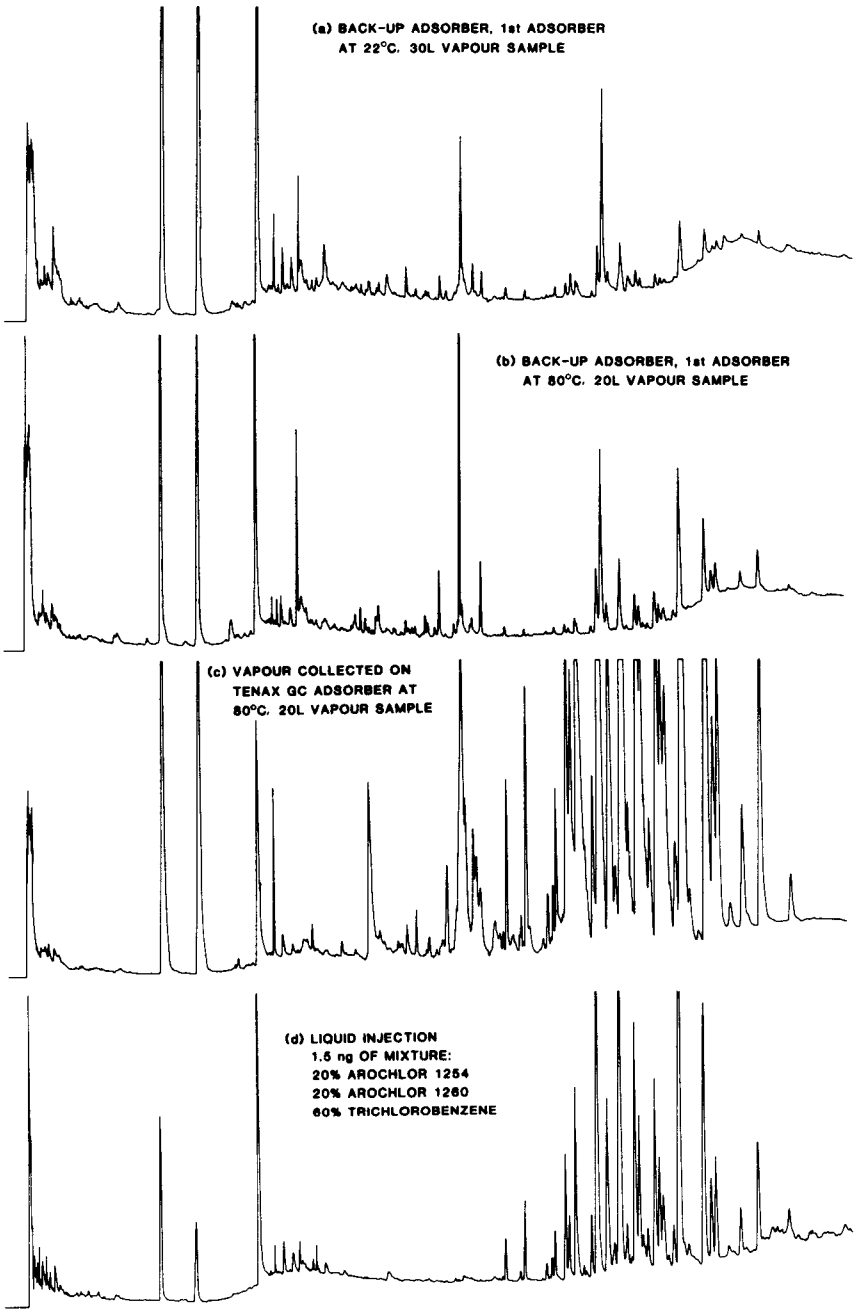

FIGURE 2. CHROMATOGRAMS OF PCB ANALYSIS.

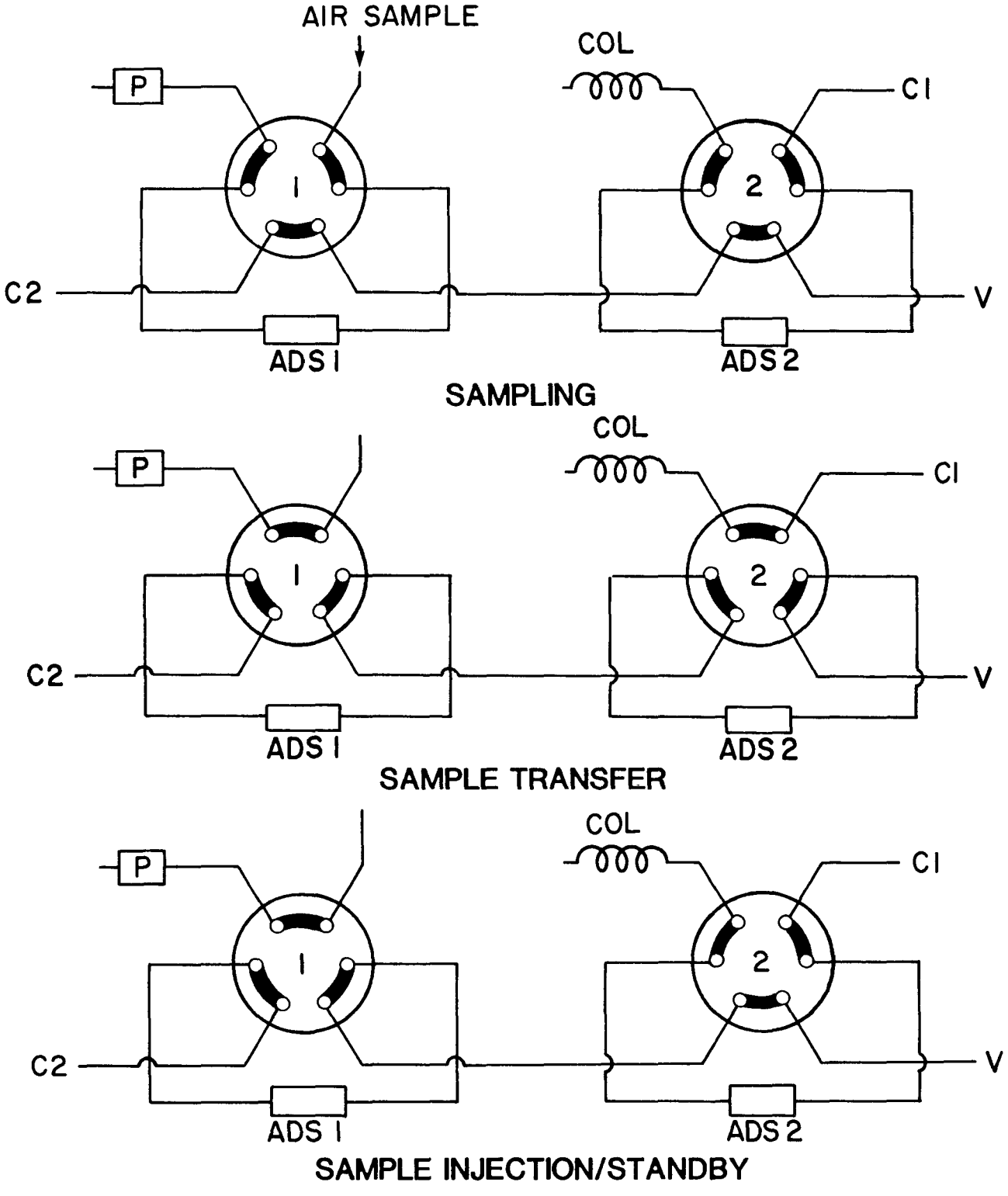

FIGURE 3. SAMPLER CONFIGURATION.

C1, C2 - CARRIER GAS; ADS 1, ADS 2 - FIRST- AND SECOND-STAGE ADSORBERS; P - AIR PUMP; V - VENT.

THE RATIO OF BENZO(A)PYRENE TO PARTICULATE MATTER IN SMOKE FROM PRESCRIBED BURNING

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INTRODUCTION

Although forest burning is prescribed widely across the United States, it is most commonly practiced in the Northwestern and the Southern United States.[1,2] In 1978, approximately 37 million metric tons of forest fuels on all forest ownerships were burned by prescription; approximately 12.5 million metric tons were burned in the South.[3] This burning produces an estimated 0.6 million metric tons of total suspended particulate matter (TSP) annually in the United States. Of that total, about 0.2 million metric tons of TSP originate in the South.[3]

Considerable uncertainty exists over the estimation of benzo(a)pyrene (BaP) produced by prescribed burning. Forest and agricultural burning were estimated by the National Academy of Sciences to emit 127 metric tons per year in 1968, but that figure was reduced to 9.5 metric tons per year in 1972.[4] In a 1977 report, EPA estimated BaP emissions from prescribed burning to be 4.5 metric tons nationally, which was 0.5 percent of the BaP from all sources.[5]

Early data gathered by the Southern Forest Fire Laboratory suggested that the amount of BaP emitted might also vary with the fuel condition and method of burning. In a series of experimental fires conducted by McMahon and Tsoukalas, the ratio of BaP to TSP was found to be much higher among simulated backing fires than among simulated heading fires in pine needle fuel (Table 1).[4] The measurements were made in a special combustion chamber at the Southern Forest Fire Laboratory (Figure 1). Backing fires are spreading fires that progress into the wind and heading fires are those that progress with the wind. Both types of fires are commonly prescribed.

A serious limitation in these results was that they represented only one fuel type burned by prescription in the South. Perhaps more important, they represented a fire environment in which pine needles were isolated from all natural variations in conditions of duff, soil, moisture, and wind. Questions were raised. Are the order of magnitude differences between BaP/TSP ratios from backing and heading fires seen in laboratory fires also characteristic of fires in natural forest settings? What is the range of BaP/TSP ratios for some other fuels commonly prescribed burned in the South? The study described here was directed toward these questions.

METHODS

Experimental Design

In the forest, several factors, which can be selected or measured prior to a prescribed burn, are believed to influence BaP and TSP production. These factors fall into two broad categories: fuel conditions and weather conditions. The fuel conditions are fuel type, fuel load, and moisture content. Weather conditions are fire type (or wind direction), wind velocity, and relative humidity.

In this field experiment, we examined the effect of fire type and fuel type only. For comparison with the laboratory experiment, we incorporated three levels of fuel loading for one fuel type--pine needle litter. The statistical design chosen was a factorial experiment (2 fire types x 4 fuel types) with an unbalanced incidence matrix. The two fire types examined were backing and heading fires. The four fuel types examined were pine needles (litter of pure slash pine needles), hardwood litter (mixed hardwood leaves and pine needles), broomsedge (pine-needle litter with broomsedge understory), and palmetto (pine-needle litter with palmetto understory).

The plots burned in each fuel type were approximately 5m by 25m. With the exception of the pine-needle fuel, 6 plots were burned in each fuel type--3 replicate backing fires and 3 replicate heading fires. In the case of the pine-needle fuel, each of 3 levels of loading was treated separately, giving a subtotal of 18 pine needle fires. The statistical analysis was appropriately adjusted for this unbalanced incidence of fuel types. In all, 36 individual plots were burned and sampled. Results were subjected to statistical analysis of variance.

The Sampler

A light, portable sampler was designed to collect, simultaneously, samples of total suspended particulate matter, benzo(a)pyrene, and combustion gases. The sampling train consisted of five units: a glass-fiber filter holder, a polyurethane foam (PUF) trap, two personal pumps, and a gas bag (Figure 2). The sampler, assembled from components and attached to a long aluminum pole, was designed for portability and safety. On one end was an air-intake probe which could be extended into the smoke plume directly over the flaming zone. The probe was positioned by the operator so that its temperature rarely exceeded 60°C by raising or lowering the probe above the flames. On the other end of the pole were the pumps and other electrical components which were less resistant to heat. The person who carried the sampler could walk near the advancing fire line holding the probe within the plume of emissions directly above the flames.

The sampling probe (Figure 3), consisted of four main parts: filter holder, PUF trap, thermocouple and anemometer. The open-faced aluminum filter holder contained a 47-mm glass-fiber filter. The exit of the holder fed directly into a PUF trap constructed of PVC pipe and end caps. The trapping material was polyurethane foam in 3 cylindrical plugs (30-mm diameter by 35-mm length) prepared in advance by soxhlet extraction with methylene chloride. We expected most, if not all, BaP to be trapped on the glass-fiber filter; but to be safe, we placed the PUF plug into the sampling train to trap any BaP in the vapor phase as well.[6,7] The filter holder and PUF trap were attached by a "quick-disconnect" to an extension tube running to the pumps. A thermocouple was placed on the probe very near the entrance to the filter holder with a temperature readout in sight of the person using the sampler. The thermocouple was used to monitor the temperature of gases entering the sampling probe. A Biram anemometer, not used in this study, was located adjacent to the sampling probe and could be used to determine average windspeed flowing by the sampler.

On the other end of the sampler (Figure 4), a Dupont P-4000 pump, powered the probe's air flow with a flow rate of 4.0 liters per minute. A smaller pump, a Dupont P-200, pulled a constant proportion of the exhaust gases from the main pump into a 2.5 liter aluminized gas bag at a flow rate of 0.12 liter per minute. Thermocouple and time readouts were also located here. About 1 to 5 mg of TSP and 1 to 2 liters of gases were collected for subsequent analysis.

TSP was determined gravimetrically while the concentrations of carbon monoxide (CO) and carbon dioxide (CO_2) were determined by a nondispersive infrared technique. CO and CO_2 values, while not used in this study, could be used to estimate emission factors by the carbon balance technique as reported by Ward, et al.[8] BaP trapped in the TSP and PUF was determined by a routine method validated for wood smoke at the Southern Forest Fire Laboratory.[9] In this method, BaP was recovered from the TSP and PUF by soxhlet extraction with methylene chloride and quantified via high performance liquid chromatography on a bonded octadecyl column. The limit of detection was about 1.34 ng BaP and the limit of quantitation was about 2.02 ng. A precision of better than 10% was typical at the BaP levels determined.

RESULTS AND DISCUSSION

Benzo(a)pyrene appeared to be trapped completely by the sampler's glass-fiber filter. In only one PUF analysis out of 12 did BaP exceed the limit of quantitation (2.02 ng). And this one case was thought to be due to leakage of TSP rather than breakthrough of BaP. In separate tests, samples of TSP were held for BaP analysis for at least 4 months under refrigeration without significant degradation.[9]

For the pine-needle fuels, the trends of the ratios of BaP to TSP in the field were similar to trends reported in the laboratory (Table 1). For example, backing fires produced higher ratios than heading fires, except for backing fires with heavy fuel loads. Also, ratios decreased with increasing loading of needles. In the field, however, the ranges in observed values (7 to 45 µg per gram) were far less than in the laboratory (2 to 274 µg per gram). The unusually high values of ratios for laboratory backing fires were, we believe, because conditions for pyrosynthesis of BaP were more favorable in these fires.

What are the conditions that influence formation of BaP during prescribed burning? Strong experimental evidence suggests that BaP pyrosynthesis within the flame envelope is governed by temperature, oxygen concentration, and length of time BaP precursors remain inside the flame.[10,11] If the flames are too hot (above 1000°C) and turbulent, BaP levels are low because oxidation is favored over pyrosynthesis. On the other hand, if temperatures are low (below 600°C), as often occurs in smoldering combustion, the BaP precursors do not cyclize to the 5-ring BaP structure. The optimum temperature for BaP pyrosynthesis

is near 800°C.[12,13] In prescribed burning, our evidence suggests that the conditions that favor BaP pyrosynthesis are low-intensity fires in which flaming combustion predominates over smoldering combustion. These conditions are produced in light fuel loadings that burn with relatively nonturbulent flames.

When BaP/TSP ratios were listed by fire type and fuel type, the range of values was less than an order of magnitude (Table 2). Over the four fuel types, no significant difference was found between ratios from backing and heading fires. A mean of 23 µg per gram for backing fires and 25 µg per gram for heading fires showed this clearly. However, there was a significant difference among mean values by fuel type. We cannot explain the variation among fuel types at this time. However, we believe that it is caused by a combination of fuel characteristics such as fraction of green fuels, fuel bed porosity, fuel loading, and chemical composition, which contribute to fire behavior factors such as reaction intensity and fire line intensity. Additional work is planned.

The mean BaP/TSP ratio of all 36 fires in the experiment was 24 µg per gram with a relative standard deviation of 0.47. In another study by Ward, et al.[14] currently in progress in the Pacific Northwest, a BaP/TSP ratio of 15 µg per gram with a relative standard deviation of 0.49 has been determined from 27 TSP samples. These samples were obtained from burning unpiled forest residues (slash burning). Applying these new ratios (24 and 15) to the fuel and TSP data available from Chi, et al.[3], we calculate a new annual BaP production of 11 metric tons for prescribed burning in the United States. Although this new value is still an approximation, we believe it to be accurate within a factor of two and a significant improvement over previous estimates because of the new information available on BaP/TSP ratios.

CONCLUSIONS

1. The ratio of BaP/TSP averaged 24 µg per gram with a relative standard deviation of 0.47 in four forest fuels common to the Southeast.
2. Significant differences were not found between heading and backing fire types, but were found amongst the fuel types.
3. BaP production from prescribed burning is estimated to be 11 metric tons annually.

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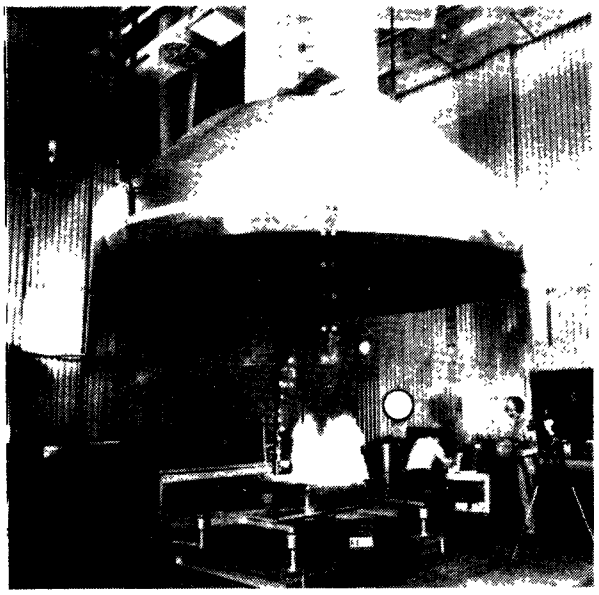

Figure 1. Bed of pine needles burning in combustion chamber at Southern Forest Fire Laboratory.

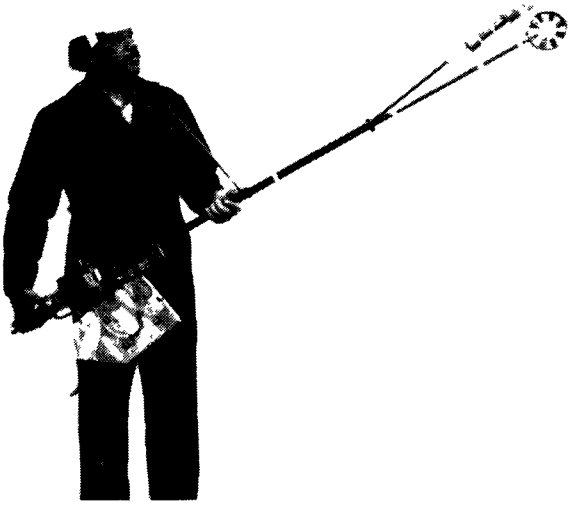

Figure 2. Portable smoke sampler.

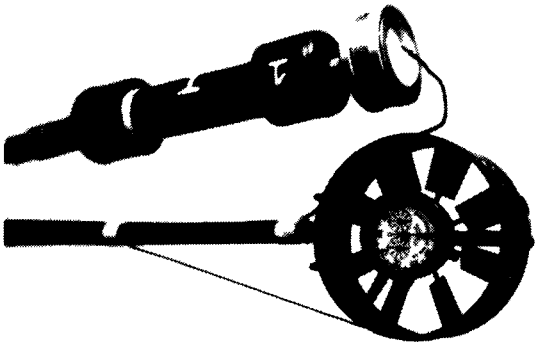

Figure 3. Portable smoke sampler, probe unit.

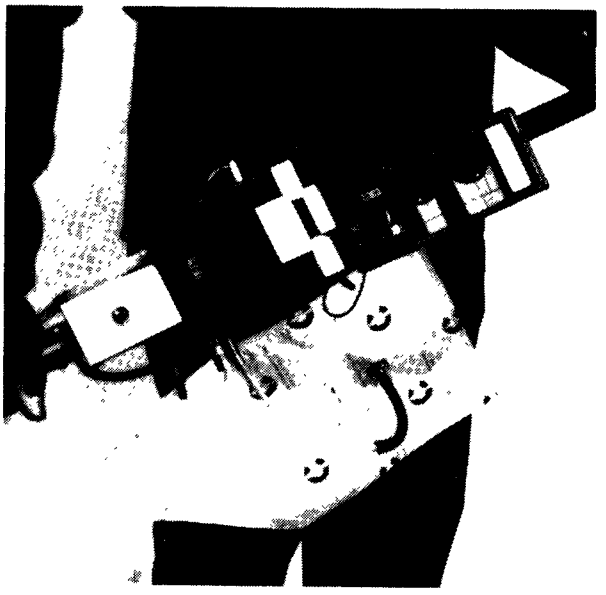

Figure 4. Portable smoke sampler, control unit.

TABLE 1. RATIO OF BENZO(A)PYRENE TO TOTAL SUSPENDED PARTICULATE MATTER FROM BURNING PINE NEEDLES IN THE LABORATORY AND FIELD

Fire type and fuel loading	Laboratory fires		Field fires	
	Fuel load* kg/m^2	Ratio µg/g	Fuel load kg/m^2	Ratio µg/g
Backing fires				
Light load	0.5	274**	0.3	45
Median load	1.5	135	1.3	14
Heavy load	2.4	98	1.6	7
Mean value	1.5	169	1.1	22
Heading fires				
Light load	0.5	3	0.3	24
Median load	1.5	2	1.3	11
Heavy load	2.4	2	1.5	11
Mean value	1.5	2	1.0	15

* In the laboratory, fuel load referred to kilograms per square meter of pine needles placed on the burning rack; however, in the field, fuel load referred to the difference in the average kilograms per square meter of pine needle litter (6 replicates) before and after the fire.

** Ratio values for laboratory fires which were taken from reference 4 were recalculated. The correct ratio for the backing fire with light load should be 318 µg per gram and not 274 µg per gram.

TABLE 2. RATIO OF BENZO(A)PYRENE TO TOTAL SUSPENDED PARTICULATE MATTER ARRANGED BY FUEL TYPE AND FIRE TYPE

Fuel types	Fire Types					
	Backing fires			Heading fires		
	Ratio* µg/g	Number of Replicates	Relative** Standard Deviation	Ratio µg/g	Number of Replicates	Relative Standard Deviation
Pine needle	22	9	1.00	15	9	0.60
Hardwood	9	3	0.44	13	3	0.18
Broomsedge	17	3	0.23	13	3	0.30
Palmetto	44	3	0.40	60	3	0.14

* Ratios are reported in micrograms of benzo(a)pyrene per gram of total suspended particulate matter.

** Relative standard deviation (coefficient of variation) is the ratio of the standard deviation of the replicates to the mean.

VOLATILE ORGANIC SAMPLING TRAIN (VOST) DEVELOPMENT AT MRI

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The purpose of this presentation is to describe volatile organic sampling train (VOST) technology presently in use at Midwest Research Institute (MRI). We hope this information will help you avoid many of the problems MRI encountered when it first sampled for volatile organics using Tenax traps.

Early in 1983 MRI received a task on an EPA Office of Toxic Substances program to evaluate the emissions from hazardous waste incinerators. We started the program using a commercial conditioner, desorber, and Tenax traps. The Tenax in the trap (Figure 1) was held in place with plugs of glass wool, and the traps were stored in test tubes with Teflon-lined caps. The traps were connected to the sampling system using Swagelok fittings with Teflon front and back ferrules. A laboratory evaluation for compound retention was performed and the system appeared to be working. After our first field test, however, we found that the blanks contained almost the same levels of volatile organics as our samples. A frantic search was initiated to eliminate the problem while the test program continued. We employed a multi-approach attack, obtained very low blanks, and adopted a procedure which is still being used.

To our knowledge, MRI has had more experience with the VOST as applied to source measurements than any other organization. Because this experience has yielded additional information, we have developed what we believe is a better understanding of the VOST's problems. We now know, for example, that many of the steps, originally incorporated in the procedure to eliminate the high blanks, are unnecessary. The major difficulties with using the VOST will be getting the cartridges clean, knowing when they are clean, and keeping them clean.

The successful use of the VOST requires good cartridge design. We designed the MRI double-walled cartridge (Figure 2) to minimize the contamination which we felt was coming from outside the tube. Tests show however that even the

double-walled cartridge does not completely protect the cartridge from contamination. With this knowledge, we are investigating a new simplified design (Figure 3).

Our first VOST runs were made on incinerators with wet scrubbers. We were having difficulty during our analysis because there was high water retention in the cartridges. We found that most of the water was contained in the glass wool used to retain the Tenax. To solve this problem, a system of C clips and stainless steel screens was developed to hold the Tenax in the traps. This retention system kept the Tenax compressed, with a surprising but now understandable improvement in cartridge performance. Keeping the Tenax compressed eliminated voids and channeling in the resin bed. The result was cartridges which were more uniform in their compound retention and which were significantly improved in their retention capacity.

Another way we modified the original Tenax tube system was the method of connecting the tubes to the system. We found that the Swagelok fittings with Teflon front and back ferrules we originally used frequently broke the tubes when tightened sufficiently to obtain a leak-free system. We therefore used the end plates in the double-walled design to obtain a seal with the tubes and attached the end plates to the system using VCO fittings.

In the new tube design, we are attempting to use Ultra-Torr fittings which use an O ring. While we were trying to reduce the blanks, we placed a cartridge filled with the Viton O rings and desorbed them into the mass spectrometer. High levels of hydrocarbons were detected. We decided to condition the O rings in a vacuum oven to remove the volatile material. When the first batch of O rings was removed from the oven, about half had turned to black glass, indicating that the vendor had mixed Viton and rubber O rings together. We changed to a vendor that color-coded its O rings (Viton is tan). Because we have not yet checked volatiles run with the new O rings, to be safe we are continuing to treat the new rings. It appears that we may be able to employ Teflon O rings in the Ultra-Torr fittings in place of Viton for even better performance.

Let us summarize the advantages and disadvantages of the two MRI tube designs and the original all-glass commercial tube design. The MRI double-walled design gives reproducible results, provides low water retention, is rugged, protects the exterior of the tube from contamination, goes in the system one way

only, and does work. It is, however, heavy, large, expensive to construct, and requires more time to recycle. (The cartridges are disassembled and only the inside tube is placed in the desorber, so the cartridge must be reassembled.) The new simplified MRI tube design will have the same advantages as those of the double-walled design but have the added advantages of being smaller, lighter, and lower in cost. It will probably require some type of outside protection in the field such as being wrapped in aluminum foil. A system to assure proper orientation of inlet to inlet will also be desirable. It is currently untried. The original commercial all-glass tube design using C clips and stainless stell screen in place of the glass wool should perform as well as the new simplified MRI design, and the different sized ends will assure proper orientation. Replacement glass tubes will be more expensive because one end must be drawn down, but the sampling train (metal parts) will cost less because of the smaller fittings on one tube end. The small tube end will also be more fragile.

A fourth tube design (Figure 4) has been proposed in the VOST protocol. We believe this new commercial tube design is unacceptable. Because the tube is necked down to 1/4 in. on each end, it is necessary to hold the Tenax in place with glass wool plugs, with the attendant disadvantages.

It has been our experience that for good conditioning, especially in the case of used cartridges, it is essential that the gas be forced to pass through the cartridges. In the commercial unit that is presently available for cartridge conditioning, the gas does not normally pass through the cartridges but flows around the tube. We understand that the manufacturer has developed a modification which forces the gas through the cartridges. If you decide to use this conditioner, we strongly recommend that you use the cartridge flow-through modification. We have found that many cartridges that have been used still fail the purity check after two 8-hr conditioning periods using the unmodified system. These same cartridges will clean up, however, after only 4 to 8 hr when the purge gas goes through the cartridge. We have been informed that some users have solved the cleanup problem by discarding the approximately $10 worth of Tenax in each cartridge after it has been used once, an approach you may wish to take.

We recommend adopting the one-step conditioning and monitoring technique (Figure 5) regardless of which cartridge design is used. The one-step procedure

consists of passing hydrocarbon-free nitrogen at 30 mL/min through the cartridge while it is heated at 200°C. The exit gas stream from every tube is checked at regular intervals using a flame ionization detector (FID) until the hydrocarbon level approaches the lower detection limit (LDL). Using the one-step technique, you know when the cartridges are clean. This permits stopping the conditioning when most of the cartridges pass the purity check. In addition, all components of the cartridge can be cleaned (conditioned) at the same time. This has the added advantage of not requiring stringently clean facilities for cartridge assembly. If you elect to condition and perform the purity check separately, you will find it necessary to recycle cartridges through the desorber until they pass the purity check.

A manifold for conditioning the new tube design is shown in Figure 6. Each manifold holds 10 tubes in the conditioning oven, so that with four manifolds 40 tubes can be conditioned at a time.

We do not agree with the introduction of a chromatographic column during the cleanup procedure, as proposed in the VOST protocol. We do not see how it improves the method, and it has a number of disadvantages. Use of a column increases the time required for each purity measurement from the present 2 min to at least 30 min. Use of a column also significantly reduces the sensitivity of the measurement. When using an FID, the hydrocarbon response is additive so that the lower detection limit is the sum of all components eluted. If the cartridge contains, for example, 15 components just below the 0.2 ng level, they would pass using the column technique. With the FID only, the response would equal 3 ng and would fail to pass. Another disadvantage concerns column contamination. If you use a column when checking cartridges that have collected field samples, you will find that high boiling hydrocarbons are slowly accumulated in the column. This will cause an increase in the background hydrocarbon level. It will, therefore, be necessary to stop and bake out or replace the column at frequent intervals.

The only method we have found that protects clean cartridges is to store them over activated charcoal or under water. Tests have demonstrated repeatedly that neither the double-walled MRI cartridges nor the all-glass cartridges stored in a Teflon-capped test tube will remain uncontaminated. After conditioning,

the cartridges should be placed under water or over charcoal as soon as they reach room temperature. As an added precaution, we maintain the purge gas flow on the cartridges until they are cool.

As indicated in the VOST protocol, and as has been done by users of all-glass tubes in the past, the tubes are capped and placed in Teflon-lined screw-capped test tubes after sampling for shipping and storage. We question this procedure. Any contamination on the exterior of the Tenax tubes, if carried to the inside of the test tubes, will migrate to the Tenax.

Since we found that volatile organics diffused through the O ring seals on the double-walled design, we also believe that storing the tubes after sampling in screw-capped test tubes over charcoal should be avoided.

The original MRI train is described in the VOST protocol. The train is being improved and modified to use the new MRI cartridge and the type of lubricant free valve required by EPA (Figure 7). The valve manufacturer recommends the use of a small amount of lubricant to maintain leak-free operation. We determined modest amounts of Apiezon grease in hydrocarbon sampling trains, will neither add to nor remove measurable quantities of hydrocarbons from the gas stream. However, the use of greases has been forbidden by EPA.

The addition of a third valve to the train will permit carrying out all the required operations without having to remove or replace various components. The valves may be arranged in such a manner that only one valve is in the system during the leak check.

In summary, MRI believes the VOST procedure can be simple and straightforward, as shown in the following steps:

- Clean new metal parts with suitable solvent.
- Sonicate all components in hot detergent solution.
- Rinse with water and oven-dry.
- Assemble cartridges in clean area.
- Condition at 200°C with 30 mL/min of hydrocarbon free gas.

- Check exit gas of each tube at intervals using FID.
- Stop conditioning when hydrocarbon level approaches lower detection limit.
- For cartridges that do not pass after 8 hr, fill with fresh Tenax and recycle.
- Cool with gas flowing, cap, and store over activated charcoal.
- Protect outside of tube while sampling with aluminum foil.
- After sampling, cap and store tubes under water until analyzed.

If benzene or toluene is to be measured, the cartridges should be conditioned as close as possible to the sampling time and analyzed as soon as possible. Cartridges for benzene or toluene should be stored under ice water after conditioning and until analyzed. For samples not requiring benzene or toluene analysis, storage over charcoal after conditioning and under water after sampling should be sufficient. However, it would probably be a good idea to keep cartridges cold when possible.

Our presentation has been limited to the sampling train. Our analytical procedure remains basically the same as reported to the contractor who prepared the protocol. The one exception is that we have discontinued using the commercial desorber. In its place we are connecting inlet and outlet fittings directly to the Tenax tubes (Figure 8) so that the purge gas must pass through the tube. The tube is then heated by a small resistance heater placed around the glass tube. Using this system we have decreased the repeatability of standardization from 10 to 2%.

In conclusion, I would like to acknowledge the following MRI personnel who made significant contribution during this work: Paul Gorman, Greg Jungclaus, Gil Radolovich, George Scheil, Bob Stultz, George Vaughn, and Ken Wilcox.

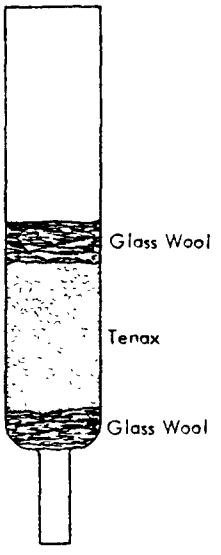

Figure 1. Original commercial trap.

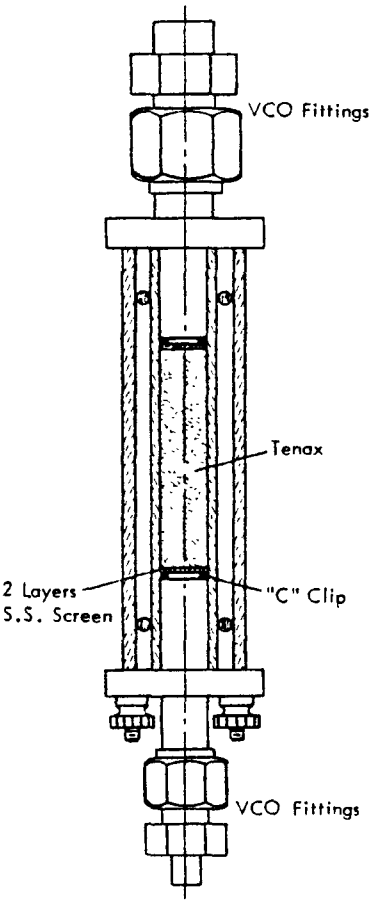

Figure 2. MRI double-walled cartridge.

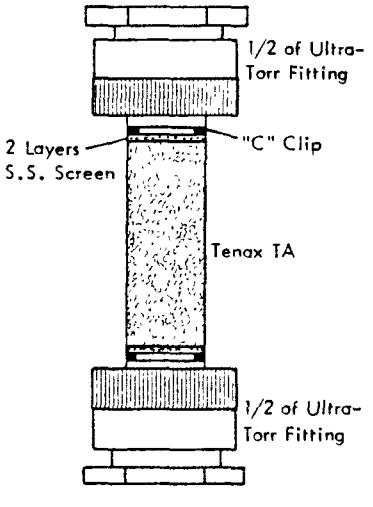

Figure 3. New simplified MRI trap.

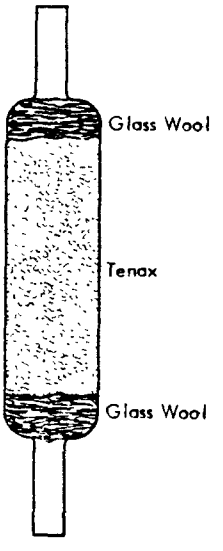

Figure 4. New commercial trap.

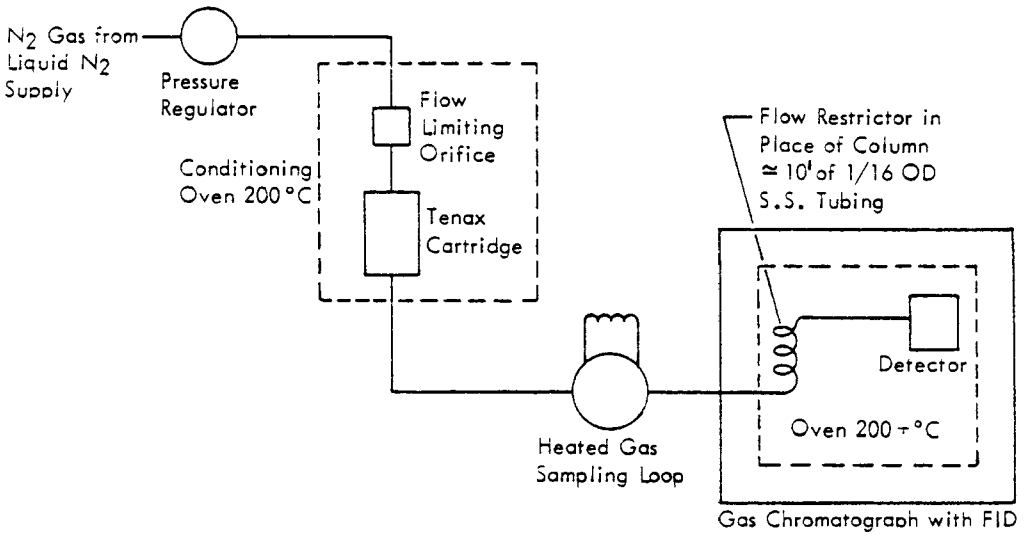

Figure 5. One-step conditioning and monitoring technique.

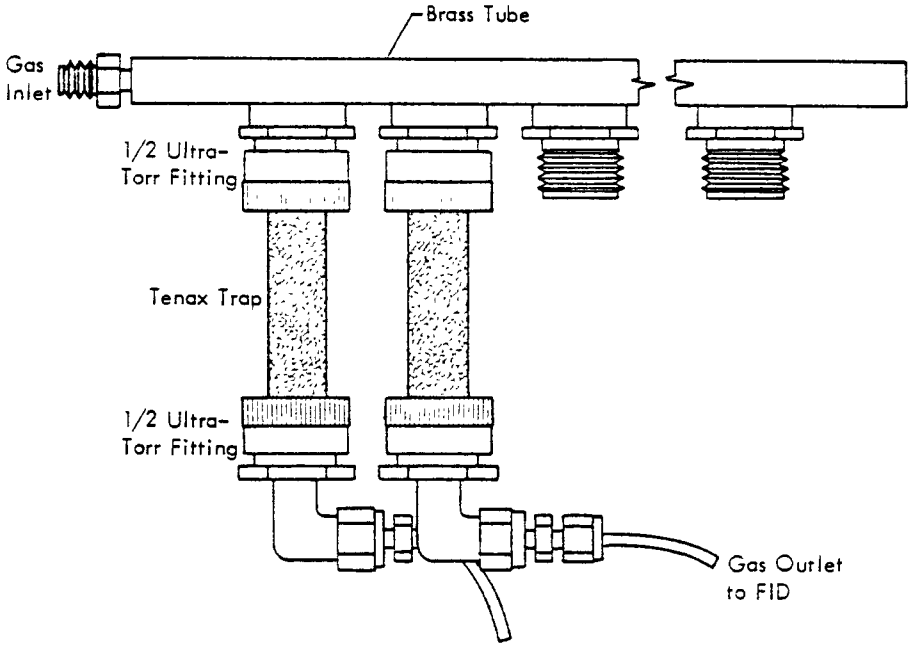

Figure 6. New MRI conditioning manifold.

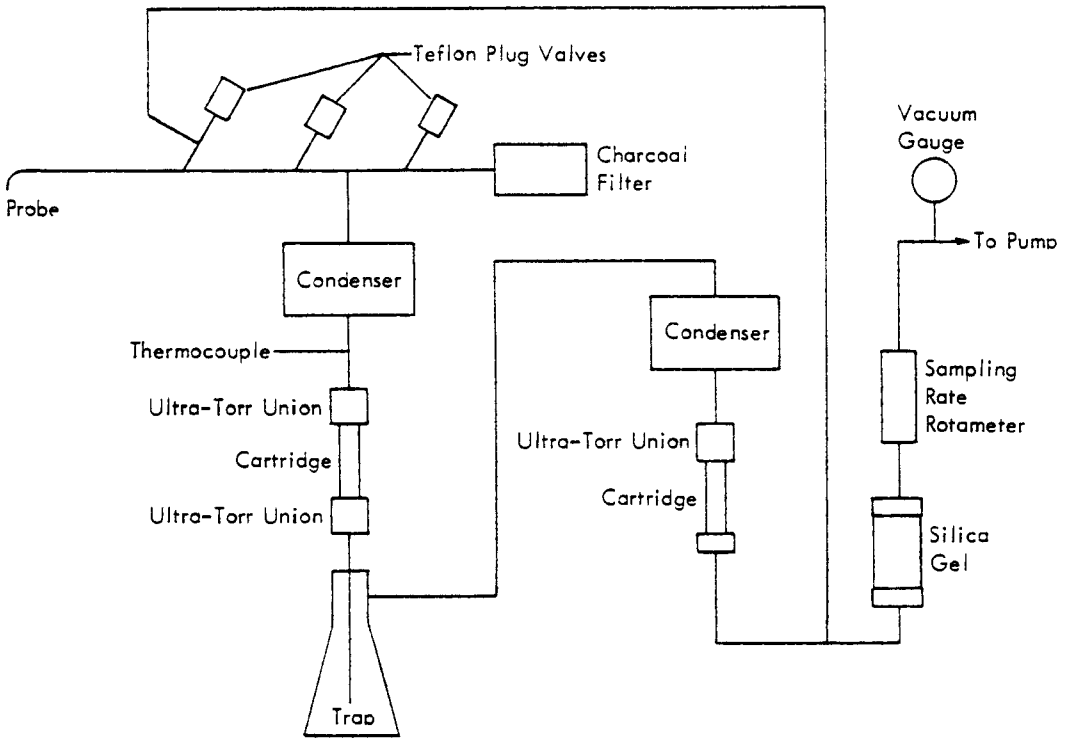

Figure 7. New VOST sampling train.

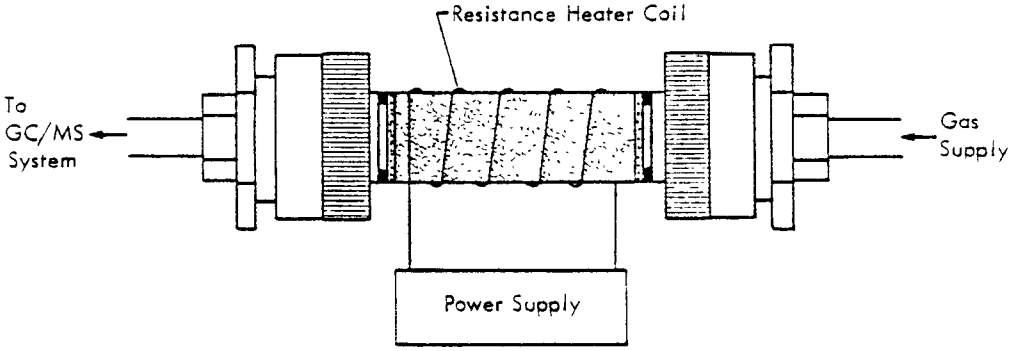

Figure 8. New desorber

AN EVALUATION OF INSTRUMENTAL METHODS FOR THE ANALYSIS OF VINYL CHLORIDE IN GASEOUS PROCESS STREAMS

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INTRODUCTION

This presentation describes a project conducted by Midwest Research Institute (MRI) and funded by the Environmental Protection Agency (EPA) to provide background information for the development of performance specifications for continuous analyzers for hazardous organic pollutants. The project has two main purposes: to assess the state of the art in continuous monitoring for vinyl chloride (VC) and to measure the actual performance of two different analyzers over a period of 6 months.

The test design (Figure 1) has the analyzers connected with a calibrator to substitute calibration gases of 0, 5, and 9 ppm VC for the sample gas once each day and a digital data logger designed by MRI to provide a phone modem link to transmit data back to MRI on request, with backup records on a printed log and magnetic tape. The system operates unattended; only a twice-monthly supply visit is made unless the phone link checks indicate the need for a repair trip to the site.

ANALYZER SELECTION

One of the analyzers to be tested is an existing EPA furnished process gas chromatograph (GC) (Applied Automation). This unit has a 30-cm backflush column of 1/16-in. stainless steel tubing packed with n-octane Durapak for removing heavy organics, followed by a 30-cm analytical column of 1/16-in. stainless steel tubing packed with Porasil C to separate VC from other light organics; a flame ionization detector (FID); and an analog preset time window integrator. The system also has a sample conditioning section, gas sampling valve, and control system for automatic, repetitive sampling and analysis.

A review of currently available instruments was conducted to select the second analyzer. Several techniques are commercially used for continuous monitoring of VC such as gas chromatography, infrared, and electrochemical sensors. Only gas chromatography has the necessary sensitivity and selectivity for measuring VC near the current 10 ppm standard in process streams in the presence of significant amounts of ethylene dichloride and other organics. A growing number of VC analyzers are using photoionization detectors (PID) in place of an FID with some use of electron capture detectors. Digital integrators are also gradually replacing analog systems for peak analysis with occasional use of measurements for peak height instead of peak area.

A process GC with a PID and a digital integrator was selected as the best choice for the second analyzer. The PID has potentially better sensitivity to VC than an FID and little response to potential interferences such as ethyl chloride. The PID, as opposed to an FID, requires no special supply gases, and the PID is not as easily poisoned as an electron capture detector. Peak height measurements suffer from nonlinearity problems whereas digital integration matches the growing use of microprocessor controlled analyzers.

More than half the cost of purchasing a second process GC is needed to duplicate the valves, column, and other basic hardware to support a detector and integrator. Since the PID is a nondestructive detector, an in-line PID could be added to the existing system. A simple switching relay allows either integrator to be selected. Adding a PID and digital integrator to the existing system thus saves considerable money and has the added advantage of allowing better discrimination of any differences between the types of detectors and integrators by having the control system alternate each integrator with each detector. Thus, a revised analyzer system was assembled (Figure 2). The added modules were a Model PI52 PID with a 10.2 eV lamp (HNU Systems, Inc.) and a Model BC-2 instrument control computer (Action Instruments).

LABORATORY TESTS

Before proceeding to the field test, a series of experiments was completed in the laboratory to determine optimum operating conditions and possible interferences, and a matrix test of the analyzer control variables was conducted. The typical VC reactor product gas contains significant concentrations of ethylene and ethylene dichloride, as well as VC, and smaller amounts of other light

chlorinated hydrocarbons. Small amounts of chlorine and hydrochloric acid are also present which required the replacement of all stainless steel in the sample conditioning system with Monel, Teflon, or Knyar parts. Test mixtures of the compounds (Table 1) were prepared with permeation tubes at about 10 ppm with similar concentrations of VC and were sampled by the process GC. The backflush column rejected most of the compounds, and the positive interferences had shorter retention times than VC with at least partial separation. Although the FID response to chloromethane was similar to that to VC, the PID response was less than 1% of the equivalent VC response.

During preliminary testing the BC-2 digital integrator system developed severe problems due to a lack of isolation from electrical noise. The computer was having nonrecoverable system crashes about once an hour and the probable cost of remedial action was excessive. Fortunately the MRI data logger, based upon an Epson HX-20 briefcase computer matched with a Wintek MCS analog interface, was functioning well in the same environment. The excellent line isolation of a Nicad-powered computer together with the optical isolation and reset capabilities of the Wintek system allowed reliable recovery from noise. The logger system could measure the detector signals with the addition of a simple amplifier and had sufficient idle time during each analysis cycle to perform the necessary peak integration. Therefore, the logger was reprogrammed to perform the digital integration task as well as to log the results and communicate with MRI.

The reliability of this modified system proved satisfactory and the matrix test of control variables was conducted. The variables can be separated into variables affecting the entire analyzer (Table 2) and variables affecting only part of the system (Table 3). Each variable was tested by measuring a VC standard gas at the optimum condition and then at reasonable steps higher and lower than the optimum. A strong effect showed a change of more than three standard deviations from the average concentration at the optimum condition, and no effect showed a change of less than one standard deviation. Since the entire analyzer is pneumatically driven, the air pressure effects occurring only at lower pressure are not surprising.

The analog integrator measures the baseline at a fixed time just before the VC peak and integrates any signal above that baseline until the fixed stop time.

Since the two detectors measure the peaks at slightly different times, a change in the integration windows or the retention time will affect each detector differently. The digital integrator program first scans the chromatogram for the peak maximum nearest the expected time of the VC peak, jumps forward by a preset offset to begin searching for a level baseline at the start of the peak, performs a similar operation to find the end of the peak, and subtracts the average baseline from the area under the peak. The program is insensitive to changes in the offsets or the factors used to set the minimum width and flatness of the baselines. Although the PID has no readily controlled unique variables, the FID is sensitive to changes in the flame hydrogen supply pressure and thus to its flow rate.

FIELD TEST

While the complete instrument system was undergoing a 1-month reliability test in the laboratory under simulated field conditions, the final arrangements for the field installation were completed. The test design required that the analyzers be operated for a period of 6 months at a VC monomer production facility with three 5-day periods of equivalence tests comparing the analyzers with EPA Method 106. The primary difficulty in selecting a test site was that all the plants contacted had gas streams which were either much less than 1 ppm or at concentrations of at least 1,000 ppm VC. The analyzer was finally installed on a reactor offgas stream with a nitrogen dilution tee to bring the VC concentration within the 1 to 10 ppm range needed for equivalency testing.

Only partial data are available since the test period does not end until late May. Figure 3 shows linear regression lines from the 20, 1-hour equivalence tests in the initial test series. The analyzer abbreviations shown in these figures refer to PID (P), FID (F), digital integration (D), and analog integration (A). All four detector-integrator channels read lower than the reference method at low concentrations. As a further check of equivalence the Method 106 integrated bag was also connected to the analyzer sample inlet. This detects differences caused by variations in the Method 106 sampling rate or sudden changes missed during the 150-second analyzer cycle. The results from the integrated bag measurements (Figure 4) indicate the same bias pattern.

After a series of tests the problem was isolated to the Porasil C analytical column. The column has a short retention time for VC but the uncoated silica was causing nonuniform adsorption. After replacing the analytical column with a Porapak Q-S column the nonlinearity disappeared. After resetting the system timing, the analyzer operated for about 1 month before the second equivalence test.

During the second test series the direct monitor readings (Figure 5) show some scatter but random bias. The integrated bag readings (Figure 6) have less scatter. An examination of the individual test runs indicates that the integrated bag concentrations are biased toward the initial sample concentration caused by a higher than normal flow rate during the first few minutes as the pressure within the bag enclosure stabilizes.

Data recovery efficiency is shown in Figure 7. The daily data sets are checked for outliers by measuring the standard deviation of the differences between the simultaneous pairs and rejecting any pair which exceeds four standard deviations. The over-range readings were caused by changes within the host monomer plant which upset the sample dilution ratio. Data recovery for November and December was affected by bad weather which produced repeated flameouts when the plant instrument air supply failed. During February the sample gas input overloads were so severe that the integrator skipped cycles. During April the data logger malfunctioned when a power supply in the data logger analog interface failed. The power supply was successfully replaced.

Finally, Figure 8 shows the daily bias and precision results for the test period following the analytical column replacement. The number shown below each set of error bars is the average VC concentration for that month. The different detector-integrator combinations show little overall bias with reference to the analyzer's original FID with analog integration. A more detailed analysis will be made after the test period is completed.

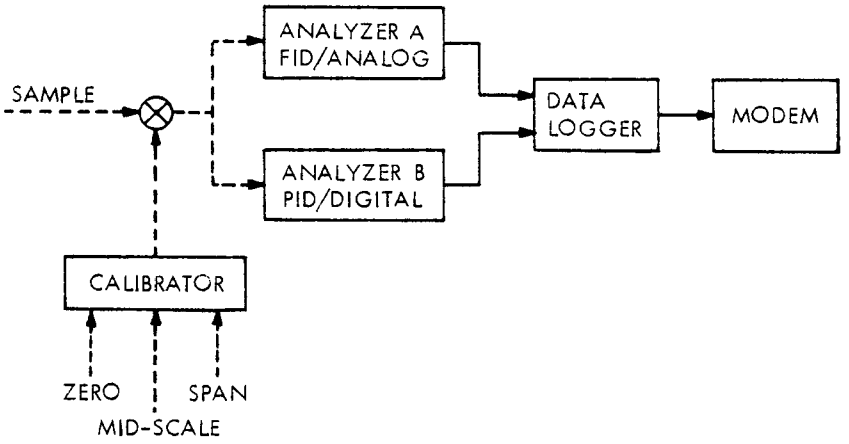

Figure 1. Original schematic of analyzer system.

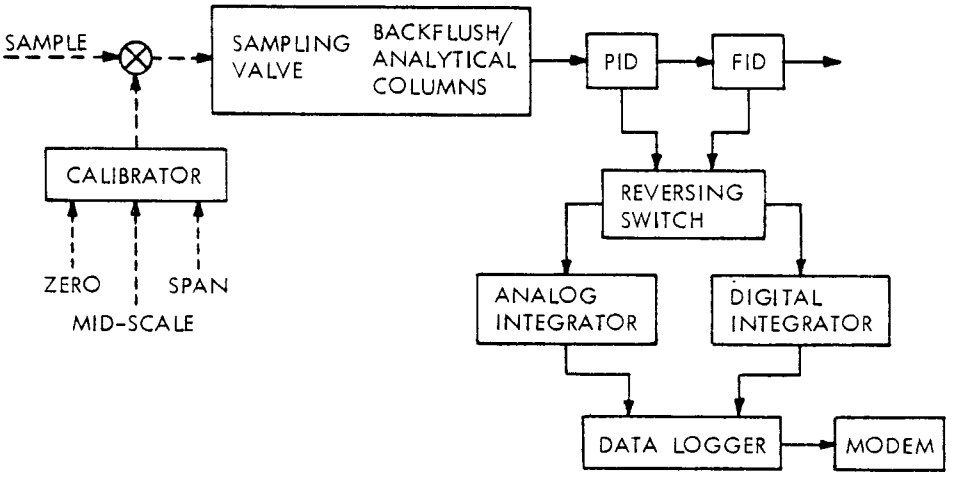

Figure 2. Revised schematic of analyzer system.

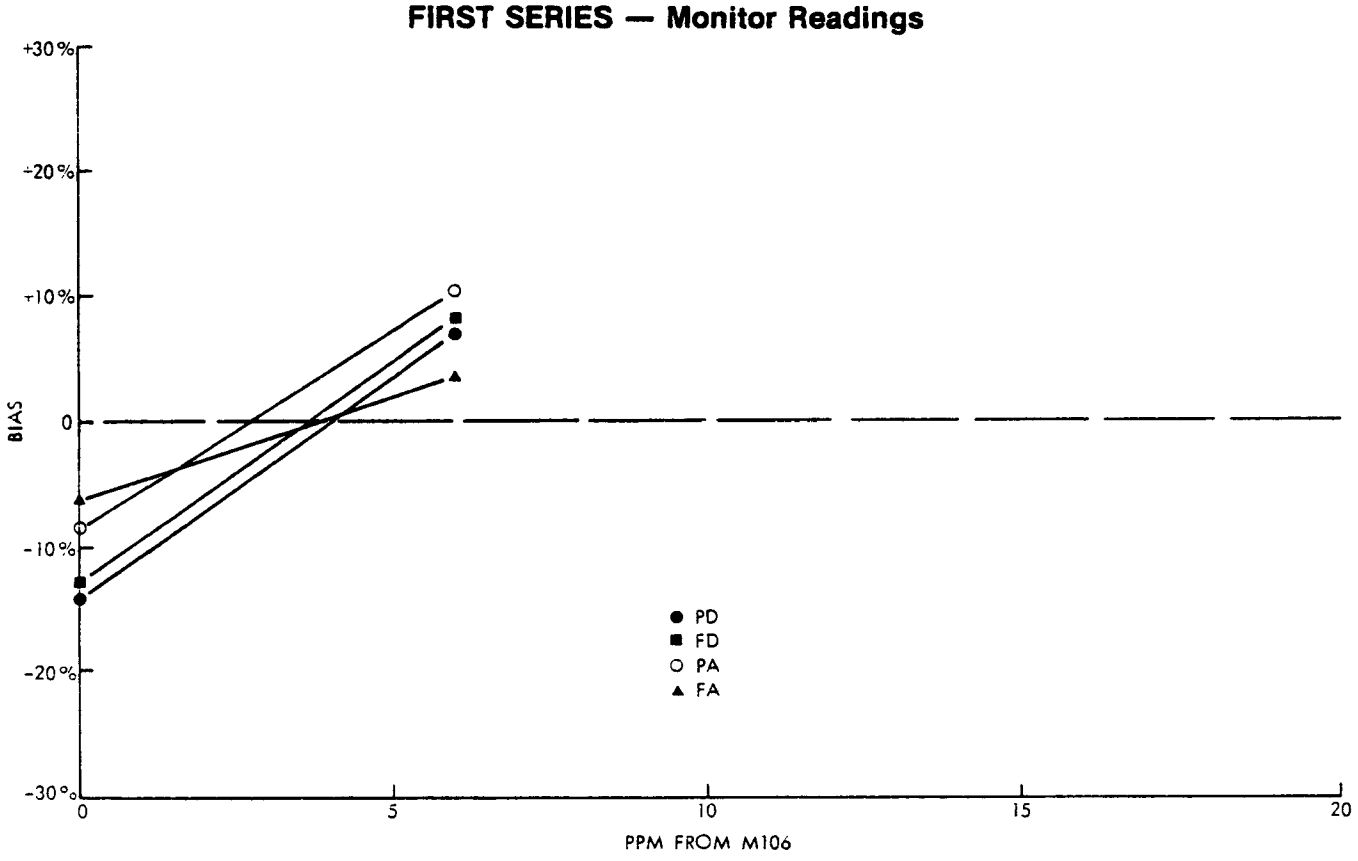

Figure 3. Bias of analyzer direct readings for the first equivalence test.

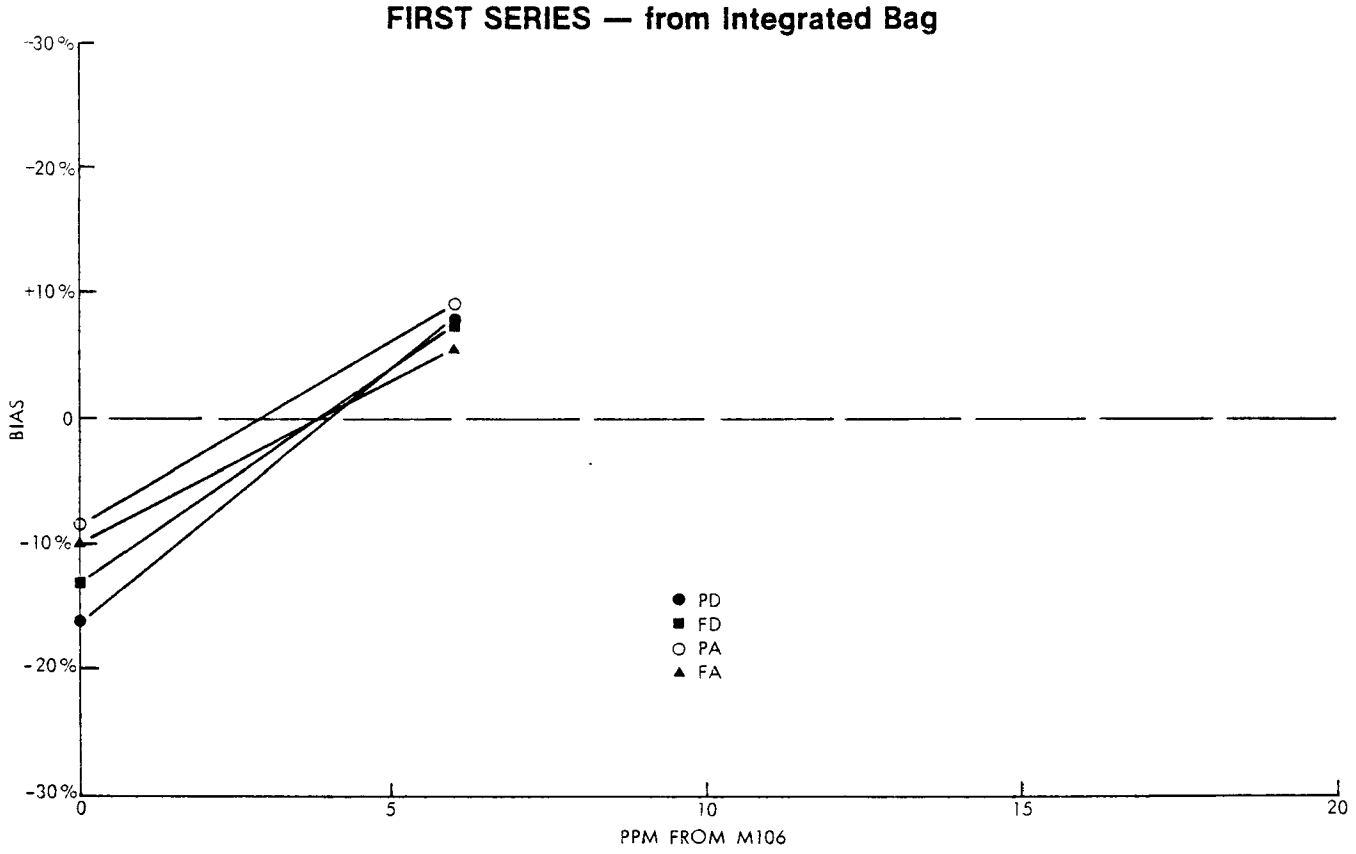

Figure 4. Analyzer bias when sampling from the integrated bags for the first equivalence test.

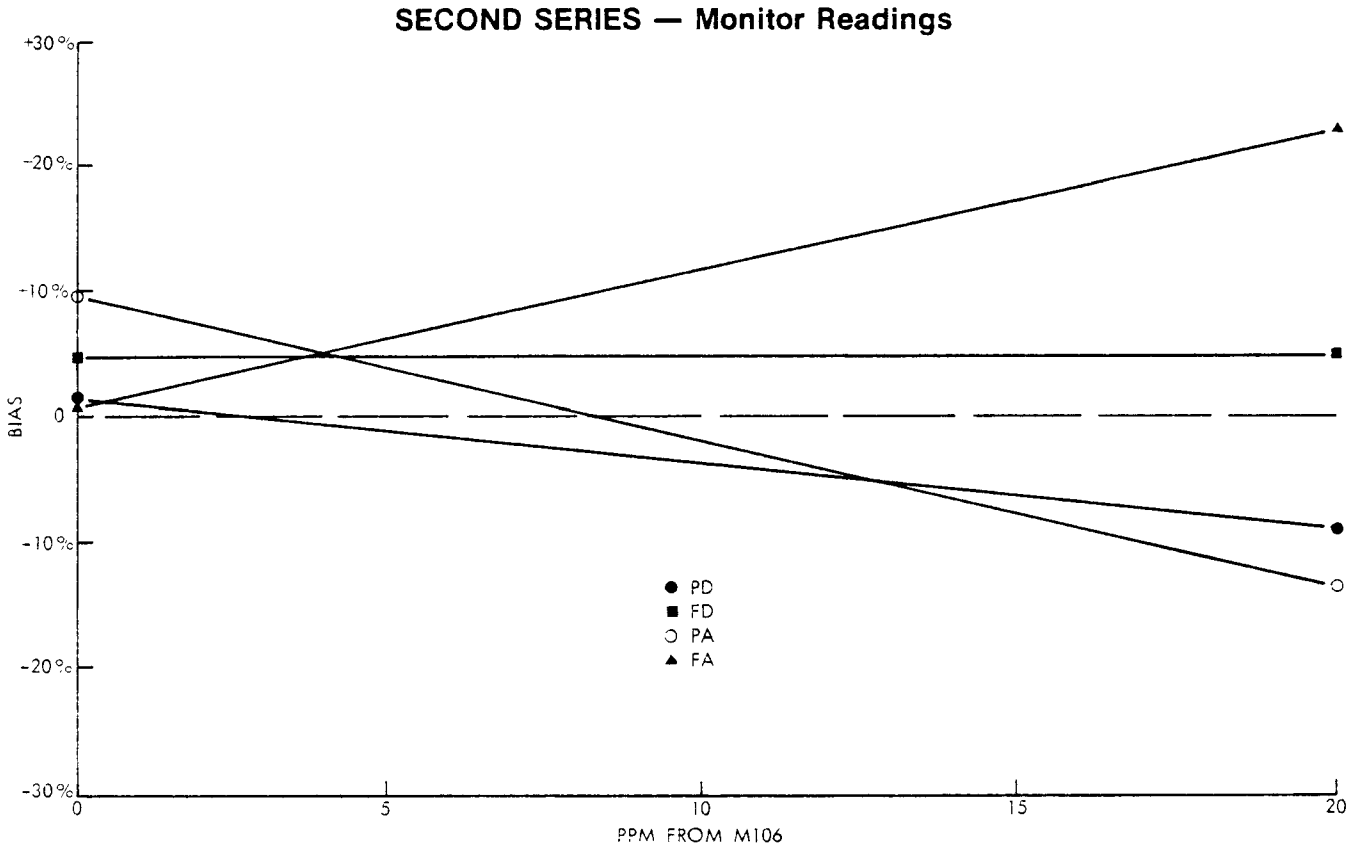

Figure 5. Bias of analyzer direct readings for the second equivalence test.

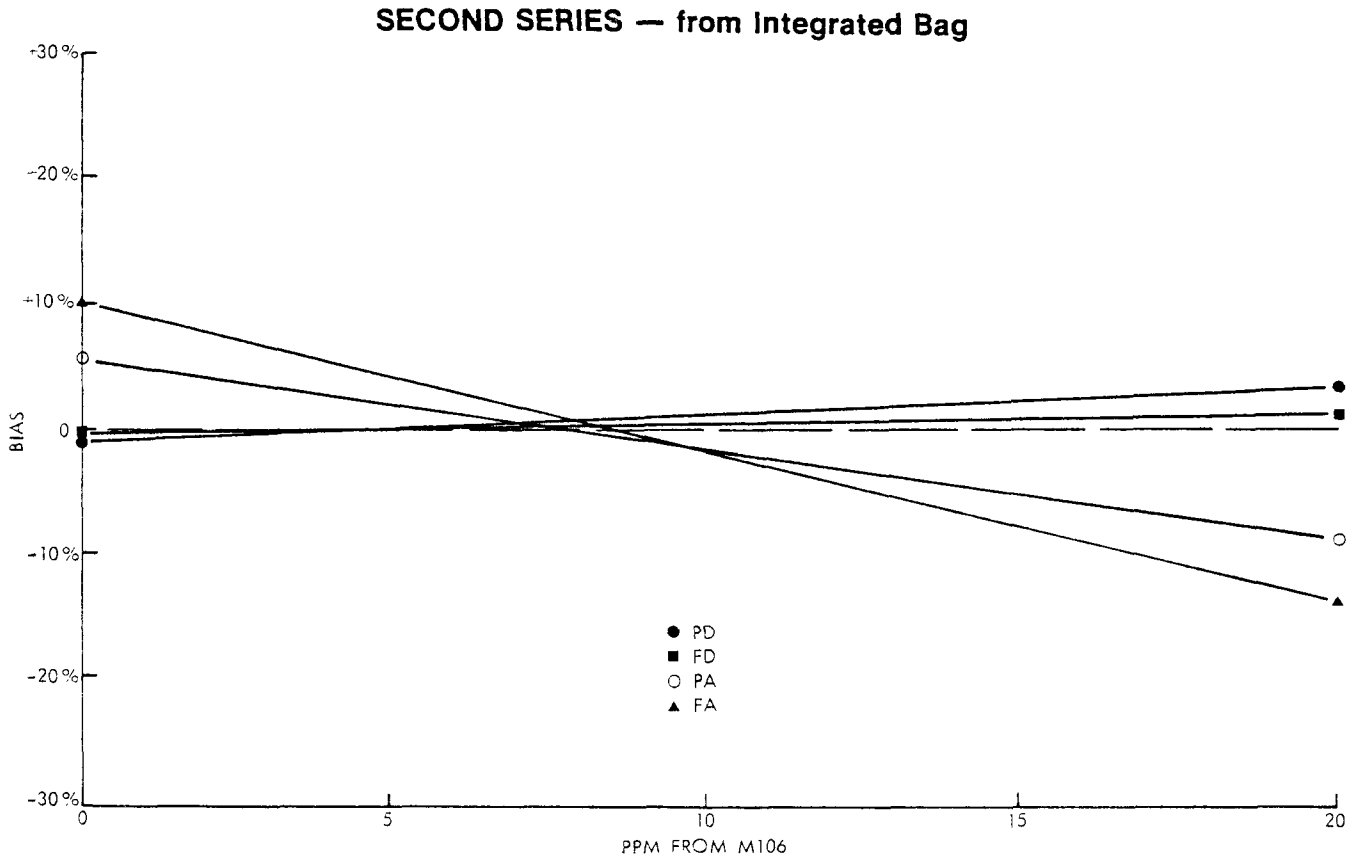

Figure 6. Analyzer bias when sampling from the integrated bags for the second equivalence test.

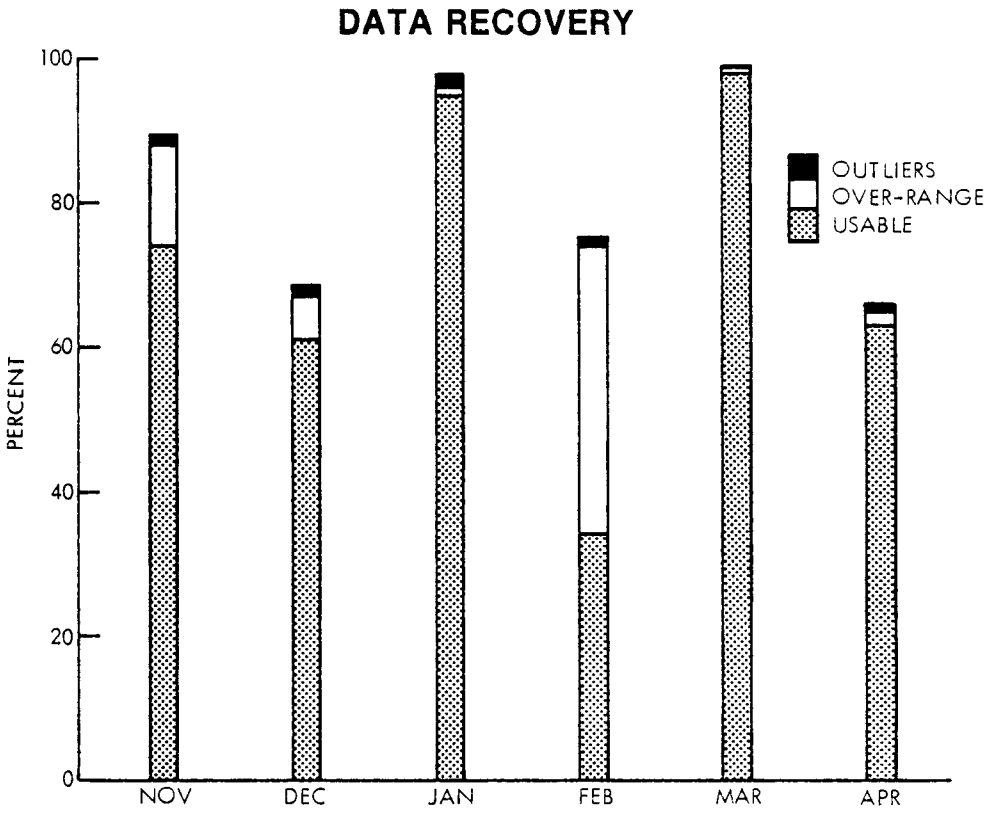

Figure 7. Average monthly data recovery of complete data sets.

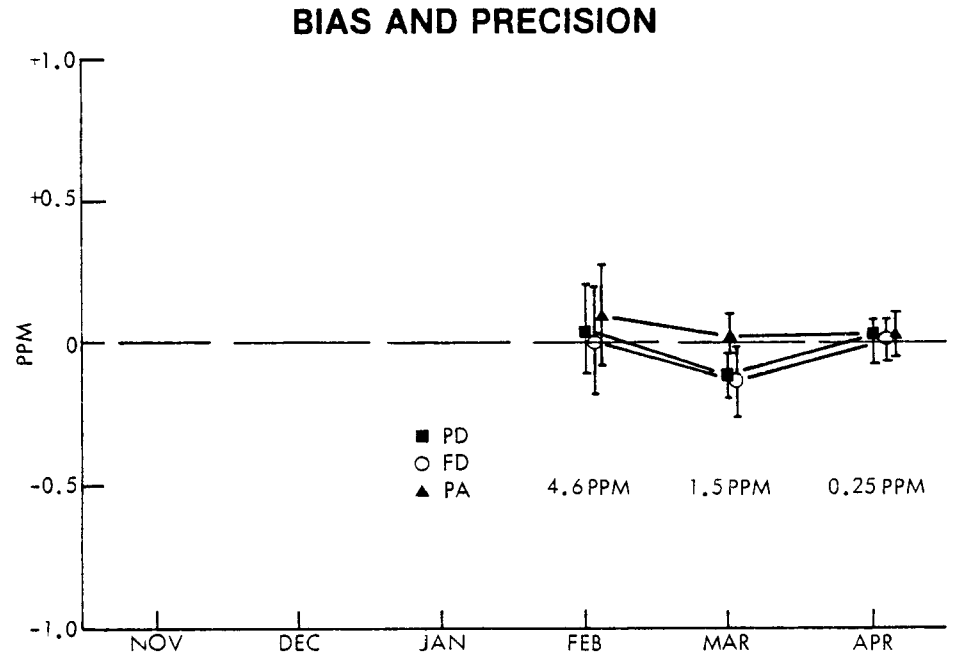

Figure 8. Analyzer bias, compared to the FA channel, and precision.

TABLE 1. TEST FOR INTERFERENCES

Compound	Effect
Dichloromethane	None
Acetaldehyde	None
cis-1,2-Dichloroethane	None
1,1-Dichloroethane	None
Chloroethane	None
Chloroform	None
Chloromethane	FID only
Isobutane	Both

TABLE 2. EFFECT OF GENERAL INSTRUMENT VARIABLES

Variable	Effect
Backflush time	Strong
Carrier pressure	Strong
Main air pressure	Strong-low
Valve air pressure	Moderate-low
Oven air pressure	None

TABLE 3. EFFECT OF SPECIFIC INSTRUMENT VARIABLES

Variable	Effect
Analog integration	
Integration stop time	Moderate-PID
Integration start time	Weak
Digital integration	
Baseline scan forward	Weak
Noise factor	None
Leading edge offset	None
Trailing edge offset	None
FID detector	
Fuel pressure	Strong
Flame air pressure	None

OVERVIEW OF SEMICONDUCTING GAS SENSING DEVICES

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The measurement of low concentrations of gases in air and of chemicals in water is becoming of increasing importance. For this reason, there is a need to develop less expensive equipment to make these measurements. Low cost, quick and easy-to-use sensors with sufficient selectivity, sensitivity and durability are needed. Now, more and more attempts are being made to satisfy these requirements through the use of sensors made from semiconductors and transistors. These sensors have several potential advantages such as, miniaturization, speed and long service life.

We believe a new type of gas detector, an integrated silicon sensor or sensor-on-a-chip, will be introduced into many new applications in the next few years. The purpose of this paper is to give an overview of some of the present work and predict future developments.

The object of the work on integrated sensors is to take advantage of the advances made in recent years in the microfabrication of various potential sensors, such as ion-selective field-effect transistors (ISFET) and metal-oxide-semiconductor field effect transistors (MOSFET). Bergveld[1] was first to propose a sensor based on a modification of a MOSFET where the gate metal was replaced by an aqueous solution. This resulted in a device in which the channel conductance appeared to be a function of the ionic concentration of the solution. Bergveld called this device a CHEMFET or an ion sensitive field effect transistor. Since this work, other researchers - Zemel[6], Lundstrom[3], Senturia[5], Krey, et.al.[2] - have prepared and tested these devices as sensors.

A metal-oxide-semiconductor field effect transistor (MOSFET) is shown in Figure 1. The substrate material is p-type silicon with a source and drain of n-silicon. The gate is a metal film evaporated over a thin insulating layer of

SiO_2. With no voltage on the gate, the source and drain are insulated from each other. When a positive voltage is applied to the gate, electrons are attracted to the surface of the silicon. This produces a thin conductive surface layer of induced n-type material (electrons) which now forms a channel connecting the source and drain. The number of electrons is directly proportional to the gate voltage so that the conductivity of the channel increases with gate voltage.

How does the MOSFET act as a sensor for a gas? One example is the mechanism proposed by Lundstrom[3] for the detection of hydrogen. It is known that a number of metals, palladium and platinum, adsorb and dissolve hydrogen. This occurs at the gate surface. Lundstrom explains: "Some of the hydrogen atoms diffuse through the thin metal film and are adsorbed onto the metal - SiO_2 interface. An equilibrium develops between the number of adsorbed hydrogen atoms on the surface and those at the interface. The number of adsorbed hydrogen atoms on the surface depends not only on the hydrogen present in the atmosphere, but also on the other gases present. The hydrogen atoms at the interface are polarized and this gives rise to a dipole layer which corresponds to a voltage drop ($\triangle V$) which is added to the external voltage Vg." This is shown in Figure 2 for a palladium MOSFET, and in Figure 3 for a palladium MOS capacitor.

Figure 4 illustrates the voltage necessary to keep a small, constant drain current on an n-channel Pd-MOSFET. This is called the threshold voltage and it depends on the hydrogen pressure and temperature. Structures such as those shown in Figures 2 and 3 have been used as sensors to detect gases in air as low as 5 PPB for H_2, 50 PPB for H_2S and 100 PPB for ammonia.

Non-hydrogenous gases cannot diffuse through the gate and, therefore, they cannot be detected by the sensor developed by Lundstrom. To detect carbon monoxide, for example, Krey and co-workers[2] modified the transistor to have a palladium gate with holes. In this way, carbon monoxide was able to reach the metal-oxide interface. When carbon monoxide is adsorbed at the Palladium-SiO_2 interface, a rise in the dipole layer occurred just as with hydrogen. Again, the threshold voltage increased with carbon monoxide pressure.

Although these palladium gate MOSFETs look very promising as sensors for hydrogen and carbon monoxide, there are some remaining problems. Lundstrom has reported that storage in oxygen gives a slow response the first time this sensor

is exposed to hydrogen. In some instances, a drift in threshold voltage due to so-called negative bias stress instability or hole trapping occurs. Another problem is poor palladium adhesion caused by phase changes in the palladium under high hydrogen pressure, even at low temperatures.

In addition to metal gate MOSFETs, Senturia[5] and researchers at Siemens in Germany[4] have worked with polymer and organic semiconductor coatings deposited on the gate region. Some minor success was achieved by the Siemen researchers but the objective of producing a usable gas sensor for gases such as CO, CO_2, SO_2 and NO with sufficient sensitivity, reproducibility and stability was not achieved.

The relative value of organic and inorganic sensing materials is yet to be defined. Many variables are important in this work - composition, film thickness, surface chemistry, and topography; therefore, much more work needs to be done to develop better gas sensors. Lundstrom, Zemel and others have outlined several areas of research needed to improve the sensitivity and selectivity of gas sensors:

1. Metals and polymer coatings on the gate
2. Doping of gate metals
3. Porous gates
4. Insulator thickness
5. Insulator composition: SiO_2, Si_3N_4, Al_2O_3
6. Bulk composition
7. Device packaging.

The sensor work is interdisciplinary and now it appears that there is an increasing emphasis being placed on bringing together workers in the fields of chemistry, physics and electronics. The performance of chemical sensitive devices is only limited by the selection of the proper chemistry. This is a relatively new area for research and development. It has a high risk, but the potential payoff should also be high.

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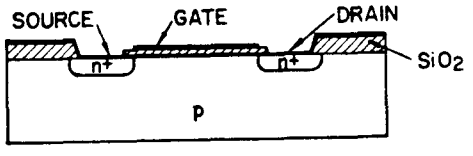

Fig. 1. Cross Section of a MOSFET.

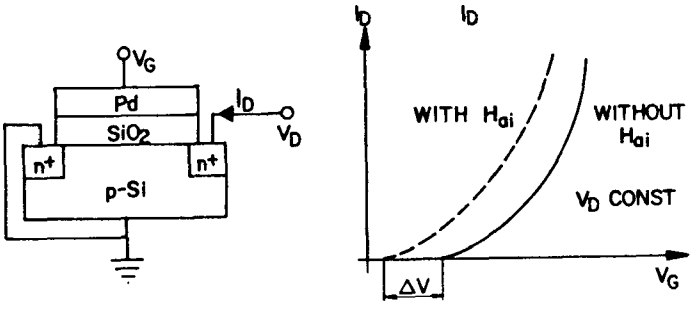

Fig. 2. Hydrogen Sensitivity of a Pd-MOS Transistor (from Ref. 3).

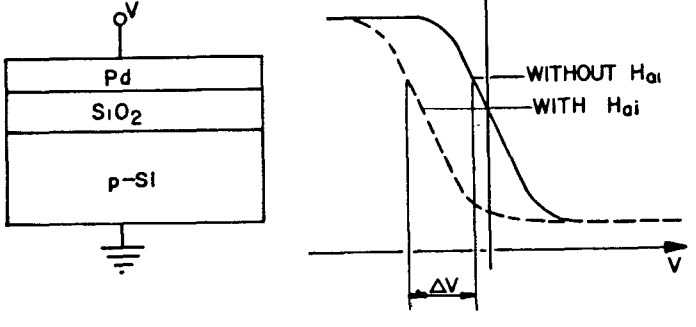

Fig. 3. Hydrogen Sensitivity of a Pd-MOS Capacitor (from Ref. 3).

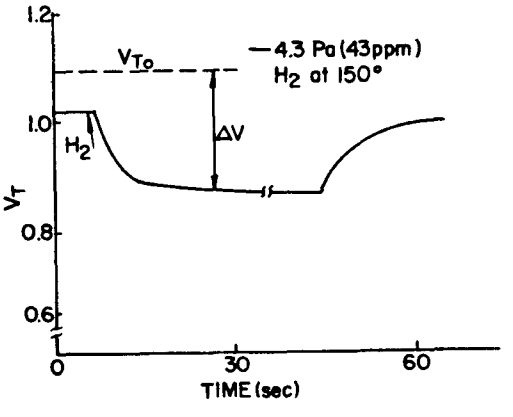

Fig. 4. Response of Pd-MOSFET to Hydrogen (from Ref. 3)

EXAMINATION OF CALIBRATION PRECISION CALCULATIONS AND PROTOCOLS FOR AIR MONITORING DATA

by James B. Flanagan

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Environmental Monitoring and Services Center
Chapel Hill, NC

The Clinical Environmental Laboratory (CEL) is an EPA research facility located on the campus of the University of North Carolina in Chapel Hill. CEL has been extablished for the study of the effects of exposure to priority pollutant gases on human subjects. Standard air monitoring equipment is used to monitor and control the pollutant gas levels during exposure sessions. These instruments are calibrated every few days using automated 3-point calibrations. Old calibration constants are superseded whenever a new calibration is performed.

This paper examines the hypothesis that by increasing the size of the ensemble of calibration data points, the net accuracy and precision of exposure session averages will improve as a result of the corresponding reduction in the calibration confidence interval. Ozone instrument calibrations provide actual data with which the theory is tested. It will be shown that drift and instrument nonlinearity complicate predictions made on the basis of simple statistical theory.

THE LINEAR REGRESSION MODEL

The following linear regression model is assumed for the instrument calibrations:

$$y_i = B\,x_i + C \qquad (1)$$

During calibration, the paired y_i and x_i values are assumed known, and the B and C constants are calculated from the ensemble of data pairs. The following assumptions are the basis for elementary linear regression applications:

1. Instrument response is linear in concentration.
2. The error variance of the output is independent of level.
3. Random errors are small compared to the total variation in levels.
4. The error in y is Normally and Independently Distributed.
5. Error in x is negligible relative to error in y.

PRECISION ESTIMATION FOR LINEAR REGRESSION

The confidence interval is a statistical estimate of the region about the calibration line in which a specified percentage (e.g., 95%) of additional (x,y) points taken under specified conditions would lie. Points taken subsequent to calibration are referred to in this paper as "probe" points. A "probe" of the calibration precision may be either a single data point or an average of a number of data points. In order to correctly assess the confidence interval about a regression line, the following additional conditions must be specified:

1. Estimating the Population Variance. If an instrument is calibrated without any knowledge of previous precision history, it is necessary to estimate the instrument's variance from the calibration data itself. In this case, it is necessary to use Student's t statistics to estimate the confidence region.

If (1) the instrument has a known history from which a prediction of its variance can be made, and (2) it can be statistically shown that the calibration is representative of the same variance, then the confidence interval can be derived using Gaussian probability tables.

2. "Probing" the Confidence Interval. Calibration curves are made using individual data points, such as 2-minute averages. The confidence interval for subsequently acquired "probe" points is dependent upon the method used to acquire these points. A For example, when the confidence interval for an hourly average is required. This confidence interval will be substantially narrower than the confidence interval for a 2-minute average. The following four equations represent the different cases:

Population Variance Unknown; Single Sample "Probe" of Precision:

$$p = t_{n-2} \cdot s_y \cdot (1 + 1/n + (x - x_m)^2/S_{xx})^{1/2} \quad (2)$$

Population Variance Unknown; q-sample Mean "Probe" of Precision:

$$p = t_{n-2} \cdot s_y \cdot (1/q + 1/n + (x - x_m)^2/S_{xx})^{1/2} \quad (3)$$

Population Variance Controlled; Single Sample "Probe" of Precision:

$$p = z \cdot \mathrm{sigma}_y \cdot (1 + 1/n + (x - x_m)^2/S_{xx})^{1/2} \quad (4)$$

Population Variance Controlled; q-sample Mean "Probe" of Precision:

$$p = z \cdot \mathrm{sigma}_y \cdot (1/q + 1/n + (x - x_m)^2/S_{xx})^{1/2} \quad (5)$$

where,

s_y - sample standard deviation of y about the regression line,
$sigma_y$ - population standard deviation of y variate,
z - Gaussian probability statistic for specified probability level,
t_{n-2} - student's t value for n-2 degrees of freedom,
x_m - mean value of x used in regression line data set,
x - any particular observation of x,
S_{xx} - sum of squares of $(x-x_m)$ for all x values,
q - number of points averaged for the "probe",
n - number of calibration points used in the regression line,
p - confidence interval half-width.

TESTING THE STATISTICAL PRECISION THEORY

Calibrations of CEL gas analyzers are done approximately every other day and results are archived. This provides a data set which can be used to test the theory of the single-point "probe" of calibration precision. First, a data set is designated as the calibration ensemble; data points from the next succeeding calibration are designated as "probe" data points. Next, differences are calculated between the calibration curve and the "probe" points. Finally, the confidence interval of the method can be investigated by accumulating ensembles of these differences and evaluating these by appropriate statistical means. If the basic assumptions listed above hold exactly, the statistical characteristics of the ensembles of differences should be exactly described by equations (2) - (5).

The actual ensembles of experimental data are constructed by taking a "moving window" j calibrations wide to calculate the B and C constants. The data points for the calibration immediately following are taken as "probe" points, and the differences added to the respective ensembles for each concentration/voltage level. The window is then moved one calibration forward in time, and a new set of j calibrations consisting of j-1 of the previously used calibrations and one new point is used to derive a second set of calibration constants. The window is moved in this manner until N differences are collected.

In the absence of bias, the mean squared error should equal the variance, and the ensemble mean would be zero. In the presence of bias, the mean square error exceeds the variance and the mean error is nonzero.

The standard deviation of the ensemble of differences should be related to the confidence interval. For a single-point "probe," such as the case here, the "theoretical" standard deviation would be:

$$E.S.D. = sigma \cdot (1 + 1/n + (x_i - x_m)^2/S_{xx})^{1/2} \quad (6)$$

where,

sigma - the true (unknown) standard deviation of the y variate,

E.S.D - expected standard deviation of an ensemble of n deviations at concentration level x_i,

n - number of individual points used in the regression: if j three-point calibrations are combined, then n=3j,

x_i - x-value: zero, midpoint, span, etc.

Figure 1 shows a plot of mean and standard deviation of the ensemble of differences computed as a function of number of combined calibration curves, j, used to derive B and C. The data are for a Bendix Ozone analyzer Model 8002, 0.1 ppm range, using the j most recent calibrations to form the ensemble of calibration points for the regression. Each point plotted is based upon an ensemble size of N=12 difference values. Also shown is the theoretical curve (E.S.D.) for the standard deviation given by eqn. (6). The solid curves in the figure refer to the expected standard deviation of eqn. (6), with the value of "sigma" being obtained by forcing the line through the first point. Examination of Figure 1 yields the following observations:

1. Agreement between the theoretical and experimental standard deviation curves as a function of j, the number of 3-point calibrations forming the regression set, is moderately good. This gives some confidence in the applicability of the theory represented by equations (2) - (5) to the CEL data.

2. The mean value of the differences increases as number of calibrations used to derive the regression coefficients B and C increases. Furthermore, for the midpoint data, the mean difference starts out negative, goes through zero and becomes positive at larger j values. Two effects appear to cause this behavior:

   a. Systematic drift leads to increasing mean error when older calibrations are included in the calculation of the regression lines.

   b. Nonlinearity of the instrument biases the mean deviation for the midpoint data.

3. The assumption of independence of variance from the concentration level is clearly violated. Physically, this probably arises from random flow and pressure errors which are simply "amplified" more at higher concentration levels.

PRECISION AND ACCURACY FOR SESSION AVERAGES

The work above used only a single point "probe" of the calibration precision; we have not yet addressed the precision for session averages, which is the actual quantity of interest. By using equations (2) - (5) above, we may make an estimate of the confidence interval when the "probe" is a mean of many 2-minute averages which comprise a session average. The correction factor for converting from a confidence interval for 2-minute averages to a confidence interval for session averages can be expressed as the ratio of eqn. (5) to eqn. (4), assuming that the session average is composed of q data points:

$$\text{Ratio of Improvement} = \frac{(1/q + 1/n + (x - x_m)^2/S_{xx})^{1/2}}{(1 + 1/n + (x - x_m)^2/S_{xx})^{1/2}} \qquad (7)$$

This ratio of improvement is applied directly to the ensemble Standard Deviations shown in Figure 1 to obtain the corresponding Standard Deviations in Figure 2. Since the bias may be assumed to be unaffected, the Mean Errors plotted in Figures 1 and 2 are identical. Total Error in Figure 2 is obtained as the square root of the sum of the squares of the corrected Standard Deviation and the Mean Error.

Since the Standard Deviation in Figure 2 is decreased, the bias error has more relative importance in the Total Error. Thus, the relative effect of drift and nonlinearity on precision for session averages is significantly greater than for individual 2-minute averages.

In summary, the data from the CEL gas data base illustrate the improvement in net precision and accuracy attainable by using larger calibration ensembles. Although combining historical calibration data points reduces the width of the calibration confidence interval, the systematic bias caused by drift and nonlinearity reduces the amount of improvement in total accuracy attainable.

REFERENCES

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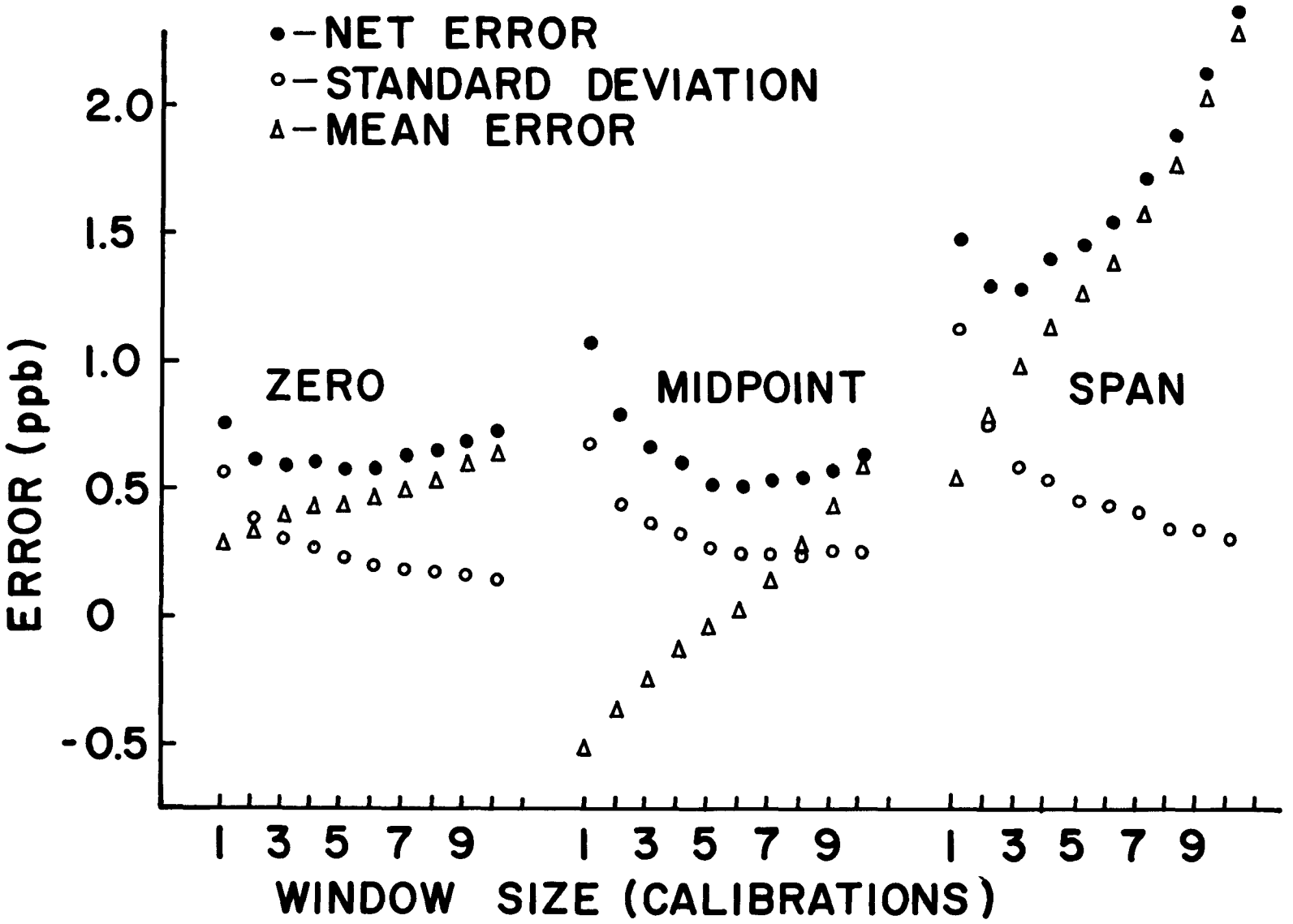

Figure 2. Errors associated with Session Means (q=60) as a function of number of historical calibrations included in regression ensemble.

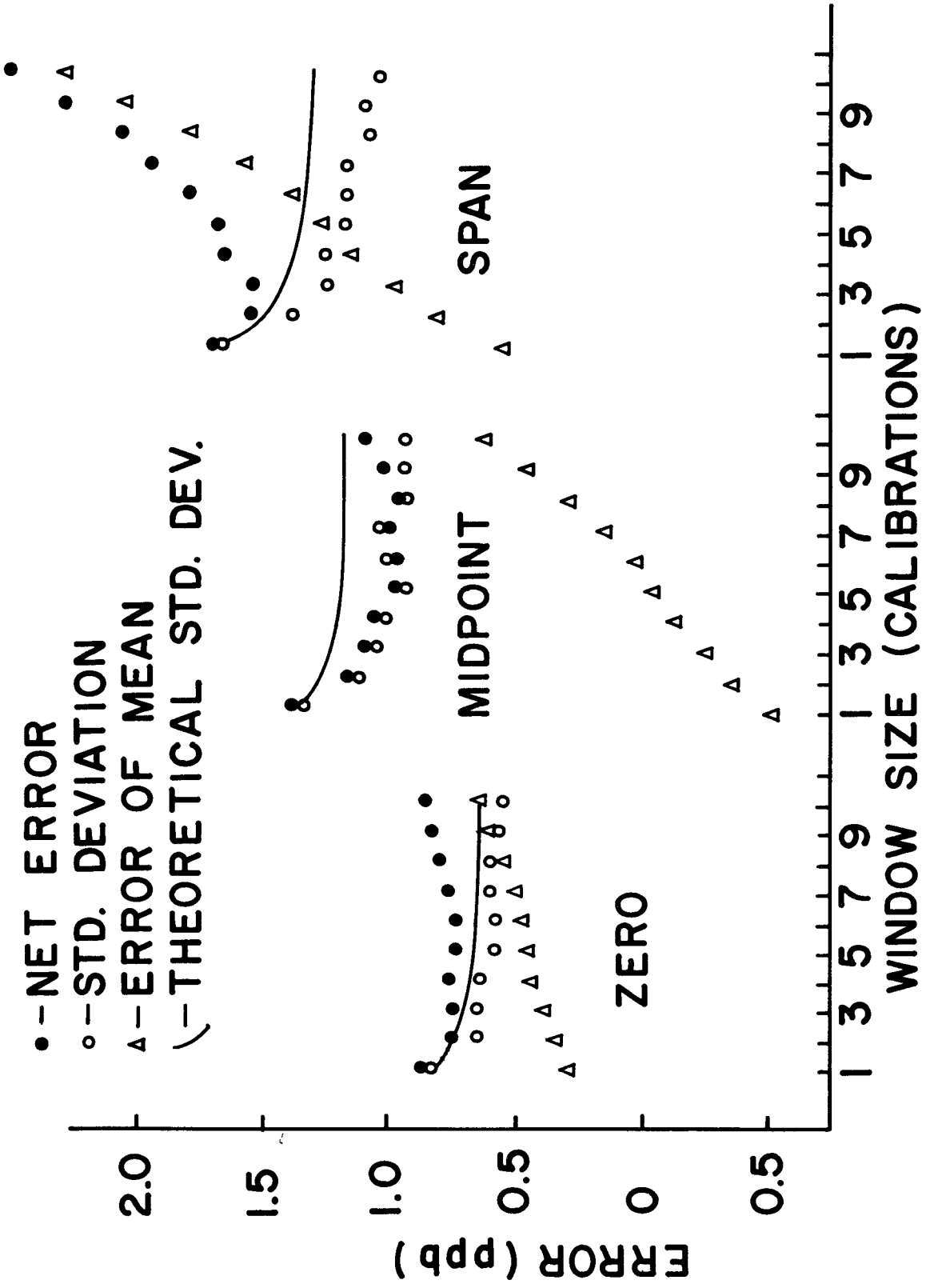

Figure 1. Errors associated with 2-minute averages as a function of number of historical calibrations included in regression ensemble.

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