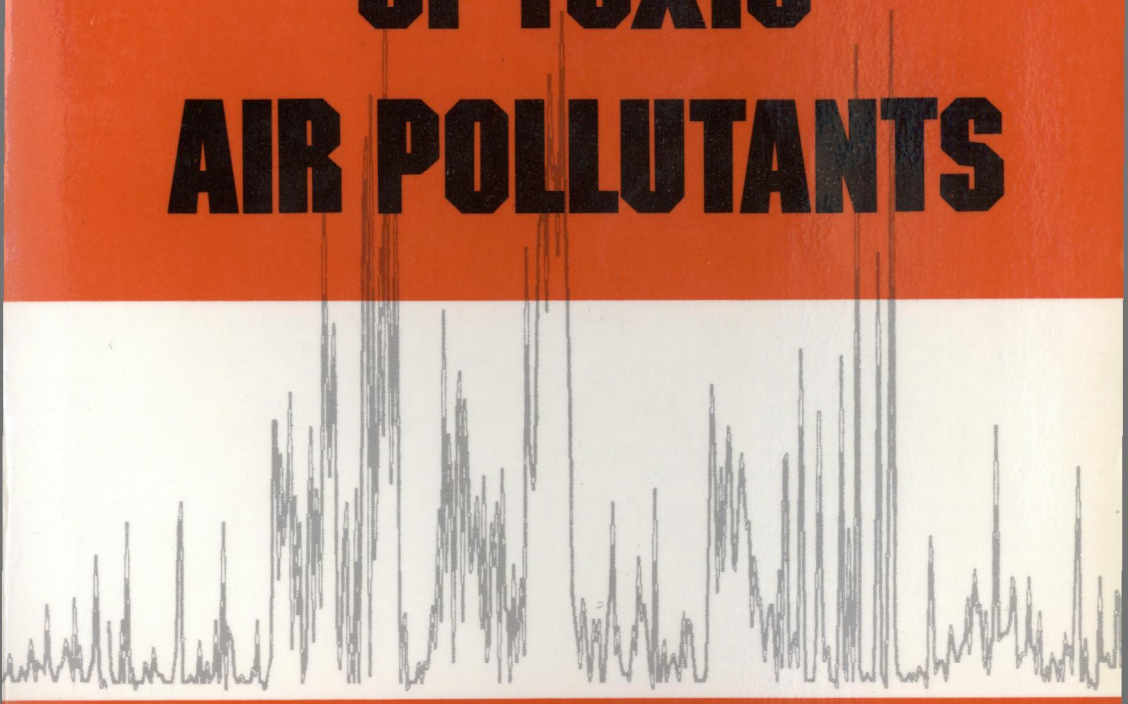
Proceedings of the 1986
EPA/APCA Symposium on

MEASUREMENT OF TOXIC AIR POLLUTANTS



U.S. Environmental Protection Agency's
Environmental Monitoring Systems Laboratory
Air Pollution Control Association

EPA/600/9-86/013
April 1986

Proceedings of the 1986 EPA/APCA Symposium on

MEASUREMENT OF TOXIC AIR POLLUTANTS

Sponsored by the
U.S. Environmental Protection Agency's
Environmental Monitoring Systems Laboratory
and the
Air Pollution Control Association

Raleigh, North Carolina
April, 1986

APCA Publication VIP-7

EPA Report No. 600/9-86-013

PROCEEDINGS OF THE 1986 EPA/APCA SYMPOSIUM ON MEASUREMENT OF TOXIC AIR POLLUTANTS

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PREFACE

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. EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, is responsible for research and development of new methods, techniques, and systems for detection, identification, and characterization of pollutants in emission sources and in indoor and ambient environments; implementation of a national quality assurance program for air pollution measurement systems; and supplying of technical support to Agency regulatory programs

A joint conference cosponsored by APCA's TP-6, TP-7, TT-9 Technical Committees and EPA's Environmental Monitoring Systems Laboratory was held in Raleigh, North Carolina, April 27-30, 1986. The technical program consisted of 95 presentations, held in ten separate technical sessions, on the recent advances for the measurement and monitoring of toxic and other contaminants found in ambient and source atmospheres. Covering a wide range of measurement topics and superbly supported by 16 instrumental exhibitors and other consulting service laboratories, the symposium was enthusiastically received by nearly 600 attendees from the United States and other countries.

This conference, the sixth in a series arranged each year by EPA/RTP, but the first jointly sponsored by EPA and APCA, was arranged with the following primary objective: to provide a forum for the exchange of ideas on the recent advances for the acceptably reliable and accurate measurement and monitoring of toxic and other pollutants found in ambient and source atmospheres.

The responses to this symposium represent an encouraging first step to the enhancement of our current measurement and monitoring capabilities. Presentations included: 1) Measurement of Indoor Toxic Air Contaminants; 2) Measurement of Semi-Volatile and Volatile Organic Pollutants in Ambient Air; 3) Chemometrics and Environmental Data Analysis; 4) Acidic Deposition-Nitrogen Species Methods Comparison Study; 5) Measurement of Hazardous Waste Emissions; 6) Measurement of Wood Stove Emissions; 7) Source Monitoring; and 8) General Papers Related to Quality Assurance and Particulate Measurements.

R. K. M. Jayanty and Seymour Hochheiser
Technical Program Chairmen

CONTENTS

MEASUREMENT OF INDOOR TOXIC AIR CONTAMINANTS

Indoor Air Quality Measurements: Emerging Technologies	J. J. Wesolowski	1
A Method to Measure Exposure to Passive Smoking	S. Katharine Hammond	16
Passive Smoking: Survey Analysis of Office Smoking Areas Versus Climatic Chamber Studies	Charlene W. Bayer	25
Airborne Viable Microorganisms in Office Environments: Sampling Protocol and Analytical Procedures	J. A. Otten	36
Intercomparison of Sampling Techniques for Toxic Organic Compounds in Indoor Air	C. W. Spicer	45
Passive Sampling Devices for NO_2	James D. Mulik	61
Development of an Adsorption/ Thermal Desorption Technique Coupled with GC/MS for the Monitoring of Trace Organic Contaminants in Indoor Air	Cecilia C. Chan	71
Measurement of Organic Emissions from Indoor Materials--Small Chamber Studies	Bruce A. Tichenor	86
Approaches to Air Pollution Monitoring and Control in Submarine	MVR Koteswara Rao	95
Total Volatile Organic Compounds (VOC) in the Indoor Air of East Tennessee Homes	Richard B. Gammage	104
Indoor Pollutants in 70 Houses in the Tennessee Valley Area: Study Design and Measurement Methods	C. S. Dudney	116
Source Emissions Database for Indoor Air Pollution	Jane M. Crum	128

MEASUREMENT OF SEMI-VOLATILE ORGANIC POLLUTANTS IN AMBIENT AIR

Problems Associated with Sampling for Semivolatile Organic Chemicals in Air	Robert G. Lewis	134
Field Evaluation of Phase Distribution of PAH	Robert W. Coutant	146
Evaluation of a Denuder-Based Gas/Particle Sampler for Chlorinated Organic Compounds	N. D. Johnson	156
Pesticides and Other Organics in Fog	D. E. Glotfelty	168

Ambient Monitoring of Semivolatile Organics Using High-Volume Sorbent Samplers--Critical Quality Control Features and Other Considerations in Sample Collection and Network Design	Gary T. Hunt	176
Analysis of Polyurethane--Florisil Cartridges to Monitor Polychlorinated Biphenyls in Ambient Air	Tom W. Campbell	205
Evaluation of the EPA High-Volume Air Sampler for Collection and Retention of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans	Fred L. DeRoos	217
Measurements of Hazardous Air Pollutants in the Emissions of German Municipal and Industrial Waste Incinerators and Afterburner Chambers	Edgar Heckel	230
Application of Orifice Meter to Ambient Dioxin Sampler	Frank D. Buckman	239
Application of Supercritical Fluid Chromatography to the Analysis of Semivolatile Organic Compounds in Airborne Particulate Matter	Robert D. Zehr	250
Development of Improved HPLC Analyses for Nitrated Polycyclic Aromatic Hydrocarbons and Quinones from Airborne Inhalable Particulate Matter	Arthur Greenberg	259
Electrochemical Detection in the HPLC Analysis of Nitro-Polynuclear Aromatics	Barbara B. Kebbekus	269
Instrumentation for Sampling and Characterization of Toxic Gaseous and Some Particulate Air Pollutants	Joseph P. Krasnec	275

MEASUREMENT OF VOLATILE ORGANIC POLLUTANTS IN AMBIENT AIR

Signatures of Atmospheric Aerosols: Cohesion of Changes in Organic Compound Concentrations	Robert E. Sievers	287
Receptor Modeling: A Promising Alternative to Traditional Source Apportionment Methods	Glen E. Gordon	304
Preconcentration and Analysis of Atmospheric Organics Using a Carbon Hollow Tube--Gas Chromatography System	G. P. Cobb	314

Analysis of Vinyl Chloride Monomer in Ambient Air by Gas Chromatography	Jeffrey C. Rogers	326
Continuous Ambient Monitoring of Vinyl Chloride in the Part Per Billion Range Utilizing the Photovac 10S Gas Chromatograph	Joseph J. Kliment	330
Ambient Monitoring for Eight Toxic Air Pollutants at Three Sites in Philadelphia	Edward Chasz	335
Industrial Emission Impacts in the New Jersey Environment: Results from a Study Near a Barrel and Pail Manufacturing Plant	John Jenks	351
Implementing a Quality Assurance Program for Sampling and Analysis of Ambient Air Toxics Compounds	William E. Oslund	364
NMOC Concentrations Measured Aloft	Hal Westberg	375
Field Applicability and Precession of a Whole-Air Sampling Method for Ambient Air Volatile Organic Compound Determination	Dennis D. Lane	385
Canister-Based VOC Samplers	William A. McClenny	402
Comparison of 0600-0900 am Hydrocarbon Compositions Obtained from 29 Cities	William A. Lonneman	419
An Air Sampling System for Measurement of Ambient Organic Compounds	Dave-Paul Dayton	431
1984 and 1985 Nonmethane Organic Compound Sampling and Analysis Program	Robert A. McAllister	442
Self Service Station Vehicle Refueling Exposure Study	Andrew E. Bond	458

CHEMOMETRICS AND ENVIRONMENTAL DATA ANALYSIS

Computer Assisted Interpretation of Gas Chromatography/Mass Spectral Data from Complex Mixtures	W. J. Dunn, III	467
Applications of Information Theory and Pattern Recognition to Gas Chromatography-Mass Spectrometric Analysis of Toxic Orgaic Compounds in Ambient Air	Donald R. Scott	476
Using Three Dimensional Graphics to Visualize Multivariate Scientific Data	S. L. Grotch	488
Source-Receptor Analysis of Volatile Hydrocarbons Collected in New Jersey	Mardi Klevs	500

Estimating Specific Source Exposures to Toxic Air Pollutants — Sylvia A. Edgerton — 513

ACIDIC DEPOSITION-NITROGEN SPECIES METHODS COMPARISON STUDY

Performance and Results of the Annular Denuder System in the Sampling and Analysis of Ambient Air Near Los Angeles — J. E. Sickles, II — 522

GENERAL SESSION

A Simplified TEM Analysis Method for Asbestos Abatement Projects — George Yamate — 534

A Near Real-Time Instrument for Monitoring Total, Combustible, and Ash Particulate from Incinerators — Richard E. Gibbs — 542

Ambient Atmospheric Concentrations of Toxic Metal and Toxic Organic Species in New York State Urban Environments — Robert Whitby — 554

A Continuous Isokinetic Gas/Mist Sampler for Flue Stream Extractive Analysis — Jan E. Kolakowski — 574

Defining Ambient Impact of Volatile Organic Compounds Emitted from an Automobile Assembly Facility — Peter E. Dahlgren — 594

Quality Assurance for Non-Routine Air Measurement Programs: EPA's Experience with the National Dioxin Study — Richard V. Crume — 601

Alkalinity Testing of Hi-Vol Filters by a New Method — Rita M. Harrell — 615

Precision and Accuracy of State and Local Agency Ambient Air Monitoring Data — Raymond C. Rhodes — 627

MEASUREMENT OF HAZARDOUS WASTE EMISSIONS

Some New Cost-Effective Approaches for Measuring Organics Associated with Hazardous Wastes — R. B. Gammage — 639

Surface-Enhanced Raman Spectroscopy: Detection of Hazardous Chemical Pollutants — T. Vo-Dinh — 651

A Flux Chamber/Solid Sorbent Sampling System for Volatile Organic Air Emission Monitoring from Hazardous Waste Land Treatment Systems: Field Results — R. Ryan Dupont — 662

Application of Capillary Gas Chromatography/Mass Spectrometry to the Volatile Organic Sampling Train (VOST) Assay to Facilitate Characterization of Products of Incomplete Combustion	Thomas A. Buedel	674
Evaluation of the Semi-VOST Method for Measuring Emissions from Hazardous Waste Incinerators	Joann Rice	685
Determination of Organic and Inorganic Chlorine in Used and Waste Oils	Alvia Gaskill, Jr.	701

MEASUREMENT OF WOOD STOVE EMISSIONS

Evaluating the Field Performance of High Efficiency and Catalytic Wood Stoves	S. Morgan	713
A System to Obtain Time Integrated Woodstove Emission Samples	James E. Houck	724
Residential Wood Combustion Impacts on Indoor Carbon Monoxide and Suspended Particulates	Mallory P. Humphreys	736
A Refinement of the Potassium Tracer Method for Residential Wood Smoke	James W. Buchanan	748

SOURCE MONITORING

Toxic Air Pollutant Emission Measurement Techniques for Non-Steady-State Processes: A Case Study with Ethylene Oxide	Pankaj R. Desai	755
A Universal Sample Introduction System Suitable for VOC Analysis in Ambient Air, VOST, Water and Solid Samples	Thomas J. Wagner	764
Evaluation of Method 25 Nonmethane Organic Analyzer Design	Maurice Jackson	780
Development and Validation of Source PM10 Measurement Methods	Ashley D. Williamson	792
Studies of Measurement Methods for Chlorine and Chlorine Dioxide Emissions from Pulp Bleach Plant Operations	Robert P. Fisher	804
Laboratory and Field Evaluation of a Modified EPA Method 5 Train and Atomic Absorption Spectrometry for the Measurement of Cadmium in Stationary Source Stack Gases	R. F. Moseman	817

Sampling and Analytical Method for Measuring Methylene Chloride Emitted from Stationary Sources	A. L. Sykes	826

GENERAL SESSION

A Sensitive Direct Measurement NO_2 Instrument	H. I. Schiff	834
Direct Ambient Nitrogen Dioxide Measurement by Visible Light Absorption	John Jung	845
A Comparison of Methodologies for the Extraction of Sulfate Ion from Size-Differentiated Particles Collected on Filter Media	Dennis D. Lane	856
Fourier Transform Infrared Spectroscopy (FTIR) Ammonium Sulfate Analysis on Teflon Air Filters	Martin J. Pollard	865
Sublimation Sources for Nitrous Acid and N-Compounds in Air	Robert S. Braman	875
Utilization of a Class I, Non-Specific Adsorbent, Carbotrap, for the Prediction of Sampling	William R. Betz	882
Development of Data Quality Indicators for Toxic Air Pollution Measurements	Gary L. Johnson	893
Index		903

INDOOR AIR QUALITY MEASUREMENTS: EMERGING TECHNOLOGIES

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Measurement techniques must be geared to the specific needs of the environmental programs they serve. Some of the differences among the three programs on air quality (occupational, outdoor, and indoor) will be outlined and the implications for measurement technologies will be discussed. Two examples of emerging measurement technologies will be given. The first is the development of the Ames Salmonella assay using a desiccator for the detection of vapor-phase mutagens from indoor sources. Data for emissions from a gas range, a kerosene heater, the process of frying hamburgers, and cigarette smoke will be presented. The second technique is the use of immunoassays (similar to those used for the detection of infectious agents) using monoclonal antibodies for the detection of airborne toxics in environmental and clinical specimens. The immunoassay approach may provide simple, rapid, and cost-effective analysis of large numbers of samples. Preliminary data on the development of antibodies to various nitroarenes are discussed.

INDOOR AIR QUALITY MEASUREMENTS: EMERGING TECHNOLOGIES

Introduction

Measurement techniques should be geared to the needs of the environmental program they serve (e.g. indoor, outdoor, or occupational) and, indeed, within a given program to specific tasks (e.g. source apportionment, monitoring, mitigation, etc.). Although Indoor Air Quality (IAQ) measurement studies have appeared in the literature for years, it has only been recently that numerous and extensive field and laboratory studies have been reported. Thus, a solid tradition of methods development, quality assurance, and standardization of methods has not been established yet for this fledgling field. The beginning of such a tradition may be emerging (note the activities of the ASTM sub-committee on Indoor Air for example). To some extent this may be due to the fact that many of the scientists involved in IAQ studies have been, or still are, associated professionally with the outdoor and occupational fields, thus bringing to the IAQ field years of experience in methods development, standardization, and quality assurance. Although there is a great deal of commonality associated with the outdoor, indoor, and occupational fields, there are also many differences, some of which will influence the directions of emerging measurement technologies. This paper will discuss some of these differences and give two examples of emerging measurement technologies.

Air Sampling Strategies

Characterization of indoor, outdoor, and occupational air each requires a different air sampling strategy. Table I displays differences in locations of measurement sites. One can reasonably characterize outdoor pollution or determine attainment of outdoor air quality standards with a relatively small number of research or monitoring locations within an air basin. This is not true for the occupational or indoor programs, particularly the latter which demands that a rather large subset of a given microenvironment be sampled to characterize air quality. This creates a more pressing need for inexpensive and rapid measurement methods than required by outdoor programs. Table II shows differences in types of measurements and instrumentation characteristics. Again the demands made by the indoor program are the most severe. Table III shows some of the differences with respect to the sources of pollution. These differences demand different emission measurement approaches. Consider the differences in measuring emissions from automobiles (gm/mile), industrial stacks (gm/hr), and building materials (gm/hr/m^2).

Bioassays for Organic Chemicals

One area of particular concern to those responsible for method development is organic measurements. Although there are many specific organic compounds that must be measured in the workplace, most individual sites will have processes that emit a small number of chemicals at a time. In outdoor air the organic mix can be quite complicated. However, the indoor environment offers the greatest organic measurement challenge, since the number of organic compounds as well as the concentrations are usually greater indoors than outdoors, particularly for office buildings (1). Thus besides methods for specific compounds it will be useful to have methods with broad specificity which detect classes of compounds (e.g. the Ames bioassay as a measure of chemical mutagens). Although such surrogate methods are certainly useful in the occupational and outdoor programs, the special needs of the IAQ problem may provide the major driving force to the measurement community to develop and standardize these methods.

This paper will describe two relatively new and non-traditional approaches to the measurement of air pollution which we believe will be important parts of the emerging measurement technology. The two are the Ames bioassay and immunoassays. The paper will conclude with a suggestion for combining these methods to determine the contribution of specific mutagens to the total mutagenicity of a complex environmental mixture.

The Ames Bioassay

The Ames bioassay has been used successfully in characterizing outdoor air for a number of years (2, 3, 4, 5). However, only a few studies in the indoor environment have been carried out (6, 7, 8). This is partly due to the lack of sensitivity of the standard plate assay and the difficulty of using high volume samplers indoors to collect sufficient samples. The recent development of the microsuspension assay, a modification of the standard test which is about ten times more sensitive than the original, makes feasible the mutagenic characterization of indoor air (9).

To demonstrate the sensitivity of the test, indoor/outdoor (I/O) mutagenicity ratios were obtained for a three-story Berkeley office building. Samples were taken at 8-hour intervals using an automated dichotomous sampler operating at 50 lpm. The results are given in Figure 1 and show clear diurnal patterns. The mean indoor/outdoor (I/O) ratio is 0.7, suggesting that indoor concentrations are influenced primarily by outside sources (smoking is not permitted in the building). In fact, this modification of the test is sensitive enough to allow two-hour time resolution (10).

Almost all the efforts thus far to estimate the mutagenicity of air using the Ames assay have focused on particulate matter. Those characterizing the vapor phase have usually yielded only qualitative results (11). This does not imply the vapor phase is not important, but rather that the standard Ames test lends itself more readily to characterizing the particulate phase. However, the amounts of vapor phase organics are much greater than organics in POM. In order to begin to rectify this situation, we have developed a desiccator system using the standard plate assay. The method was first tested in a study of the mutagenicity of the vaporous (as well as particulate) emissions from various indoor sources. The work was carried out in a 35 m^3 environmental chamber (cf. Figure 2), and was done in cooperation with the Lawrence Berkeley Laboratory. Particulate matter was collected on 47 mm diameter EPM 2000 fiberglass filters at a flow rate of 45 lpm. For vapor phase mutagen detection, polluted air from the chamber was passed through a desiccator containing Salmonella plates at a flow rate of 0.5 lpm. Particles were prefiltered with a glass fiber filter (EPM 2000). The particulate mutagenicity was obtained using the microsuspension method, while the vapor mutagenicity was measured using the desiccator plate method. More experimental details can be found in references 12 and 13.

The data are displayed in Figures 3 and 4. The particle phase mutagenicity was highest for strain TA98 (with or without metabolic activation). The reduction of activity for TA98NR suggests the presence of certain nitroarenes in the emissions. The vapor phase mutagenicity was much higher for TA100 than TA98. Caution must be exercised in making comparisons between particle and vapor phase mutagenicity since the relation between the microsuspension and the desiccator methods has not been established. The figures do demonstrate that the desiccator method is sensitive enough to obtain vapor phase emission mutagenicity.

Immunoassay Methods For Chemical Analysis

The introduction stressed the need for simple, rapid, and inexpensive methods for detection and quantitation of organic chemicals. This section discusses efforts to develop such methods, using modifications of immunoassay techniques used in the fields of virology to detect viruses, and clinical chemistry to detect drugs. The preliminary work described here will focus on efforts to prepare monoclonal antibodies that bind to certain nitroarenes. These direct acting mutagens were chosen because of their importance in environmental samples, particularly as a result of the combustion process of diesel engines (14, 15). Recent analysis of urban aerosols also suggests that some nitroarenes are formed in the atmosphere (16).

Immunoassays use antibodies as a probe for detecting naturally occurring antigens such as viruses and bacteria. Although there are a number of different types of immunoassays, they all have as a basis the measurement of the competition for binding to antibody between an unknown amount of the specimen antigen and a known amount of labelled antigen. Antigens are usually labelled with radioactive or fluorescent molecules to aid detection. The crucial step in developing an immunoassay for a small organic molecule is the production and characterization of antibodies to the chemical of interest. The discussion to follow will refer to the development and characterization of antibodies to the nitroarenes, but it should be noted that the technique is applicable to a large number of compounds. (Indeed there is a sizable literature on pesticides (17)). More detail on immunoassay techniques is found in reference (18).

Figure 5 gives a scheme of the general steps that are followed in the development of monoclonal-antibody based immunoassays, for the detection and quantitation of organic compounds. The process consists of several stages:

i.) induction of antibody-producing cells in mice by immunization with the compound of interest;

ii.) establishment and cloning of these cells in culture;

iii.) characterization of the antibodies secreted in the cultures with respect to sensitivity and specificity of binding to the compound of interest.

Antibody Production

The first step in the production of antibodies is the inoculation of animals with the antigen of interest. Organic compounds, (referred to as haptens), must first be chemically conjugated to carrier proteins before they can be used to elicit an immune response in animals. Hapten-protein conjugates were made for nitrofluoranthene using keyhole limpet hemocyanin (KLH) and bovine serum albumin (BSA).

The nitrofluoranthene hapten was made by nitrating fluoranthenebutanoic acid (19), conversion to the methyl ester and chromatography on silica gel. This separated the non-nitrated starting material from the various isomers of nitrofluoranthene butanoic acid methyl ester. These isomers were resolved by normal-phase high performance liquid chromatography (Figure 6). HPLC analysis determined that the mixture contained five nitrated isomers whose structures were determined by proton NMR after ester hydrolysis (Figure 7).

The nitrofluoranthene butanoic acid isomer mixture was conjugated with protein by the mixed anhydride method (see reference 18 for details). This hapten-protein conjugate was next inoculated into mice. The immune response of the mouse causes B lymphocytes in the spleen to become programmed to secrete antibodies directed against the conjugate. Some lymphocytes secrete antibody to the protein carrier portion of the conjugate, others to the nitrofluoranthene portion.

Cell Fusion, Screening and Cloning

Three to four days after inoculation the animal is sacrificed, and the cells are teased from the excised spleen. These cells are then "immortalized" by fusion with mouse myeloma cells (cf. ref. 18). These fused cells are apportioned into multi-well plates for culturing. Cells that grow in these wells are called hybridomas, because they have acquired genetic traits from both the immunized spleen cells and the myeloma. These hybrids can be grown in culture indefinitely.

Next, a screening procedure is used to seek out cells producing antibodies to the hapten of interest, if indeed any have been produced. The hybridomas growing in the multi-well plates are screened by a qualitative nitrocellulose spot immunoassay (20).

In those fusions where numerous positive wells are observed, a competition enzyme-linked/immunosorbent assay (ELISA) is then performed to select those wells with the greatest specificity to the analyte of interest. (cf. ref. 18). Those wells with the greatest reaction with the antigen (analyte) of interest and the least competition from similar antigens (analytes) are chosen for cloning.

The purpose of cloning is to select individual hybridoma cells which secrete the desired antibody and then grow these cells as single clones. This is done by serially diluting the hybridoma culture and splitting it into hundreds of separate wells (using 96-well culture plates) so that there is approximately one living hybridoma cell in each well. After clones divide to give several hundred cells each, the wells are screened with the nitrocellulose spot assay to determine which clones are indeed making the desired antibodies.

Antibody Characterization

The antibody produced must be characterized with respect to two important properties: 1) the ability of the antibody (Ab) to react with the antigen (Ag), and 2) its ability to cross react with different antigens (analogous to interference properties in chemical methods). The complexing of Ab and Ag is described by an association (or affinity) constant, which determines the sensitivity of the immunoassay. It is measured by using different amounts of antibody and antigen and measuring the amount of the resulting complex. This is done by using standard immunoassays such as ELISA or radioimmunoassays. The cross-reactivity to different compounds (and hence the specificity to the molecule of interest) is also determined by using competition immunoassays with compounds closely related to those of interest.

It should be noted that in the present examples, the mouse was immunized by injection with the conjugate containing several isomers (e.g. all five isomers of nitrofluoranthene). Different clones gave antibodies of varying specificity and affinity, including some which cross-reacted with molecules of substantially

different structures from that of the immunogen. For example, two clones were highly specific for 7- and 8-nitrofluoranthene, respectively, and showed negligible cross-reactivity with all other nitroarenes tested as competitors. Those reacting preferentially with the 3-isomer of nitrofluoranthene (3-NF), on the other hand reacted equally well with 1-nitropyrene, possibly as a result of the 1-nitronaphthalene moiety in common to these two molecules. Among these latter clones was at least one which cross-reacted with 2-nitrofluoranthene (2-NF) and at least two which showed no reactivity with 2-nitrofluoranthene. The immunization of even a single mouse is thus capable of producing a "library" of monoclonal antibodies with a useful spectrum of reactivities. Figure 8 shows the results of two radioimmunoassays carried out for one of these clones. In the first assay, tritium labeled 3-NF was mixed with antibody and various amounts of unlabeled 3-NF. The amount of radioactive Ab:Ag complex was measured. Increasing the amount of unlabeled 3-NF decreases (inhibits) the measured radioactivity since the 3-NF competes with the ^{3}H-3-NF for the antibody (not enough antibody is added for binding all the ^{3}H-3-NF plus unlabeled 3-NF). The second curve is a similar experiment done with ^{3}H-3-NF plus unlabeled 2-NF. The figures indicates that 2-NF does not compete with ^{3}H-3-NF for the antibody. This 3-NF curve is analogous to the "standard curve" used in calibrations for chemical methods. Note that only thirty-five nanograms of 3-NF caused a 50% inhibition. The detection limit is even less (five-ten nanograms). We believe this method can be made several orders-of-magnitude more sensitive through technical modifications.

Advantages of the Immunoassay Method

Although chemical methods using sophisticated analytical instrumentation have achieved impressive levels of sensitivity and specificity in recent years, they are often slow, expensive, and usually require extensive sample preparation or clean-up procedures. The last not only adds complexity to the technique but also risks underestimating the concentration through inadvertent loss of analyte. Antibody-based detection techniques have the following advantages, which should make them useful compliments to the more traditional chemical methods:

i.) sensitivity: Many immunoassays currently used in clinical chemistry detect in the picogram range: some model systems have detected as little as a few attograms (10^{-18} gm) (21).

ii.) specificity: At one extreme, the use of monoclonal antibody technology has allowed us to produce antibodies specific for individual isomers of a single compound. Other antibodies cross-react with a variety of compounds of similar structure. This could be very useful in environmental studies in which detection of a broad structural catagory is desired. An example would be the detection of dibenzodioxins or polychlorinated biphenyls, which possess numerous isomers with potential health effects.

iii.) speed and ease-of use: It is important to separate the development of monoclonal immunoassays from their use. Although their development requires a major research effort, once operational, such assays should permit the analysis of many hundreds of samples per day without the need for highly skilled workers or expensive equipment.

iv.) standardization: The immunoreactivity of conventional (polyclonal) antibodies obtained from individual immunized animals is variable.

Once a hybridoma cell is "immortalized", however, it provides a constant source of invariant antibody which could be shared and standardized among laboratories.

Although there is much to be done to completely characterize and validate the immunoassay method, the advantages of the method appear sufficient to warrant the effort.

Combining Immunoassays and Bioassays

Both the immunoassay and the Ames bioassays described above should prove useful in characterizing indoor air quality as well as emissions from outdoor sources. The former will be most useful in detecting specific compounds or classes of compounds, while the latter mostly will be used for establishing relative mutagenicity. In order to identify the mutagens, i.e. the specific compounds causing the mutagenicity, as determined by the Ames test, we plan to combine the two methods as follows.

Environmental samples will be split and one half treated with antibody before both portions are subjected to the Ames assay. If antigen (hapten) specific to the antibody used is present in the sample, the mutagenicity of the treated half will be less than the untreated. The amount of inhibition will depend on the quantity of this chemical present. The proposed system should be useful, for example, in the detection of nitrofluoranthene isomers which are known to have high specific mutagenicities, but occur at low levels which are marginally detectable by physico-chemical methods. Such specific compounds may make a substantial contribution to the total mutagenicity, but cannot be discriminated by conventional Ames assays which measure only total mutagenicity. Of course, this strategy of antibody-mediated activity may also be generalized as an adjunct to a wide variety of physico-chemical methods. For example, half a sample could be treated with a specific antibody, or panel of antibodies, prior to HPLC analysis and the suppression of specific chromatographic peaks (as compared to the spectra of the non-treated half) would provide identification. It should be noted that conclusive identification of a suppressed peak will depend on the completeness of our knowledge of antibody cross-reactivities (analogous to the "interference" properties of a chemical method).

This approach would be most useful in "accounting" for the mutagenicity of environmental samples, i.e. determining the percentage of the total mutagenicity caused by the presence of specific chemicals. This "mutagenicity balance" would be analogous to the "mass balance" achieved for total suspended particulate matter.

Summary and Conclusions

The paper has attempted to demonstrate some of the differences among measurement needs for the indoor, outdoor, and occupational environments. It also gave two examples of emerging measurement technologies, one the reasonably well-developed Ames bioassay and the other a novel approach using monoclonal immunoassays. We anticipate that new measurement technologies will emerge based on these approaches, and they will compliment the traditional physico-chemical approaches. Thus, the successful environmental laboratory of the future will require a multi-disciplinary staff and view.

Acknowledgements

We appreciate the efforts of Felipe Moteclaro, Her-Lin Su, and Jun-Zhuo Liu in carrying out much of the laboratory work in developing the immunoassay method.

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TABLE I. LOCATIONS OF MEASUREMENT SITE

Occupational:	Worksite - Either Personal or Area Sampling
Outdoor:	Air Basin Sampling - Need Sufficient Number of Stations to get Averages Representative of Community Air.
Indoor:	Many Different Types of Microenvironments (Residences, Mobile Homes, Schools, Offices, Planes, etc.)

TABLE II. MAJOR MEASUREMENT NEEDS

	Types of Measurements	Special Instrumentation Characteristics
Occupational:	Mainly Chemicals (≈ 500)	Portable Personal Relatively inexpensive
Outdoor:	Meteorological Parameters Chemical (O_3, CO, NO_2, SO_2, TSP, Pb, Some Organics)	In general can be relatively noisy, expensive, and large
Indoor:	Air Exchange Chemical (Many) Biological (Fungi, Molds, Bacteria, Viruses) Tobacco Smoke	Portable Personal Relatively inexpensive Quiet

TABLE III. SOURCES OF POLLUTION

Occupational:	Worksite (Process oriented)
Outdoor:	Mobile, Stationary (Point and Extended)
Indoor:	Outdoor infiltration, consumer products, building materials, people and their activities, pets

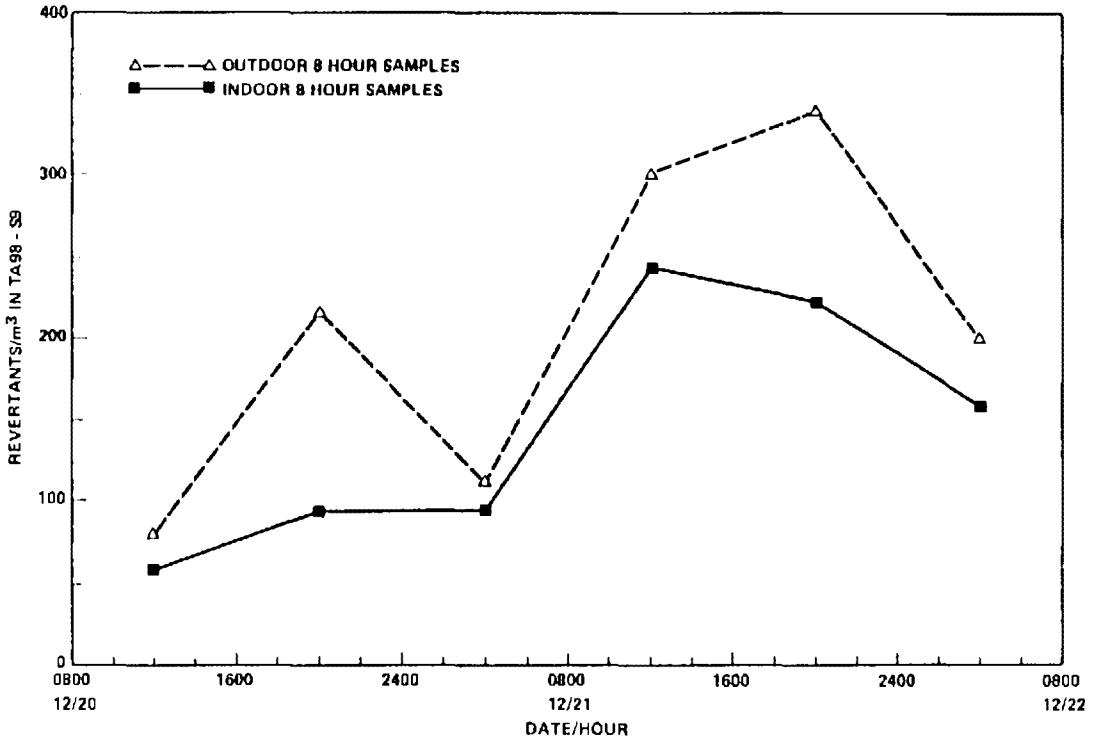


Figure 1. Mutagenicity of particles less than 2.5 μm aerodynamic diameter using a modification of the Ames test without metabolic activation inside and outside a Berkeley office building.

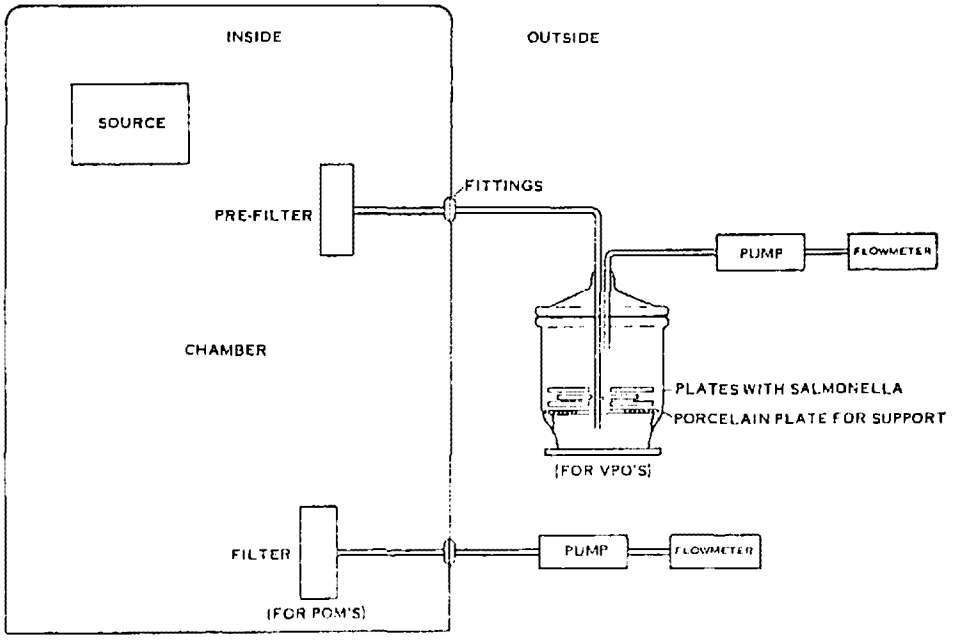
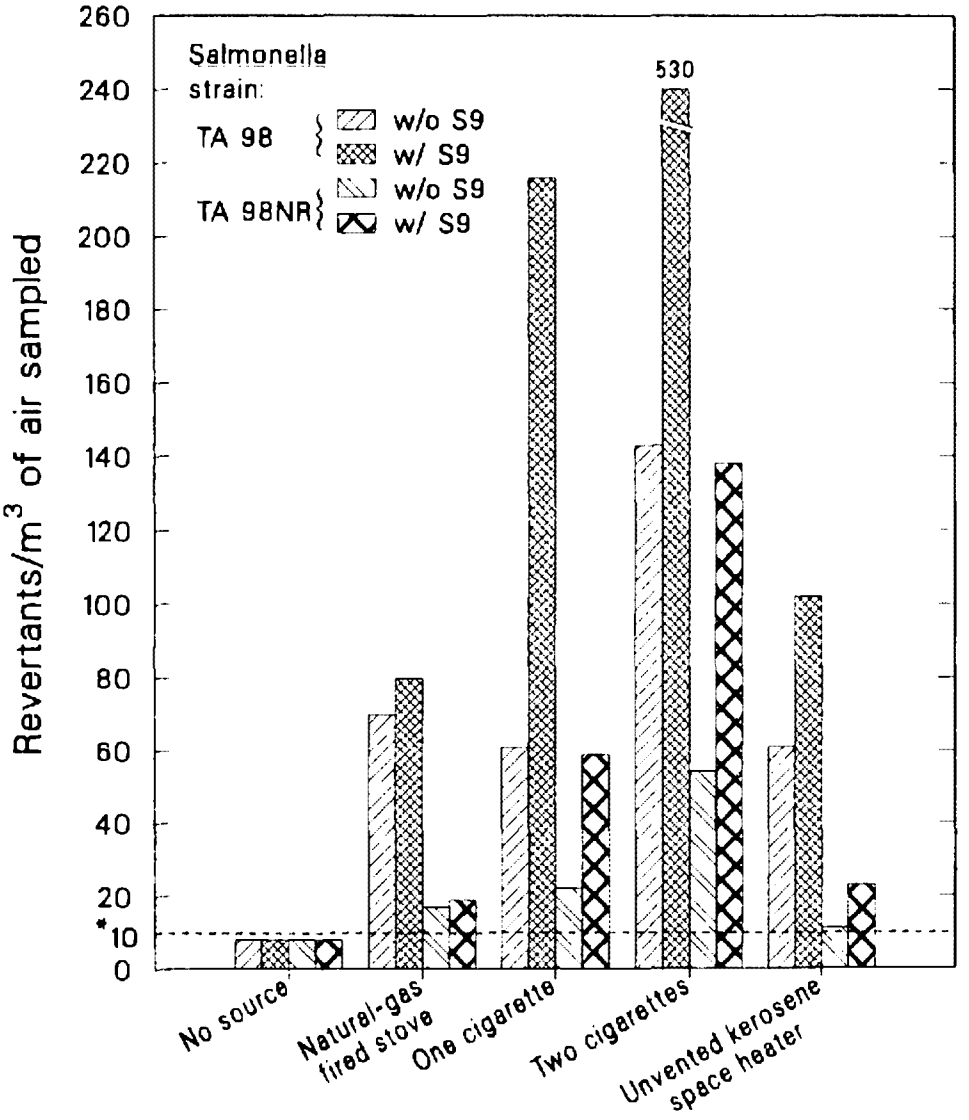
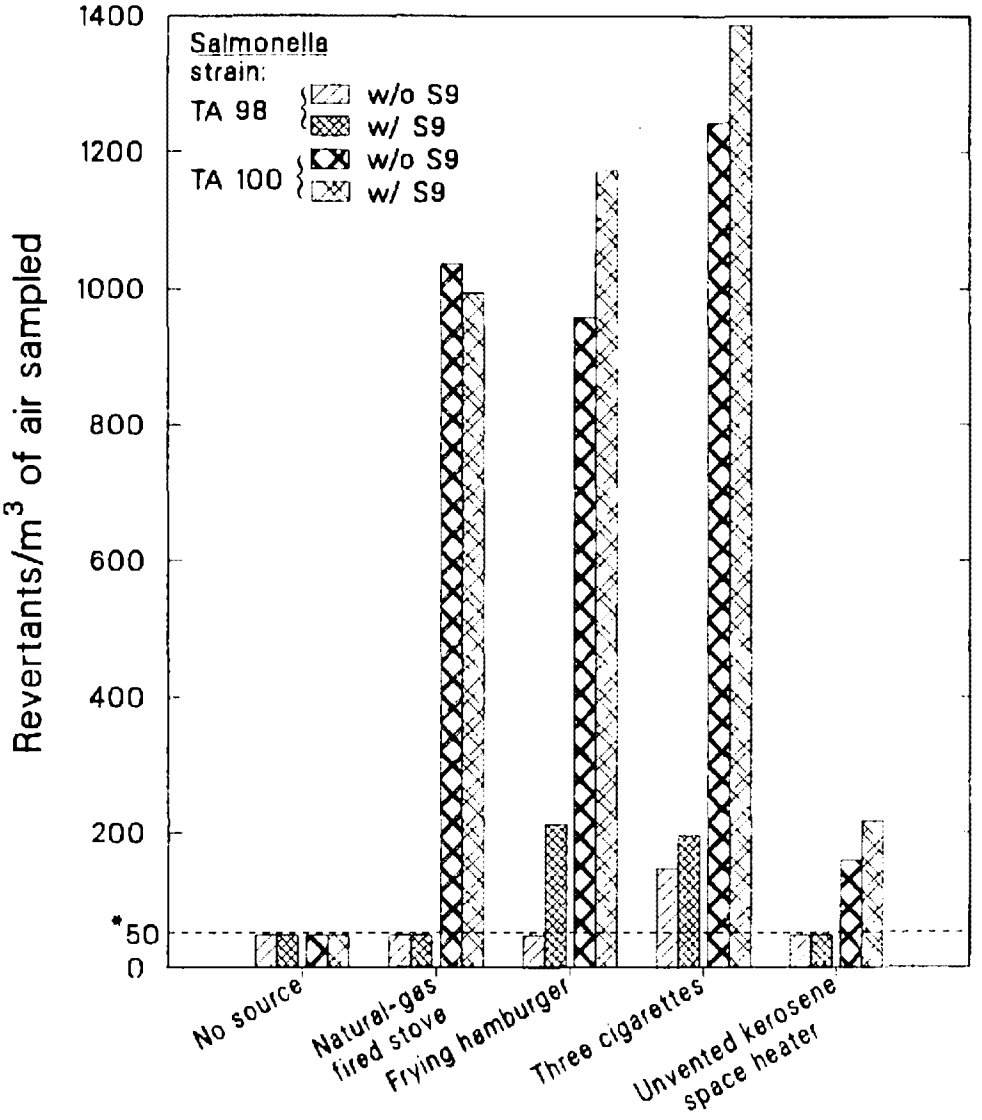


Figure 2. A schematic drawing of the chamber experiments for collecting vapor-phase organic (VPO) and particulate organic matter (POM) samples.



Nominal mutagenic threshold

Figure 3. Particle-phase mutagenicity emitted from various sources. Sources were operated in a 35 m^3 environmental chamber and samples were collected on fiberglass filters at a flow rate of 45 lpm.



*Nominal mutagenic threshold

Figure 4. Vapor-phase mutagenicity emitted from various sources. Sources were operated in a 35 m^3 environmental chamber. After prefiltration, air from the chamber was passed over plates in a desiccater at a flow rate of 0.5 lpm.

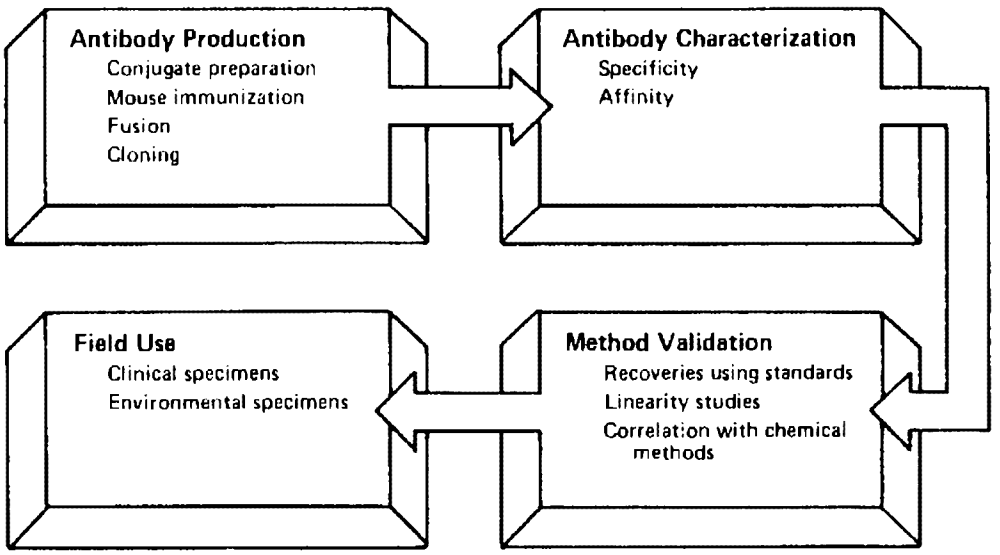


Figure 5. Scheme for the development of monoclonal antibody-based immunoassays for the detection and quantitation of organic compounds.

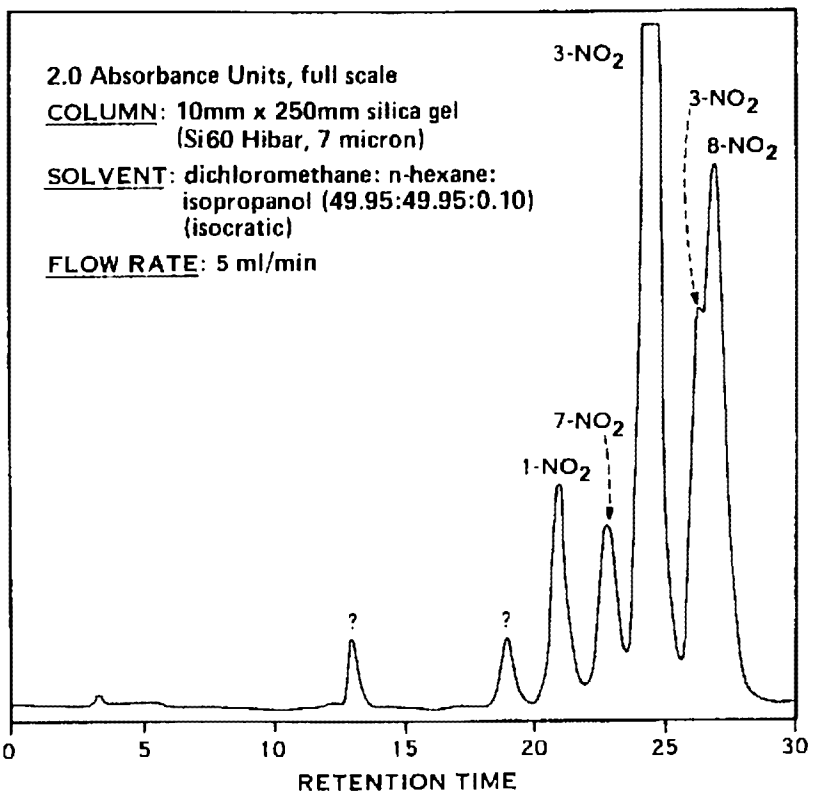


Figure 6. HPLC elution profile of methyl esters of nitrofluoranthene-butanoic acid.

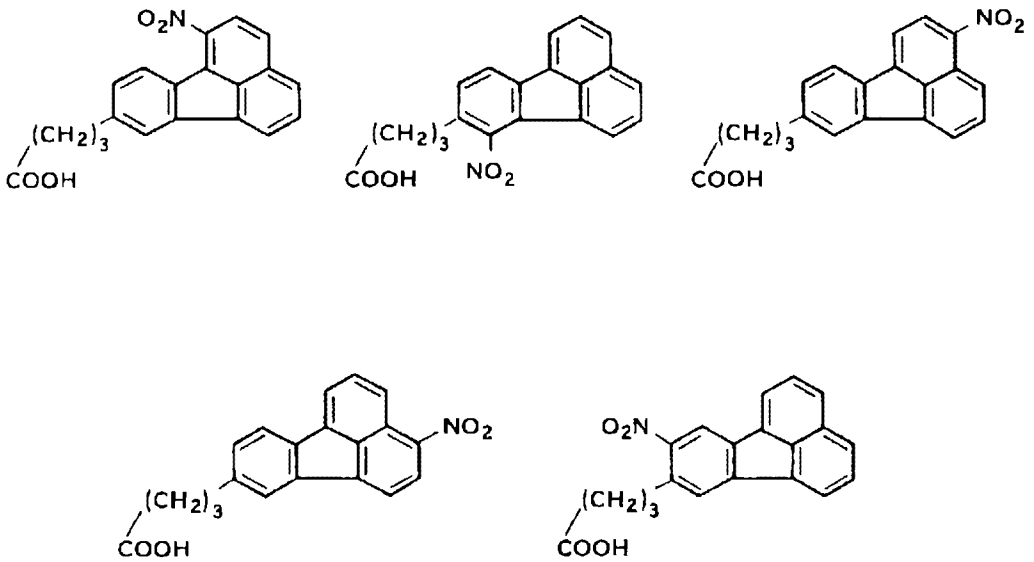


Figure 7. The five isomers of nitrofluoranthenebutanoic acid.

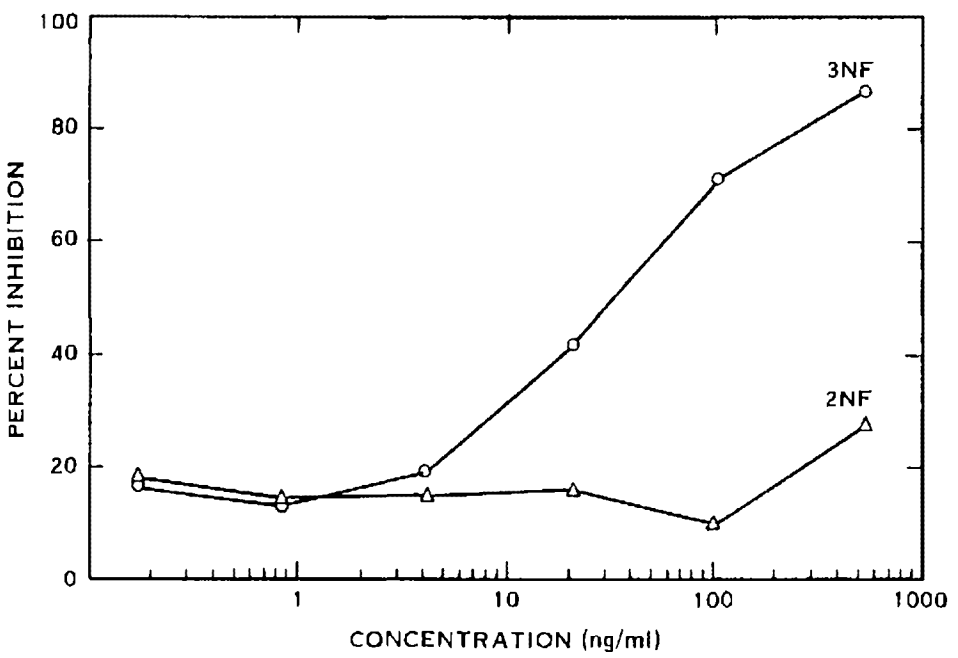


Figure 8. Inhibition of 3H-3-nitrofluoranthene-antibody binding by unlabeled 3-nitrofluoranthene (o) and 2-nitrofluoranthene (Δ) in a competitive radioimmunoassay.

A METHOD TO MEASURE EXPOSURE TO PASSIVE SMOKING

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Concern about the health effects of passive smoking and the large segment of the population exposed to environmental tobacco smoke (ETS) have contributed to the need to develop a method to measure exposure to ETS. Because tobacco smoke is complex mixture, it is difficult to measure. Nicotine was chosen as a marker in these studies because, unlike other markers often used, tobacco smoke is the only important source of nicotine. Nicotine was collected efficiently on filters treated with sodium bisulfate; it was then desorbed and analyzed by gas chromatography with nitrogen selective detection. This method can detect 1 ug nicotine/m^3 in samples collected in one hour. The method was tested in an environmental chamber in which people smoked selected brands of cigarettes. The ambient nicotine concentrations were found to be similar despite the fact the cigarettes had varying nicotine yields in the mainstream smoke. The ratio of nicotine to particulate matter in ETS was also found to be constant. Personal samples of nicotine exposure were collected from the breathing zone of office workers who were found to be exposed to up to 28 ug/m^3 of ETS throughout an eight hour work day.

A METHOD TO MEASURE EXPOSURE TO PASSIVE SMOKING

Introduction

Environmental tobacco smoke (ETS) is an important component of indoor air pollution. Concern about the health effects of passive smoking and the large segment of the population exposed to ETS have contributed to the need to develop a method that would assess that exposure.

Measuring passive smoking is important for several reasons. Several governmental agencies have already regulated or are considering regulating smoking in public places. One method often used is segregating smokers from non-smokers. Although such separation is widely used, the effectiveness in reducing the exposure of nonsmokers to ETS has not been studied. Such a study would require a method to measure ETS.

Epidemiological studies which examine the possible adverse health effects of passive smoking have been hampered by the lack of a good measure of exposure to ETS. Without such a measure, epidemiological studies have classified people into exposed and unexposed groups based on other data. In many studies the nonsmoking spouses of smokers are compared with the nonsmoking spouses of nonsmokers. For instance, Hirayama[1] reported a higher risk for lung cancer among wives of smokers than among wives of nonsmokers. A similar study[2] in the United States failed to find such an association. Such studies assume that nonsmoking spouses of nonsmokers are unexposed to ETS. However, these people may be exposed to ETS at work, in restaurants and bars, at meetings, and even at Bingo parlors. Such misclassification underestimates any possible health effect which might be observed. Among couples in which neither partner smoked, forty to fifty percent of the individuals reported some exposure to passive smoking, and for fifteen percent the exposure lasted over ten hours per week.[3]

Questionnaires are another method commonly used to categorize people's exposure to ETS. However, individuals' perceptions of tobacco smoke exposure vary. Some people are quite sensitive to ETS and may report exposure in a situation which others do not notice at all. Probably those who are most exposed to passive smoking are generally least sensitive to it, and so answers to questionnaires can be quite misleading. In one study[3] nearly half of the nonsmoking wives of smokers reported no exposure to passive smoking in their homes, yet eighty-three percent of their husbands reported smoking ten or more cigarettes daily. Clearly an objective measure of exposure to ETS would enhance epidemiological studies.

Cigarette smoke is a complex mixture of thousands of compounds, and so a marker for ETS is needed. Several of the components of ETS have been used as tracers. Carbon monoxide is easy to measure and is a major component of ETS. However, there are many other sources of carbon monoxide, including gas water heaters, gas stoves and grills, and automotive exhaust. These produce carbon monoxide at levels comparable to that found in ETS, and so apportioning the carbon monoxide among the

sources would be required. This is difficult. Several studies have demonstrated that particle concentration rises with smoking, and so the concentration of particulate matter has been used as a marker for ETS. However, there are also many other sources of particles in the environment. This problem of lack of specificity for ETS plagues many of the other possible tracers. Some of the other substances used as markers for ETS include aromatic hydrocarbons, nitrogen oxides, acrolein, and polonium-210. Tobacco specific nitrosamines exist, but they are present in very low concentrations, and so their measurement is difficult.

We chose to examine nicotine as a candidate for an ETS tracer for several reasons. First, ETS is the only important source of nicotine in the environment. Secondly, nicotine is present in high levels in ETS, and sensitive methods are available for the analysis of nicotine, so even very low levels of ETS should be quantifiable.

Nicotine presents several challenges. The first is the variability of nicotine among different brands of cigarettes. Nicotine reduction in mainstream smoke is achieved by filtering the smoke, increasing ventilation, and other changes in the design of the cigarettes[4]. Much less variablity is found in the nicotine levels of sidestream smoke[5]. The variability of nicotine in ETS was tested in the experiments described in this report.

The second challenge is to collect the nicotine sample efficiently. One method that has been used frequently is to collect the nicotine with the particles on a filter. Badre et al.[6] demonstrated that nicotine spiked onto a filter is rapidly volatilized and lost during sampling. These investigators collected nicotine efficiently from cigarette smoke with three bubblers in series. Although this method is useful for area samples, bubblers are not appropriate for personal smapling, as the bubblers are awkward and subject to spillage and breakage. Two methods have been reported which collect nicotine on adsorbents. NIOSH[7] has published a method which uses XAD-2 resin and is intended to sample nicotine in occupational settings. Muramatsu et al.[8] report the use of an adsorbent sampler (Uniport-S coated with 10% silicon OV-17) designed to sample nicotine from ETS at low levels. For our own research we needed to collect both nicotine and particles, the latter for subsequent mutagenic and chemical analysis. However, adsorbent tubes may collect inefficiently at the higher flow rates used in respirable dust sampling (1.7 Lpm) and may generate excessively high pressure drops which strain the personal sampling pumps. Therefore we designed a two stage sampler in which two filters are held in series within a single cassette. The first collects particles and the second is treated with sodium bisulfate to collect vapor phase nicotine. After the laboratory development of this method, the collection efficiency was tested in an environmental chamber with ETS generated by smokers in the chamber. Then the sampler was used in the field with workers in offices and other locations as well as in a few public places. The development of this method is described in detail in another paper[9], but will be summarized here.

Experimental Methods

Particulate material was collected on a pre-weighed 37 mm Teflon coated glass fiber filter. Vapor phase nicotine was collected downstream on a similar filter which had been treated by saturating it with an aqueous solution of 4% sodium bisulfate. The two filters were contained within one cassette and were separted by a stainless steel support screen and a Teflon o-ring. For a subset of samples collected in the chamber a second treated filter was placed downstream from the first treated filter in order to check for possible breakthrough of the nicotine. Air was sampled at 1.7 Lpm with personal sampling pumps. For field samples a 10 mm nylon cyclone was employed to remove non-respirable dust from the particulate matter collected. The efficiency of the treated filter alone, which might be used when there was no need to collect the particles separately, was tested by assembling cassettes with two treated filters in series.

After sampling, nicotine was desorbed from the treated filters with an aqueous solution containing 5% ethanol. The nicotine free base was formed by adding sodium hydroxide. Nicotine was then concentrated by liquid/liquid extraction into 250 ul of ammoniated heptane. The solution was vortexed for one minute between each addition. An aliquot of the solution was removed and analyzed by gas chromatography with a nitrogen selective detector. Nicotine was extracted from the particles with dichloromethane; 200 ul of ammoniated heptane was added and the dichloromethane evaporated under nitrogen. An aliquot was then analyzed by gas chromatography.

Samples were analyzed on one of two gas chromatographs (GC): the first was a Shimadzu GC-7A GC equipped with nitrogen selective detector, Shimadazu FTD-7 and a Shimadzu autosampler, AOC-7; the second was a Hewlett Packard 5890 GC with a nitrogen detector. All integrations were performed on a Hewlett Packard 3392A integrator. A six foot long, one eighth inch diameter stainless steel column of Chromosorb W coated with 10% Apiezon L containing 3% KOH was used to analyze the nicotine. The column temperature was 225 °C. Because the nitrogen detectors were both found to be somewhat unstable, a standard solution was run before and after each sample.

An all aluminum environmental chamber with a total volume of 34 m^3 was used in experiments testing the efficiency of the sampler and the levels of nicotine generated by different brands of cigarettes. The temperature, humidity, ventilation, and mixing in the chamber were all carefully controlled. The fresh air ventilation rate for all experiments was set at approximately 2.5 air changes per hour. A recirculation rate of 1000 L/sec was used to ensure near ideal mixing and thus prevent any horizontal concentration gradient of the generated air contaminants in the chamber. The chamber was maintained at a temperature of 23 °C and a relative humidity of 50%. During all experiments four smokers occupied the test chamber. They smoked cigarettes serially at the rate of 8 cigarettes per hour over a period of 5 hours. Each cigarette was smoked for 7.5

minutes; this provided a continuous source with one cigarette being smoked at any given point in time.

Four brands of cigarettes with varying rated nicotine contents in the mainstram smoke, as reported by the Federal Trade Commisssion, were used in these experiments. Each experiment employed only one brand of cigarette. The cigarettes were conditioned prior to smoking at a temperature of 23 °C and a relative humidity of 50%. They were weighed before and after smoking, without butts, to determine the toal amount of tobacco consumed during air sampling.

Results

The desorption of nicotine from the treated filter and the concentration into heptane was found to be greater than 95% efficient for different levels of nicotine ranging from 0.04 ug to 50 ug added to the filter. The particles contained only 2.7% of all the nicotine recovered in these chamber experiments. The first treated filter collected 97.3%, and the second, backup, treated filter collected less than 0.1%. Therefore, the treated filter was judged to be efficient in collecting nicotine. In experiments in which the sampler consisted only of two treated filters, without the front filter to collect particles, there was slightly more nicotine on the second treated filter, ranging from 1 to 5% of the total. Thus, the treated filter alone was also efficient in collecting nicotine.

The limit of detection by the GC with nitrogen selective detection was 0.01 ug per filter. Recovery studies were performed as low as 0.04 ug nicotine added to a filter. The limit of detection of nicotine in air would depend on the sampling rate and time. If a conservative analytical limit of detection of 0.1 ug nicotine is assumed, and samples are collected for one hour at 1.7 Lpm, nicotine levels in air as low as 1 ug/m^3 can be measured. Lower levels can be detected with longer sampling times.

The nicotine yields in mainstream smoke of the cigarettes tested ranged from 0.1 to 1.3 mg per cigarette (Table I). Despite this wide range, the ambient nicotine concentrations generated by smoking these cigarettes under controlled conditions showed much less variability, with values between 77 and 111 ug/m^3. The total particulate mass also did not vary as much among the different brands of cigarettes as might be expected from mainstream yield data. Additional chamber studies[10] with ten different brands of cigarettes confirm this consistency. Furthermore, the ratio of nicotine to total particulate mass demonstrated even less variability, with an average value of 0.073 ± 0.009.

Table II presents the nicotine concentrations found in personal samples worn by railroad workers throughout an eight hour work day. Exposure to ETS, as measured by nicotine, depends both on the number of cigarettes smoked and the job, or, more accurately, the degree of enclosure. The repair workers spend most of their time outdoors, and so nonsmoking repair workers had very little exposure to ETS. By contrast,

nonsmoking office workers were exposed to between 0.1 and 28.2 ug nicotine/m^3, with a mean exposure of approximately 8 ug/m^3 for 18 workers. The importance of the degree of enclosure or ventilation in determining exposures to ETS can be demonstrated by the different exposures on two successive days of a freight car repair worker who was also a heavy smoker. On each day this man smoked 17 cigarettes during the work shift. On the second day he worked in a confined space, inside a freight car he was repairing, and his exposure to ETS was nearly ten times as great as on the first day, when he worked outdoors. It is important to remember that the samplers are measuring exposure to environmental tobacco smoke, and not mainstream smoke inhaled directly through the cigarette by the smoker, which is much more concentrated.

A few, not especially representative, samples have been collected in some public places. Nicotine levels found ranged from less than detectable when no smoking occurred, through a few ug/m^3 with light smoking, to 60 ug/m^3 in places with heavy smoking.

Discussion

The treated filter method described here is suitable for personal sampling and is quite sensitive. Nicotine levels as low as 1 ug/m^3 can be measured in one hour samples. This compares to a senstivity of approximately 0.4 ug/m^3 for one hour samples collected on adsorbent and thermally desorbed, as reported by Muramatsu et al.[8]

Little difference was found in the levels of nicotine generated by cigarettes with widely varying nicotine concentrations in mainstream smoke. Also, the ratio of nicotine to particulate matter generated by the cigarettes showed even less variability among the different brands. Therefore, nicotine appears to be an appropriate marker for ETS from different brands of cigarettes.

The levels of nicotine found in offices in this study ranged from 0.1 to 48 ug/m^3 time weighted average over an eight hour day. These are similar to values found[8] in offices sampled by other efficient collectors of nicotine, in which concentrations ranged from 9 to 32 ug/m^3 in one office and from 14 to 26 ug/m^3 in another. The few restaurants and bars evaluated in this study had nicotine levels ranging from less than detectable for those with no smoking to 60 ug/m^3, which compares with values measured by other researchers[6] in cafes of 25 to 52 ug/m^3.

Several research questions remain to be answered. The method of collecting nicotine reported here does not distinguish between vapor phase nicotine and nicotine originally in the particulate phase and stripped from the particles during sampling: both forms of nicotine would be collected by the treated filter. The distribution of nicotine between the vapor phase and the particulate phase in ETS must be determined. Nicotine in mainstream smoke is primarily in the particulate phase, but sidestream smoke has a higher pH than mainstream, and so a greater proportion of the nicotine

would be in the more volatile, free base form. If nicotine is present in the vapor phase in environmental tobacco smoke, it might serve as a marker for the vapor phase, which contains many toxic compounds including several carcinogenic volatile nitrosamines. The fact that the ratio between nicotine and particulate matter varied so little among the different brands of cigarettes tested in the chamber indicates that nicotine may serve as a marker for the particulate phase as well. Additional research must be conducted to see if the ratio remains consistent under varying environmental conditions including temperature, relative humidity, ETS concentrations, and with different surfaces.

Although nicotine may be a marker for ETS, it is not of intrinsic interest. The composition of ETS, which is an aged mixture of sidestream smoke and exhaled mainstream smoke, must be studied further. The compounds of interest from a public health perspective must be identified, their levels in ETS measured, and ratios between their concentrations and that of the tracer materials established.

Levels of nicotine and other components of ETS in homes and in public places should be measured. The use of an ETS-specific tracer such as nicotine can be used to determine the levels of ETS to which a nonsmoker is exposed in various settings. Data must be collected to determine the effectiveness of methods proposed to control public exposure, such as increased ventilation and the establishement of smoking and nonsmoking sections of restaurants and airplanes.

Models to estimate ETS levels must be developed. This will require further information on the determinants of ETS concentrations, including number of cigarettes smoked over given time periods, infiltration/ventilation rates, room size, number of people, and deposition of markers such as nicotine by surfaces and possible re-emission.

Acknowledment

Research described in this article was conducted under contract to the Health Effects Institute (HEI), an organization jointly funded by the United States Environmental Protection Agency (EPA) (Assistance Agreement X812059) and automotive manufacturers. It is currently under review by the Institute. The contents of this article do not necessarily reflect the view of HEI, nor do the necessarily reflect the policies of EPA or automotive manufacturers. Additional support for this work was obtained from the National Institutes of Health through Grant ES-00354.

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TABLE I.

NICOTINE LEVELS FOUND IN

ENVIRONMENTAL TOBACCO SMOKE

	Mainstream Nicotine Yield, mg/cig.	Ambient Nicotine Concentration, ug/m^3
Cigarette A	1.3	107
Cigarette B	1.1	111
Cigarette C	0.3	101
Cigarette D	0.1	77

TABLE II.

NICOTINE LEVELS BY JOB AND NUMBER OF CIGARETTES SMOKED

REPAIR WORKERS		OFFICE WORKERS	
# cig.	Nicotine, ug/m^3	# cig.	Nicotine, ug/m^3
0	0.0 to 0.3	0	0.1 to 28.2
14	16.1	9	48.0
9	3.8	9	25.1
17	4.2 (outside)		
17	41.1 (inside)		

PASSIVE SMOKING: SURVEY ANALYSIS OF OFFICE SMOKING AREAS VERSUS CLIMATIC CHAMBER STUDIES

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Tobacco smoke is recognized as a contributor to indoor air contamination. However, the extent of involuntary exposure to environmental tobacco smoke (ETS) is difficult to establish due to several factors. These include: the complexity of smoke composition, the variability of ETS composition, and the similarity of ETS constituents to those emitted from other sources of airborne contaminants. A study was undertaken to investigate these factors of ETS exposure. In this preliminary study, the smoking areas of several office facilities were investigated for the presence of volatile organic compounds (VOCs) which could be related to only ETS contamination. No attempts were made to relate the findings to quantitative amounts of ETS or other building factors.

Survey analyses were conducted in smoking areas of three office buildings for the presence of VOCs. Collection was on Tenax and Porapak Q with subsequent analysis by thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS). Nicotine was collected on cold Petri dishes and analyzed by gas chromatography with thermionic nitrogen-phosphorous detection. Inductively coupled plasma spectrometry was used to identify metals in the particulate portion. The compounds detected in the offices were compared with those identified from collection of smoke from an idling cigarette in a sidestream chamber.

The VOCs detected in the offices of each building were similar. Common VOCs detected included 1,1,1-trichloroethane, toluene, xylenes, and hydrocarbons. In several smokers' offices pptv levels of nitrogenous compounds were detected which are not common to the indoor atmosphere, but which have been identified

in cigarette smoke. These include: pyrrolidine, 2-methyl-1H-pyrrole, and 2-methylpropyl cyanate. Several metals, such as cadmium, chromium, and nickel, which are known to be present in mainstream cigarette smoke were detected in the offices of two smokers.

Additional investigations are planned to search for better methods for determination of ETS. Chamber studies will be employed which will closely simulate actual room conditions, but eliminate other unknown indoor contaminant sources.

INTRODUCTION

Environmental tobacco smoke (ETS) is recognized as a contributor to indoor air contamination. ETS can be defined to be a combination of sidestream smoke and exhaled mainstream smoke. The smoke is one of the most prevalent aerosols and is a major source of total suspended particles in the indoor atmosphere (1). Numerous acute and chronic health effects have been attributed to involuntary smoking, such as eye and throat irritation, headaches, rhinitis, chronic obstructive pulmonary disease, cardiovascular disease, and lung cancer (2).

The passive smoker is exposed to ETS. The extent of this exposure is difficult to establish due to several factors. These include the complexity of smoke composition, the variability of ETS composition, and the similarity of ETS constituents to those emitted from other sources of airborne contaminants. It is often difficult to determine if the source of indoor air contamination in an office environment is resulting from ETS or another contaminant source. Over 3000 volatile organic compounds (VOCs) have been identified in tobacco smoke (3). Many of these compounds are also emitted from other sources. Respirable particulates can result from numerous sources other than tobacco smoke such as combustion systems and construction materials. A study was undertaken to investigate these problems and to attempt to differentiate VOCs resulting from ETS from those outgassing from other sources in the building. In this preliminary study, the smoking areas of several office facilities were examined for the presence of VOCs which could be related to ETS contamination. No attempts were made to relate the findings to quantitative amounts of ETS or other building factors.

EXPERIMENTAL

Survey analyses were conducted in smoking areas of three office buildings for the presence of VOCs and nicotine. These results were compared to those obtained in nonsmoking areas and with outside samples. The data was also compared with that obtained from an idling cigarette enclosed in a sidestream chamber.

Preparation of Sampling Materials. VOCs were collected on both Tenax (60/80 mesh) and Porapak Q. Extensive cleanup of both adsorbents was required before sampling. The adsorbents were Soxhlet extracted in methanol for 24 hours and dried under a nitrogen stream. Two hundred mg Tenax or 500 mg Porapak Q were packed into glass sampling tubes which had been washed and baked in an oven. The tubes were then baked in a manifold under a helium flow for at least 18 hours. The Tenax tubes were baked at 270C, and the Porapak Q tubes were baked at 150C. The tubes were stored in air-tight containers for storage and carrying to-and-from the sampling site.

Nicotine was collected on glass Petri dishes. Prior to analysis the dishes were washed with soapy water, baked, and rinsed with methanol.

Sampling and Analysis

VOCs. VOCs were collected with personal sampling pumps calibrated to 100cc/min. Samples were collected for 4 hours and were collected in duplicate. Analysis was by thermal desorption/capillary gas chromatography/mass spectrometry (TD/GC/MS) using a Finnigan OWA GC/MS interfaced with a Tekmar Model 5000 thermal desorber. The thermal desorber was equipped with a cryofocusing unit. Samples collected on Tenax were desorbed at 250C for 8 minutes. Samples collected on Porapak Q were desorbed at 150C for 8 minutes. Compound identification was primarily by mass spectral matching with the National Bureau of Standards Library. Authentic standards were used whenever available. (More complete methods of analysis will be supplied by the authors upon request.)

Nicotine. Nicotine was collected on cold Petri dishes using a method by Williams, et al. (4). The dish was rinsed with 2 mls methanol. The extracts were analyzed by injection on a capillary Hewlett-Packard 5890 gas chromatograph equipped with a thermionic nitrogen-phosphorous specific detector (GC/NPD). The system was interfaced with a Nelson Analytical data-handling system.

Sidestream Chamber Samples. The sidestream chamber was designed by R. G. Griffith of the Tobacco Research Institute. The chamber consists of a glass tube with teflon ends. The cigarette is held in place in one teflon end-piece. Puffing was achieved with a solenoid valve operated by a cam-timer. This end piece also has an entrance for a stream of air for combustion. The other teflon end-piece has a sampling port. Collection was on Tenax and Porapak Q. Whole smoke collected by drawing the smoke directly onto the adsorbent tube. The cigarette smoke was also divided into the particulate and gaseous phases by placing a Cambridge filter in-line prior to the adsorbent tube. The adsorbent tubes were analyzed by TD/GC/MS as described above. The Cambridge filter was desorbed with methanol and analyzed by GC/NPD as described above.

Metals Analysis. In two of the offices, studied, a PVC filter was added to the sampling train for the determination of airborne metals. The filters were acid digested and analyzed on a Perkin-Elmer Model 6000 inductively coupled plasma spectrometer (ICP).

RESULTS

Chamber Studies

Nitrogen pyrolyzates were the primary compounds identified (Figure 1). Nicotine was the major component detected in the whole smoke. Nicotine was also the major nitrogenous component detected in the particulate phase analyzed by GC/NPD (Figure 2).

Offices Complexes

Complex 1. Three offices were surveyed in the first building: 1) a nonsmoker's office (2) an inner office with one smoker (3) an outer office with two smokers. Almost identical reconstructed ion chromatograms (RIC) were obtained for office 1 and office 2 (Figure 3). Common VOCs detected in the office buildings were identified in the ppbv range as shown in Table 1. The smoker in office 2 was a light smoker, only smoking four cigarettes during the sampling period. A similar RIC was obtained for office 3, but a few compounds were detected which are not common in the indoor atmosphere and have been detected in ETS such as 6-chloro-2H-pyran-2-one, pyrrolidine, and tetrahydrofuranmethanol.

Complex 2. Two offices of smokers were surveyed for VOCs. In a third office, only nicotine sampling was done. The two offices examined for VOCs were on different floors of the building. In office 1, the smoker was present during the entire sampling period and a cigarette was idling during the entire sampling period. In office 2, the smoker was present only a short period of the sampling time. Again similar RICs (Figure 4) were obtained. Similar VOC backgrounds were found in both offices. Office 1 did contain pptv of nitrogenous compounds not normally detected in the indoor atmosphere including 2-methyl-1H-pyrrole and 2-methylpropyl cyanate, which are suspected to originate from ETS.

Complex 3. The third office building was a much older, recently remodeled complex. Four offices of smokers were analyzed. Offices 1 and 2 were analyzed for VOCs on Tenax under identical conditions to those under in Complexes 1 and 2. The offices 3 and 4 were sampled for VOCs on both Tenax and Porapak Q with a PVC filter added to the sampling train. Office 1 was inner office with poor ventilation and no windows. Office 2 was an outer office with one window. Figure 5 shows the RICs obtained for these two offices. No differences were detected in the VOC chromatographic pattern detected, nor were any unique VOCs detected which could be attributed to ETS. Tenax was found to be a better adsorbent for the less volatile compounds, and Porapak Q was a better adsorbent for the more volatile compounds.

The PVC filter in the sample train used in offices 3 and 4 was analyzed for the presence of several metals known to be present in ETS. The results are shown in Table 2. The data is not correlated to chamber studies, outside samples, or nonsmokers' offices. Metals found in ETS were present, but not all of them in as appreciable quantities as expected particularly cadmium.

Nicotine

The nicotine concentrations are shown in Table 3. In Complex 1 no difference in nicotine concentrations were detected between the nonsmoker's office and the smoker's office 2. This could result from circulation of the nicotine in the ventilation system. In Complex 2 no differences were detected between the smoker's offices 1 and 2 in nicotine concentration. The third office which was sampled only for nicotine showed significantly higher levels of nicotine. In Complex 3 only offices 1 and 2 were sampled for nicotine. Higher levels of nicotine were detected in the office with the poorest ventilation. Two nonsmokers' offices were sampled for nicotine in a fourth building in which there was very little smoking. No nicotine was detected in these two offices.

Figure 2 shows the chromatographic trace of the GC/NPD analysis of the particulate fraction of the chamber studies. Nicotine is the primary component.

CONCLUSIONS

This preliminary study has formed the basis for continued research into differentiating ETS exposure from that resultant from other contaminant sources. Several VOCs were detected in smoking areas which are not commonly detected in the indoor atmosphere and are not known to outgas from other sources. A few of these are shown in Table 4. It is not possible to say that these VOCs originated from the ETS, but these compounds were identified in the chamber tobacco smoke samples. Additional studies are planned using chamber studies which will closely simulate actual room conditions, but eliminate other unknown indoor contaminant sources. These studies will be used to try to identify VOC markers for ETS as well as find better analytical methods of analysis for ETS.

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2. J. L. Repace, "A Quantitative Estimate of Nonsmokers' Lung Cancer Risk from Passive Smoking," Environment Int., 11: 3 (1985)

3. V. Norman, Recent Advances in Tobacco Science, vol. 3, 31st Tobacco Chemists' Research Conference, Greensboro, NC, 1977, pp. 28-58.

4. D. C. Williams, J. R. Whitaker, and W. G. Jennings, "Measurement of Nicotine in Building Air as an Indicator of Tobacco Smoke Levels," Environ. Health Persp., 60: 405 (1985).

TABLE 1

COMMON VOCS IDENTIFIED IN OFFICE BUILDINGS

COMPLEX 1

COMPOUND	CONCENTRATION (PPBV) NONSMOKER	SMOKER 1	SMOKER 2
1,1,1-Trichloroethane	0.07	0.05	0.02
Benzene	0.05	nd	0.01
Trichloroethene	0.03	0.05	0.01
Toluene	0.24	0.19	0.16
O-Xylene	0.05	0.06	0.02
p-Xylene	0.02	0.02	0.01
Octane	0.01	0.01	0.01
Tetrachloroethene	0.01	0.02	0.02

TABLE 2

AIRBORNE METALS IDENTIFIED IN SMOKERS' OFFICES

METAL	UG/CIG (3)	IDENTIFIED IN SMOKERS' OFFICES OFFICE 1 (MG/M^3)	OFFICE 2 (MG/M^3)
Chromium	0.0014	0.0007	0.0005
Zinc	0.36	0.0002	0.0002
Cadmium	0.12	nd	0.0001
Lead	0.24	0.0012	nd
Copper	0.19	0.0015	0.0048
Nickel	0.080	0.0001	0.0001
Iron	0.042	0.0088	0.0075
Manganese	0.003	0.0001	0.0002
Silicon	No Data Available	0.0011	0.0015

TABLE 3
NICOTINE CONCENTRATIONS

	NG/M^2 - MIN
Complex 1	
Smoker's Office 1	49.6
Smoker's Office 2	6.04
Nonsmoker's Office	6.09
Complex 2	
Smoker's Office 1	7.14
Smoker's Office 2	7.56
Smoker's Office 3	12.2
Complex 3	
Smoker's Office 1	11.3
Smoker's Office 2	6.23
Complex 4	
Nonsmoker's Office	nd
Nonsmoker's Office	nd

TABLE 4
SEVERAL VOCS IDENTIFIED IN CHAMBER STUDIES AND OFFICE SURVEYS

Pyrrolidine
6-Chloro-2H-pyran-2-one
Tetrahydrofuranmethanol
2-Methyl-1H-pyrrole
2-Methylpropyl cyanate
Nonanol
Dimethylundecane
Methylnaphthalene

FIGURE 1. CHAMBER SAMPLES OF CIGARETTE SMOKE

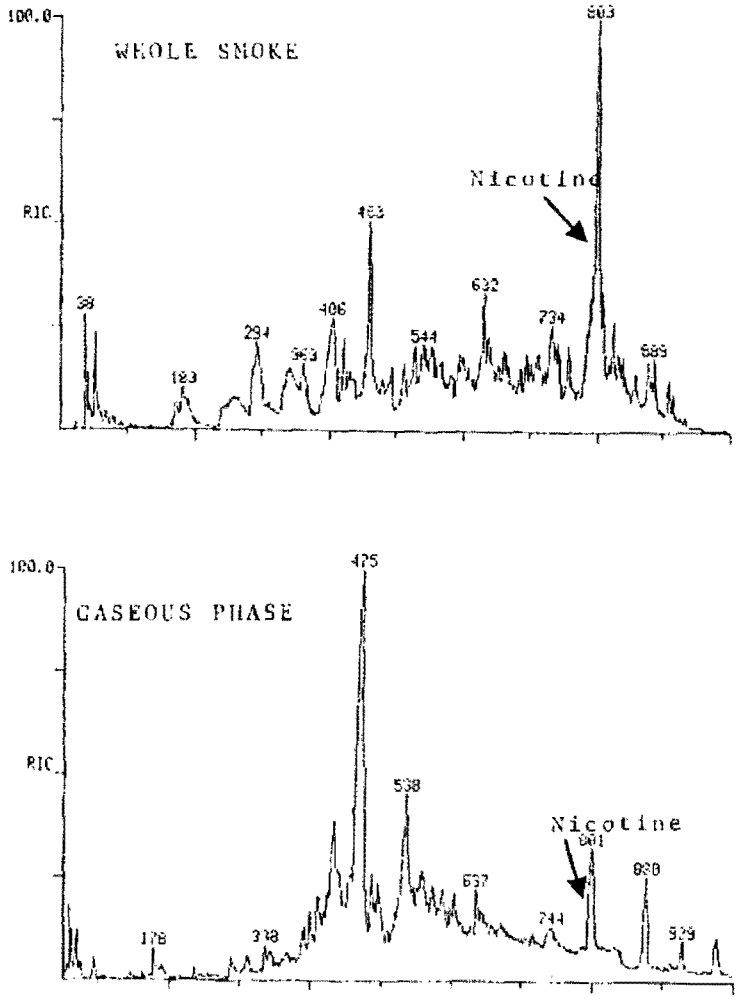


FIGURE 2. GC/NPD ANALYSIS OF PARTICULATE FRACTION

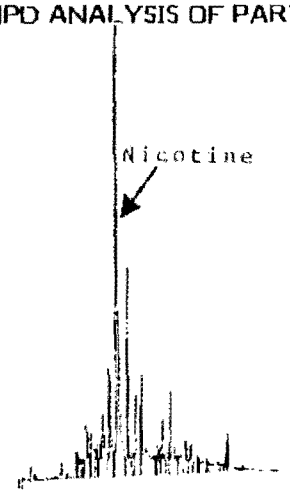


FIGURE 3. RICs FROM OFFICES IN COMPLEX 1

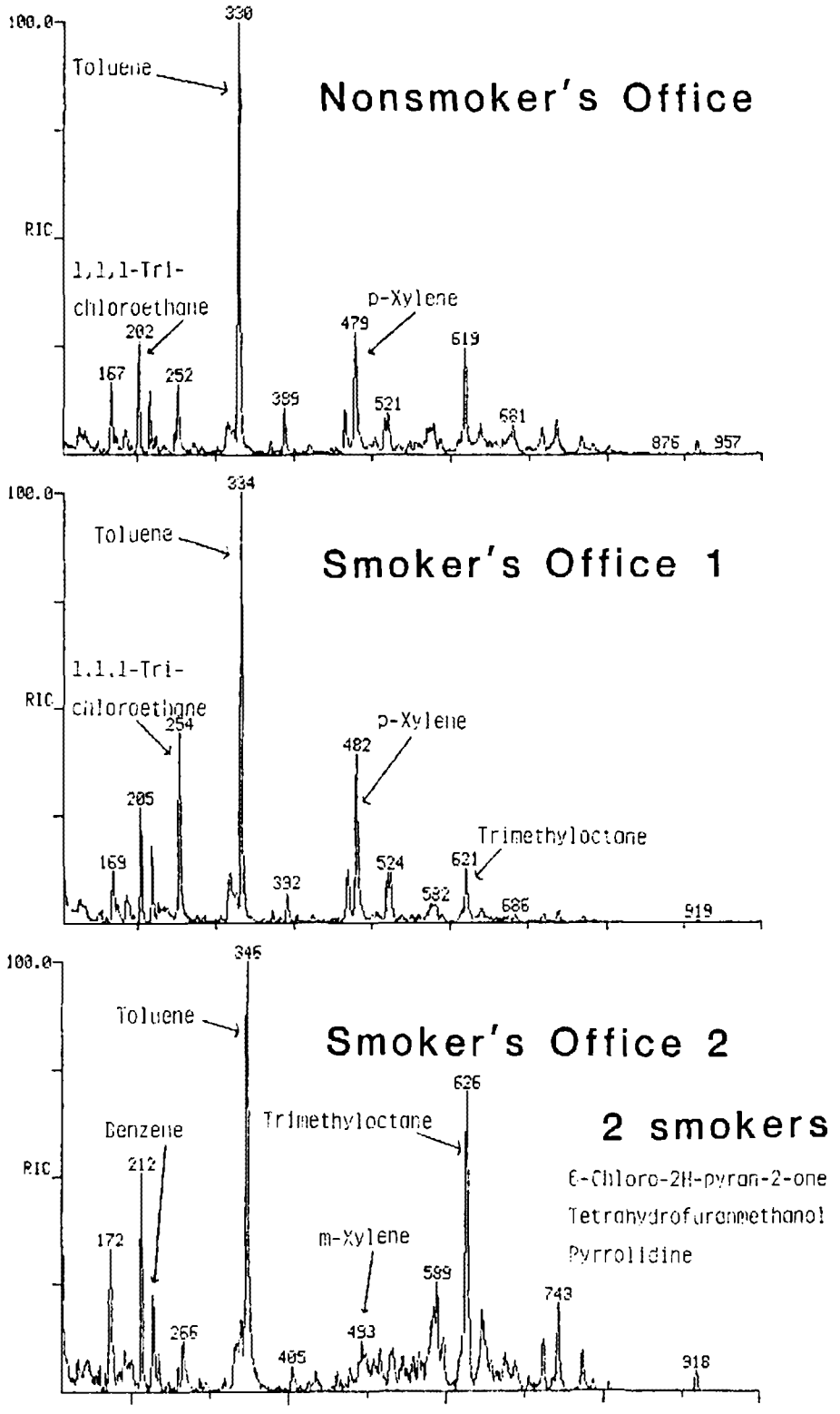
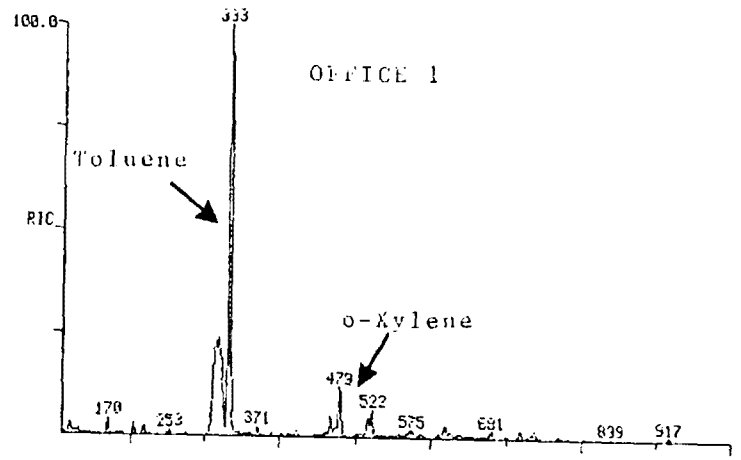


FIGURE 4. RICs FROM COMPLEX 2



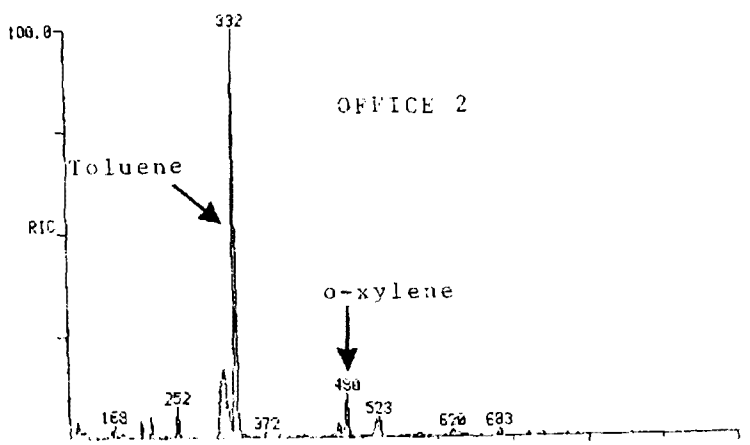
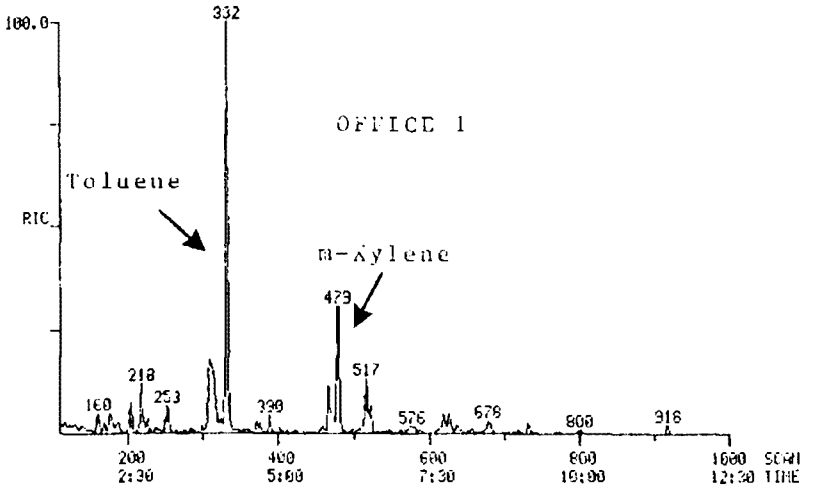
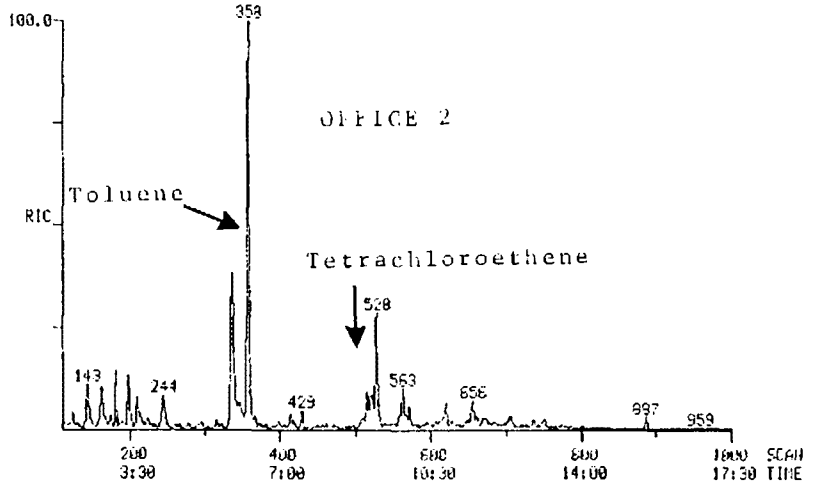


FIGURE 5. RICs FROM COMPLEX 3





AIRBORNE VIABLE MICROORGANISMS IN OFFICE ENVIRONMENTS: SAMPLING PROTOCOL AND ANALYTICAL PROCEDURES

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A general objective of the American Conference of Governmental Industrial Hygienists' (ACGIH) Committee on Bioaerosols is the development of specific protocols for the sampling and assessment of bioaerosols in workplace environments. The procedures and equipment for collecting samples of bioaerosols is much like that used to sample other airborne particles. However, the processing of collected bioaerosols is less well defined and is very dependent on the unique characteristics of the sampled material and the response sought.

The ACGIH Committee on Bioaerosols has developed a draft sampling protocol and analytical procedures for airborne viable microorganisms in office environments where workplace-related illnesses such as hypersensitivity pneumonitis, humidifier fever, and allergies (due to bioaerosols) are reported. The following items are specified in this draft protocol: (a) Rationale for initiating airborne monitoring, (b) Sampler selection, (c) Culture media selection, (d) Sampling strategy, (e) Handling and processing of collected microorganisms, (f) Data interpretation and (g) Remedial actions.

Our Committee is considering the development of bioaerosol sampling protocols for a number of other workplace environments such as research animal facilities, agricultural silos and elevators, and passenger aircraft. The bioaerosol sampling protocol for offices may serve as a model for protocols to be developed in these and other diverse occupational environments.

INTRODUCTION

The draft protocol presented here is based on the premise that air sampling would be initiated only after medical or clinical reports indicate the existence of workplace-related illness such as hypersensitivity pneumonitis, humidifier fever, and allergies that are likely due to bioaerosols. Because illnesses may be caused by a diverse array of agents such as bacteria, thermophilic actinomycetes, fungi, and protozoans, sampling may be very complex when the etiologic agent has not been determined.[16,20] Dose response data relating airborne exposure to these agents and illness are unavailable. However, if the clinical symptoms are reasonably well defined and local sources of non-microbial irritants have been obviated, the assessment of viable airborne microorganisms, as described herein, can be a useful phase in assessing the hygienic status of an office environment and is a necessary precursor to determining contamination sources and selection of appropriate remedial measures. This protocol is not applicable for the collection of highly fastidious pathogens that are optimally isolated by means other than air sampling (eg., *Legionella pneumophila*). Air sampling as described herein is used to confirm the presumption that illness is likely due to bioaerosols and no generalization that air sampling should be done on a routine basis should be drawn.

EXPERIMENTAL METHODS

Sampler Selection, Calibration, and Disinfection

Sampler Selection

N6-Andersen: The Andersen[a] viable impactor is generally accepted as the standard instrument for collection of airborne viable particles in environments where the concentration of bioaerosols is normally low.[5] A modified single stage version of the Andersen sampler referred to as the NIOSH-6 (N6) Andersen sampler[14] can be used in place of the original multistage impactor[3] and results in equivalent volumetric data with fewer plates. In the N6 Andersen sampler a Petri dish containing culture media is placed on top of the instrument base plate. Stage 6 is then sealed to the base plate with electrical tape or elastic bands. The standard Andersen inlet is not used. The protocol described in this paper utilizes the N6 Andersen sampler.

Use of other impactors: The utility of other viable impactors such as the Spiral Air System,[b] Biotest,[c] Microban[d] and slit samplers[e] is recognized. These as well as other impactors may be used in place of the N6 Andersen sampler. However, their collection efficiency relative to the N6 Andersen

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[a]Andersen 2000 Inc., P.O. Box 20769, Atlanta, GA 30320.

[b]Spiral System Instruments, Inc., 4853 Cordell Ave., Bethesda, MD 20814.

[c]Biotest Diagnostics Corp., 6 Daniel Rd. E., Fairfield, NJ 07006.

[d]Ross Industries, Inc., Midland, VA 22728.

[e]Mattson-Garvin Co., 130 Atlantic Drive, Maitland, FL 32751.

sampler as used in this application should be known before they are routinely used. This may sometimes be determined by reference to published data.[13] If the efficiency of other instruments is significantly different than the N6 Andersen sampler, data should be adjusted to reflect airborne concentrations that would have been obtained if the N6 Andersen sampler had been utilized. In cases where medical reports indicate illness due to a lower or distal airways exposure, size classification of collectate into respirable and nonrespirable particles may also be desirable. In the latter case, the use of a two-stage Andersen sampler is recommended.[12] Aerosol sampling devices which operate on the principles of filtration and impingement have many successful applications in aerobiology,[8] and can be used in office environments provided that each is carefully calibrated with respect to the N6 Andersen sampler. Filter cassette samplers are not recommended for bacteria due to potential low viability resulting from drying. Where bacteria are of interest, impingers with appropriate media are useful substitutes for N6 Andersen samplers.

Sampler Calibration

Samplers must be calibrated to air flow rates recommended by the manufacturer. Air flow rate through samplers should be checked on a daily basis during use in the field.

Sampler Disinfection

Ideally, the N6 Andersen sieve plate should be sterilized before use at each sampling location. For use in the field, decontamination by immersion in 70% ethanol for one minute will suffice. Excess ethanol should be drained away and the sieve plate should be uncovered to allow it to dry thoroughly before its next use. It is imperative to clean the sampler and inspect sieve plate jets for blockage before use. Other methods of disinfection as recommended by manufacturers are acceptable. For samplers where manufacturer's directions are not available, disinfection methods must be devised and carefully tested before routine sampler use.

Culture Media

Media are described for the detection of three classes of microorganisms, namely fungi, bacteria, and thermophilic actinomycetes. These media are recommended because they provide good general support for growth of microorganisms. However, specific media may be required for the growth and identification of certain microorganisms.

Culture Plates and Media: For the N6 Andersen sampler use sterile 100 × 15 mm plastic Petri dishes containing 45 ml of media[4] or use sterile glass Petri dishes as designed for the Andersen sampler and add 27 ml of media.[3] For other samplers follow the manufacturer's directions.

Media for General Detection and Enumeration of Fungi: "Malt extract agar" - ingredients per liter of distilled water.

Malt extract	20 g
Peptone	1 g
Dextrose	20 g
Agar	20 g

Media for General Detection and Enumeration of Bacteria and Thermophilic Actinomycetes: BBL "trypticase soy agar" or equivalent - 40 g per liter.

Additional Media: Other general media for the culture of fungi, bacteria, and thermophilic actinomycetes may be used. However, equivalency to the media listed above in terms of supporting growth of microorganisms collected in an office environment should be known.[7]

Culture media must be checked for sterility and the ability to support the growth of the organisms being collected. This is especially important if media are not purchased from a commercial source. A 0.1 ml inoculum of a suspension of the test organisms should be spread on appropriate media and incubated at the appropriate temperature. Organisms for fungal sampling include *Cladosporium cladosporioides*, *Alternaria alternata*, and *Aspergillus fumigatus*. *Thermoactinomyces vulgaris* is a common thermoactinomycete, and *Staphylococcus epidermidis*, *Streptococcus salivarius*, *Escherichia coli*, and *Bacillus subtilis* are common bacteria that are useful in media testing. These microorganisms should be obtained from a source that normally supplies quality assurance organisms.

Sampling Strategy

The primary objective of sampling is to identify the source of airborne microorganisms so that effective corrective action may be undertaken. Reported sources of airborne microorganisms include outdoor input sources; components of the heating, ventilation and air-conditioning (HVAC) system; office furnishings and equipment; portable appliances (eg., cool mist vaporizers); building occupants.

For most situations at least 0.1 m^3 of air should be sampled. Duplicate or triplicate samples should be obtained for each culture medium used at each location including control sites for each variable that may affect the bioaerosol level. Some variables may include: humidifier on or off; fan coil unit operating with dirty or clean filter; occupants present or absent.

Air samples should be collected near potential sources such as diffusers, fan coil units, office furnishings, and portable applicances; within the return air chase and air supply plenum of the HVAC system, and near occupants both with or without symptoms of building-related disease. In addition, air samples should be collected in the outdoor air away from obvious sources of bioaerosols and in the vicinity of bioaerosol sources such as cooling towers.

Sampling should be carried out in relation to the likely source of bioaerosol contamination in the office environment. The following illustrates one possible sampling sequence:

Sample before the HVAC system is turned on and before occupants arrive for work.

Sample before occupants arrive for work at a time when the HVAC system is operating.

Sample at the time of maximal occupancy (HVAC system on).

Sample after occupants leave (HVAC system off).

Sample in relation to normal changes in HVAC system operational parameters or before and during artificial manipulation of the HVAC system.

Handling and Processing of Air Samples

Samples can be processed by the investigator or by a reference laboratory. If an outside laboratory is used, obtain the advice of a microbiologist or a consultant experienced in microbiological techniques and the handling and processing of airborne microorganisms. Obtain information on the procedures to be used for shipping and transport of exposed and control plates to the microbiological laboratory before sampling is initiated. Make sure the laboratory is experienced in processing samples from your type of equipment.

Malt extract agar for fungi should be incubated for 3 to 7 days at 25°C under 12 hours of ultraviolet illumination per day. Trypticase soy agar for bacteria should be incubated for 2 days at 35°C. Trypticase soy agar for thermoactinomycetes should be incubated at 55°C for 3 days.

For enumeration of counts leading to the determination of total colony-forming units (CFU) per m^3 using the N6 Andersen sampler, note the 400 possible impaction sites for colony growth on the culture plates utilized. Avoid duplicate counts at single impaction sites. Avoid counting colonies that grow at sites other than the 400 impaction locations. For example, do not count colonies found along the margin of the culture plate or between obvious impaction sites. Adjust raw colony counts by using the positive hole table found in reference 3. The same cautions apply for other culture plate impactors. When using dilution cultures of filter eluates or impinger fluid, dilute to the level of 10 to 50 colonies per plate.

Total CFU per m^3 is determined from culture plate impactors as follows:

$$\frac{\text{CFU}}{m^3} = \frac{\text{Adjusted* number of colonies on plate}}{\text{Total volume of air sampled in cubic meters}}$$

*Positive hole adjustment.[3]

If a sampler other than the N6 Andersen is used, adjust this value by dividing by the relative efficiency of your sampler (eg., if a sampler is 50% as efficient as the N6 Andersen, divide by 0.5).

Total count measurements for 25°C fungi, 35°C bacteria, and 55°C thermophilic actinomycetes should be made. If a reference laboratory is used, the industrial hygienist must provide data to the laboratory on the volume of air sampled in obtaining the air samples. The laboratory should provide a report on the total CFU/m^3 of viable particles at each sample site before proceeding with more analysis. Alternatively, the laboratory can provide the industrial hygienist with average plate counts for each sampling site and the industrial hygienist can calculate the total viable count.

RESULTS AND DISCUSSION

If the total count at the affected person's area equals or exceeds 10000/m^3, proceed to remedial actions discussed later. If the total count is less than

$10000/m^3$, or if clinical or research studies would benefit by identification of the source of the etiologic agent(s), the following identification procedures may be employed. All fungi present at >70 CFU/m^3 should be identified.

The presence of any dominant fungus not present in outdoor air at the affected person's area without indication of allergic response from outdoor particles can lead to a presumption of a building-related source. If a building-related source is found, proceed to remedial actions.

Bacteria: As an initial bacterial screen, specify that the laboratory identify and enumerate (CFU/m^3) the following:

Bacillus spp.
Gram negative rods
Other predominant bacteria

If Bacillus spp. or gram negative rods are dominant at the affected person's area without indication of allergic response from outdoor particles, a presumption of a building-related source can be made. As a second screen, identify and enumerate all bacteria >70 CFU/m^3.

High levels of any bacteria at the affected person's area but not in other indoor locations may be indicative of poor ventilation or overcrowding. For example, airborne Streptococcus salivarius has been suggested as an indicator of respiratory pollution.[24] If a high level of one or more species of bacteria are found at the affected person's area, proceed to remedial actions.

Thermophilic Actinomycetes: Enumerate all thermophilic actinomycetes. Identify those present at >70 CFU/m^3.

The presence of thermophilic actinomycetes in indoor environments has been associated with outbreaks of hypersensitivity lung illness.[11] Proceed to remedial actions.

Recommendations for Remedial Actions

Since water may serve as an excellent menstruum for growth of microorganisms, it can act both as a source of contamination and also as its amplifier. Therefore, the following actions are recommended:

Remove stagnant water and slimes from building mechanical systems; when the system is off disinfect with a chlorine solution.

Eliminate water spray systems in air handling units.

Substitute steam for cold water humidifiers.

Eliminate the use of cold mist vaporizers.

Prevent water leaks or floods.

Keep indoor relative humidity below 70%. For locations where cold surfaces are in contact with warm air keep indoor relative humidity below 50%.

Discard porous building materials and office furnishings that are visually contaminated with fungi.

Replace HVAC system filters at scheduled intervals.

Control by dilution.

Upgrade the collection efficiency[2] of air handling unit filter banks.

Provide suitable (clean, filtered) outdoor air in amounts >10 liters per second per occupant.

Affected or sensitized personnel may have to be reassigned temporarily to another work environment. If illness persists in the workplace even after remedial actions, affected personnel need to be permanently reassigned to another area.

Additional samples should be collected to document if the remedial actions taken were effective.

If the aforementioned control measures fail and if the sampling protocol and analytical procedures for airborne viable microorganisms fail to identify the source of bioaerosol contamination, the following agents could be responsible for illness: nonviable spores,[15,23] protozoans,[10] mycotoxins,[9] endotoxins,[22] and submicron particulate antigens.[6,21] Competent advice should be sought for measurement and control of these microbial agents.

Acknowledgement: This is a condensed version of an article that appeared in Applied Industrial Hygiene, Vol. 1, Number 1, April, 1986. Permission to publish in these proceedings was granted by the American Conference of Governmental Industrial Hygienists, Inc.

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INTERCOMPARISON OF SAMPLING TECHNIQUES FOR TOXIC ORGANIC COMPOUNDS IN INDOOR AIR

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People spend a major fraction of their time indoors, and there is concern over exposure to volatile organic compounds present in indoor air. This study was initiated to compare several VOC sampling techniques in an indoor environment. The techniques which were compared include distributive air volume sampling, high and low rate passive sampling, and whole air collection in canisters. The study focused on ten target compounds:

chloroform	toluene
1,1,1 trichloroethane	tetrachloroethylene
benzene	styrene
bromodichloromethane	p-dichlorobenzene
trichloroethylene	hexachlorobutadiene

Altogether, ten separate 12-hour sampling experiments were conducted. Two experiments sampled the background air of the residence. For the other eight experiments, the indoor air was spiked with the target compounds. Three different spike levels were utilized to cover a range of target compound concentrations. The nominal spike concentrations were 3, 9, and 27 ng/L for each of the ten target compounds. Statistical analysis of the sampling results indicates generally high correlation coefficients (greater than 0.90) between the methods. The most notable exception was benzene, which had lower correlation coefficients. In general, the distributed air volume sampling technique and the low rate passive technique measure concentrations less than or equal to the canister method.

INTERCOMPARISON OF SAMPLING TECHNIQUES FOR
TOXIC ORGANIC COMPOUNDS IN INDOOR AIR

Introduction

There has been an increasing need to measure volatile organic compounds in air. This need has been especially great for hazardous organic species in indoor air. A variety of approaches have been utilized for collection and analysis of hazardous organic pollutants in air. One of the most widely used sampling technique is collection of Tenax solid adsorbent. This study employed an active Tenax sampling technique developed by Walling[1,2] and Walling and Bond [3], in which four samples are collected simultaneously at different flow rates. This technique is termed distributed air volume sampling.

Collection of whole air samples in passivated canisters is another technique which has been employed for volatile organic species sampling. This study employed a canister sampling procedure reported by Oliver et al.[4] and Holdren et al.[5].

Passive collection of volatile organic chemicals is a very attractive means of sampling, especially in performing human exposure studies. Small stainless steel cylinders containing Tenax adsorbent behind a diffusion barrier have proven to be very successful for sampling a wide range of compounds, when used under appropriate conditions[6]. Both high sampling rate and low sampling rate devices were employed in the present study.

All of the techniques noted above have been employed for ambient air sampling, and some have been used to sample indoor air. The study reported here has compared these methods for the first time in an indoor environment, with the emphasis placed on a number of hazardous organic chemicals observed in indoor air.

Overview of Study Design

The intercomparison of volatile organic compound sampling techniques was carried out in an unoccupied residence. The techniques which were compared include distributive air volume sampling, high and low rate passive sampling, and whole air collection in canisters. Samples were collected in duplicate for each technique except the canister procedures; each canister sample was analyzed twice, to provide an estimate of analytical precision for this sampling medium. All samples were analyzed within three days of collection by GC/MS. The study focused on ten target compounds:

chloroform	toluene
1,1,1 trichloroethane	tetrachloroethylene
benzene	styrene
bromodichloromethane	p-dichlorobenzene
trichloroethylene	hexachlorobutadiene

Altogether, ten separate 12-hour sampling experiments were conducted. Two experiments sampled the background air of the residence. For the other eight experiments, the indoor air was spiked with the target compounds. Three different spike levels were utilized to cover a range of target compound concentrations. The nominal spike concentrations were 3, 9, and 27 ng/L for each of the ten target compounds. Spiking was accomplished by vaporizing an initial charge of the ten-compound mixture into the furnace blower duct to achieve the approximate spike concentration. Throughout the remainder of the 12-hour period, the target compounds were continuously introduced into the duct from a gas cylinder at a rate calculated to make up for dilution caused by infiltration. Continuous operation of the furnace blower and several oscillating fans located throughout the house was used to provide thorough mixing, and also to provide the air velocity required for efficient operation of the passive devices.

For the distributive air volume technique, one blank was run for each sample (i.e. per set of four tubes). The blanks were transported to the field, but were not opened or handled prior to analysis. Duplicate samples were collected using a second distributive air volume collection system, and both the high and low rate passive samples were collected in duplicate. Temperature, relative humidity, and air exchange rate were monitored during each experiment.

All samples and blanks have been analyzed on the same GC-MS system to minimize the uncertainty in the analytical portion of the measurements so that the comparison could focus on the sampling techniques.

Experimental

The residence used for these experiments is located in the Upper Arlington suburb of Columbus, OH, approximately 10 km northwest of downtown. The test house was unoccupied during this study, and has been used for the past year for heating, ventilation, and air infiltration experiments. The house is a three bedroom, two bath ranch constructed in 1963. All sampling was conducted in the living room of the residence.

Sampling Methodology for Target Organic Compounds

Distributed Air Volume (DAV) Sampling. Sampling with Tenax adsorbent tubes was accomplished with the system shown in Figure 1. For experiments 1 through 5, the mass flow controllers were adjusted so that nominal air

volumes of 5, 10, 15, and 20 liters were collected over the 12-hour sampling period. For experiments 6 through 11, nominal sample volumes of 5, 10, 20, and 40 liters were collected. Actual volumetric flow rates were measured before and after each experiment. Duplicate sets of Tenax adsorbent tubes were collected during all ten experiments. These tubes consisted of packed glass cartridges as used with the Volatile Organic Sampling Train (VOST) System developed by EPA for stack sampling. Tenax for the VOST-type cartridges was purchased from Alltech Associates. The material was then transferred to the individual glass cartridges. Within 48 hours before use, the sampling cartridges were cleaned by heating (240°C) under a helium purge (50 ml/minute). When not being used for sampling or analysis, all Tenax cartridges were stored at room temperature in one-gallon metal cans containing a layer of charcoal.

A sample blank was carried along with each set of four Tenax cartridges. The blank cartridge was not removed from its storage container but simply accompanies the four adsorbent tubes to the test site and then back to the laboratory for analysis.

Canister Sampling. Six-liter stainless steel canisters (Demaray Scientific Instrument, Ltd.) were used for collecting integrated whole air samples. A stainless steel pump (Metal Bellows Corp., Model-158 or 151) directs flow into the sample canister. The sampling rate is controlled with a mass flow controller (Tylan, FC-260). A stainless steel tube restrictor (0.03 inch i.d. by 6 inch length) was positioned upstream of the mass flow controller to prevent pump oscillations from affecting the mass flow. The sample flow was set so that a final canister pressure of 10 psig was achieved (i.e. 10 cc/min for a 12-hour sample period). Duplicate analyses were performed on each canister sample.

In preparation for sampling, the canister was sequentially filled (15 psig) and evacuated (25 in. of Hg.) five times using zero air (Aadco, Inc.) as the flushing gas. After the fifth evacuation, the canister was sealed, transferred to a higher vacuum system and pumped down to 0.1 torr. A liquid nitrogen trap was utilized in this system to prevent contamination from the pump oil. An oven (100°C) was also used to bake out the canisters during evacuation.

Passive Sampling Devices (PSDs). Two types of passive sampling devices (PSDs) were utilized in this study. Both are stainless steel cylinders filled with 0.4 g Tenax GC. The device shown schematically in Figure 2 was designed to have a relatively high sampling rate for organic compounds. This device, which has been characterized by Lewis et al.[7], employs a 200-mesh stainless steel screen as the diffusion barrier.

The second type of device is similar to that shown in Figure 2, except that the 200-mesh screen is replaced by a stainless steel plate with a single 0.5 mm hole in the center. This device was designed to have a reduced sampling rate.

The sampling rates for PSDs employing reversible adsorption are dependent on the specific design of the device as well as the retention volume of each organic compound with respect to Tenax. Based on the design specifications of these devices and the 12-hour exposure time used in this study, the effective sample volumes for each target compound are shown in Table 1. A time weighted average sampling rate was used to compute the volumes for the high rate PSD, because the rate decreases with time for some compounds over the 12-hour sampling period. The computation is based on the development by Coutant et. al[8].

Before sampling, the PSDs were cleaned by baking at 200°C for at least two hours in an oven designed to hold ten PSDs. During bakeout, the PSDs were exposed to a flow of 100 ml/min of hydrocarbon-free N_2. Following cleanup, the PSDs were stored in a stainless steel cylinder which was purged with hydrocarbon-free N_2 and pressurized through a quick-connect fitting. The PSDs were transported to and from the residence in this device, and the blank PSDs were kept in the cylinder at the residence during sampling.

Three high rate and three low rate PSDs were employed for each experiment. Two devices of each type were analyzed; the third was collected as a backup. One of each PSD type was transported to the residence for use as a blank. These PSDs were not removed from the transfer cylinder.

Efficient operation of the PSDs requires movement of air around the device to replenish the boundary layer which is depleted by sampling. Following the recommendation of Lewis et al.[7], we operated the furnace blower and three oscillating fans in the living room during each experiment. This provides linear velocities of 25-35 $ft\text{-}min^{-1}$ at the location of the PSDs.

Additional measurements which were made to complement the organic species sampling intercomparison included temperature, relative humidity, NO/NO_x, and air infiltration rate. These measurements were made in the living room simultaneously with the organic species sampling. Temperature and relative humidity were monitored with an EG&G Model 911 unit. The concentrations of NO and NO_x were monitored with a CSI Model 2200 portable chemiluminescence instrument. Readout from both of these instruments was recorded on two Weather/Measure dual channel recorders.

Air infiltration rate was measured by the decay method, using SF_6 as the inert tracer. The concentration of SF_6 was measured every 30 minutes throughout each 12-hour experiment with a Hewlett Packard Model 5790 electron capture gas chromatograph with a 1 cc sampling loop and an automated gas sampling valve.

An example of the results from the 10 intercomparison experiments is provided in Table 3. The Table lists the experiment number, date, spike level, measured air exchange rate, average temperature, average relative humidity, and the mean NO and NO_2 concentrations over the 12-hour sampling period. Table 3 also reports the sample volumes, blank-corrected concentrations, and blank values for the various sampling techniques. A complete listing of the data may be found in Reference 9.

Analysis Methods

The instrumentation used in this effort consisted of an Extranuclear Simulscan quadruple mass spectrometer interfaced to Hewlett Packard 5710A gas chromatograph. Data acquisition and reduction was performed using an on-line Finnigan INCOS 2300 data system. Sample analyses were performed by thermal desorption of the adsorbent (passive and distributive air volume samplers) or direct sampling (canister) into cryogenic trap. Distributive air samples were desorbed at 200°C for ten minutes while purging with helium at 80 ml/min. Passive monitors were desorbed at 150°C for 15 minutes with an equivalent helium flow. The lower desorption temperature for the passive monitors was selected to minimize thermal degradation of sensitive compounds due to the stainless steel passive monitor housing. The canister was sampled through approximately 1 meter of Nafion tubing resulting in a dry sampling volume of 1.0 liter.

The cryogenic trap consists of a 20 cm loop of 1/8 in. OD stainless steel tubing packed with 60-80 mesh silanized glass beads. The trap was maintained at 87°K with liquid Argon during the cryofocussing step. The cryotrap was then heated to 160°C while back flushing with 3 ml/min of helium for a period of seven minutes. The cryotrap eluent was routed to a Hewlett Packard 50 m crosslinked SE 30 wide bore thick film fused silica capillary column using a 6-port valve maintained at 100°C. The initial column temperature was -20°C.

Following cryotrap desorption, the column was temperature programmed at 8°C/min to 200°C. GC/MS acquisition was initiated after a six minute delay. Electron impact ionization was used with the instrument scanning from m/z 46-270 with a 0.5 second cycle time.

Data reduction was performed automatically using in-house developed software. This involved retention driven reverse search for the target analytes followed by integration of characteristic extracted ion current profiles. Quantification was performed by comparison to the chromatographic peak areas of a known standard. Calibration and performance check analyses were done by cryotrap sampling a known volume from an aluminum compressed gas cylinder containing 1.0 ppm in each of the target analytes. The concentration of benzene in the calibration cylinder was found to be within 6% of the calculated value based on direct comparison with an NBS primary standard cylinder.

Results

The dates of the ten experiments and the nominal spike levels are shown in Table 2. Some of the target compounds were present in the background air in the residence, contributing significantly to the total residence concentration during the spiking experiments.

An example of the results from the 10 intercomparison experiments is provided in Table 3. The Table lists the experiment number, date, spike level, measured air exchange rate, average temperature, average relative humidity, and the mean NO and NO_2 concentrations over the 12-hour sampling period. Table 3 also reports the sample volumes, blank-corrected concentrations, and blank values for the various sampling techniques. A complete listing of the data may be found in Reference 9.

Analysis of Results

The statistical methods were taken from linear regression analysis. The canister method was chosen as the reference method throughout. This means that the results from the three Tenax methods (DAV, high rate PSD, and low rate PSD) were used as the dependent variable and the canister results as the independent variable in the regression. The canister and Tenax means were paired by experiment for each compound. The experimental design for the DAV Tenax was complicated by a number of factors and various types of averaging were done before performing the regression analysis. Details and justification for the regression analysis are given in the appendix of Spicer, et. al. (Reference 9).

The two statistics of greatest interest from the regression analysis are the slope of the Tenax vs. canister regression line and the correlation coefficient between the canister and Tenax means. The slope is interpreted as a measure of the agreement between the two methods in any comparison. If the intercept is 0, a slope less (greater) than one indicates that the Tenax mean is, generally, lower (higher) than the canister mean. A correlation coefficient close to one indicates that the canister and Tenax means are approximately linearly related over all experiments. That is, the resultant means from the measurements by the two methods show the same relative peaks and valleys over all experiments.

Figures 3, 5, and 6 are summaries of the slope (agreement) for all three Tenax methods, while Figure 4 shows the correlation coefficients, for DAV Tenax for all compounds. The compound numbers on the horizontal axis refer to the compounds as listed in the 'Overview of Study Design' section. The retention of the compounds increases from left to right. There are several conclusions that have been drawn from the statistical analysis that are illustrated in the figures:

1) The slope (agreement) results for DAV are shown in Figure 3. Note that ± one standard error bars are drawn on the figure.

   a) (9) p-dichlorobenzene and (10) hexachlorobutadiene had slope estimates less than one and the estimates were within two standard errors of one.

   b) (3) benzene, (6) toluene and (7) tetrachloroethylene had slope estimates greater than one and the estimates were within two standard errors of one.

   c) The five other compounds had slope estimates less than one and the estimates were more than two standard errors from one.

   d) (8) styrene was the only one of the ten compounds with an intercept estimate (0.79 ng/L) more than two standard errors from zero.

   e) The more detailed statistical analysis indicated that for the DAV Tenax, the slopes for (1) chloroform, (2) 1,1,1-trichloroethane, and (10) hexachlorobutadiene shown in Figure 3 do not adequately represent the experiment and these results should be qualified.

2) The low rate PSD slope estimates (Figure 5) show that all slope estimates were less than one and all intercept estimates were within two standard errors of zero. With the exception of (3) benzene, the slope estimates for all compounds were not within two standard errors of one.

3) The high rate PSD slope estimates (Figure 6) are as follows:

   a) (3) benzene had a slope estimate less than one and within two standard errors of one.

   b) (1) chloroform and (4) bromodichloromethane had slope estimates less than one but these estimates were not within two standard errors of one.

   c) The seven remaining compounds had slope estimates greater than one and were not within two standard errors of one.

   d) (10) hexachlorobutadiene was the only compound with an intercept estimate (-1.53 ng/L) more than two standard errors from zero.

4) The correlation between Tenax means and canister means was generally large (>0.90) for all Tenax methods. The most notable exception was (3) benzene, which had relatively small correlation coefficients for all Tenax methods.

Precision estimates were obtained for the three Tenax methods by pooling the variance of replicates over all experiments for PSD and DAV and over all nominal volumes for DAV. The precision estimate is taken as the square root of the pooled variance estimate. The compounds that showed precision estimates greater than 2.0 ng/L were:

(3) benzene for the DAV and low rate PSD Tenax

(6) toluene for all three Tenax methods

(7) tetrachloroethylene for the DAV and high rate PSD Tenax

(10) hexachlorobutadiene for the low and high rate PSD

Precision estimates for the duplicate canister sample analyses were less than 1.2 ng/L for all compounds.

NOTE: Results for analysis of the canister samples and the low rate PSD samples have been corrected for a calibration error since the symposium presentation.

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TABLE 1. 12-HOUR SAMPLE VOLUMES FOR HIGH RATE AND LOW RATE PASSIVE SAMPLING DEVICES

Target Compound	High Rate PSD Volume (L)	Low Rate PSD Volume (L)
chloroform	8.28	1.80
1,1,1-trichloroethane	5.19	1.53
benzene	17.9	2.01
bromodichloromethane	28	1.70
trichloroethylene	16.6	1.89
toluene	40.3	1.92
tetrachloroethylene	36.2	1.86
styrene	46	1.81
p-dichlorobenzene	41	1.53
hexachlorobutadiene	31.4	1.25

TABLE 2. NOMINAL SPIKE LEVELS FOR INDOOR INTERCOMPARISON EXPERIMENTS

Experiment No.	Date	Nominal Spike Level (ng/L)
1	June 12, 1985	background
2	June 18, 1985	3
3	June 24, 1985	3
4	June 26, 1985	9
5	July 1, 1985	9
6	July 8, 1985	27
7	July 10, 1985	27
9	August 20, 1985	background

TABLE 3. RESULTS FROM INDOOR INTERCOMPARISON STUDY EXPERIMENT 6

Experiment No. 6
Date: July 8, 1985

Organic Spike Level: High
Measured Air Exchange Rate: 0.045 hr^{-1}

Average Temperature, °C 27°
Average Relative Humidity, percent 37
Average [NO], ppb NA
Average [NO_2], ppb NA

Sampling Techniques	Sample No.	Sample Volume, l	Reported Units	Target Chemicals: Chloroform	1,1,1-Trichloroethane	Tetrachloroethylene	Bromodichloromethane	Trichloroethylene	Benzene	Toluene	Styrene	p-Dichlorobenzene	Hexachlorobutadiene
Integrated Canister--Sample 1	C-3	1.0	ng/l	23.1	21.0	29.5	15.7	15.7	26.4	32.3	11.2	11.3	18.7
Integrated Canister--Sample 2	C-3	1.0	ng/l	23.8	20.7	30.3	15.9	16.0	27.9	33.7	11.6	11.8	17.0
Distributed Air Volume--System 1	T-20	5.22	ng/l	21.3	21.8	31.6	16.2	16.6	28.1	38.5	13.7	13.5	17.4
Distributed Air Volume--System 1	T-19	10.20	ng/l	22.8	19.8	29.4	15.9	15.5	26.3	36.6	13.4	12.8	18.3
Distributed Air Volume--System 1	T-13	19.60	ng/l	18.9	17.4	22.4	12.9	13.3	24.7	30.1	11.2	10.7	15.9
Distributed Air Volume--System 1	T-14	39.90	ng/l	11.9	15.0	27.6	14.0	13.7	25.5	34.1	12.0	11.6	18.0
Distributed Air Volume--System 2	T-1	4.78	ng/l	21.5	18.6	28.7	14.6	15.4	24.5	34.7	12.7	12.4	15.6
Distributed Air Volume--System 2	T-4	9.10	ng/l	17.7	16.0	24.4	11.1	11.8	21.6	29.7	11.3	11.2	16.5
Distributed Air Volume--System 2	T-8	18.90	ng/l	18.6	17.1	25.7	12.6	13.4	25.1	32.6	11.7	11.2	16.7
Distributed Air Volume--System 2	T-7	39.80	ng/l	10.0	15.1	28.1	13.4	14.9	25.1	31.7	12.1	11.9	18.6
DAV Blank	MCT-1		ng	--	0.3	--	--	--	3.1	0.2	--	0.6	--
DAV Blank	MCT-2		ng	--	0.3	--	--	--	0.5	0.1	<0.1	--	--
High Rate Passive Sampler	87	*	ng/l	15.9	57.6	39.2	13.3	19.0	18.9	47.3	16.9	18.5	24.6
High Rate Passive Sampler	90	*	ng/l	15.7	56.7	43.0	13.2	20.3	21.0	50.5	17.5	19.4	31.4
High Rate Passive Sampler		*	ng/l										
HRPS Blank	93		ng	--	26.8	--	--	0.9	0.8	3.4	0.3	--	--
Low Rate Passive Sampler	B208	*	ng/l	14.7	15.5	14.8	11.3	9.9	17.9	14.8	6.6	7.3	11.2
Low Rate Passive Sampler	B206	*	ng/l	15.2	15.5	15.9	11.8	10.7	18.8	15.9	7.1	6.6	< 1.1
Low Rate Passive Samoler		*	ng/l										
LRPS Blank	B211		ng	<0.1	6.8	0.2	<0.1	1.0	1.2	2.0	0.2	0.1	<1.8
			High Rate PSD	8.3	5.2	36.2	28	16.6	17.9	40.3	46	41	31.4
			Low Rate PSD	1.80	1.53	1.86	1.70	1.89	2.01	1.92	1.81	1.53	1.25

NA Not available
NR Not reported due to interference or high blank

*Sampling rate for PSDs varies with compound. Sample volume for 12 hour collection period, in liters;

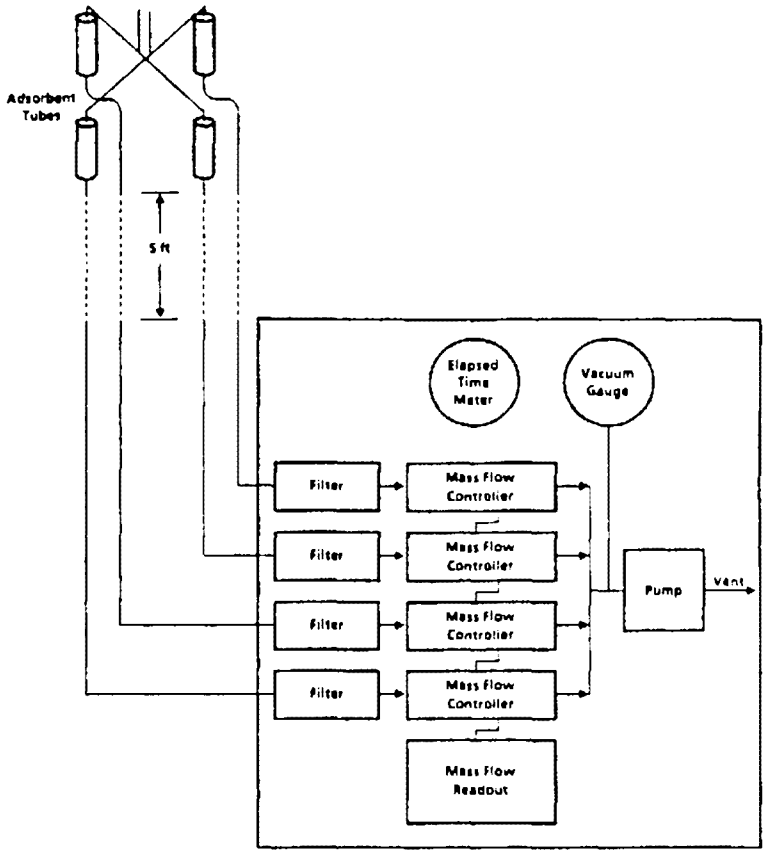

Figure 1. Diagram of distributive air volume sampler.

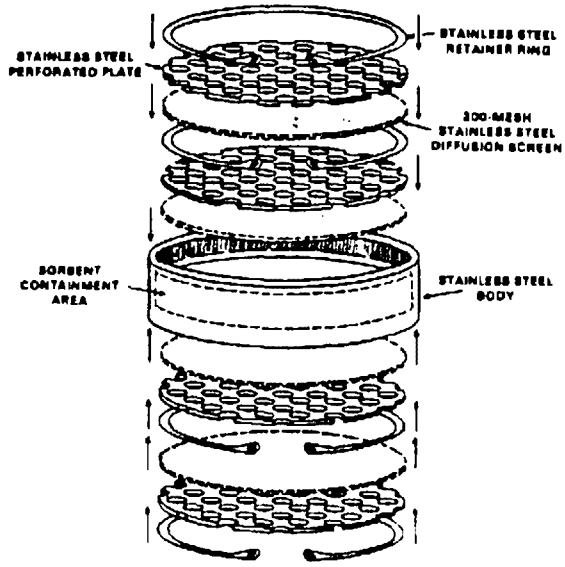

Figure 2. Thermally desorbable passive sampling device.

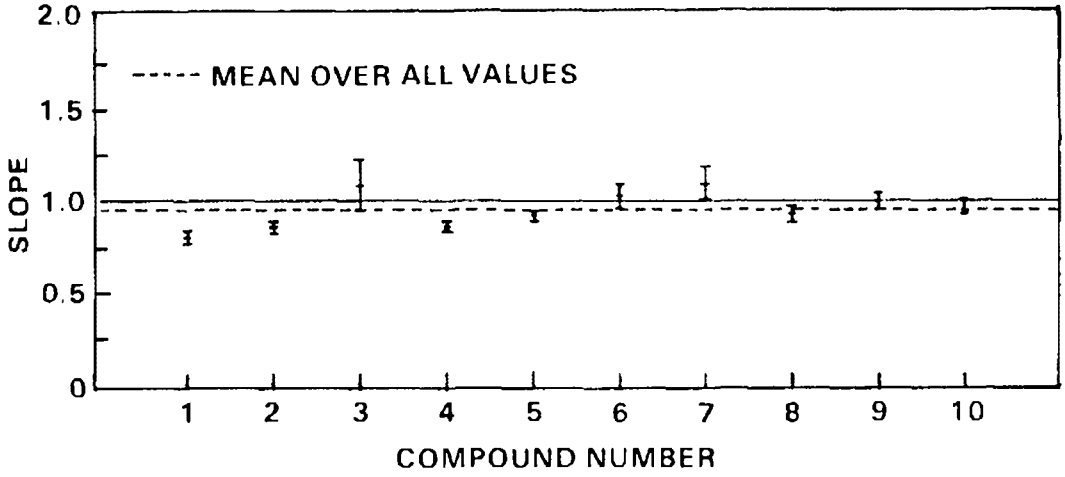

Figure 3 AGREEMENT: Tenax distributed air volume and canister slope plus and minus one standard error from the linear regression of Tenax mean vs canister mean.

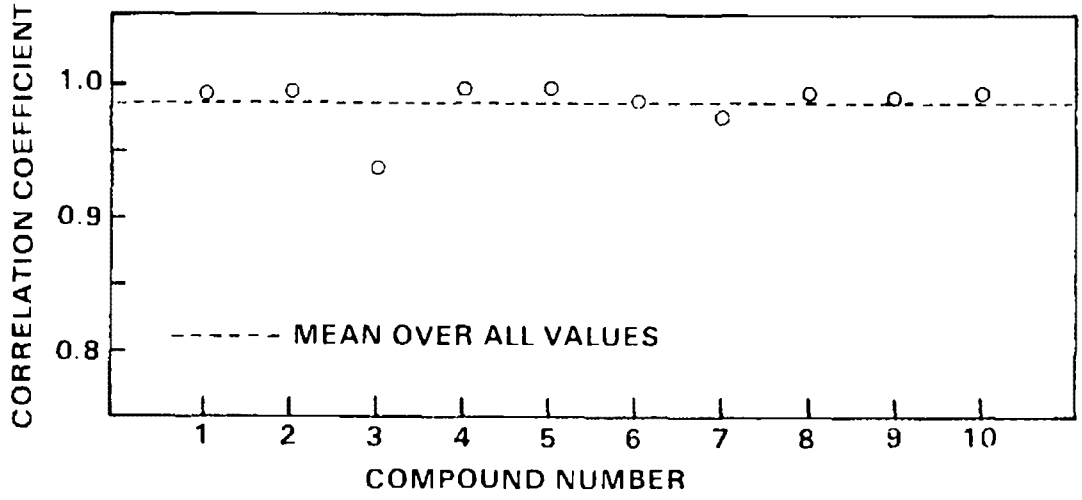

Figure 4 CORRELATION. Tenax distributed air volume and canister correlation of Tenax mean and canister mean.

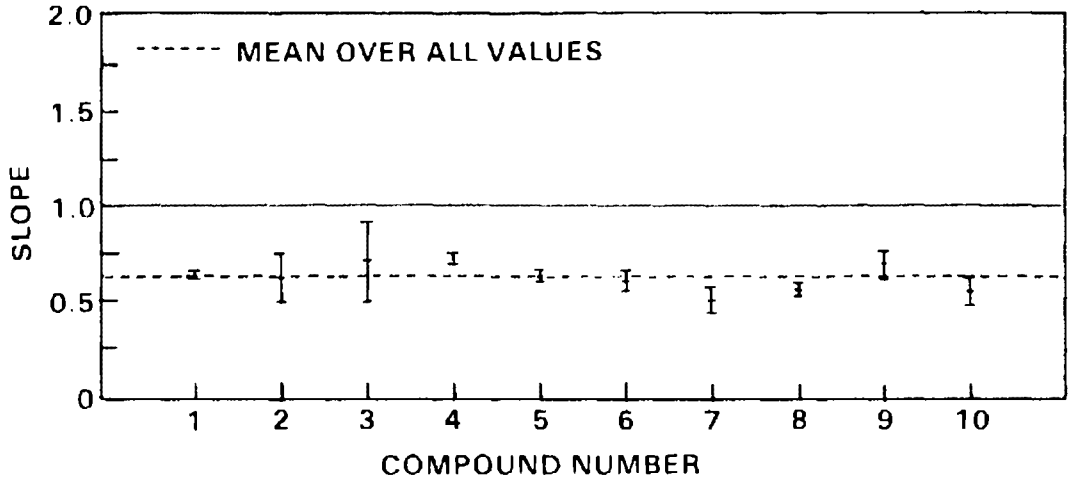

Figure 5 AGREEMENT Tenax low rate personal sampling and canister slope plus and minus one standard error from the linear regression of Tenax mean vs canister mean.

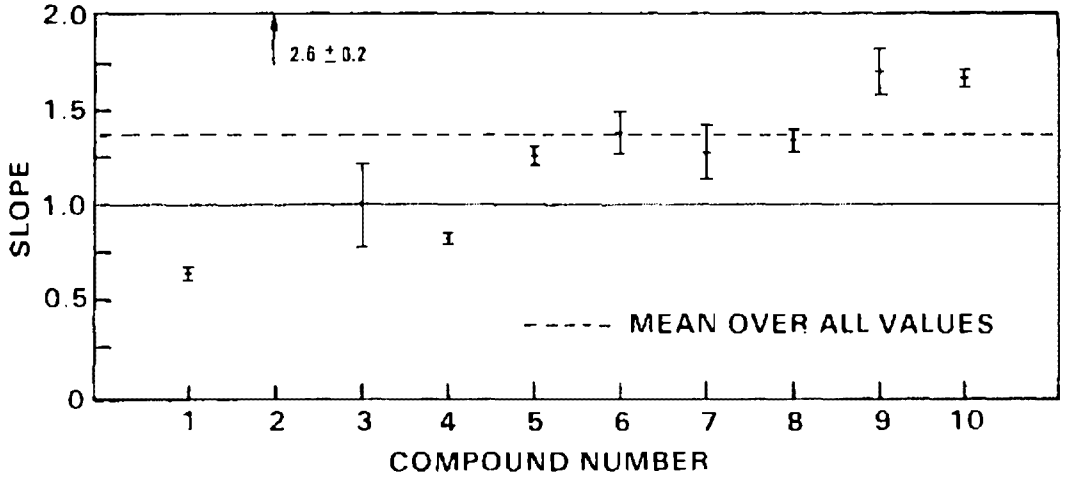

Figure 6 AGREEMENT Tenax high rate personal sampling device and canister slope plus and minus one standard error from the linear regression of Tenax mean vs canister mean.

PASSIVE SAMPLING DEVICES FOR NO_2

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ABSTRACT

For the past several years considerable progress has been made in the development of passive sampling devices (PSDs) for the collection and analysis of both inorganic and organic pollutants from air. This paper describes the status of EPA's program in developing a passive sampling device for the collection and analysis of NO_2 for application primarily in indoor air environments.

INTRODUCTION

In the past, active sampling devices have been the method of choice for the collection of NO_2 from ambient air. Active sampling devices are flow-through devices that require a mechanical means (pump) to move the sample to the collection medium. In recent years interest has been increasing in the use of diffusion-based passive sampling devices (PSDs) for the collection of NO_2 from air. PSDs are more attractive for indoor air because of their characteristics of small size, quiet operation (no pump), and low unit cost. Wallace[1] and others have shown that the air quality inside buildings, where people spend 90% of their lives, is considerably different from outdoor air. Therefore, fixed monitoring stations do not always reflect the actual concentrations of pollutants that people come in contact with in their daily lives. Epidemiologists believe that to determine health effects of NO_2 on humans, the sampler must be either worn by people or be in close proximity to where people spend most of their time -- indoors. Since most people do not wish to carry noisy pump samplers on their person or have them near where they work, sleep, eat and play, passive samplers may well be the answer. Another important criterion in developing a PSD for NO_2 is that it should be capable of doing 8 to 24 hr

time weighted averages in order to obtain meaningful health effects data. Commercially available passive sampling devices for NO_2 lack the sensitivity to obtain the 8 to 24 hr time weighted average data that is needed. The Palmes[2] NO_2 diffusion tube is a PSD that has been used effectively since 1976 in many studies monitoring high exposure levels of workers to NO_2. The Palmes tube shown in Figure 1 is a 2.8" by 3/8" acrylic tube that contains 3 metal screens coated with triethanolamine (TEA) as the sorbent. NO_2 is collected on the sorbent by Ficks 1st law of diffusion.

$$M = D \frac{A}{L} (C_\infty - C_0)$$

where

M = mass flow cm^3/min
D = diffusion coefficient cm^2/min
A = cross sectional area of diffusion channel cm^2
L = length of diffusion channel cm
C_∞ = conc of NO_2 in air surrounding PSD
C_0 = conc of NO_2 at surface of sorbent.

After sampling is complete, a color reagent is added to the tube, mixed, developed and the result color is measured s rophotometrically. Since the Palmes NO_2 tube been used effectivel long term studies (5 to 7 days), it was logi to try to improve the itivity to make it applicable for 8 to 24 hr studies. The main reason for the low sensitivity of the Palmes NO_2 tube is that it has an effective sampling rate of ~ 1.0 cc/min. There are basically three ways to improve the sensitivity of any passive sampling device:

1. Increase the sampling rate by making the A/L ratio larger in Ficks equation.

2. Concentrate the sample.

3. Use a more sensitive analytical technique.

One or more of the aforementioned approaches to increase PSD sensitivity were used in our research on developing potential indoor air NO_2 passive method. The four methods that were studied are listed blow:

1. Modified Palmes tubes with ion chromatographic (IC) analysis and a concentrator column -- Washburn University -- Cooperative Agreement No. CR11532-01.

2. EPA-PSD with Palmes tube chemistry and ion chromatographic analysis without a concentrator column -- In-house Contractor -- Northrop

3. Passive version of commercially available Thermosorb NO_2 cartridge with morpholine chemistry -- Contract No. 68-02-4127 -- Thermedics, Inc.

4. Ag/AgO on Chromosorb P and chemiluminescence analysis -- Battelle -- Columbus -- Contract # 68-02-4127

Another method that appears to have potential as a NO_2 passive sampling device in indoor air is the Yanigisawa[3] filter badge, but it was not investigated because of time and funding constraints.

It is important to emphasize that this paper is intended only to present the status of EPA's multi-faceted program to develop a passive sampling device (PSD) for the collection and analysis of NO_2 in indoor air. It is hoped that one or more of these techniques will become a useful method for monitoring NO_2 in indoor environments. Each of the methods studied will be described with emphasis on those methods that appear to have the best potential. Each method described will be a subject of either an EPA final report available from NTIS or a journal publication.

METHODOLOGY

The first approach considered was to improve the sensitivity of the Palmes NO_2 tube using ion chromatographic (IC) analysis and a concentrator column.

This work was done by Dr. Donald Miller of Washburn University under Cooperative Agreement No. CR11532. Theoretically, ion chromatography with a concentrator column should have reduced the minimum detectable quantity (MDQ) from 300 PPB-hr to 4 PPB-hr. Upon laboratory evaluation the MDQ was only reduced to 30 PPB-hr ± 20%, which is still adequate for 8 to 24 hr time weighted data. Apparently, sample concentration produced more problems than it solved. For example, the concentration step caused CL^- to interfere with resolution of the NO_2^-. It became necessary to build a special extraction apparatus to extract the nitrite ion from the TEA-coated screens in order to prevent handling contamination. The acrylic tube of the Palmes NO_2 device was found to act as a sink or a source of NO_2 depending on how well it was cleaned. Finally, stainless steel tubes were recommended to minimize contamination in order to obtain the necessary minimum detectable quantity of NO_2 for indoor air measurements. These added steps make this method too cumbersome to recommend for routine analysis of NO_2 in indoor environments.

A second method that appeared to have the sensitivity required was the Thermosorb cartridge that was originally designed for nitrosamine collection followed by GC-TEA[4] chemiluminescence analysis. Thermedics, Inc. under Contract No. 68-02-4084 determined the feasibility of using the Thermosorb NO_2 active cartridge in the passive mode with morpholine as the sorbent. Morpholine reacts with NO_2 to form nitrosomorpholine which can be easily analyzed at the sub parts-per-billion level with a GC-TEA chemiluminescence monitor. Initial testing involved converting the Thermosorb NO_2 active cartridge into a passive device simply by capping one end, removing the cap and enclosure from the other end, and coating the felt pads in the cartridge with morpholine. Although representative NO_2 data were obtained, it was not repeatable, probably because of the volatility of the morpholine which allowed it to diffuse from the matrix. The morpholine chemistry and acidic pH also turned out to be non-compatible with a variety of supports including various gels, polymers and latexes. Attempts were made to use another passive sampling device from GMD Systems, Inc. with morpholine chemistry. Unfortunately, the morpholine was also not compatible with the membrane of the GMD badge and severe loss in diffusion rates was observed. It is possible that additional research on using morpholine as the collecting reagent for NO_2 may still be successful, but the initial problems found in this feasibility study, along with the marked success of two other passive methods that were investigated, indicate that further work on this project is not warranted.

The third approach was to modify the EPA-PSD that was originally developed for the collection and analysis of volatile organic compounds[5] and

to convert it into a PSD for NO_2. This work was done by our in-house contractor, Northrop, Inc. (Dennis Williams). A schematic of the EPA-PSD is shown in Figure 2. This device is now commercially available from Scientific Instrumentation Specialists, Inc., Moscow, Idaho. To convert the device into a NO_2 PSD the Tenax was removed and replaced with triethanolamine-coated glass fiber filter paper. The analytical technique was ion chromatography (IC) without a concentrator column.

After exposure, the triethanolamine-coated filter paper is extracted with 10 ml of distilled deionized water and an aliquot is injected directly into the ion chromatograph with no concentration step. A typical ion chromatogram is shown in Fig. 3.

The primary advantage of the EPA-PSD for NO_2 with Palmes tube chemistry is that ion chromatography can be used without a concentrator column and still attain the 30 PPB-hr MDQ needed for indoor air monitoring. The concentrator column is not needed because the effective sampling rate of the EPA-PSD is 154 cc/min as compared to ~ 1 cc/min for the standard Palmes tube.

The EPA PSDs were evaluated in a NO_2 exposure chamber in sets of 5 at concentrations ranging from 20 $\mu g/m^3$ to 460 $\mu g/m^3$. The NO_2 concentration in the exposure chamber was continuously monitored with a Bendix NO_x chemiluminescent monitor.

Fig. 4 is a linear regression plot of NO_2 generated (as measured by a Bendix NO_x monitor) versus NO_2 found by ion chromatographic analysis. Each point is an average of 5 PSD-NO_2 values sampled at that concentration for 24 hrs. The correlation coefficient of .9955 is excellent over the range studied (20 $\mu g/m^3$ to 460 $\mu g/m^3$). Fig. 4 also shows that 91 $\mu g/m^3$ of nitric oxide and a relative humidity of 57% have no deleterious effect on the efficiency of the EPA-PSD. Additional interference studies are necessary, such as higher humidities and peroxyacetyl nitrate (PAN), although PAN probably would not be a pollutant found in indoor atmospheres.

Fig. 5 is a plot of total µg of nitrite found by IC on the TEA glass fiber filter versus sampling time while maintaining the concentration of NO_2 at 58 PPB or 109 $\mu g/m^3$.

The fourth method that was investigated as a possible passive sampling device for NO_2 involves collection on Ag/AgO coated on an inert support followed by thermal desorption into a chemiluminescent monitor. This work is being done by Dr. Robert Coutant of Battelle-Columbus. While such a thermally reversible sorbent would be ideally suited for use in the EPA-PSD, it is also equally applicable to active sampling. The active sampling mode appeared to be the quickest means of determining the feasibility of collecting NO_2 on Ag/AgO followed by thermal desorption into a chemiluminescent monitor. The sorbent tubes used in the active sampling mode were 2" by 1/4" O.D. stainless steel with quick disconnect fittings. Collected samples of NO_2 were thermally desorbed into a chemiluminescent monitor. Quantitation was achieved by comparing peak areas with responses obtained with known NO and NO_x samples. A variety of solid supports were investigated as the media on which to coat the Ag/AgO. Chromosorb-P was selected as the support media for the Ag/AgO because it was the support that showed the least absorption of NO_2 as shown in Table 1.

A series of runs was conducted with varying levels of NO and NO_2 concentrations of the order of 200 ppbv. In these experiments the sample gas was drawn directly through the sample tube with a by-pass system in place to permit periodic monitoring of the sample composition. NO concentrations varied from about 200 ppbv to 2.5 ppmv. In all cases the NO_2 was essentially 100 percent removed from the sample stream and no removal of NO could be detected. Desorption following each run showed only single peaks at temperatures of 150-200°C. Attempts were made to electronically integrate the desorption peaks for quantitation purposes, but interfacing and improvement of the peak quality proved beyond the scope of this feasibility study.

Additional runs for quantitation were therefore made with manual control of temperature programming and manual integration of stripchart outputs. For these runs the temperature was increased at approximately 100°/min to 200°C and was then held constant at 200°C until desorption was complete. A sample output from one of these runs is shown in Figure 6 (reconstructed from stripchart readings). In this figure the NO_x output is shown at the bottom and the NO signal is shown at midscale (zeroed at midscale). It can be seen that the principal component of the effluent is NO_2. The minor amount of NO seen in this figure may have resulted from thermal conversion on the stainless steel tube surface. Results of these runs are summarized in Table 2.

For the most part these results reflect efficient collection and recovery of NO_2 with little evidence of interference by NO. In the case of the tube that was pretreated with CO_2, there is no evidence for interference by this compound, even after the system had been exposed to approximately 3.8 L-atm of pure CO_2. This same tube was used for the last two samples cited in Table 2 with no consistent impairment of performance. The low desorption efficiency for the last sample in Table 2 is believed to be due to an experimental artifact.

CONCLUSIONS

The additional sample handling problems produced by using a concentrator column and ion chromatographic analysis with the Palmes NO_2 diffusion tube make this methodology less than desirable even though the MDQ was decreased to 30 PPB-hr.

The approach of using morpholine to collect NO_2 as nitrosomorpholine in a passive Thermosorb device coupled with GC-TEA chemiluminescence analysis is still possible, but the incompatibility of morpholine with various polymers and the volatility of morpholine producing stability problems will be difficult to overcome.

The modified EPA PSD with Palmes tube chemistry coupled with ion chromatography and no concentrator appears to be a viable passive sampling method for the collection of NO_2 in indoor air. The minimum detectable quantity (MDQ) of 30 PPB-hr that is attainable with this methodology is adequate for 8 to 24 hr time weighted averages of NO_2. Additional interference studies are planned along with field comparison studies, particularly with the new portable Scintrex LMA-3 continuous NO_2 monitor based on luminol chemiluminescence that is being evaluated as a real-time monitor to measure peak concentrations in indoor air.

The solid sorbent method (Ag/AgO on Chromosorb-P) that is capable of reversible thermal adsorption of NO_2 into a chemiluminescent monitor is perhaps the most attractive method for the collection and analysis of NO_2 because of its potentially high sensitivity and versatility in that it can

be used for both active and passive sampling. Based on observed peak areas from the limited feasibility study described herein for a sample collected at 50 cc/min for 15 minutes, 3 ppbv could be easily detected. If the sorbent were used in the EPA-PSD that samples at 154 cc/min a minimum detectable quantity of < 1 ppbv could be achieved. The major advantage of this technique is that no sample pretreatment is necessary and analysis can be completed in 10 minutes.

The results of the feasibility study or collecting NO_2 with Ag/AgO were limited but showed significant potential for sampling and analysis of NO_2. Research will continue on this project with a focus on use of Ag/AgO in passive sampling devices. Obviously, shelf life, relative humidity and other possible interferents (PAN, NH_3, etc.) will be studied. Plans are to fabricate a more formalized but flexible analytical system and thermal desorption interface. The scope of the additional studies will encompass both controlled laboratory experiments and limited field studies.

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5. R. G. Lewis, J. D. Mulik, R. W. Coutant, G. W. Wooten, and C. R. McMillin, "Thermally Desorbable Passive Sampling Device for Volatile Organic Chemicals," Analytical Chemistry, 1985, 57:214-219.

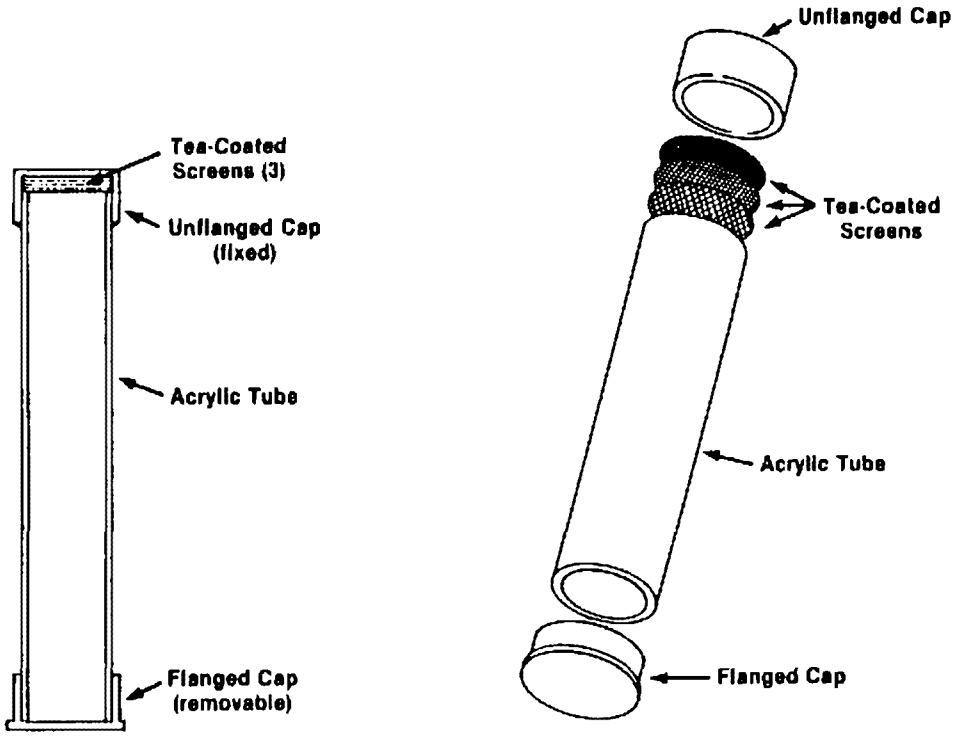

Figure 1. Assembled view (left) and exploded view (right) of Palmes NO_2 diffusion tube sampler.

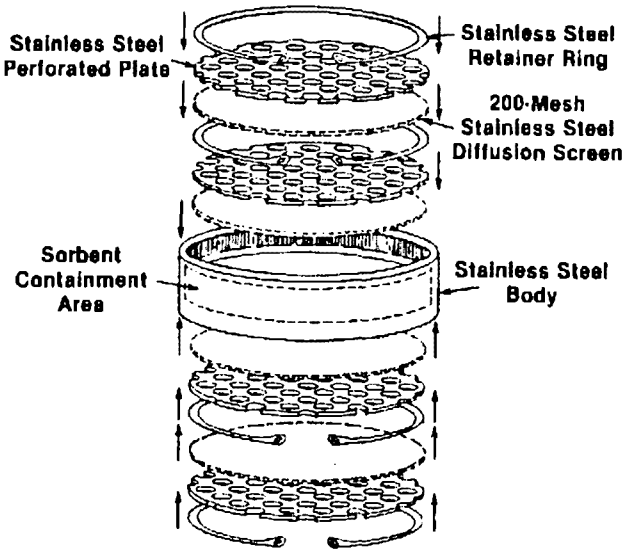

Figure 2. NO_2 passive sampling device.

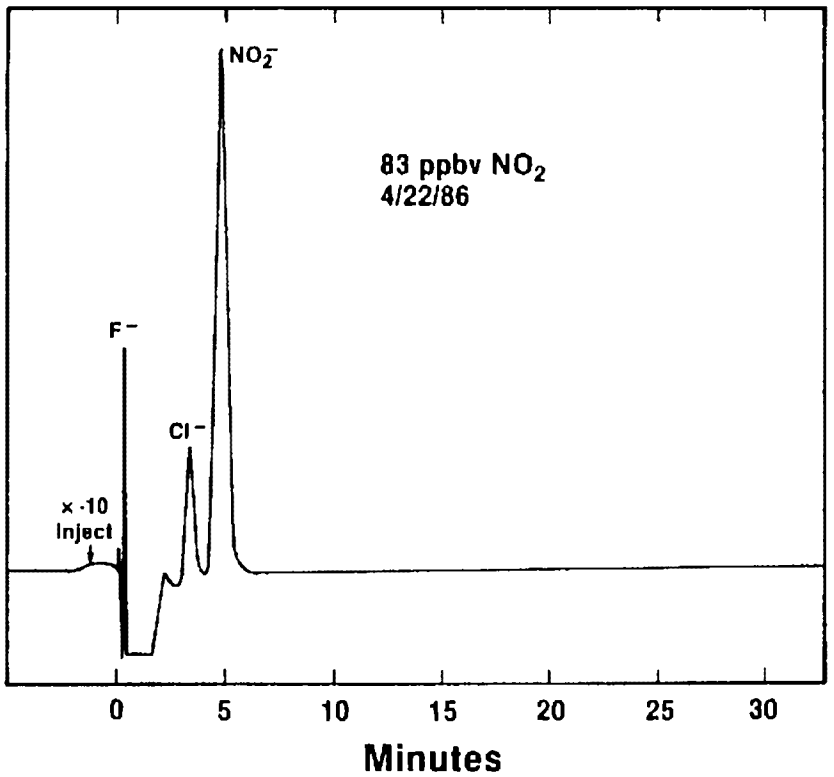

Figure 3. Typical ion chromatogram of TEA-NO_2 extract.

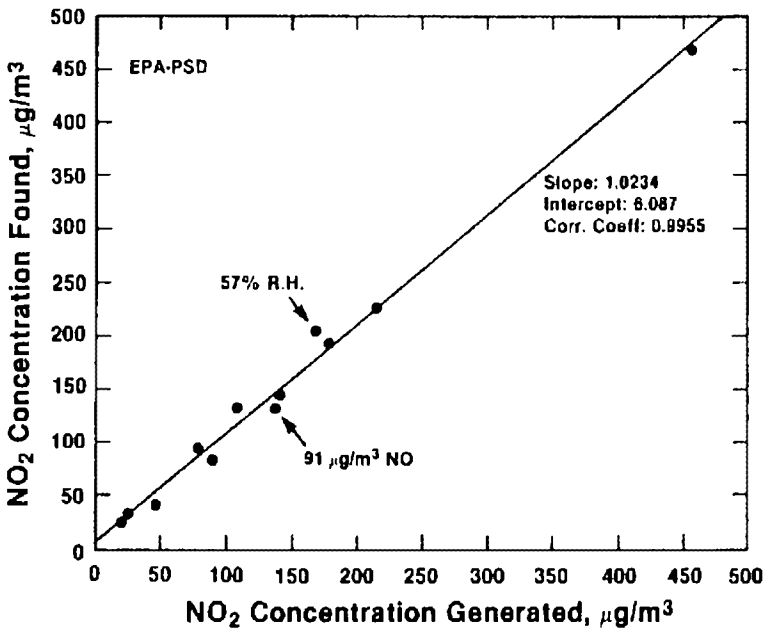

Figure 4. Plot of NO_2 found by IC vs. NO_2 generated.

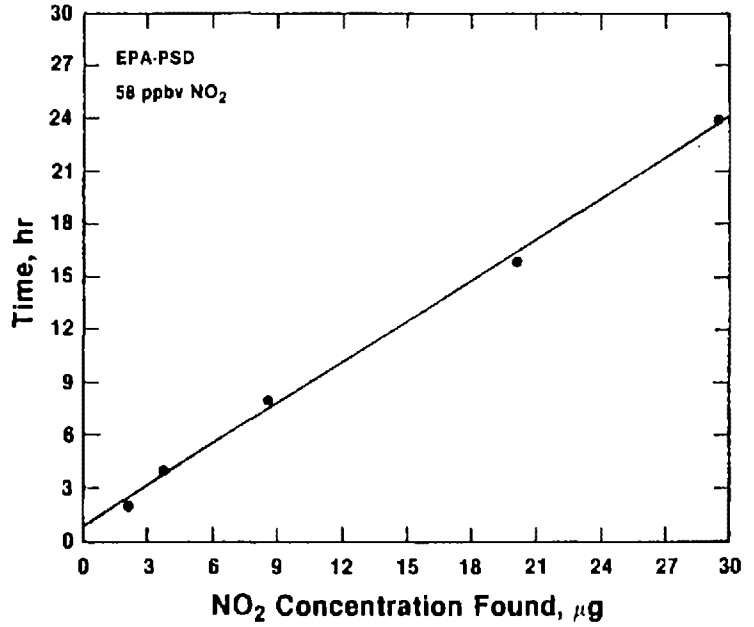

Figure 5. NO_2 concentration found by varying the sampling time.

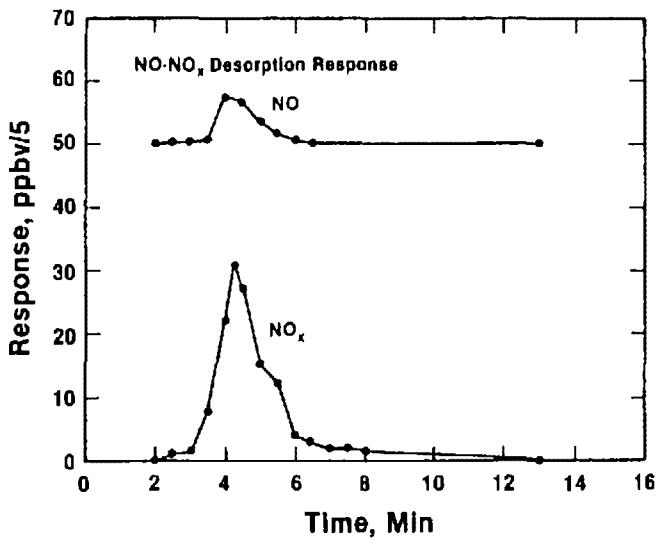

Figure 6. Sample recording of analytical response Ag/AgO on Chromosorb-P.

Support	Treatment	Percentage Removal of[a]	
		NO_2	NO
Fisher Alumina	None	100	100
Supelco Alumina	None	80	75
Supelco Alumina	Water Washed	65	62
Supelco Alumina	Nitric Acid Washed	95	87
Quartz Beads	None	12	9
Porasil B	None	24	16
Chromosorb P	None	8	0

[a]Challenge mixture of approximately 200 ppbv NO + 200 ppbv NO_2.

Table 1. Sorption of NO_x by candidate support media.

Sample Source[a]	NO ppbv	NO_2 ppbv	NO_2 Dose nL	NO_x Recovered, nL	Eff. Percent
A	200	200	70.0	67.6	96.5
A	200	200	59.5	57.3	96.3
A[b]	200	200	193.0	137.0	81-89
A[b]	200	200	175.0	154.0	88-100
B	200	200	91.0	83.6	92.0
C	20	40	171.0	166.0	97.0
C	0	60	262.0	136.0	52.0

[a] A = Standard cylinder source of NO with 50 percent titration of NO with O_3.
B = Same source as A, but with pretreatment of tube with 100 percent CO_2.
C = Laboratory air.

[b]Discrepancy between NO and NO_x outputs.

Table 2. Summary of quantitative NO_2 sampling runs for Ag/AgO on Chromosorb-P.

DEVELOPMENT OF AN ADSORPTION/THERMAL DESORPTION TECHNIQUE COUPLED WITH GC/MS FOR THE MONITORING OF TRACE ORGANIC CONTAMINANTS IN INDOOR AIR

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The use of multi-layer sorbent cartridge coupled with thermal desorption technique in the collection and analysis of both volatile and semi-volatile organic compounds in the indoor environemt is described. The performance of the sorbents with reference to the adsorption characteristics, breakthrough potential, retention of the organics, and artifacts released from the adsorbents during the thermal desorption process are evaluated to determine their suitability for use.

Overall recoveries and reproducibity of most of the organics desorbing from the cartridge are generally satisfactory, except for a few compounds which either appeared to be decomposed or were not desorbed very efficiently under the experimental conditions. Very little memory effect is observed in the sorbent cartridges and the internal traps for volatile organics, wheras retention in the traps and the original cartridge was detected in the semi-volatile compounds. Limits of detection were determined for 52 compounds: most of them in the ppt or low ppb range based on the volume sampled.

INTRODUCTION

The presence of toxic organics in the indoor environment has been the subject of increasing concern over the quality of air in both residences and workplaces. Due to the continuous emission of contaminants from building materials and man-made activities(1-3), pollutants can accumulate in tightly sealed buildings, and since most people spend a large fraction of their time indoors, long term exposure of even trace levels to toxic contaminants may ultimately create a health problem.

To characterize and measure a broad spectrum of organic pollutants in indoor air, a number of methods have been employed. These methods include freeze concentration (4), impinger collection (5), and sorbent trapping (6). A preconcentration step is usually necessary in monitoring trace levels of organics due to the limited sensitivity of analytical instruments. In some cases, the entire sample is required for analysis to achieve an adequate sensitivity. As a result, the thermal desorption technique has gained widespread acceptance in recent years for the analysis of minute quantities of hazardous organics in ambient air. This approach generally offers better sensitivity; eliminates the use of solvents and requires very little handling. Previous studies in this area have been conducted to evaluate this technique using Tenax as the trapping media for volatile organic vapours (7-12). Some of these studies (6,7,13) have indicated a poor adsorption efficiency of Tenax for very volatile organics; and hence a requirement for backup sorbents.

This paper evaluates the use of a multi-layer sorbent cartridge for the collection and analysis of a wide range of organic contaminants in ambient air using the thermal desorption technique. The desorption conditions, memory effect, adsorption characteristics, breakthrough volumes and artifacts resulting from the process have been investigated. In addition, the possibility of extending this technique to cover the semi-volatile organics has also been examined.

EXPERIMENTAL

Materials

Packed sorbent cartridges (20 cm long, 6 mm OD, 4 mm ID), constructed of pyrex glass and containing multi-layer sorbents were obtained from Envirochem Inc. (Kemblesville, Pa.) or were prepared in-house. Tenax-TA (60/80 mesh) was purchased from Alltech Assoc. (Deerfield, Il.); Ambersorb XE-340 (30/60 mesh) was obtained from Rohm and Haas Inc. (Philadelphia, Pa.). Silicone coated glass beads (60/80 mesh) and charcoal (60/80 mesh) were acquired from Chromatographic Specialities Ltd. (Brockville, Ontario). The glass beads were prepared for use by extraction with methylene chloride and heating in an oven at 350°C. The other sorbents were thermally desorbed at 20°C below their maximum temperature for 2 hours in a sorbent tube conditioner, while being purged continuously with high purity nitrogen at a flow rate of 50 ml/min prior to use.

All analytical standards were obtained from Aldrich Chemicals (Milwaukee, Pa.) and Chem Service (West Chester, Pa.). In most cases, the

purity of the standards was determined by GC/MS prior to their use in this study.

Apparatus

Analyses were performed using an Envirochem concentrator model 780B. This unit was interfaced with a Finnigan 3300 mass spectrometer equipped with a model 9500 gas chromatograph and data system. The plumbing of the concentrator was modified in-house, so that splitting of the sample was completely eliminated to achieve better sensitivity and reproducibility. An automatic desorber unit was attached to the Envirochem concentrator, with a separate module controlling the temperature and timing of the desorption process. The desorber unit consisted of five major components: a sleeve heater which accommodated the sorbent cartridge, an injection port, a high temperature four port valve, a heated transferline to the valve compartment of the concentrator, and a temperature controller. Carrier gas was allowed to enter from the side of the injection port and flow through the sorbent cartridge at 40-50 ml/min. Introduction of standards into the sorbent tube or internal trap of the concentrator for calibration was achieved through the injection port. The temperature module, equipped with the desorber unit, controlled the rate and timing of the desorption process. This allowed the temperature to either rise rapidly (approximately 100°C/min), or ramp at a pre-set time of 20, 40, 60 minutes to the maximum desorption temperature.

The concentrator contained two internal glass traps of different bore size. The primary trap was large bore, which permitted a preliminary concentration of the compounds of interest from the high flow of carrier gas during the initial desorption cycle. At the end of the desorption, an auxiliary carrier gas was used to purge any residual organics in the transfer lines into the primary trap. The primary trap was then thermally desorbed, with the retained compounds being transfered to the secondary small bore trap, which was approximately 1/10th the capacity of the first. The small bore trap, which contained glass beads, Tenax, silica gel, Ambersorb XE-340 and charcoal, allowed for an efficient injection of the compound of interest to the capillary due to the relatively high linear velocity through the small inside diameter of the trap, even at the relative low flow rates required by the capillary. The combination of the small bore trap, a rapid trap heating rate (approximately 1000°C/min), and selected sorbent materials, produced a discrete narrow-band plug of sample for deposit on the head of the column.

Preparation and Packing of the Sorbent Tube

Pyrex glass tubes (20 cm long, 6 mm OD and 4 mm ID) were soaked in detergent, followed by rinsing with both tap and distilled water. The empty tubes were then silanized with 5% dimethyldichloromethane in hexane, rinsed thoroughly with tap water, distilled water and acetone, and left to dry in a clean oven maintained at 200°C. The glass tubes were filled with approximately 0.3 gram of silicone coated glass beads (60/80 mesh) obtained from Chromatographic Specialities Ltd. and baked in a tube conditioner at 425°C for an hour with a high purity nitrogen purge of 50 ml/min. Silanized glass wool plugs (DMCS treated) were used to retain and separate the adsorbents.

Tenax TA (Alltech Assoc. 60/80 mesh, 0.07 gram) was then added to the tubes followed by conditioning at 350C with 50 ml/min of nitrogen for two hours. The Tenax layer was observed to shrink after conditioning, and the tubes were therefore agitated with a vibrograver to settle the packings again.

Ambersorb 340 (Rohm and Haas Inc. 30/60 mesh, 0.15 gram) and charcoal (Chromatographic Specialities Ltd., 60/80 mesh, 0.23 gram) were added consecutively to the sorbent tubes, with thermal baking at 350°C for two hours with nitrogen after each addition to get rid of the contaminants. The sorbent tubes were positioned in the conditioner in such a way that the newly added adsorbent was always on the exit end of the gas flow, hence any breakdown products during the conditioning would not be released into other adsorbent layers.

After conditioning, the sorbent tubes were immediately placed in clean screw-capped test tubes that had previously been heated and purged with nitrogen. The test tubes were then stored in second glass container filled with nitrogen and tightly sealed to avoid contamination.

Preparation of Composite Standards

A stock volatile standard solution was prepared by injecting approximately 200-300 ul of each contaminant into a 10 ml reactiflask fitted with a Minnert valve which provided complete protection and easy access via a hypodermic needle. After all the components had been added the composite solution was agitated to ensure homogeneity. Aliquots of the resulting solution were removed, and either injected into a helium-filled bottle equipped with a septum top to produce gaseous standards or further diluted in glass distilled methanol to give concentrations of 50-75 ng/ul for each of the components.

A stock semi-volatile composite standard solution was prepared by accurately weighing about 10 mg of each component and dissolving in 10 ml of acetone in a graduated volumetric flask. Secondary standard solutions were obtained by diluting the stock solution in methanol to give approximate concentrations of 50 - 100 ng/ul for each component.

Introduction of the composite standards onto the sorbent tubes was achieved by two methods. In the first method, the composite standard was diluted to the appropriate concentrations and injected directly onto the glass bead layer of the sorbent tube. The orientation of the tube was such that the glass beads were facing the injection port. After injection, a stream of helium was allowed to pass through the sorbent tube for 10 minutes.

The second method involved injection of appropriate aliquots of the gaseous standards that were prepared in the bottle into a clean sorbent tube through the injection port of the desorber at room temperature. Again, the sorbent was purged with helium prior to the analysis. The total amount of each standard loaded on the sorbent tube was calculated from the concentrations and the volume of the composite standard used.

Thermal Desorption of the Organics

In a typical thermal desorption analysis, the sorbent tube was placed in the sleeve heater such that the carrier gas flow through the tube was in the reverse direction of the flow used to collect the sample. The tube was then secured on both ends with Graphite/ Vespel ferrules. A high flow of helium was allowed to pass through the sorbent tube while, at the same time, the temperature was immediately raised to the maximum desorption temperature. Adsorbed organics were released from the packing materials into the primary trap of the concentrator and subsequently the GC/MS system. Concentrator conditions were: transfer lines at 280°C; initial purge time of 2 minutes; sorbent tube desorbed at 280°C for 12 minutes with helium flow of 50 ml/min; trap 1 desorbed at 300°C with a flow of 50 ml/min; trap 2 desorbed at the same temperature with helium flow of 2 ml/min onto a 30 m J & W DB-5 fused silica column (1.0 um film thickness, 0.25 mm ID) maintained at 40°C. Desorption time for the semi-volatile organics was set at 20 minutes and at a desorption temperature of 300°C.

An alternative desorption condition was also used in this study to determine the effect of temperature on component recovery. Under this condition, the temperature was ramped at 20°C/min to the maximum desorption temperature and held for 20 minutes to allow complete desorption of the high boiling organics from the sorbent tube. A major advantage of this method was that the recoveries of some heat labile compounds such as p,p-DDT, diazinon and BHC's were improved significantly.

The 2 minute purge with carrier gas was very critical, as this step ensured that oxygen in the sorbent tube was completely removed before increasing the temperature. Hence any oxidative reaction during the thermal desorption process could be eliminated.

RESULTS AND DISCUSSION

The choice of an effective adsorbent is usually based on the following requirements: low background; good collection efficiency; ability to desorb quantitatively, reproducibly and efficiently during the thermal desorption process; and high breakthrough volume. Polymeric adsorbents, in particular Tenax-GC, have been demonstrated in a number of studies to be an excellent sorbent for a wide variety of organics in ambient air (9-11). However, a major disavantage of Tenax-GC is its relatively poor adsorption efficiency for very volatile organics. To solve this problem, a backup sorbent or cartridge is required for sampling highly volatile organics. In the present work, the use of multi-layer sampling cartridges was evaluated to determine the sorption characteristics and its usefulness in air analysis. A broad spectrum of organics of different physiochemical properties was selected to thoroughly test this technique. The following sorbents were used in the cartridge: glass beads (for high boiling compounds); Tenax-TA (for medium to medium low boiling compounds); Ambersorb XE-340 (for volatile compounds) and activated charcoal (as a backup for very volatile compounds).

The results obtained from the thermal desorption study of the volatile and semi-volatile organics using the multi-layer sorbent cartridges are depicted in Table I. In these experiments, a composite solution of organics was introduced through a heated injection port onto the sorbent cartridge, and subsequently desorbed into the GC/MS system. For volatile organics, a

rapid temperature ramping rate (100 ^{o}C/min), in conjunction with a high flow of carrier gas (50 ml/min) through the sorbent tube, appeared to provide good recoveries and reproducibility for most of the volatile organics. With the exception of bromobenzene, which appeared to be degraded prior to entering the GC/MS system, quadruplicates using the same composite standard generally agreed within 10%, although in a few cases one sample of the quadruplicate set was slightly different from the rest to result in larger coefficient of variation. The response of the carbon tetrachloride was also found to be significanltly lower than the other chlorinated hydrocarbons although the recovery and reproducibility data were quite good. The method detection limits using the Finnigan 3300 GC/MS system averaged about 6 ng per cartridge, slightly better for the aromatics such as benzene, toluene and xylenes.

Application of thermal desorption technique to semi-volatile organics was not as successful as the volatile organics using the present system. This class of compounds generally showed greater variation, lower recoveries and higher detection limits. For example, high boiling compounds such as benzo(ghi)perylene either were not detected, or in the case of benzo(a)pyrene, exhibited very poor response. p,p' DDT appeared to breakdown during the thermal desorption process and 2,4-D, which normally requires derivatization to be analysed by gas chromatography, was not detected. In addition, responses of nicotine, pyrethrin and pentachlorophenol were very poor. The latter two compounds were also shown to have a high coefficient of variation (24.3% and 30.2% respectively). A slow temperature ramping rate (20°C/min) during the thermal desorption appeared to improve the recovery of p,p'-DDT and pyrethrin. However, the desorption time had to be extended significantly under this condition to desorb the high boiling compounds.

In spite of the problems encountered with some of the compounds in this catagory, the rest of the semi-volatile organics were found to show good results. Recoveries of these compounds generally ranged from 70-80% with a coefficient of variation less than 20%. Diazinon, which is reported to decompose at temperatures higher than 120°C, was found to have a 95% recovery.

The major problem in the analysis of the semi-volatile organics was in large part due to the desorption device used in this study. The compounds investigated consisted of both heat labile compounds and high boiling compounds. To efficiently desorb the high boiling compounds without significant degradation of the heat labile compounds, a short transfer pathway coupled with an optimum temperature and fast heat transfer from the heat source to the sorbent bed were required. In addition, sufficient desorption time should be allowed at the maximum desorption temperature to enable complete removal of the organics from the sorbents. Unfortunately, in these experiments, the organics had to pass through two internal traps, a number of transfer lines, and two valving systems which have an upper temperature limit of 250°C. Any cold spot in the system may eventually cause condensation of the high boiling organics. Although the internal traps of the concentrator were desorbed at 320°C, the desorption time could not be controlled. Consequently, recoveries and reproducibility of the high molecular weight compounds were not very satisfactory.

Evaluation of the Adsorption Characteristics

To better understand the role of the multi-layer sorbents in the adsorption of a wide range of organics, a series of experiments were conducted to examine the adsorption characteristics of each packing material. In this study, a sorbent tube train, which consisted of 5 tubes in sequence (glass beads, Tenax TA, Ambersorb XE-340, activated charcoal and a backup sorbent cartridge) was attached to a gas chromatograph inlet. The amount of packing materials in each tube was proportional to the corresponding amounts in a regular cartridge.

A known concentration of the volatile organics in gaseous form was then introduced into the sorbent train using the standard loading method as described. The sorbent train was left for a pre-determined period of time to allow a known large volume of carrier gas to pass through the system. The collection efficiencies of the adsorbents with passage of 10, 50, 100, and 500 litres of carrier gas were then determined and the relative percent retention in each adsorbent was calculated. This experiment was conducted using approximately 150 ng of each component and a flow of 450 ml/min of nitrogen carrier gas at 20°C.

The collection characteristics of the multi-layer sorbents are presented in Table II and III, where the organics found in each layer are expressed as a percentage of the total values of the sorbent train. As expected, most of the volatile organics are poorly retained by glass beads. Except at lower gas volumes for some less volatile compounds such as dichlorobenzenes, trichlorobenzenes and naphthalene, glass beads are completely ineffective in adsorbing the volatile compounds. The collection efficiencies of Tenax-AT for most of the organics under investigation are quite acceptable at low gas volumes. Increasing the volume of carrier gas through the sorbent train is observed to have a major effect: a higher percentage of the relatively volatile organics was detected in the Ambersorb layer instead of the Tenax layer. This effect is more noticeable with the low boiling compounds such as acetone, diethyl ether, methylene chloride and 1,1-dichloroethylene. No significant difference is observed in the breakthrough of the semi-volatile compounds from the Tenax layer at all gas volumes.

Ambersorb XE-340 is generally effective in retaining the more volatile organics, although breakthrough of some of these compounds is possible at high gas volumes. This carbonaceous adsorbent has a chemical composition intermediate between that of activated carbon and polymeric adsorbents, and unlike activated carbon, it can efficiently desorb many types of organics compounds. This superior adsorption capacity, coupled with the low retention for water, makes this synthetic polymer an ideal backup sorbent for Tenax. Unfortunately, a major drawback of this adsorbent is noted in its inefficiency in retaining water soluble compounds such as the alcohols and ketones at high gas volume. To compensate for the breakthrough of the polar compounds, activated charcoal was used as a final backup layer. Examination of the compounds retained in the charcoal layer indicates that this sorbent increases the overall adsorptivity of the cartridge by retaining the polar compounds and the very volatile organics.

The backup sorbent tube used in this study was to ensure that any breakthrough of the organics from the multi-layer sorbents could be detected.

Breakthrough into the backup sorbent tube was not observed with gas volumes up to 100 litres but at 500 litres, small amounts of some of the more volatile compounds were found in the backup sorbent tube.

Memory Effect

One major consideration of the thermal desorption technique is the possible retention of organics in the original sorbent tube, or the trapping system in the concentrator. To determine this retention behaviour, the volatile standard in vapor form, and the composite semi-volatile standards, were loaded into sorbent cartridges which were then desorbed into the concentrator under the conditions described in the experimental section. The trapping system and the sorbent tubes were desorbed once and then re-analysed to determine the effectiveness of the desorption process. Table IV illustrates the memory effect after the analysis of spiked sorbent tubes.

In these experiments, the desorption of the volatile organics from the sorbent cartridges are shown to be quite effective. Overall relative recoveries of over 90% were achieved with very little retention in either the original sorbent cartridge or the internal traps of the concentrator. However, for the semi-volatile fraction, an erratic retention pattern was observed. Due to the design of the concentrator used for this work, as described in the previous section, non-volatile organics generally do not pass through the system as efficiently as the volatile organics. Retention in the sorbent cartridges or the trapping system was common for the polar and the high boiling compounds. It should be noted that in this study the results are expressed in relative percentage. Hence any irreversible adsorption on the sorbents and traps, degradation during the desorption cycle, or reaction between the organics are not accounted for.

An attempt was also made to load the sorbent cartridges with volatile standards prepared in methanol to examine the memory effect resulting from this method. In contrast to the results obtained by loading the sorbent cartridge with gaseous standards, this experiment appears to have more carryover of the organics in the sorbents. A possible explanation is that the volatile organics in methanol solution may penetrate may be carried by methanol and penetrate deeper into the packing materials, and consequently are more difficult to be desorbed. This effect is evident by the proportion of polar compounds retained in the original sorbent tube. Based on these results, it is obvious that using liquid standards for volatile compounds is unacceptable in this technique.

Artifacts from the Adsorbents

The background contribution from adsorbents is a major drawback when using the thermal desorption technique for high sensitivity analysis. Tenax is known to release a number of components during the thermal desorption process (7,14), which may cause interferences with the identification and quantitation of unknown organic compounds. To investigate the occurrence of the artifacts from the multi-layer adsorbents used in this study, newly packed multi-layer sorbent tubes and individual adsorbents were analysed.

Multi-layer sorbent tubes were found to release a number of degradation products such as aromatic hydrocarbons, sulfur dioxide, carbon dioxide, phenol, benzaldehyde and acetophenone. Of the four adsorbents tested, Ambersorb XE-340 was observed to have the highest background. The major compounds in the backgound included benzene, styrene, toluene, xylenes, sulfur dioxide, naphthalene, acetophenone and C_3 benzenes. Tenax TA was also found to release a number of aromatics such as toluene, styrene, xylene, phenol and benzaldehyde. A relatively low backgound was found for glass beads and activated charcoal. Except for Ambersorb XE-340 the background usually decreased drastically after one thermal desorption cycle. For Ambersorb, a longer conditioning with carrier gas at elevated temperature was necessary to reduce the background.

Sulfur dioxide originates from the Ambersorb layer which is a synthetic carbonacous adsorbent prepared from cross-linked divinyl benzene which has been sulfonated prior to controlled pyrolysis. It is, therefore, suspected that sulfur dioxide is a decomposition product of the sulfonated resins. This compound appears to persist despite continuous conditioning of the resins, but fortunately, this compound elutes in the early part of the chromatogram and hence does not interfere with other compounds.

Based on these findings, it is concluded that a thorough conditioning of the sorbent tube is mandatory prior to use. In addition, an sorbent tube blank should be analysed prior to the sampling, otherwise false positive or false quantatition results will be obtained for these compounds.

CONCLUSION

The multi-layer sorbent cartridge, which contains glass beads, Tenax-TA, Ambersorb XE-340 and activated charcoal, proved to be quite effective in adsorbing a wide range of organics from the air stream. The performance is slightly less than ideal for polar compounds and also for very volatile compounds at high sampling volumes (> 100 litres). Overall recoveries and reproducibity of most of the volatile organics desorbing from the cartridge are generally good, except for bromobenzene which appeared to be degraded prior to entering the GC/MS system. The semi-volatile fraction was observed to have a few problems due to the design of the instrument. With the exception of the chlorophenols, phenoxy acids and the very high boilers, the rest of the organics under investigation were found to be satisfactory.

In general, very little memory effect is observed in the sorbent cartridge and the internal traps during a thermal desorption cycle of the volatile organics. However, for the semi-volatile fraction, retention in the traps and the original sorbent cartridge was detected. Breakthrough of volatile organics was not observed at a sampling volume of 100 litres with a flow rate of 450 ml/min. Hence, a maximum of 100 litres of sampling volume is recommended using this type of sorbent cartridge at levels of 50 ppt to 10 ppb. If the air sampled is suspected to have volatile organic loading of more than 10 ppb, reduced volumes should be taken. In addition, a duplicate sampling at a lower volume will be necessary to check for breakthrough. Since non-volatile organics are usually present at lower concentrations and thus require a large volume of air, it is recommended that they should be sampled

separately to avoid breakthrough of the volatile fraction.

ACKNOWLEDGEMENT

This research was supported by Health and Welfare Canada under contract no. 05SV.H4001-4-N0015. In-house manuscript review by Pierre Beaumier and Bill Burgess is gratefully acknowledged.

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TABLE I

RECOVERIES, REPRODUCIBILITY AND DETECTION LIMITS OF ORGANICS USING THERMAL DESORPTION TECHNIQUE

NO.	COMPOUND	QUANT ION 1	QUANT ION 2	REC. (%) [a]	C.V. (%) [b]	MDL Ng/Cartridge [c]
1	ACETONE	58	43	85	11.8	6
2	DIETHYL ETHER	59	74	93	4.7	6
3	ACRYLONITRILE	53	52	90	14.9	8
4	METHYLENE CHLORIDE	84	49	60	6.1	6
5	1,1-DICHLOROETHYLENE	61	96	119	9.6	6
6	1,1-DICHLOROETHANE	63	65	98	4.9	6
7	2-BUTANONE	56	74	72	9	6
8	HEXANE	57	86	92	8.7	6
9	CHLOROFORM	83	85	93	7.8	6
10	BUTANOL	56	43	95	5.7	6
11	BENZENE	78	77	92	4	4
12	CARBON TETRACHLORIDE	82	117	93	7.8	8
13	1,2-DICHLOROPROPANE	63	76	83	7.7	6
14	TRICHLOROETHYLENE	130	132	98	14.1	6
15	BENZALDEHYDE	77	106	93	2.8	6
16	1,1,1-TRICHLOROETHANE	130	132	89	15.2	6
17	TOLUENE	91	92	93	4.7	4
18	ETHYLENE BROMIDE	107	109	86	6	10
19	TETRACHLOROETHYLENE	129	169	92	6.8	6
20	FURFURAL	95	96	76	9.2	8
21	CHLOROBENZENE	112	114	97	4.7	6
22	1,3 & 1,4-DIMETHYL BENZENE	106	91	83	2.5	4
23	STYRENE	104	77	87	4.8	4
24	1,2-DIMETHYL BENZENE	106	91	75	6.1	4
25	1,1,2,2-TETRACHLOROETHYLENE	164	166	77	8.3	8
26	CHLOROTOLUENE	126	128	86	3.6	8
27	PENTACHLOROETHANE	83	84	100	3.2	10
28	1,3-DICHLOROBENZENE	146	111	92	8.3	4
29	1,4-DICHLOROBENZENE	146	111	84	5.6	4
30	1,2-DICHLOROBENZENE	146	111	86	4.1	4
31	1,2,4-TRICHLOROBENZENE	180	182	100	2	6
32	BROMOBENZENE	156	77	ND	-	
33	NAPHTHALENE	128	102	80	3.9	8
34	PHENOL	94	66	94	9.1	8
35	1,2 METHYL PHENOL	108	94	83.9	11.5	20
36	METHYL NAPHTHALENE	142	140	106	13.1	10
37	NICOTINE	84	-	37	9.2	75
38	HEXACHLOROBENZENE	282	284	86	12.2	8
39	DIETHYL PHTHALATE	149	177	102.3	11.9	10
40	LINDANE	181	217	80.3	9.1	10
41	DIAZINON	179	181	94.8	12.7	12
42	PHENANTHRENE	178	177	112.2	7.6	10
43	DIBUTYL PHTHALATE	149	121	87.3	10	12
44	PYRETHRIN	123	164	83.1	24.3	75
45	PENTACHLOROPHENOL	264	266	ND	-	75
46	FLUORANTHRENE	202	101	99.5	10	15
47	TRIBUTYL PHOSPHATE	155	99	111.5	6.8	10
48	BENZO (GHI) PERYLENE	276	138	ND	-	NA
49	P,P'-DDT	235	165	ND	-	NA
50	BENZO(A)PYRENE	252	126	40	37.8	75
51	METHYL STYRENE	118	91	84.7	8.9	8
52	2,4-D	162	220	ND	-	NA

a - Average of four determinations
b - Coefficient of variation
c - Minimum Detection Limit

TABLE II

ADSORPTION CHARACTERISTICS OF MULTI-LAYER SORBENTS WITH DIFFERENT GAS FLOW

(RELATIVE %)

COMPOUND	10 L PASSED					60 L PASSED				
	GLASS B	TENAX	AMBERSORB	CHARCOAL	BACKUP TUBE	GLASS B	TENAX	AMBERSORB	CHARCOAL	BACKUP TUBE
ACETONE	-	21.0	79.0	-	-	-	19.7	80.3	-	-
ACRYLONITRILE	-	32.7	71.6	-	-	-	-	100.0	-	-
METHYLENE CHLORIDE	-	11.3	83.7	-	-	-	16.0	84.0	-	-
1,1-DICHLOROETHYLENE	-	18.8	81.2	-	-	-	-	100.0	-	-
1,1-DICHLOROETHANE	-	11.6	88.4	-	-	-	-	100.0	-	-
2-BUTANONE	-	80.0	20.0	-	-	-	-	100.0	-	-
HEXANE	-	91.6	8.4	-	-	-	62.4	37.6	-	-
CHLOROFORM	-	29.6	70.4	-	-	-	17.4	82.6	-	-
BENZENE	-	89.1	10.9	-	-	-	28.9	71.1	-	-
CARBON TETRACHLORIDE	-	47.5	52.5	-	-	-	17.4	82.6	-	-
1,2-DICHLOROPROPANE	-	100.0	-	-	-	-	59.7	40.3	-	-
TRICHLOROETHYLENE	-	100.0	-	-	-	-	66.3	33.7	-	-
BENZALDEHYDE	-	89.3	10.7	-	-	-	68.1	31.9	-	-
1,1,1-TRICHLOROETHANE	-	100.0	-	-	-	-	100.0	-	-	-
TOLUENE	-	94.7	5.3	-	-	-	96.7	3.3	-	-
ETHYLENE BROMIDE	-	100.0	-	-	-	-	100.0	-	-	-
TETRACHLOROETHYLENE	-	100.0	-	-	-	-	100.0	-	-	-
FURFURAL	-	100.0	-	-	-	-	100.0	-	-	-
CHLOROBENZENE	-	98.8	1.2	-	-	-	98.2	0.8	-	-
1,3 & 1,4-DIMETHYL BENZENE	-	97.6	1.9	-	-	-	98.6	1.4	-	-
STYRENE	0.5	100.0	-	-	-	-	100.0	-	-	-
1,2-DIMETHYL BENZENE	-	100.0	-	-	-	-	91.0	9.0	-	-
1,1,2,2-TETRACHLOROETHYLENE	-	100.0	-	-	-	-	100.0	-	-	-
CHLOROTOLUENE	-	100.0	-	-	-	-	100.0	-	-	-
PENTACHLOROETHANE	-	100.0	-	-	-	-	100.0	-	-	-
1,3-DICHLOROBENZENE	6.4	93.6	-	-	-	-	100.0	-	-	-
1,4-DICHLOROBENZENE	4.7	95.3	-	-	-	-	100.0	-	-	-
1,2-DICHLOROBENZENE	5.7	94.3	-	-	-	-	100.0	-	-	-
1,2,4-TRICHLOROBENZENE	9.1	90.9	-	-	-	-	100.0	-	-	-
NAPHTHALENE	10.9	89.1	-	-	-	1.1	98.9	-	-	-
BROMOBENZENE	-	-	-	-	-	-	-	-	-	-

TABLE III

ADSORPTION CHARACTERISTICS OF MULTI-LAYER SORBENTS WITH DIFFERENT GAS FLOW

(RELATIVE %)

COMPOUND	100 L PASSED					500 L PASSED				
	GLASS B	TENAX	AMBERSORB	CHARCOAL	BACKUP TUBE	GLASS B	TENAX	AMBERSORB	CHARCOAL	BACKUP TUBE
ACETONE	-	11.0	89.0	-	-	-	7.4	52.0	17.5	23.1
ACRYLONITRILE	-	-	100.0	-	-	-	-	100.0	7.9	-
METHYLENE CHLORIDE	-	11.5	52.2	36.2	-	-	1.4	92.4	6.2	-
1,1-DICHLOROETHYLENE	-	-	95.6	3.2	-	-	21.3	68.4	7.2	3.2
1,1-DICHLOROETHANE	-	-	93.6	5.4	-	-	-	37.2	62.8	-
2-BUTANONE	-	55.5	43.5	-	-	-	-	77.0	23.0	-
HEXANE	-	14.1	72.1	13.8	-	-	-	23.0	77.0	-
CHLOROFORM	-	9.2	84.9	4.9	-	-	5.9	62.7	22.2	9.2
BENZENE	-	0.6	98.1	1.3	-	-	11.7	75.4	12.9	-
CARBON TETRACHLORIDE	-	4.0	96.0	-	-	-	-	100.0	-	-
1,2-DICHLOROPROPANE	-	11.0	89.0	-	-	-	12.8	87.2	-	-
TRICHLOROETHYLENE	-	4.8	95.2	-	-	-	7.9	92.1	-	-
BENZALDEHYDE	-	100.0	-	-	-	-	90.9	6.3	3.0	-
1,1,1-TRICHLOROETHANE	-	4.7	90.4	4.7	-	-	-	100.0	-	-
TOLUENE	-	5.9	92.3	1.7	-	-	50.8	47.9	0.9	0.4
ETHYLENE BROMIDE	-	92.8	7.2	-	-	-	-	100.0	-	-
TETRACHLOROETHYLENE	-	63.5	36.5	-	-	-	-	100.0	-	-
FURFURAL	-	100.0	-	-	-	-	100.0	-	-	-
CHLOROBENZENE	-	93.8	6.2	-	-	-	90.9	57.9	9.1	-
1,3 & 1,4-DIMETHYL BENZENE	-	97.2	2.9	-	-	-	98.9	0.6	0.5	-
STYRENE	-	99.9	0.1	-	-	-	98.0	1.2	0.8	-
1,2-DIMETHYL BENZENE	-	100.0	-	-	-	-	99.1	1.6	0.4	-
1,1,2,2-TETRACHLOROETHYLENE	-	100.0	-	-	-	-	100.0	-	-	-
CHLOROTOLUENE	-	100.0	-	-	-	-	100.0	-	-	-
PENTACHLOROETHANE	-	97.3	2.7	-	-	-	100.0	-	-	-
1,3-DICHLOROBENZENE	-	100.0	-	-	-	-	97.4	2.6	-	-
1,4-DICHLOROBENZENE	-	100.0	-	-	-	-	99.1	0.9	-	-
1,2-DICHLOROBENZENE	-	100.0	-	-	-	-	98.2	1.9	-	-
1,2,4-TRICHLOROBENZENE	-	100.0	-	-	-	-	100.0	-	-	-
NAPHTHALENE	-	100.0	-	-	-	-	100.0	-	-	-
BROMOBENZENE	-	-	-	-	-	-	-	-	-	-

TABLE IV

MEMORY EFFECT OF ORGANICS (RELATIVE %)

NO.	COMPOUND	% RECOVERED FROM THE SORBENT TUBE	% RETAINED IN THE TRAPPING SYSTEM	% RETAINED IN THE SORBENT TUBE
1	ACETONE	97.9	-	2.1
2	DIETHYL ETHER	100.0	-	-
3	ACRYLONITRILE	100.0	-	-
4	METHYLENE CHLORIDE	100.0	-	-
5	1,1-DICHLOROETHYLENE	100.0	-	-
6	1,1-DICHLOROETHANE	100.0	-	-
7	2-BUTANONE	100.0	-	-
8	HEXANE	100.0	-	-
9	CHLOROFORM	100.0	-	-
10	BUTANOL	100.0	-	-
11	BENZENE	96.9	3.1	-
12	CARBON TETRACHLORIDE	100.0	-	-
13	1,2-DICHLOROPROPANE	100.0	-	-
14	TRICHLOROETHYLENE	100.0	-	-
15	BENZALDEHYDE	100.0	-	-
16	1,1,1-TRICHLOROETHANE	100.0	-	-
17	TOLUENE	98.7	1.3	-
18	ETHYLENE BROMIDE	100.0	-	-
19	TETRACHLOROETHYLENE	100.0	-	-
20	FURFURAL	100.0	-	-
21	CHLOROBENZENE	100.0	-	-
22	1,3 & 1,4-DIMETHYL BENZENE	98.6	0.6	0.8
23	STYRENE	100.0	-	-
24	1,2-DIMETHYL BENZENE	100.0	-	-
25	1,1,2,2-TETRACHLOROETHANE	100.0	-	-
26	CHLOROTOLUENE	100.0	-	-
27	PENTACHLOROETHANE	100.0	-	-
28	1,3-DICHLOROBENZENE	100.0	-	-
29	1,4-DICHLOROBENZENE	100.0	-	-
30	1,2-DICHLOROBENZENE	100.0	-	-
31	1,2,4-TRICHLOROBENZENE	100.0	-	-
32	BROMOBENZENE	NA	NA	NA
33	NAPHTHALENE	100.0	-	-
34	PHENOL	98.6	0.4	1.0
35	O-CRESOL	96.9	1.5	1.6
36	METHYL NAPHTHALENE	95.1	3.8	1.1
37	NICOTINE	0.0	96.8	3.2
38	HEXACHLOROBENZENE	99.4	0.6	-
39	DIETHYL PHTHALATE	98.3	1.7	-
40	LINDINE	100.0	-	-
41	DIAZINON	100.0	-	-
42	PHENANTHRENE	95.6	4.4	-
43	DIBUTYL PHTHALATE	100.0	-	-
44	PYRETHRIN	100.0	-	-
45	PENTACHLOROPHENOL	34.4	42.5	3.1
46	FLUORANTHRENE	77.5	2.9	20.6
47	TRIBUTYL PHOSPHATE	100.0	-	-
48	BENZO (GHI)PERYLENE	37.5	-	62.5
49	P,P,-DDT	NA	NA	NA
50	BENZO (A) PYRENE	26.2	63.9	9.9
51	METHYL STYRENE	95.5	2.3	1.8
52	2,4 D	NA	NA	NA

MEASUREMENT OF ORGANIC EMISSIONS FROM INDOOR MATERIALS -- SMALL CHAMBER STUDIES

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Indoor Air Quality (IAQ) is receiving increased attention by researchers and regulators as a critical component of the total exposure of humans to a variety of air pollutants. Volatile organic compounds in the indoor environment have been measured at concentrations exceeding those found in the outdoor air. Emissions data for indoor sources of these compounds are largely unavailable. EPA's Air and Energy Engineering Research Laboratory is conducting studies in small environmental chambers to develop such emissions data. The studies include GC measurements of a variety of organic compounds emitted from selected indoor materials (e.g., particle board, flooring adhesive, caulking compounds). Environmental conditions (i.e., temperature, humidity, air exchange rates) are varied, and their influence on emission rates is determined. Data are presented on emissions from a clear acrylic latex caulk with silicone. These data show the variation in concentrations and emission factors over time for total measured organics and selected organic species.

MEASUREMENT OF ORGANIC EMISSIONS FROM INDOOR MATERIALS--SMALL CHAMBER STUDIES

Introduction

Indoor Air Quality (IAQ) is receiving increased attention by researchers and regulators as a critical component of the total exposure of humans to a variety of air pollutants. Studies in both the United States and Europe have shown indoor concentrations of several pollutants at levels in excess of outdoor ambient concentrations[1]. A variety of indoor sources have been implicated as causes of these high concentrations. Combustion sources (e.g., cigarettes, wood stoves, kerosene heaters) emit NO_x, CO, and particulates. Natural sources can cause elevated levels of radon and microorganisms. Building materials and consumer products are potential sources of a wide variety of organic emissions, including formaldehyde.

In 1983, Congress mandated that EPA, in cooperation with other Federal agencies, develop plans and conduct research on IAQ. This work, initiated in fiscal year 1984, has included activities in measurement/monitoring, health effects, and source characterization. As part of EPA's research on source characterization, the Air and Energy Engineering Research Laboratory is conducting studies in small environmental chambers to develop organic emissions data on a variety of building materials and consumer products commonly used in homes.

Our research on small chamber evaluation of organic emissions from indoor materials has several objectives:

- develop techniques for rapid screening of products for organic emissions;
- determine the effect of environmental variables (i.e., temperature, humidity, air exchange) on emission rates;
- rank various products and product types vis-a-vis their emissions profiles (e.g., emission factors, specific organics emitted);
- provide compound specific data on various organic sources to guide field studies and assist in evaluating "sick buildings;"
- provide emissions data for the development and verification of models used to predict indoor concentrations of organics;
- develop data useful to manufacturers and builders for assessing product emissions and developing control options.

Sanchez, et al.[1] have reported on the performance of the test chambers with respect to control of environmental variables and recovery of organic emissions. Merrill, et al.[2] presented protocols for screening materials via headspace analyses using GC/MS. Dunn[3] proposed models and statistical methods for evaluating organic emissions data collected from the chambers. Previous papers[1,3] focused on the evaluation of emissions from a water based floor adhesive with emphasis on total measured organics. This paper reports on tests conducted on a clear acrylic latex caulk with silicone. Data are presented on both total measured organics and selected organic species.

Experimental Facility

Design and construction of EPA's Environmental Test Chamber (ETC) facility was completed early in 1985. The basic components of the system are shown schematically in Figure 1 and include the following sub-systems: clean air conditioning and delivery, Environmental Test Chambers (two at 166 liters each), sampling manifolds, and sample concentration on Tenax and charcoal. A permeation system for quality control is included. The environmental variables are monitored and controlled via a microcomputer based system; sampling is automated by the same system. Organic analyses are conducted by thermal desorption, concentration via purge and trap, and gas chromatography using FID. A separate microcomputer provides GC data analysis. Sanchez, et al.[1] provided a complete description of the facility. They also reported on the initial system shakedown and mechanical performance testing. A series of 10 randomly ordered tests (including two replicates) were conducted over the following ranges of environmental variables: temperature, 23 to 40°C; relative humidity, 40 to 60 percent; and air flow, 1.3 to 6.5 liters/min. These tests showed that the system can hold environmental variable setpoints to within the following limits: temperature, ±0.1°C; relative humidity, ±0.7 percent; and air flow, ±0.7 percent of reading.

Experimental Methods

Headspace Evaluation

Prior to testing in the Environmental Test Chamber, the material is evaluated via headspace analysis. The material to be tested is spread on a glass slide and placed in a 1 liter Teflon-coated chamber. Nitrogen at a flow rate of 50 ml/min is passed through the chamber for 30 minutes. The exhaust from the chamber is collected on a Tenax cartridge. The cartridge is then analyzed by the thermal desorption technique. GC/MS analysis of the gas provides information on the composition of the emissions from the material being tested. The total mass scan for each of the major peaks in the reconstructed chromatogram is interpreted with the aid of computer searching, comparison to the Aldermaster eight-peak index, comparison to the mass spectra of known compounds available in the EPA/NIH library of mass spectra, and/or application of "first principles" for interpretation of mass spectral fragment patterns, per McLafferty[4]. The GC/MS conditions are shown in Table I.

Environmental Test Chamber (ETC) Evaluation

A 4.89 g sample of caulk was spread evenly over a 19 cm square aluminum plate and placed in the ETC. At 1440 hours on 8/16/85, the incubator was closed and flow through the ETC was initiated. Environmental conditions were set at:

Temperature = 23°C
Relative Humidity = 50%
Air Flow = 5 liters/min
Air Exchange Rate = 1.8/hr

The test was continued until 1230 hours on 8/19/86, a period of 70 hours. Nine samples were collected on Tenax and analyzed via GC/FID after thermal desorption and concentration. GC/FID conditions are shown in Table II.

Results

Headspace Analysis

The results of the GC/MS analysis of the caulk headspace gas are shown in Table III. The compounds, including molecular weight and composition, are listed in order of elution from the GC. These identifications are from library searches; approximately 70-80 percent of the identifications are assumed to be correct.

ETC Emissions

Figure 2 shows the concentration vs. time for total measured organics, three organic species, and the remaining unidentified compounds. Figure 2 shows that the total measured concentration reaches 3000 $\mu g/m^3$ within the first hour, then drops rapidly to less than 300 $\mu g/m^3$ after 4 hours. Within 10 hours, the total measured concentration is reduced to less than 150 $\mu g/m^3$.

In order to evaluate how the compositions of the measured emissions vary over time, Figure 3 was prepared. Figure 3 presents the organic species data as a percentage of total measured emissions. Note that the C-4 and C-7 compounds are initially major contributors to the total measured organics. After approximately 3 hours, the C-8 compound becomes the major organic component. These results show that the organic emissions over time will vary for individual compounds. Such a result is not surprising, because individual compound vapor pressures will impact emission rates. As the concentrations of individual compounds vary, their partial pressures will also vary, and their contributions to the total emissions change. The changing composition of the chamber air also affects the vapor pressure evaporative driving force. Finally, the vaporization at the surface of the caulk changes the vertical concentration profile within the caulk. Since the caulk is assumed to be homogeneous at application, such changes in the vertical profile will also impact the emissions of individual species. Thus, while the changing composition of the emissions is not surprising, its empirical verification provides insight into the problem.

Emission factors ($\mu g/g$-hr) can be calculated for total organics, as well as for individual species, by multiplying the concentration by the chamber air flow and dividing by the sample weight. By integrating such curves over time, cumulative mass emissions over time can be plotted. Figure 4 shows the results of such calculations for the caulk sample ETC test. These data provide insight regarding the cumulative exposure to the total measured organics as well as individual species per gram of caulk. Note that over the total test period, the C-8 compound contributed approximately 42 percent of the total measured emissions; the C-4, C-7, and unidentified remainder contributed approximately 16 percent, 21 percent, and 21 percent, respectively.

Quality control checks for organic recovery were conducted on the system using hexane as the standard addition compound. For nine QC checks, the average recovery was 97.6 percent, with a standard deviation of 16.9 percent. The environmental setpoints were controlled as follows, based on 300 data points at 5 minute intervals:

Temperature; mean = 23.0°C, standard deviation = < 0.1°C
Relative Humidity; mean = 51.4 percent, standard deviation = 2.5 percent

Flow Rate; mean = 4.0 liters/min,
standard deviation = < 0.1 liter/min.

The slight increase in the relative humidity was caused by the water evaporated from the caulk during the test.

Conclusions

Environmental chamber testing of materials for organic emissions can provide useful information on the concentration, composition, and cumulative mass emissions of total and individual organic compounds. The changes in the variables over time can be documented. Further research is required to identify critical parameters affecting chamber emissions for a variety of building materials and consumer products. Research is underway to determine how changes in environmental variables affect emissions.

Acknowledgments

The research reported here was conducted at EPA's Air and Energy Engineering Research Laboratory supported by a contract to Acurex Corporation. The headspace analyses were conducted by Ray Steiber of EPA/AEERL. Mark Mason of Acurex conducted the ETC testing and GC analyses.

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3. J. Dunn, "Models and Statistical Methods for Gaseous Emission Testing of Static Sources in Well-Mixed Chambers." Presented at Workshop on Characterization of Contaminant Emissions from Indoor Sources, Chapel Hill, NC, May 1985.

4. F. W. McLafferty, Interpretation of Mass Spectra, 2nd ed., The Benjamin/Cummings Publishing Company, Inc., 1973.

TABLE I - GC/MS CONDITIONS

Instrument:	HP 5993 (Modified to accept a gas-phase sample)
Data System:	21 MX computer
Column:	60/80 Carbopack B/1% Carbowax 2 m x 0.2 mm ID glass column
Temperature Program:	40°C for 3 min to 200°C at 10°C/min Final hold 40 min
Injection:	Direct: 1 ml gastight syringe
	Purge and trap: HP Model 7875A
Temperatures:	
Injection:	250°C
Transfer Line:	150°C
Scan Range:	35-350 m/z at 2 sec/scan
Carrier Gas	Helium, Grade 5.0; 25 ml/min.

TABLE II - GC/FID CONDITIONS

Instrument:	Tracor 222 Gas Chromatograph with a flame ionization detector
Data System:	Perkin-Elmer 7500 Computer with LCI 100 Integrator
Column:	60/80 Carbopack B/1% SP-1000 10 ft x 2 mm ID glass
Temperature Program:	50°C for 5 min to 22.5°C at 10°C/min, 15 min final hold
Temperatures	
Clamshell	190°C
Purge and Trap Concentrator:	190°C
Detector:	250°C
Gases	
Nitrogen:	30 ml/min
Hydrogen:	40 ml/min
Air	400 ml/min

TABLE III - COMPOUNDS TENTATIVELY IDENTIFIED BY HEADSPACE ANALYSIS OF CAULK (GC/MS)

Compound	Molecular Weight	Composition
Acetone	58	C_3H_6O
Methyl Ethyl Ketone	72	C_4H_8O
Methyl Propionate	102	$C_5H_{10}O_2$
Ethyl Propionate	102	$C_5H_{10}O_2$
Dimethyl Pentene	98	C_7H_{14}
C-6 Ester	116	$C_6H_{12}O_2$
Butanone	116	$C_6H_{12}O_2$
Toluene	92	C_7H_8
C-8 Alkene	112	C_8H_{16}
Dimethyl Cyclohexane	112	C_8H_{16}
C-8 Alkene	112	C_8H_{16}
Butyl Propionate	130	$C_7H_{14}O_2$
N-Octane	114	C_8H_{18}
Dimethyl Benzene	106	C_8H_{10}
C-8 Alcohol	130	$C_8H_{18}O$

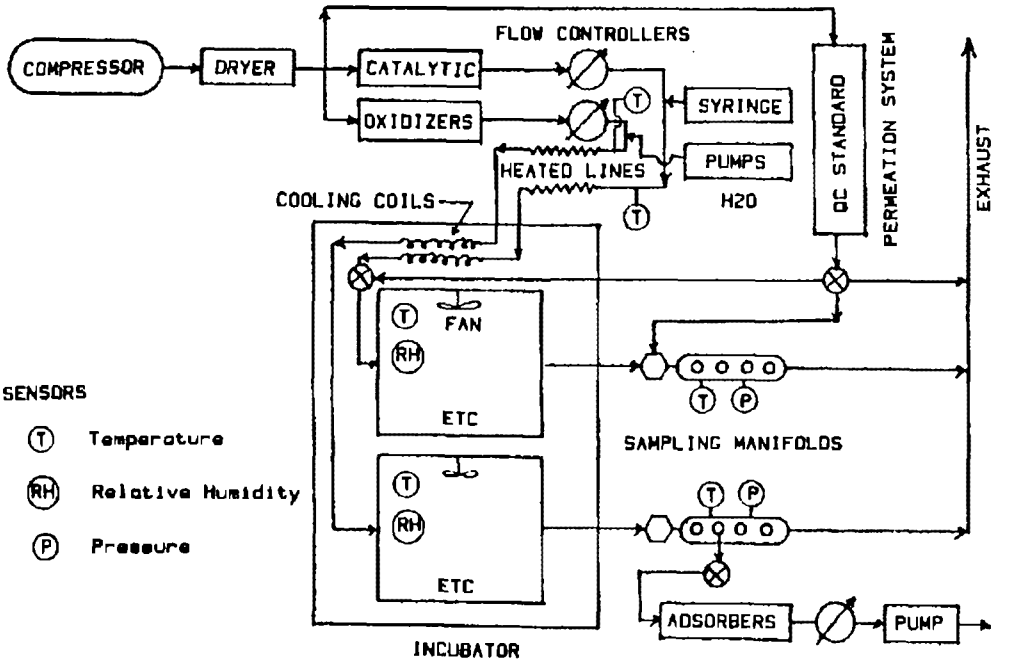

Figure 1. Test facility including environmental test chambers (ETC).

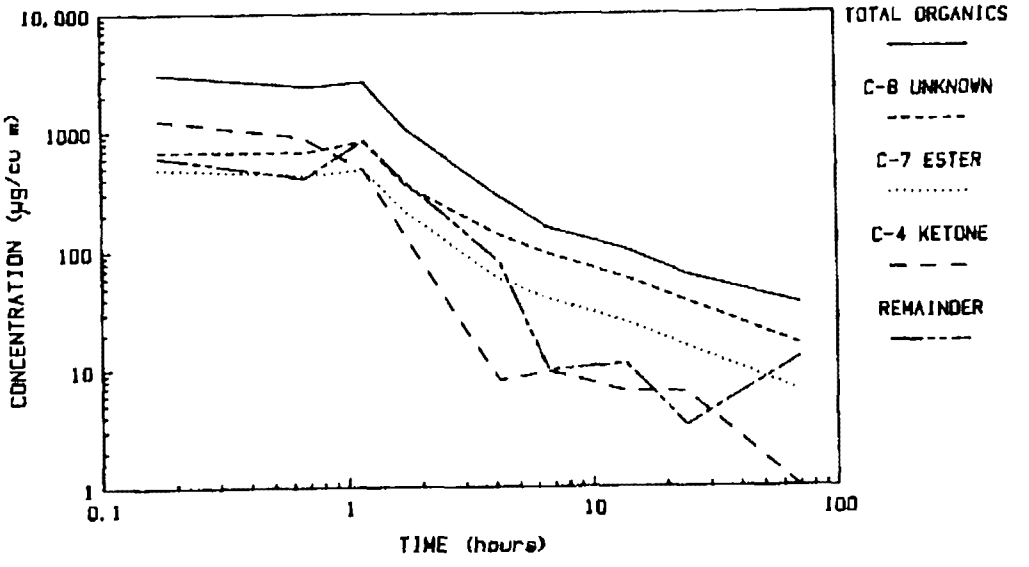

Figure 2. Chamber (ETC) concentration vs. time
T = 23C RH = 50% Air Exch. = 1.8/hr

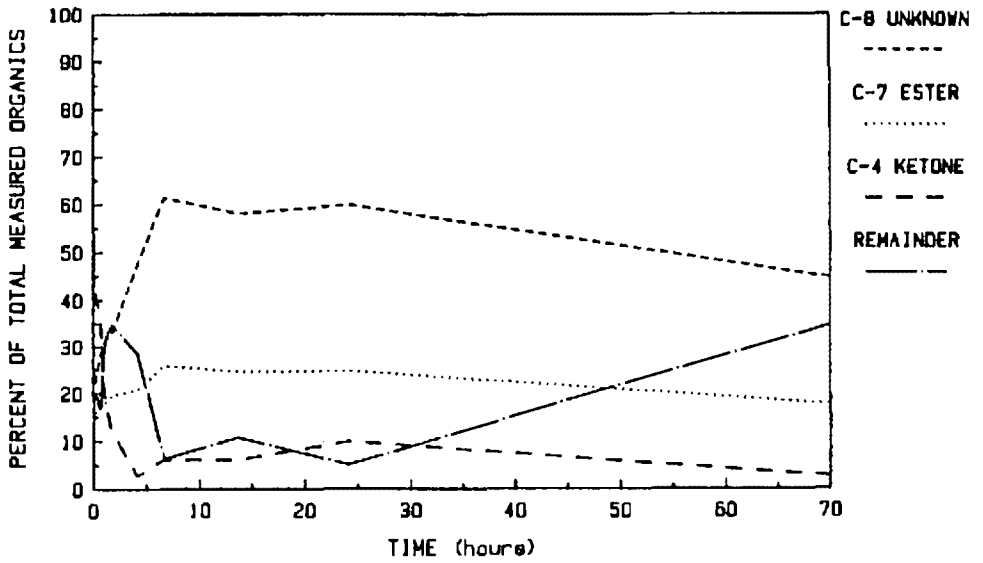

Figure 3. Emission composition vs. time
Clear Acrylic Latex Caulk w/Silicone

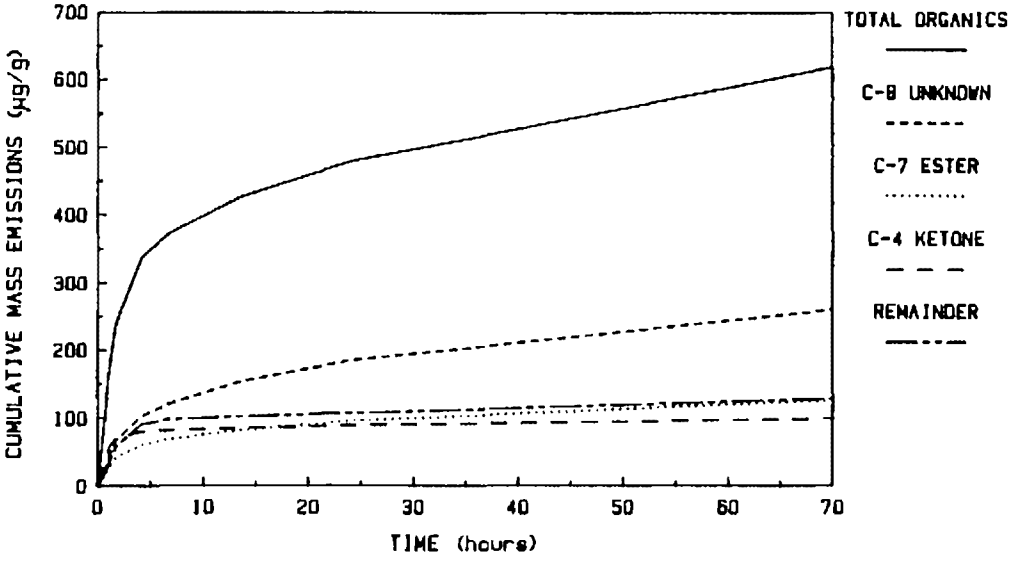

Figure 4. Cumulative emissions vs. time
T = 23C RH = 50% Air Exch. = 1.8/hr

APPROACHES TO AIR POLLUTION MONITORING AND CONTROL IN SUBMARINE

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The environment inside a submarine is of 'confined type' and the crew are subjected to discomforts as regards habitability, health, psychological stress and contamination with toxic gases (that generate from operating machinery, batteries, refrigeration, degreasing agents and paints). During snorting, toxic gases such as carbon dioxide, hydrocarbons, oxides of nitrogen, mercaptans,and chlorine are generated; and when the boat is diving, the build up of carbon dioxide is on the increase, while oxygen depletion occurs. Besides, hydrogen, stibine, aerosol of sulphuric acid are formed. Prolonged exposure of man to this atmosphere is risky and impairs his efficiency. It has, therefore, become necessary to establish the levels of these gases and vapours by monitoring the air in compartments.

During the course of work, the preparation and calibration of chemical detector tubes for chlorine, stibine, mercaptans, sulphuric acid aerosol and nitric oxide are taken up and the findings are reported herein. The usefulness of adsorbents e.g. activated carbon and molecular sieves, which are capable of holding large quantities of pollutant gases is also discussed. All these measuring devices and adsorbent columns help in the establishment of maximum allowable concentrations (MAC) for toxic gases and vapours that are generated in the closed chambers under tropical waters.

APPROACHES TO AIR POLLUTION MONITORING AND CONTROL IN SUBMARINES

INTRODUCTION

The comfort in habitation inside closed compartments of a sea-going vessel largely depends on the environment. The environment inside a submarine is subject to contamination with gases generating from machinery, and men. Some of these gases or vapours are toxic and they impair the working efficiency of the crew; they also react with the materials used in submarines, especially poison the catalysts in hydrogen burners, chemicals in carbon dioxide adsorbing systems and others. In addition, gases such as hydrogen, benzene and organics cause explosion when their level go beyond a limit.

CONTAMINANTS AND CONTROL

Contaminant sources: Atmospheric contaminants are generated from the materials of construction, operation of the equipment and from human physiological activities. In Table I the possible sources of toxic contaminants are shown[1]. It is seen that a majority of these are generated in processes that are essential to keep the submarine operation. The formation of these compounds in the submarine depends on the extent of machinery, operation as well as on the quality of materials used. The contaminants are divided into three groups as shown in Table II. In group I, a variety of organic compounds with carbon, hydrogen and oxygen have been placed. Group II comprises of acidic and alkaline toxic gases, majority of them inorganic in nature. Vapours with hetero-atoms of sulphur, nitrogen and halogens and possessing neutral character have been placed in group III. Based on this classification the monitoring and control measures to be adopted have been organised.

Disturbance of normal environment: The normal environment in submarine has the following constituents of air (excluding moisture: v/v at atmospheric pressure). Nitrogen-70.05% , Oxygen 20.90%,Carbon dioxide 0.03%, Argon 0.93%, other gases 0.09%. When submarine machinery operates in full swing, toxic gases are generated gradually; men breathe oxygen and exhale carbon dioxide, batteries generate hydrogen and the normal environment gets disturbed. A typical rate of consumption of oxygen per man per hour is 27 litres, and release of carbon dioxide 25 litres. The build up of carbon dioxide to 1% and above in environment occurs in about 7 hours of submerged condition and reduction of oxygen to 18% takes place in about 24 hours of continuous diving.

Monitoring devices: Currently most of the submarines are fitted with automatic analysers for continuous measurement of oxygen, carbon dioxide and hydrogen. In addition, chemical detector tubes for the rapid measurement of toxic gases such as carbon monoxide, organic vapours, stibine, chlorine, nitric oxide etc are also provided. A continuous record is thus maintained.

Maximum allowable concentrations (MACs): The present threshold limit values (TLVs) designed by American conferences of Government Industrial Hygiene for in contaminants pertain to 8 hour exposure (daily) or 40 hour exposures (weekly) at work places and are not directly applicable to the subjects working in closed compartments[2]. Hence these standards are modified not only with reference to total exposure but also applying due weightage to the total exposure but also applying due weightge to the total personnel, ambient temperature, movement restriction, oxygen concentration, fatigue, combined effects of contaminants and their toxicity. Hence the TLVs are modified by a factor of 10 or more for exposure in submarines. Table III gives a few values for some important gases[3].

Control of contaminants: Attention must be given to control each type of contaminant that generates ing the submarine while under snorting or diving conditions. In the snorting condition, purging of these occurs due to ventilation, but in the diving mode, effective control measures have to be adapted. Noteworthy systems based on principles of physical adsorption, chemisorption and catalytic combustion of toxicants are available. Modifications of these for greater efficiency are still in progress. Thus, the contaminants listed in Group I to III of Table II are usually adsorbed on materials such as activated carbon, molecular sieves, depending upon the molecular weight and kinetics. Low molecular compounds in group I which escape physical adsorption can be completely oxidised on catalysts to carbon dioxide or water. In the case of some substances in Group II and III, a process of conversion to simpler molecules followed by chemisorption can be resorted. All Group II substances are controlled by adsorption processes. Some of the new approaches in environmental monitoring and contaminant control in submarine spaces have been to develop sensitive detectors and effective adsorption systems. Experiments were, therefore, carried out towards achieving this objective. In this scheme four detector tubes[4], namely, chlorine, stibine, mercaptan and nitric oxide were prepared.

EXPERIMENTAL METHODS

The scheme involves the preparation of chemical detector tubes[4] and other devices for the measurement of toxic gases. These devices are used in laboratory test chambers in order to assess their suitability.

DEVELOPMENT OF DETECTOR TUBES

Silica gel: Silica gel (BDH make, non-indicating type, 70 mesh) is boiled with concentreated nitric acid for 48 hours, and washed with distilled water several times to free from acid till it shows a pH 5.0. The gel is dried in air-oven at 110°C and stored in air tight bottle. This is used as a support for the indicating chemical. The guard silica gel (30 mesh) which is used to protect the indicator-impregnated silica gel in detector tubes is also processed in a similar manner. In Table IV are shown the different indicator chemicals used in

the preparation of detector tubes and their performance. The glass tubes chosen for the fabrication of detector tubes are made of Pyrex/Corning glass of 10 cm length and 4 mm internal diameter. The tubes are thoroughly cleaned with chromic acid followed by water, dried and kept ready for filling. The tubes are sealed one end by means of a blow burner and a glasswool strip is introduced from the open end into the tube towards the closed end.

From the open end, the guard silica gel is introduced in order to fill a length of 1 cm. Subsequently, the indicator impregnated silica gel is introduced to fill a length of 3 cm followed by the guard silica gel once again to 1 cm length. A glasswool plug is again placed and the open end is now sealed. A 5 cm linear scale sticker is wrapped on the tube to offer measurement of length of colour.

LABORATORY EVALUATION

Chlorine: Chlorine gas required for evaluation is produced on reaction from hydrochloric acid and potassium permanganate, followed by scrubbing through water to free the gas from hydrogen chloride. The quality of chlorine present in this stock gas is estimated by colorimetric method. An aliquot of chlorine is drawn from this into a Drager test chamber (3 litres capacity) and an equilibrium mixture of chlorine with dry air is made. The detector tube is connected to the chamber containing gas mixture, the change in colour (from colourless to yellow) is followed and the tube calibrated.

Stibine: Stibine required for evaluation of detector tube is made by reduction of antimony powder with nascent hydrogen (from zinc and hydrochloric acid). The gas admixed with hydrogen is collected by downward displacement of water. The concentration of stibine in this stock gas is estimated by reaction of an aliquot sample with silver nitrate. An aliquot of stock gas is diluted with dry air in test chamber and the stibine tube is calibrated. The colour changes from colourless to pale pink on reaction with stibine.

Mercaptan: Ethyl mercaptan (bp.35°100 mg) is mixed with dry air in a 10 litres glass aspirator, and this constitutes the stock gas. An aliquot of this is further diluted in another 10 litres glass aspirator. Air is sucked into the detector tube in order to calibrate the mercaptan tube. The colour change is from orange to pale green.

Nitric oxide: Nitric oxide required for calibration of detector tube is prepared from reaction of copper turnings with 1:1 dilute nitric acid. The resulting gas which contains nitrogen dioxide is passed through water and nitric oxide alone is collected by downward displacement of water. The concentration of nitric oxide in this stock gas is estimated by colorimetric method. An aliquot gas mixture from stock gas is further diluted with dry air and used to calibrate the detector tube in the same manner described above. The colour change in detector tube is from colourless to red.

Lead dioxide impregnated GF Paper: This device is developed in the laboratory for the purpose of monitoring sulphur dioxide during cruises. Lead dioxide is coated on both sides of the glass fibre(GF) paper to cover an area (10 x 10 cm) and subsequently dried in a vacuum desicator. The papers are hung at a central location where sulphurous aerosols are expected and on completion of cruise, the sulphation rate is estimated by gravimetric method. A laboratory correlation between sulphur dioxide and sulphation rate in a static test chamber is also established.

Multi-stage adsorption columns: A multi stage adsorption assembly, prepared from copper oxide-manganese oxide, activated carbon and molecular sieve (4A^{o} type), is set up for conversion of carbonmonoxide and hydrocarbon, and complete adsorption of carbon dioxide from the environment.

RESULTS

The characteristics of chemical detector tubes for chlorine, stibine, mercaptan and nitric oxide are recorded in Table IV. The performance of the tubes as well as the lead dioxide coated GF paper are quite satisfactory when examined in environmental test chambers.

CONCLUSIONS

A review comprising the sources of generation of toxic air pollutants in closed compartments, their effect on men working in these spaces, their maximum allowable concentrations, the monitoring and control techniques, has been made. The development of monitoring devices, namely chemical detector tubes for a few gases, e.g. chlorine, mercaptans, stibine and nitric oxide and their evaluation in environment test chambers has been described. The usefulness of lead dioxide impregnated GF papers for measurement of sulphurous vapours indoor spaces has been brought out. A multi-stage adsorption assembly for conversion and subsequent adsorption of end products in respect of hydrogen, hydrocarbons and carbon monoxide, which has potentialities in the control processes has also been described.

ACKNOWLEDGEMENTS

The author expresses sincere thanks to Dr. R. Krishnan, Director and Dr.A.A. Karande, NCML, Bombay for discussions and encouragement.

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TABLE I - POSSIBLE SOURCES OF MAIN CONTAMINANTS IN SUBMARINE COMPARTMENTS

Contaminant	Possible source
Carbon dioxide	Respiration, burning of organics
Carbon monoxide	Burning of oils, smoking
Sulphur dioxide	Burning of fuels
Hydrogen sulphide, mercaptans	Burning of fuels
Organics(hydrocarbons)	From fuels, solvents,cleaning agents
Ethylbenzene,xylene, TCE, methanol,ethanol	Paints, solvents, lub oils
Triaryl phosphate	Compressors, lubricating oils
Freons	Leaks of refrigerents
Chlorine	Freon decomposition
Hydrogen chloride	Freon decomposition
Oxides of nitrogen	Burners, ESPs
Hydrogen	Batteries
Stibine	Batteries
Sulphuric acid aerosol	Batteries
Ammonia	Scrubbers, sanitary tanks, cooking
Acetaldehyde,acetone, lactic acid, butyric acid, ketones.	Humans

TABLE II - CLASSIFICATION OF IMPORTANT CONTAMINANTS

Group I C,H,O compounds	Group II Acid or alkaline type	Group III neutral gases
Benzene, Toulene Xylene, Gasolene vapours, acetal dehyde, Methyl ethyl ketone, acetone, hexane, pentane, hydrogen, methane	Chlorine, Hydrogen fluoride, Ammonia, nitrogen dioxide, Hydrogen chloride, sulphur dioxide, hydrogen sulphide, carbon dioxide.	Freons Vinyl chloride Trichloroethylene, Stibine

TABLE III-INCIDENCE OF CONTAMINANTS IN SUBMARINE COMPARTMENTS AND THEIR MACs(K.F.SCHAEFER, 1964)

Contaminant	Highest concentrations found	MACs
Carbon dioxide	1.1%	5.0%
Carbon monoxide	38 ppm	100 ppm
Chlorine	1.0 ppm	1 ppm
Stibine	1.0 ppm	0.1 ppm
Hydrogen	1.75%	4.0%
Freon (Dichloro difluro methane)	70 ppm	1000 ppm
Hydrocarbons	25 ppm	500 ppm
Sulphur dioxide	-	5 ppm
Ammonia	>1.0 ppm	100 ppm

TABLE IV - CHARACTERISTICS OF CHEMICAL DE TECTOR TUBES

Type	MAC ppm	Range ppm	Indicator chemicals	Colour changes	Performance in test chambers
Chlorine	1	0.0-5.0	O-tolidine	colourless to yellow	responds to 0.1 ppm
Stibine	0.1	0.0-1.0	Silver diethyldithiocarbamate impregnated	colourless to pink	responds to 0.1 ppm
Ethyl mercaptan	-	0.1-2.0	Isatin - conc.H_2SO_4	Orange to pale green	-
Nitric oxide	-	1.0-5.0	2-naphthylamine and sulphanilic acid	colourless to red.	-

TOTAL VOLATILE ORGANIC COMPOUNDS (VOC) IN THE INDOOR AIR OF EAST TENNESSEE HOMES*

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Measurements of total VOC were made in the wintertime in eight homes in East Tennessee. The mean concentration of total VOC indoors was 1.03 mg/m^3 with a range in concentration of 0.09-3.67 mg/m^3. The corresponding values for air samples collected out of doors were 0.08 mg/m^3 and 0.003-0.44 mg/m^3. Hence the indoor-to-outdoor ratios of concentrations were about 10:1. There were marked differences in both the total loadings and complexities of VOC between different homes and temporally within a given home. About 10L samples of air were drawn through composite sorbent traps containing Tenax GC and two different carbonaceous resins. The trapped VOC were desorbed thermally and analyzed by GCFID. The counts from all peaks in the chromatograms were integrated and used to estimate total VOC relative to the FID response to a standard composed of chlorinated and non-chlorinated, aliphatic and aromatic hydrocarbons. The highest volatility VOC that we measured and included in our definition of total VOC were C4+ alkanes, C1+ chlorinated hydrocarbons, and C2+ oxygenated hydrocarbons. Consideration is given to the types of compound that should be included in definitions of total VOC.

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*Research sponsored jointly by the Consumer Products Safety Commission Division of Health Sciences under Interagency Agreement DOE No. 40-11961-81, CPSC 84-1161 and by the Office of Health and Environmental Research, U.S. Department of Energy under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

Introduction

As a class, the volatile organic compounds (VOC) found indoors have probably changed more dramatically in the past few decades than any other category of indoor air pollutant[1]. This change is due primarily to a post-World War II proliferation in the types and quantities of synthetic organic chemicals that are used in building, furnishing, and household and personal consumer products. Many of these items emit trace and higher amounts of a variety of VOC to the extent that indoor concentrations are nearly always higher than outdoors[2]. It is now generally conceded that exposure of the general population to VOC in indoor air in the home and at work far outweighs in importance exposure to VOC in the outdoor air [2].

There are several different forms of health concern. Some VOC, such as benzene, methylene chloride, and tetrachloroethylene, are known or suspected human carcinogens. Will lifelong indoor exposure to trace amounts of these compounds have deleterious health consequences? Other VOC, such as formaldehyde, hexane, and ethyl benzene, have irritating or sensitizing potential. On the other hand, complex mixtures of VOC that are commonly encountered indoors can cause mucous membrane irritability[3] and reduced mental alertness[4]. These effects were produced by 22 component VOC mixtures at a total 5 mg/m^3 concentration. Such a concentration can be found, for example, in new homes[3].

There is reason to believe that complex mixtures of VOC are sometimes implicated in episodes of health complaints called tight building syndrome[5]. Synergistic effects between different VOC may be exacerbating adverse human responses[6]. This property adds importance to the inclusion of measurements of total VOC concentrations in protocols for studying VOC in indoor air.

Some persons can become chemically sensitized to airborne pollutants. For such persons their quality of life can be anything from mildly to severely degraded. At worst the affliction can become permanently debilitating. The role that can be suspectedly played by VOC has yet to be determined with objectivity.

We here report measurements of total VOC that include compounds of widely varying boiling point and chemical functionality (e.g., methylene chloride, bp 40°C; acetone, bp 56°C; and hexadecane, bp 287°C). Formaldehyde is a example of an important and ubiquitous indoor VOC not included in our measurements.

Definition of Total VOC

From a review of the literature it is clear that there is no concensus on which individual or groups of VOC should be specifically included in total VOC measurements. Because of the potential for synergistic effects in human reactions to complex mixtures of VOC it seems wise to include, in the definition of total VOC, compounds with as wide a range of volatilities and chemical functionalities as possible.

The types of VOC found most frequently in indoor air should be included in the total VOC. These types include alkanes, alkylated benzenes, terpenes, alcohols, ketones, and chlorinated hydrocarbons[3]. Gasoline vapors are a ubiquitous and often abundant component of VOC indoors[7]. Furthermore, the predominant compounds common to all gasoline vapors are butane, isobutane, pentane, and isopentane[8]. Provision, we think, should be made for inclusion of these four compounds in a total VOC measurement. We advocate this even though a mixture of these four compounds does not produce renal toxicity and/or renal cancer in exposed animals[9]. Such adverse renal effects are produced by exposures to the whole gasoline vapors[10].

Individual toxic compounds should surely be included in the total VOC measured. Methylene chloride is such an example; its ability to produce cancer in animals seems to be clearly established[11]. Methylene chloride is also a commonly occurring and abundant member of the class of chlorinated VOC[12]; it is a common ingredient of spray propellant and paint stripper.

These reasons suggest that the most valuable definition of total VOC should include alkanes (C_4+), benzene and alkylated benzenes, organic chlorides (C_1+), terpenes, and oxygenated (C_2+) species such as aldehydes, ketones, alcohols, and acetates. The sorbent traps and analytical techniques should accordingly be tailored for measurement of such VOC.

Previous studies indicate that quite often the meaning attached to total VOC has been the sum of those VOC that the author happened to measure with his particular system for sampling and analysis. At one extreme, Lamb et al.[13] included ethane and acetylene in their measurements of C_2-C_{10} hydrocarbons. Those using Tenax sorbent usually claim quantitative sampling only for n-hexane and higher boiling VOC[12]. Sometimes the values of total hydrocarbons have been given without reference to the limitations of the sampling or analytical technique[14]. For future measurements of total VOC linked to health complaints or general surveys it would certainly be advisable for the indoor air quality research community to develop a more uniformly acceptable definition of total VOC.

Experimental Methods

The VOC in 10L samples of air were collected by drawing air through triple sorbent traps. The three sorbents were, in order of encounter by the sampled air, Tenax GC followed by Carbopak B coated with 1% SP-1000 and finally 30-50 mesh Ambersorb XE-340. The organic polymer Tenax GC preferentially sorbs the lower polarity organic vapors with boiling points greater than 60°C. The Carbopak and Ambersorb pick up the very volatile polar and non-polar compounds. Each of these polymeric materials adsorbs VOC reversibly. Thus the VOC can subsequently be extracted quantitatively by heating.

The trap configuration and dimensions are drawn in Figure 1. Further details about sorbent and trap preparation, air flow rates, and sampling volume are contained in reference 15.

The VOC were desorbed thermally at 200-220°C and trapped in a sampling loop cooled in liquid nitrogen. The sampling loop was then warmed to 25°C for 10 minutes and its contents flushed into a gas chromatograph (60m J&W DB5 fused silica capillary column with a 1 micron film thickness of methyl-5% phenyl silicon) with a flame ionization detector. The temperature of the loop and capillary column were then raised at 2°C per minute to 230°C.

To estimate the total VOC in indoor air samples, the counts from all peaks in the GCFID chromatograms were integrated. Conversions to total VOC were based on the mean FID response per μg of a standard mixture of chlorinated and non-chlorinated, aliphatic and aromatic hydrocarbons. This mean response was close to the FID response per μg of toluene.

Eight homes from a larger set of homes studied in East Tennessee[16] were selected for these measurements of total VOC. The characteristics of the houses are listed in Table I.

Results

Collection and analytical efficiencies were determined for some individual VOC. Some of the highest volatility VOC included in our measurement of total VOC were quantified with the following approximate efficiencies: butane 70%, pentane 85%, acetone 90%, and methylene chloride 100%. Less volatile VOC were collected and analyzed with essentially 100% efficiency.

The values for total VOC, measured largely during the winter months of 1984, are listed in Table II. The mean concentration of total VOC in indoor air was 1.03 mg/m^3 with a range in concentration of 0.09-3.67 mg/m^3. The corresponding values for air samples collected out-of-doors were 0.08 mg/m^3 and 0.003-0.44 mg/m^3. The differences are about 10-fold in favor of more highly concentrated total VOC in indoor air as opposed to outdoor air.

Variations in the complexity as well as the concentrations of VOC are shown in the chromatograms of Figures 2 and 3. The major components contributing to the total VOC were often C_4-C_{12} alkanes, toluene, C_2- and C_3-substituted benzenes, and C_{10}-terpenes. On occasion, other compounds were seen as major components and identified by mass spectroscopy. For example, in house No. 5, a siloxy compound, octamethylcyclotetrasiloxane (furniture polish), was sometimes in abundance.

Discussion

The VOC that were trapped by a triple sorbent cartridge of Tenax, Carbopak, and Ambersorb have been measured to give quantitative values of total VOC. The highest volatility components we measured include C_4+ alkanes, C_1+ chlorinated hydrocarbons, and C_2+ oxygenated hydrocarbons. The values for total VOC are not in absolute mg/m^3 units but rather in mg/m^3 units equivalent to the GCFID response to a standard mixture of VOC which, in turn, closely mimicked the FID response to toluene.

The indoor/outdoor ratios of the total VOC we measured were about 10:1. This finding is in broad agreement with other studies where total VOC were being evaluated[12,13,17]. Remarking on the general findings of higher indoor concentrations, Wallace stated that different studies show remarkable agreement on the point that essentially every organic compound measured has higher indoor levels than outdoors, often 10 times higher[2].

The mean indoor concentration of total VOC that we measured in wintertime was about 1 mg/m^3. Similar measurements of total VOC in northern Italian homes gave a higher mean value of about 3 mg/m^3[12]. The lower value in our homes reflects perhaps the lower temperatures and hence vapor pressures of VOC that prevail in the wintertime compared to the other warmer seasons (e.g., the low value of 0.09 mg/m^3 inside house No. 85 was during a cold spell in January 1984). The low indoor value of 0.09 mg/m^3 for house No. 86 during December 1984 is also probably something of an anomaly that contributed to downward biasing of the mean total VOC concentration; this lakehouse had been uninhabited and unheated since the previous summer.

There appears to be little obvious relationship between the values of total VOC and the house characteristics listed in Table I. Another finding of note is that between different houses, the VOC show wide variations in both concentration and complexity. Furthermore, there can be marked changes in concentration and complexity of VOC over time within a given house. These differences are evidenced in Table II and Figures 2 and 3.

Acknowledgement

The principal author registers his appreciation for the continued support and advice given by Dr. Kailash C. Gupta, Division of Health Effects, U.S. Consumer Product Safety Commission, during the entire period of this study.

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TABLE 1. CHARACTERISTICS OF EIGHT HOMES MONITORED FOR CHLORINATED AND OTHER HYDROCARBONS

House No.	Age (yrs)	[1]Occupants	House Type	Size (ft^2)	Air Conditioning	Insulation	Floor Covering	Attached Garage
05	3	2 adults	3-level frame	2000	heat pump	fiberglass	vinyl -carpet	yes
08	7	2 adults	3-level frame	2500	heat pump	UFFI	vinyl -carpet	yes
10	39	3 adults (smoke 7 packs per week)	2-level frame	2000	window a/c electric heat -wood stove	other	carpet -hardwood	no
24	5	2 adults	4-level frame	3000	heat pump -woodstove	UFFI	carpet	yes
36	5	2 adults 2 children	2-level frame	3000	heat pump	fiberglass	vinyl -carpet	yes
39	22	2 adults (smoke 10 packs per week)	3-level frame	4000	electric resistance heating, coal-fired stove, window air conditioner	UFFI	tile -hardwood -carpet[3]	no
[2]85	2	2 adults	1-level frame	2000	heat pump	fiberglass	vinyl -carpet	yes
86	2	2 adults (weekend/ summer use)	5-level frame	1500	heat pump	fiberglass	vinyl -carpet	no

[1]regular occupants were non-smokers except for 2 smokers in both houses No. 10 and 39
[2]only house/garage with "no" stored paints, lacquers, thinners, gasoline, etc.
[3]carpet and stove produced VOC (p. 47 of ref. 16)

TABLE II. TOTAL VOC (MG/M^3) ESTIMATED FROM THE TOTAL GCFID CHROMATOGRAMS

House No.		Concentration (mg/m^3) February 1984	August 1984	December 1984
05	living room	1.48	0.71	1.11
	bedroom	3.67	-	-
	outside	0.44	0.01	0.00(3)
08	family room	1.18	-	0.26
10	living room	1.56	-	1.02
	bedroom	0.24	-	-
24	living room	0.50	-	1.49
	bedroom	0.40	-	-
36	living room	-	-	0.15
	bedroom	0.88	-	-
	outside	-	-	0.00(9)
39	living room		-	0.24
	outside	0.01	-	0.00(5)
85	living room	1.70	-	0.09 (January 1985)
	bedroom	0.78	-	-
86	living room	0.74	-	0.09
	bedroom	0.75	-	-

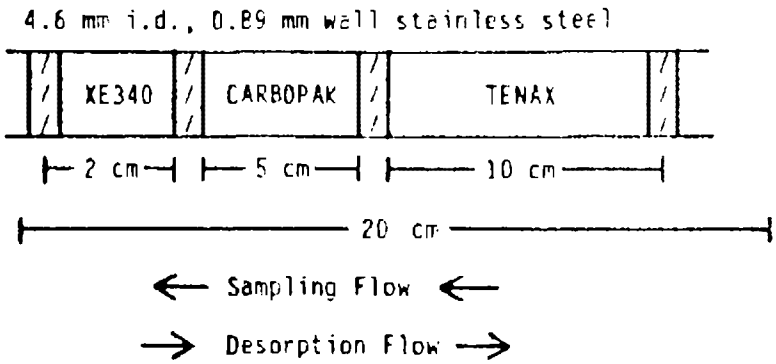

Figure 1. Schematic of trap configuration.

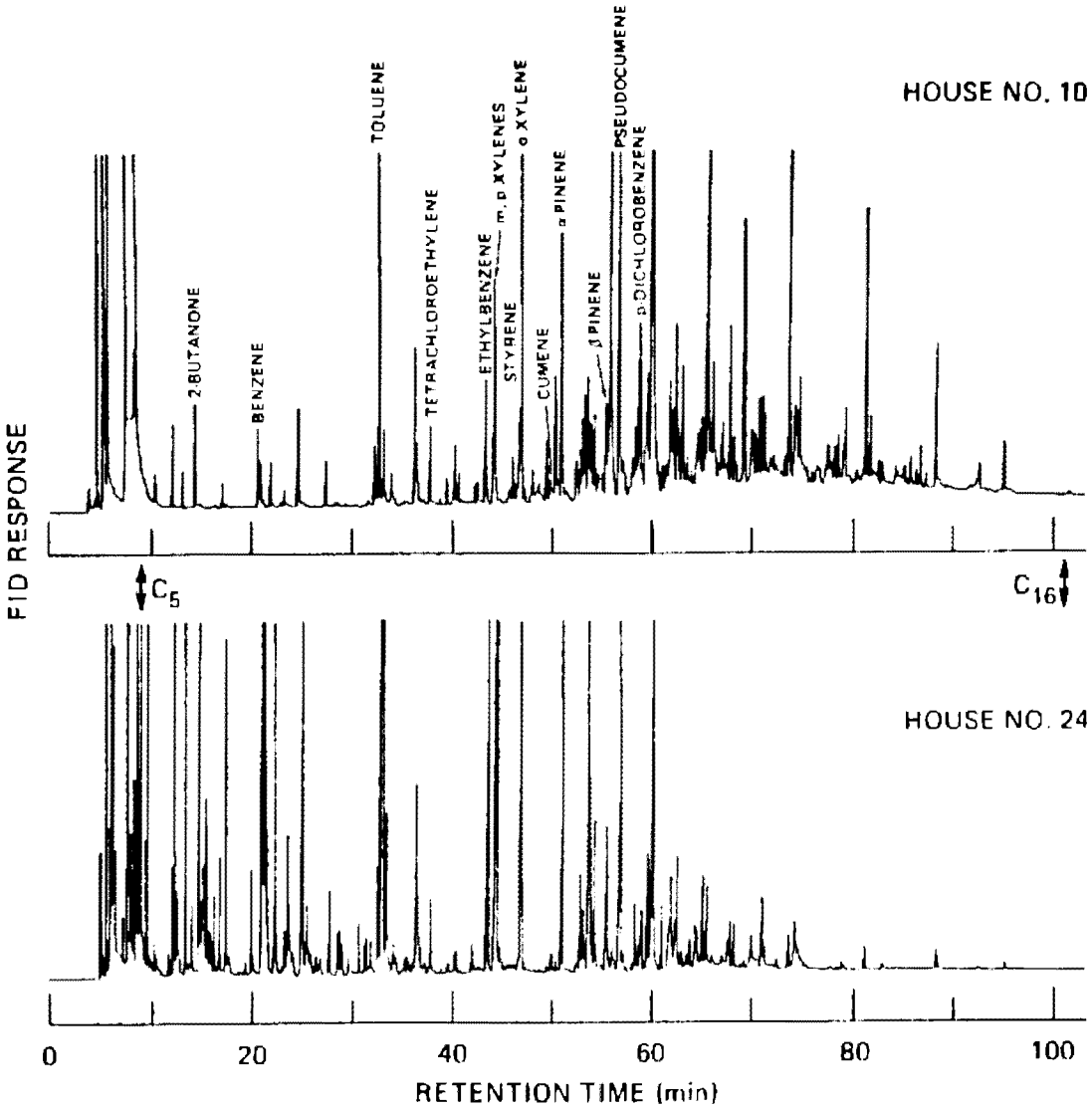

Figure 2. GCFIC chromatograms showing the complexity of indoor VOC and some compound identifications.

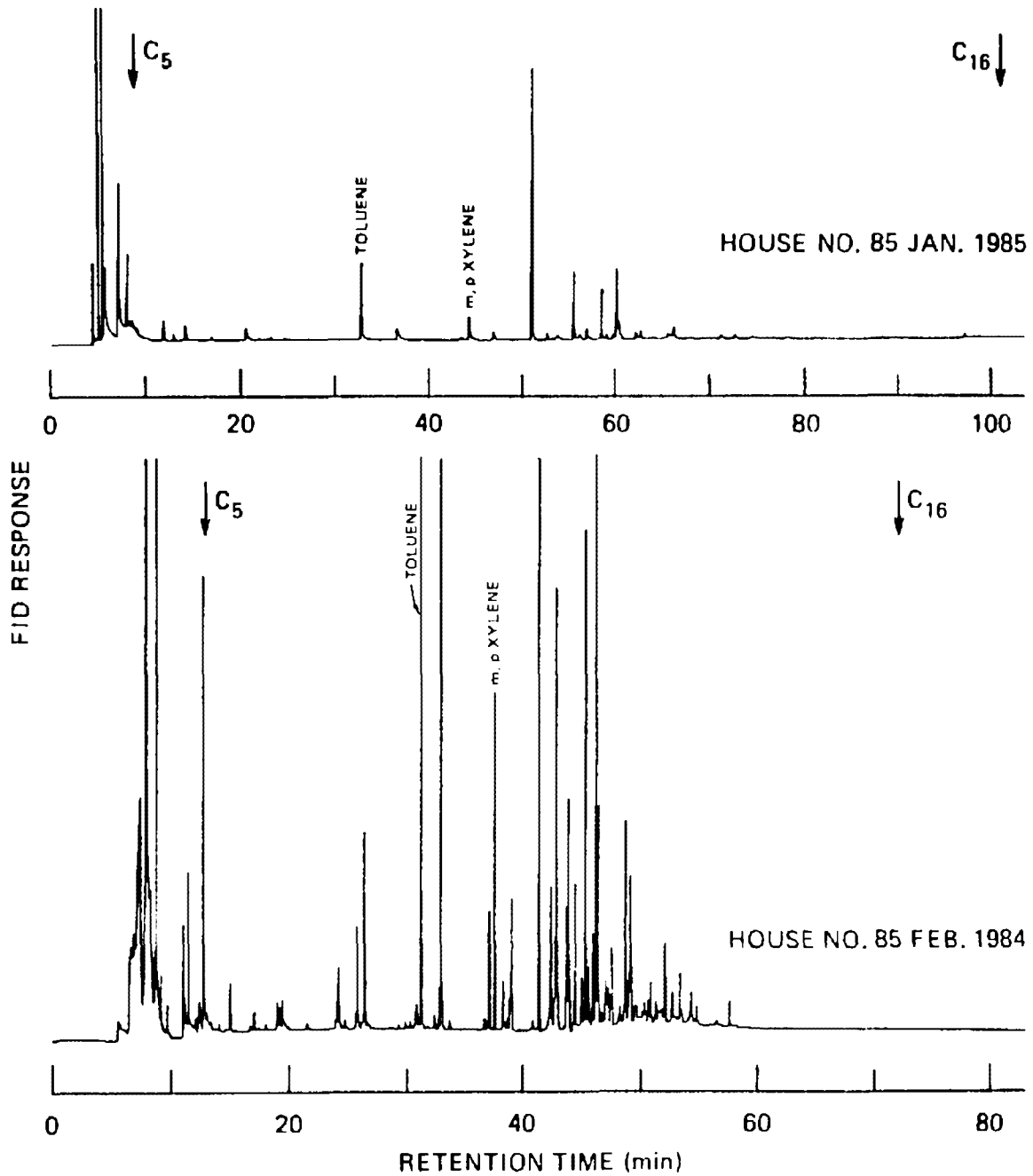

Figure 3. Marked change in the load of VOC occurring over one year in the indoor air of house no. 85.

INDOOR POLLUTANTS IN 70 HOUSES IN THE TENNESSEE VALLEY AREA: STUDY DESIGN AND MEASUREMENT METHODS

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Levels of nitrogen dioxide, formaldehyde, vapor-phase polynuclear aromatic hydrocarbon compounds, respirable particles, radon and other parameters related to indoor air quality are being measured with passive monitors in a year-long study of indoor air quality in 70 houses in the Tennessee Valley area. Criteria for house selection included presence of a lower level with cement floor and one or more block walls in contact with the soil and proximity to one of four cities in the region (Knoxville, Chattanooga, Birmingham, and Florence). By design, most of the houses in the study are in the same neighborhood as at least one other house in the study. Houses range in age from newly constructed to about forty years old, typically have more more than 2000 square feet of finished floor space, and encompass a garage in the lower level in most cases.

Six houses near Knoxville were especially selected for intensive study. An instrumented measurement and data acquisition system was used during the

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summer of 1985 to make a nearly continuous record of oxides of nitrogen, oxides of carbon, formaldehyde, particulate matter, ozone, air exchange rate, and air movement. Simultaneously, passive monitors identical to those used throughout the study were deployed with increased replication in the houses.

Introduction

Because people spend a lot of time in their homes, residential environments can account for much of the total exposure to some pollutants. Studies of indoor pollutant levels in occupied homes are necessary to provide a measure of the residential component of total exposure to pollutants. Indoor pollutants of concern include nitrogen dioxide, polynuclear aromatic hydrocarbon compounds (PNAs), formaldehyde, volatile organic compounds (VOCs), and particles in the respirable size range (RSPs). A study is under way in the Tennessee Valley area to examine levels of the above pollutants, as well as radon and its progeny, in 70 houses in four states during a one-year period.

Since World War II there has been an explosion in the number of organic chemicals used in construction and consumer products by American industry. Organic and inorganic chemicals can frequently be detected in the air of American homes. Sources of these chemicals in the residential environment include building products, consumer products and solvents, unvented combustion, and natural emissions from plants and animals. Many of these chemicals are toxic to varying degrees; over 59,000 different chemicals are listed in a recent edition of the Registry of Toxic Effects of Chemicals Substances.[1]

There have been relatively few previous studies on levels of indoor non-radioactive pollutants in homes of the Tennessee Valley area. Spengler et al.[2] studied personal exposures to respirable particles in the vicinity of Kingston and Harriman, Tennessee. The levels in homes where cigarettes were smoked were generally about twofold higher than in non-smoking homes. Also, personal exposures were more highly correlated with exposure levels measured in homes than with levels measured outdoors. In 1982, a year-long study of indoor air quality in forty houses near Knoxville, Tennessee, was conducted.[3] Formaldehyde levels in most houses exceeded 100 ppb on at least one occasion. Levels were higher in newer houses. The concentrations of various organic chemicals were found to be about tenfold higher indoors than outdoors. Also, a greater diversity of chemical species were detected in indoor samples compared to outdoor samples. Carbon monoxide and nitrogen oxides were usually less than 2 ppm and 20 ppb, respectively, except during episodes of unvented combustion or of automobile operation in attached garages.

To investigate the range of levels of several indoor pollutants and factors that influence indoor air quality in houses, a year-long study of 70 houses in four states began in the summer of 1985. The portion of the study dealing with radon and radon progeny has been described elsewhere.[4] This paper will provide an overview of the study design, experimental methods, and example results from the first quarter of the study.

Selection of Houses

Houses in the vicinity of one of four cities, Knoxville and Chattanooga in Tennessee and Florence and Birmingham in Alabama, were

selected for the study. Twelve counties are represented in these clusters: Anderson, Knox, and Roane counties in upper East Tennessee; Hamilton (TN) and Walker (GA) counties near Chattanooga; Shelby and Jefferson counties in central Alabama; Colbert, Lauderdale, and Madison counties in northwestern Alabama; and Lee and Itawamba counties in northeastern Mississippi. The number of homes in the vicinity of each city was limited to twenty or less due to limited numbers of both staff and radon progeny samplers.

Volunteers for the study were solicited using different methods with varying degrees of success. Direct solicitation by either mail or phone was completely unsuccessful in uncovering suitable houses. Seminars describing indoor air quality research at the Oak Ridge National Laboratory were presented to academic, industrial, and professional groups. Several interested attendees at these seminars volunteered for the study. Interviews were provided to the news media in several cities and subsequent news coverage induced other interested individuals to contact us. Most houses included in the study resulted from the efforts of volunteers who, in turn, solicited their neighbors to participate in our study. This approach resulted in a clustering of study houses within neighborhoods which reduces the travel time needed to make measurements.

The principal criterion for house selection was the presence of a lower level with cement floor and block walls in contact with the soil. This allows comparison of upstairs data and downstairs data and is especially important for the radon component of the study. In addition, we tried to avoid houses with technologically enhanced sources of radon.

Additional criteria were used in the selection of the six houses closest to Knoxville, Tennessee, because these houses were subjects of special study during the summer of 1985. The selection of these houses is described in Table I.

Measurement Methods

The schedule of measurements being made in this study are summarized in Table II. The sampling schedule involves quarterly visits to all houses. Each quarter each house is visited two times, about a week apart. Integrating sampling devices are installed during the first visit and are retrieved during the second visit. In addition, during the second visit nitrogen dioxide samplers are installed and the homeowner returns them to us by mail after one week. The same two sampling locations are used in each house each quarter, one on the level of the house in contact with the soil and one on the floor immediately above. A small metal rack is used to hold the passive samplers at each location.

The passive samplers used for nitrogen dioxide and PNAs have been described elsewhere.[5,6] The samplers used for formaldehyde were obtained commercially.[7,8] Water vapor concentration is measured using gravimetric analysis of molecular sieve in a diffusion-controlled sampling tube. Precision of the passive samplers, other than those for PNAs, was estimated during the summer of 1985 by installing them in triplicate in the six houses in the vicinity of Knoxville, Tennessee. VOCs, with volatility less than the volatile components of gasoline, were sampled using cartridges containing three sorbent materials: 30-50 mesh Ambersorb XE-340, 60-80 mesh Carbopak B coated with 1% SP-1000, and 35-60 mesh Tenax GC.[9] Air was passed through the cartridge for 30 minutes at a rate of 1 L/min. Average rate of air exchange during the week-long sampling interval is estimated using the perfluorocarbon tracer technique developed by Dietz et al.[10]

Some measurements are only made in selected houses. For example, particles in the respirable size range (i.e., less than 2.5 microns) are monitored in about a dozen houses each quarter, using an impactor developed by the Harvard School of Public Health.[11] Each quarter, hygrothermographs are placed in ten to twenty of the houses to monitor humidity and temperature. In forty of the homes, air exchange will be estimated during one visit using tracer decay experiments.[12]

During the summer of 1985, data were taken in each of the six houses near Knoxville, Tennessee, using an instrumented measurement and data acquisition system. Instruments for nitrous oxide, nitrogen oxides, carbon monoxide, carbon dioxide, ozone, formaldehyde, and freon (i.e., the tracer used for nearly continuous recording of air exchange rate) sampled from an air stream pumped cyclically from sites in a bedroom, the kitchen, the basement, and outside of the house. At a single location, a hotwire anemometer and a ten stage cascade impactor monitored air velocity and particulate levels indoors. Each of these instruments was moved sequentially between the bedroom, kitchen, and basement locations. An automated data acquisition system sampled all instruments, controlled valves to sample air from all sites sequentially, and controlled release of freon tracer to monitor air exchange rates. Levels of freon were maintained between preset limits which were determined from instrument detection limits and safe exposure levels. The duration of one measurement cycle including all four measurement sites was 100 minutes. The measurement and data acquisition system was installed at each house for about a week and useful data were taken during about two to six days at the various houses.

Two questionnaires have been developed for use in the study. The homeowners were queried during one visit concerning many characteristics of the house that affect indoor air quality. Such characteristics include age, building materials, weatherization measures, combustion sources, ventilation practices, heating and cooling practices, and air cleaning devices. Another questionnaire is administered in each house after each quarterly sampling interval to determine what unusual activities occurred that might have affected the data just collected.

More detailed information on the status of weatherization measures in these houses is being sought. Each homeowner is requested to authorize an energy audit by the home energy conservation program of the local electric utility. For those houses that agree, these audits will provide an expert assessment of house features such as insulation, storm doors and windows, caulking, weatherstripping, and the heating, ventilating, and air conditioning system.

Example Results and Discussion

The only results presently available from this ongoing study are some preliminary results from the detailed study made of six local houses during the summer of 1985. Selected results from measurements with passive integrating devices and with active devices will be presented in this section.

Generally, passive integrating monitors for formaldehyde, nitrogen dioxide, and water vapor were exposed in triplicate at five locations at each house. Those locations were basement, bedroom, a central upstairs

location, kitchen, and outdoors. The results for formaldehyde, nitrogen dioxide, and water vapor are presented in Tables III, IV, and V, respectively.

The precision of passive samplers used for nitrogen dioxide, formaldehyde, and water vapor was estimated from the analysis of variance of results from triplicate exposures in the six local houses. The precision, defined here to be one standard deviation, of formaldehyde samplers was 19 ppb based on analysis of 90 measurements with a mean concentration equal to 80 ppb. The precision of the nitrogen dioxide samplers was 1.5 ppb based on analysis of 74 measurements with a mean concentration equal to 6.0 ppb. The precision of the water vapor samplers was 1.8 g/m3 based on analysis of 49 measurements with a mean concentration equal to 11 g/m3.

The air velocity in the vicinity of the sampling face of diffusion-limited samplers is an important factor in their proper function. Figure 1 depicts air velocity recorded in House 917 during a 24-hour period spanning two days during the summer of 1985. The instrument used could not resolve velocities less than about 4 cm/sec. For most of the sampled interval, the air velocity was less than 5 cm/sec but it ranged up to almost 15 cm/sec. These preliminary results may indicate that passive monitors intended for indoor monitoring applications should be evaluated for sampling efficiency when air movement is between 3 and 15 cm/sec.

The rate of exchange between indoor and outdoor air can affect indoor air quality. Figure 2 shows the levels of freon detected at three locations in House 917 during a 22-hour period spanning two days during the summer of 1985. The air exchange rates after the first injection of tracer are 0.17, 0.14-0.20, and 0.17 air changes per hour in the basement, bedroom, and kitchen, respectively. The rates after the second injection are 0.09, 0.10, and 0.10 air changes per hour at the same three sampling sites. The magnitude of the change in air exchange rate within a 22-hour period is noteworthy.

Respirable particles were monitored at four houses near Knoxville, Tennessee, during the summer of 1985 (Table VI). Within houses, the levels are relatively uniform. In house 905, more than 250 cigarettes were smoked weekly and the levels of particulate matter reflect the presence of that source. In contrast, the levels in House 942 are quite low, presumably, reflecting the operation of an electrostatic precipitator.

Future Work

The results that will be obtained from 70 houses in four states will yield information on the range of levels of NOx, HCHO, humidity, vapor phase PNAs, air exchange rates, and respirable particles in houses in the north central portion of the southeastern region of the US. In addition, analysis of the data from the detailed instrumented measurements in the six local houses will allow comparison of results from passive integrating monitors with near continuous records of instrumental measurements.

Information on factors potentially influencing residential air quality is also being collected. It will be possible to examine correlations of pollutant levels with air exchange rates determined either during a short period using passive decay of a tracer or during a one-week period using average concentration of a tracer that is continuously released. The possible correlations with house characteristics such as age, size,

location, materials, and weatherization will be examined. Temporal factors such as temperature and wind speed will be considered. For those houses found to have the highest levels, preliminary studies will be done to characterize the sources. Clearly, such houses would be attractive candidates for studies of mitigation measures.

Acknowledgements

This manuscript was prepared by Oak Ridge National Laboratory (ORNL), operated by Martin Marietta Energy Systems, Inc., on behalf of the U.S. Department of Energy (DOE), as an account of work sponsored by the Tennessee Valley Authority (TVA), the U.S. Environmental Protection Agency (EPA), the U.S. Consumer Product Safety Commission (CPSC), and Alabama Power Company (APC). Neither ORNL, DOE, TVA, EPA, CPSC, APC, or the U.S. Government, nor any person acting on their behalf: (a) makes any warranty or representation, express or implied, with respect to the information contained in this manuscript; or (b) assumes any liabilities with respect to the use of, or damage resulting from the use of any information contained in this manuscript.

A study of this magnitude cannot succeed without assistance from many sources. Most important are the homeowners, without whose patience this entire study would not continue. The authors gratefully acknowledge the assistance of C. Clark, C. R. Daffron, and M. A. Cohen in some of the field survey trips. Dr. J. D. Spengler and coworkers at the Department of Environmental Science and Physiology at the Harvard School of Public Health are providing the laboratory analysis of nitrogen dioxide passive samplers and perfluorocarbon tracer samplers. Dr. T. Vo-Dinh and coworkers at the Health and Safety Research Division of the Oak Ridge National Laboratory are providing the laboratory analyses of the vapor-phase PNA dosimeters. Dr. J. P. Harper of the Tennessee Valley is arranging for the energy audits and has provided many useful discussions. L. G. Watson has assisted with preparation of the manuscript.

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Table I. Characteristics of Study Houses in Knoxville Area.

House Number	Principal Selection Criterion	Age (Yrs)	Other Characteristics
905	Heavy use of cigarettes	9	Extensive pressed wood products
917	New house and furnishings	<1	Wood stove
922	Nearly new house	3	Cigarettes, wood stove
936	Few indoor sources	22	Solvents stored outdoors
942	Electrostatic precipitator	13	Wood stove
958	Natural gas combustion	19	Cigarettes, car restoration hobby shop

Table II. Summary of Measurement Schedule.

Frequency	Duration	Pollutant	Technique	Sample Pumped
		All Houses		
Quarterly	<1 hour	Radon	Modified Lucas Cell	Yes
		Rn Progeny	Alpha Spectroscopy	Yes
Quarterly	One week	NO_2	Ethanolamine sorbent	No
		Water vapor	Weight Gain	No
		Rn Progeny	Modified TLD	Yes
Summer/Winter	One week	Formaldehyde	Bisulfite sorbent	No
		PNA vapor	Phosphorescence	No
Quarterly	3 months	Radon	Track etch	No
		Six Houses, Five Sites per House, Summer, 1985		
Every 100 minutes	15 min.	NO/NO_x	Chemiluminescence	Yes
	CO	Electrochemical Cell	Yes	
		CO_2	Infrared Absorption	Yes
		O_3	UV Absorption	Yes
		Particles*	Weight Gain	Yes
		Formaldehyde	Pararosaniline	Yes

*Three sites at 4 houses, one site at one house, and not used at one house.

Table III. Concentrations of Formaldehyde (ppb).

House:	905	917	922	936	942	958
basement	160	60	30	70	90	60
	170	70	30	60	90	60
	140	50	50	80	100	90
bedroom	180	70	130	60	100	80
	150	60	100	50	110	80
	150	60	150	50	110	90
central upstairs	240	90	130	60	100	70
	280	80	130	70	90	90
	140	130	160	60	90	80
kitchen	110	90	150	40	90	90
	160	80	110	50	90	90
	170	70	110	60	90	80
outdoor	0	10	10	10	0	0
	0	10	10	0	0	10
	0	30	20	10	0	10

Table IV. Concentrations of Nitrogen Dioxide (ppb).

House:	905	922	936	942	958
basement	5	4	2	10	15
	6	3	2	8	11
	7	3	2	8	
bedroom	5	3	3	8	8
	5	2	2	8	12
	6	2	3	7	12
central upstairs	5	2	3	8	14
	5	2	3	8	9
	5	2	3	8	11
kitchen	5	2	3	8	10
	5	3	3	9	10
	5	3	3	8	
outdoor	5	7	5	6	10
	6	8	6	6	11
	5	7	6	8	10

Table V. Concentrations of Water Vapor ($\mu g/m^3$).

House:	905	917	922	936	942	958
basement	11.0	14.0	14.0	9.0	9.9	10.0
	11.0	14.0	14.0	9.0	10.0	10.0
	11.0		14.0	9.0	9.9	10.0
bedroom	10.0	14.0	9.6	8.7	10.0	8.9
	9.9	14.0	13.0	8.8	10.0	9.1
	9.9		13.0	8.8	10.0	9.1
central upstairs	10.0	14.0	13.0	8.8	9.9	8.8
	10.0		13.0	7.7	9.9	8.0
	22.0		13.0	8.7	10.0	8.8
kitchen	9.9	13.0	13.0	9.0	10.0	9.0
	9.9	14.0	13.0	8.9	10.0	9.0
	9.9		13.0		10.0	9.0

Table VI. Concentrations of Respirable Particles ($\mu g/m^3$).

House	Kitchen	Bedroom	Basement
905	91	71	73
936	17	20	16
942	<2	<2	<2
958	30	2*	32

* Suspected instrument problem.

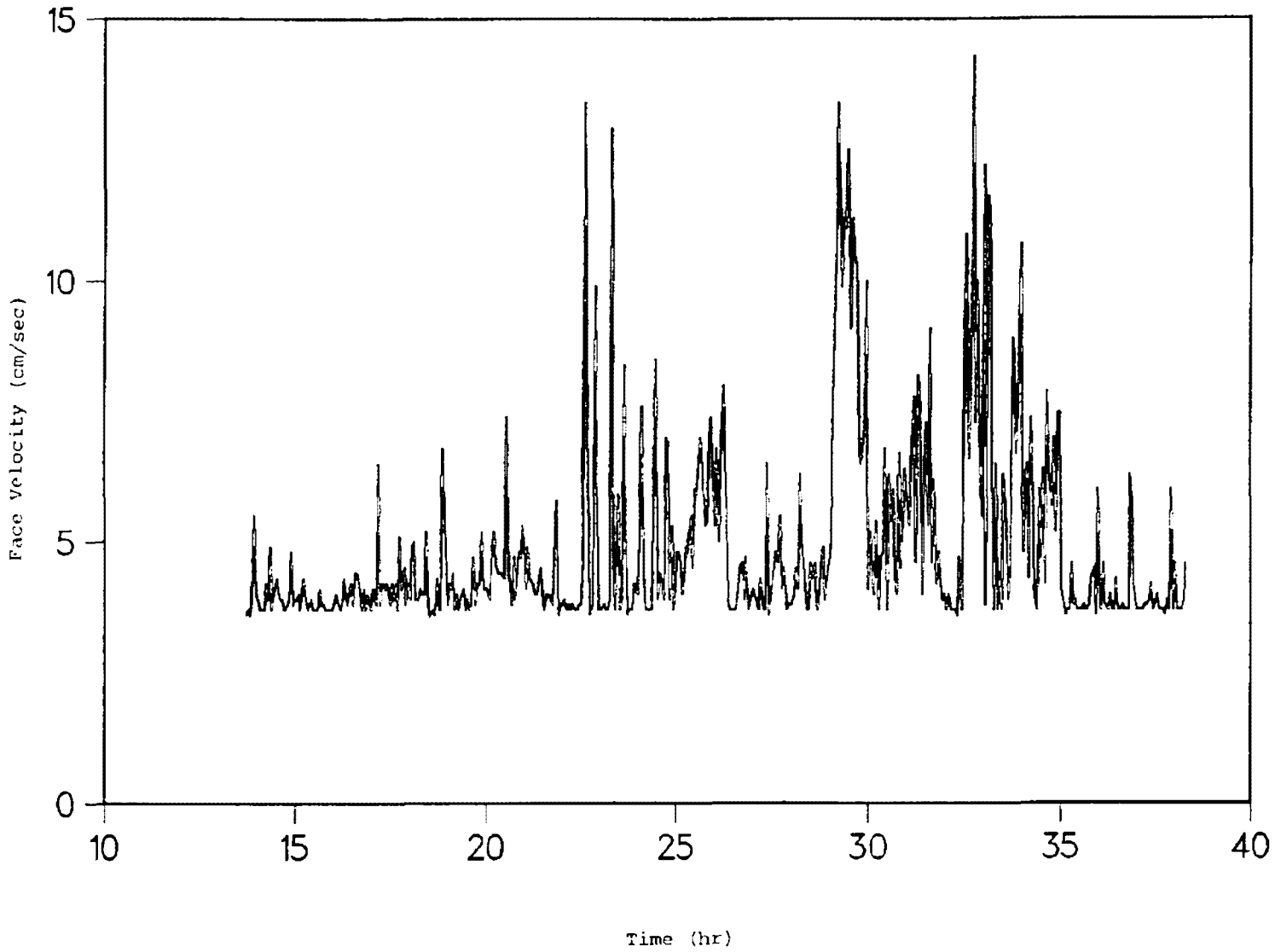

Figure 1. Record of air velocity in House 917 during 24 hours spanning two days in August, 1985.

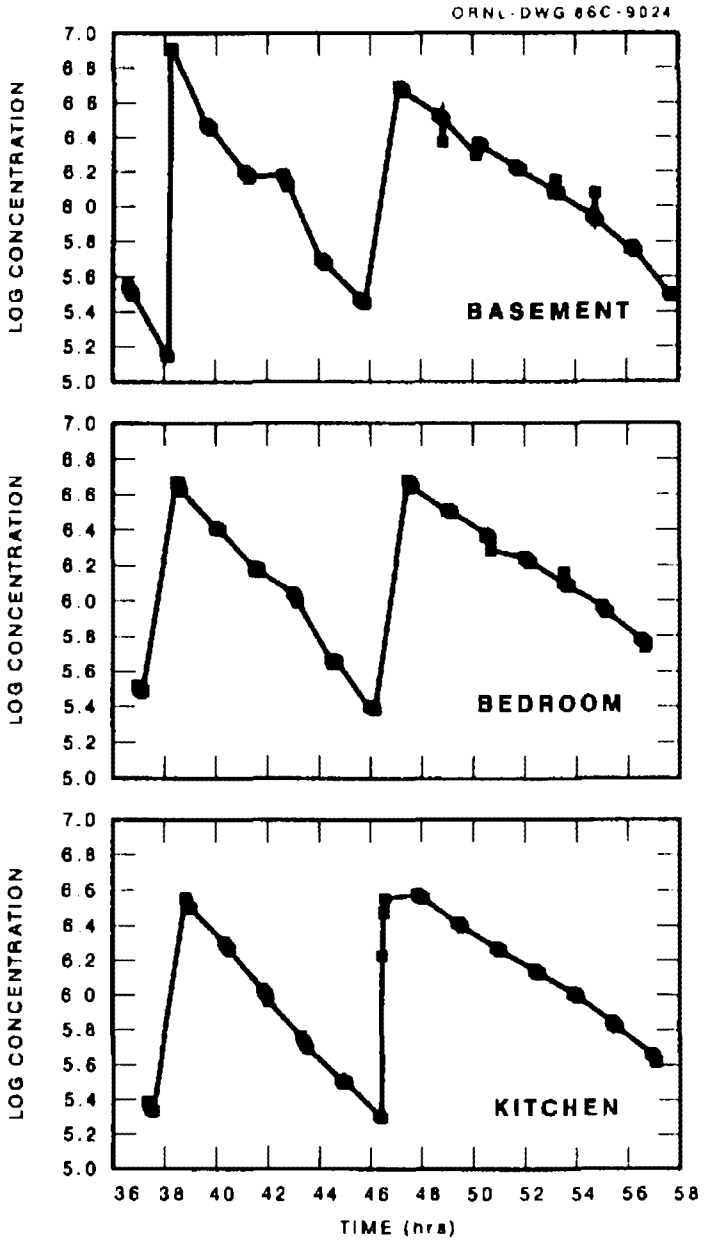

Figure 2. Records of freon concentrations at three locations in House 917 during 22 hours spanning two days in August, 1985. Tracer was injected at approximately 37 and 46 hours.

SOURCE EMISSIONS DATABASE FOR INDOOR AIR POLLUTION

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ABSTRACT

This paper describes a computerized database for experimental results on indoor air pollution sources and their emission factors. The database allows for convenient searches on such topics as indoor source, source class, and pollutant. Users of this database have access to information including: emission factors for air pollutants of indoor sources; and conditions, sampling methods, and analytical techniques of each experiment. The abstracts and data for these experiments are scheduled to be available in mid-1986 in a dBase III version and in a Clipper-compiled version for IBM and compatible microcomputers.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

SOURCE EMISSIONS DATABASE FOR INDOOR AIR POLLUTION

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Background

Indoor concentrations of pollutants vary significantly depending on many factors including the prevalence and character of indoor air pollution sources. The importance of these sources has been recently emphasized by energy conservation techniques which decrease the infiltration of ambient air and allow the concentrations of harmful chemicals to accumulate in the indoor environment. Thus, experiments that measure emissions from possible indoor air sources (i.e., source characterization studies) are necessary in indoor air pollution research.

Source characterization studies are experiments in which single possible indoor air sources (e.g., insulation, kerosene heaters, paints, personal care products) are placed inside a hood, chamber, or house, and are exposed to specified conditions to determine the quantity of chemical compounds emitted or offgassed. The value determined is called an emission factor, with units for material sources of mass of pollutant per mass of source per period of time (μg/g hr), or mass of pollutant per surface area of source per period of time (μg/cm^2 hr). For combustion sources the units are μg/kJ, μg/kg, or μg/hr.

The Hazardous Air Technology Branch (HATB) of the U.S. Environmental Protection Agency's Air and Energy Engineering Research Laboratory (AEERL) recognized the need to gather available source characterization experimental data into a computerized database to provide the medium for data transfer and data consistency. This database is a result of that recognition. It compiles abstracts of articles published on indoor air source characterization, and catalogs data on sources, pollutants, conditions, sampling methods, and analytical techniques of each experiment.

It is designed to reach a broad spectrum of users in a widely accessible, and extremely user-friendly manner. The database will be available in a dBase III and a Clipper-compiled version. The Clipper-compiled version may be used on any IBM or compatible microcomputer disk operating system (DOS) with or without dBase III. The dBase III version is the original programming language and requires a copy of the dBase III

software. Accessibility on the IBM and compatible microcomputer allows the user to have the entire system in his/her own office or laboratory.

Anticipated users of this database (including other source characterization researchers, monitoring teams, builders and architects, policy makers, consumer groups, and private industry) may use the database to evaluate results of completed studies and plan future endeavors. Monitoring teams may use the database to attribute high concentrations to specific sources within the structure. Health-related professionals may plan epidemiologic studies based on data retrieved from the database. Builders and architects may refer to specific building construction materials. Manufacturers may view pollutants off-gassed by consumer products and home furnishings. Individuals studying control technology may use the database for insights on source modification, pre-treatment, or removal.

Structure

The hierarchical structure for the data set is composed of five databases which give information on: (1) the journal article, the test facility, and the abstract (BIBLIO); (2) the source tested (SOURCE); (3) the conditions of the experiment (COND); (4) the sampling and analytical techniques (SAMPLE); and (5) pollutants, emission factors, and related data (POLL). These are arranged and connected as follows:

```
                    BIBLIO
                   /      |
              SOURCE     SOURCE
             /      |          |
         COND      COND       COND
        /    |          |     /    |
    SAMPLE     SAMPLE   SAMPLE SAMPLE  SAMPLE
   /   /   |     |        |      |     /     |
POLL POLL POLL  POLL     POLL   POLL POLL   POLL
```

This structure is designed to fit experiments where, in a single journal article, data may be reported on tests of one or several sources, conditions, sampling and analytical methodologies, or pollutants.

The five databases are connected by four tying numbers. These numbers allow data to be linked, arranged, and searched on any one or several of the five database levels.

Use Of The Database

The only command the user needs to type to begin the programs is IASE in the Clipper-compiled version, or DO IASE in the dBase III version. (IASE is an acronym for the Indoor Air Source Emissions database.) The main program immediately displays the following menu from which the user may make a numerical selection:

1. USE HELP.
2. ADD NEW RECORDS TO THE FILES.
3. DO PRE-PROGRAMMED SEARCHES.
4. DO DETAILED SEARCHES.
5. DISPLAY ABSTRACTS.
6. EXIT.

The most popular selection will be the pre-written programs for searching the database (Option 3).

Pre-written Programs

The pre-written programs allow the user to search the database by:

1. SOURCE CLASSES.
2. SOURCES.
3. POLLUTANTS.
4. SOURCE CLASSES AND POLLUTANTS.
5. SOURCES AND POLLUTANTS.

No previous computer experience or further instructions are necessary. If a user decides to search by one of these five possibilities, a submenu appears displaying all options available in the database. He/she simply selects the number of the option desired. For example, if the user chooses to search by pollutants, the list available would include:

1. NITROGEN DIOXIDE.
2. NITRIC OXIDE.
3. CARBON MONOXIDE.
4. CARBON DIOXIDE.
5. SULFUR DIOXIDE.
6. FORMALDEHYDE.
7. BENZYL CHLORIDE.
8. BENZAL CHLORIDE.
9. N-HEXANE.
10. N-DECANE.

Similarly, if the user chooses to search by sources (Option 2), the list of options would include:

1. UNVENTED CONVECTIVE KEROSENE SPACE HEATERS.
2. UNVENTED RADIANT KEROSENE SPACE HEATERS.
3. UNVENTED RADIANT GAS SPACE HEATERS.
4. UREA FORMALDEHYDE FOAM INSULATION.
5. CIGARETTES.
6. PARTICLEBOARD.
7. CHIPBOARD.
8. GYPSUMBOARD.
9. CAULKING COMPOUND.
10. DRAPERY FABRIC.

A list of available source classes appears if option 1 or 4 is chosen. The classification system is covered later in this paper.

The user then has the option to:

1. DISPLAY EXTENSIVE DATA.
2. DISPLAY LIMITED DATA.

Option 1 displays all of the data included about that experiment -- details about the source, sampling methodology, experimental conditions, the test facility, the analytical techniques, etc. A limited data display shows only specific information; e.g., the sources, pollutants, and emission factors involved.

Additional Features

Additional programs are written and are accessible from the original menu. One of these selections (Option 4) allows the user to search the database while limiting specific experimental parameters; e.g., temperature ranges or ventilation rates. Another feature (Option 2) allows researchers to add their own data into the database. Option 5 displays abstracts of the publications from which the data were retrieved.

If the user has a copy of dBase III, knowledge of the programming language, and the dBase III version of this database, additional manipulations of the data are possible. These will be covered in the user's manual.

Data Inconsistency

In reviewing articles, data inconsistency became an apparent problem. Important information (e.g., temperature, humidity, and air exchange rate) was often omitted from the publications. Terms such as emission factors were also in various units. Currently the data stored in the database include only data published in the original article. The units are converted for consistency on key fields within the condition and pollutant

databases (COND and POLL). Since the database also serves as a repository for on-going source characterization studies, its presence may allow for more consistencies in the future.

Source Classification

In an attempt to list the indoor air sources, a classification system was attempted. The major catogories listed by the author are: combustion, material, and activity sources. (Activity sources are those sources which involve a personal or mechanical action within the facility during testing, as opposed to passive material sources.) These categories were subdivided into classes. For combustion sources, similar fuel types exhibit similar emissions. In classifying material sources, similar compositions or major compositions were placed into the same class. Since activity source characterization data have not been reviewed at this time, activity sources have not been subdivided. Some of the subdivisions currently in use are:

COMBUSTION SOURCES	MATERIAL SOURCES
TOBACCO	PLASTICS
GAS	WOOD PRODUCTS
KEROSENE	ADHESIVES/SEALANTS
WOOD	TEXTILES
COAL	APPLIED COATINGS
FUEL OIL	INSULATION
OTHER COMBUSTION	PERSONAL CARE PRODUCTS
	HOUSEHOLD CHEMICALS
	MASONRY/ROCK/STONE
	LIVING THINGS
	OTHER MATERIAL

Contents Of The Database

Currently approximately 40 articles are prepared for entry into the database. A large portion of these articles address combustion sources, especially kerosene and gas space heaters. The database also contains several works on formaldehyde emissions from material sources, particularly pressed wood products. Very little data are available on organic emissions from material or combustion sources, and no entries are currently reviewed for activity sources.

Conclusions

The indoor air problem is a complex one that requires coordination among several disciplines including those interested in health effects, indoor concentrations, and specific sources. The indoor air source emissions database strives to make source characterization information accessible to all groups. It is scheduled for release in mid-1986.

PROBLEMS ASSOCIATED WITH SAMPLING FOR SEMIVOLATILE ORGANIC CHEMICALS IN AIR

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Semivolatile organic chemicals (SVOCs) may be distributed between the gaseous and particulate-associated phases in air. Filtration sampling will not provide accurate measurements of particulate organic loadings due to post-collection volatilization problems. When back-up vapor traps are added, the samplers may efficiently collect both phases, but will not maintain their integrity, so that results will not realistically reflect airborne distributions. Consequently, great care should be exercised in both sampling and data interpretation. Experimental systems have been developed which may provide some insight into the true phase distributions of several SVOCs. However, a practical method for such monitoring is probably not in the immediate future.

DISCUSSION

The term "semivolatile organic chemicals" is used to broadly describe organic compounds which are too volatile to be collected by filtration air sampling but not sufficiently volatile for thermal desorption from solid sorbents. SVOCs can be generally classified as those having saturation vapor pressures (p_0) at 25°C falling between 0.1 torr (mm of Hg) and 10^{-7} torr. Many monitoring proposals for SVOCs presume that these compounds will be associated with airborne particulate matter and that they will remain associated with (be retained by) the particulate matter after collection on filters. Both assumptions are faulty. Once contaminated particles are entrained into the atmosphere, partitioning of the SVOCs into the gas phase will commence by non-classical vaporization. The extent of loss of a given SVOC from the suspended particles in transit to a sampler placement site will depend on its vapor pressure, on the distance traveled, and to a lesser degree, on the temperature, humidity, wind velocity and particle size. Of the organic compounds which remain adsorbed on particles after collection on the filter, only the least volatile (e.g., benzo-a-pyrene) will be efficiently retained.

Vapor pressures are not known for all SVOCs. However, p_0 values can be calculated for some of them using published heats of vaporization and other physical constants.[1,2] Comparisons with known vapor pressures for compounds of similar molecular structure can be used to estimate others. Approximate p_0 values (published and/or calculated) for some typical organic chemicals which may be found in the air are shown in Table I.

The chlorobenzenes, chlorotoluenes and other chlorinated organics listed in Table I are structurally and chemically similar to PCBs, DDT and other organochlorine pesticides for which there is substantial published air sampling data. These compounds are more volatile than most of the organochlorine pesticides. As early as 1966, Abbott et al.[3] reported that such pesticides vaporized from 0.22 μm membrane filters when air was drawn through them at 15 L/min. Bjorklund et al.[4] designed a high-volume (280 L/min) sampler to separately collect particulate and gaseous forms of airborne pesticides. It was equipped with a glass fiber filter, followed by a support-coated liquid sorbent bed. However, they found that when DDT was introduced as a mixture of gaseous (28%) and aerosol (78% on talc) forms, 90.6% of the insecticide was found in the vapor trap and only 9.3% on the filter. Beyerman and Erkrich[5] found that 90-100% of DDT, DDD, dieldrin and lindane (γ-BHC or γ-hexachlorocyclohexane) passed through a glass fiber filter. Lewis[6] added 19 organochlorine and organophosphate pesticides with p_0 values ranging from 10^{-3} to 10^{-7} torr to glass fiber filters coated with airborne particulate matter and pumped unfiltered ambient air through the filters for 24 hours. The result was the loss of 95 to 100% of the pesticides from the filters. Recent experiments with chlorinated dibenzodioxins showed that TCDD was nearly quantitatively (ca. 95%) vaporized under essentially the same conditions.[7] The vaporized TCDD was quantitively trapped on a polyurethane foam (PUF) back-up trap.

Although polynuclear aromatic compounds (PNAs) are generally believed to be introduced into the atmosphere as particles, and often occluded deep within particles, published literature indicates substantial losses from volitilization occurs on sampling. Davis et al.[8] and Guerin et al.[9] reported 40 to 90% evaporative losses of fluoranthene and pyrene and small losses of less volatile PNAs from standard Hi-Vol filters at ca. 500 L/min. Likewise PNAs with $p_0 > 10^{-8}$ torr were heavily lost from vapor-spiked urban particulate matter in dynamic studies performed with glass fiber filters.[10]

When investigators have employed samplers designed to separately collect gas phase and particulate-associated organic compounds from ambient air, compounds with $p_0 > 10^{-7}$ torr have been found primarily in the vapor traps of these samplers. For example, Bramesberger and Adams[11] found that 76 to 84% of a 2,4-D herbicide aerially applied in the northwest United States was collected in the vapor trap of a low-volume sampler (1 L/min) which was constructed to remove particulates by means of a rotating impactor. In 1972, EPA used a modified high-volume sampler with a back-up vapor trap to sample for pesticides ($p_0 = 4 \times 10^{-3}$ to 2×10^{-7} torr) in three states (New York, Texas and Florida).[12] The samplers were operated for 24-hour periods at 280 L/min during the 12 month study. Only rarely were any pesticides found on the filters. Billings and Bidleman[13] used a similar high-volume filter sampling system employing a PUF vapor trap to measure PCBs and pesticides in ambient air. They reported the following average percentages of each compound found in the filter: Aroclor 1016 ($p_0 \cong 10^{-4}$ torr), < 2%; Aroclor 1254, < 6%; chlordane < 2%; and p,p'-DDT, 17%. Jackson and Lewis[14] used a high-volume sampler (225 L/min), which pulled air through a glass fiber filter followed by a PUF vapor trap, to monitor the air in connection with the removal of PCB-contaminated soils in North Carolina. Samplers

situated 30 meters downwind of excavation activities showed that the majority (50-90%) of the Aroclor 1260 released into the air was collected by the PUF. Only in one case was more PCB (59%) found on the filter than in the vapor trap, and this resulted from excessive windblown dust created by a mechanical sweeper. In these studies, the samplers were turned off about one hour after digging operations ceased. Had sampling continued for substantially longer periods, even less PCB would probably have been detected on the filters.

Cautreels and van Cauwenberghe[15] used a low-volume sampler (7 L/min) with a glass fiber filter and a Tenax-GC trap to study PNA phase distribution in the air in Belgium. They found that PNAs with $p_0 > 10^{-6}$ torr were found primarily in the vapor trap and those with $p_0 < 10^{-9}$ torr were mostly on the filter. Similar results were obtained by Yamasaki et al. [16] in Japan and Keller and Bidleman[17] and Galasyn, et al.[18] in the U.S., all using high-volume samplers with glass fiber filters backed with polyurethane foam traps. The findings of these four independent investigations relative to several compounds covering the p_0 range of 10^{-4} to 10^{-9} torr are shown in Table II. Thrane and Mikalsen used a modified Hi-Vol sampler which pumped air at 400 L/min through a glass fiber filter and tandem PUF plugs to sample air in Norway between mid-September and mid-December.[19] Their results showed that only 5% of the total PNAs collected was on the filter, while 70% and 25% were collected on the front and back PUF a low volume (1.7 L/min) system employing filters (glass fiber or silver membrane) and Tenax GC cartridges. Of 50 PNAs detected, 29 were found only on the Tenax vapor trap, 11 were distributed between the filter and vapor trap, and 10 were found only on the filter.

Unfortunately, none of the previously cited studies can answer the question as to the real distributions of SVOCs in the ambient air. Currently-used sampling devices cannot truly distinguish between gaseous and particulate-associated organic chemicals with vapor pressures greater than 10^{-6} to 10^{-8} torr.

If present theories are correct, however, many SVOC's should not be associated to a substantial extent with airborne particulate matter in steady-state atmospheres. The partitioning of an organic chemical between the gas phase and particulate matter in the atmosphere is primarily a function of its saturation vapor pressure.[21] The composition of the airborne particulate matter and environmental conditions have relatively little effect on this partitioning under normal circumstances.[22] Equilibrium distributions between gas and particulate-associated (surface-adsorbed) phases can be calculated from Junge's equation:

$$\Phi = c\theta / (p_0 + c\theta),$$

where Φ is the ratio of the amount of organic compound on the particulate matter to that in both the gaseous and particulate-associated phases, θ is the surface area of the particulate matter per unit volume of air, and c is a constant which depends on the molecular weight and heat of condensation.[21] This equation would suggest, therefore, that organics with $p_0 > 10^{-4}$ torr would exist almost entirely in the gas phase and those with $p_0 < 10^{-8}$ torr would be nearly all in the particulate-associated phase in the atmosphere. Figure 1 shows a plot of Φ vs θ, with vapor pressure isobars superimposed. θ values for clean (remote), rural and urban atmospheres are indicated.

Junge's equation does not take into account the effects of temperature on the phase distribution of airborne organic chemicals in the atmosphere. However, Bidleman[23] has recently applied a mathematical treatment developed

by Yamasaki et al.[16] to predict partitioning ratios as a function of air temperature as they apply to air sampling. The Yamasaki equation is:

$$\log A(TSP)/F = a-b/T,$$

where A is the quantity of an organic chemical collected in the vapor trap and F is the amount on one filter, (TSP) is the concentration of total suspended particulate matter, T is the temperature in °K, and a and b are empirically-derived constants. This equation does not distinguish between equilibrium distributions in the atmosphere and those that occur due to volatilization from the filter. A plot of this equation for Aroclor 1254 is shown in Figure 2 along with points derived from high-volume air sampling using glass fiber filters and PUF at sites in three states and Sweden. As can be seen, the A/F ratio for Aroclor 1254 is 4000 at 25°C compared to 200 at 0°C. Similar plots for chlordane would show an A/F of 20,000 at 25°C and 300 at 0°C and predict A/F ratios of over 10^5 for HCB and lindane (γHCH) at 25°C.

Gaseous compounds present in the atmosphere from fugitive emissions (or from evaporative desorption from suspended particulate matter) may, of course, be adsorbed from the air onto airborne particles. The rate of sorption would be dependent on the frequency of collisions between suspended particles and the gaseous molecular species in the great air mass medium, but the efficiency of this process is questionable.[24] The mechanics of atmospheric gas-particle interactions are complex and are governed by a host of chemical, physical, and environmental factors, including the number and size of particles, temperature, air mixing, photoreactivity, and chemical reactivity. Only a very small fraction of the collisions between gas molecules and particles will lead to adsorption. Highly carbonaceous material, such as that emitted from coal-burning stacks, will, of course, adsorb organic compounds far more efficiently than highly siliceous particles, such as airborne sandy soil. Some clue as to the efficiency of the process may be found in the calculations of Judeikis and Siegel.[25] Using a modified particle-gas collision equation containing both adsorption and desorption parameters, they calculated that for conditions of adsorption without reaction, only 10^{-7}% of a gas originally present at 1 ppm would be adsorbed after several days' exposure to air levels of 100 μg/m^3 of airborne particulate matter of the type normally found in the ambient atmosphere. As they noted, this is no longer than the mean life of particles in the troposphere.[26]

In contaminated atmospheres near pollution sources (particularly dust producing), more particle-associated organics would be anticipated. Monitoring of these atmospheres with current methodology, however, would be unlikely to reveal this distribution since post-collection volatilization would bias the sample towards the gas phase.

Several recent investigations[9,27,29] have been directed at designing air samplers which will differentiate between gaseous and particulate-associated SVOCs. All of these have led to the development of prototype samplers which employ the principle of denuder tube separation. While such systems may afford a better estimate of the amounts of particulate-associated chemicals, post-collection volatilization processes still remain a problem. In addition, a second, collocated sampler capable of collecting both phases may be necessary to determine gas phase concentrations by difference.

CONCLUSIONS

Since currently-used air sampling methodology does not permit the separate determination of phase-distributed organics, only total airborne concentra-

tions of SVOCs can be determined. For this purpose, an air sampler having a particle filter and gas phase adsorbent system combination should be employed. However, the material collected on the filter should be combined with that collected on the adsorbent for analysis. While separate analyses may sometimes yield positive results, these results could not be interpreted to accurately reflect distributions between the gas and aerosol phases at the time of collection. When sampling in the vicinities of dust-producing operations, rapid volatilization of many SVOCs from dust entrained into the air would be expected, so that all or much of these compounds may be lost from airborne particulate matter before reaching the sampling devices. Quantities remaining associated with the collected particulate matter may be quickly stripped off the filters. Therefore, even if sampling were terminated shortly after a dust excursion, filter losses may be significant and unpredictable. Even if no losses occurred, following such a scenario, the quantities of compounds collected during a brief episode would likely be below analytical detection limits or indistinguishable from the same or similar chemicals in the area background air.

It can be logically argued that the physical state of potentially hazardous SVOCs may not be significant from a public health standpoint. The assumption that chemicals associated with inhalable particles (IP) capable of penetrating to the nasopharyngeal and tracheo-bronchial regions present a greater potential health risk than do gaseous chemicals is apparently based on the belief that the gases will be largely exhaled, while the particles will be retained. Gas phase deposition of SVOCs onto surfaces, particularly of plants, is apparently quite efficient.[26,43] Deposition in the mucosa of the nasopharynx and alveolar sacs should be even more efficient. In this event, lipid-soluble organic chemicals would be rapidly absorbed into the blood. Particulate-bound organics would likely be released into the circulatory system much more slowly (i.e., in much smaller doses). In any event, the same processes that contribute to the volatilization of particulate-associated organics in the air and from sampler filters would be operational in the respiratory tract, so that evaporative desorption may occur before deep-lung penetration.

In summary, attempts to determine the SVOCs (or any organic compound with $p_o > 10^{-7}$ to 10^{-8} torr) on particulate matter collected by filtration sampling should be discouraged for the following reasons:

1. They will be largely unassociated with airborne particulates under equilibrium conditions. The degree of association under non-equibrilium conditions will vary widely with transport distances, temperature, humidity, particle size, and particle concentrations.

2. Existing sampling methodology will not permit accurate determination of organic loadings on total or respirable particulate matter. Even under non-equilibrium conditions where SVOCs are associated with airborne particles, they would be vaporized from particulate matter collected on filters.

3. Gas phase SVOCs may present an equal or greater potential risk to human health than particle-associated SVOCs.

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TABLE I. SATURATION VAPOR PRESSURES* OF SOME ORGANIC COMPOUNDS AT 25°C

Vapor Pressure mm Hg	Chemical Class: Chlorinated	Oxygenated or Nitrogenous	Normal Alkanes	Polynuclear Aromatic
1	Monochlorotoluenes	Benzaldehyde	Decane	
10^{-1}	p-Dichlorobenzene Hexachlorobutadiene	Toluene-2,4-diisocyanate Aniline Toxaphene	Dodecane	Quinoline
10^{-2}	Tetrachlorobenzenes 2,4,5-Trichlorophenol 2,4-D isopropyl ester	Nicotine p-Chloroaniline	Tetradecane	Naphthalene
10^{-3}	Pentachlorobenzene	p-Nitroaniline	Hexadecane	Anthracene
10^{-4}	Aroclor 1242 Pentachlorophenol Heptachlor	Diazinon Butyl phthalate	Octadecane	Phenanthrene
10^{-5}	Hexachlorobenzene Chlordane Aroclor 1260	Parathion Carbaryl	Eicosane	
10^{-6}	Dieldrin 2,3,7,8-Tetrachloro-dibenzodioxin		Hexacosane	Fluoranthene
10^{-7}	DDT	Di(2-ethylhexyl)-phthalate		Benz(a)-anthracene
10^{-8}			Nonacosane	Chrysene
10^{-9}				Benzo(a)-pyrene
10^{-10}				Benzo(ghi)-perylene
10^{-12}				Coronene

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* Published or calculated. (See references 1, 2, and 30 through 42.)

TABLE II. COMPARATIVE MEASUREMENTS OF VAPOR/PARTICULATE DISTRIBUTES OF PNAs IN AMBIENT AIR

Investigators	% in Vapor Trap	Temp. (°C)
I. Cautreels & Van Cauwenberghe, Belgium (1978)[15] (GFF/Tenax, 7 L/min, 72 hr/3wks)		
Phenanthrene + Anthracene	96 avg	10.2 avg
Pyrene	67	
BaP + BeP + Perylene	12	
II. Yamasaki et al., Japan (1982)[16] (Hi-Vol, Gff/PUF, 800 L/min, 24 hr)		
Phenanthrene + Anthracene	96 - 100	7 to 30
Pyrene	92 - 99	
BaP + BeP + Perylene	0 - 20	
III. Keller & Bidleman, U.S.A. (1982)[17] (Hi-Vol, GFF/PUF, 500 L/min, 24 hr)		
Phenanthrene	92 - 98	-14 to +19
Pyrene	70 - 80	
BaP	0 - 5	
IV. Galasyn et al., U.S.A. (1984)[18] (Hi-Vol, GFF/PUF, 1100 L/min(?), 14-24 hr.)		
Phenanthrene	93 - 100	(12 mos.
Pyrene	54 - 97	New Hampshire)
BaP	0	

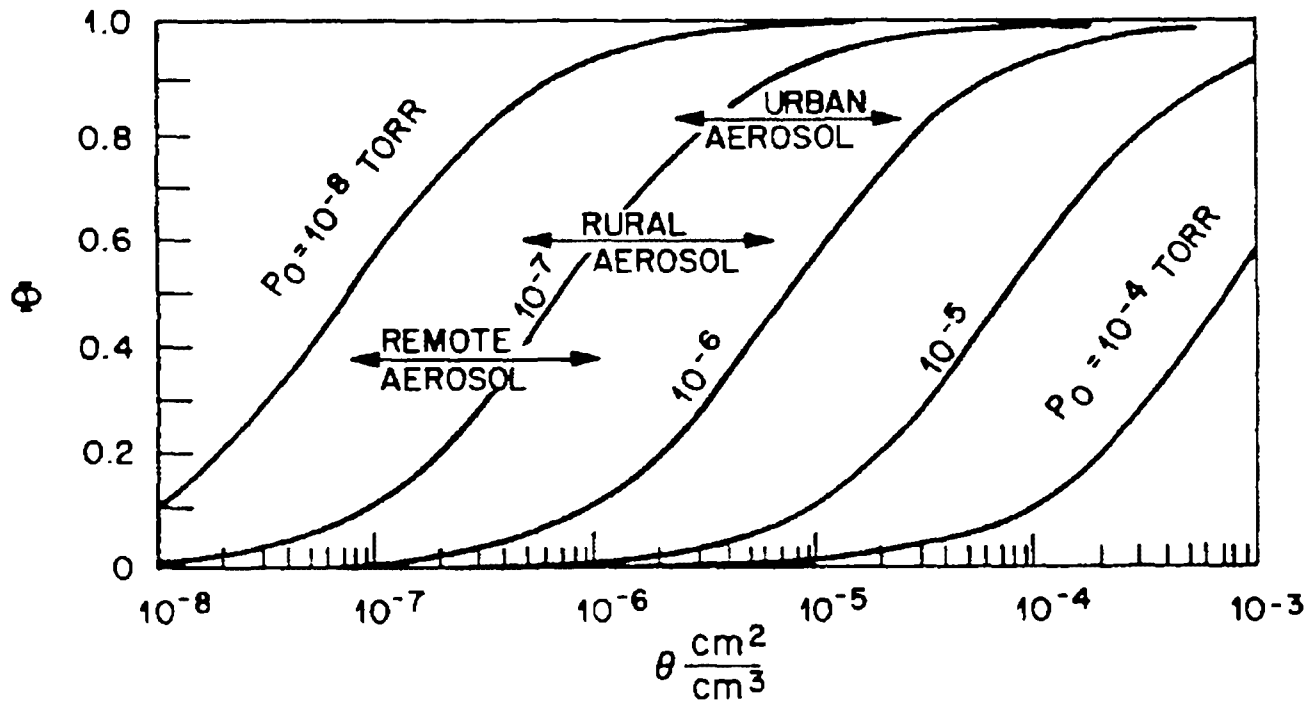

Figure 1. The fraction (Φ) of atmospheric organic chemicals adsorbed on suspended particulate matter as a function of surface density (Θ) and vapor pressure (p_o). (Reference 21)

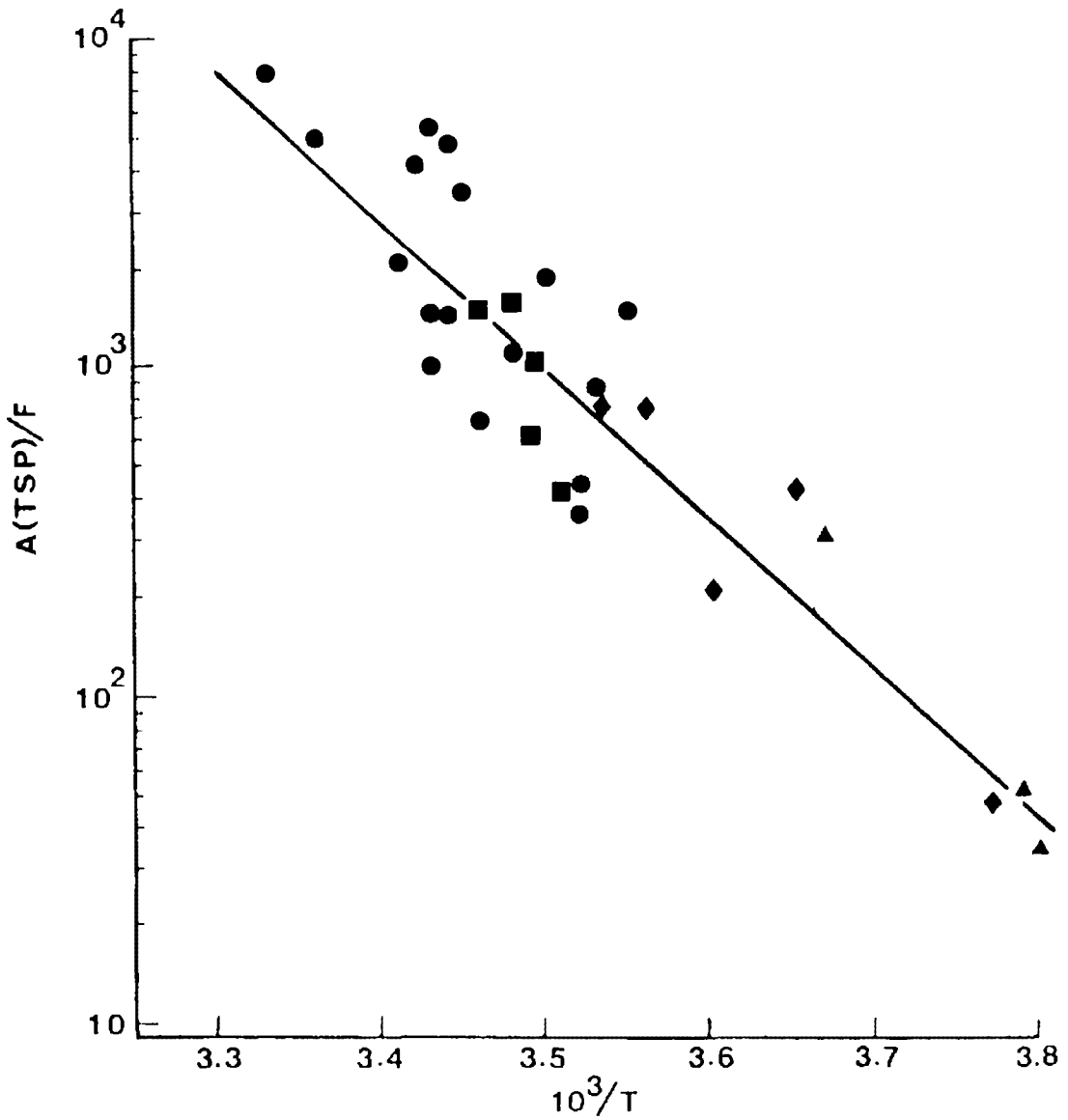

Figure 2. Relationship of gas phase to filter-retained ratios (A/F) of Aroclor 1254 to air temperature. Superimposed points derived from air samples taken in Columbia, SC (●), near a New Bedford, MA landfill (■), in Denver, CO (▲) and in Stockholm, Sweden (♦). (Reference 23)

FIELD EVALUATION OF PHASE DISTRIBUTION OF PAH

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A series of field sampling experiments was conducted using parallel modified EPA samplers, with one of the samplers equipped with a multiple tube denuder for removal of vapor phase PAH. Analytical results for the PAH collections on the filters and in the PUF backup traps for the two samplers were interpreted in terms of the amounts of each PAH (1) in the vapor phase; (2) associated with the particulate matter; and (3) volatilized or condensed during the sampling process. Results indicate that appreciable quantities of phenanthrene, anthracene, fluoranthene, pyrene, and to a lesser extent benzo(a)anthracene and chrysene exist in the vapor form in the atmosphere, and that these compounds are subject to vaporization/condensation during the sampling process. No evidence was found for vaporization of the benzopyrenes or heavier PAH. Apparent adsorption energies and estimates of the equilibrium vapor concentrations of these species in the atmosphere are derived from the data.

FIELD EVALUATION OF PHASE DISTRIBUTION OF PAH

Introduction

Many polycyclic aromatic hydrocarbons (PAH) are known or suspected carcinogens. The determination of concentrations of PAH in ambient air is therefore of considerable importance to the characterization of air quality. The task of sampling PAH is complicated by the fact that many PAH have equilibrium vapor concentrations that are considerably higher than their normal ambient air concentrations. This implies a temperature and concentration dependent distribution of such PAH between particulate and vapor phases, and also suggests the possibility for artifact occurence due to volatilization during the sampling process.

From the viewpoint of human health risk assessment, it is importnat to distinguish between the vapor and particle bound PAH. Traditional sampling methods have used only filtration to collect ambient aerosol. More recently, the use of backup polyurethane foam (PUF) (or other vapor sorbents) cartridges to collect vapor passing through the filter has become more popular. This approach however ignores the possibility of artifact formation as a result of either condensation or vaporization during the sampling process.

In a previous study for EPA, a laboratory study was conducted to determine the potential for existence of various PAH in the vapor phase in the atmosphere and to determine the potential for artifact formation as a consequence of high volume sampling processes. A research grade sampler capable of operating at a flow rate of 15 L/min was developed to investigate the phase distributions of PAH in the ambient atmosphere. The purpose of the current program was to use this sampler to evaluate phase distributions and artifact formation during sampling of ambient atmospheres. This work was conducted in two phases with air sampling during (a) the summer months of 1985 and (b) the winter months of 1986.

Experimental Approach

To achieve the objective of this task, a series of field sampling experiments was conducted on a laboratory roof at Battelle's Columbus Division in Columbus, Ohio. For these experiments, two samplers were operated in parallel. The first sampler was the standard EPA sampling train developed for semivolatile organic compounds[1] which is equivalent to the General Metals Works PS-1 sampler. The train consists of a filter and PUF cartridge for series collection of particulate bound and vapor phase PAH. The second sampler was similar, but incorporated a multiple tube denuder (described below) ahead of the filter. Filter and PUF samples were analyzed by GC/MS from each these samplers, with the following comparisons being made:

1. The two filter samples are nominally identical, with differnces reflecting excess artifact due to volatilization under the essentially vapor free conditions existing with the denuder sampler.
2. Assuming efficient removal of vapor phase PAH in the denuder, the PUF analysis from the second

sampler should reflect the total volatilization artifact (normal artifact plus excess).

3. The PUF analysis from the first sampler yields the vapor phase PAH plus the normal volatilization artifact.

The results therefore yield the following information for each of the PAH found:

1. The total PAH concentration in the sampled atmosphere.
2. The fractional distribution of each PAH in the vapor and particulate phases.
3. The artifact for each PAH as caused by volatilization during sampling.

Sampling periods were nominally 24-h, with analyses being conducted for phenanthrene, anthracene, pyrene, fluoranthene, benzo(a)anthracene, chrysene, benz(a)pyrene, benz(e)pyrene, cyclopenta(c,d)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene, and coronene.

Denuder Assembly

The denuder consisted of a parallel bank of 7 stainless steel tubes, 61 cm long with the diameter of each tube being 1.5 cm. The assembly was interfaced with the standard EPA sampler using a 15 cm transition section (see Figure 1). The inner surface of each tube was cleaned and recoated with 5g of high vacuum silicon grease (Dow Corning) before each sampling run. All internal surfaces of the sampler were cleaned with methylene chloride prior to each sampling run.

Initial tests of the denuder system were made using naphthalene as the challenge PAH. Air laden with naphthalene vapor was pumped through a single denuder tube at a rate of 2 L/min, with the input and output concentrations being monitored by gas chromatography. Results of these tests showed an initial removal efficiency of 89 percent (theoretical efficiency = 87-92 percent), and a capacity to remove several tens of micrograms without significant decline in removal efficiency.

Filters

Filters were 104 mm QAST (quartz fiber) filters obtained from Pallflex. These were baked at 350 C for 6h and were stored individually between similarly treated watchglasses that were sealed with Teflon tape.

Polyurethane Foam (PUF) Cartridges

PUF cartridges were cleaned by compression rinsing using 50 cycles in toluene followed by 50 cycles in 10 percent ether in hexane and acetone. The PUF plugs were then extracted in a Soxhlet extractor with acetone for 16h and were dried under vacuum at room temperature. After drying, each PUF plug was individually wrapped in hexane-washed aluminum foil and was stored in a glass jar closed with a Teflon-lined cap. Typically, PUF plugs were used within 24h after cleanup.

Sample Extraction

All PUF and filter samples were extracted immediately after removal from the samplers. These samples were Soxhlet extracted using 400 ml methylene chloride and 800 ml of 10 percent ether/hexane for at least 16h or until the solvents were clear. After extraction, the solutions were reduced to 1 ml using a Kuderna-Danish apparatus. The extracts were then transferred to Chromflex tubes and were further concentrated to 100µl for PUF samples. Prior to analysis, the internal standard, 9-phenylanthracene, was added to yield a concentration of 1 µg/ml.

GC/MS Analysis

A Finnigan 4500 GC/MS operated in an EI mode was used for analysis. A bonded-phase fused-silica capillary column (Ultra #2, crosslinked 5 percent phenylmethylsilicone) was used in both the GC oven and the ionization source. Data acquisition and processing were performed using a Finnigan/INCOS Model 2100 data system.

Standard solutions containing the target compounds and the internal standard were prepared at four concentration levels (0.1, 0.5, 2.0, and 5.0 µg/ml) for generation of calibration curves. The molecular ion peaks of the target compounds were monitored by the MS. Identification of target compounds was based on detection of the molecular ion coupled with comparison of retention time relative to that of the internal standard.

Results

Summaries of the summer and winter results are shown in Tables 1 and 2 respectively. In these tables, the apparent vapor and artifact levels are given as percentages of the total amounts found for each PAH. Although the detailed distributions for each PAH vary over a considerable range, the total of the vapor plus the artifact yields numbers very similar to those of reported by Van Cauwenberghe and co-workers[2].

Discussion

While it is convenient to express the data in terms of percentages of the total, as in Tables 1 and 2, this approach is misleading and indeed is inconsistent with the fundamental concepts of adsorption and equilibrium processes. An alternative approach is to consider the apparent vapor pressure of each PAH relative to the equilibrium vapor pressure of the pure compound at the same temperature.

The apparent vapor pressure can be expressed in terms of the free energy of vaporization from the adsorbed state, and therefore in terms of the entropy and enthalpy of vaporization. The entropy of vaporization from the adsorbed state is dominated by the change in translational entropy (at least for low energy volatilization processes) and is therefore much the same as the entropy of vaporization of the pure compound. The enthalpy change can be expressed as the normal vaporization enthalpy plus some excess enthalpy change that is related to the excess energy of adsorption. Therefore, we express the vapor concentrations of the adsorbed phase and the pure compound respectively as

$$\ln C_{va} = A - (\Delta H_n + \Delta H_e)/RT \qquad (1)$$

and

$$\ln C_{vo} = A - \Delta H_n/RT \qquad (2)$$

where R is the gas constant (1.987 cal/mole-deg) and T is the absolute temperature. The ratio of C_{va}/C_{vo} is therefore given by

$$\ln C_{va}/C_{vo} = -\Delta H_e/RT \qquad (3)$$

In view of the chemical similarity of the PAH compounds included in the current study, it might be expected that ΔH_e would be the same for all of those compounds found to have significant vapor phase concentrations. Table 3 shows values of ΔH_e calculated from the observed vapor phase concentrations for the summer data and the equilibrium vapor concentrations[3].

It can be seen from the values given in Table 4 that the apparent excess energies of adsorption fall in a fairly narrow range, with no significant differences between the various compounds. The values for chrysene are slightly low, but we believe this is due to the limited and somewhat questionable literature values for the vapor pressure of this compound. Omitting these questionable data, the overall average of apparent excess adsorption energies for the summer data is 5.8+/-0.5 kcal/mole. A similar treatment of the winter data yields an average of 3.9+/-0.7 kcal/mole. This slight drop in the adsorption energy for the winter data is consistent with the fact that surface coverages observed for the winter data were considerably higher than those for the summer data.

Inasmuch as the winter study has only recently been completed (March 1986), these data and the combined summer/winter data set has not yet been fully analyzed. In pursuing this analysis, we have noted however that the observed distributions of PAH between particulate bound and vapor phase material are well-correlated using the Dubinin-Radushkevich isotherm which has proven so useful in describing adsorption of volatile sorbates on carbonaceous sorbents[4].

Conclusions and Recommendations

The current work indicates that the 3 and 4-ring PAH exist to a large extent in the vapor phase in ambient air, and that appreciable artifact formation can occur as a result of volatilization (or condensation) of these compounds. This finding is consistent with the conclusions of other authors, but the current work provides a means for distinguishing beween artifact and vapor. The results are internally consistent when viewed from the perspective of thermodynamic equilibrium. It is expected that complete analysis of the current data will result in a means for estimating phase distributions of ambient PAH under a variety of sampling conditions.

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TABLE 1. SUMMARY OF PAH VAPOR PHASE AND ARTIFACT LEVELS (SUMMER DATA)

Chemical	Ranges		Median	
	Vapor	Artifact	Vapor	Artifact
Phenanthrene	22-78	22-70	39	60
Anthracene	4-58	34-92	26	71
Fluoranthene	25-56	38-65	32	48
Pyrene	4-72	22-83	43	47
Cyclopenta(c,d)-pyrene	--(a)	--	--	--
Benzo(a)-anthracene	21-47	11-48	26	13
Chrysene	2-43	20-50	18	38
Benz(e)pyrene	NA	NA	0	0
Benz(a)pyrene	NA	NA	0	0
Indeno(1,2,3-c,d)-pyrene	NA	NA	0	0
Benzo(g,h,i)-perylene	NA	NA	0	0
Coronene	NA	NA	0	0

(a) Apparent concentration too low to yield consistent results.

TABLE 2. SUMMARY OF PAH VAPOR PHASE AND ARTIFACT LEVELS (WINTER DATA)

Chemical	Ranges		Median	
	Vapor	Artifact	Vapor	Artifact
Phenanthrene	35-70	18-62	57	32
Anthracene	43-71	14-28	57	21
Fluoranthene	48-63	7-33	60	15
Pyrene	38-62	14-33	58	25
Cyclopenta(c,d)-pyrene	--(a)	--	--	--
Benzo(a)-anthracene	--(a)	--	--	--
Chrysene	--(a)	--	--	--
Benz(e)pyrene	NA	NA	0	0
Benz(a)pyrene	NA	NA	0	0
Indeno(1,2,3-c,d)-pyrene	NA	NA	0	0
Benzo(g,h,i)-perylene	NA	NA	0	0
Coronene	NA	NA	0	0

(a) Apparent concentration too low to yield consistent results.

TABLE 3. CALCULATED VALUES OF EXCESS ENERGY OF ADSORPTION
(ΔHe in kcal/mole)

Chemical	Run Number					
	624	710	716	718	723	729
Phenanthrene	6.9	5.7	--	6.3	6.5	6.7
Anthracene	6.7	7.7	--	6.8	7.5	9.1
Fluoranthene	5.7	5.3	5.8	5.4	5.7	5.9
Pyrene	5.5	5.5	7.6	6.5	--	--
Benzo(a)-anthracene	--	5.5	5.3	5.8	5.2	6.4
Chrysene	--	3.8	4.0	4.6	5.1	6.2

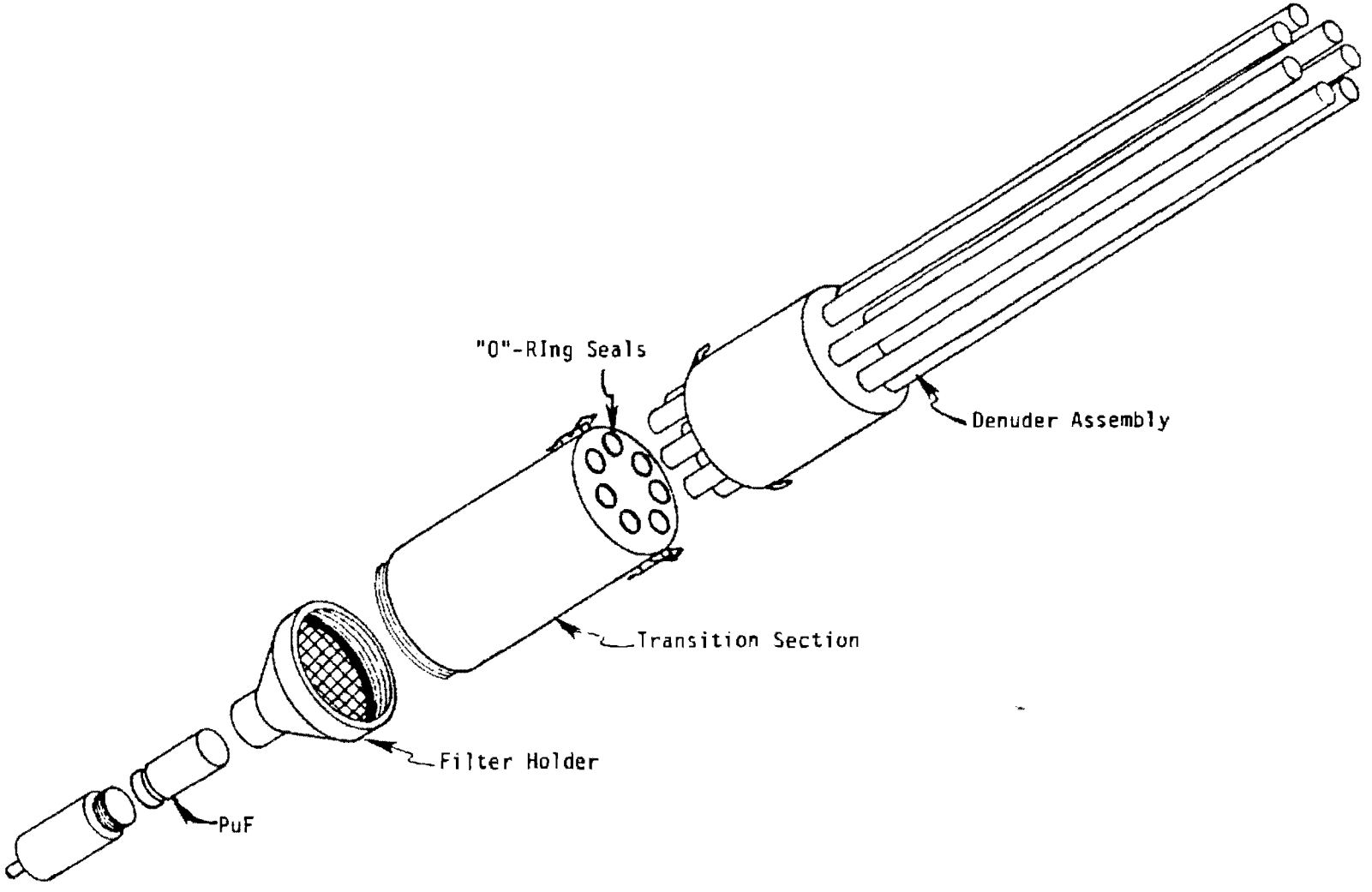

Figure 1. Modified EPA sampler.

EVALUATION OF A DENUDER-BASED GAS/PARTICLE SAMPLER FOR CHLORINATED ORGANIC COMPOUNDS

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Abstract

Semi-volatile organochlorine compounds in classes such as PCBs and some pesticides are perceived to exist in the atmosphere in both the particulate and vapour phase. An accurate knowledge of the distribution between phases is important in defining deposition mechanisms to water bodies and/or human exposure to residues. A prototype sampling system has been developed which separates the vapour fraction of such compounds by an annular denuder prior to particulate collection by filtration. Packed backup adsorbers collect any material that may escape the filter. The denuder has been adapted to a dichotomous sampler and vapour fractions are defined by the net difference in amounts collected by this unit and a conventional filter/adsorber sampler that is operated in parallel. Laboratory evaluations indicated that generated vapours of selected target compounds, such as hexachlorobenzene (HCB) and lindane (γ-HCH), were efficiently retained by the denuder at various temperature and relative humidity conditions. On the basis of field evaluations, sub-ng/m^3 concentrations of these compounds were consistently found at a suburban location near Lake Ontario. Only trace amounts were found in particulate matter collected by either sampler. However, measurements by denuder difference suggested that a large fraction of HCB, and to a lesser extent α- and γ-HCH, was associated with the airborne particulate phase but can be readily volatilized during the filtration process.

Introduction

The occurrence of pesticides, PCBs and numerous other substances in remote water bodies, as well as the Great Lakes, is considered primarily to result from atmospheric transport and deposition[1]. However, input mechanisms are not well defined. The compounds HCB and lindane have been selected for study here since they are regularly detected in surface waters and in rainfall. Although production and fungicidal use of HCB has declined in recent years, it occurs in waste during production of several chemicals. Lindane continues to be used extensively as an insecticide in some countries outside of North America. Both species are perceived to exist in the atmosphere as vapour and as adsorbed components of particulate matter.

Background airborne concentrations are reported to be within a range of 0.03 to 0.23 ng/m^3 for HCB and 0.01 to 0.5 ng/m^3 for lindane and in some urban/rural locales, where measurements have been conducted at a distance from sources, concentrations were only slightly higher[2,3]. Tenax has been found to be a suitable adsorbent for such compounds and was demonstrated to provide better collection efficiency than polyurethane foam, for example[3]. Most investigators have concluded that these compounds occur predominantly in the vapour state but some imply that such conclusions may be influenced by the sampling methods being used since vapour pressures (i.e., ~10^{-5}mm Hg at room temperature) suggest that both vapour and particle phases could exist[4]. Because of the numerous factors that can affect vapour/particle equilibria and the complex nature of airborne particulate matter, it is recognized that currently-available sampling techniques (e.g, conventional filter/adsorber samplers) may not adequately distinguish between phases due to probable disruption of equilibria during filtration. For example, vapour loss from filtered material could occur by volatilization or, conversely, the potential exists for adsorption of gaseous constituents onto particles during sampling.

Improved sampling methods, based on diffusion denuders, have been developed in recent years for partitioning specific inorganic or organic vapours from particulate matter. Although volatilization may still occur, an efficient denuder should limit any tendency for adsorption of vapour onto exposed particles during sampling. A single annular denuder, which resulted in greater collection efficiency for SO_2 than predicted for a cylindrical tube, also has been investigated[5]. This permits the use of smaller configurations with greater flow rates than normally obtained with a series of parallel tubes, thus enhancing the sensitivity of measurements.

The major objective of this study was to develop a denuder sampling method for determining the vapour/particle fraction of high molecular weight organochlorine compounds in ambient air, and to evaluate the sampler performance characteristics under both laboratory and field conditions using the candidate species HCB and lindane.

Sampler Design

The design of the prototype sampling system has been reported earlier[6] and is briefly discussed below. As shown in Figures 1 and

2, the annular denuder, enclosed within an aluminum shell, is attached to a dichotomous sampler (Train A). This unit is operated in parallel with a conventional filter/adsorber reference sampler (Train B). Each unit contains a 10 µm dichotomous sampler inlet to remove large particles and both are operated at a flow rate of 16.7 L/min. for a desired sampling period (i.e., normally 24-hours). In Train A, vapour phase constituents are removed by the denuder that contains six concentric pyrex tubes (60 cm length, 2 mm gaps) in a pyrex holder with adsorbent surfaces coated. Filter-retained species are determined by analysis of the fine and coarse particles collected by filters in the dichotomous sampler and the single filter of the reference sampler. Heat-cleaned glass fibre filters were selected. Packed adsorbers, each containing two sections of Tenax resin, are positioned behind the filters of both units in order to retain constituents that may volatilize from particles during filtration. The sampler was designed to provide the following:

- the constituent vapour fraction, as retained by the denuder, by defining the net difference between the combined filter and backup adsorber analyses of the two trains,

- the fraction associated with particulate matter within a given size range by the combined filter/adsorber analyses of the dichotomous unit, and

- the total airborne concentration of the target compound by combined filter and adsorber analyses of the reference unit.

This sampling system has been evaluated in both laboratory and initial field experiments as discussed in the following sections.

Experiment Methods and Evaluations

Vapour Generation and Measurements

A dynamic vapour generator was fabricated to continuously supply vapours of target compounds at concentrations representative of rural areas using a diffusion tube approach. Crystals of HCB and lindane were placed in separate vessels containing diffuser tubes, allowing the vapour concentration of each compound to be controlled by the dimensions of the diffuser tube, the temperature of the diffuser assembly (maintained at 20°C) and the volumetric flow rate of pre-cleaned dilution air (maintained at a flow greater than 16.7 L/min.). Actual concentrations generated were determined by sub-sampling a portion of the airstream at a manifold using small adsorbent collectors or by simultaneously passing the entire airstream of the vapour generator outlet through an adsorbent cartridge that was extracted and analyzed.

Tenax GC resin was selected for packed-bed adsorbent cartridges as described elsewhere[6]. Cartridges were heat-cleaned between use at 300°C while purging with prepurified nitrogen that was also passed through a gas purification system. Several other precautions were taken (e.g., scrupulous cleaning of cartridge glassware, storage in dedicated coolers at 4°C, etc.) to ensure satisfactory blank levels. Analysis of the target compounds was performed by packed-column gas chromatography

with electron capture detection (GC-ECD). During laboratory evaluations, the adsorbent was extracted by Pesticide Grade hexane and aliquots were injected directly into the GC system.

Denuder Coating Evaluations

Procedures were developed to coat surfaces of denuder tubes and several different types of coatings were evaluated for adsorption properties. After initial screening experiments with single tubes, the most appropriate coating was selected for the annular denuder. This consisted of crushed Tenax (finer than 200 mesh) deposited onto a silicone gum. The coating was applied to the surfaces of the concentric tubes to a length of 55 cm while a portion at the inlet was left uncoated (i.e., where turbulence can be expected). The theoretical denuder length was derived on the basis of calculations reported by Possanzini et al[5]. A visually smooth, thin and even distribution of Tenax was obtained and coating deposits, were estimated to be approximately 0.73 mg/cm^2. In addition, coatings remained intact when subjected to water rinsing and heating to 300°C.

Vapour removal efficiency tests were conducted for 24-hour periods by connecting the denuder and attached backup adsorber to the outlet of the vapour generator such that the entire airstream passed through the denuder. Inlet vapour concentrations were monitored simultaneously by analysis of adsorbers connected at two manifold ports and any breakthrough of the denuder was determined by analysis of the backup adsorber. The denuder was usually heat-cleaned at 300°C between tests. Experiments, in which case the entire vapour generator and sampling devices were installed in a controlled environmental chamber, were conducted at various temperatures and relative humidities.

Potential aerosol losses were evaluated by passing a known concentration of submicron sodium fluoride aerosols through the denuder using a fluid atomization generator. In repeated tests, the salt particles were trapped on preweighed filters located before or after the denuder and any loss was determined by gravimetric difference between the two filters. Fluoride analysis by ion chromatography also was done to confirm the mass balance and detect the presence of aerosol in the coating.

Field Studies

An initial field evaluation of the sampling system was conducted by measuring target compound concentrations in several tests at Sheridan Park in Mississauga (i.e., a rural/suburban location near Lake Ontario). In some cases two denuder units were operated concurrently with the reference sampler and measurements were conducted for 24-hour periods when no rain was predicted. In addition, two samples were collected 1 km downwind of an agricultural chemical producer located adjacent to Lake Ontario that formulates and supplies organochlorine pesticides.

Denuder filters and adsorbent cartridges were heat-cleaned before use and target compounds (i.e., HCB, α and γHCH) in collection media were analyzed by capillary column GC-ECD. During field evaluations, filters and Tenax adsorbers were extracted with hexane and extracts were

preconcentrated and eluted through Florisil as a cleanup step prior to GC injection. In addition, filters were weighed on a microbalance before and after use in order to define any aerosol loss in the denuder.

Results and Discussion

Vapour Generation and Collection

Vapours of HCB and γ-HCH were generated continually at room temperature using the diffusion vapour generator with clean air dilution. Packed Tenax adsorbers were found to efficiently retain the target compounds on the basis of both laboratory vapour generation tests and cartridge spiking. For example, a large fraction of these compounds was retained in the first of two Tenax cartridges positioned in series. In most instances, recovery by hexane extraction was greater than 80% (i.e., with or without extract cleanup and preconcentration) and low blank levels (i.e., <1 ng/cartridge) were generally obtained with the cleaning procedures being utilized. Although visual degradation of Tenax occurred during heating (i.e., yellow colouration), adsorptive performance did not appear to be affected and cartridges were used repeatedly.

The range of concentrations generated for laboratory denuder evaluations throughout the study (low ng/m^3 levels) are summarized in Table 1. Series A was conducted to establish the performance characteristics of the vapour generator and Series B provided vapour concentrations that were considered more representative of the ambient levels to which the denuder would be exposed. In both series, the mean concentrations of target compounds measured were similar to those calculated. Although daily variations were found, the mean concentration of HCB was practically identical to the theoretical amount, while the measured average lindane concentration was approximately 25% higher than expected. When considering the low concentrations involved, this agreement provided confidence in both the vapour generation and measurement methods being used.

Vapour Removal by Denuders

Various types of coatings on single pyrex tube denuders were evaluated by determining the difference between the denuder inlet and outlet vapour concentrations. For example, different types and thicknesses of silicone gums as well as solid adsorbents such as crushed Florisil and Tenax, attached by either a sodium silicate or a silicone gum binder, were tested for a denuder length of 40 cm (i.e., a theoretically suitable length). Vapour breakthrough was observed for some of these coatings. However, efficient removal was demonstrated for the combined coating of crushed Tenax and silicone gum which also furnished other desirable properties (e.g, tight adherence, smooth and even consistency, heat resistance, hydrophobic surface). Hence, this coating was selected for annular denuder performance evaluations.

Results of a test series using the annular denuder are shown in Table 2. Essentially complete vapour removal was demonstrated for the denuder (55 cm length) at the laboratory conditions tested. Efficient removal

was proven for at least a 96-hour collection period and both compounds were efficiently retained on the denuder, as found by passing clean air through the denuder for 24 hours after the 96 hour loading. Performance of the denuder was further assessed by generating vapours over temperature and relative humidity ranges of 3 to 41°C and 10 to 80%, respectively. Although practically complete removal was found at low and room temperature for both low and high humidities, partially reduced collection efficiency was evident for HCB at abnormally high temperatures (i.e., 41°C) and substantial breakthrough of lindane occurred. Hence, somewhat reduced vapour collection efficiency by the denuder may be expected under extremely hot summer conditions.

In addition, aerosol generation tests were conducted by subjecting a horizontally-positioned denuder to high mass loadings of sub-micron NaF aerosols. The mean difference between the filter collections before and after the denuder was found to be only 3%. This indicated effective aerosol penetration and minimum surface impaction. Fluoride analysis in filters and extracts of the coated and uncoated section of the denuder confirmed the mass balance and indicated that most of the small aerosol fraction that was retained was trapped on the coated portion of the denuder. These data, in conjunction with the small diffusion coefficients of fine aerosol, suggest that only a small fraction of aerosol mass can be expected to be retained by the denuder.

Field Evaluations

During field evaluations of the sampling system over a 4 month elapsed time, mean daily temperatures and humidities ranged from 0 to 22°C and 50 to 85%. The overall mean particulate concentration (< 10 μm in size) was 22 $\mu g/m^3$ comprising 60% fine particles (see Table 3). On the basis of comparative loadings between the reference and denuder units (i.e., Trains A and B) and two dichotomous units (i.e., one without a denuder), average data suggest that no substantial particle losses occurred in the denuder. However, on some occasions up to 50% difference was found, especially during low loadings. This may not necessarily be attributed to loss on the denuder coating but could also relate to filter weighing uncertainties and losses in other components of the sampling system. In general, individual differences in particle capture were less than 20% and the average difference was less than 5%.

Total airborne concentrations of three target compounds in Mississauga, as determined with the reference unit, are shown in Table 4. It is evident that concentrations were similar between days and the sub-ng/m^3 levels found were similar to those reported in other studies. No dependence on wind direction was evident. This denotes a ubiquitous, low -level occurrence at this location characteristic of background locales. Lindane concentrations were usually an order of magnitude lower than the other compounds and often around the detection limit of the method (i.e., approximately 0.05 ng/m^3). On the other hand, lindane concentrations were found to be higher than HCB and α-HCH and primarily in the vapour phase when measured downwind of an agricultural chemical formulating plant.

Only small amounts of HCB and sometimes lindane were occasionally

detected directly in filtered particles of either sampling unit and the largest amounts were found in backup Tenax adsorbers of the reference unit. However, all three target compounds (especially HCB) were often found in various amounts in backup adsorbers positioned after filters downstream of the denuder which was previously demonstrated to remove vapours of these compounds at such ambient conditions. It was deduced from these measurements that the target compounds originally attached to airborne particulate matter were subjected to volatilization and blow-off during sampling. Data in Table 4 show the average 'particulate-associated' fractions of these compounds found by 12 denuder-difference measurements and expressed as a percent of the total concentrations. These data suggest that a relatively large fraction of HCB (~60%) was associated with airborne particulate matter at this location. Lesser and more variable amounts of particulate-associated α- and γ-HCH were found by this technique. This corresponds to some degree with the difference in vapour pressures of these compounds since HCB is reported to be at least a factor of two lower than the other compounds. Hence, it appears that considerable disruption of the vapour/particle equilibrium of these compounds can occur by the filtration process.

In six tests, data are available for two denuder units that were operated concurrently with the reference sampler (see Table 5). Similar results of the particulate fractions usually were found for HCB and α-HCH, as derived by denuder difference, while large variations were evident for lindane (i.e., related to measurements near the detection limit of lindane). From a Student "t" test, based on paired replication at the 95% level, no significant difference was found between these denuder measurements. Although one set of high HCB values (i.e., Test 8) cannot be readily explained, the favourable agreement between sets was encouraging. Because denuders were used repeatedly with heat cleaning between tests, the possibility of reduced vapour collection efficiency with denuder age (i.e., used 25 times) was suspected. However, results of three additional vapour removal efficiency tests, that were conducted in the laboratory after field testing, confirmed complete HCB retention by the same denuder. Hence, these subsequent data provided further confidence in the measurement system. The values shown must be regarded as upper limits since complete vapour removal efficiency by the denuder under all field conditions remains as a basic assumption. Nevertheless, the method is considered to provide a more representative indication of the particulate-associated fraction of these compounds in air which otherwise may be underestimated by direct filter analysis only.

In addition, the magnitude of the particulate-associated fraction of HCB when normalized with total particulate loadings was found to increase with decreasing ambient temperature. This could be expected from changes in vapour pressure with temperature as previously reported by Bidleman and Foreman[4] and work of other investigators. More data would be required to accurately define this apparent trend but it is evident that such dependencies are necessary to consider in predicting the predominant physical state of such compounds in a given area.

Conclusions

An alternative sampling method for determining gas/particle distributions of airborne organochlorine compounds has been developed and evaluated. Specific findings of this evaluation are:

- a Tenax-coated annular denuder was demonstrated to efficiently remove HCB and lindane vapours at representative ambient concentrations under most atmospheric conditions. Reduced collection efficiency can be expected at abnormally high temperatures,

- only minimal particle loss occurred in the denuder (<5% on average) which suggests effective vapour/particle separation by the annular design,

- airborne concentrations of HCB and α-HCH (mean 0.3 ng/m^3) and γ-HCH (mean 0.05 ng/m^3) were similar between days and were consistent with other reported values for similar locations. These data suggest a general, low-level background occurrence of such compounds. Lindane concentrations were higher and predominantly in the vapour phase near a suspected source,

- although only small amounts of HCB and lindane were occasionally detected in filtered particulate matter, measurements by denuder difference suggest that these compounds readily volatilize from particles during sampling. The mean particulate-associated fractions that were deduced during the study period were 66% HCB, 22% α-HCH and ~36% γ-HCH. The fraction of HCB associated with particulate matter was found to increase with decreasing ambient temperature. These fractions are regarded as upper limits that require substantiation by further measurements.

Hence, initial field data infer that the relative magnitude of the vapour phase fraction of such compounds may be overestimated when determined by conventional filter/adsorber measurements and that particulate deposition of HCB, for example, may be of somewhat greater significance than generally perceived.

Acknowledgements

The support of Drs. W.M. Strachan and F. Onuska, Canada Centre for Inland Waters is gratefully acknowledged as is the contribution by several staff members of Ontario Research Foundation. The study was conducted with the financial support of Supply and Services Canada (Unsolicited Proposals Program), The Great Lakes Water Quality Program and the Atmospheric Environment Service of Environment Canada.

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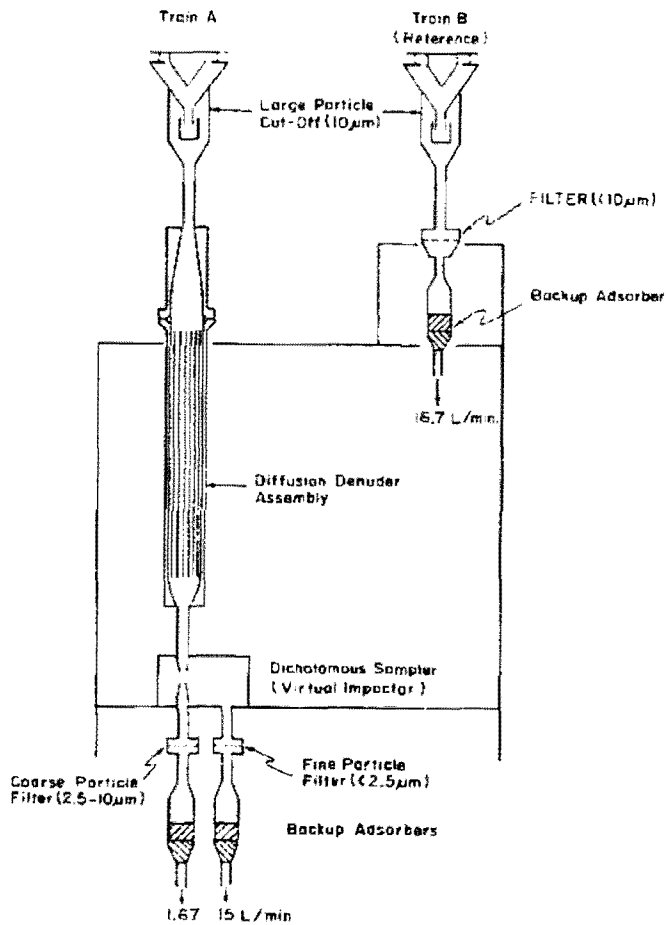

FIGURE 1. SCHEMATIC DIAGRAM OF GAS/PARTICLE FRACTIONATING SAMPLER.

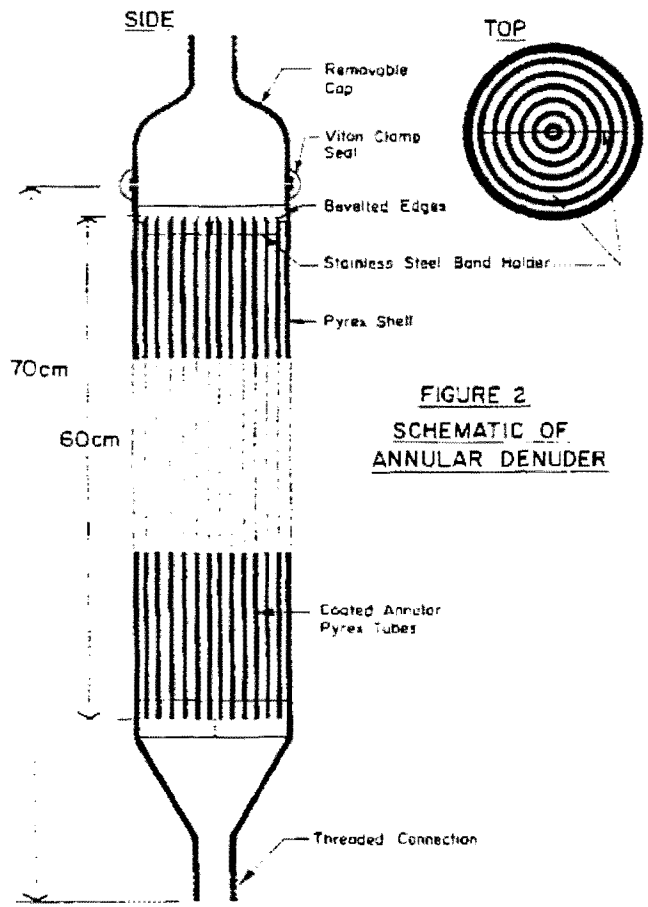

FIGURE 2
SCHEMATIC OF
ANNULAR DENUDER

TABLE 1

Vapour Generator Test Results (ng/m^3)

Test Series	No. of Measurements	Calculated Concentrations HCB	Calculated Concentrations γ-HCH	Measured Concentrations HCB	Measured Concentrations γ-HCH
A	34	2.4	7.5	2.5 (±1.5)	10 (±3.6)
B	43	0.6	0.8	0.7 (±0.4)	1.0 (±0.5)

TABLE 2

Vapour Removal by Denuder - 24 Hour Laboratory Tests

Denuder Coating and Length	No. of Tests	Ave. Removal Eff. (%) HCB	Ave. Removal Eff. (%) γ-HCH
Tenax/Silicone Gum - 40 cm	4	82	69
Silicone Gum - 55 cm	2	56	70
Tenax/Silicone Gum - 55 cm*	7	99	100

* No breakthrough after 96-hour test

TABLE 3

Airborne Particulate Concentrations (μg/m^3)
Reference vs Denuder

Sampler Type	No. of Samples	Fine	Coarse	Total (<10 μm)
Reference	10	-	-	22
Denuder/Dichot.	10	13	8	21
Reference/Dichot.	2	14	11	25
Denuder/Dichot.	2	13	10	23

TABLE 4

Total Airborne Concentrations and the Fraction Associated with Particulate Matter

Sampling Method	No. of Samples	HCB	α-HCH	γ-HCH*
Total Concentration by Reference (ng/m^3)	12	0.3 ±0.2	0.3 ±0.1	0.05 ±0.05
Filter-Retained Fraction by Reference (%)	12	<10	N.D.	N.D.
Particulate Fraction by Denuder Difference (%)	12	66	22	~36

* Near method detection limit [mean near source concentration = 0.5 ng/m^3 (12%)]

TABLE 5

Comparison of Two Denuders Operated Concurrently (Particulate-Associated Fraction Measured by Denuder Difference - %)

Test No.	Denuder	HCB	α-HCH	γ-HCH
8	1	100	N.D.	~33
	2	100	N.D.	~66
9	1	71	14	~33
	2	80	14	~33
10	1	53	12	N.D.
	2	68	3	~67
11	1	65	N.D.	N.D.
	2	70	-	-
12	1	70	22	~82
	2	43	7	N.D.
17	1	57	69	~19
	2	62	40	~ 6

PESTICIDES AND OTHER ORGANICS IN FOG

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ABSTRACT

Sampling and analyzing atmospheric fog is important for several reasons, not the least of which is that it provides an opportunity to examine the vapor-particle-moisture distribution of atmospheric organics in a natural system. We built a vehicle-mounted, high-volume rotating screen collector for collecting liter-sized samples of fog water. When we collected fog, we also collected interstitial gases and unactivated particles using a high-volume dichotomous impactor. These fog water and interstitial air samples allowed us to measure air/water distribution coefficients. From samples collected at Beltsville, Maryland, and at various locations in the Central Valley of California, we have learned that fog contains a variety of pesticides, plasticizers, flame retardants, industrial chemicals, and combustion products. Fog-water concentrations of many of these compounds greatly exceed their concentrations in rain. Measured air/water distributions show marked enrichment into the liquid phase, especially of volatile, insoluble chemicals. The reasons for this enhanced partitioning are not yet known. It is clear, however, that ground contact and sedimentation of fog provides an avenue for ready movement of fog-entrained organics from the atmosphere to the surface.

INTRODUCTION

Pesticides are present in the atmosphere because they drift during application and volatilize following application. These pesticides possess a wide range of physicochemical properties and reactivities, and like other organics are removed from the atmosphere by chemical reaction or by redeposition at the surface. Thus, their atmospheric fate is determined in part by their association with atmospheric moisture. For example, pesticides are found in rain. It is usually assumed, consonant with Henry's Law, that the concentration in rain will be proportional to the concentration in air (of a vapor-phase species). Attempts to verify this hypothesis lead to variable results for a variety of possible reasons, one of which is that air and rain samples collected to make these measurements may represent different air masses. Fog, which is a cloud in contact with the ground, offers a convenient opportunity to measure environmentally-meaningful air/water distribution coefficients, provided appropriate samples of the fog liquid and the associated interstitial air can be obtained.

Fog consists of liquid droplets ranging in size from about 2 μm to 60 μm, with the volume-median-diameter being about 25 μm. These liquid droplets represent only a small portion of the total atmospheric moisture in fog, the larger portion being present as water vapor. Sampling methods to collect fog liquid will therefore be based upon some type of inertial impaction. Several devices for collecting fog liquid have recently been described (1-3). The low liquid water content of fog, typically only 0.1 g m^{-3}, means that a large volume of air must be processed in order to collect enough water to have a realistic chance of isolating and identifying pesticides and other organics in fog. We designed and built a high volume atmospheric fog extractor, shown in Figure 1, that depends upon inertial impaction of fog droplets upon rotating stainless steel screens, and can process more than 4,000 m^3 hr^{-1}. Laboratory tests have shown that this device is more than 99% efficient for droplets larger than 4 um, and in actual operation collects between 0.2 to 2.0 L hr^{-1} depending upon the liquid water content of the fog.

Interstitial air was sampled using a high-volume dichotomous sampler. The original sampler has been described in detail (4). We modified the sampler orifices to increase the cutoff diameter up to about 8 μm, and added a sampling train to trap organic vapors. A diagram of this modified sampler is shown in Figure 2. The total system flow rate was about 0.5 m^3 min^{-1}. Ten percent of the flow passed through the second, large orifice and carried fog droplets out of the system. The droplet-free air passed first through a glass fiber (GF) filter to remove unactivated aerosol particles, then through solid adsorbent vapor traps. About 90% of this flow passed through a 7.5-cm diameter x 7.5-cm deep bed of porous polyurethane foam. The remaining 10% passed through a 20 g bed of Chromosorb 102. These air sampling media (GF filter, polyurethane foam, and Chromosorb 102) were extracted in a soxhlet for 6 hr using 1:1 hexane/acetone.

Fog-water samples were filtered through GF filters to remove solid particles, then fortified with 20 g L^{-1} Na_2SO_4 and extracted with dichloromethane as prescribed by a validated multiresidue procedure (5). The filtered solids were soxhlet-extracted for 12 hr in subdued light using dichloromethane.

Concentrated water and air sample extracts were separated into four fractions of increasing solute polarity by normal-phase HPLC using a hexane-to-methyl-t-butyl ether gradient (6). Pesticide components were detected and measured using element-selective gas chromatography: Hall 700A

Electrolytic Conductivity Detector (halogen and nitrogen), Thermionic Selective Detector (nitrogen and phosphorus) and Flame Photometric Detector (phosphorus and sulfur). Positive confirmation was achieved by one or more of the following: quantitative agreement between two element-selective detectors, GC/mass spectrometry, or specific chemical derivatives.

RESULTS

One interesting feature of fog is that, under some circumstances, it may be very acid. The chemistry responsible for acid fog has been thoroughly studied and is now well known (7). In certain regions of the Central Valley of California, fog acidity is reportedly controlled by a precarious balance between sources of acid species ($SO_4^=$ and NO_3^-) and agricultural sources of NH_3 which keeps the pH higher (8). This is especially true for the eastern side of the southern valley, where cattle feedlots are numerous. Consonant with this, we found that fog in this area was much less acid (pH range 5 to 7) than fog at Beltsville, Maryland (pH range 2.5 to 4.5). Representative values are shown in Table I. The acidity of Beltsville fog is caused primarily by sulfuric acid; on most occasions, the $SO_4^=$-to-NO_3^- ratio was greater than 2. The acidity of fog may either directly or indirectly affect the partitioning of atmospheric organics. For example, the uptake of certain N-containing organics may be controlled by acid/base reactions. On the other hand, if changing pH alters the character of surface-active material associated with the aqueous droplet, uptake of even neutral organics may be affected.

Fog also contains atmospheric particulate material. The solid particles, which may have originally been condensation nuclei, or were simply captured subsequent to fog formation, exhibit size ranges and distributions typical of ambient aerosol particles. Both particle concentration and size distribution may change during a fog event, and particle loads as high as 150 mg L^{-1} were observed at Beltsville. The values shown in Table I are more typical. Samples collected in the Central Valley were generally cleaner than those collected at Beltsville, reflecting the small population density, fewer vehicles, and fewer residential heating sources. It is possible that these aerosol particles could be the source of, or be involved in the partitioning of organics in fog, although the data thus far show that pesticide adsorption to these solid particles is small.

A number of organics have been identified in fog. For example, carbonyl compounds, which are ubiquitous products of hydrocarbon oxidation and are readily soluble in water, were reported by Grosjean and Wright (9) to be present in Los Angeles fog at mg L^{-1} levels. Of the carbonyl compounds identified, formaldehyde was the most concentrated, up to 2.3 mg L^{-1}. Hydrometeor scavenging of gas-phase carbonyls is the major source, but particulate carbonyl and droplet-phase oxidation products are other possible sources. The reaction of aldehydes with HSO_3^- to form hydroxyalkylsulfonates could be important in atmospheric water droplets when SO_2 is present (10).

Hydrocarbons and aldehydes are oxidized in the atmosphere to organic acids. Kawamura and Kaplan (11) reported that fog water concentrations of volatile organic acids (C_1 to C_7) were consistently higher than their concentrations in rain, the fog water concentrations being in excess of 100 μM. Nearly all of the volatile acid component was comprised of formic, acetic, and propionic acids. Kawamura, et al. (12), found some twenty dicarboxylic acids in fog, including cis and trans unsaturated, saturated, normal, branched, and aromatic. Oxalic, succinic, and malonic were the dominant diacids. The total dicarboxylic acid concentration in fog was reported to be about 65 μM.

In our fog samples, we have thus far only examined the dichloromethane-extractable neutral organics. Such compounds include a number of well known and widely distributed environmental contaminants. For example, we found a number of phthalate esters, which are used as plasticizers and are ubiquitous environmental contaminants. We also identified tributyl-phosphate (TBP) and 2-ethylhexyl diphenyl phosphate. These may be representative of another group of compounds, the trialkyl, alkylaryl, and triaryl phosphate esters, which are used as flame-retardant plasticizers (13). Compared to phthalate esters, phosphate ester plasticizers are less frequently reported in environmental samples. TBP occurs extensively in fog and rain, especially at Beltsville. The Central Valley samples only occasionally had small amounts of TBP. We found a number of polynuclear aromatic hydrocarbons in the Beltsville fog samples, possibly derived from local wood burning residental heating sources.

Table II reports concentrations of selected pesticides in fog water and interstitial air for the California samples. In January, when these samples were collected, the organophosphorus insecticides, parathion, diazinon, and chlorpyrifos, are used in dormant sprays on fruit trees. DEF is used in the late fall in the extensive southern valley cotton-growing area as a cotton defoliant. Pendimethalin is a dinitroaniline herbicide used to control grasses and certain broadleaf weeds. We also found small amounts of methidathion, malathion, atrazine, and simazine. Fewer pesticides (diazinon, malathion, methyl parathion, atrazine, simazine, alachlor, and metolachlor) were found at Beltsville, reflecting the less diverse agriculture of the area.

Paraoxon forms by oxidation of parathion on dry soil and in air. It is a potent cholinesterase inhibitor and, therefore, toxic. The average concentration in California fog water reported in Table II is dominated by one particularly high value, more than 180 ppb, found in the Lodi sample. Small amounts of the oxygen analogues of methidathion, chlorpyrifos, and diazinon, were also found. It may be that these oxygen analogues form directly in fog water.

Table II shows that the measured distribution of the pesticides between fog water and the interstitial air strongly favored the water phase, and that large aqueous-phase enrichments can occur. These enrichments are defined as the ratio of the concentration in fog water to concentration in air, divided by the ratio of solubility to vapor pressure of the pure chemicals (i.e., the reciprocal of Henry's law coefficient). In other words, an aqueous-phase enrichment of 300 means that there is 300 times more pesticide in the fog-droplet solution than would dissolve in pure water at the same vapor concentration. The organophosphorus insecticides were enriched by factors of several hundred. The less polar, less soluble DEF and pendimethalin were enriched more than 2000-fold. Neglecting the high Lodi value, paraoxon is enriched no more than a factor of 10. The reason for these high aqueous-phase enrichments is not known.

We would note that the pesticides and other neutral organics that we've identified thus far account for well less than 1% of the total dichloromethane-extractable organic matter given in Table I. We would also note that, because of ground contact and the high deposition velocity of fog, most of this organic matter will end up at the surface on soil and vegetation.

ACKNOWLEDGMENTS

The authors thank Mr. Michael McChesney (UC-Davis), and Ms. Anne Lucas and Mr. Pat Freeman (ARS-Beltsville) for their technical assistance. We also thank Dr. Barbara Leonhardt and Mr. Dave DeVilbis (ARS-Beltsville) for mass spectrometric confirmations.

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Table I. AEROSOL PARTICLES, DICHLOROMETHANE-EXTRACTABLE ORGANIC MATTER, AND pH OF SELECTED FOG SAMPLES.

Location	pH	Particle Load	Organic Matter
		$mg\text{-}L^{-1}$	
Corcoran, CA.	6.70	6	7
Parlier, CA.	5.40	15	12
Lodi, CA.	6.05	37	38
Beltsville, MD (A)	3.16	53	0.7
Beltsville, MD (B)	2.51	ND[a]	55
Beltsville, MD (C)	2.42	13	4.5

[a] ND = not determined.

TABLE II. THE CONCENTRATION OF SELECTED PESTICIDES IN FOG WATER AND ASSOCIATED INTERSTITIAL AIR, THEIR MEASURED AIR/WATER DISTRIBUTION COEFFICIENTS, AND THEIR AQUEOUS-PHASE ENRICHMENTS FOR THREE FOG EVENTS IN THE SAN JOAQUIN VALLEY.

Pesticide	Concentration: Fog water ($\mu g\text{-}L^{-1}$)	Concentration: Air ($ng\text{-}m^{-3}$)	Air-to-water Distribution ($\times 10^{-6}$)	Aqueous-Phase Enrichment[a]
Parathion	23.2	4.0	0.24	310
Chlorpyrifos	2.6	6.2	2.5	190
Diazinon	16.8	3.9	0.24	310
Paraoxon[b]	65.0	0.18	0.03	88
DEF	0.52	0.08	0.15	2200
Pendimethalin	2.5	2.1	0.74	2400

[a] Aqueous-phase enrichment is defined in the text.

[b] Paraoxon is the oxygen analogue of parathion. The values given for paraoxon are dominated by a very high concentration ($180 \mu g\text{-}L^{-1}$) found in fog water collected near Lodi, CA. The average for the Corcoran and Parlier samples, was $5.1 \mu g\text{-}L^{-1}$. For these two samples, the average aqueous-phase enrichment was 7.3.

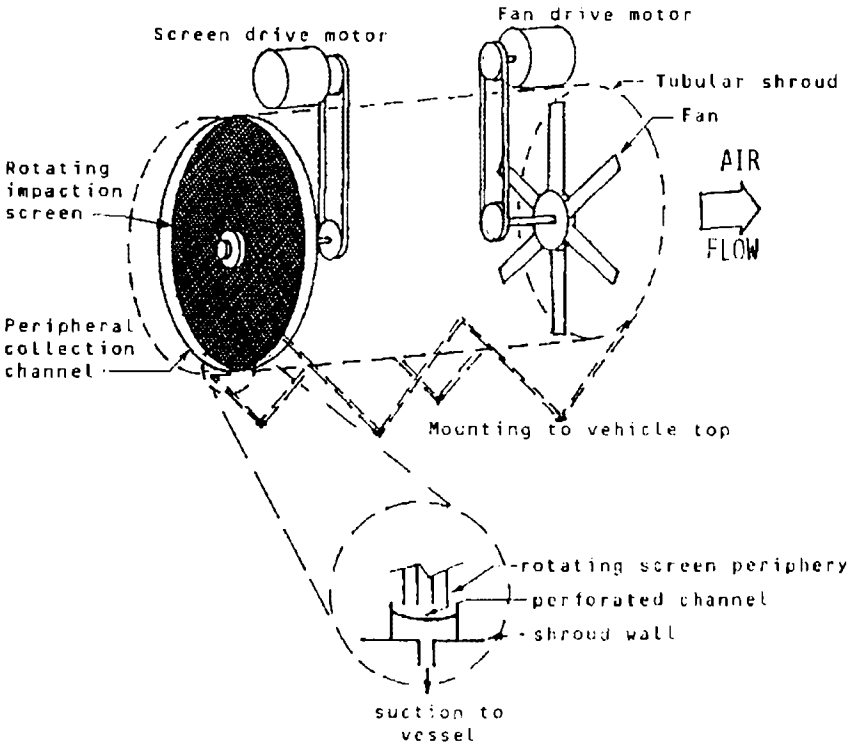

Figure 1. High volume atmospheric fog extractor.

Figure 2. High-volume dichotomous impactor for sampling the interstitial pestide vapors in fog.

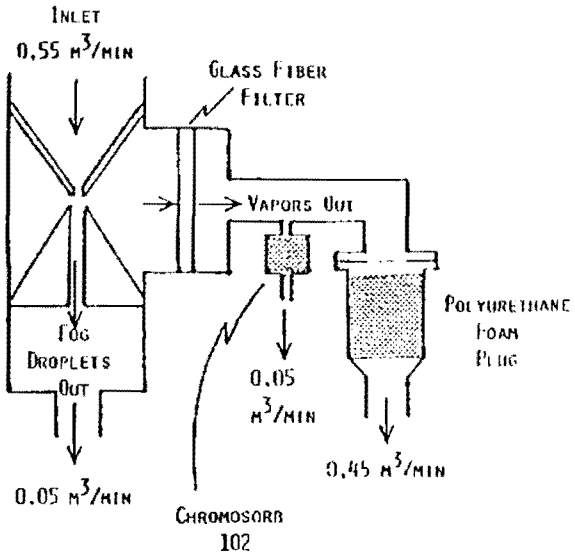

Figure 3. Sampling locations (■) in the Central Valley of California

AMBIENT MONITORING OF SEMIVOLATILE ORGANICS USING HIGH-VOLUME SORBENT SAMPLERS - CRITICAL QUALITY CONTROL FEATURES AND OTHER CONSIDERATIONS IN SAMPLE COLLECTION AND NETWORK DESIGN

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ABSTRACT

Much interest is currently focused on the occurences, distribution, transport and fate of trace concentrations (ng/m^3, pg/m^3) of a wide variety of semivolatile organics in the ambient atmosphere. This is particularly true in the case of chlorinated aromatic species such as PCBs, PCDDs, PCDFs, chlorinated benzenes and others. These sensitivity requisites frequently mandate the use of high-volume sorbent samplers in conjunction with gas chromatography/mass spectrometry and/or selective GC detectors.

The overall complexity of the combined sample collection and analysis scheme mandates the use of a stringent quality assurance/quality control system to govern the collection of reliable monitoring data at trace concentrations (pg/m^3 to ng/m^3). This presentation will provide a comprehensive review of some of the more critical quality control features in the sample collection process as well as other considerations requisite to the design of an air monitoring network for the collection of semivolatile organics in ambient atmospheres. Particular emphasis will be placed on the following features: (1) Sorbent media quality including a review of the most commonly used collection media; actual data on classical media contaminants, what are they and how to control them. (2) Data Precision and how to establish it for the combined sampling and analysis scheme. How to apply it in the evaluation of actual monitoring data. (3) Air matrix/media effects - The effects of physical and chemical properties of the air matrix on the sample collection process will be presented. (4) Ambient background - What is it and how can it be determined? Types of background data will be presented and discussed.

It is intended that this presentation will serve as a guidance document to both existing and potential users of this monitoring technology to familiarize them with some of the more critical ingredients in the network design, sample collection and resultant data evaluation processes.

INTRODUCTION

High-volume air sampling techniques provide an effective means to preconcentrate trace atmospheric contaminants to concentration level commensurate with existing state-of-the-art analytical methodologies. In an historic sense high-volume air sampling techniques have been in use for over 25 years commencing with their use in the determination of total suspended particulates (TSP) to their present use in the collection of trace concentrations of toxic semivolatile organics in ambient air. For many years these techniques were employed primarily in the collection of ambient particulate matter and polycyclic aromatic hydrocarbons known to be associated with ambient particulate matter. Subsequent to these early applications high-volume sampling methods were employed in investigations of the distribution, occurrences, transport and fate of a variety of chlorinated hydrocarbons in the marine atmosphere. While much of these preliminary applications focused on the collection and analysis of the particulate fraction only, more recently, the sample collection system has been modified to contain a solid sorbent cartridge situated downstream of the particulate filter to promote more efficient collection of vapor phase species.

Much interest continues to be focused on the occurrences, distribution, transport and fate of a wide variety of semivolatile organics in the ambient atmosphere. Much of this interest in recent years is spurred by public concerns over fugitive emissions of toxic organics from inactive hazardous waste sites, hazardous waste treatment storage and disposal facilities as well as selected chemical manufacturing and processing facilities. For instance, such requisites are frequently required to monitor fugitive air releases from inactive hazardous waste sites particularly during site remediation activities. Additionally, both recent and pending "air toxics" regulations at the federal and state level have focused on both point source and fugitive releases of these same contaminants. This has been particularly true in the case of chlorinated aromatic species such as PCBs, PCDDS, PCDFS, chlorinated phenols, chlorinated benzenes and others. The enhanced toxicological concerns associated with trace concentrations of these compounds in conjunction with their general tendency to occur in low ppt concentrations in the atmosphere (prompted by low vapor pressures as well as historical usage rates) warrant monitoring requisites in the pg/m^3 to ng/m^3 range. Such sensitivity mandates in turn generally require the routine use of state-of-the-art sample collection and analysis procedures. These requisites for instance have created much interest in the use of high-volume sorbent samplers (e.g., General Metal Works PS-1) typically in conjunction with gas chromatography/mass spectrometry (GC/MS) and/or selective GC detectors (e.g., ECD, FID, PID, NPD, FPD, HECD) to provide data commensurate with the aforementioned sensitivity requirements.

The overall complexity of a combined sample collection and analysis scheme such as this mandates the use of a stringent quality assurance/quality control system to govern the collection of reliable monitoring data at trace concentrations (pg/m^3 to ng/m^3). This presentation will provide a comprehensive review of some of the more critical quality control features in the sample collection process as well as other considerations requisite to the design of an air monitoring network for the collection of semivolatile organics in ambient atmospheres. Particular emphasis will be placed on the following features:

- <u>Sorbent Media Quality</u> - This will include a review of the most commonly used collection media; actual data on classical media contaminants, what are they and how to control them.

- Data Precision - How to establish it for the combined sampling and analysis scheme and how to apply it in the evaluation of actual monitoring data. Data collected under actual field conditions employing collocated samplers will be presented. This data in conjunction with data available in the open literature will be used to develop precision goals for the combined sample collection and analysis scheme.

- Air Matrix/Media Effects - The effects of physical and chemical properties of the air matrix on the sample collection process will be presented. This will include the impact of ambient temperatures on the vapor/particle distribution of semivolatile species as well as a review of potential in-situ chemical reactions arising from interactions between either the sorbent media or sorbed components and reactive atmospheric fixed gases (e.g., NO, NO_2, O_3, etc.).

- Ambient Background - What is it and how can it be determined? Types of background data will be presented and discussed. A case history will be presented to illustrate the role of various types of background measurements in the data evaluation process. Global background data for a number of "classical" chlorinated organics will be presented in an effort to establish "how clean is clean".

- Particle/Vapor Phase Partitioning - The concept of the actual vs the "perceived" distribution will be discussed as well as the environmental factors controlling it (e.g., vapor pressure Vp, particulate loading ($\mu g/m^3$), particle surface chemistry).

It is intended that this presentation will serve as a guidance document to both existing and future users of this monitoring technology so as to familiarize them with some of the more critical ingredients in the network design, sample collection and resultant data evaluation processes. Attendant to these objectives a detailed bibliography for each of the aforementioned topics is provided along with this manuscript to serve as a reference source to potential users and other interested members of the scientific community.

POLYMERIC SORBENTS AS COLLECTION MEDIA

Perhaps the most critical component in the sample collection system is the sorbent cartridge itself, which is typically fitted into the sampler throat downstream of the particulate filter. Some of the more critical considerations in the effective use of sorbents as collection media for semivolatile organics in ambient air include sorbent selection, sorbent collection efficiency and retention efficiency for the components of interest and sorbent quality.

While a wide variety of solid sorbent media are commonly used in ambient air sampling, only a select few of these have been used extensively in high-volume air sampling applications. With the exception of florisil (magnesium silicate) non-polymeric solid sorbents including charcoal, alumina, and silica gel are not commonly used collection media in high-volume air sampling applications.

Conversely, the majority of those commonly used collection media can be categorized as polymeric sorbents. The enhanced sorption capacity of these materials for organics in conjunction with their hydrophobic properties, optimum mesh size, (suitable for passage of large volumes of

ambient air without developing pressure differentials (e.g., "back pressure"), their compatibility with a variety of organic solvent systems as well as their widespread availability and relatively low cost make them ideal candidates for the collection of trace concentrations of semivolatile organics in ambient air. Some of the more common polymeric sorbent products employed in the sample collection process include polyurethane foam (PUF), Amberlite XAD-2, and Tenax®. Despite the aforementioned advantages to the use of polymeric sorbents as sample collection media there are several distinct disadvantages peculiar to the use of these materials. These include "native" sorbent contamination levels and potential contamination attributable to artifact formation during the sample collection process. Perhaps the single most deleterious property associated with the use of polymeric sorbents as collection media is the contamination associated with the product as received from the manufacturer. Users are therefore urged to familiarize themselves with the native sorbent contamination issue. Pertinent subject matter including contaminant chemistry, its sources and how to control it are provided in the discussion to follow.

Sorbent Quality, Contaminant Chemistry and Pretreatment

The majority of synthetic polymers, as received from the manufacturer, can be expected to contain measurable or perhaps significant quantities of one or more of the following types of chemical contamination: (a) residual monomers (b) artifacts of the polymer synthetic process (e.g., starting materials, catalysts, by-products, etc.), (c) chemical preservatives to inhibit chemical or biological degradation. For these reasons, all sorbent materials should undergo rigorous cleanup procedures prior to use. Numerous sorbent preparation procedures are available in the literature capable of reducing contamination to levels compatible with the eventual end use of the sorbent. Users are cautioned, however, that due to the significant contamination often encountered, that any cleanup procedure can at best only minimize these contaminants, often times leaving measurable quantities of organics characteristic of the respective polymer. In addition, while numerous cleanup procedures are available for establishing resin quality, the subsequent storage and handling of these materials can promote reappearance of contamination. Users are, therefore, urged to familiarize themselves with the chemical nature of polymeric sorbent contaminants as well as proper cleanup, storage and handling procedures.

<u>Amberlite XAD Resins</u> - Amberlite® XAD resins for instance are synthetic adsorbents structurally comprised of a styrene-divinylbenzene copolymer. Due to the polymeric production process users are cautioned that these resins do contain significant quantities of preservatives and monomers as received from the manufacturer, Rohm and Haas.[1,2]

Analyses of representative extracts of each of two types of Amberlite® resins (XAD-2 and XAD-4) employing gas chromatography/mass spectrometry (GC/MS) consistently indicate the presence of significant concentrations of a variety of aromatic hydrocarbons including alkylated derivatives of benzene, stryrene, naphthalene and biphenyl. A comprehensive listing of these contaminants including their approximate concentrations in each sorbent matrix is provided in Table I[3]. Note that the contaminants listed in Table I show a marked structural similarity to the characteristic parent structure of the Amberlite® polymer repeating unit as shown in Figure 1. The predominance of benzene, styrene, naphthalene and biphenyl derivatives suggests that the extractable contaminants are either residuals from the resin manufacturing process (e.g., starting materials or secondary by-products) or artifacts

from the degradation of the polymer itself during storage and handling,subsequent to the manufacturing process. In either case prospective resin users are cautioned that XAD resins must undergo rigorous clean up prior to use in actual environmental sampling regimes. The most widely accepted clean up procedures are those employing sequential solvent extraction in a soxhlet apparatus[4,5]. As shown in Figure 2, a continuous extraction scheme employing a sequence of water, methanol and methylene chloride can virtually eliminate chromatographable organic extractables associated with the sorbent matrix. Furthermore, it has been our experience that Amberlite® resin contamination is qualitatively consistent from lot to lot as received from the manufacturer. This is perhaps attributable to the patented synthetic process employed by Rohm and Haas in the manufacture of the Amberlite® resin product line.

Polyurethane Foam - Flexible polyurethane foams (PUF) constitute a generic class of polymeric sorbents that have by far been the most extensively used collection media in high-volume air sampling applications. PUF, unlike other polymeric sorbents, which are generally manufactured by a single patented process, are synthesized via any one of a number of patented processes. The most common pathways employ organic isocyanates (aliphatic or aromatic) and a polyol as starting materials as shown in Figure 3. In addition a number of chemical additives are generally introduced during the synthetic process to impart particular chemical or physical properties to the final foam product as shown in Figure 4[6,7]. (High molecular weight halogenated organics for example are typically added to impart fire retardant properties to the foam)[7]. Some of the more commonly used chemical ingredients are listed in Table II. As a consequence polyurethane foam products can be expected to contain a number of these chemical additives as well as other synthetic artifacts as received from the supplier. Furthermore, the quality of flexible foam products will vary markedly from supplier to supplier as well as from manufacturer to manufacturer.

Polyurethane foams unlike other polymeric sorbents also tend to be a non-homogeneous product containing a number of additives and artifacts in variable quantities from lot to lot. Our experience, however, indicates that these contaminants can be sufficiently reduced to permit trace organic analysis by employing a sequential solvent extraction procedure in conjunction with stringent quality control criteria prior to actual use. This observation is consistent with the experience of other investigators who have used flexible foams extensively in analytical environments.

A reconstructed ion chromatogram (GC/MS) containing extractable contaminents isolated from a typical lot of foam is shown in Figure 5. The qualitative composition of the extractable contaminants were provided by combined gas chromatography/mass spectrometry. Contaminant profiles were identical for each of the two solvent systems employed, methylene chloride (100%) and ethyl ether/hexane (5/95). The contaminant chemistry shown here and again in Figure 6 in several instances is consistent with the manufacturing process data shown earlier in Table II; most notably the presence of residual toluene diisocyanate (starting materials; see Figure 6) an aliphatic amine (possible reaction catalyst) as well as a commercial antioxidant (substituted phenol).

On account of the wide diversity in polyurethane foam (PUF) manufacturing processes and likely contaminant chemistry users are cautioned that sorbent quality control is more critical than with other synthetic polymers such as the aforementioned Amberlite® XAD series. Every effort should be made to procure PUF products consistently from the

same manufacturers, preferably in each instance from the same production lot. Moreover, it is our recommendation that due to inconsistencies in manufacturing practices first-time foam users should solicit the advice of other satisfied and experienced users in the selection of a sorbent supplier.

In any case it is imperative that native sorbent contamination be reduced significantly prior to use of the collection media in actual air sampling schemes. In practice these materials cannot be removed entirely but can only be lowered sufficiently so as to permit subsequent analysis and achieve the requisite detection limits. In all instances, users of polymeric type sorbents are urged to familiarize themselves with sorbent contaminant chemistry in order to recognize spurious data points arising from the use of improperly cleaned or mishandled resins. Furthermore, rigorous quality control measures including field blanks, and sorbent contamination tolerance criteria, should be instituted to both curtail and permit recognition of contamination arising from sorbent use.

It has further been our experience that rigorous sorbent pre-treatment procedures (e.g., soxhlet extraction, thermal desorption) in concert with a well-established quality control program will successfully control potential contamination effects arising from the sample collection media, itself. Furthermore, a well executed quality control program will permit identification of spurious data points attributable to media contamination when and if they do occur.

AIR MATRIX PROPERTIES AND THEIR EFFECTS ON THE SAMPLE COLLECTION PROCESS (MATRIX/MEDIA EFFECTS)

In a similar manner to all other types of air sampling techniques the collection of atmospheric semivolatile organics is very strongly influenced by the physical and chemical properties of the air matrix, itself. A generic summary of some of the more prominent physical and chemical features of the air matrix are provided in Table III. For instance physical properties of the air matrix such as ambient temperature directly influence the partitioning of semivolatile organics between the particle and vapor phases. The discussion to follow will constitute a review of some of the more prominent chemical and physical features of the air matrix and their effects on the sample collection process. Particular attention will be focused on ambient temperature effects, the role of ambient particulate matter, in-situ chemical artifact formation involving reactive atmospheric fixed gases and both sample collection media as well as analytes deposited on the collection media.

Physical Properties of the Air Matrix and Matrix/Media Effects

As shown in Table III prominent physical features of the air matrix include the influence of ambient temperature, particle size, and particle mass loading. Each of these factors provide strong influences not only in the actual distribution and behavior of semivolatile organics in the ambient atmosphere, but also directly effect the "perceived" behavior of these same constituents under the dynamic conditions of high-volume air sampling.

Ambient Temperature Effects. Ambient temperature during the sample collection process is the most significant factor governing the distribution of organics between particulate matter and the corresponding vapor phase. Ambient temperatures almost exclusively govern the actual vapor phase/particulate distribution of organics in ambient air[8]. Furthermore, temperature by virtue of its role in establishing component

vapor pressures (Vp), is the most important factor governing the distribution of semivolatile organics between filter and sorbent under high volume air sampling conditions[8-10].

This same relationship in turn also dictates the collection efficiency and retention or breakthrough volume of solid sorbent type samplers. A number of recently published studies have, in fact, shown that a 5°C rise in ambient temperature effectively reduces the breakthrough capacity (m^3) of semivolatile organics (e.g., PAHs and chlorinated pesticides) on polyurethane foam by 50% under high-volume air sampling conditions[8,9]. Hence, unanticipated rises in temperature during an extended ambient sampling period or complete failure to take the temperature factor into account can significantly reduce the efficiency of a sorbent sampler. The net result will be an undefined loss of analyte(s) and a corresponding reduction in the observed concentrations. As a consequence, it is advisable to calculate the necessary sorbent capacity requirements based on requisite sample volumes prior to the conduct of an actual field sampling program. Sufficient excess breakthrough capacity (e.g., component retention capacity) should be factored into the sampler design so as to accommodate the complete volatility range of the components of interest as well as seasonal and temporal temperature fluctuations peculiar to the sampling location.

Particulate Matter. (Size and Concentration) The physical properties of suspended particulate matter as well can play a significant role in the actual distribution of organics between the vapor and particulate phases. There is for example a direct correlation between the quantity of organics condensed on particulate matter and the particle surface area itself.

For instance, the available surface area in a 500 $\mu g/m^3$ grain loading of 1 μ particles is ten times greater than the surface area available in an identical grain loading of 10 μ particles. Hence, both particle size and mass loading govern directly the particle surface area available for condensation of organics.

Recent work by Yamasaki[10] strongly suggests that the particle/vapor distribution of semivolatile organics in ambient air and in particular polycyclic aromatic hydrocarbons is related to the ambient particle loading or TSP concentration. These findings have been corroborated by You and Bidleman[9] and Keller and Bidleman[8].

Chemical Properties of the Air Matrix and Matrix/Media Effects

The chemical composition of the air matrix can give rise to the following types of chemical interactions: (1) those involving chemical reactions between components of the air matrix and the collection media, (2) those involving chemical reactions between components of the air matrix and analytes sorbed on the collection media. Either of these interactions can in turn result in the one or more of the following:

- Component degradation - reduction in concentration of component of interest.
- Component enhancement - production or net increase in the concentration of a component of interest.
- Component synthesis - production or synthesis of a new compound that is not native to the actual air matrix.

Chemical Reactions Involving the Air Matrix and the Sample Collection Media. By far the majority of combined air matrix/media effects occur via either chemical reactions between air matrix components and the collection media or via chemical reactions between two or more components of the air matrix with the collection media (e.g., filter, sorbent) acting as a reaction substrate.

Based on a combination of our own experience and the experience of others as provided in the open literature the predominant matrix/media chemical interactions are those involving naturally occurring fixed gases such as O_3, NO_2, SO_2, NO and either polymeric sorbents or particulate filters.

General types of reaction pathways include the following: 1) continuous exposure of polymeric sorbents such as Tenax and XAD-2 to ambient concentrations of reactive gases (e.g., O_3, NO_2, Cl_2, NO, SO_2) can result in the formation of oxygenated aromatic derivatives 2) formation of inorganic salts ($SO_4^=$, NO_3^-) from reactions between filter media and reactive air matrix constituents (e.g., HNO_3, SO_2). Further examples of these and other matrix/media chemical interactions are summarized in Table IV.

Chemical Reactions Involving the Air Matrix and Analytes Adsorbed on the Collection Media. The sample collection media (e.g., sorbent, filter) can also act as a substrate promoting chemical reactions between two or more constituents of the air matrix. While this phenomena can perhaps occur on any one of a number of suitable media the majority of the citations in the open literature report on insitu chemical reactions between fixed gases in the air matrix (O_3, NO_2, SO_2 etc.) and semivolatile organics sorbed on particulate matter or the filter media. Generally these reactions involve the nitration of PAH homologues while sorbed on the surface of ambient particulate matter from exposure to atmospheric N_xO_y derivatives. In these instances the resultant products are nitro derivatives of the corresponding PAH isomer. Recently, investigators have also reported on chemical reactions between reactive gases (O_3, Cl_2) and analytes adsorbed directly on solid sorbent collection media. In this case reaction mechanisms are identical to those discussed earlier involving atmospheric gases and the polymeric sorbent itself.

A summary of these and other pertinent references on the subject of chemical reactions between constituents of the air matrix and analytes sorbed on the sample collection media are provided in Tables V and VI.

Photochemical Effects (hv). The influence of sunlight (hv) on the integrity of selected analytes sorbed on ambient particulate or particulate filters is well documented. This phenomena for instance has been shown to promote the insitu degradation of photochemically active species such as polycyclic aromatic hydrocarbons (e.g., B(a)P) while sorbed on ambient particulate matter. Similar behavior may result when other photochemically active species sorbed on solid sorbents or particulate filters are exposed to sunlight or room light. As a consequence, when sampling analytes known to be photochemically active, precautions should be taken to shield sampling media (e.g., particulate filters) from sunlight or room light, particularly during transport, storage and handling procedures.

DATA EVALUATION CRITERIA

Perhaps one of the more critical aspects of any ambient monitoring campaign is the ultimate interpretation and disposition of the data product. This generally consists of a formal evaluation of the available data base as directed by the program objectives in an attempt to ascribe significance to ambient concentrations of semivolatile species. Typically monitoring program are designed and executed to satisfy either of two primary objectives.

- Assess air quality in the site vicinity in an attempt to evaluate health impacts posed by the source. This approach is commonly employed during remedial investigations at hazardous waste sites. This approach generally consists of both off site and perimeter monitoring along upwind and downwind vectors. In these instances measured ambient concentrations particularly along the downwind vectors, are compared to existing health regulatory guidelines or standards. Data may also be evaluated using risk assessment methodologies.

- A purely quantitative assessment of site or facility emissions as a means to estimate the incremental impact of the source on air quality in the site vicinity. This approach generally consists of ambient monitoring along both upwind and downwind vectors. This approach is exclusively quantitative and does not infer comparison of the data product to existing health effects data or ambient air quality guidelines (AALs).

While monitor placement along prevailing wind vectors (e.g., upwind and downwind) serves as the primary means in accomplishing either of the above objectives similar considerations must be offered for the role of existing background concentrations as well as the ultimate precision and accuracy of the monitoring methodology itself. Each of these two types of data are an essential component in ascribing significance to actual ambient measurements collected in the vicinity of the site or facility under investigation. Further discussion on the role that each of these data evaluation tools can play in the design and implementation of ambient air monitoring networks as well as their role in the data product assessment process are provided here.

What is Background?

From an air quality perspective background is a relative term generally considered to be a measure of the existing concentrations of the components of interest at a specific site or within a given geographical region. These concentrations are in turn a sum or aggregate of all source contributions (e.g., area, point, fugitive, etc.) other than that attributable to the source in question. In order to assess the incremental impacts of any area source such as a hazardous waste site on air quality in the site vicinity it is imperative that each of several types of background measurements be evaluated. A summary of these is provided in Table VII. Further discussion pertinent to each of these categories is provided below.

Historical Background Data - Site Specific. This information generally consists of existing air monitoring data specific to the site in question. These data are generally suitable for comparison purposes but due to disparities in seasonal, temporal, and meteorological parameters as well as incongruities in sampling and analysis procedures it is not recommended that existing data bases alone be used to establish background

concentrations at a given site. These data bases, if available, can provide some indication of existing conditions at the site/facility as well as the historical impact of site specific activities on air quality in the site vicinity. If such data is unavailable, a baseline background monitoring program might be useful. Such a program would generally be conducted prior to the commencement of site reclamation activities and would consist of upwind, downwind and on-site monitoring stations. Its purpose would be to establish the existing impact of the site, if any, on air quality in the site vicinity without the perturbations of a site restoration program or facility process operations. The data collected during such a campaign would of course be done using sampling and analysis procedures identical to those anticipated for use during the site/facility investigation.

Historical Data Bases - Geographical Region. In addition to historical air quality data specific to the site itself, some consideration should e given to background data pertinent to the geographical region in which the site is located.

Site-specific and/or Regional Background Data - "Real Time". Naturally the most important background measurements will be those that assess the relative contribution of the source itself to existing air quality in the site vicinity during actual site remedial activities. The location of the background monitors should be selected after consideration of site meteorology and source configuration. Locations predominantly upwind of the site should be identified. These monitors must be well removed from the waste site area sources and in the least likely direction of transport. To account for general variability in wind direction it is recommended that monitors be situated around the entire site perimeter both upwind and downwind of the most likely wind vector(s). Periodic review of the wind direction data will determine which monitor(s) are designated as upwind or background monitors during a particular time period. If significant other point or area sources are in close proximity to the waste site, background monitors may be required to assess the contribution from these other sources, as well. Background monitors may also be placed at off-site rural and urban locations to provide data for eventual comparison to data collected in the site vicinity. Again, it is imperative that each of these monitors be configured in an identical fashion to all others in the network and that they operate for an equivalent time period to all others in the network. All subsequent sample handling and analyses should be done in an identical fashion such that differences in reported concentrations are attributable to actual differences in air concentrations only.

An illustrative example of an actual regional ambient monitoring network incorporating both the site specific and regional background concepts is provided in Figures 7 and 8[21]. As shown 21 high-volume air sampling stations were situated throughout the New Bedford, Mass. metropolitan area on each of two test days in September of 1982 as part of a regional PCB monitoring program. Monitors were situated along upwind and downwind vectors in the vicinity of several known or suspected PCB contaminated area sources, as well as in a number of preselected urban and rural background locations. Note in particular the PCB concentration profiles on each of the two test days in the vicinity of the New Bedford Sewage Sludge Incinerator (POTW), the upper Acushnet/Aerovox region, and along the eastern and western perimeters of the Acushnet River Estuary. Further comparison of these site specific PCB concentration profiles to site specific, regional background, and historical background values are provided in Figure 9. As shown site specific concentrations are again provided for the New Bedford Sewage Sludge Incinerator (POTW) and the

upper Acushnet River/Aerovox Region, and contrasted to regional background values specific to both the New Bedford and Fairhaven metropolitan areas. Historical background data are also provided characteristic of both U.S. and Canadian urban centers.

Historical Data Bases - Other Geographical Regions. These data bases contain concentrations of components of interest collected in other geographical regions such as other urban and rural sites, other hazardous waste sites or "pristine" type areas (e.g., open ocean) where atmospheric concentrations are regarded to be minimum values. These data bases by far contain the majority of the existing ambient air quality data for semivolatile organics on a worldwide basis. Global background data for PCBs[21,22] and some commonly occurring organochlorine pesticides[23-34] are provided in Figures 10 and 11, respectively. As shown, ambient concentration ranges are contrasted for open ocean (marine) atmospheres, as well as coastal/rural and urban locations.

In summary it is advisable that existing background data from other urban and rural sites be considered during the course of any air monitoring campaign. A number of pertinent references on existing air quality data are provided in the bibliography immediately following this manuscript. These references should provide the reader with an overview of typical concentrations for a variety of organics in urban and rural locations worldwide. Perhaps they can supply the framework for further data gathering and eventually provide a working definition of: what is background?

Data Precision Guidelines and Goals

The overall precision and accuracy of the montoring data is an integral component in the data evaluation process. The absence of this information precludes a proper assessment of the monitoring data and accordingly limits the ultimate values of the data package as we cannot ascribe significance to measured ambient concentrations. In fact, despite the present availability of a wide variety of measurement data using high-volume sorbent samplers for monitoring semivolatile organic in ambient air, little formal guidance is provided pertinent to precision and accuracy goals and objectioves goevrning these measurements.

Precision Data - Collocated Field Samplers. A data summary from the available open literature, as defined by collocated high-volume sorbent samplers, is provided in Table VIII. As shown, the highest percent difference (D) in data can be ascribed to those paramaters generally regarded as complex chemical mixtures, such as PCBs. Lewis[35], et al, reports 20 percent D values for collocated PCB samplers, while Billings and Bidleman[36,37] provide values spanning from 12-15% expressed as a % Relative Standard Deviation (RSD) between collocated sampler pairs, Conversely, % RSD values for single analytes, again as reported by Billings and Bidleman, span from 8-10% (RSD) for selected organochlorine pesticides. As shown in Table VIII, sampler precision data spans from 10-40% for the majority of those components listed. While it appears, based on these data, that data precision goals of 10-20% are achievable, we feel that more prudent and pragmatic precision goals such as ± 30-50% are warranted. Again, based upon our own experiences and the experience of other researchers, it is advisable that precision data as much as possible should be established on a project-by-project basis. As discussed herein this is necessitated by the high variability in air matrix properties within an extended sampling period (e.g., ambient temperature) and their marked effects on the sample collection process (e.g., component vapor pressure and sorbent collection

efficiency/"breakthrough"). Additionally due to the non uniformity of sampling and analyses procedures presently in use and the unavailability of formal precision requisites save for a limited number of organochlorine compounds and PAHs, the existing precision data is neither transferable nor adequate for all present and future monitoring needs.

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TABLE I

CHEMICAL CHARACTERIZATION AND QUANTITATION OF ORGANIC CONTAMINANTS EXTRACTED FROM AMBERLITE XAD-RESINS [3]

Compound Name	Concentration[a] µg/g XAD-2	XAD-4
methylbenzene (toluene)	ND	10000
dimethylbenzene isomer	ND	53
diethylbenzene isomer	102	ND
4-ethyl-1,2-dimethylbenzene	D	D
triethylbenzene isomer	D	490
ethenylbenzene (styrene)	19	D
1-ethenyl-4-ethylbenzene	320	5700
1-ethenyl-3-methylbenzene dimethylbenzene	15	1800
1-ethenyl-3-5-dimethylbenzene	D	ND
2-ethenyl-1,3 dimethylbenzene	D	ND
1,4- or 1,3-diethenyl benzene	45	5960
1- or 3-methylindene	67	3470
naphthalene	470	6870
1- or 2-ethylnaphthalene	D	710
1,1'-biphenyl	69	1300
1,1'-biphenyl 12- or 3-methyl	D	90
1,1'-biphenyl, dimethyl isomer	D	ND
benzene, 1,1'-methylene bis	D	ND
benzene, 1,1'-ethylidene bis	130	55
benzene, 1,1'-(1,2-ethenediyl)bis(e)	D	67
ethane, 1,1-bis(p-ethylphenyl)	26	ND

[a]denotes component detected but not quantitated. ND component not identified in lots examined (<5 µg/g).

TABLE II

TYPES OF INGREDIENTS COMMONLY USED IN THE POLYURETHANE FOAM MANUFACTURING INDUSTRY[6,7]

Diisocyanates

2,4-Toluene diisocyanate - TDI
2,6-Toluene diisocyanate - TDI
4,4'-Diphenylmethane diisocyanate - MDI
Hexamethylene diisocyanate - HDI

Blowing Agent (Halogenated alkanes/water)

Trichloro fluoromethane
Methylene chloride

Fire Retardants

Tris(2-chloroethyl) phosphate
Tris(2,3-dibromopropyl) phosphate
Diammonium phosphate
Antimony oxides

Foam Stabilizers/Surface Active Agents

Silicone oils
Silicone-glycol copolymers
Phenol 2,6-bis (1,1-Dimethylethyl)-4-methyl
(Commercial Antioxidant)

Cross-Linking Agent (Triols/polyethers/alkanolamines)

Glycerol
Triethanolamine
pentaerythritol

Catalyst(s) (Tertiary amines)

Triethylendiamine
Triethylamine
Dimethylpiperazine
N,N-Dimethyl cyclohexylamine

TABLE III

CRITICAL PHYSICAL AND CHEMICAL PROPERTIES OF THE AIR MATRIX

Physical Properties

- Ambient temperature
- Particulate mass loading
- Particle size distribution

Chemical Properties

- Fixed Gases - HNO_3, NO_2, SO_2, O_3, H_2O
- Particulate composition - surface chemistry
- Photochemical Intensity (hv)

TABLE IV
CHEMICAL REACTIONS BETWEEN THE AIR MATRIX AND THE SAMPLE COLLECTION MEDIA - SOME PERTINENT EXAMPLES

Air Matrix Type/Composition	Media Type	Summary of Results - Reaction Products	References
Ambient air w/ O_3, NO_2	TENAX-GC (diphenyl phenylene oxide)	Low levels of O_3 and NO_x react w/polymer. Major products formed are benzaldehyde, acetophenone, and phenol. Minor products formed are o-hydroxyacetophenone and ethylene oxide.	[11]
Ambient air w/ SO_2/ SO_3	TENAX-GC	Reaction of polymer with SO_2/SO_3 mixture resulted in the formation of benzaldehyde, acetophenone and phenol.	[11]
Ambient air w/ CL_2	TENAX-GC	Reaction of polymer with Cl_2 resulted in formation of benzaldehyde, acetophenone and phenol.	[11]
Stack gas containing HNO_3, NO, N_2O, and SO_2	TENAX GC	Reaction of polymer with either HNO_3 or NO resulted in the formation of 2,6-diphenyl-p-quinone.	[12,13]
Stack gas containing NO_2, NO (nitric oxide)	XAD-2 (polymer of styrene-divinyl benzene)	Products of reaction between NO and XAD-2 sorbent were as follows: Benzoic acid, ethylbenzaldehyde, dimethyl benzaldehyde, ethylphenylethanone, dimethylbenzoic acid, C_3-benzoic acid, 2-hydroxy -3-nitro-benzoic acid, diethylphthalate, dibutylphthalate and diphenoxybenzene.	[14]
Stack gas containing NO_2 (nitrous oxide)	XAD-2	Products of reaction between NO_2 and XAD-2 sorbent were as follows: benzoic acid, ethylbenzaldehyde, (C_4)-benzene, nitrophenol, ethylbenzoic acid, dinitrotoluene.	[14]
Stack gas containing NO (nitric oxide) or NO_2 (nitrous oxide)	TENAX-GC	Products of reaction between NO or NO_2 and TENAX sorbent were as follows: 2, 6-diphenylquinol, C_3H_7CO or C_5H_{10} adduct to 2, 6-diphenyl quinone, C_3H_7CO or C_5H_{10} adduct to 2,6-diphenylquinol.	[14]
Ambient air containing SO_2 and/or HNO_3	Glass fiber filters, microquartz filters, Teflon (zefluor) filters	Artifact particulate sulfate and nitrate formed on quartz and teflon filters from reaction between filter and atmospheric gases (HNO_3, SO_2).	[15]
Ambient air containing O_3	TENAX (diphenyl phenylene oxide)	Cyclohexadiene-d_8 benzene-d_6 and three isomers of $C_6D_{10}O$ formed from reaction between O_3 and cyclohexene-d_{10}.	[11]
Ambient air containing Cl_2	TENAX	2-chlorocyclohexanol-d_{10} and two isomers of dichlorocyclohexane-d_{10} formed from reaction between Cl_2 and cyclohexene-d_{10}.	[11]
Ambient air containing Cl_2	TENAX	Styrene-d_8 dichloride and two isomers of a-chloro styrene-d_7 formed from reaction between Cl_2 and styrene-d_8.	[11]
Ambient air containing O_3	TENAX	Benzaldehyde-d_6 and benzoic acid-d_6 formed from reaction between O_3 and styrene-d_8.	[11]

TABLE V
CHEMICAL REACTIONS BETWEEN THE AIR MATRIX AND ANALYTES COLLECTED ON THE SAMPLING MEDIA SOME PERTINENT EXAMPLES

Chemical Class Monitored/Affected	Air Matrix Type/Composition	Media Type	Summary of Results - Reaction Products
Benzo(a) pyrene (PAHS)	Ambient air - sunlight	Glass fiber filter	Study suggests that B(a)P decomposes upon continued exposure to sunlight during prolonged sampling periods.
Polycyclic aromatic hydrocarbons (PAHS)	Ambient air containing NO/NO_2	Glass fiber filters with soot particles	Data suggests that nitro-PAH derivatives are formed.
Polycyclic aromatic hydrocarbons (PAHS)	Ambient air containing O_3 (ppm)	Filters with diesel particulate matter	Oxygenated-PAH derivatives are formed.
Polycyclic aromatic hydrocarbons (PAHS)	Ambient air and stack gases containing NO_2 HNO_3 or SO_x	Filters with particulate	No effect from exposure to 200 ppb of O_3. Exposure to 1 ppm NO_2 caused degradation of pyrene, benzo(a) anthracene and benzo(a) pyrene. Products formed were 3-nitropyrene, 10-nitro B(a)A and 6-nitro B(a)P. Exposure to HNO_3 resulted in the formation of same nitro-PAH derivatives.
Polycyclic aromatic hydrocarbons (PAHs)	Ambient air w/ O_3 and NO_2	Filter with particulate	Presence of 1 ppm NO_2 caused degradation of pyrene, benz(a) anthracene and benzo(a) pyrene. Degradation from exposure to O_3 was somewhat limited.

TABLE VI

SELECTED CHEMICAL REACTIONS (IN-SITU) BETWEEN ATMOSPHERIC FIXED GASES AND ANALYTES SORBED ON SUBSTRATE

Reactive Gas	Substrate/Reactant	Product(s)	Reference
N_2O_5	Pyrene	1-NO_2 Pyrene	[16]
	Perylene	3-NO_2 Perylene	
	Naphthalene	1-NO_2 Naphthalene	[17]
NO_2	Perylene	3-NO_2 Perylene	[18]
	Benzo(a)pyrene	1-NO_2 B(a)P	
		3-NO_2 B(a)P	[18]
		6-NO_2 B(a)P	
NO_2,HNO_3	Benzo(a)anthracene	10-NO_2 B(a)A	[19]
	Benzo(a)pyrene	6-NO_2 B(a)P	
O_3	Benzo(a)pyrene	B(a)P 4,5-oxide	[20]

TABLE VII

TYPES OF BACKGROUND DATA

Historical

- Geographical Region
- Site Specific
- Other Sources, Geographical Regions, Global

Actual ("Real Time")

- Site-Specific (Upwind and Off-Site)
- Geographical Region

TABLE VIII

PRECISION DATA - COLLOCATED HIGH VOLUME

SORBENT (PUF) SAMPLERS

Parameter	% D[a]/RSD[b] (N)	Reference
PCBS	20 (7) %D	Lewis, 1985
Aroclor 1016	14 (7) %RSD	Billings and Bidleman, 1980
Aroclor 1254	14 (9) %RSD	Billings and Bidleman, 1980
Aroclor 1016	12 (9) %RSD	Billings and Bidleman, 1983
Aroclor 1254	13 (11) %RSD	Billings and Bidleman, 1983
Aroclor 1252	30 (10) %D	Hunt, 1986
PAHS	24 (6) %D	Hunt, 1983
PAHS	40 (12) %D	Thrane, 1981
Chlordane (Cis and Trans)	10 (12) %RSD	Billings and Bidleman, 1983
HCB	10 (12) %RSD	Billings and Bidleman, 1983
P,P'-DDE	9 (4) %RSD	Billings and Bidleman, 1983
Toxaphene	8 (12) %RSD	Billings and Bidleman, 1983

a % D = % Difference;

$$\frac{X_2 - X_1}{\left(\frac{X_2 + X_1}{2}\right)}$$

b % RSD = Relative Standard Deviation

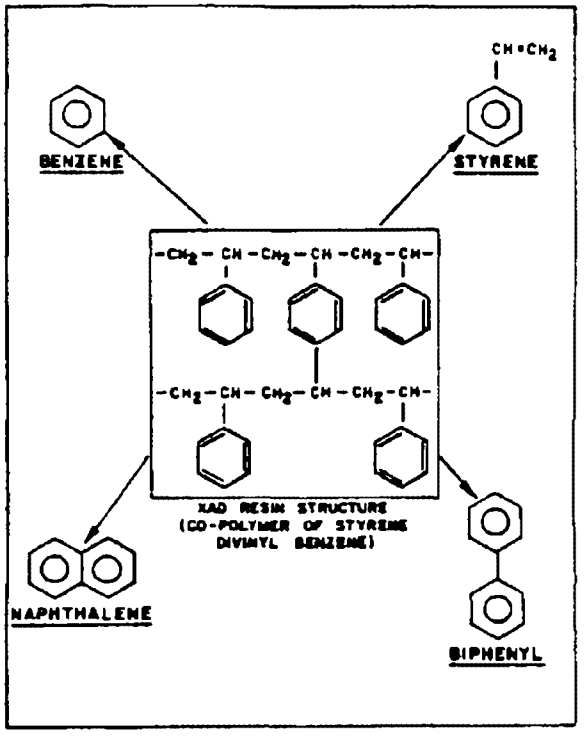

Figure 1 Comparison of XAD-2 Polymer Repeating Unit with Parent Structures of Typical Contaminant Species

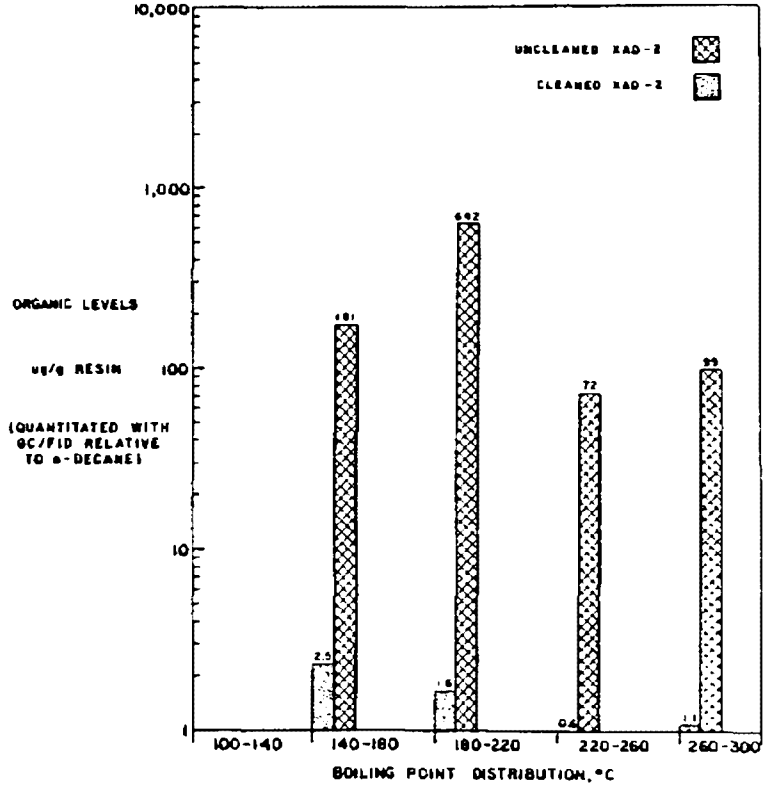

Figure 2 Comparison of Extractable Organic (CH_2Cl_2) Levels in Uncleaned and Cleaned XAD-2 Resin

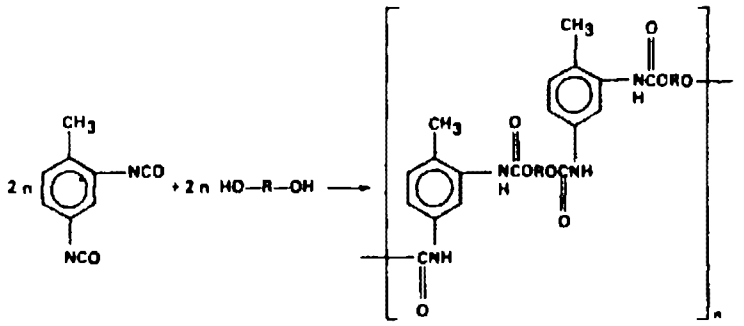

Figure 3 The Synthesis of Polyurethane Foam - Typical Reaction Sequence Involving an Aromatic Isocyanate (TDI) and a Triol

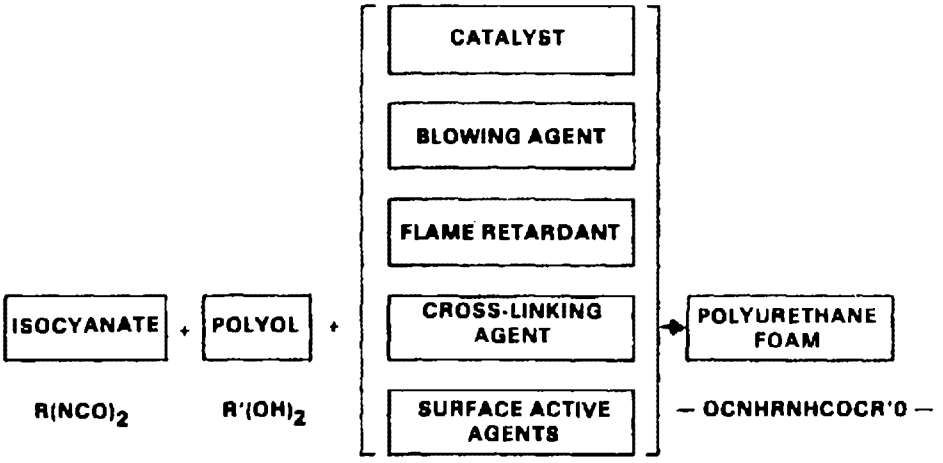

Figure 4 Polyurethane Foam Manufacturing Process - General Synthetic Pathway

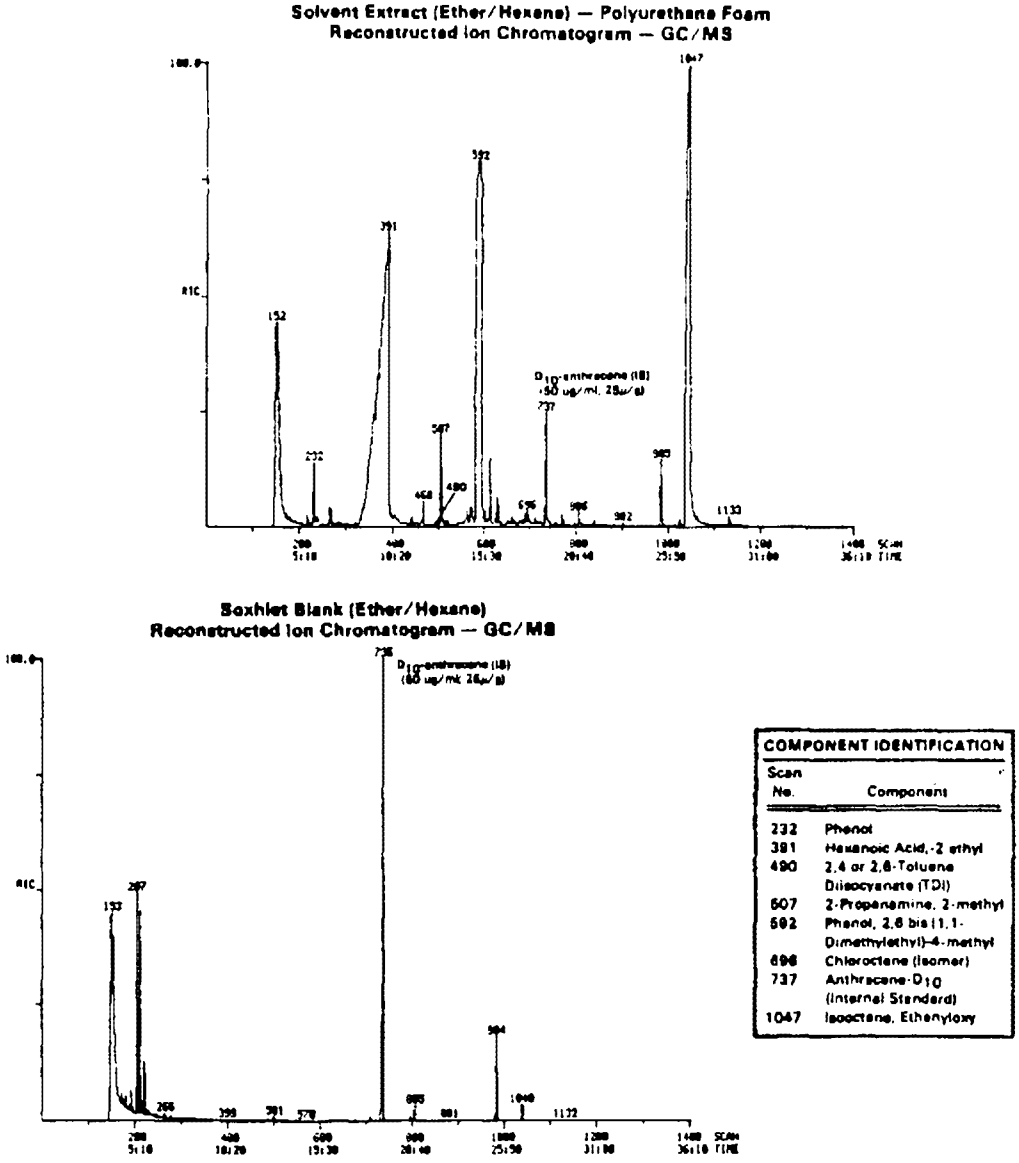

Figure 5 Extractable Organic Profile (Ethyl Ether/Hexane, 5/95) of a Random Lot of Flexible Polyurethane Foam - Reconstructed Ion Chromatograms (GC/MS)

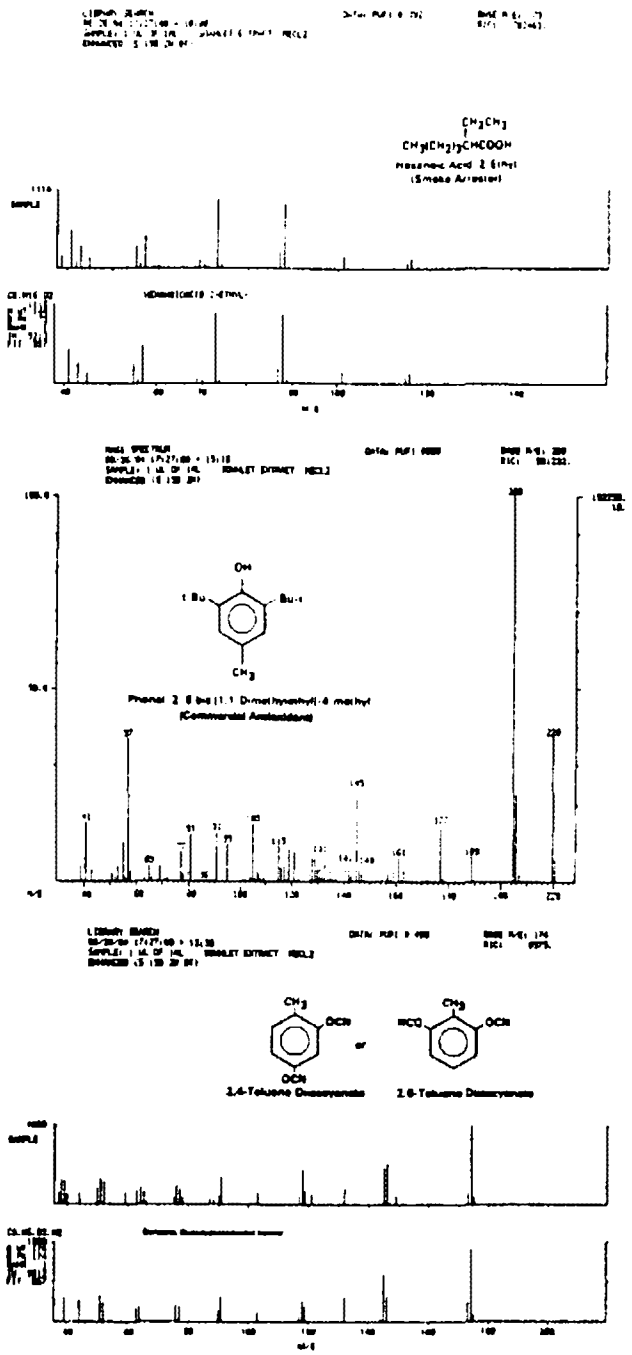

Figure 6 Mass Spectra Data - Selected Organic Extractables (Methylene Chloride) Isolated From a Random Lot of Polyurethane Foam

(Temp = 23°C)

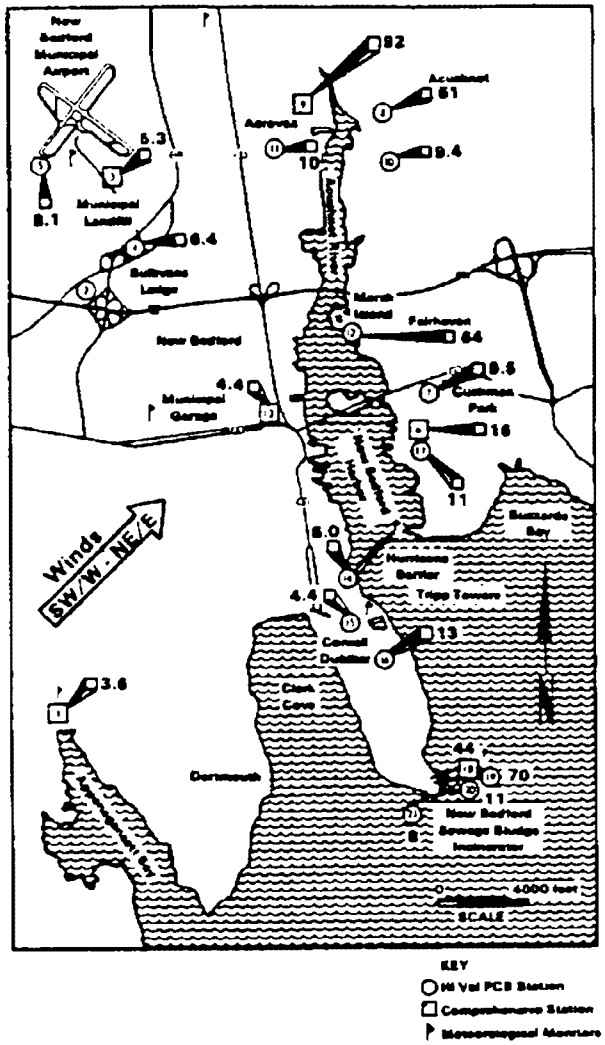

Figure 7 Ambient PCB Concentrations - ng/m^3
New Bedford, Mass Sept. 3, 1982

(Temp = 24°C)

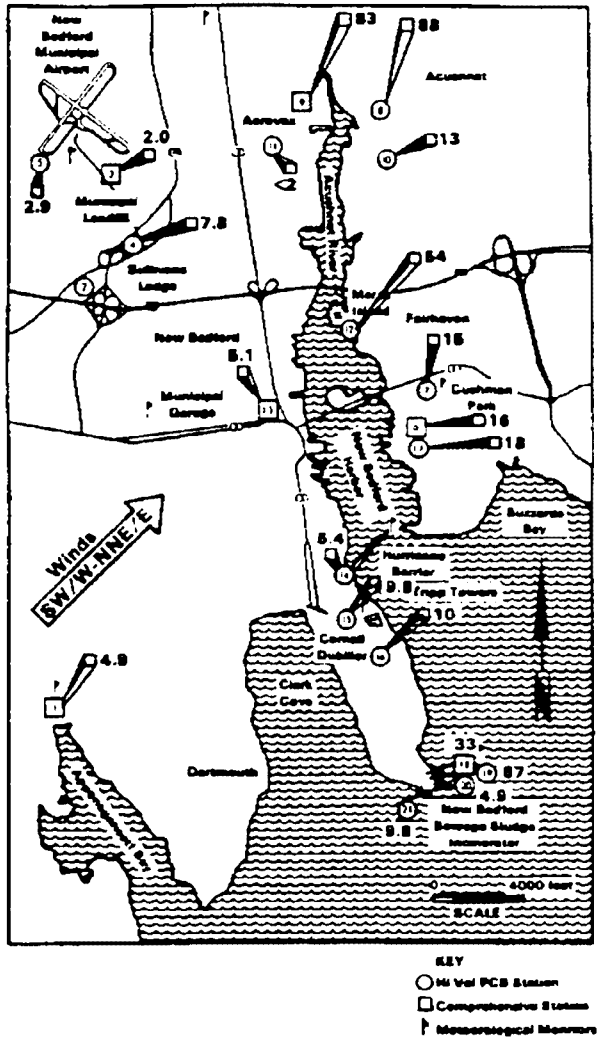

Figure 8 Ambient PCB Concentrations - ng/m^3
New Bedford, Mass Sept. 9, 1982

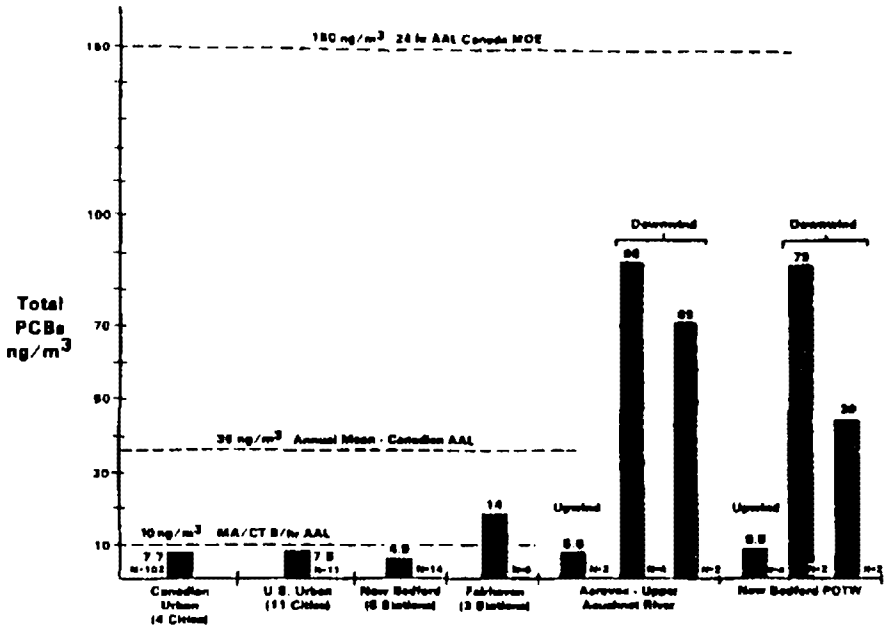

Figure 9 Ambient PCB Concentrations - New Bedford, Mass Sept. 1982 Comparison of Data to Site Specific and Historical Background Values.

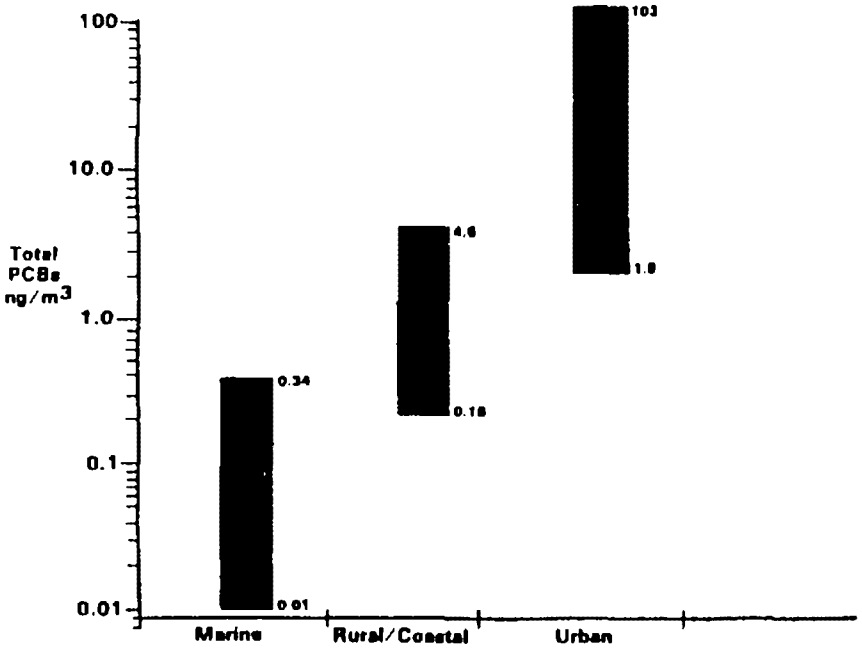

Figure 10 Global Background Data - PCBs

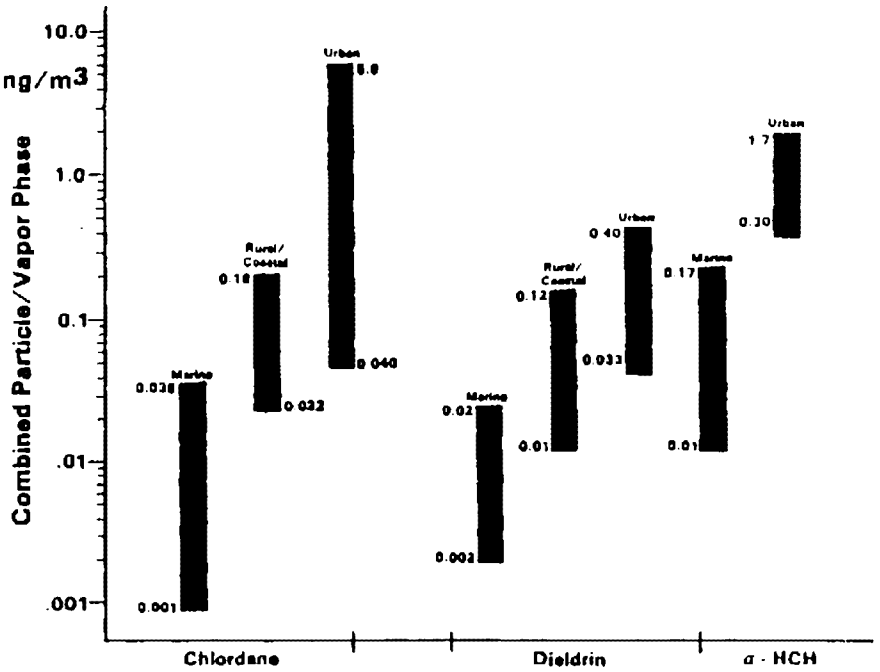

Figure 11 Global Background Data - Selected Organochlorine Pesticides

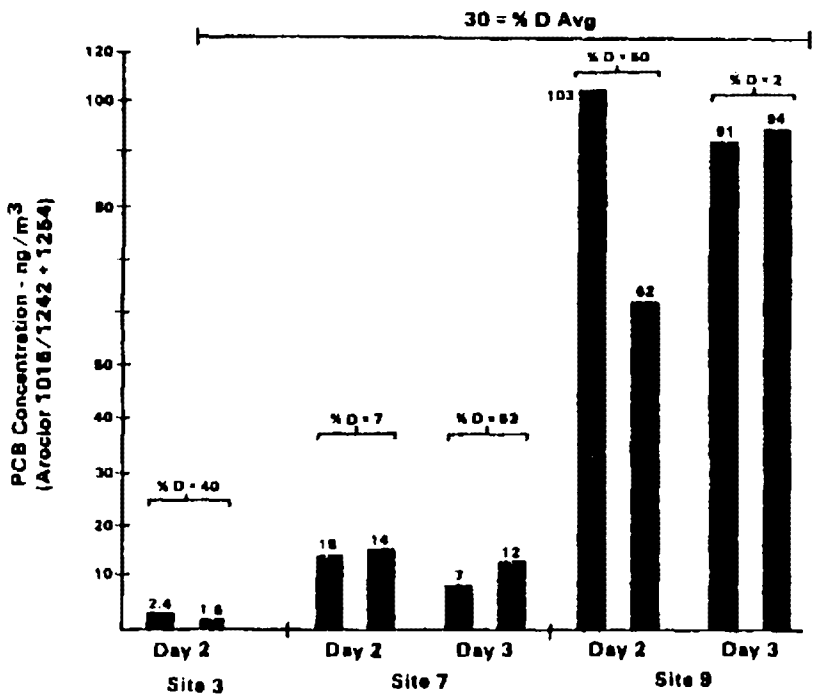

Figure 12 Collocated Sampler Precision Data - Ambient PCB Monitoring New Bedford, Mass (9/82)

ANALYSIS OF POLYURETHANE - FLORISIL CARTRIDGES TO MONITOR POLYCHLORINATED BIPHENYLS IN AMBIENT AIR

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Polychlorinated biphenyls (PCBs) are present in ambient air from several sources. By monitoring air for PCBs, processes which release PCBs into the environment can be detected and controlled. Radian Corporation, in cooperation with the Illinois EPA, has developed a procedure to monitor PCBs in air.

Samples were collected by pumping a measured volume of air through a glass cartridge containing a quartz fiber filter followed by Florisil sandwiched between two polyurethane foam plugs. The cartridges were then spiked with ^{13}C-labeled surrogates of mono-, tetra-, octa-, and deca-chlorobiphenyl. The recovery of these surrogates is a measure of the accuracy of the analysis. The cartridge was then extracted with 60:40 acetone:hexane in a Soxhlet extractor. The extract was cleaned using alumina and mercury and spiked with the internal standard.

The high resolution gas chromatographic-mass spectrometer-single ion monitoring (HRGC-MS-SIM) analysis was done following calibration with a mixture of 10 representative PCB congeners. The responses of the selected congeners were used to represent the respective homolog group. A 3 point calibration was run from 0.1 to 2.5 ug/mL. The instrument detection limit was <100 pg for each PCB congener. Quantitation was based on the major ion of the molecular ion cluster with a second ion of the cluster used for confirmation. The PCBs found in air samples do not commonly have the congener ratio found in Aroclor mixtures and must be quantified by a method which does not require direct comparison with an Aroclor for quantitation.

ANALYSIS OF POLYURETHANE - FLORISIL CARTRIDGES TO MONITOR POLYCHLORINATED BIPHENYLS IN AMBIENT AIR

Introduction

Polychlorinated biphenyls (PCBs) have been regulated in the United States since 1976 by the Toxic Substances Control Act (TSCA) PL 94-469 (U.S. Congress 1976). It was soon recognized that incidentally generated PCBs and weathered PCBs commonly do not have the congener ratio found in any Aroclor or other commercial product and quantitation using a classic Aroclor-based analysis method gives inaccurate results.[1]

The 209 possible PCB congeners are made up of 10 isomer groups or homologs of formula $C_{12}H_{10-n}Cl_n$ where n = 1 to 10. The appeal of GC-MS as a PCB analysis method is that the mass spectrometer can confirm the identity of a compound eluting from a gas chromatograph as a PCB. Quantitation of PCBs by GC-MS is of continuing interest.[2,3] The full potential of the GC-MS method is realized by methods which quantitate PCBs by homolog.[4]

The Radian sampling and analysis protocols were developed from the air monitoring work of Billings and Bidleman,[5,6] the high volume air sampler work of Lewis and coworkers,[7,8] and the GC-MS work of Erickson and coworkers.[9] The EPA extraction method was used as a starting point.[10] The purpose of this work was to validate a method useful for ambient air monitoring studies required by the State of Illinois EPA.

The method validation study was divided into three phases. The first phase established the ability to recover both surrogates and native PCBs in the absence of the sampling cartridge. Modifications in the extraction procedure were incorporated to enhance recoveries of low molecular weight PCBs. These modifications included the use of a micro-Snyder column concentration step and a nitrogen blowdown to final volume.

Phase 2 was designed to evaluate possible matrix effects on the recovery of PCBs. This was accomplished by pre-extraction of sampling cartridges, spiking with appropriate native and labeled materials, and determining method recoveries.

Phase 3 was designed to evaluate the method using an Aroclor PCB mixture comprised of predominantly lower molecular weight isomers (Cl_1 through Cl_4). Aroclor 1232 was chosen for this phase.

This report presents a detailed analytical procedure for use in future studies, as well as a discussion of the results of the validation study.

Experimental Method

Step 1. Extraction and Concentration:

1) Prepare a polyurethane foam-Florisil glass sampling cartridge (PUFP) as described by Lewis and Jackson.[8]

2) Clean the PUFP for 24 hours in a Soxhlet extractor using 500 mL of 60:40 acetone:hexane.

3) Dry the PUFP in a vacuum at room temperature and collect the sample as required using the high volume sampler.[8]

4) Add the surrogate spiking solution to the prepared PUFP and extract with 500 mL of 60:40 acetone:hexane in a Soxhlet extractor.

5) Allow the extract to cool after the extraction is complete. Rinse the condenser with the extraction solvent and drain the Soxhlet apparatus into the collecting round-bottom flask. Filter the extract and dry it by passing it through a 4 inch column of sodium sulfate which has been washed with the extracting solvent. Collect the dried extract in a 500 mL Kuderna-Danish (K-D) flask fitted with a 10 mL graduated concentrator tube. Wash the extraction flask and sodium sulfate column with 100-125 mL of the extracting solvent.

6) Add 1 or 2 clean boiling chips to the K-D flask and attach a three-ball Snyder column. Pre-wet the Snyder by adding about 1 mL of solvent to the top. Place the K-D apparatus on a steam or hot water bath so that the concentrator tube and the entire lower rounded surface of the flask are bathed in hot water or vapor. Adjust the water temperature as required to complete the concentration in 20-30 minutes. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for about 10 minutes.

7) Rinse the K-D apparatus with a small volume of solvent.

8) Remove the concentrator tube from the K-D flask and attach to it a micro Snyder column. Further concentrate the extract, on the hot water bath, to a volume of 2-3 mL.

9) Allow the concentrated extract to cool, remove the micro Snyder column and set aside the extract for subsequent alumina column clean-up.

Step 2. Alumina Column and Mercury Clean-Up:

1) Prepare the chromatographic column as follows: Place a glass wool plug at the bottom of a 10 mm i.d. chromatography column. Add 9 g of Activity Grade IV basic alumina to the column, and gently tap the column to settle the packing. Add 10 mL of hexane to the column and allow the hexane to drain to the level of the packing. Discard this eluate. NOTE: Do not allow the column to dry.

2) Quantitatively transfer the extract from step 1 and 3 x 1 mL of hexane rinses to the top of the alumina. Allow the sample and rinses to drain to the level of the packing. Collect this eluate into a 10 mL graduated concentrator tube.

3) Place an additional 10 mL of hexane onto the column and collect this eluate into the same concentrator tube.

4) Evaporate the combined eluate under a gentle stream of dry nitrogen at room temperature to approximately 10 mL.

5) Remove the Snyder column and add 2-3 drops of elemental mercury to the concentrated extract. Swirl the mixture thoroughly on a Vortex mixer for about 15 seconds.

6) Transfer the organic phase to a 2 mL, conical reaction vial. Evaporate the extract at room temperature under a gentle stream of dry nitrogen to a final volume of 200 uL.

7) Cap the vial securely and store the extract in a refrigerator at 4°C

until GC-MS analysis. NOTE: During all N-evap steps, do not apply heat in an attempt to compensate for cooling caused by evaporation.

Step 3. Analysis by HRGC-MS:

1) PUFP extracts are chromatographed on a high resolution 60 meter DB-5 capillary GC column, and analyzed by MS SIM. During the chromatographic run, the mass spectrometer is used to sequentially monitor the ions as shown in Table 1.

2) PCB isomers are identified using the criteria presented in Table 2. The correct intensity ratio of the two major ions in the molecular isotope cluster and maximization of the two ions within 3 MS-SIM scans is the major homolog identification criteria used. A ±20% range around the theoretical intensity ratio is considered acceptable.

3) Table 3 lists PCB congener standards used for quantitation and for determining spike recoveries. The HRGC-MS-SIM system is calibrated in the range of 0.1-2.5 ng of PCB per GC peak. This calibration takes the form of the measurement of response factors (RFs) for each PCB congener with respect to the chrysene-d_{12} internal standard (phenanthrene-d_{10} or pyrene-d_{10} may also be used). Thus, the PCB congener concentrations measured for spike recoveries are based on the actual response factors for the selected congeners. For quantitiation of samples containing other congeners, the response of the selected congeners is used to represent all congeners of that homolog.

Quality Control (QC) Considerations. The analyst should demonstrate, through the analysis of reagent blanks, that the entire analytical system is free of interferences. The following steps should be incorporated to ensure control of the analysis:

1) All samples and blanks should be spiked with isotopically labeled surrogates prior to extraction. Spiking surrogates are:

   - $^{13}C_6$-4-monochlorobiphenyl,
   - $^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl
   - $^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl, and
   - $^{13}C_{12}$-decachlorobiphenyl.

2) Analysis of extraction duplicates should be performed at the rate of 10%.

3) Spiked blank PUFP should be analyzed at the rate of one per sample set or 5%. These blanks should be spiked with known amounts of Cl_1-Cl_{10} PCB congeners to validate accuracy of the analysis.

4) Reagent blanks should be generated at the rate of one per sample set or 10%. These blanks should be spiked with the isotopically labeled surrogates.

5) The mass spectrometer should initially be tuned to meet instrument PFTBA specifications.

6) The GC-MS system should then be tuned to pass the criteria[11] for 50 ng of DFTPP injected onto the GC. Since all PCB quantitation ions are >180 amu, only those DFTPP ions above 180 amu will be required to pass DFTPP specifications.

7) The GC-MS should then be calibrated by analysis of the PCB-standard (Table 3) at three concentrations. The recommended concentrations are 0.1 ng/ul, 0.5 ng/ul and 2.5 ng/ul. Response factors are generated at all three levels and averaged to yield a single RF value to be used in determining concentration of PCBs.

8) All sample extracts, blanks and standards should be spiked with the internal standards: phenanthrene-d_{10}, chrysene-d_{12} or pyrene-d_{10}. Internal standard spiking should be performed in the range of 100 to 200 ng.

9) An aliquot of the surrogate spiking solution utilized during extraction should be analyzed to determine surrogate RFs. Surrogate recoveries should be measured in each extract. The acceptable range for surrogate recovery is 50-150%.

10) Duplicate injecting of sample extracts should be performed at the rate of one per sample set or 5%.

11) The final analysis of the day should be a 0.5 ng/ul standard. This will allow the analyst to monitor any drift in the analytical system. RFs from this analysis should agree within ±20% from average RFs determined by 3-point calibration.

Results

Analysis of congener spiked samples without alumina clean-up, versus phenanthrene-d_{10}, gave poor chromatography. After basic alumina chromatography, pyrene-d_{10} was added as the internal standard and satisfactory results were obtained. The alumina clean-up was used on subsequent samples. It was also observed that our Finnigan split-splitless capillary injector showed discrimination with mass so these and subsequent samples were analyzed using on-column injection to give a uniform detection limit of <100 pg congener per injection.

PUFP samples were spiked in duplicate with Cl_1 through Cl_{10} PCBs at two levels. The low level spike was 50 ng per congener. The high level spike was 500 ng per congener. The recoveries of the individual congeners ranged from 60 to 100% (Table 4). The carbon-13 surrogate recoveries ranged from 60 to 86% for these samples (Table 5).

The Cl_1 and Cl_2 PCB recoveries suggest there is some of loss occurring during some phase of the analysis. Recovery of these two compounds averaged 65%. Caution should be exercised when concentrating any extract for PCB analysis due to the greater volatility of the Cl_1 and Cl_2 homologs. All other analytes were recovered at >80% showing good accuracy of the method. The mean standard deviation was 6.1%, showing excellent precision of the method.

Two PUFP were selected for duplicate spiking with Aroclor 1232. The Aroclor 1232 spike consisted of 15 ul of 50 ppm stock onto the PUFP. This resulted in a nominal concentration of 750 ng Aroclor per sample. However, the bias in the HRGC-MS analysis of the Aroclor 1232 standard solution resulted in a nominal measured concentration of 440 ng per PUFP. Since the standard may contain impurities and since the concentration of those congeners present at below the detection limit cannot be determined, this low bias is not surprising. Another factor which can influence the concentration found is the representativeness of the response factor of the congener selected to represent the

homolog group. The standard value of 440 ng per PUFP was used to calculate percent recoveries of the two samples. Aroclor 1232 homolog recoveries ranged from 57-95% (Table 6). Recovery of the monochlorobiphenyl species averaged 59%, suggesting some loss of these compounds during the concentration phase. The precision and accuracy shown by the duplicate Aroclor analysis is comparable to the congener spike study.

All samples were spiked prior to extraction with the following isotopically labeled surrogates:

- $^{13}C_6$-4-monochlorobiphenyl at 100 ng,
- $^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl at 250 ng,
- $^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl at 400 ng, and
- $^{13}C_{12}$-decachlorobiphenyl at 500 ng.

Overall surrogate recoveries ranged from 60-95%. These results are found in Table 7. Recovery of the $^{13}C_6$-4-monochlorobiphenyl surrogate averaged 66%. This supports the previous results from the Aroclor 1232 and Cl_1-Cl_{10} spiked samples, that a loss of the lesser chlorinated (Cl_1 and Cl_2) species is occurring.

Conclusions

The extraction and analytical procedures described give precise and accurate PCB analyses. The recoveries of low molecular weight PCBs (the mono, and dichloroisomers) are susceptible to losses at the concentration steps, and care is needed to ensure that the recovery of these isomers is maximized. The use of a labeled chlorobiphenyl surrogates is required to monitor losses as previously described by Erickson and Stanley.[9]

Acknowledgments

We thank Robert Hutton and Jim Buckert of the State of Illinois EPA and Mitchell Erickson of Midwest Research Institute for very helpful advice in the method development.

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TABLE 1. IONS MONITORED IN SEQUENTIAL FASHION FOR PCB ANALYSIS

Group 1 Start/Stop(1) 12.0 /23.0		Group 2 Start/Stop 23.0 /25.0		Group 3 Start/Stop 25.0 /27.0		Group 4 Start/Stop 27.0 /35.0	
M/Z	Dwell(2)	M/Z	Dwell	M/Z	Dwell	M/Z	Dwell
188.0	25	208.0	25	212.0	25	236.0	25
190.0	25	212.0	25	290.0	25	240.0	25
194.0	25	256.0	25	292.0	25	360.0	25
196.0	25	258.0	25	304.0	25	394.0	25
212.0	25	260.0	25	324.0	25	396.0	25
222.0	25	290.0	25	326.0	25	398.0	25
224.0	25	292.0	25	328.0	25	428.0	25
226.0	25	294.0	25	360.0	25	430.0	25
256.0	25	302.0	25	362.0	25	432.0	25
258.0	25	304.0	25	364.0	25	440.0	25
260.0	25	324.0	25	394.0	25	442.0	25
290.0	25	326.0	25	396.0	25	462.0	25
292.0	25	328.0	25	398.0	25	464.0	25
294.0	25	360.0	25	428.0	25	466.0	25
302.0	25	362.0	25	430.0	25	495.8	25
304.0	25	364.0	25	432.0	25	497.0	25
306.0	25	394.0	25	440.0	25	499.8	25
324.0	25	396.0	25	442.0	25	507.8	25
326.0	25	398.0	25	462.0	25	509.8	25

(1) Minutes.
(2) Dwell time in milliseconds.

TABLE 2. PCB IDENTIFCATION CRITERIA

Homolog	Expected RT Range (min)	Major Molecular Isotope Ions (1) and Relative Intensities (2)		Ion Intensity Criteria	
		M1 (100%) (4)	M2 (RI%)	Theoretical Ratio of M1/M2 Intensities	Acceptable Range (3)
Cl_1	16-19	188 (100)	190 (33)	3.0	2.4- 3.6
Cl_2	18-22	222 (100)	224 (66)	1.5	1.2- 1.8
Cl_3	19-23	256 (100)	258 (99)	1.0	0.8- 1.2
Cl_4	20-25	292 (100)	290 (77)	1.3	1.0- 1.6
Cl_5	21-26	326 (100)	328 (66)	1.5	1.2- 1.8
Cl_6	23-27	360 (100)	362 (82)	1.2	0.98-1.5
Cl_7	25-30	394 (100)	396 (98)	1.0	0.8- 1.2
Cl_8	27-32	430 (100)	428 (87)	1.1	0.9- 1.4
Cl_9	28-33	464 (100)	462 (76)	1.3	1.0- 1.6
Cl_{10}	30-33	498 (100)	500 (87)	1.2	0.9- 1.3

(1) These ions must coelute within the same 2-3 MS cycles, i.e., 1-2 seconds.
(2) Based on chlorine isotope theoretical abundance.
(3) ±20% around expected ratio.

TABLE 3. PCB STANDARD MIXTURE

Congener	(IUPAC Number)[12]
2-Chlorobiphenyl	(1)
3,3'-Dichlorobiphenyl	(11)
2,4,5-Trichlorobiphenyl	(29)
2,2',4,4'-Tetrachlorobiphenyl	(47)
2,3'4,5',6-Pentachlorobiphenyl	(121)
2,2',3,3',6,6'-Hexachlorobiphenyl	(136)
2,2',3,4,5,5',6-Heptachlorobiphenyl	(185)
2,2',3,3',4,4',5,5'-Octachlorobiphenyl	(194)
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	(206)
2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	(209)

TABLE 4. PCB CONGENER SPIKE RECOVERY STUDY(1)

Sample -	Low Spike PUFP I(2) ng	(%)	Low Spike PUFP II(2) ng	(%)	High Spike PUFP I(3) ng	(%)	High Spike PUFP II(3) ng	(%)	PUFP Blank ng	Average Recoveries avg.	std. dev
Congeners											
Cl_1	34	(68)	30	(60)	320	(64)	300	(60)	<10 each	63	±4
Cl_2	38	(76)	36	(72)	360	(72)	380	(76)	<10 each	74	±2
Cl_3	46	(92)	38	(76)	400	(80)	420	(84)	<10 each	83	7
Cl_4	44	(88)	40	(80)	380	(76)	420	(84)	<10 each	82	5
Cl_5	42	(84)	32	(64)	440	(88)	440	(88)	<10 each	81	±11
Cl_6	46	(92)	46	(92)	380	(76)	440	(88)	<10 each	87	±8
Cl_7	44	(88)	46	(92)	400	(80)	440	(88)	<10 each	87	±5
Cl_8	50	(100)	48	(96)	380	(76)	460	(92)	<10 each	91	±11
Cl_9	46	(92)	44	(88)	420	(84)	480	(96)	<10 each	90	±5
Cl_{10}	42	(84)	42	(84)	400	(80)	440	(88)	<10 each	84	±3

(1)All values in this table were calculated using average response factors with pyrene-d_{10} as an internal standard.
(2)All congeners have a nominal concentration of 50 ng each. Recoveries based upon this value.
(3)All congeners have a nominal concentration of 500 ng each. Recoveries based upon this value.

TABLE 5. CARBON-13 SURROGATE RECOVERIES

Carbon-13 Congeners	Low Spike PUFP I	Low Spike PUFP II	High Spike PUFP I	High Spike PUFP II	PUFP Blank
Cl_1	67%	60%	67%	63%	66%
Cl_4	85%	85%	74%	85%	84%
Cl_8	85%	79%	74%	84%	85%
Cl_{10}	86%	79%	65%	86%	83%

TABLE 6. AROCLOR 1232 DUPLICATE SPIKE RECOVERY DATA

Congeners	Aroclor Spike Std. ng	(%)	Aroclor Spike PUFP I(1) ng	(%)	Aroclor Spike PUFP II(1) ng	(%)
Cl_1	166	--	100	(60)	94	(57)
Cl_2	76	--	64	(84)	58	(74)
Cl_3	104	--	102	(98)	80	(78)
Cl_4	94	--	90	(95)	74	(78)
Cl_6	<10 each		<10 each		<10 each	
Cl_7	<10 each		<10 each		<10 each	
Cl_8	<10 each		<10 each		<10 each	
Cl_9	<10 each		<10 each		<10 each	
Cl_{10}	<10 each		<10 each		<10 each	

(1) Percent recoveries are versus the Aroclor 1232 spike standard value.

TABLE 7. SURROGATE RECOVERIES IN DUPLICATE AROCLOR 1232 SPIKED SAMPLES

Carbon-13 Congeners	Aroclor Spike PUFP I	Aroclor Spike PUFP II
Cl_1	70%	64%
Cl_4	93%	80%
Cl_8	95%	90%
Cl_{10}	87%	87%

EVALUATION OF THE EPA HIGH-VOLUME AIR SAMPLER FOR COLLECTION AND RETENTION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS

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The High-Volume Air Sampler, developed by the U.S. Environmental Protection Agency for sampling of semivolatile organic compounds, was evaluated to determine its efficiency for collection of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). The evaluation was carried out by generating air streams containing known concentrations of two PCDD/PCDF isomers which were sampled over a 24 hour period. The desorption of PCDD/PCDF isomers from spiked particulate matter and the retention efficiencies of six selected PCDD/PCDF isomers spiked onto PUF and silica gel prior to sampling were also determined.

The sampler exhibited good collection efficiencies for the PCDD/PCDF isomers spiked into the gas stream. The majority of the tetrachlorinated isomer spike was found on the PUF cartridge, while the octachlorinated isomer spike was collected on the filter. When the two isomers were spiked directly onto particulate matter, the same trend was observed. The tetrachlorinated isomer was desorbed from the filter during sampling and collected on the PUF cartridge, while the octachlorinated isomer remained on the filter. The six PCDD/PCDF isomers spiked onto either the filter or the adsorbent cartridge prior to sampling were also retained in the sampler with their distribution being determined by their relative volatility.

EVALUATION OF THE EPA HIGH-VOLUME AIR SAMPLER FOR COLLECTION AND RETENTION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS

INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are two classes of tricyclic compounds that are often found in the environment[1]. Certain isomers, those substituted in the 2, 3, 7, and 8 positions, are toxic at the parts-per-trillion (ppt) level in some animal species. The LD_{50} level for 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8TCDD), for example, is approximately 600 ppt in the male Guinea pig.[2,3]

A major source of PCDD and PCDF has been commercial processes that involved the production or use of chlorinated phenols (CP) or polychlorinated biphenyls (PCB). During the production of CP and PCB, trace quantities of PCDD or PCDF were often formed as unwanted side products. These low levels of PCDD and/or PCDF often entered the environment through commercial products such as herbicides, pesticides, or electrical utility dielectrics.[4,5] Recent production techniques and restrictions on the use of PCB have greatly reduced these sources of contamination.

Combustion sources have also been shown to emit PCDD and PCDF into the environment. Precursor compounds, including CP and PCB, are readily converted to PCDD and PCDF during combustion which are subsequently released into the atmosphere. Incinerators which burn municipal and industrial wastes are particularly rich in precursor compounds which produce a variety of PCDD and PCDF isomers.[6] Although it is probable that the majority of the PCDD and PCDF emissions come from a limited class of precursor compounds, there is evidence that most combustion involving chlorine will produce PCDD and PCDF.[7]

Due to the toxicity[2], mutagenicity[8], and carcinogenicity[9] of selected PCDD and PCDF isomers, their detection and quantification in the environment is of major concern. In order to assess ambient air levels of these compounds, it is essential that an accurate, reproducible, and efficient sampling technique be available. The goal of this work was to evaluate the EPA High-Volume Air Sampler[10] for collection of PCDD and PCDF isomers.

Three types of experiments were carried out during the evaluation of the EPA High-Volume Air Sampler. The first set of experiments determined the ability of the sampler to collect PCDD and PCDF isomers that had been spiked into the ambient air stream entering the sampler. The second set of experiments measured to desorption of PCDD and PCDF isomers from spiked particulate matter that occurred during sampling. The third set of experiments measured the retention efficiencies for PCDD and PCDF isomers that had been spiked into the sampler prior to sampling.

EXPERIMENTAL METHODS

Gas Phase Collection Experiments

The gas phase collection efficiency of the sampler was measured by sampling ambient air streams containing known concentrations of 1,2,3,4-tetrachlorodibenzo-p-dioxin (1,2,3,4-TCDD) and of octachlorodibenzofuran (OCDF).

Three concentrations were used during the evaluation. The spiked gas streams were generated by vaporizing dilute hexane solutions of the two isomers using the apparatus shown in Figure 1. The spiking system consisted of a micrometering pump and a vaporizing assembly connected by a fused silica capillary tube. The vaporizer was constructed from a six-inch length of quartz capillary tubing which was resistively heated at the end by a coil of nichrome wire. During operation the spiking solution was introduced at a flow rate of 1 µl/min with the vaporizer tip being maintained at 70°C.

The experimental setup for the collection efficiency experiments is shown in Figure 2. A carbon filter was used to purify the air entering the spiking apparatus to assure that ambient levels of PCDD/PCDF would not interfere with the experiments. A critical orifice was interfaced to the inlet to allow the flow to be monitored. The flow rates during the sampling sessions were typically between 5-6 ft^3 (0.14-0.17 m^3/min). The three gas phase concentrations of the PCDD/PCDF isomers were approximately 0.8 ng/m^3, 0.08 ng/m^3, and 0.008 ng/m^3.

Particulate Desorption Experiments

An estimate of the desorption of PCDD/PCDF isomers from the filter during sampling was made by spiking known quantities of 1,2,3,4-TCDD and OCDF onto particulate matter loaded filters which were then used to sample approximately 325 M^3 of clean ambient air. The experimental setup is shown in Figure 3. After sampling, the filters and adsorbent cartridges were analyzed and the distribution of the PCDD/PCDF isomers in the sampler was calculated. The filters were loaded with approximately 9 mg of particulate matter prior to spiking by sampling ambient air.

Two spiking levels were used for these experiments. The high level spike was 12 ng of 1,2,3,4-TCDD and 27 ng of OCDF, while the low level spike was 1.6 ng of 1,2,3,4-TCDD and 2.2 ng of OCDF. Four filters were prepared at each spike level. Two of the filters, referred to as dynamic filters, were used for the desorption experiments. The other two filters, referred to as the static filters, were held during the sampling period and then extracted along with the dynamic filters. The static filters were used to determine the extraction efficiency of the PCDD/PCDF isomers from the particulate matter.

PUF and Silica Gel Retention Experiments

The ability of the sampler to retain PCDD/PCDF was evaluated by spiking the sampler module with selected isomers and then sampling approximately 325 M^3 of clean ambient air. The spikes were deposited either directly onto the PUF adsorbent cartridges or onto clean filters. The PCDD/PCDF isomers used for these experiments were: 1,2,3,4-TCDD, 1,2,4,8-TCDF, 1,2,3,4,7,8-HexaCDD, 1,2,3,6,7,8-HexaCDF, OCDD, and OCDF. The spike levels were either 150 ng or 5 ng per isomer. The experimental set up for the retention study is shown in Figure 4.

The use of silica gel as an alternate adsorbent was also evaluated. The PUF was replaced with approximately 30 g of 35-70 mesh silica gel which was held in the sampling cartridge using pyrex glass wool plugs. The quantity of silica gel was limited by the flow rate that could be achieved with the air pump.

Analytical Methodology

The levels of PCDD/PCDF were quantified using capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The sample preparation consisted of spiking the samples with isotopically labelled internal standards followed by Soxhlet extraction with benzene. Coextracted interferences were removed using acid/base modified silica gel and alumina column chromatography.[11] The operating parameters of the HRGC/HRMS are summarized in Table 1.

RESULTS

Gas Phase Collection Experiments

The results from the Gas Phase Collection experiments, in percent of spike collected, are summarized in Table 2. The 1,2,3,4-TCDD was found predominantly on the PUF adsorbent with only a minor portion of the spike being collected on the filter. The majority of the OCDF however, was found on the filter. These results can be explained on the basis of the relative volatilities of the two isomers[12] or differing degrees of affinity for particulate matter.

The high recoveries (>100%) observed for the 1,2,3,4-TCDD at the lower spike levels resulted from interfering compounds, presumably degradation products, that were coextracted from the PUF.[13] The average detection limit for 1,2,3,4-TCDD in the PUF extracts was approximately 500 pg/sample while the average detection limit in the filter extracts was 10 pg/sample. The low recoveries observed for the OCDF in several of the experiments may have resulted from adsorption of the spike on the walls of the sampler.

Desorption Experiments

The results from the Desorption Experiments are summarized in Table 3. The recoveries of the spiked compounds in the static experiments were quantitative within ±20% as were the recoveries of the high level spikes in the dynamic experiments. The average recovery of the 1,2,3,4-TCDD in the low level dynamic experiments was 160%, which was probably due to interfering compounds.

PUF and Silica Gel Retention Experiments

The results from the retention experiments are summarized in Tables 4-7. Tables 4 and 6 contain the data from the experiments in which the spikes were deposited onto the filters, while Tables 5 and 7 contain the data from the adsorbent spikes. In general the total recoveries for the retention experiments were quantitative within approximately ±30%.

CONCLUSIONS

The EPA High-Volume Air Sampler was found to be an efficient sampler for PCDD and PCDF isomers, however relatively high levels of interfering compounds were present in the PUF extracts. These interferences limited its use to levels above approximately 100 pg/M^3. The distribution of the isomers in the sampler was dependent upon the volatility of the particular isomer. The more volatile isomers were collected on the

adsorbent while the less volatile isomers were collected on the filter. The total recovery of the spikes was essentially quantitative.

The PCDD and PCDF isomers also appear to desorb from particulate matter collected on the filter. The degree of desorption is dependent upon the volatility of the particular isomer and its affinity to particulate matter. Although the particulate matter was spiked with solvent solutions of selected isomers rather than by gaseous adsorption, it is probable that PCDD and PCDF isomers will desorb from actual samples. Additional work will be required to determine the effects of spiking technique, temperature, and surface characteristics on desorption.

Silica gel was found to have approximately the same retention efficiency as PUF for PCDD and PCDF isomers. The background interference levels in silica gel are relatively low, therefore it should allow lower levels of detection to be achieved. Additional work will be required to determine the effects of humidity on the retention efficiency of silica gel.

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TABLE 1. HRGC/HRMS OPERATING PARAMETERS

Mass Resolution	9,000–12,000 (M/ΔM, 10% valley definition)
Electron Energy	70 eV
Accelerating Voltage	6,000 volts
Source Temperature	200°C
Preamplifier Gain	10^7 volts/amp
Electron Multiplier Gain	$\sim 10^6$
Transfer Line Temperature	280°C
Column	DB-5 60M
Injector Temperature	300°C
Column Temp—Initial (3 min)	160°C
Column Temp—Program	30°C/min
Column Temp—Final	290°C
Carrier Gas	Helium
Flow Velocity	~25 cm/sec
Injection Mode	Splitless
Injection Volume	2 μL

TABLE 2. SUMMARY OF GAS PHASE COLLECTION EXPERIMENTS USING POLYURETHANE FOAM

	Recovery of 1,2,3,4-TCDD (%)			Recovery of OCDF (%)		
Spike Level (pg/M³)	Filter	PUF Cartridge	Total	Filter	PUF Cartridge	Total
800	7.0	110	120	52	2.6	55
800	2.4	97	99	22	0.65	23
800	11	120	130	79	ND	79
75	17	124	140	22	ND	22
75	2.2	150	150	100	ND	100
75	16	160	180	97	ND	97
8	ND	86	86	110	ND	110
8	ND	180	180	110	ND	110
8	ND	270	270	120	ND	120

ND = Not Detected
Limit of Detection Approximately 500 pg/Isomer/Sample for PUF
Limit of Detection Approximately 10 pg/Isomer/Sample for Filters

TABLE 3. SUMMARY OF GAS DESORPTION EXPERIMENTS (PARTICULATE LOADED FILTER)

Conditions	Spike Level	1,2,3,4-TCDD (%)			OCDF (%)		
		Filter	PUF	Total	Filter	PUF	Total
Static	High	110	NA	110	77	NA	77
Static	High	110	NA	110	88	NA	88
Static	Low	100	NA	100	100	NA	100
Static	Low	100	NA	100	96	NA	96
Dynamic	High	5.1	92	97	77	1.5	79
Dynamic	High	6.8	77	84	77	1.3	78
Dynamic	Low	3.7	150	150	100	ND	100
Dynamic	Low	5.9	180	190	99	ND	99

High Level = 12 ng 1,2,3,4-TCDD and 27 ng OCDF
Low Level = 1.6 ng 1,2,3,4-TCDD and 2.2 ng OCDF
NA = Not Analyzed
ND = Not Detected
Limit of Detection Approximately 500 pg/Isomer/Sample for PUF
Limit of Detection Approximately 10 pg/Isomer/Sample for Filters

TABLE 4. SUMMARY OF PUF RETENTION EXPERIMENTS (FILTER SPIKES)

Spike Level	Sample	TCDF	TCDD	HxCDF	HxCDD	OCDF	OCDD
150 ng	Filter	0.3	1.5	4.2	9.9	56	88
	PUF	73	95	110	110	21	16
	Total	73	97	110	120	77	100
150 ng	Filter	0.3	1.8	4.7	9.2	55	83
	PUF	95	98	94	90	36	14
	Total	95	100	99	99	91	97
150 ng	Filter	0.4	2	5.4	12	59	88
	PUF	78	90	100	89	17	9.8
	Total	78	92	110	100	76	98
5 ng	Filter	2	0	0	4	21	32
	PUF	90	120	91	100	74	57
	Total	92	120	91	100	95	89
5 ng	Filter	0	0	0	0	29	45
	PUF	76	88	100	110	69	57
	Total	76	88	100	110	98	100
5 ng	Filter	1	0	3	4	27	45
	PUF	72	81	86	100	70	88
	Total	73	81	89	100	97	130

TABLE 5. SUMMARY OF PUF RETENTION EXPERIMENTS (CARTRIDGE SPIKES)

Spike Level	TCDF	TCDD	HxCDF	HxCDD	OCDF	OCDD
150 ng	31	108	40	90	110	108
150 ng	70	99	79	96	97	100
150 ng	67	104	75	100	107	110
	$\bar{x}$ = 56%	104%	65%	95%	105%	106%
5 ng	81	122	120	135	105	97
5 ng	94	112	114	124	120	112
5 ng	96	105	108	117	109	100
	$\bar{x}$ = 90%	113%	114%	125%	111%	103%

TABLE 6. SUMMARY OF SILICA GEL RETENTION EXPERIMENTS (FILTER SPIKES)

Spike Level	Sample	TCDD	HxCDF	HxCDD	OCDF	OCDD
150 ng	Filter	3.7	5.8	43	68	96
	Silica Gel	77	65	78	18	2.0
	Total	81	71	120	86	98
150 ng	Filter	4.9	7.8	60	61	99
	Silica Gel	75	49	73	27	3.1
	Total	80	57	130	88	100
150 ng	Filter	4.9	6.6	27	54	88
	Silica Gel	69	73	124	17	2.3
	Total	74	80	150	71	90
5 ng	Filter	1.6	7.1	9.4	83	99
	Silica Gel	61	68	120	7.6	6.9
	Total	63	75	130	91	110
5 ng	Filter	1.3	4.1	6.2	76	106
	Silica Gel	88	74	100	7.8	6.7
	Total	89	78	110	84	110
5 ng	Filter	1.8	5.9	7.1	91	127
	Silica Gel	73	46	29	8.8	6.7
	Total	75	52	36	100	130

TABLE 7. SUMMARY OF SILICA GEL RETENTION EXPERIMENTS (CARTRIDGE SPIKES)

Spike Level		TCDD	HxCDF	HxCDD	OCDF	OCDD
150 ng		92	4	101	90	104
150 ng		89	47	105	97	101
150 ng		89	61	138	99	101
	$\bar{x}$ =	90%	37%	115%	95%	102%
5 ng		92	38	127	110	118
5 ng		81	64	132	98	119
5 ng		92	118	163	108	128
	$\bar{x}$ =	88%	73%	141%	108%	122%

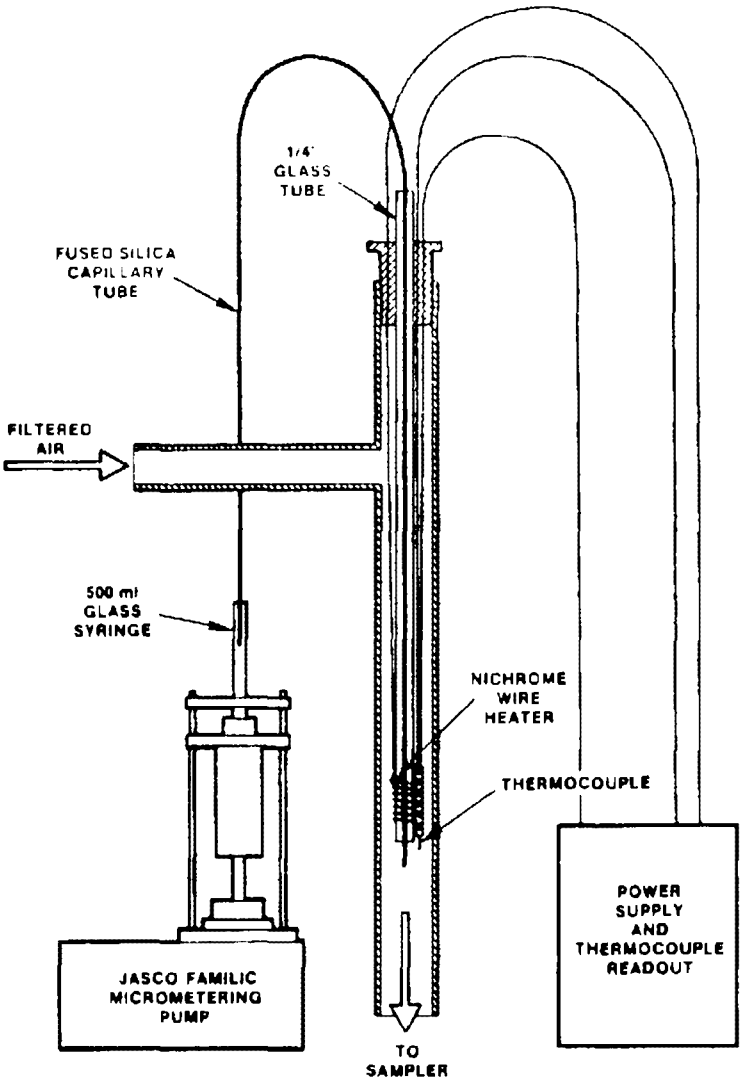

FIGURE 1. AIR STREAM SPIKING APPARATUS

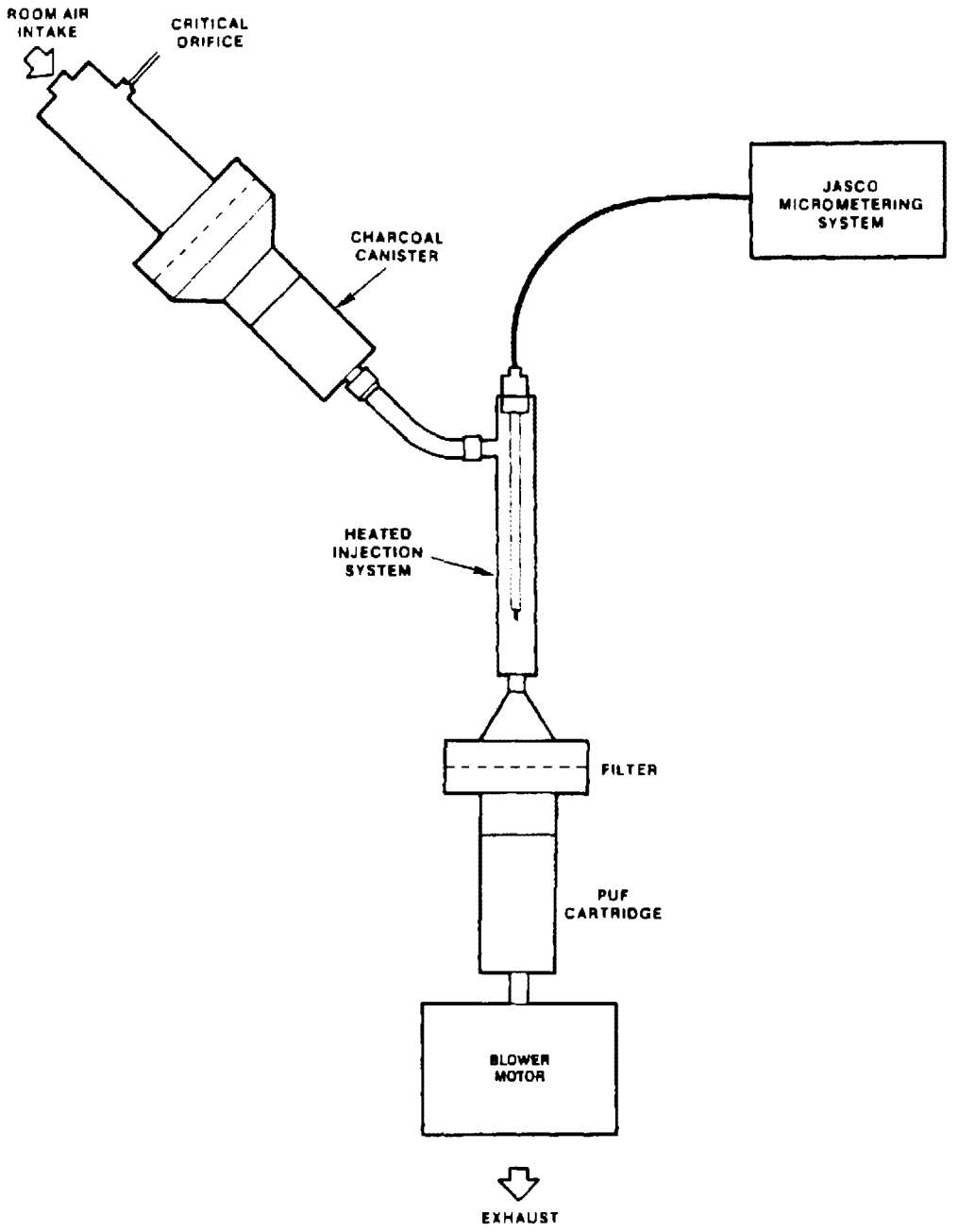

FIGURE 2. EXPERIMENTAL SETUP FOR COLLECTION EFFICIENCY STUDY

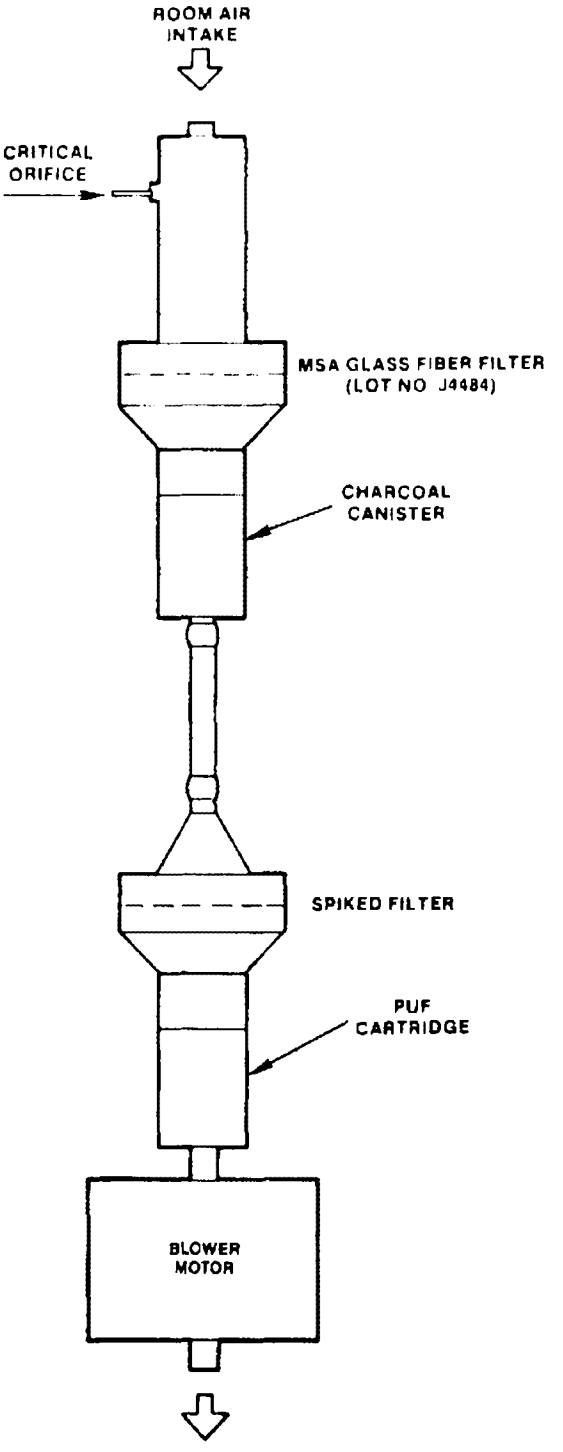

FIGURE 3. EXPERIMENTAL SETUP FOR DESORPTION STUDY

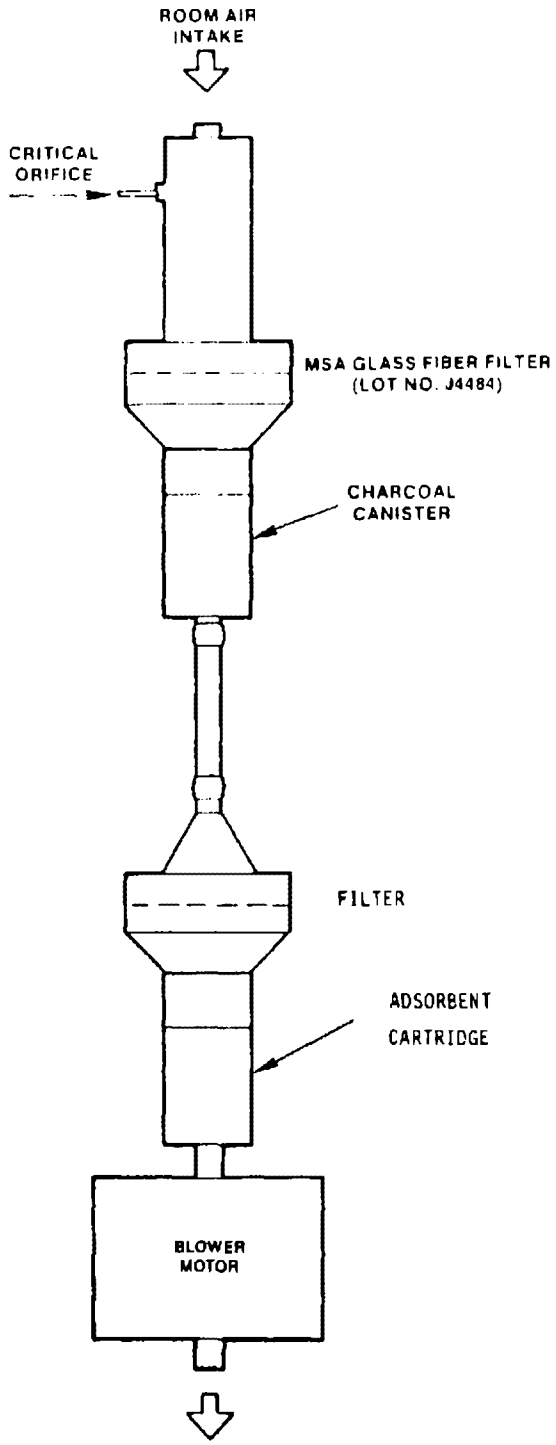

FIGURE 4. EXPERIMENTAL SETUP FOR RETENTION EFFICIENCY STUDY

Measurements of Hazardous Air Pollutants in the Emissions of German Municipal and Industrial Waste Incinerators and Afterburner Chambers

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At the end of the last decade the discussion arose in the aftermath of the Seveso accident concerning the release of chlorinated DIOXIN and DIBENZOFURAN into the environment from operating municipal and industrial waste incinerators. In consequence of this discussion, the Landesanstalt für Immissionsschutz (State Institute of Immission Control, LIS) of the state of Northrhine Westphalia (NRW) was the first institution in the Federal Republic of Germany to conduct an investigation of all major municipal and industrial waste incineration plants in NRW during the period 1979/80.

No traces of Tetrachlorodibenzodioxin (TCDD) were detected in the solid particulates of the flue gas at nine incineration plants. However the incinerator at Iserlohn emitted TCDD at concentrations much higher than the detection limit.

Following a report of the German Federal Environmental Protection Agency (Umweltbundesamt) in 1984, which revealed a few high recordings (e.g. 52 ppb TCDD) of fly ash samples, the Government of Northrhine Westphalia ordered further testing. Now the main aim was the analysis of slag and fly ash samples. Other state governments followed soon the example set by Northrhine Westphalia. Consequently several extended programs on the Dioxin/Dibenzofuran theme were initiated. Some of the results are discussed in the following.

A schematic representation of a waste incinerator is shown in Figure 1. Deviations from this scheme follow in case of special purpose applications, e.g. for the combustion of polychlorinated biphenyls (PCB).

A summary of the investigations of the waste incinerators in Northrhine Westphalia is shown in Table I. The results of 11 municipal waste incinerators are collectively listed because the observed data indicate that dioxins and dibenzofurans could not be detected in either the slag or the scrubber sludge or the fly ash (micro dust). Also 2,3,7,8-TCDD and 2,3,7,8-TCDF could not be determined in the filter dust. However, other dioxins and dibenzofurans were found at all incineration plants. The maximum value in the fly ash was 0.075 ppb of 2,3,7,8-TCDD and in the slag 0.013 ppb of 2,3,7,8-TCDD. The latter values were observed at the Iserlohn plant which has been separately listed for this reason in Table I. One can assume that no nominal amount of 2,3,7,8-TCDD is released with the slag in the environment. The sign "<" in Table I means that all observed values are equal or smaller than that particular value.

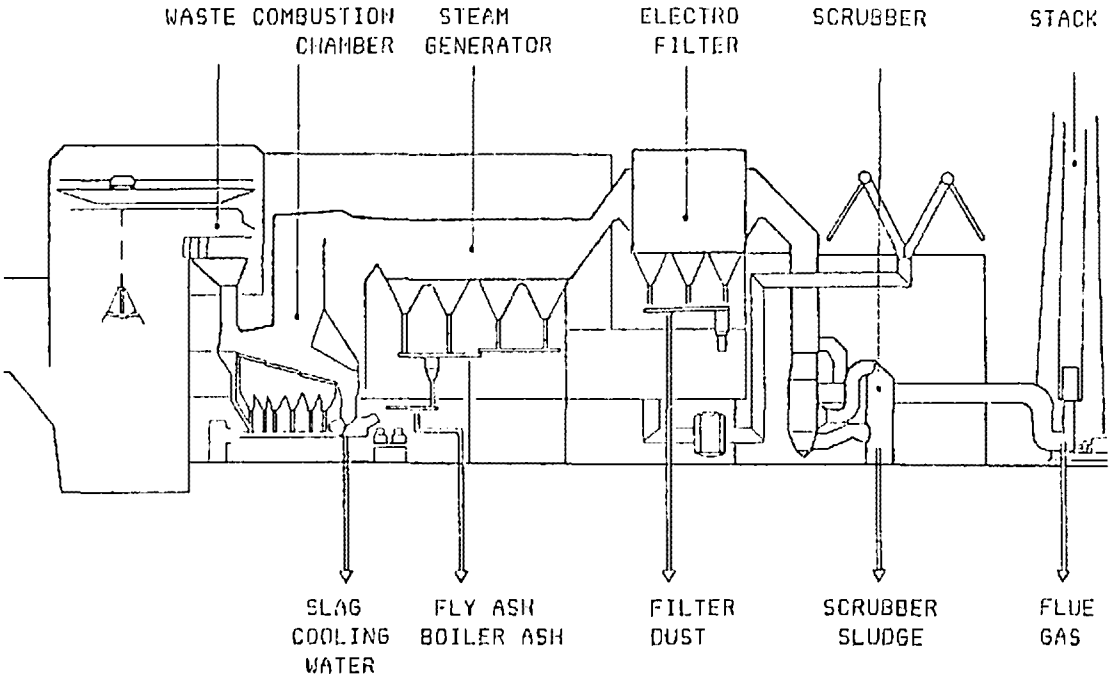

Figure 1. Schematic Representation of a Waste Incineration Plant(1)

Table 1. PCDD/PCDF concentrations of the filter dust, slag, scrubber sludge and fly ash of 12 municipal (MWI) and of 2 hazardous (HWI) waste incinerators in Northrhine Westphalia.

PLANT	MATERIAL	2,3,7,8-TCDD	Σ PCDD (3 - 8)	2,3,7,8-TCDF	Σ PCDF (3 - 8)
11 MWI	FILTER DUST (µG/KG)	<0.01	4 - 330	<0.05	10
	SLAG "	<0.01	<0.2	<0.01	<0.6
	SCRUBBER SLUDGE "	<0.01	<0.3	<0.01	<0.6
	FLY ASH (nG/m^3)	<0.0008	<0.2	<0.15	<0.25
MWI at ISERLOHN	FILTER DUST (µG/KG)	0.075	177	1.2	107
	SLAG "	0.013	-	-	-
	SCRUBBER SLUDGE "	<0.01	0.10	<0.01	<0.6
	FLY ASH (nG/m^3)	0.014	57.8	0.21	58.5
HWI at LEVERKUSEN (PCB,etc.)	FILTER DUST (µG/KG)	<0.01	2.5	<0.01	2.0
	SLAG "	<0.01	2.3	<0.01	1.5
	SCRUBBER SLUDGE "	<0.001	<0.001	<0.001	<0.001
	FLY ASH (nG/m^3)	<0.005	0.60	0.005	1.04
HWI at BERGKAMEN (Hospital W., Solvents,etc)	FILTER DUST (µG/KG)	-	-	-	-
	SLAG "	<0.001	<0.001	<0.001	<0.001
	SCRUBBER SLUDGE "	<0.02	<0.04	<0.02	<0.02
	FLY ASH (nG/m^3)	0.05	21.0	0.018	14.0

Table I contains for the sake of clarity information only on two of the four hazardous waste incinerators investigated by the LIS because the results resemble each other very nearly.

The plant in Leverkusen is operated by the BAYER AG and it is permitted to burn PCB and Dioxin/Dibenzofuran containing materials. Only 3 other incinerators (BASF AG, GSB in Bavaria, HIM) are licenced for the combustion of such hazardous substances in the Federal Republic of Germany. The incinerator at Bergkamen belongs to the SCHERING AG and serves primarily the company in the removal of plant site waste. Representatively for these hazardous waste incineration plants, Table II provides some technical data of the plant at Leverkusen.

Table II. Some technical Information of the BAYER AG Waste Incineration Plant in Leverkusen (2).

Waste Intake:	120 l drums with solid waste Liquid waste via special injection system
Rotary Kiln:	7 RPM, 1000 - 1200 °C, 11 % Oxygen appr. 1 h retention time of slag in kiln Water cooling of slag
Afterburner Chamber :	> 1200 °C Retention time > 18 sec Total retention time > 22 sec
Heat Exchanger :	Flue gas cooling to 320 - 350 °C

Electrostatic filter, quenching w. water to 60 °C, rotary washer, alkaline jet washer, water droplet separator, 100 m stack.

Combustion Efficiency > 99.9999 %
2,3,7,8-TCDD < 0.01 - 1 ppb depending on matrix

The data on the industrial waste incinerator demonstrate that both a sufficient high temperature and an extended retention time lead to a total destruction of chlorinated hazardous waste. Model experiments (3) on incomplete combustion corroborate these findings, e.g. the formation of 2,3,7,8-TCDD from the following chlorinated organics at 600 °C:

5.000 µG/G 2,4,5-Trichlorophenol
2.000 µG/G 2,4,5-T
200 µG/G Herbizide Tormona 90

Most of the previous investigations on waste incinerators neglected the gaseous portion of the flue gas after it has passed through the scrubbers since it was believed that dioxins and dibenzofurans exhibit no significant volatility. A recent publication (1) and our

own measurements revealed that a major portion of these chlorinated compounds escape uncontrolled through the stack. A summary of the results of these investigations is provided in Tables III to V .

Table III: PCDD/PCDF concentrations (nG/m^3) of the gaseous portion of the stack gases of 1 hazardous (HWI) and 3 municipal (MWI) waste incinerators at the city of Hamburg (1).

PLANT	DATE	2,3,7,8-TCDD	Σ PCDD (3 - 8)	2,3,7,8-TCDF	Σ PCDF (3 - 8)
HWI	4.16.84	<0.002	247	3	176
Borsig St.	4.17.84	<0.002	151	8	240
MWI 1	4.09.84	0.2	144	3	153
Borsig St.	4.11.84	0.2	170	3	167
MWI 2	5.10.84	0.7	97	2	287
Stellinger	5.02.84				
Moor	DUST:	0.1	45	3.4	159
	GAS :	0.45	86	0.23	204
MWI 3	5.04.84	0.07	37	0.9	92
Stapelfeld	5.15.84				
	DUST:	<0.002	1.0	<0.002	1.4
	GAS :	0.096	53.5	0.6	132
	5.17.84	0.1	36	1.4	103

Table IV. PCDD/PCDF concentrations (µG/kG) of the filter dust, fly ash and slag of the municipal waste incinerator at Stapelfeld in the city of Hamburg (1).

DATE	MATERIAL	2,3,7,8-TCDD	Σ PCDD (3 - 8)	2,3,7,8-TCDF	Σ PCDF (3 - 8)
5.04.84	FILTER DUST	0.02	75	0.02	22
	FLY ASH	<0.01	9.5	0.03	6.2
	SLAG	<0.01	0.15	<0.01	0.4
5.15.84	FILTER DUST	0.01	23	0.03	6.2
	FLY ASH	0.01	1.5	0.01	0.64
	SLAG	<0.01	0.12	<0.01	0.07
5.17.84	FILTER DUST	0.01	25.5	0.01	7
	FLY ASH	0.01	0.7	0.01	0.63
	SLAG	<0.01	-	<0.01	-

Table V. PCDD/PCDF concentrations (nG/m^3) of the gaseous and the solid phase of the flue gas from a waste and a sludge incinerator of a large industrial plant. Samples were taken from flue gas after passage of the scrubber.

PLANT	MATERIAL	2,3,7,8-TCDD	ΣTCDD	2,3,7,8-TCDF	ΣTCDF
WASTE INCINERATOR	Solid Phase	0.002	0.069	0.007	0.214
	Gaseous Phase	<0.003	<0.003	<0.003	0.14
SLUDGE INCINERATOR	Solid Phase	0.001	0.029	0.010	0.165
	Gaseous Phase	0.001	0.001	0.08	0.02

Investigations of the formation of DIOXINS in large industrial waste incinerators have shown that the dioxins formed during the combustion of PVC containing waste cannot be related to its presence in waste.

Several authors (4,5,6,7) reported on the formation of chlorinated dioxins from wood (lignin) or garbage and chlorine contained in organic and inorganic materials when the combustion does not occur under optimum conditions. However these conditions prevail in almost any kind of waste independently of the presence of PVC (8).

An estimate of the surplus of Cl-ions in solid waste with reference to the dioxins in the stack gases revealed - based on REIMANN's (9) data of the net-balance of chlorine of an incinerator plant - that in solid waste free of PVC a Cl-ion surplus of 3*10^9 exists compared to 12*10^9 in waste containing PVC. Since this difference is not significant, the contribution of PVC to the formation of dioxins can be neglected in municipal waste incineration plants.

The German Federal Environmental Protection Agency (Umweltbundesamt) concluded from investigations of 5 municipal and 1 hazardous waste incineration plant: "There exists no connection between HCl concentration and the contents of PCDD and PCDF in the fly ash"(10). Similar results were obtained by KARASEK et al.(11) when he increased the PVC content by 300 % at a municipal incinerator in Paris, France.

A study group initiated by the German UMK (Environmental Ministerial Conference) concluded in a report on "Dioxin and Waste Incinerators" that there exists no significant risk from waste incinerator operations.

The New York City Department of Sanitation also reported (12):"PVC has never been shown to be a precursor of PCDF/PCDD, and the HCl

liberated by PVC combustion comprises only part of the total amount of chlorine in municipal solid waste. Therefore, at this time, the removal of PVC from incoming solid waste stream would not be expected to affect the PCDF and PCDD emissions from the stack".

No formation of dioxin was observed during the combustion of solid PVC at elevated temperatures. A study in the laboratories of the Solvay Company in Belgium (13) on pure PVC and PVC used in the manufacture of bottles revealed no indication of the presence of traces of dioxins during the combustion at temperatures ranging from 408 to 850°C. The detection limit was 10 µG dioxin/KG of burnt PVC (10 ppb).

Olie et al.(14) pointed out that "attempts to generate measurable amounts of chlorinated dioxins and dibenzofurans by burning PVC alone were not successful". These results were also corroborated by an US-Canadian study (15) on the combustion products of PVC at 800-950°C. No dioxins were found.

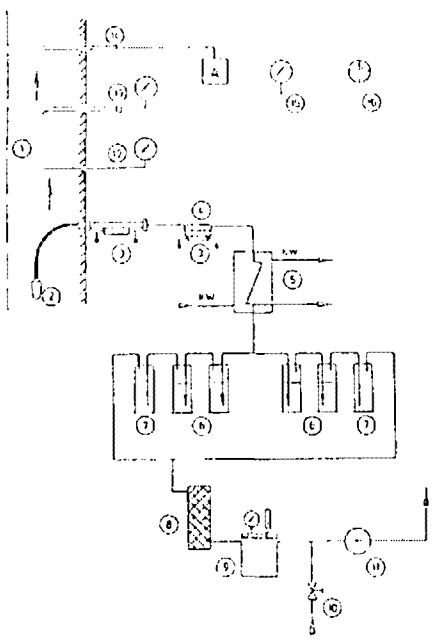

Figure 2. Stack Gas Sampling Unit for Investigations on Dioxin/Dibenzofuran

1. Stack
2. Sampling Probe Gas/Solids
3. Heater
4. Micro Filter
5. Cooler + Condenser
6. Impinger,ice cooled
7. Droplet Separator
8. Dryer
9. Gas Meter
10. Bypass Valve
11. Pump
12. Temperature Sensor
13. Differential Pressure Meter
14. Oxygen Analyzer
15. Barometer
16. Timer

The sampling requires special precaution because of relatively large volume rates whereas at the same time the use of small quantities of absorber liquid is desirable. There exist only a few methods to collect samples of fly ash and gaseous components simultaneously. No standard procedure for measuring polychlorinated dioxins or dibenzofurans at incinerators are known. Therefore the methods employed are mainly based on standard procedures for sampling filter dust or fly ash whereby high volume sampling equipment has to be used. Ballschmiter et al. (1) are using an assembly of more or less standard equipment which is shown in Figure 2. Our technicians employ very similar instruments, only the materials of the probes are different. Whereas Ballschmiter et al. uses for the separation of dust from gaseous components a glass fiber thimble of the type 603 gK, the IWL employs membrane filters 50 K, type SN 13400 distributed by the Satorius company. For the adsorption of the gaseous portion are either methoxyethanol (1) or 1,2-ethanediol suitable.

Standard GC-MS techniques were routinely used for the chemical analysis of the dioxins and dibenzofurans.

Despite the clear indication that no harm to the public is expected from the safe operation of waste incinerators, the resistance against the building and operation of such plants is inconceivable. Since the same opposition is growing against open landfills, the orderly removal of waste has become a first rate political issue in several states of the Federal Republic of Germany.

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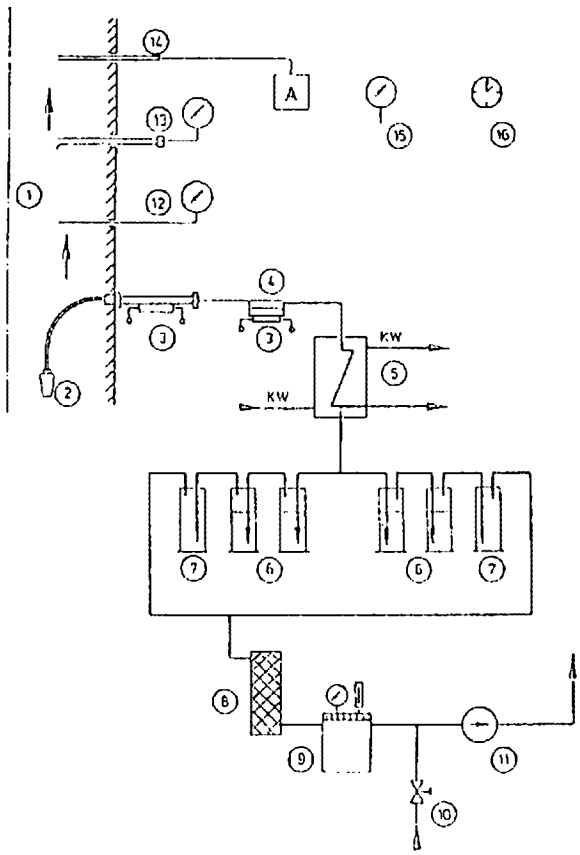

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APPLICATION OF ORIFICE METER TO AMBIENT DIOXIN SAMPLER

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The New York State Departments of Environmental Conservation and Health are providing lead roles in the determination of extremely toxic substances found in ambient air on a statewide basis. Samplers have been assembled from components and housed in standard high volume air sampler shelters. Calibrated air flow rates must be maintained and measured by field operators over a long-term study designed to document background levels of dioxins and furans. Preliminary quality assurance reviews and results from collocated samplers indicated flow rates reported were neither uniform nor stable resulting in possible invalidation of the results from difficult and expensive analytical procedures and loss of important data.

In an effort to develop an air flow check system which would be reliable, stable, rugged, easy to use, and affordable, an orifice assembly previously used with a stack testing train was modified and tested for this application. The device was installed in series with the sampling train, located between the vacuum pump and the charcoal scrubber which is used to protect the pump from any potential breakthrough of dioxin spiked sample cartridges. Results of testing indicated that an orifice size of 7/32" opening with pressure taps connected to a standard oil filled manometer yielded good mid-range readings at the desired flow rate of 1 cfm.

The orifice assembles are easily calibrated and certified using existing wet test meter reference flow procedures developed for stack test trains; and when permanently installed in the sampling train, simplify routine flow and leak check procedures. As an added benefit there is no potential to contaminate the cartridge while making flow measurements. This approach appears to be a viable solution to other applications of toxic samplers where constant flow rates must be maintained and measured over a long period of time under adverse conditions. Results of quality assurance audits and details of field calibrations can be reported in a similar format to those used for other criteria contaminants like lead.

APPLICATION OF ORIFICE METER TO AMBIENT DIOXIN SAMPLER

Introduction

The State of New York is currently investing several million dollars in modernization and expansion of the statewide air monitoring system to include selected toxic substances, acid rain components and criteria air contaminants. It is essential that all air monitoring equipment operate properly, be checked and certified at least annually, and have standardized operational and quality assurance procedures. One objective of this project is to develop samplers which can be maintained and measured by existing field operators with available components which are reliable, stable, rugged, easy to use and affordable. The research testing plan is to determine existing levels of field performance, propose and apply modifications where required, verify results in the field, and finally document procedures for inclusion in quality assurance manuals.

Ambient sampling for toxic substances in New York State was initiated in 1982 for toxic organic species including BHC's, PCB's, BAP and phthalates[1]. Vacuum pumps were used to draw ambient air through solid sorbent (florosil) packed cartridges to trap the compounds for subsequent laboratory analysis as described by Narang[2]. The sampling period was 24 hours and required air flow rates of approximately 0.5 cfm were obtained by maintaining pump vacuum well above critical. The accurate determination of actual flow through these units was crucial to final laboratory calculation of toxic substances concentrations. The major problem encountered with cartridge flow calibrations was the fact that the florosil sampling media would loosen up with handling and shipping. Initial flow calibrations performed in the laboratory with a freshly packed cartridge would differ from the final exposed cartridge tests, the latter indicating higher flows. In addition, since these lab flow tests were performed at an assumed pump vacuum well above critical, it was often discovered that actual pump vacuum conditions in the field were markedly different dependent on pump condition and system leakage. As a result, it became essential to develop field flow quality assurance audit procedures to insure accurate cartridge sampling flow rates were being reported[3]. Actual flows were determined by utilizing a dry gas meter calibrated against a primary standard wet test meter. The dry gas meter was connected to the cartridge inlet at the start of each sampling run for two consecutive 10-minute flow checks. This data was recorded and forwarded to the laboratory with each cartridge.

Project Requirements

This procedure was satisfactory until 1984 when a statewide program to sample for ambient levels of dioxins and dibenzofurans using protocols developed by O'Keefe and others[4,5] was initiated. New sampling cartridges were utilized which were larger and consisted of two stages: a glass fiber particulate filter and a teflon chamber containing silica gel "spiked" with dioxins for breakthrough analysis purposes. Because anticipated ambient concentrations of dioxin would be extremely low, namely picograms per cubic meter, purity in the sampling train became paramount. Since the dry gas meters used for field audits were once used in stack test systems, it was decided not to use them for the dioxin sampler for fear of introducing unwanted contamination. New dry gas meters could not be used because of their affinity to become "doped" by the sampled air itself. Consequently, an alternate flow calibration method had to be developed.

Available mass flow meters were evaluated, but because of the high pressure drops experienced at sampling flows of about 1 cfm, their use would have created additional calibration problems and consequently, they were not considered acceptable for this application. In addition, these components were not considered reliable when maintained in an outdoor environment for long periods of time. Rotameters were also suggested but past experiences[6] in using orifice meters as a substitute for the visi-float in our high volume air sampler network directed us away from this alternative. Additional experiences of using orifice meters for calibration of dichotomous samplers and in stack sampler applications led us to believe this device should be tested for possible application to the samplers.

Due to the large geographic distances involved in the network, bench testing was to be performed and documented in our calibration standards lab in Albany before any field modifications could be implemented. Also, because of the relatively high cost for each analysis (approximately $2200 per sample), any changes proposed for the field sampling protocol had to be inherently free from potential contamination or invalidation of the sample run. Field-proven techniques used in conjunction with existing standard methods for compliance monitoring were to be applied wherever practical to extend resources and reduce complexity.

Experimental Method

After careful consideration, it was decided to use an orifice which would be installed downstream from the sampling cartridge between the vacuum pump and the cartridge as shown in Figure 1. This device offered an additional important advantage in that it could be easily decontaminated at the completion of testing. Available 8" oil filled manometers were to be used requiring an orifice which yielded good mid-range readings at the desired flow, i.e., about 5" water total at 1 cfm. An existing stack test orifice assembly was to be modified for testing, by drilling out the orifice for the desired characteristics. If repeated tests with the modified orifice yielded satisfactory results, it could be concluded that this device was a viable solution to flow calibration assurance.

Since there were only a limited number of the modified orifices available and we needed a total of five, we borrowed an orifice design described by EPA[7] which had been used to calibrate dichotomous samplers. These were modified slightly by requiring 7/32" drill size openings. These orifices were manufactured for us at a cost of $150 each from the specifications shown in Figure 2.

Prior to installation, each orifice was to be calibrated and certified by our Quality Assurance Laboratory utilizing the protocol described in EPA QA Handbook[8]. The test data for each orifice would also be analyzed to determine correlation coefficient values. The generated intercepts and slopes for each set of orifice data that accompany the orifice to the sampling site would enable rapid flow determination by utilizing the following formula:

$$Q_{act} = A \times \Delta H^{B}$$

where: Q = flow in cfm at actual conditions
A = intercept
ΔH = manometer reading in inches of water
B = slope

After the permanent installation of these orifices in the field sampling train, the effectiveness of simplified flow checks and operation in addition to reducing the potential for leaks were to be determined by comparison to previous flow rates reported.

Results

From the initial testing performed an orifice size of 7/32" was determined to produce the desired nominal flow rate of 1 cfm through the sampling cartridge when used with conventional vacuum pumps. Pump vacuum was varied from approximately 16" to 22" mercury in a total of four steps to generate the calibration and linear regression data. Typical orifice meter calibration reproducibility is illustrated by the results of the five tests shown in Table I for orifice #1. Limits for calculating flow for a 95% confidence interval were demonstrated to be better than ±5% indicating excellent repeatability for the individual tests performed.

Figure 3 is a summary of the five different orifice meter calibration curves which demonstrates the relationship of flow to manometer reading is linear within the range of pump vacuum used. The high level of correlation reported in Table II also illustrates this point. It was not prudent to batch calibrate all the orifice meters because it appeared that each one has a unique slope and intercept. This is most likely due to the tolerances used when machining and fabricating. Each orifice meter had to be number engraved in order to maintain calibration data.

The calibrated orifices were installed on the field dioxin samplers in January 1986. Since the sampling frequency is normally monthly, there are only a limited amount of reported data available[9]. To determine the actual effect of flow rates reported by operators, Figure 4 is the history of actual flow rates reported at each site for the past two years. The lack of uniformity and stability is obvious, but appears to have improved after January 1986. As a result of the use of the orifice meters the operators can now perform a simple leak test on the entire sampling train by plugging the cartridge filter inlet and observing if the manometer reading drops to zero. This benefit has totally eliminated the chance that a significant portion of the total volume of the air sampled could be the result of leaking connectors. Actual field protocol is to run the sampler for five minutes both before and after the cartridge has been exposed to the sample volume to record starting and ending flows. Results to date indicate no change in manometer readings before, during or after 48 hour sampling runs.

Conclusions

Processing of a precise volume of ambient air for the analysis of trace levels of toxic, semi-volatile organics like dioxins and furans is now an easy task with the application of the orifice meter to the sampling train. Utilization of an orifice device for flow determination is not a new idea, but because of its simplicity, lack of frequent calibration and maintenance requirements, and field proven reliability, it will continue to be useful for a multitude of monitoring purposes.

Its application for toxic monitoring has provided an affordable, trouble-free solution to the vexing problems of sampling train contamination and leak checking. This study has demonstrated that this simplistic device is inherently free from the inadequacies mentioned with the previous schemes. This approach can be used over a wide variety of desired flow dates by sizing the vacuum pumps and orifices according to the flow rates desired.

Samplers which utilize solid sorbent packed columns have been tested at flow rates approaching 10 cfm by using larger orifices and vacuum pumps. The use of a polyurethane foam (PUF) insert within our orifice meter equipped high volume air sampler filter holders also appears to work well. Sampling flow rates of 28 cfm have been observed while operating the standard high volume sampler motor at 90 volts.

The modification of existing equipment to sample for additional contaminants has the unique advantage of providing an in-place sampling network with minimal start-up and operational costs. Also, quality assurance programs can be implemented with protocols and training that are currently in use for criteria pollutants like lead. We would encourage EPA and others to consider the orifice meter technique as the recommended method for maintaining and measuring constant air flow rates for all types of manual samplers.

Acknowledgements

The authors wish to acknowledge Don Gower, Ed Savoie, Bill Webster and Dick Gibbs for administrative and technical support of this project. The authors thank Stephanie Liddle, Gary Lanphear and Ben Hill for aid in preparation of manuscript and graphics.

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Table I. Orifice Meter #1 Calibration Reproducibility

Test No.	A(Intercept)	B(Slope)	Q(CFM Flow) [Calculated for ΔH=3.3"]	Correlation
a	11.59	.7557	1.00	.9996
b	11.57	.7582	1.01	.9992
c	11.44	.7658	1.01	.9999
d	11.62	.7496	1.00	.9998
e	11.36	.7611	.99	.9997
Mean	11.51	.7581	1.00	.9996
Standard Deviation	.111	.0060		
Limits for 95% Confidence				Note: Confidence Intervals using Students "t" Distribution
Upper	11.82	.7748	1.05	
Lower	11.20	.7414	.96	t_4=2.776

Table II. Individual Orifice Meter Calibration Results

Orifice Meter #	A(Intercept)	B(Slope)	Q(CFM Flow) [calculated for ΔH=3.3"]	Correlation
1	11.51	.7581	1.00	.9996
2	10.57	.7442	.91	.9999
3	11.09	.7240	.93	.9997
4	11.56	.7723	1.03	.9999
5	10.06	.7564	.88	.9999

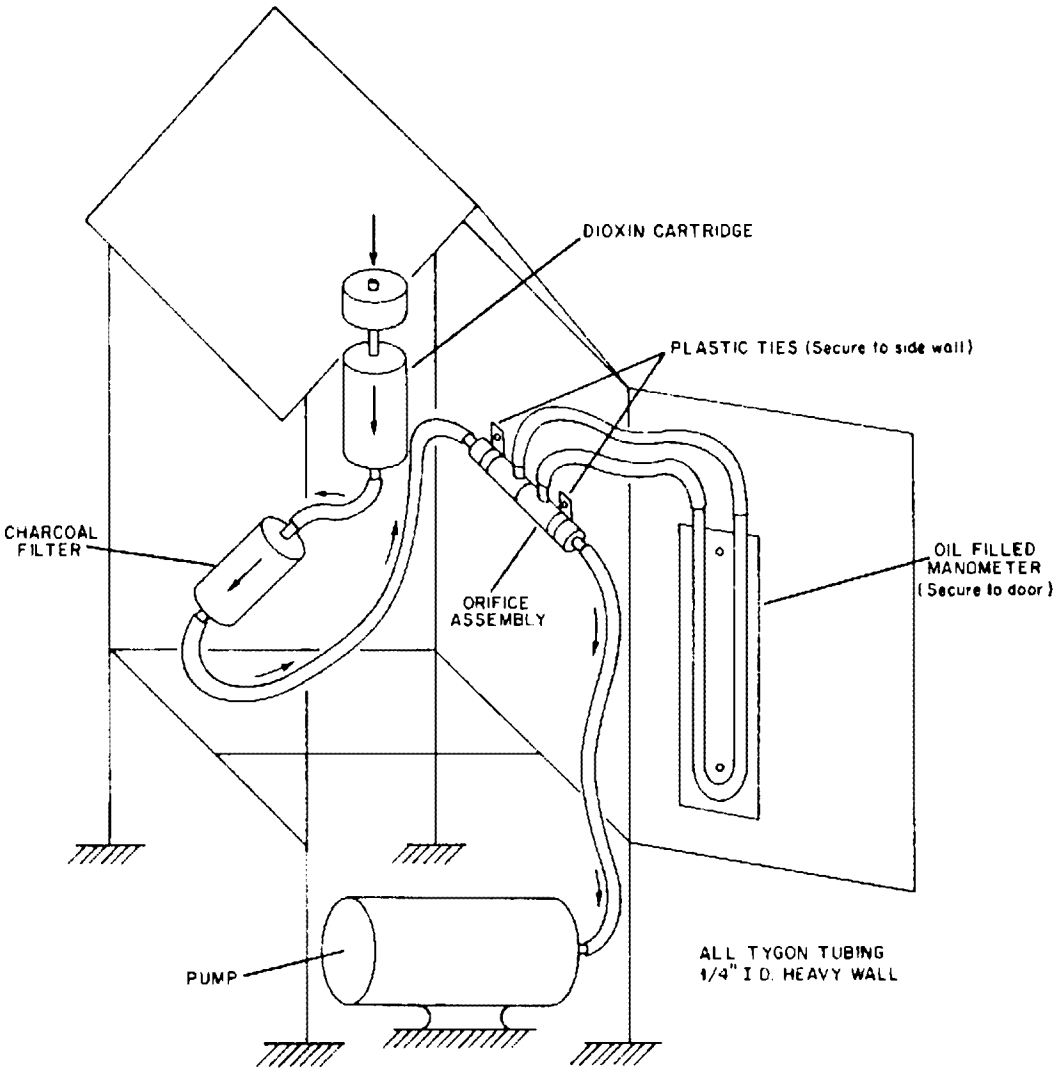
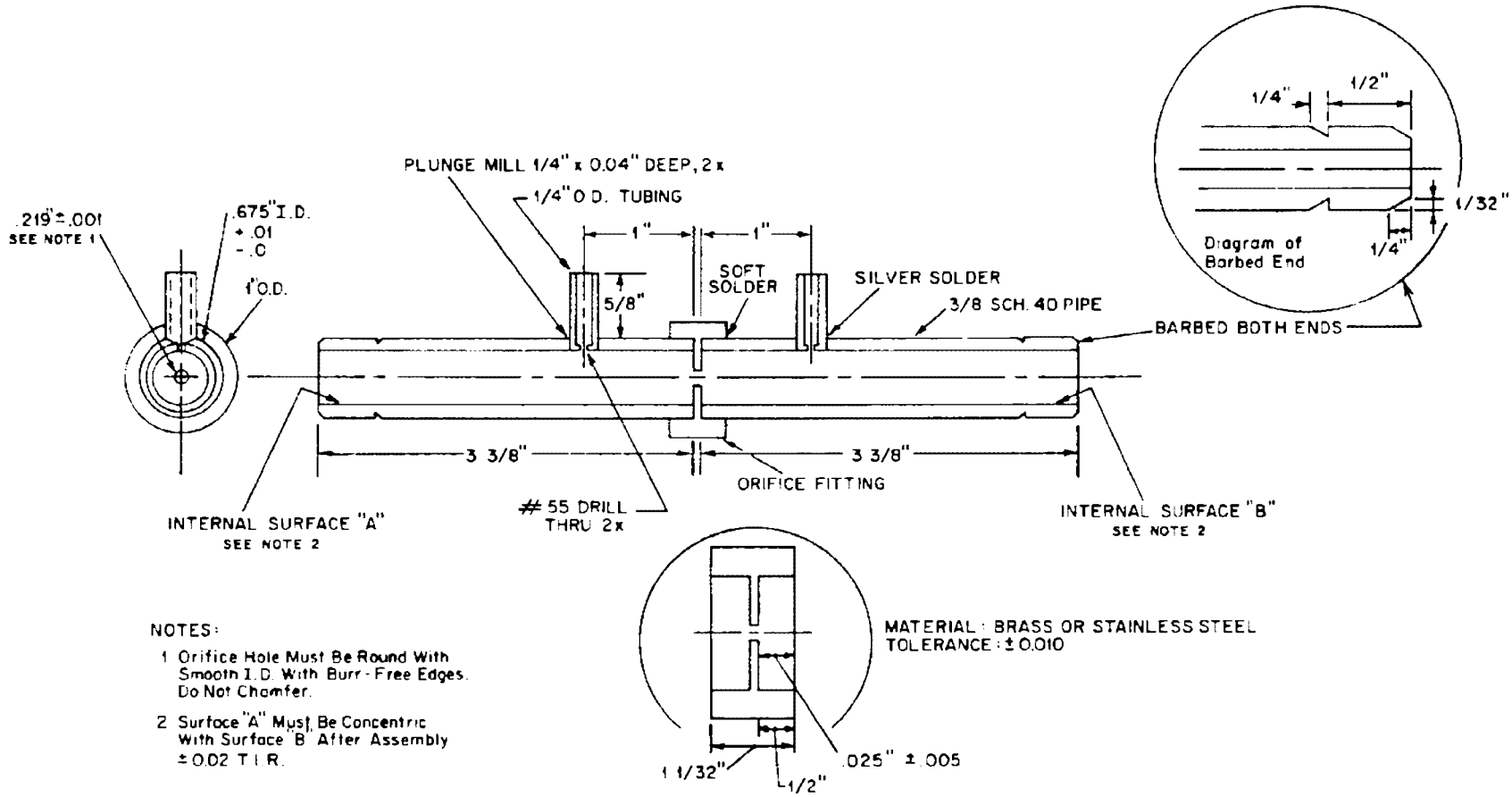


Figure 1
DIOXIN SAMPLING ASSEMBLY



NOTES:

1. Orifice Hole Must Be Round With Smooth I.D. With Burr-Free Edges. Do Not Chamfer.
2. Surface "A" Must Be Concentric With Surface "B" After Assembly ± 0.02 T.I.R.

Figure 2 Details of Construction For Orifice Assembly

FIGURE 3

ORIFICE METER CALIBRATION GRAPHS

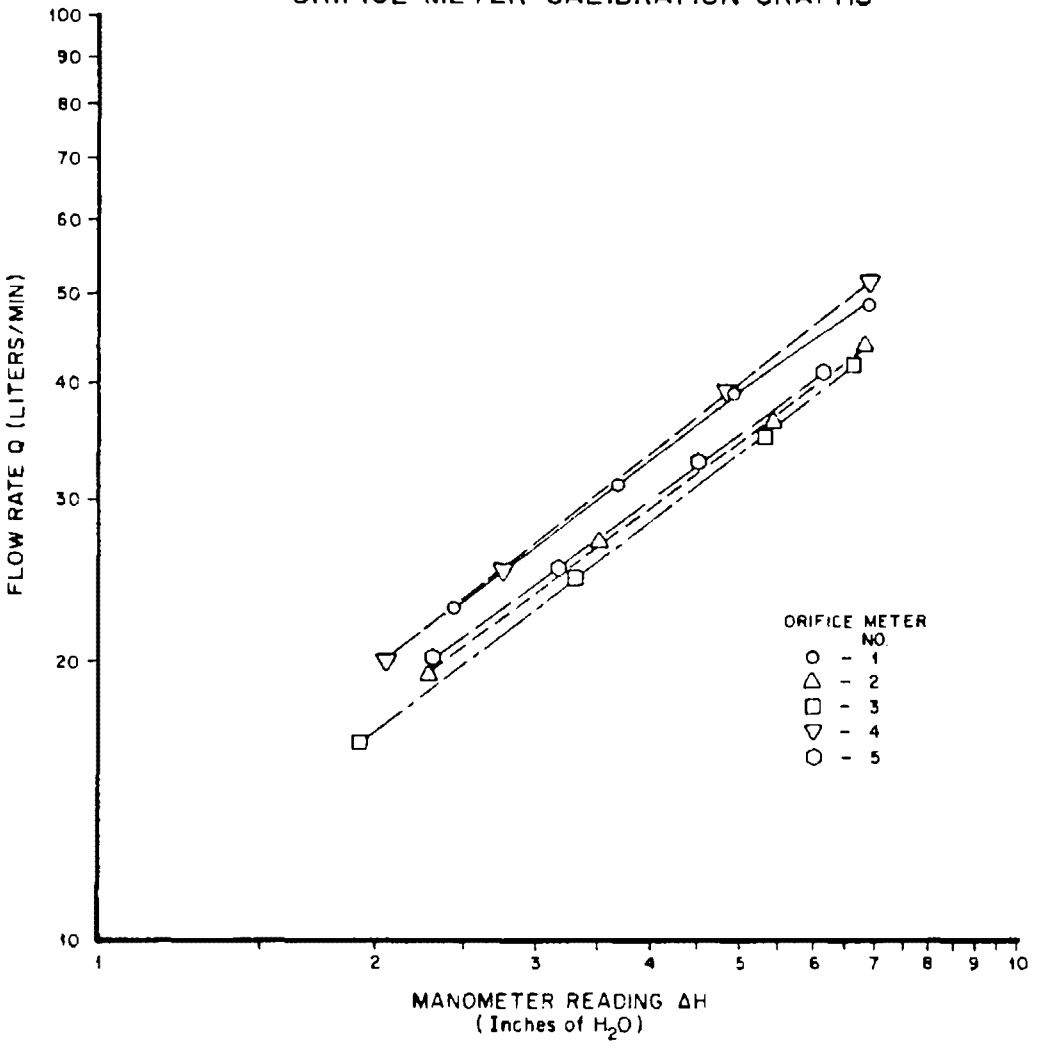
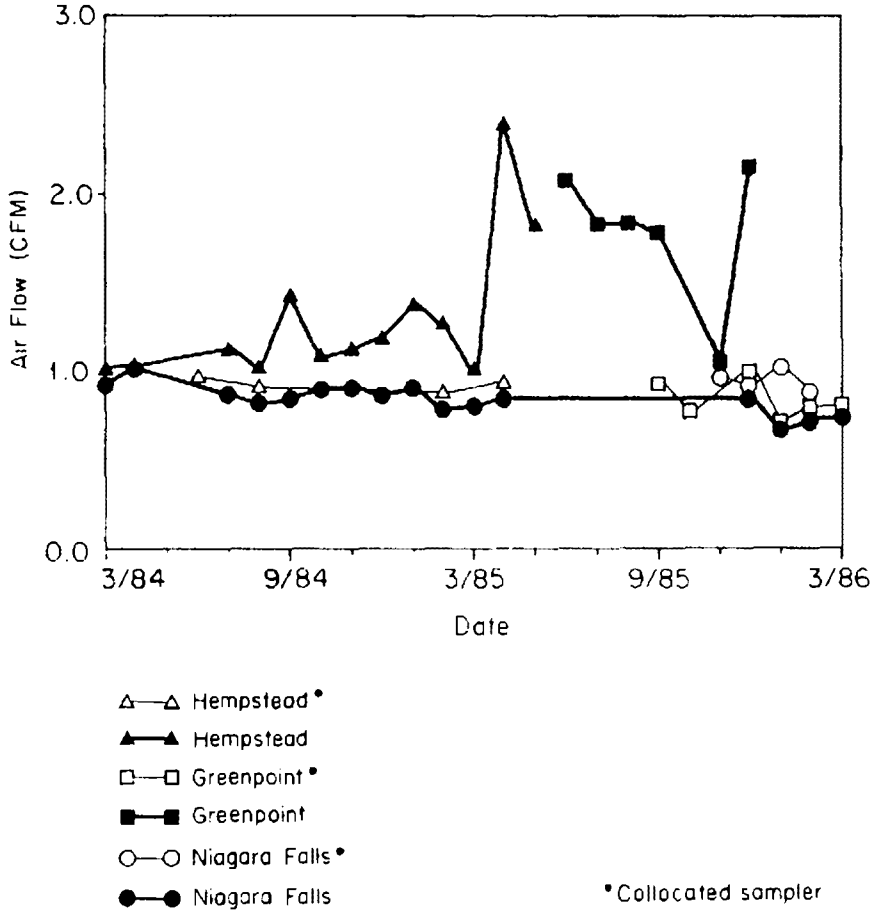


Figure 4

Reported Sample Air Flow Rates for Dioxin Samplers



APPLICATION OF SUPERCRITICAL FLUID CHROMATOGRAPHY TO THE ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS IN AIRBORNE PARTICULATE MATTER

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A commercial packed column supercritical fluid chromatograph has been used to analyze several air particulate samples for semivolatile organic compounds. Analyses are rapid and require low temperatures. The variable wavelength ultraviolet detector supplied with the instrument has low sensitivity and requires that samples be large and undergo extensive sample cleanup.

APPLICATION OF SUPERCRITICAL FLUID CHROMATOGRAPHY TO THE ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS IN AIRBORNE PARTICULATE MATTER

Introduction

One of the major missions of the Environmental Monitoring Systems Laboratory of the Environmental Protection Agency is to evaluate the application of new techniques for the measurement of air pollutants. This paper describes some of our work to date using supercritical fluid chromatography (SFC) to analyze semivolatile organic compounds in airborne particulate matter.

Experimental Methods

Equipment

The chromatography equipment is a Hewlett-Packard Model 1082 B Liquid Chromatograph equipped with two high pressure solvent pumps, a manual valve injector, a heated column oven, and a programmable variable wavelength UV detector. Modifications to permit the use of supercritical fluids as mobile phases have been described[1] and will only be outlined here. The pumpheads are insulated and cooled by a circulating ethylene glycol-water mixture at -20°C. A heat exchanger is installed between the column and the UV detector to eliminate light scattering caused by the turbidity of supercritical fluids. The flow cell in the UV detector is designed for high pressure operation. System pressure is maintained by a precision back pressure regulator placed after the UV detector. Two precision pressure gauges are provided to monitor system pressure: one is connected to the flow stream before the valve injector; the other measures pressure between the UV detector and the back pressure regulator.

Commercially available packed HPLC columns were used. A Vydac TP 201 octadecyl-silane (ODS) column was used for most of the work reported, but several other columns were investigated briefly; including Hypersil-ODS, Zorbax-ODS, Lichrosorb RP-8, Waters μ-CN, and Zorbax-SIL columns. Mobile phases initially consisted of industrial quality liquid carbon dioxide passed through a 2.5 cm ID x 50 cm column of silica gel. Later, "SFC-Grade" liquid carbon dioxide (Scott Specialty Gases, Inc.) became available and was used. The oven temperature was 40°C, above the initial temperature of carbon dioxide (31°C).

Methanol-carbon dioxide mixtures were prepared by weight in a 1-liter stainless steel sampling cylinder. Critical temperatures and pressures of these mixtures were calculated using mole fraction-weighted linear combinations of critical temperatures and pressures of carbon dioxide and methanol[2]. When methanol-carbon dioxide mixtures were used, the column oven temperature was set at 65°C.

to ensure that the mobile phase remained supercritical. The chromatograph was programmed to change the mobile phase composition from 1% to 10% methanol-carbon dioxide (w/w) by a linear gradient. The variable-wavelength UV detector was programmed to change monitoring wavelengths to allow selective detection of each successive component eluting from the chromatographic column. Peaks from unknown samples were tentatively identified by comparison of retention times at specific wavelengths with those obtained from standard solutions. Quantitation was carried out by manual measurement of peak heights. Capacity factors (k') were calculated according to the relationship

$$k' = \frac{t - to}{to}$$

where t is the component retention time and to is the solvent retention time.

Sample Extraction and Cleanup

Filters and samples of National Bureau of Standards (NBS) SRM 1649 (Urban Dust) were weighed into pre-extracted cellulose extraction thimbles and extracted with methylene chloride for 16-24 hours in a Soxhlet extractor. The solutions were then concentrated and solvent-exchanged into cyclohexane or hexane. Diesel exhaust extracts in methylene chloride were solvent-exchanged into hexane.

Several cleanup methods were attempted. Partitionings with nitromethane or dimethyl sulfoxide were tried and abandoned because of interferences and low recoveries. Fractionation over silica gel in a flash chromatography column[3] gave satisfactory results. Standard mixtures were eluted quantitatively with 1/1 methylene chloride/hexane. Chromatograms of unknown samples were free of obvious interferences.

Results and Discussion

The polycyclic aromatic hydrocarbons (PAH) used as reference standards in this work are shown in Table I. These PAH have from 3 to 7 fused aromatic rings and have a molecular weight range from 178 to 300. Each is frequently found in air particulate samples; and several are proven or suspect carcinogens or mutagens.

The effect of varying the system pressure on compound retention is shown in Figure 1. Retention times and capacity factors of individual compounds decreased as system pressure increased at constant temperature. Separation between adjacent peak pairs was not affected by system pressure. Variation of system pressure in SFC appears to have effects analogous to those obtained by variation of temperature in gas chromatography. Figure 2 shows that, within the range investigated, increasing temperature caused retention times and capacity factors

to increase, an effect opposite to that observed in gas chromatography. Separation of adjacent peaks was not affected by changing temperature. Use of methanol-carbon dioxide mixtures (up to 10% w/w) as the mobile phase greatly shortened retention times and lowered capacity factors.

Of the columns used in this work, the Vydac TP 201 ODS column was most retentive for the PAH studied. Figure 3 shows baseline resolution of all ten components using supercritical carbon dioxide as the mobile phase. The PAH isomers benz(a)anthracene (BaA)-chrysene (CHRY); and benzo(a)pyrene (BaP)-benzo-(e)pyrene (BeP) were readily separated on this column. Under the chromatographic conditions used, coronene (COR) eluted in approximately 2 hours. The wide separation of all components suggested that carbon dioxide-methanol gradients could be used to reduce analysis time while maintaining adequate chromatographic resolution.

Gradient operation and separation of the 10-component mixture is depicted in Figure 4. Coronene eluted after about 15 minutes, and the total analysis time was reduced to approximately 30 minutes including time for mobile phase equilibration after the gradient run. All components were baseline separated. Each peak represents from 13 to 18 ng per individual PAH injected on column.

The sample cleanup procedure and subsequent SFC analysis have been applied to several sample types. In cases where independent analytical data are available, the results obtained by SFC agree to within about 10% of values obtained by the independent methods. Figure 5 is a chromatogram of the PAH fraction from the NBS SRM 1649 (Urban Dust). The SFC-derived concentrations of benz(a)-anthracene (2.3 μg.g) and benzo(a)pyrene (2.5 μg/g) are 90% of the certified concentrations: 2.6 μg/g and 2.9 μg/g, respectively. This chromatogram illustrates that the variable wavelength UV detector used with the SFC has low sensitivity for trace environmental analysis. Even though large samples were used and gave high recoveries of PAH, the chromatographic peaks are close to the limits of detection (twice peak-to-peak noise).

PAH from a diesel exhaust extract are shown in Figure 6. This chromatogram shows the presence of benz(a)anthracene (BaA), benzo(b)fluoranthene (BbF), and benzo(e)pyrene (BeP), and possibly benzo(a)pyrene. There is no evidence for higher molecular weight PAH. The rising baseline at the later stages of the chromatogram was present in the blank and probably was due to impurities in the industrial quality carbon dioxide used in the mobile phase.

Figure 7 shows the PAH from a filter from the National Filter Analysis Network (NFAN). Peaks indicate benzo(b)fluoranthene (BbF), benzo(e)pyrene (BeP), benzo(a)pyrene (BaP), benzo(g,h,i)perylene (BghiP), and coronene (COR).

The amount of BaP found in this chromatogram (9.02 μg/filter) is 98% of the value obtained in the original analysis by thin layer chromatography (9.18 μg/filter)[4].

Conclustions

This work demonstrates that SFC provides rapid analysis for semivolatile organic compounds in environmental samples. Chromatographic resolution is moderate and is similar to that found in conventional HPLC. Low oven temperatures are required for elution of semivolatile compounds. However, the low sensitivity of the variable wavelength UV detector requires that large or concentrated samples be used, along with labor-intensive sample cleanup.

Acknowledgements

We thank Dr. Roy Zweidinger of the Atmospheric Sciences Research Laboratory, EPA, for the gifts of diesel exhaust extracts; and Jeffrey R. Adams of Northrop Services, Inc., for the NFAN filters and extracts.

References

1. D. R. Gere, R. Board, and D. McManigill, "Supercritical Fluid Chromatography with Small Particle Diameter Packed Columns", Anal. Chem., 736-740 (1982).
2. P. A. Peaden and M. L. Lee, "Supercritical Fluid Chromatography: Methods and Principles", J. Liq. Chromatog., 5(Suppl. 2): 179-221 (1982).
3. W. C. Still, M. Kahn, and A. Mitra, "Rapid Chromatographic Technique for Preparative Separations with Moderate Resolutions", J. Org. Chem., 43: 2923-2925 (1978).
4. D. H. Swanson, "Standard Operating Procedure for Ultrasonic Extraction and Analysis of Residual Benzo(a)Pyrene from Hi-Vol Filters", EMSL/RTP-SOP-EMD-015, Revision 1 (June, 1982).

PAH Reference Compounds

Anthracene	Benzo[b] fluoranthene
	Benzo[e] pyrene
Fluoranthene	Benzo[a] pyrene
Pyrene	
Benz[a] anthracene	Benzo[ghi] perylene
Chrysene	Coronene

Table I. PAH used in this work

Retention Varies with Pressure

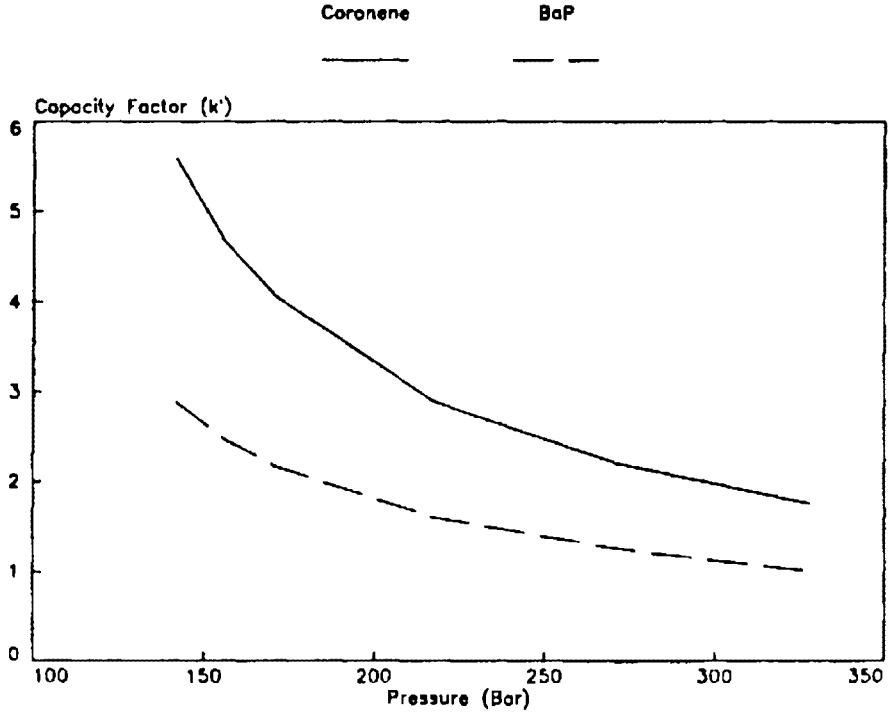

Figure 1. Dependence of retention on system pressure

Retention Varies with Temperature

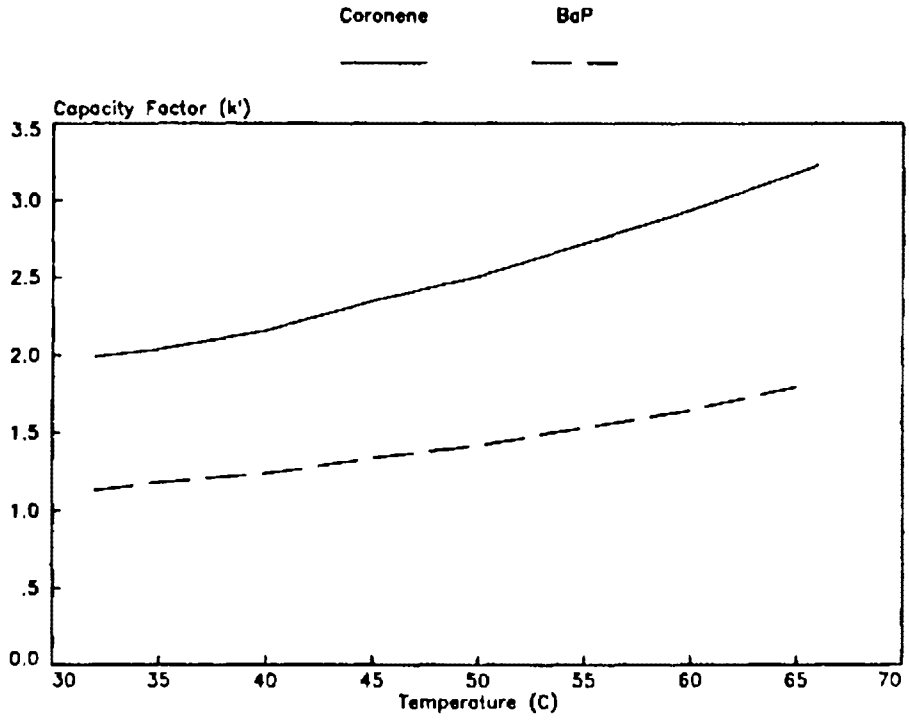

Figure 2. Dependence of retention on oven temperature

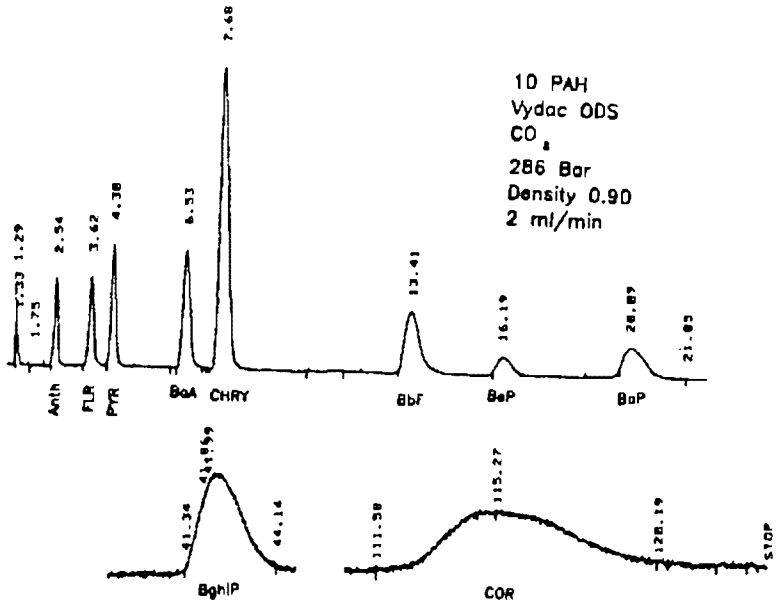

Figure 3. Chromatogram of standard mixture, carbon dioxide mobile phase

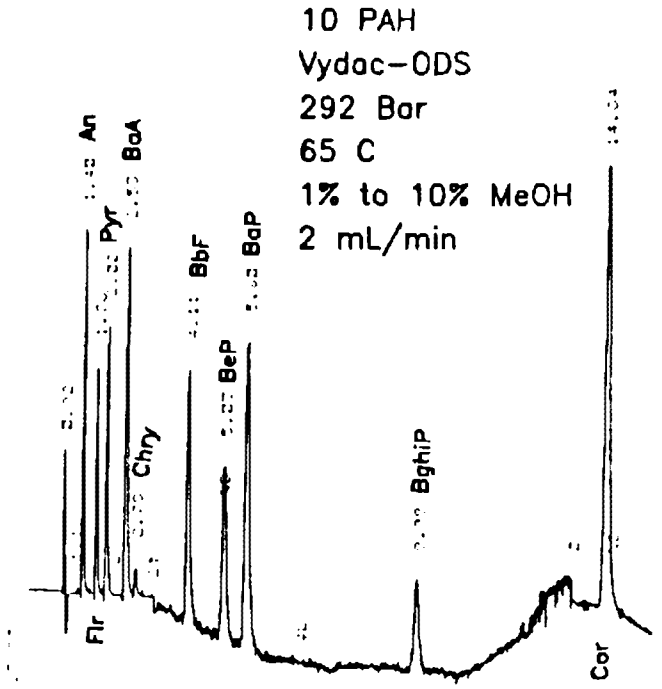

Figure 4. Chromatogram of standard mixture, gradient elution

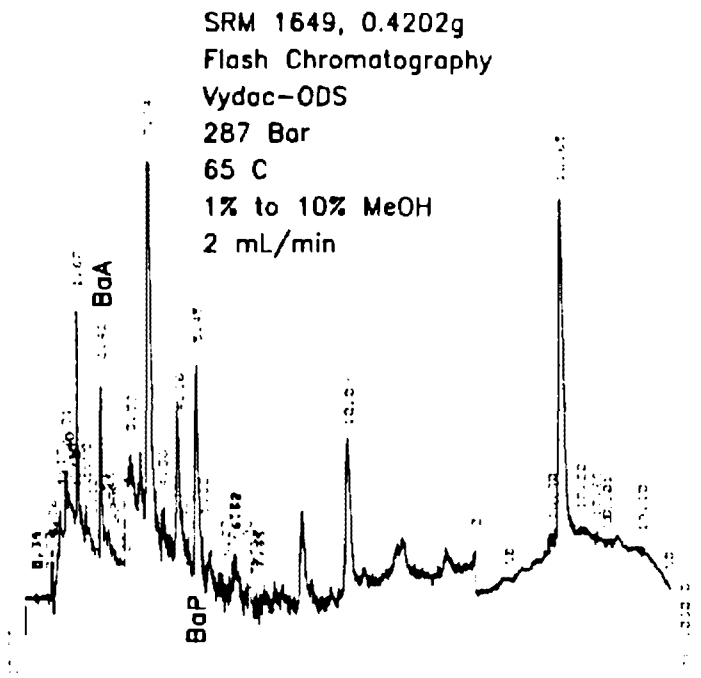

Figure 5. Chromatogram of SRM 1649 extract

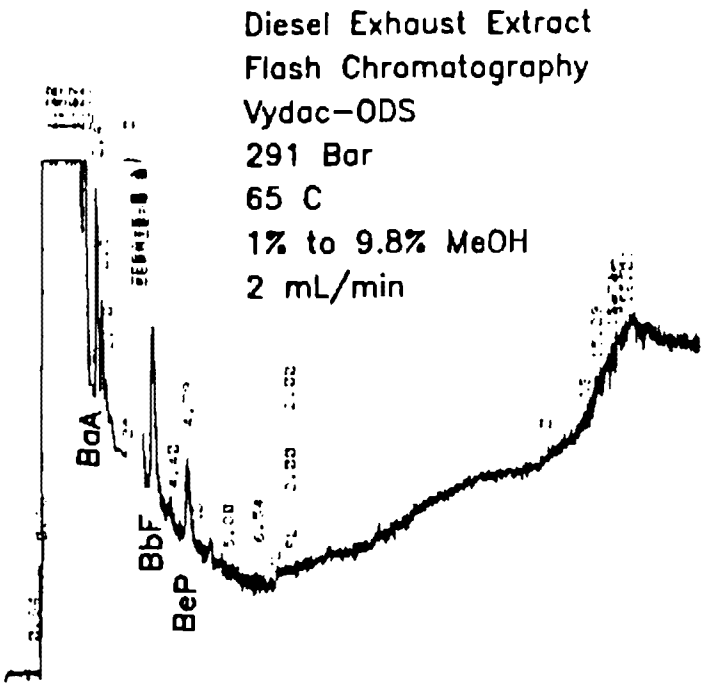

Figure 6. Chromatogram of diesel exhaust extract

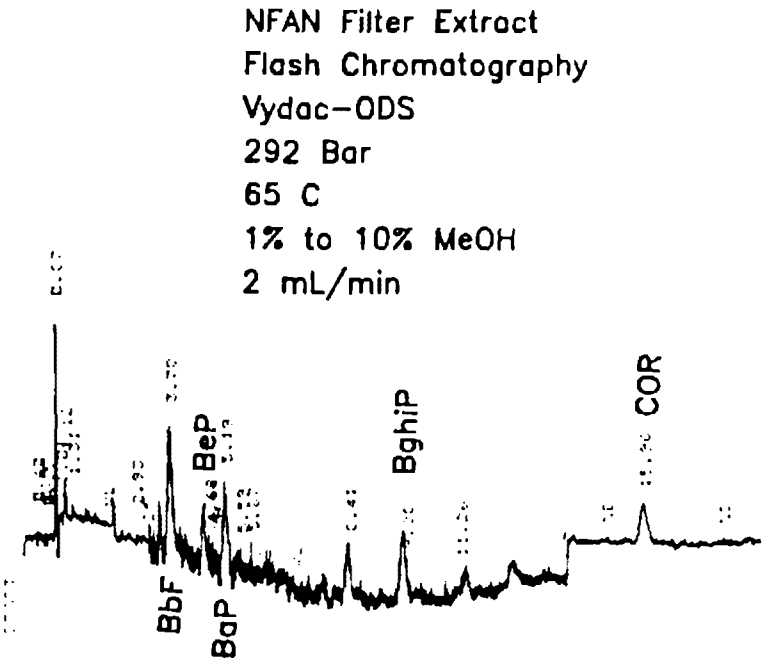

Figure 7. Chromatogram of extract of NFAN filter

DEVELOPMENT OF IMPROVED HPLC ANALYSES FOR NITRATED POLYCYCLIC AROMATIC HYDROCARBONS AND QUINONES FROM AIRBORNE INHALABLE PARTICULATE MATTER

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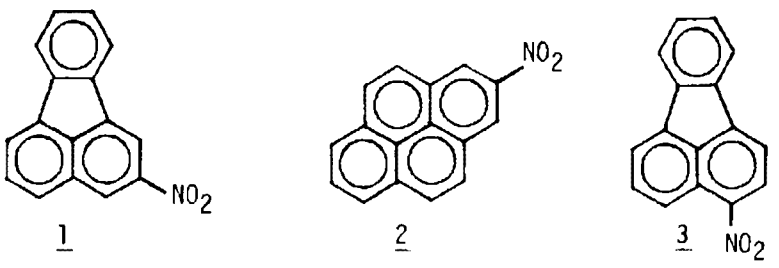
Nitrated polycyclic aromatic hydrocarbons (nitro-PAH), extracted from airborne inhalable particulate matter and separated by thin layer chromatography, are analyzed using HPLC. The analytical technique is a modified version of that reported by MacCrehan and May in which nitro-PAH are reduced on a post-analytical column filled with zinc and silica whereby amino-PAH are formed and monitored using fluorescence. The same technique has also been applied to the analysis of selected PAH quinones since the resulting dihydroquinones are frequently much more fluorescent than the starting material. As other groups have previously noted, most of the mutagenic activity of the extracts of airborne particulates is found in the more polar fractions. Among the compounds reported by other researchers are the hydroxynitro-PAH. We have synthesized a nonpolar member of this class, 1-nitropyren-2-ol, and find it in airborne particulates. The mutagenicities of a number of nitro-PAH and related molecules are also reported.

Introduction

Polycyclic aromatic hydrocarbons (PAH)[1] have long been used as surrogates for the carcinogenic activity of airborne dust, with benzo(a)pyrene frequently employed as the class archetype.[2,3] However, in recent years it has become quite clear that unsubstituted PAH are not the most important contributors to mutagenicity or carcinogenicity of air particulates.[4-6] Thus, attention has been focussed on nitro-PAH[7] such as 1-nitropyrene. These compounds are found in relative abundance in diesel particulate matter. For example, the levels of 1-nitropyrene and related compounds are typically one to two orders of magnitude lower than PAH concentrations. However, the certified concentration of 1-nitropyrene in the U.S. National Bureau of Standards SRM 1650 (Diesel Particulate) is about twenty times greater than that of benzo(a)pyrene.

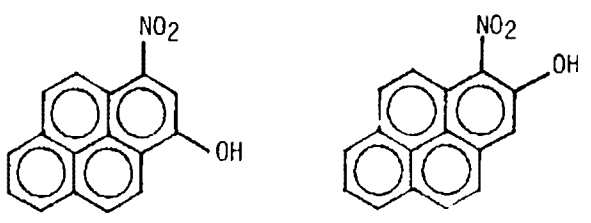
In contrast to the PAH which must be metabolized in order to be mutagenic, many nitro-PAH are powerful direct mutagens. In fact, some of these compounds, e.g. dinitropyrenes, are among the strongest known carcinogens.[7] Nitro-PAH found in airborne particulates could have their origin in a) generation during combustion, b) reactions of PAH during atmospheric residence, c) reactions of particulate-bound PAH on filters as an artifact during the sampling process. Although the extent of atmospheric reaction may not be very great, the high biological activity of some of these compounds is reason for concern.

Evidence for atmospheric nitration of PAH can be presented by noting reports of 2-nitrofluoranthene (1) and 2-nitropyrene (2) in airborne particulates.[8-10] These compounds are not found in source particulates nor are they formed in the usual simulation experiments, e.g. PAH on particulate-laden filters exposed to NO_2 or nitric acid. Previous reports of 3-nitrofluoranthene (3) are now known to be incorrect and it is the 2-nitro isomer (1) that is found.



1 2 3

The nitro-PAH, while more polar than the parent PAH, are still relatively nonpolar molecules. However, recent investigations[4-6] have shown that the greatest amount of mutagenic activity is found in more polar fractions.[4-6,11,12] Polar nitrated substances appear to play an especially important role.[11] A group of hydroxynitro-PAH (HNP), including 3-nitropyren-1-ol ("1,3-HNP, 4) as well as 1,6-HNP and 1,8-HNP may be responsible for a significant fraction of this activity. These substances are direct mutagens. A related compound, 1-nitropyren-2-ol (5), has been synthesized via photochemical reaction of



4 5

1-nitropyrene in acetonitrile.[13] It is an indirect mutagen requiring S9 activation and showing activity comparably to benzo(a)pyrene; this unusual behavior is attributed to intramolecular hydrogen bonding.[14]

Another natural depot for atmospheric PAH is the corresponding PAH-quinones formed via atmospheric oxidation. Pierce and Katz[15] reported levels of these compounds that were about an order of magnitude lower than even such reactive PAH as benzo(a)pyrene. The quinone levels were a greater percentage of the PAH levels during the summer season.

Experimental Methods

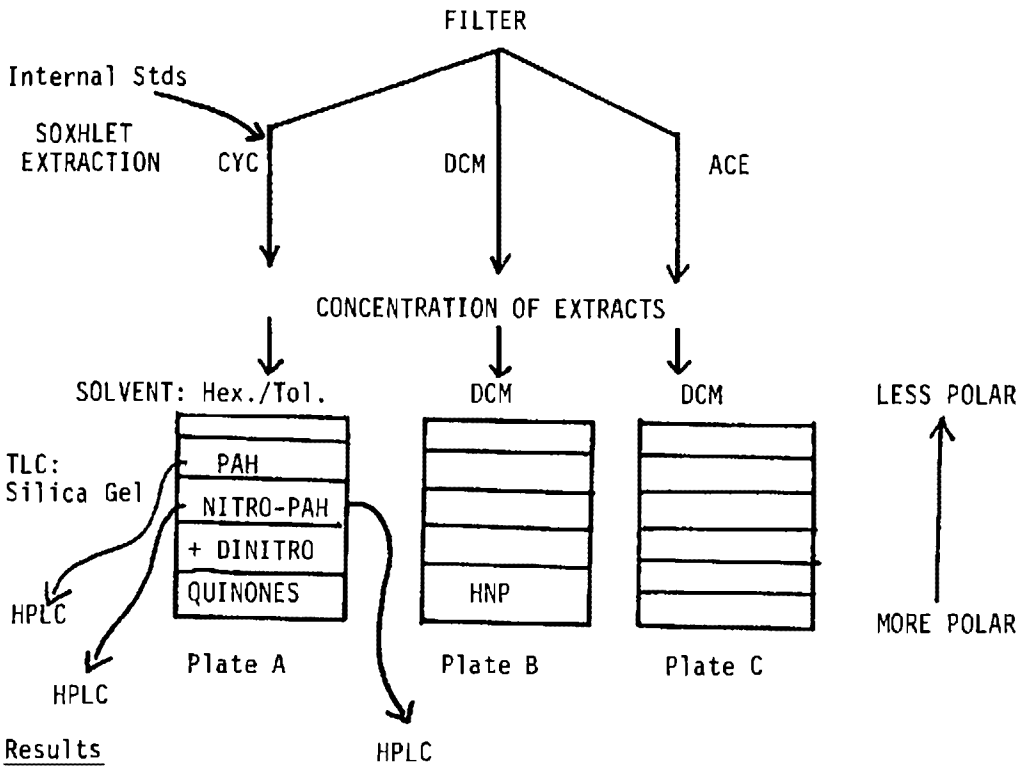
Inhalable airborne particulates (AD_{50} 10 micron) are collected on pre-fired quartz filters for 24-hour periods beginning at midnight on the roof of a two-story building in Newark, New Jersey at the residential/industrial location described in earlier discussions of the ATEOS project.[16] The filters are returned to the laboratory in envelopes and immediately soxhlet extracted or stored in the dark at -10 C for a brief period. Soxhlet extraction is done sequentially using cyclohexane (CYC), dichloromethane (DCM) and acetone (ACE). All solvents are HPLC grade. Internal standards, 9-methyltriptycene and 2-nitrotriptycene are added to the cyclohexane extract and the sample concentrated under reduced pressure to about 1 ml. The concentrate is the streaked along a 10 cm line on a silica gel GF TLC plate (Analabs, Inc.) and developed using 1:1 hexane/toluene. Zones on the TLC plate are noted using fluorescence as a guide and standard compounds to assign classes to zones. The sources of PAH have been described previously.[17] Pentacyclic quinones were purchased from the National Cancer Institute Chemical Repository as were most of the nitro-PAH. Tetracyclic quinones were purchased from the Aldrich Chemical Company. A mixture of 1,3-, 1,6-, and 1,8-hydroxynitropyrenes was a gift from Dr. Louise Ball, University of North Carolina and 2-nitrofluoranthene was a gift from Drs. Barbara Zielinska and Janet Sweetman, University of California Riverside. 1-Nitropyren-2-ol was synthesized and purified according to the published procedure.[13]

The PAH section of the TLC plate (plate A, Figure 1) is scraped and the adsorbent washed with tetrahydrofuran freshly distilled from lithium aluminum hydride. The PAH class was then analyzed via gradient HPLC using conditions previously described.[17] The results will not be described in the present paper.

Analysis of nitro-PAH is also done using HPLC with slight modifications of the method of MacCrehan and May.[18] The nitro-PAH section of TLC plate A is scraped and the adsorbent washed first with cyclohexane and then with methanol and the washings are combined and the solution concentrated. Analysis by gradient HPLC employs the Separations Group Vydac TP201 column with the acetonitrile/ammonium acetate buffer (pH 5.4) solvent system.[18] We run the solvent from 65 % to 90 % aqueous acetonitrile rather than to 100 % since this seems to lessen precipitation of salts. The column is temperature controlled to 15 C and detection is done with two UV channels (280 and 365 nm) and one fluorescence channel (360 nm, excitation; long pass, 440 nm emission). Rather than the reducer column described by MacCrehan and May,[18] we have designed disposable columns filled with zinc and silica.

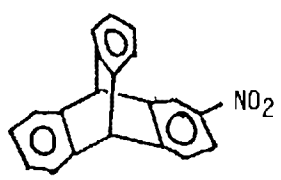
Analysis of PAH-quinones is done by washing the quinone section of TLC plate A and performing the same HPLC procedure as employed for nitro-PAH. (See Figure 1 for schematic of analysis). Previously, Pierce and Katz[15] published a "wet" chemical analysis of PAH-quinones. The present procedure is faster and is also quantitative relying on the fact that the dihydroquinones produced by reduction are stable in the closed, oxygen-scrubbed system.

Figure 1. Separation scheme applied to extraction of classes of organic pollutants from inhalable airborne particulate matter.



Results

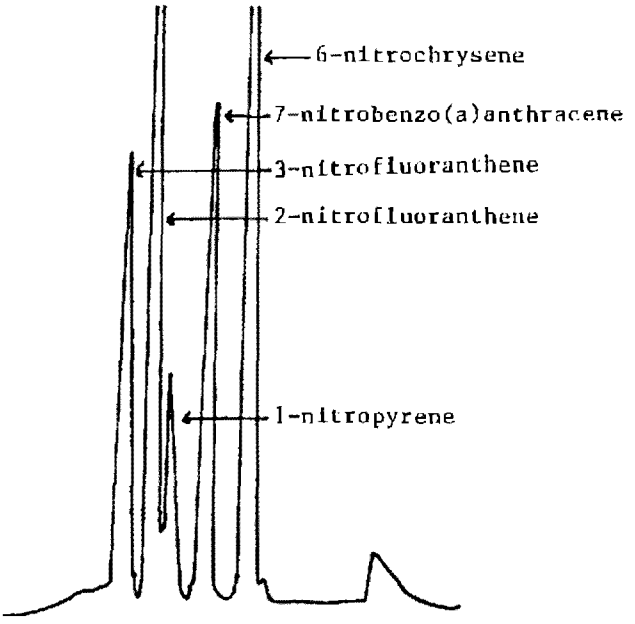
In the analysis of nitro-PAH, 2-nitrotriptycene (6) was employed as the internal standard in the manner in which we employ 9-methyltriptycene for the PAH.[17] Both compounds are spherical and elute early. Compound 6 reduces to the amino compound quantitatively. 2- Nitrotriptycene as well as the 2,6- and 2,7-dinitro derivatives are found to be nonmutagenic (Table I). The nitro derivatives of triptycene were synthesized according to published methods.[19]



6

Figure 2 is an HPLC chromatogram of a standard group of nitro-PAH. We are able to separate 2-nitrofluoranthene (1) and 3-nitrofluoranthene (2) under these conditions. In a complex sample, peak assignment is not always obvious and peak ratios often provide help in discrimating compounds. The peak ratios for 2-nitrofluoranthene are: 280/365 = 6.60; 280/FLUOR = 1.73; 365/FLUOR = 0.26. The peak ratios for 3-nitrofluoranthene are: 280/365 = 2.50; 280/FLUOR = 0.94; 365/FLUOR = 0.37. Taken along with an estimated tolerance of ± 25 % in the peak ratios, it is clear that peak assignments are possible but not as clear cut as they are when mass spectrometry is employed. The abundance of the m/z 217 (M - NO) fragment is 2 % for 1 and ca 40 % for 3. Kebbekus and Hawthorne[20] have achieved a degree of selective electrochemical detection for these isomers. Nevertheless, the peak ratios and relative magnitudes of the concentrations (i.e. 2-nitrofluoranthene levels are reported to be as much as

Figure 2: HPLC chromatogram (280nm detector) of selected nitro-pah-



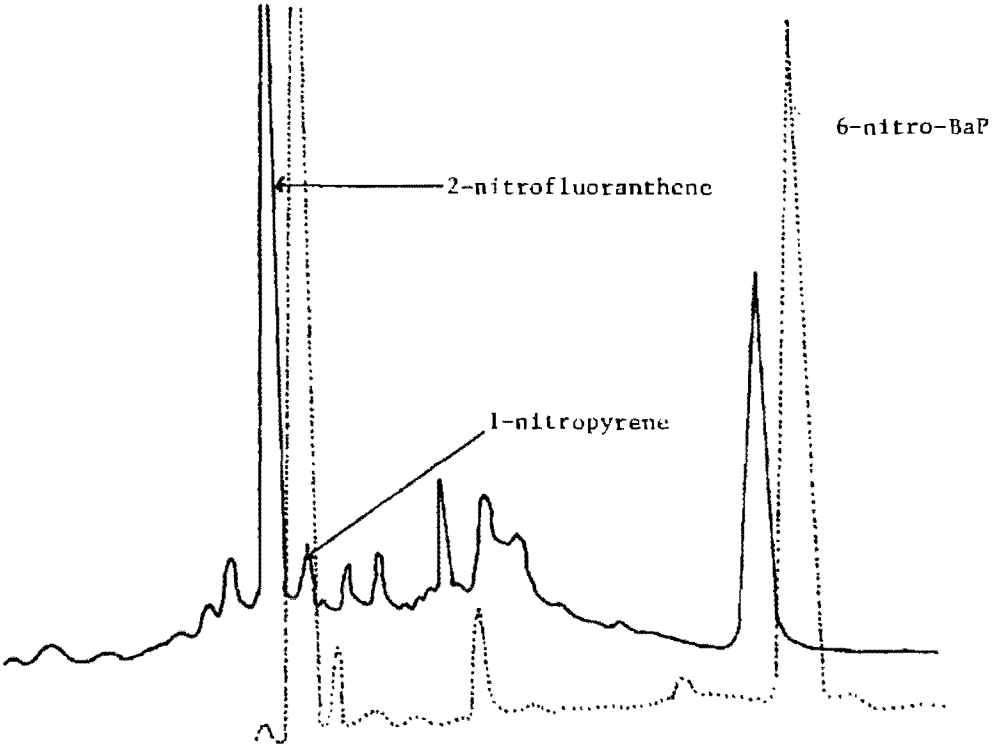


Figure 3: HPLC chromatogram of extract of Newark airborne particulate matter monitored at 280nm UV and Fluorescence(---), 360nm excitation and greater than 440nm emission with the aid of a reducer column

an order of magnitude higher than 1-nitropyrene levels[8]) lead us to conclude that we are finding 2-nitrofluoranthene. Figure 3 is an HPLC chromatogram of an environmental extract. The high level of 2-nitrofluoranthene relative to other nitro-PAH is apparent.

Analysis of 1-nitropyren-2-ol (5) is accomplished through separation via TLC of the nonpolar cyclohexane extract. In contrast to the other HNP, 5 is nonpolar due undoubtedly to the intramolecular hydrogen bonding previously postulated[13,14] which is also the source of its red color which allows monitoring at 546 nm, a fairly selective wavelength. Figure 4 shows an HPLC chromatogram of a Newark cyclohexane extract fraction from plate A monitored at 546 nm. 1-Nitropyren-2-ol is present and may be the end-product of atmospheric reaction by 1-nitropyrene in the presence of sunlight by analogy, by no means foolproof, with the photochemical synthesis in solution. The other hydroxynitropyrenes mentioned earlier are more polar and are likely to be present on the most polar sections of TLC Plate B (see Figure 1).

In agreement with the study of Lofroth et al[14], 1-nitropyren-2-ol is found to be an indirect mutagen only with reactivity comparable to that of benzo(a)-pyrene. The fact that TA98 NR (+S9) does not reduce mutagenicity is also consistent with their conclusion that the nitro group is not involved in the metabolism of this carcinogen.[14] Table I lists the mutagenic properties of 5 and other nitro-PAH tested in this work. The results compare well with those of other research groups.

PAH-quinones are found in the more polar fractions of TLC plate A (Figure 1), although their distribution between cyclohexane and dichloromethane extracts is not yet quantitated.Figure 5 shows the separation of eight isomeric pentacyclic quinones. UV absorbance at 280 nm and 365 nm is apparent but little fluorescence is observed without the reducer column. Figure 6 shows an HPLC chromatogram with the reducer column in place. It is clear that the pentacyclic dihydroquinones are much more fluorescent than their precursors.

Conclusions

HPLC using a post-analytical reducer column is a convenient technique for analysis of both nitro-PAH and PAH-quinones. HPLC also differentiates 2-nitrofluoranthene and 3-nitrofluoranthene and the presence of the former compound on ambient airborne particulates is confirmed. 1-Nitropyren-2-ol can also be analyzed using selective detection at 546 nm and/or the reduction/fluorescence technique. It is found in ambient airborne particulates and may be a photoreaction product of airborne 1-nitropyrene. 2-Nitrotriptycene is a useful internal standard for nitro-PAH analysis since it has novel HPLC properties, is quantitatively reduced and is nonmutagenic.

Acknowledgements

We thank the Office of Science and Research of the New Jersey Department of Environmental Protection for support of this project. We thank Clint Brockway, Diane Dudacik, and Roman Pazdro for their assistance in the laboratory.

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Figure 4: HPLC chromatogram of whole Cyclohexane extract of Newark sample at 546nm

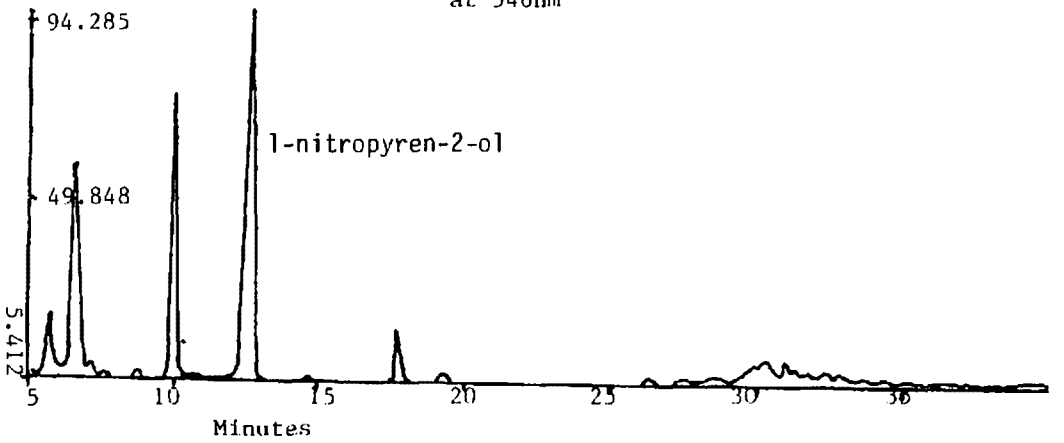


Table I. Mutagenicities of selected nitro-PAH in Revertants/ng.

Compound	This Study TA98(-S9)	TA98(+S9)	TA98NR	Other Studies[8,14] TA98(-S9)	TA98(+S9)	TA98NR
Benzo(a)pyrene	--	.063	.082	--	.0140	--
1-Nitropyrene	1.0	ND	.08	1.9	.23	.14
2-Nitrofluoranthene	.92	ND	.16	4.0	--	--
3-Nitrofluoranthene	13.4	ND	2.9	22.0	--	5.6
1-Nitropyren-2-ol	ND	.072	.061*	<.002	.10	--
3-Nitroperylene	.18	1.06	1.08	<.10	6.0	--
2-Nitrofluorene	.09	ND	.02	.22	est .18	.02
6-Nitrochrysene	.012	.15	.092*	<.05	.40	.006
9-Nitroanthracene	.001	ND	.001	.002	.002	est .0003
6-Nitrobenzo(a)pyrene	ND	.23	.24*	<.005	.70	--
9,10-Dinitroanthracene	.002	--	est .0005			
2-Nitrotriptycene	ND	ND				
2,6-Dinitrotriptycene + 2,7-Dinitrotriptycene	ND	ND				
2-Methyl-1-Nitro-anthraquinone	.002	.003	--			

*This is TA98NR (+S9); others are TA98NR (-S9).

Figure 5. HPLC of selected quinones without reducer column

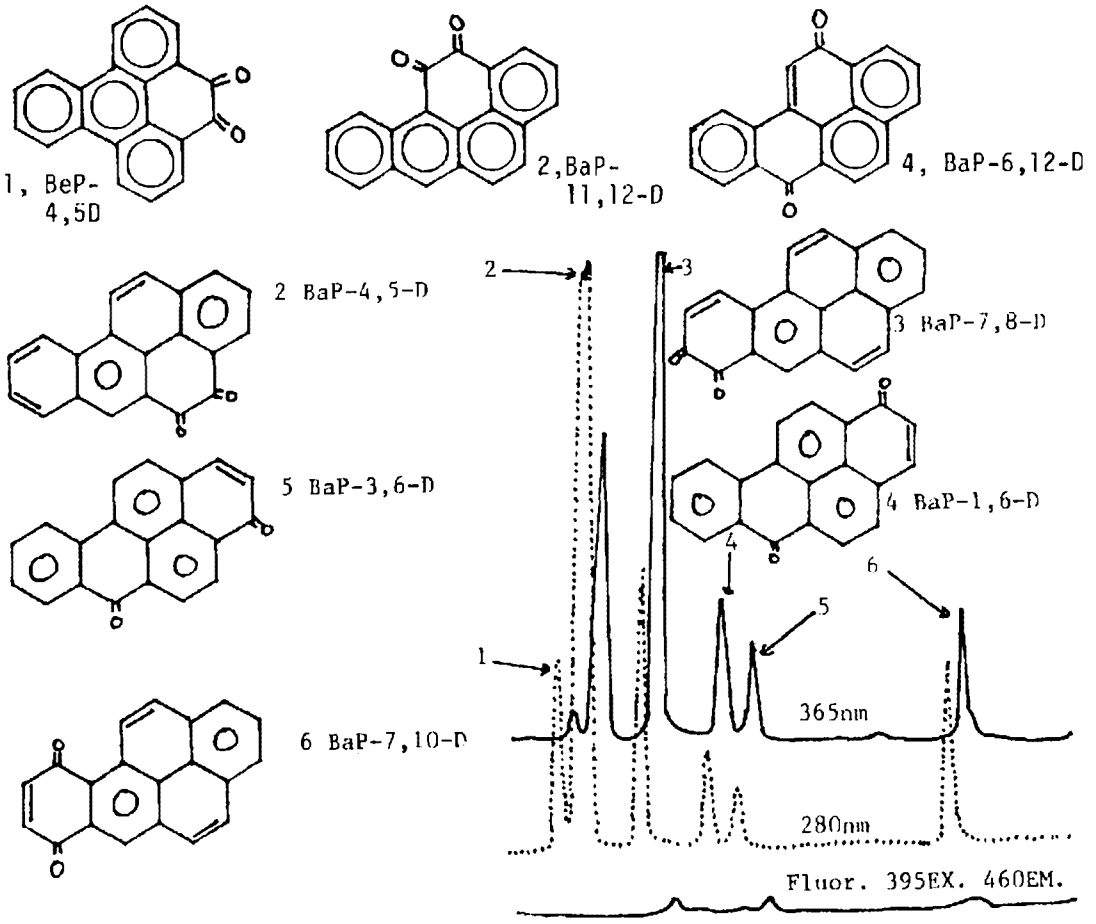
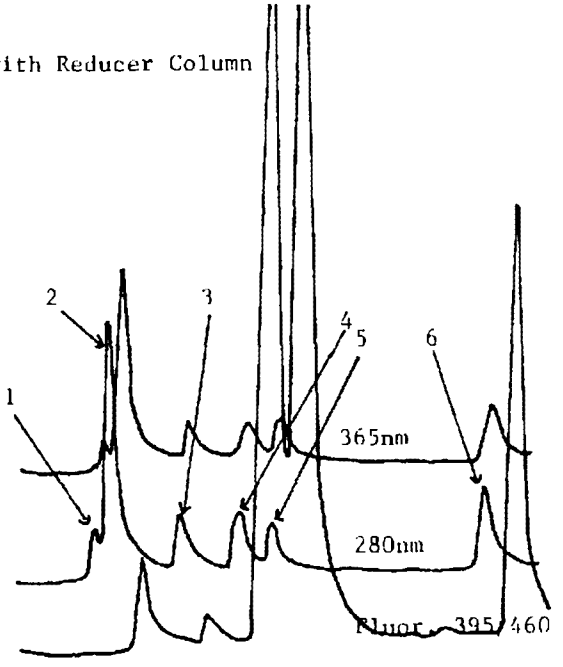


Figure 6: HPLC of Quinones with Reducer Column

1 4,5 Bep/D
2 4,5 Bap/D
11,12 Bap/D
3 7,8 Bap/D
4 6,12 Bap/D
1,6 Bap/D
5 3,6 Bap/D
6 7,10 Bap/D



ELECTROCHEMICAL DETECTION IN THE HPLC ANALYSIS OF NITRO-POLYNUCLEAR AROMATICS

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The analysis of extracts of particulate matter for oxidized forms of polynuclear aromatic hydrocarbons can be simplified by use of a detector which is selective for reducible compounds. The difficult separation of the components of this complex mixture is made simpler when the detector voltage can be adjusted so that the compounds of interest are reduced, and thereby detected, while other materials are not. The mercury drop electrode, with the HPLC column eluent flowing across its surface is used to monitor the occurrance of peaks of reducible material in the stream.

The system has been used to distinguish between two nitro-fluoranthene isomers, which are difficult to separate by HPLC.

Introduction

Particulates have long been recognised as an important component of air pollution. Total suspended particulate and smokeshade have been used as measures of air quality for years. As the components of this particulate were studied, interest has focused on some of the fractions which, while present at trace levels, appear to have significant potential for health effects. Studies of the polynuclear aromatic compounds in particulate led to interest in the products of these compounds after exposure to an oxidizing atmosphere, nitrogen oxides and ultraviolet radiation. Mutagenicity studies pointed to the conversion of the indirectly mutagenic PAH into such direct mutagens as nitroPAH[1].

The search for ever smaller amounts of certain compounds in the complex mixture presented by these environmental samples is a continuing challenge to the analytical chemist. To gain the specificity needed to identify these traces of material in the complex chromatogram, more selective detection systems are being called into use. In addition, the use of a pre-separation step to divide the extract of the organic materials into several fractions with column or thin layer chromatography is usually needed. The gas chromatograph/mass spectrograph is the method of choice for absolute identification of compounds, but these polar and rather nonvolatile compounds are difficult to separate by gas chromatography, and their mass spectra are often very similar. The compounds are more suited to liquid chromatographic separation, but detection of liquid chromatographic peaks by mass spectrometry, especially at trace levels, is not a mature technique as yet.

The use of an electrochemical detector has been suggested[2], since these oxidized compounds are amenable to reduction and the selectivity of these detectors can be adjusted by changing the reduction potential. The hanging mercury drop electrode was chosen, since it offers a wide reduction voltage range, and is not prone to surface contamination problems, which can occur with solid surface microelectrodes. The nitro-substituted PAH were selected as the first group to be tested.

Experimental

Apparatus. The model 310 polarographic detector electrode and LC flow system, powered by the 174A Polarographic analyzer was acquired from EG&G Princeton Applied Research. A Laboratory Data Control liquid chromatography pump and injector, and a Varian Variscan model 635LC UV/Visible detector completed the system. The column used for the separations was a PRP1 resin based, reverse phase column supplied by Hamilton. The signals were recorded on a strip chart recorder (Linear) and the area of the peaks was calculated using a SpectraPhysics Model 4000 integrator system.

Chemicals. The eluent is prepared from acetonitrile (Baker HPLC Grade) 90%, organic free distilled water 10%, with

0.05 mol/l of tetrabutyl ammonium chloride (Fluka), as supporting electrolyte. Standards were prepared from pure compounds obtained from the Chemical Repository of the National Cancer Institute, and the National Bureau of Standards. The 2-Nitrofluoranthene was graciously supplied by J. Sweetman and B. Zielinska, University of California, Riverside.

Procedure. The standards were prepared in acetonitrile. The eluting solution was filtered, then deoxygenated by bubbling nitrogen through the solvent reservoir, which was kept at about 50°C, to lower the solubility of gases. The solvent flow was set to 1 ml/min. Ten microliters of sample was injected onto the column, and the effluent passed first through the UV/Visible detector, monitoring the absorbance at 280 nm, then into the mercury drop electrode detector. The mercury drop is held at the selected voltage, in the range of -0.2 to -1.0 volts. The potential is measured vs a silver/silver chloride reference electrode, and a platinum wire is used as the counter electrode. A single mercury drop is used during the elution of the peaks from an injection, thus eliminating the vibrations caused when a drop is dispensed.

The DC current produced when a reducible species flows across the electrode surface is monitored on a strip chart recorder.

Results and Discussion

The linearity of response of the electrochemical detector was tested with a series of injections of nitrofluorene. The detector showed a linear peak area vs. amount response up to 100 ng injection.

To test the ability of the system to selectively detect compounds in the presence of other similar compounds, the isomeric pair 2-nitrofluoranthene(2-NFA) and 3-nitrofluoranthene (3-NFA) were selected. These two isomers have been the center of some discussion in the literature[3,4], where it has been reported that these isomers, detected in air particulates, may be artifacts formed on the collection filter by reaction with NO_3^- ions or N_2O_5. However, it has been shown experimentally that direct nitration of fluoranthene or the reaction with N_2O_5 of fluoranthene deposited on a glass fiber filter yields 3-NFA and several other isomers, but not 2-NFA. On the other hand, the gas phase reaction of fluoranthene and N_2O_5 yields only 2-NFA[5]. So, while these two isomers are difficult to separate by HPLC, it is important to determine which of them is present in an air sample. The presence of 3-NFA indicates direct emission of the compound, or possible artifact formation, while 2-NFA indicates the formation of the compound by reaction of the parent fluoranthene with N_2O_5 in the atmosphere.

A Huckel calculation was done on these two non-alternant hydrocarbons[6]. It was determined that there was a greater stabilization of the molecule when the 3-NFA was reduced to

the amine than when the 2-NFA was reduced. This indicated that the 3-NFA should be reduced at a less negative potential than the 2-NFA. The halfwave potentials could not be determined experimentally, since the amount of standard was very limited. The expected difference in halfwave potentials was not great, but a series of injections of the compounds at different potentials proved the prediction to be accurate.

At -0.7 V vs AgCl the 40 ng of the 3-NFA gave a readily measureable peak, while 68 ng of the 2-NFA was barely differentiated from the baseline noise at that potential. At -0.9 V, however, the 2-NFA was easily detected. Figure 1 shows the three chromatograms. The large peak labeled "a" is oxygen, which is present because, while the eluent is maintained oxygen-free, the samples are not deoxygenated. The peaks labeled "b" are 3-NFA in chromatogram 1 and 2-NFA in 2 and 3. Chromatogram 2 also shows the response from the UV detector, demonstrating the presence of the compound, even though almost no response was seen on the electrochemical detector at that potential.

There are several precautions to be taken when working with this detector. Since the electrochemical detector senses the quantity of reducible material in a very thin diffusion layer at the surface of the drop, any mechanical disruption of this layer will cause a erratic signal. The working electrode is a liquid drop, and so is extremely vibration sensitive. It is readily disturbed by such vibration-producing mechanical devices as pump motors. Placing vibration damping material under the electrode stand was of some help in reducing this noise. The use of the electrode in the hanging drop mode rather than the dropping mode also helped to eliminate vibrations. Attempts were made to use the system in the dropping mode, with a 1-2 sec drop time, sampling the current at the end of the lifetime of each drop. While this method eliminated the large oscillations in current seen as each drop formed and fell, the drop itself oscillated when it formed, and did not stop vibrating before the reading was taken, leading to a noisy signal.

The detector is also very sensitive to pulsations in the HPLC flow. These pulses deliver reducible material at varying rates, as well as disturbing the diffusion layer. A well damped pumping system, or a syringe pump system keeps noise low, and the lowest flow compatible with good chromatography is also helpful. The use of a microbore column is planned for future work with this system. Incomplete deoxygenation of the eluent and insufficient concentration of supporting electrolyte are also causes of high background current, high impedance, and noise in the system.

There has been little attempt to optimize the eluent or the column in our studies, since we were most interested in demonstrating the practicality of using the electrochemical detector in the reductive mode to selectively detect certain compounds. Solvent programming and a higher efficiency column are obvious improvements to be made in the system, in future work.

Conclusion.

When the separation is optimised, the electrochemical detector, as one of a series of detectors, can be used to add important information on the identities of peaks, by supplying an additional response, at a different level. The use of a UV-Visible absorbance detector in conjunction with the electrochemical detector enables the quantitation of coeluting peaks, since the magnitude of the response of the two detectors will be significantly different for each of the compounds. The electrochemical detector can be held at a potential which maximizes the response to one of the components in a coeluting peak, while being relatively insensitive to the other.

Further work is needed, however, in development of techniques to lower the noise levels in the detector, so that detection levels may be improved. A syringe pump with a microbore column is probably the best liquid chromatography system to be used with this detector. Improving the signal to noise ratio will also allow the use of differential pulse techniques, which will greatly enhance the sensitivity of the detector.

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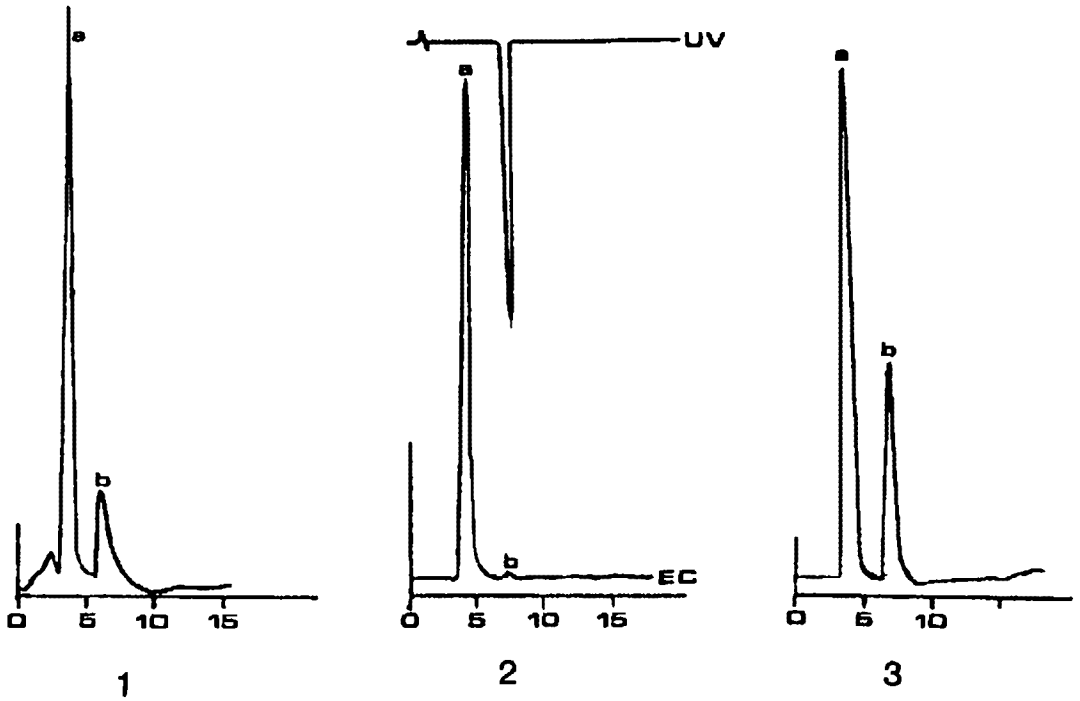

Figure 1.
a. Oxygen peak b. Nitrofluoranthene peak.
1. 40 ng of 3-NFA at -0.7 V
2. 68 ng of 2-NFA at -0.7 V
3. 68 ng of 2-NFA at -0.9 V

INSTRUMENTATION FOR SAMPLING AND CHARACTERIZATION OF TOXIC GASEOUS AND SOME PARTICULATE AIR POLLUTANTS

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A brief discussion of different approaches to sampling and monitoring of toxic air pollutants is presented. Sampling instrumentation design criteria are outlined. Grab samplers, passive samplers, personal samplers, single-use devices, in-situ measurement instruments and new, microcomputer controlled syringe and adsorbent tube samplers are compared.

The latter instruments provide automated, sequential, integrated collection of a variety of indoor and industrial pollutants, including hydrocarbon/halocarbon organic vapors, CO, CO2, HCOH, tobacco smoke, combustion and odorous mixtures, and particulate matter. In addition, the samplers can be used in indoor infiltration and air exchange studies. The instruments can be used in a complementary fashion for a variety of sampling tasks varying from simple screening tests to complex projects. These include industrial emission inventories, toxic waste site monitoring, indoor air quality, area/traffic monitoring and industrial hygiene applications. The analysis of automatically collected samples is done in a centrally located and properly equipped laboratory, typically using GC, LC and GC-MS instruments with multiple/specific detectors.

The paper describes design and operation of several samplers in some detail. Current and potential applications are also mentioned. Recently introduced passive samplers and sequential grab samplers are also described in general terms. Their use for toxic organic pollutant sampling is highlighted. The currently available sampling and analytical instruments provide for estimation of total exposure to toxic air pollutants, characterization of sources and types of pollutants in a timely and efficient manner.

INSTRUMENTATION FOR SAMPLING AND CHARACTERIZATION OF TOXIC GASEOUS AND SOME PARTICULATE AIR POLLUTANTS

Introduction

...Growing concerns about the impact of air pollutants on a large segment of the general population spending up to 80-90% of its time indoors, at work and at home, greatly intensify the interest of professionals involved in the sampling, monitoring and measurement of gaseous pollutants. The data obtained so far provides important, yet incomplete, information on the types of species present in indoor environments, the concentration distribution, and their toxicological effects (11). In order to meaningfully interpret data from pollution monitoring programs, the accuracy, reliability, and reproducibility of sampling and measuring techniques become major areas of concern. Additional demands placed on sampling programs include minimizing personnel and equipment requirements to meet specific measurement tasks, and low maintenance and replacement costs. Typical areas of interest are indoor residential and work atmospheres (1; 13; 14), industrial environments, and studies concerned with dispersion, transport and fate of toxic air pollutants (2). Most of the above activities require continuous monitoring of gases of interest, which include toxic or otherwise undesirable species. In this manner characterization of gas, and in some cases also particulate air pollutants, their sources, and estimation of total exposure can be achieved.

Description and Comparison of Currently Available Sampling Devices

...Several approaches are utilized for pollutant gas sampling. Manual grab samplers (various containers, syringes, or plastic bags) are widely used. Their advantages include simplicity and low initial cost. The drawbacks are high manpower requirements, low reliability, and unsuitability for larger studies. In some cases sampling has been semi-automated; that is, flasks or plastic bags were equipped with pumps, manifolds and timers. However, concerns about sample integrity, logistics problems and operating costs arose.

With the advent of new technologies in the 1970's, a number of smaller, continuous, gas analyzers appeared on the market. Some of them are suitable for in-situ measurements of a variety of gaseous species, particularly reactive gases such as ozone, nitric oxide, nitrogen dioxide, sulfur dioxide, and radon. Recently, highly portable, personal monitors have been introduced (10). These instruments are used for measuring carbon monoxide, carbon dioxide, hydrogen sulfide, vinyl chloride, combustible gases, ammonia, formaldehyde, ethylene oxide, and some hydrocarbons. Presently these compact units measure only relatively few gaseous species, typically at ppm or higher concentrations. In-situ measurements of toxic contaminants are highly desirable, but frequently not feasible because of the high cost, the need for skilled personnel, complicated logistics, and limited availability to a number of users. Increased demands for polluted atmosphere characterization, including measurement of gases such as formaldehyde, and measurement of indoor/outdoor air infiltration rates led to the development of low cost passive samplers, and miniature tracer gas sources (5).

Recently, as a result of U.S. EPA's research and developmental effort (4) unique, thermally desorbable passive samplers became available. These very compact, simple and rugged sampling devices can be used for monitoring of

volatile organics in ambient air, and for short (1 hr.), or long-term (8-24 hr) personal monitoring in indoor and industrial environments. The sampling concentration range extends from sub-ppb level to high ppm level. The reusable/rechargeable and cost-effective passive samplers use a series of stainless steel screens (Figure 1.) and a stable, thermally desorbable Tenax adsorbent for sampling of over 20 toxic organic gases. The samplers exhibit high equivalent pump rate, high sensitivity and multicomponent capacity. The "Summa" passivation of all exposed stainless steel components assures sample integrity and convenient thermal desorption via a stand-alone, purgeable desorber unit. These new passive samplers compare very favorably with active (pump-based) samplers and have considerably better sensitivity then the other commercially available passive samplers using active charcoal. The passive samplers are available in a standard and reduced sampling rate configuration.

Several manufacturers now provide inexpensive, single use, gas detector tubes for an approximate determination of over one hundred different gases at the ppm to % concentration. These tubes are suitable for screening and to some extent qualitative purposes rather then more accurate quantitative determinations.

Toxic Air Pollutant Sampler Criteria

...The preferred approach to toxic air pollutant sampling/monitoring uses sample collection over the desired length of time with multipurpose, versatile, and preferably automatic gas samplers. Frequently, the protocol for sampling and monitoring gaseous contaminants requires sampling environments of interest at desired times and locations (8). Operation of a number of relatively expensive in-situ analyzers can create significant logistics problems and result in considerable expenditure of resources whereas a number of lower priced automated samplers will perform at multiple locations, 24 hours a day, with no external power or consumables such as special gases required. Subsequent sample analysis can be conveniently carried out in a central, permanently based, properly equipped and staffed analytical laboratory.

The main areas of concern in the sampler construction and operation are reliability, size, procurement and operating costs. Desirable characteristics of industrial and indoor toxic gas samplers are ruggedness, continuous, unattended operation capability, and flexibility in their use. One of the few limitations imposed on the automated samplers is the reactivity of sampled gases. Ozone, oxides of nitrogen, and sulfur dioxide cannot be stored for any length of time. Other gaseous species may be collected and stored in suitable containment vessels made of polymeric materials, glass, and some metals. Frequently, sampling devices such as the plastic bags are not suitable for collection of air samples because of contamination and permeation characteristics (9), difficult handling, and overall unreliability. Most types of analyses require sample size from a few millilitres to number of litres. An automated, multi-station sampler utilizing suitably sized syringes (6), or sample tubes containing user selectable, solid adsorbent such as Tenax for efficient gas vapor trapping (3; 16), can collect necessary volume of samples for the analysis of indoor pollutants. An additional advantage of these samplers is the positive displacement mode, and high efficiency of sample collection of larger volumes of gas mixtures lending themselves to convenient syringe sample analysis or thermal/solvent desorption of sampled tubes and/or impregnated filter cartridges.

Experience with design and construction of automated, single to twelve

station samplers used in atmospheric tracer studies (7) enabled introduction of several types of samplers meeting the above criteria for collection of indoor/industrial air samples suspected of containing pollutant gases. The main advantages of automated syringe/adsorbent tube samplers are the advanced design, cost-effectiveness, average reliability of 97% (15) compared to about 60-85% for the bag samplers), compactness, and a variety of possible sampler applications.

Automated Sequential Syringe Sampler Design and Operation

...The SS-12A series, commercially available gas sampler contains an advanced timing system which allows automatic collection of twelve, sequential, time-averaged gas samples. Rack and pinion gears driven by a stepper motor mechanically actuate each syringe. In operation, the syringe plunger remains stationary while the rack and pinion drive gradually extends the syringe body. At the end of travel, the syringe needle drives into a silicone septum, and power transfers to the next syringe. Alternately, the syringe can be equipped with a multiport valve and an adsorbent tube and cycled repeatedly until desired volume of air is sampled in each sample tube. A digital clock, controlled by a quartz crystal oscillator governs the operation of the sampler. The overall time accuracy is better than + 0.001% and the station-to-station sampling time reproducibility is about + 0.01%. The time base interval (2-8 minutes) is internally selectable. A time-base multiplier (1 to 15) is incorporated in the control electronics. An operator can pre-program the unit up to 15 days ahead of the actual operation, locate it on a suitable site, and leave it unattended. The sampler will start collecting sequential, time-averaged samples (each ranging from 2 minutes to two hours) at the pre-selected time, and upon collection of each sample, seal the syringe needle to prevent diffusion or sample contamination. The adsorbent tubes are sealed with a check valve on the inlet end and the multi-port valve at the outlet end. The unit can be very quickly turned around for another sampling cycle. A rechargeable battery, which allows up to 50 hours of continuous operation, assures portability. An optional 115/230V A/C power supply kit is available. The unit is enclosed in a sturdy aluminum case, secured with two key locks, and easily portable by one person as the overall weight is approximately 15 kg (33 lbs).

The automated syringe/adsorbent tube gas sampler (Figure 2.) can be readily adapted for special operating requirements. It can be used in areas inaccessible to operators because of toxic gases or other hazards. A manifold can be attached to allow sequential sample collection from a continuous (process) gas stream, or other source. Glass, or "Summa" passivated stainless steel syringes are available for collection of gases which require an inert, non-contaminating, non-reactive surface for maintenance of sample integrity. Table II. provides a listing of recommended syringe construction and adsorbent materials for sampling a variety of pollutant gases. Sampler syringes can be equipped with integral shut-off valves in place of the needles. Optionally, two to six syringes can be collected simultaneously to provide larger sample size. An impregnated membrane filter cartridge can be installed on the syringe to provide a low-volume particulate matter sampling capability.

A microcomputer controlled SS-12B/MCC syringe sampler has been recently introduced to provide considerably enhanced sampling capabilities. A hand-held size Sharp-1500A microcomputer, with an expandable RAM memory up to 24K can be programmed in the BASIC language and further enhanced with the use of MACHINE language. A custom designed interface allows the computer (with an internal clock) to control all sampling parameters such

as the start time, lenght of sampling, stop time, setting individual sampling parameters for each sampling station, compilation of all pertinent data, i.e sample I.D. and the corresponding collection times. In addition, full control of equipment such as sampling pumps, valves, various sensors, and compillation/processing of analog or digital signals can achieved. A RS-232 interface enables data transfer for further processing or storage in a PC or a larger computer system. The microcomputer enables the SS-12B/MCC syringe sampler to collect up to twelve completely independent samples, to collect one or more duplicate samples, to provide any (user selectable) delay between samples, to deliver (inject) the collected samples via a manifold to an analytical system such as GC or GC-MS, and to operate one or more syringes as syringe pump(s). After completion of sample collection or sample delivery cycle the microcomputer LCD displays the sample I.D. #, and individual sample collection start and finish time. This information can be printed out on an accessory, portable printer, or transfered to a PC or other computer via optional RS-232 interface.

In the dual sampling mode the automated sequential syringe sampler is equipped with a mechanically actuated, multi-port valve attached to the syringe. A sampling tube containing a suitable solid adsorbent, or an impregnated filter cartridge is placed ahead of the valve and the syringe. The syringe acts as a small, fixed volume pump. The sampler electronics allows multiple, individual syringe actuation providing a flow of sampled air through the sampling tube during the active stroke, and exhaust of air that passed through the sampling tube, from the syringe to an optional secondary adsorbent tube, during the passive stroke. In this mode, several litres of sampled air can be pulled through each sampling tube, and the cycle can be repeated up to twelve times.

Automated Sequential Adsorbent Tube Sampler Design and Operation

...Two new instruments, a portable, remotely controlled adsorbent tube sampler Model ARS-7 and an advanced Model ATS-12/36 are available for a multitude of environmental sampling tasks. The ARS-7 sampler weighs less than 2.3 kg (app. 5 pounds). This model is a lightweight version of the larger ATS-12/36 sampler. It utilizes seven adsorbent tubes and simplified electronics for remote sampling in a variety of environments via proportional radio control (RC). The sampler is particularly suitable for (airborne) vertical profile sampling of air pollutants, using a tethered ballon as a sampling platform. Commercially available winch systems allow sampling from ground level to heights exceeding one mile (1.6 km.). Sampler can also be used for ground sampling that requires remote sampler placement/actuation in hazardous environments, or applications that require a grid sampling in a larger area and central control of the sampling sequence. A built-in flash unit provides a visual indication of individual sample collection.

The latest model: ATS-12/36 (Figure 3.) weighs about fourty pounds (app. 18 kg) and is designed as a multipurpose instrument. The Sharp-1500A microcomputer controls the entire operation of the sampler, including sophisticated timing functions, sampling flow rate(s), sampling parameter storage/retrieval and communication with external data systems. The sampled air or other environmental gaseous mixtures are passed through glass or metal tubes, packed with a solid adsorbent selected by the user. The choice of adsorbents include Ambersorb, Tenax, molecular sieve, activated charcoal, or other suitable materials. In addition, the sampler can be used with the standard 25 mm filter assemblies to permit gas sampling on impregnated membrane filters, or to carry out low volume particulate matter sampling. The adsorbent tubes and filter assemblies can

be used separately or simultaneously for parallel sampling tasks. A "tray" arrangement permits installation of up to three trays, each containing twelve tubes for extended sampling programs. The removable/reloadable trays come in several configurations. Adsorbent tubes are thermally desorbed in commercially available thermal desorbers, or in a stand-alone microcomputer controlled D.S.I. desorber unit (currently under development). Impregnated membrane filters or low volume particulate sampling cartridges are individually removed and solvent extracted.

The gas flow is provided by a compact, low-power pump located downstream from the sampling tubes. Several pump types are available, including microcomputer/mass-flow controlled pumps, providing a highly regulated, accurate flow in the 20-5,000 ml/min. range. A commercially available, miniature mass flow sensor and A/D and D/A converters with associated electronics are controlled by the microcomputer which varies the sampling pump operating voltage to maintain the pre-programmed sampling flow. The sampling flow is updated and displayed on the microcomputer's LCD every 2 seconds. This value is an average of ten readings taken by the microcomputer. The unit records a cumulative mass flow through the adsorbent tubes or impregnated filter cartridges and provides the total mass volume of air or other gas media for individual samples at STP. The mass flow control system can be easily calibrated. At the end of the sampling cycle the individual sample I.D. #, sampling start and sample collection time, and total mass volume can be displayed, or printed out on a portable printer. Figure 4. represents a system diagram of the ATS-12/36 adsorbent tube sampler. The sampling data can be transfered to a larger computer system via an optional RS-232 interface. Extensive software is available for the operation, calibration and diagnostics of the ATS-12/36 sampler. Custom software can be provided for special applications.

Recently, a stainless steel bellows, constant volume pump has been introduced by D.S.I. This pump provides positive displacement, continuously variable flow of gaseous mixtures in the 1 to 500 ml/min. range. The pump utilizes fixed volume bellows driven by a geared motor which is controlled by a Sharp-1500A microcomputer. Electrically actuated/computer controlled valves provide for operation of the bellows inlet and outlet ports. The design and construction of the bellows pump provide for high accuracy, reproducibility, reliabilty, and a contamination-free flow of sampled mixtures. The bellows pump can be used for calibration of other pumps or flow control devices, and can be installed in the ATS-12/36 sampler or other sampling and analytical systems.

The sampling is done sequentially, and up to thirty six samples can be collected. In addition, a remote control is available for a manual "override" of the microcomputer program by means of a cable providing DC voltage. The per-tube sampling time ranges from less than one minute to many hours. Each sampling tube is separated from the sampled media by an upstream, miniature solenoid valve and a downstream flow restrictor. Optional downstream isolation solenoid valves can also be provided. Several valve materials are available, i.e. stainless steel, brass and teflon. The tube and filter cartridge tray assemblies can be readily exchanged within a few minutes. The samplers can be placed in desired field sampling locations, suspended from suitable supports, or installed on ground or airborne sampling platforms. The sampler is powered by either a rechargeable lead/acid gel battery or a 115/230V AC power supply.

The sampler applications include on-site sampling of pollutant and tracer gases, industrial process and atmosphere sampling/monitoring, indoor pollution studies, toxic gas and waste disposal site monitoring. The sampled gases include a variety of hydrocarbons, halocarbons, and other

toxic industrial and indoor pollutants, depending upon the choice of the adsorbent media. The sampled gases can be desorbed from the tubes into the appropriate analytical systems thermally, or by means of suitable solvents.

Automated, Sequential Grab Sampler Design and Operation

...The microcomputer controlled sequential sampling mode is also applicable to grab sampling by means of "Summa" passivated stainless steel containers. A variable number (2-6) of 0.5 to 6.0 liter sampling containers is connected to a common manifold which is equipped with miniature (on/off) solenoid valves. A compact, inert sampling pump powered by a rechargeable 12VDC battery provides flow of up to app. 5l/min. of sampled gas. Flow regulation can be provided by a calibrated fixed orifice, mechanical flow controller or an electronically controlled mass flow controller. All of the sample collection timing and control functions are provided by a small, inexpensive microcomputer. The cost/benefit analysis indicates that use of a carefully selected, low cost, hand-held size microcomputer is considerably more advantageous then use of standard PC boards. A self-contained, portable automated grab sampling system can provide sequential, time-averaged sampling/monitoring (from less than one minute to many days) of point sources of pollutant gases and indoor and industrial atmospheres. In addition, it can facilitate toxic waste site monitoring, emission inventory surveys and urban atmosphere characterization. The collected gas mixtures are stored and transported in the well tested and field proven passivated stainless steel grab sampling containers which are easily removable from the sampling system. The laboratory analysis utilizes single, or multiple specific detector GC and GC-MS instrumentation.

Toxic Gas Sampler Applications

...The applications list for the passive, grab and syringe/adsorbent tube samplers is still growing. Some organizations are using the samplers in indoor pollution studies and in determining air infiltration rates (12). Other uses include industrial and process atmosphere monitoring, plant surveys, area/traffic monitoring and tracer gas studies where reliable quantitative and qualitative data is required. Table I. gives a partial listing of studies utilizing the automated, sequential gas samplers. In all cases a profile of the concentrations of sampled pollutant gases as it relates to source emissions, process evolution, air exchange rates, and time-series changes can be obtained. In addition, individual pollutants can be identified. Additional applications will develop as the users in industry, consulting firms, and regulatory agencies begin exploring the new approaches to gas/particulate contaminant collection and monitoring.

Conclusions

...Automated, time-averaged sampling of gaseous and particulate toxic pollutants is gaining acceptance in industry, with consulting firms, and regulatory agencies. Inherent reliability, efficiency, portability, and moderate cost make the automated, sequential samplers a versatile tool for a variety of air pollution studies. Utilization of the automated gas/particulate matter samplers in conjunction with reliable analytical techniques makes the estimation of total exposure to indoor and industrial pollutants, characterization of sources and types of pollutants possible in a timely and efficient manner. As a result, appropriate steps can be taken to prevent, or significantly reduce the exposure of a large number of people to harmful gas and particulate pollutants.

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TABLE 1. PARTIAL LISTING OF STUDIES USING DSI AUTOMATED TOXIC GAS SAMPLERS

Organization	Location	Time	Application
U.S. EPA/Research Triangle Institute	Research Triangle Park, N.C.	1983-84	Air Exchange Rates/ Indoor Air Quality
U.S. EPA	RTP, N.C.	1984-86	Indoor Toxic Gas Meas.
Geomet Technologies/ EPRI	Gaithersburg, Maryland	1983-85	Air Exchange Rates/ Indoor Air Quality
Rockwell Int./EMSI/ Aerovironment/EPRI	Numerous locations in continental U.S.	1982-85	SF6 Tracer Experiments (PMV&D and other)
Washington State University	Pullman, WA; U.S & foreign locations	1982-86	Air Infiltration/ SF6 Tracer Studies
Louisiana State U.	Baton Rouge, LA	1984-86	Tox. Site Monit./SF6 Exp.
Exxon Research and Engineering Company	Florham Park, New Jersey	1983-	SF6 Tracer Studies/ Industr. Atm. Sampling
California Institute of Technology	Pasadena, California	1983-1985	SF6 Tracer Studies/ Indoor Air Sampling
U.S. DOI/ Bureau of Mines	Pittsburgh, Pennsylvania	1983-	SF6 Tracer Studies/ Work Atm. Sampling
U.S. Army CRDC/RD	APG, Maryland	1984-86	Infilt./Sim. Disp. Exp.'s
Battelle PNL	Richland, Wa	1985/86	PFC Tracer/Indoor AQ
DuPont (SRL): MATS	Aiken, S.C.	1985/86	SF6 Tracer Experiments
Westec/API	Santa Barbara, CA	1985	SF6 Tracer Experiment

TABLE II. SUITABLE SYRINGE CONSTRUCTION AND SOLID ADSORBENT MATERIALS FOR TOXIC GAS POLLUTANT COLLECTION

Type or Group of Gases to be Collected	Concentration Range (Parts: Vol./Vol.)	Recommended Syringe Material	Comments
Inert, man-made gases: SF_6, Fluorocarbons (1)	10^{-12}--------10^{-3}	Polyethylene	Glass or S.S. equally suitable
Fluorochlorocarbons, Halogenated HC's (1)	10^{-10}--------10^{-6}	Passivated Stainless Steel	Tenax or other adsorbents O.K.
Hydrocarbons and Halocarbons (1)	10^{-5}--------10^{-3}	Polyethylene	Glass or S.S. equally suitable
Hydrocarbons	10^{-10}--------10^{-6}	Passivated S.S., glass suitable	Tenax or other adsorbents O.K.
CH_4, CO_2, N_2O, and most inert gases	10^{-7}--------10^{-3}	Passivated S.S.	
Toxic gases (per EPA classification) (1)	10^{-9}--------10^{-4}	Passivated S.S.	Tenax or other adsorbents O.K.
Formaldehyde	10^{-7}--------10^{-4}	Not applicable	Mol. sieve ads.
Tobacco smoke, odorous, combustion and other complex gas mixtures	10^{-9}--------10^{-4}	Passivated S.S. usable in some cases	Tenax, activated charcoal, or other adsorbents

(1) These gases can be also adsorbed on suitable solid adsorbent materials

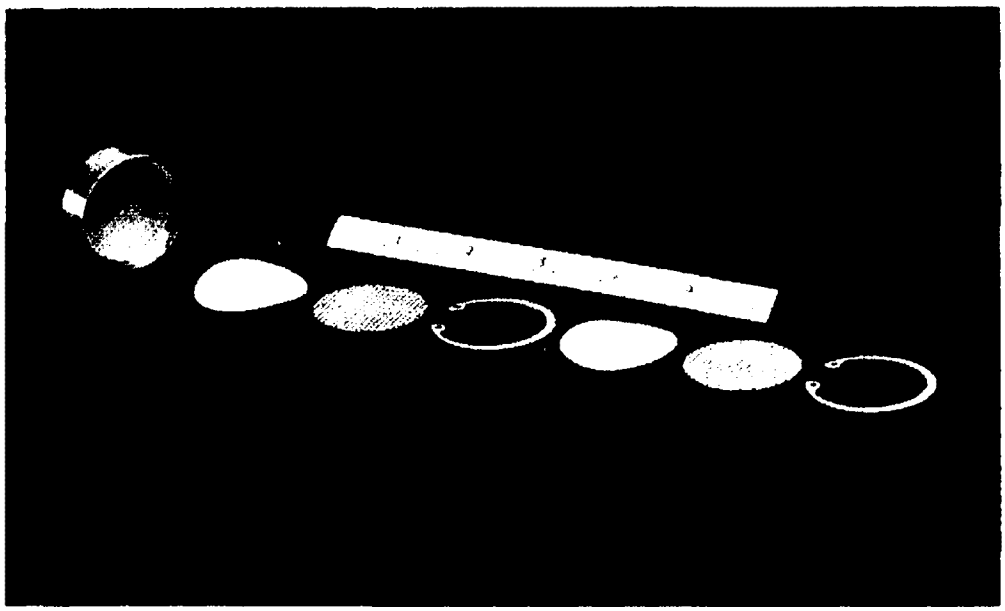

Figure 1. Disassembled standard flow reusable passive sampler.

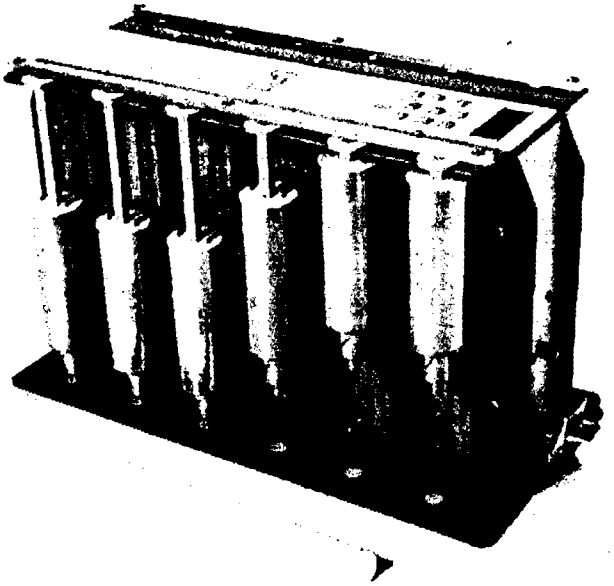

Figure 2. SS 12A-30S automated sequential syringe sampler.

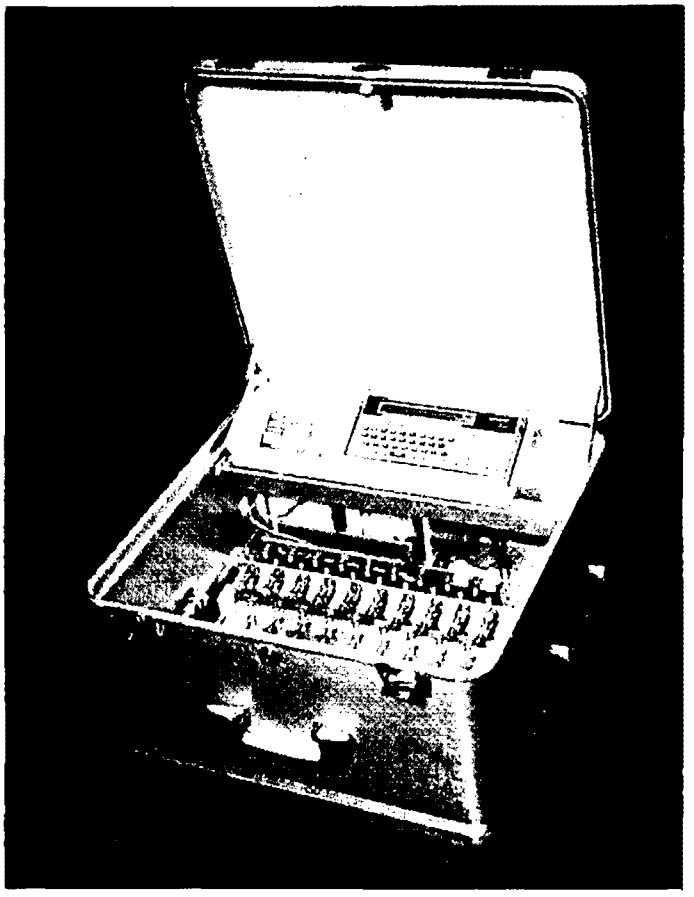

Figure 3. ATS-12/36 microcomputer controlled adsorbent tube sampler.

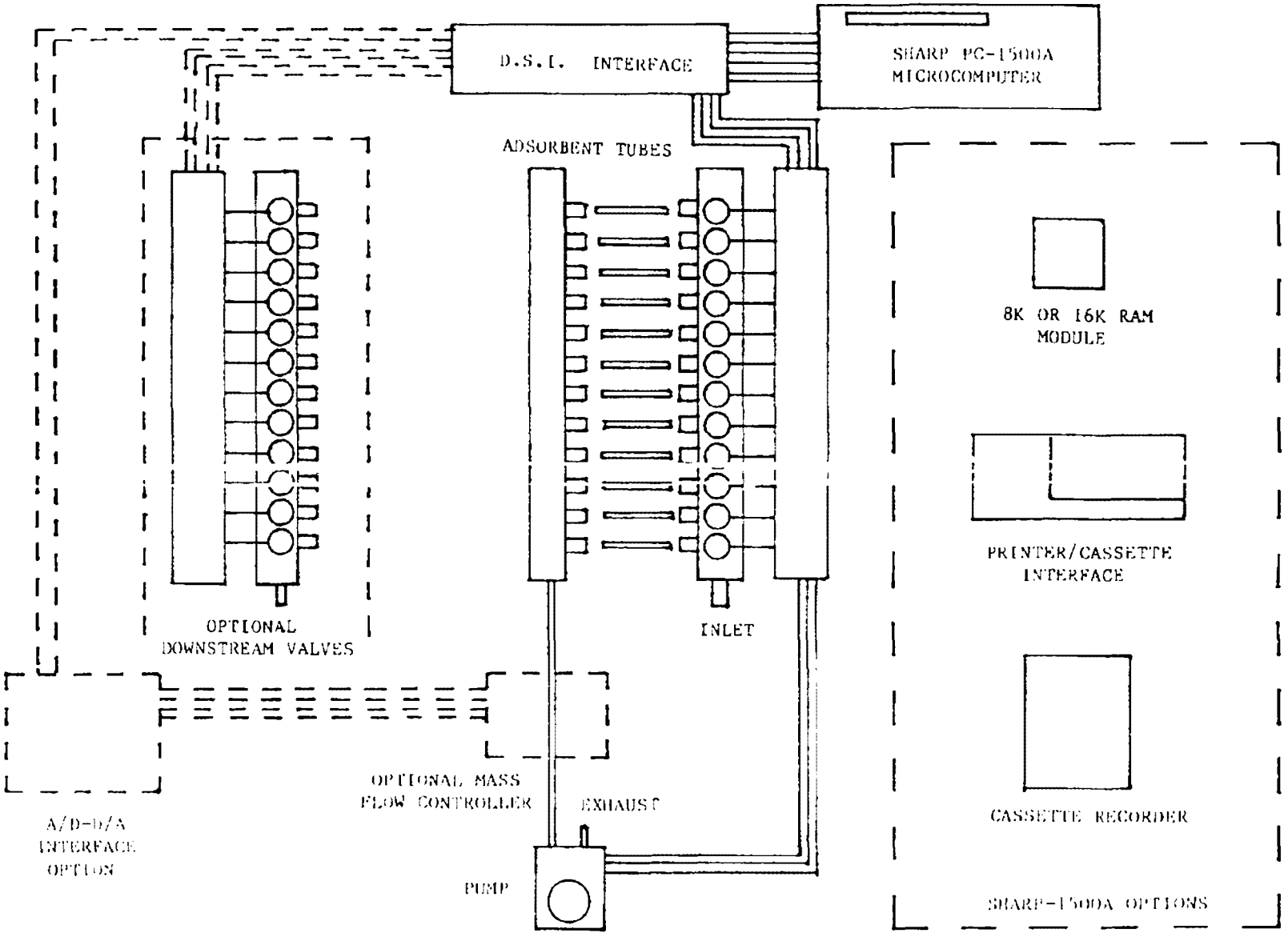

Figure 4. ATS-12/36 adsorbent tube sampler system diagram

Signatures of Atmospheric Aerosols: Cohesion of Changes in Organic Compound Concentrations

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Aerosol sources, transport, and chemical transformations were investigated using a new particle analysis technique in conjunction with factor analysis. Samples of airborne particles were collected by drawing approximately 300 L of air, for 58 min, through a small glass tube containing a quartz fiber filter. Particles were subsequently analyzed by direct thermal desorption of volatile organic compounds into a gas chromatographic column followed by separation and detection of volatile compounds. The volatile organic compounds that can be thermally desorbed from airborne particles change cohesively with time, providing information about sources, photochemical transformations and transport of aerosols. Organic compounds desorbed from particles include terpenoids from biogenic sources, alkanes from vehicular and biological sources, and aldehydes, ketones, carboxylic acids, lactones and furans from photochemical transformations and other sources. Concentrations of oxygenated species in aerosols increased markedly on sunny days relative to cloudy days or nights. Factor analysis of the variations of concentrations of 44 organic compounds in 138 one-hour samples with time and meteorology revealed characteristic signatures for photochemical activity, biological sources, and motor vehicle sources.

Introduction

In trying to better understand the processes that occur in the atmosphere affecting the emission, transport and transformations of chemicals in the atmosphere, scientists have made extensive measurements of the inorganic constituents of particles and used statistical techniques such as factor analysis to learn what they could from these species. These studies have identified factors which measure coal, oil, wood and motor vehicle fuel combustion as well as particles arising from wind blown dust, marine sea spray, refuse burning, smelters and a wide range of individual specific industrial sources.[1-5] While the earlier investigations have been very effective, they are directed principally at inorganic aerosol constituents, and, therefore, do not directly discern atmospheric processes or aerosol sources involving organic compounds.

It has been much more difficult, until now, to determine what information could be learned about sources, chemistry, and the effect of meteorological parameters on the organic constituents of aerosols. The complexity of classical methods for measurement of organic compound concentrations, with the tedious and lengthy solvent extraction and fractionation, have made it difficult to obtain information about organic composition as detailed as that available for inorganic constituents. While these analytical difficulties are not insurmountable problems, they have been prohibitive to the acquisition of large amounts of data about organic compound composition over short time intervals.

A procedure has recently been developed in our laboratory for the analysis of the volatile organic fraction of airborne particulate matter that is faster and less tedious than earlier methods.[6] Unlike earlier procedures, which utilize only a fraction of the collected sample, volatile species from the entire sample are analyzed, greatly increasing effective sensitivity. This technique involves passing approximately 300 liters of ambient air through a small glass tube containing a quartz fiber filter supported by a glass frit. After collection, particles are analyzed by direct thermal desorption of volatile organic compounds into a cryogenically cooled gas chromatography column, followed by subsequent heating of the column and detection of the eluting compounds by flame ionization or mass spectrometry. This technique was used to collect and analyze 138 particle samples and to produce organic composition data for aerosol source apportionment by factor analysis. Ozone and carbon monoxide concentrations in the air, temperature, cloud cover, wind speed and wind direction were all monitored continuously during particle sampling. The final data set used in the factor analysis calculation included these variables and the concentrations of 44 organic compounds identified in the airborne particles.

The major objectives of this study were to identify the different sources which contribute to the particulate organic composition of aerosols in an urban/residential environment, and to utilize the rapid analysis features of low volume sampling/direct thermal desorption to observe the hourly fluctuations in sources and particulate organic composition as they change with sunlight, meteorological conditions, and time.

Experimental

Equipment. Instruments for measuring ozone, carbon monoxide, wind speed, wind direction and temperature were all maintained and calibrated by the Colorado Department of Health. Information on the cloud cover during sampling was obtained

from the National Weather Service in Denver, Colorado. Carbon monoxide was monitored with a Beckman model 866 ambient carbon monoxide monitoring system (Beckman Instruments Inc., Fullerton, CA.) according to the EPA-designated reference method. Ozone was monitored with a Dasibi Environmental Corp. model 1003-RS ozone analyzer (Dasibi Environmental Corp., Glendale, CA.) according to an EPA-designated equivalent method.

Quantitation was performed with a Hewlett-Packard model 5880A gas chromatograph with flame ionization detection (GC/FID). Compound identification was performed with a Hewlett-Packard model 5892A gas chromatograph/mass spectrometer with data system (GC/MS/DS), which was modified such that the end of the chromatographic column extended into the ion source of the mass spectrometer. Both the GC/FID and GC/MS systems used helium carrier gas through a 25 m x 0.25 mm i.d. (0.25 μm film thickness), Ultra Performance fused silica capillary column, manufactured by Hewlett-Packard. The linear flow rate through the columns inside the GC/FID and GG/MS were 30 cm/sec at 300 °C and 40 cm/sec at 300 °C, respectively. The chromatographic oven temperature program was -60 °C to 0 °C at 20 °C/min, then from 0 °C to 300 °C at 5 °C/min and finally, held at 300 °C for 15 min. The injection port temperature of both instruments was 250 °C and the FID temperature was 300 °C. The mass spectrometer electron impact voltage was 70 eV.

Low volume air samples were collected with a Nutech model 221-1A gas sampling pump (Nutech Corp., Durham, NC.). The thermal desorption apparatus was constructed from a cylindrical aluminum block (7 cm diameter x 8 cm long with a 2.54 cm hole in the middle) and was fitted with a 165-Watt heating cartridge connected to an Omega 6000 thermal controller (Omega Engineering, Stamford, CT.). Exact operating conditions for the low volume sampling pump and the thermal desorption heating block have been described previously.[6]

Sampling and Analysis. Between April 18, 1985 and June 20, 1985, 138 air particulate samples were collected at the Colorado Department of Health, Pollution Control Division, Air Monitoring Station in Boulder, Colorado on the campus of the University of Colorado. The particle sampling tube was positioned approximately 5 m from ground level and within 5 m of the inlets of the ozone and carbon monoxide analyzers. Airborne particles were collected for 58 min, on the hour, with a 2 min per sample interruption used for changing the particle collection tube. After sample collection, tubes were again placed inside of screw cap culture tubes, covered with aluminum foil, sealed with a screw cap, and stored in crushed ice until they could be transferred to a freezer. The times recorded are those when the sampler was removed rather than inserted. Several 1-hr aerosol samples were collected consecutively in sessions ranging in duration from 3 to 24 h, with an average of two sessions per week. Larger samples for GC/MS analysis were also collected routinely throughout this study, but these samples were used only for compound identification. The latter samples were collected for times ranging from 1 h to 12 h resulting in collection volumes ranging from 300 to 4000 L. Field blanks were also obtained during this study by filtration of a token 10 liters of ambient air through a new, conditioned particle collection tube. Samples were stored in a freezer at -15 °C prior to analysis and were usually analyzed within 72 h after collection. Analysis involved the thermal desorption of particulate organic compounds, at a maximum temperature of 254 °C for 15 min, directly from the collected particles into a cryogenically cooled (-60 °C) fused silica capillary chromatograph column.[6]

Site Description. The Boulder site was chosen by the Colorado Department of Health as being typical of an urban, residential environment which is removed by several

miles from any heavy industrial activity. In all directions from the sampling site, for an approximate radius of 5 km, is the city of Boulder (pop. 80,000) and its surrounding residential areas. Mountains and the Roosevelt National Forest are directly west of Boulder and there are no large urban or industrial centers to the west for approximately 1000 km. Denver, Colorado, and its large metropolitan area and suburbs populated by approximately 1.5 million inhabitants, lies to the south-east, approximately 40 km from the sampling site. The countryside east of Boulder is dominated by grassland and cropland with very few trees, while the area west of Boulder has extensive conifer forestation.

Factor Analysis. Factor analysis computations were conducted using the Statistical Packages for the Social Sciences (SPSS-X) computer program.[7] Factors were extracted from Z-scored variables by the method of principal components and were later interpreted after varimax rotation.[8] The number of factors retained for the factor model was determined by inspection of the scree plot.[7] This resulted in rejecting factors with eigenvalues less than 1.2. Approximately 3% of the values in the original data table were missing, because of occasional chromatographic interferences and operator error, and these values were later replaced by substitution of mean values for that variable.

Transformations of the raw data matrix were conducted to eliminate variable discontinuities, calculate compound concentrations and to add constructed variables. The discontinuity in the wind direction, which occurs at 0 and 360 degrees, was eliminated by a modification[9] of the transformation described by Tuncel, et al.[1] This procedure results in the formation of two new wind direction variables, designated west-east and south-north, which can be described as vector components of the original wind direction in either a west to east or a south to north direction. An equivalent transformation[9] was performed on the time variable to eliminate the discontinuity at 24:00 and 0:00 h. In this instance, the deconvolution procedure results in a night-day and a dusk-dawn variable.

Two other variables were constructed and used as factor analysis parameters. These transformations were performed on selected peak integration concentration values according to the following equations.

(1) $HPI = 0.5(\sum_{odd} C19 \text{ to } C31 / \sum_{even} C18 \text{ to } C30 + \sum_{odd} C19 \text{ to } C31 / \sum_{even} C20 \text{ to } C32)$

(2) $Psum = \sum$ peak integration counts for the organic compounds in Table I.

In Equation 1 the hydrocarbon preference index, HPI, is analogous to the carbon preference index, which indicates the extent of predominance of n-alkanes with odd carbon numbers over those with even carbon numbers.[10] Because of chromatographic interferences, the entire range of normal hydrocarbons (n-C_{14} to n-C_{32}), which is normally used to calculate the carbon preference index, could not be individually measured. Equation 2 is the summation of the total area integration counts for all chromatographic peaks used in the factor analysis calculation, for each sample investigated.

Results and Discussion

Factor Interpretations. Chromatographic peaks were initially selected for integration and used in the factor analysis model based on chromatographic and practical

analytical considerations. A peak was used in the factor analysis if chromatographic resolution and contamination levels in the field blanks were all acceptable for that compound. Another criterion was that the compounds were ubiquitous, so that only very infrequently were the concentrations below the detection limit.

The organic composition of urban aerosols is often dominated by anthropogenic activity related to fossil fuel combustion. Polynuclear aromatic hydrocarbons, carboxylic acids, alkanes, and phthalate esters are often observed in airborne particulate matter and constitute the most widely studied classes of particle constituents. Several of these common aerosol components were observed in this investigation, but were not used in the factor analysis calculation because of analytical interferences. Most carboxylic acids were chromatographically unresolved from other constituents of the aerosols. In the present study, polynuclear aromatic hydrocarbons were present at concentrations that were too low for reliable flame ionization detection and phthalate esters were often observed in field blanks, so neither class of compounds was included in the factor analysis.

It is possible that some pyrolysis may accompany thermal desorption of volatile organic compounds during analysis. However, thermal decomposition under the conditions selected appears to be negligible,[9] and most of the compounds identified have been observed previously in the analysis of particles not involving thermal desorption. A total of 55 variables for 138 samples were used in the factor analysis computation. Forty-four of these variables are organic compounds associated with particles as measured by low volume sampling coupled with direct thermal desorption.[6] The range and average concentrations of the organic compounds measured, the standard deviation and the programmed temperature chromatographic retention indices are listed in Table I. Other factor analysis variables included wind speed, wind direction, cloud cover, temperature, time, carbon monoxide concentration, ozone concentration, HPI and Psum. Application of factor analysis to these 55 variables resulted in the extraction of 9 factors, all with eigenvalues greater than 1.2. A list of the variables which make up these factors is presented in Table II, along with the varimax rotated factor loadings. These combined factors account for 75.1% of the total variance in the data set, with 53.1% of the variance accounted for by the first three factors.

Each factor listed in Table II was interpreted according to the meteorological and chemical elements it contains and according to the interaction between these elements. Factor 1 was interpreted to be a photochemical factor; Factors 2 and 4 are related to different biogenic sources; Factor 3 was interpreted as a vehicular source factor; Factor 5 is a meteorological factor and Factors 6 through 9 were not interpreted. In preliminary data inspection, several factor solutions were evaluated by setting the number of factors extracted to 6,7,8,9 and 10. The relative positions and interpretations of lower factors changed with differing factor solutions but the positions and interpretation of Factor 1 through 5 remained constant. Because 53.1% of the total variance was accounted for by the first three factors, it is these factors to which the most significance should be attached.

Photochemical Factor. Factor 1, accounting for 31.3% of the variance in the data set, is the most important factor reflecting changes in the organic compound concentrations in airborne particulate matter. The organic compounds in Factor 1 were interpreted as arising principally from photochemical processes. In designating this as a "photochemical" factor, it is recognized that these compounds may arise from several processes: photolysis, secondary oxidation involving ozone, oxides of nitrogen, hydroxyl radicals, etc., and to some extent other sources such as combustion may contribute.

Factor 1 includes ozone and oxygen-containing organic compounds such as acids, aldehydes, furans, lactones and ketones. Ozone, acetic acid, n-heptanoic acid, phthalide and ethenyl benzaldehyde, are all components that are known to be produced by photochemical activity.[11-13] Other Factor 1 chemical species, such as the furans and 4-methyl-3-penten-2-one, could be inferred to be photochemical by-products based upon the presence of relevant precursors and analogous chemical reactions.[14] By contrast, Factor 1 does not contain any of the saturated alkanes, terpenoids or the higher molecular weight methyl ketones.

Further evidence for the interpretation of Factor 1 as a photochemical factor is obtained by observing the magnitude of the Factor 1 scores as a function of time of day, wind direction and atmospheric conditions for individual samples and for a large number of samples collected in consecutive hours. Inspection of the Factor 1 scores for individual samples showed that a small number of samples were dominated by a specific individual factor rather than contribution from several, or all, factors, resulting in chromatograms with distinctive "signatures". Figure 1A shows a chromatogram of a sample with a very high Factor 1 score. The organic compounds constituting Factor 1 are labeled on this chromatogram. The peak numbers on Figure 1 refer to the compounds listed in Table I. This particular sample was collected on the afternoon of June 19, 1985, between 15:00 h and 16:00 h. The wind direction was from the Denver metropolitan area (southeast) at a speed of 4 km/h. The temperature was 26.7 °C, there were no clouds to obstruct the sunlight, and the ozone concentration was relatively high at 90 ppb (ambient ozone concentrations observed in this study ranged from 2 ppb to 100 ppb with an average of 42 ppb). In general, when samples showed large concentrations of Factor 1 compounds, they were those collected during, or immediately after, atmospheric conditions which favor high photochemical activity (i.e., hot, sunny afternoons with high ozone concentrations).

Figure 2 shows the ambient ozone concentration plotted against Factor 1 scores. Since ozone is one of the constituents of Factor 1, with a factor loading of 0.8, a correlation between these variables is anticipated. This plot illustrates the extent of the relationship between ozone and the other variables contained in Factor 1 and further demonstrates the photochemical nature of this factor.

A plot of Factor 1 scores versus time of day is presented in Figure 3. This plot shows low Factor 1 scores during the night and high Factor 1 scores during the day, which is consistent with the photochemical interpretation of this factor. The persistence of Factor 1 past sunset is expected because of the lag time for particle dilution, transport and removal. In Figure 3, the solid line shows the change in Factor 1 over time for one particular sampling session, on June 18, 1985. During this sampling session, temperature, ozone concentration, and solar radiation were also increasing in a manner similar to Factor 1 scores.

The incident near-surface radiation during the sampling period was estimated by cloud cover, as reported by the National Weather Service at Stapleton airport, and confirmed by visual observations in Boulder. Cloud cover was measured on a scale from 0 to 10, with 0 indicating no clouds present, and 10 indicating complete cloud cover. Cloudy conditions (6 and higher cloud cover) and sunny conditions (4 and lower cloud cover) are designated by C and S, respectively, in Figure 3. A comparison of Factor 1 scores (from 6:00 h to 22:00 h) with cloud cover showed that 75% of the sunny days had Factor 1 scores greater then zero and 70% of the cloudy days had Factor 1 scores less then zero. In Figure 3 some of the hours with partial or full cloud cover that exhibited anomalously high Factor 1 scores were on afternoons following periods with extensive sunshine earlier in the same day.

During days with full cloud cover (cloud cover = 10), only 26% of the samples analyzed showed n-heptanoic acid concentrations greater than 40 ng/m^3 while 90% of the samples from sunny days (cloud cover = 0) had n-heptanoic acid concentrations greater than 40 ng/m^3. This suggests a very strong predominance of photochemical sources for particulate n-heptanoic acid.

Biogenic Factors. Factor 2 contains several terpenoids and other biogenic compounds as well as the west to east wind direction component and the night-day time variable. Terpenoids are well known constituents of trees and other plants[15-17] and the predominance of these compounds indicate that Factor 2 is a biogenic factor, probably forest-related. Bornyl acetate, piperitone and camphor have all been identified as being present in the trees and plants indigenous to the forested areas west of Boulder, Colorado.[15-17]

Factor 2 also shows a strong west to east wind direction relationship and a chromatogram which shows domination by Factor 2 compounds when the wind is from the west is presented in Figure 1B. This sample was collected on May 22, 1985, between 4:00 h and 5:00 h. The wind was almost directly from the west (265 °) at a speed of 2 km/h.

Factor 4 was interpreted as a second biogenic factor related to vegetative and microbial activity surrounding the sampling site. It contains the odd carbon number higher molecular weight hydrocarbons, n-heptacosane ($C_{27}H_{56}$), n-nonacosane ($C_{29}H_{60}$), n-hentriacontane ($C_{31}H_{64}$), and the constructed hydrocarbon preference variable (HPI), defined earlier to indicate the extent to which the alkanes with odd carbon number dominate. These odd-carbon hydrocarbons are constituents of grass and broad-leaf type of plants, and the excess of these compounds relative to the even-carbon analogs is often cited as indicating natural source contributions to the airborne particulate matter.[10,18]

Vehicular Factor. Factor 3 was interpreted to be from motor vehicle sources. It contains carbon monoxide and six saturated hydrocarbons from n-eicosane ($C_{20}H_{42}$), through n-pentacosane ($C_{25}H_{52}$). Saturated hydrocarbons and carbon monoxide are well-known constituents of automotive combustion and their occurrence in Factor 3 supports the vehicular source interpretation of this factor. The characteristic feature of the signature for vehicular sources is the presence of large n-alkane chromatographic peaks in the 60 to 70 minute range, Figure 1C. This sample was collected on June 19, 1985 between 7:00 h and 8:00 h. The wind was from the south-east (Denver) at a speed of 4 km/hr. The ambient carbon monoxide concentration was 0.6 ppm and the ambient ozone concentration was 28 ppb.

The interpretation of Factor 3 as arising principally from automobiles is further supported by the relationship between the Factor 3 scores and time of day. Figure 4 shows an increase in the Factor 3 score between 7:00 and 9:00 MST, which is the expected result, assuming the normal urban traffic flow. The line in this figure shows the sharp increase in Factor 3 during one sampling session. Most samples containing high concentrations of Factor 3 compounds were collected between 8:00 and 9:00 MST.

Further chemical evidence for the interpretation of Factor 3 hydrocarbons as vehicular, was obtained by collecting particle samples in downtown Denver, Colorado, during periods of high traffic volume. A chromatogram of a particle sample from this study is presented in Figure 5. Inspection of this figure clearly shows that the n-alkanes of highest concentrations in Denver are the same n-alkanes that constitute

Factor 3.

Meteorological Factor. Factor 5 is a meteorological rather than a chemical factor because it is mostly comprised of non-chemical variables. This factor consists of wind speed, south to north wind direction, temperature, cloud cover, and one chemical compound, phytone. Phytone (6,10,14-trimethylpentadecan-2-one) is a common constituent of several plants, insects and animal manure and it is, therefore, difficult to attribute a particular source to this compound. This ketone had one of the highest concentrations and was among the most ubiquitous constituents of the organic compounds in airborne particles observed in this study, and it has been observed in high concentrations by other investigators. This compound also has the highest correlation coefficient with temperature of any compound ($r = 0.70$), which may account for its clustering with the meteorological variables.

Short-term Fluctuations in the Organic Composition of Aerosol Particles. Many of the rapid changes in the composition of particulate matter observed in this study would not have been observed using techniques with particle collection times longer than one hour. In several instances, large changes were observed in the concentrations of organic compounds in the particles over a one hour period. Several of these changes were the result of wind direction shifts bringing terpenoid compounds from the west to replace the existent airborne particles. Other rapid changes were observed in the organic constituents of particles when Factor 3 vehicular source compounds increased during the morning traffic movement. The concentrations of Factor 1 compounds usually increased relatively slowly, over a period of several hours (Figure 3), but occasionally two-fold increases were observed during a one-hour time period at mid-day.

The highest factor loading of a variable determines its inclusion in a factor, but the other smaller factor loadings (Table II) were useful for verifying chemical and meteorological relationships which are independently known to exist. For example, acetic acid is known to have natural, photochemical and combustion sources, all of which contribute to its concentration in airborne particulate matter. Factor loadings of this particular compound (Table II) suggest that photochemistry is the most important contributor to acetic acid associated with airborne particles, but the Factor 3 and 4 loadings indicate that natural and vehicular sources also add to the acetic acid concentrations.

Conclusions

Factor analysis constitutes an effective method for determining the natural associations between changes in the chemical constituents of aerosols and grouping these components to reveal common sources, transport, and transformations. Factor 1 contained the ambient ozone concentration, and a variety of particulate organic oxygenates, some of which are known photochemical by-products, so this was interpreted as a photochemical factor. Particle samples collected during periods of full sunlight showed much higher concentrations of oxygenated compounds than samples collected at night or on cloudy days. During afternoons the particulate concentration of acetic acid, heptanoic acid, and other oxygenates increase, mirroring the ozone concentrations in ambient air. Factor 2 was strongly dependent upon wind direction and contained several terpenoids in the particles; it was interpreted as a transport-dependent biogenic factor arising principally from the conifers in the forested regions west of the sampling site. Factor 3 contained the ambient carbon monoxide concentration and the saturated n-alkanes, $C_{20}H_{42}$ through $C_{25}H_{52}$ in aerosol particles, and it was interpreted as a vehicular factor. The concentrations of

these hydrocarbons increased rapidly during the morning rush hour. Low volume sampling with direct thermal desorption allowed hourly fluctuations of the concentrations of organic compounds desorbed from airborne particles to be measured and short term phenomena to be observed. At mid-day, two-fold increases in the concentrations of oxygenates in particles over a one-hour period were occasionally observed. Many of the aerosol source interpretations presented in this study would not have been possible using traditional techniques with sample collection times longer than one hour.

Acknowledgments

We are grateful to the National Science Foundation for support of this research under the Grant ATM-8317948. We would also like to thank the Colorado Department of Health and the National Weather Service for providing access to their data. The assistance of Steve Arnold, Don Barbaric and Susan Martino from the Colorado Department of Health, Air Pollution Control Division was greatly appreciated. Technical assistance provided by Pamela Veltkamp and Gene Lutter is gratefully acknowledged. R.E.S. acknowledges the support of the Univ. of Colorado Council on Research and Creative Work for a faculty fellowship spent as a Visiting Scholar at the Scripps Institution of Oceanography, U.C. San Diego.

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Table I. Concentrations of Volatile Compounds from the Thermal Desorption of Urban Airborne Particles

compound	min. conc.[h] ng/m^3	max. conc. ng/m^3	mean conc. ng/m^3	standard dev.[i]	chrom. retention index[j]
Factor 1					
1-phenyl-1-penten-3-one(11)[d]	< 19	64	26	10	1583
ethenyl benzaldehyde(10)[d]	< 19	50	26	7.1	1576
heptanoic acid(7)[b]	< 30	170	59	32	1109
1,3-indandione(8)[b]	< 26	99	40	11	1342
acetic acid(2)[b]	< 210	1200	420	220	723
2,3-dihydro-5/-methyl furan(1)[b]	< 15	160	43	29	709
α-angelicalactone(5)[b]	< 32	84	46	12	870
dihydro-4,4-dimethyl/-2(3H)-furanone(6)[b]	< 19	58	27	7.9	988
phthalide[b]	< 25	58	34	8.8	1348
toluene[b]	< 8.5	49	17	8.4	788
2,5-dimethyl furan(3)[b]	< 6.4	17	8.7	2.1	768
4-methyl-3/-pentene-2-one(4)[b]	< 18	48	24	5.5	805
5,6,7,7a-tetrahydro-/4,4,7a-trimethyl-(S)/-2(4H)-benzofuranone(9)[d]	< 0.7	14	2.7	2.7	1541
Factor 2					
terpenoid(14)[e,f]	< 5.7	33	9.7	5.0	1182
bornyl acetate[b]	< 6.5	40	9.4	5.8	1283
terpenoid(17)[e,g]	< 5.7	150	29	28	1226
1-(1,4-dimethyl-3-cyclo/hexen-1-yl)-ethanone(15)[d]	< 5.7	110	16	17	1189
terpenoid(12)[e,g]	< 5.7	130	18	21	1123
n-nonanoic acid(19)[b]	< 26	56	34	7.1	1287
piperitone(18)[b]	< 5.7	28	9.1	4.0	1253
γ-heptalactone[b]	< 6.1	53	13	8.7	1173
camphor(13)[b]	< 5.7	25	8.9	4.5	1165
n-propionic acid[b]	< 260	590	340	69	817
branched acid(20)[e]	< 0.3	26	3.9	4.2	1826
Factor 3					
n-docosane(25)[b]	< 0.3	14	4.3	2.7	2200
n-tetracosane(27)[b]	< 0.3	6.3	2.1	1.1	2400
n-pentacosane(28)[b]	< 0.3	16	5.0	3.1	2500

n-tricosane(26)[b]	< 0.3	20	5.5	4.2	2300
n-eicosane(23)[b]	< 0.3	11	2.9	2.1	2000
n-henicosane(24)[b]	< 0.3	32	5.2	4.1	2100
Factor 4					
n-nonacosane[b]	< 0.7	35	7.5	5.2	2900
n-hentriacontane[b]	< 0.7	15	4.1	3.0	3100
n-heptacosane[b]	< 0.7	11	4.2	2.7	2700
Factor 5					
phytone[d]	< 0.3	71	23	17	1847
Factor 6					
2-tridecanone[c]	< 8.0	22	12	3.2	1496
2-pentadecanone[c]	< 8.0	16	9.8	2.0	1706
n-octadecane[b]	< 0.3	19	2.0	1.8	1800
Factor 7					
n-octacosane[b]	< 0.3	13	2.0	1.8	2800
n-triacontane[b]	< 0.7	15	2.9	2.1	3000
n-hexacosane[b]	< 0.3	8.3	1.5	1.5	2600
Factor 8					
γ-decalactone[c]	< 6.0	72	17	11	1470
n-nonacosane[b]	< 0.3	75	5.0	8.1	1900
Factor 9					
benzaldehyde[b]	< 19	44	27	5.9	960
5,5-dimethyl-2/(5H)-furanone[d]	< 19	50	27	7.1	956

[a]Numbers in parentheses refer to chromatographic peaks in Figure 1. GC/FID was used for compound quantitations using calibration curves derived by measuring responses from authentic standards. For compounds for which authentic standards were unavailable, quantitation was performed using calibration plots from analogous compounds, assuming a similar flame ionization response factor. Unknown terpenoids were estimated using the camphor calibration plot. [b]Compounds were identified by comparison of their mass spectra to literature mass spectra and by comparison of their mass spectra and retention times to those of authentic standards measured in our laboratory. [c]Compounds were only tentatively identified by comparison of their mass spectra to literature mass spectra and by interpolation of the expected retention time of the compounds from the retention times of homolog compounds. [d]Compounds were tentatively identified by comparison of their mass spectra to literature mass spectra. [e]Compound type was identified by mass spectral interpretation and comparing the mass spectra to the mass spectra of analogous compounds. Mass spectra are available in reference 9. [f]138 m/z was the highest mass in the mass spectra. [g]150 m/z was the highest mass in this mass spectra. [h]Values listed are the detection limits (9). [i]Values represent the standard deviation of the ambient compound concentrations in aerosols over time. Analytical precision of repetitive quantitations, as measured by percent relative standard deviation, ranges between 15 and 30% (6). [j]The programmed temperature chromatographic retention index is relative to n-alkanes.

Table II. Matrix of Factor Loadings of Chemical and Meteorological Variables[a]

	Factors								
	F1	F2	F3	F4	F5	F6	F7	F8	F9
Factor 1									
1-phenyl-1-penten-3-one(11)	0.9								
ethenyl benzaldehyde(10)	0.9								
n-heptanoic acid(7)	0.9			0.2					
1,3-indandione(8)	0.9								
acetic acid(2)	0.9		0.2	0.2					
2,3-di-hydro-5/ -methyl furan(3)	0.8			0.2					0.3
ozone	0.8	-0.2	-0.2		0.3				
α-angelicalactone(5)	0.8	0.3	0.2						
dihydro-4,4-dimethyl/ -2(3H)-furanone(6)	0.8								
phthalide	0.7		0.2		0.2	0.2		0.2	
toluene	0.7								0.4
2,5-dimethyl furan(1)	0.7	0.3		0.3			0.2	0.2	0.2
4-methyl-3/ -pentene-2-one(4)	0.7	0.3		0.3			0.2	0.2	0.2
Psum	0.7	0.5	0.3	0.3			0.2		
5,6,7,7a-tetrahydro-/ 4,4,7a-trimethyl-(S)/ -2(4H)-benzofuranone(9)	0.6		0.3			0.4			
Factor 2									
terpenoid(14)		0.9							
bornyl acetate		0.9							
terpenoid(17)		0.9						0.2	
1-(1,4-dimethyl-3-cyclo/ hexen-1-yl)-ethanone(15)		0.8						-0.2	
terpenoid(12)		0.8							
n-nonanoic acid(19)	0.3	0.7							
piperitone(18)	0.4	0.7						0.2	
γ-heptalactone	0.3	0.7		0.2					
camphor(13)		0.6							0.3
west-east	-0.4	0.6				-0.4			
night-day		0.5			-0.5	-0.5			
n-propanoic acid	0.2	0.5			-0.3			0.4	
branched acid(20)		0.5	0.4	0.2				0.3	
Factor 3									
n-docosane(25)			0.9						
n-tetracosane(27)	0.2		0.8						
carbon monoxide			0.7		-0.3				
n-pentacosane(28)	0.2		0.7	0.3	0.3				
n-tricosane(26)	0.2		0.6	0.2	0.5			0.3	
eicosane(23)			0.5	0.2		0.5			
n-heneicosane(24)	0.2		0.5	0.5					0.3

Factor 4									
n-nonacosane	0.3			0.8			0.2		
n-hentriacontane	0.3			0.8			0.2		
n-heptacosane	0.3		0.2	0.7	0.3		0.3		
HPI				0.6	0.3		-0.5	0.2	
Factor 5									
temperature	0.4			0.3	0.8				
wind speed			-0.2		0.7	-0.2			
phytone	0.3		0.3	0.3	0.6				0.3
south-north	0.4				0.5				
cloud cover	-0.3				-0.5				-0.2
Factor 6									
2-tridecanone	0.4			0.2		0.7		0.2	
2-pentadecanone	0.3	0.2				0.6			
dusk-dawn	0.4		0.3		0.3	-0.6			
n-octadecane			0.3			0.5			
Factor 7									
n-octacosane			0.3				0.8		
n-triacontane							0.8		0.2
n-hexacosane			0.6				0.6		
Factor 8									
γ-decalactone								0.8	
n-nonadecane		0.3	0.4					0.7	
Factor 9									
benzaldehyde	0.4						0.3	0.3	0.6
5,5-dimethyl-2(5H) -furanone	0.4			0.3			-0.2	0.3	0.5

[a]Only factor loadings with absolute magnitudes greater than 0.2 are reported in the table.

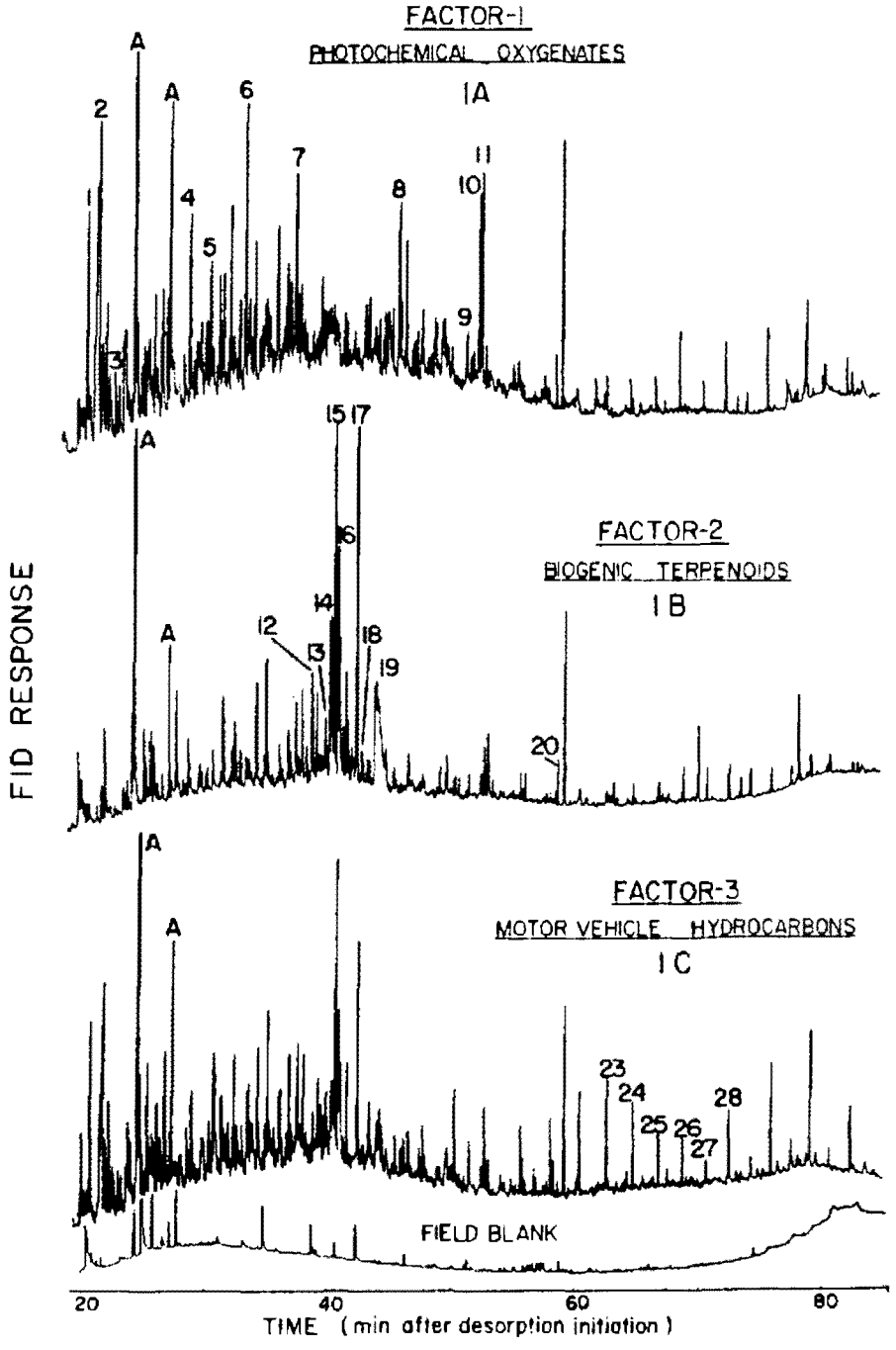

Figure 1. Chromatographic signatures of particles collected on different days dominated by organic compounds from aerosol sources dictated by: photochemistry (1A), wind direction (1B), and source strengths (1C). The numbers on this figure refer to Table I.

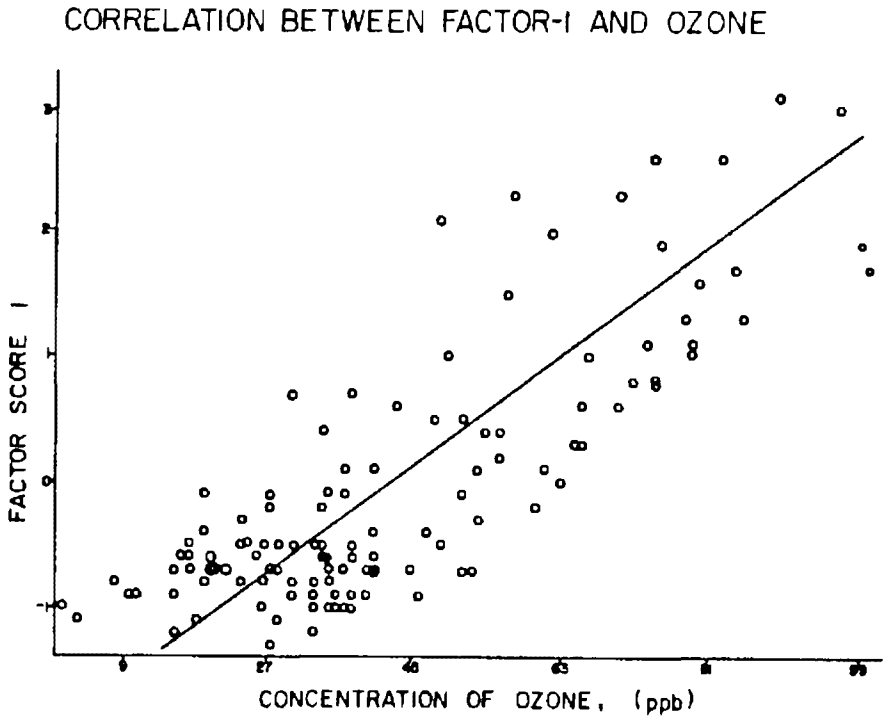

Figure 2. Relationship between Factor 1 scores and the ambient ozone concentration.

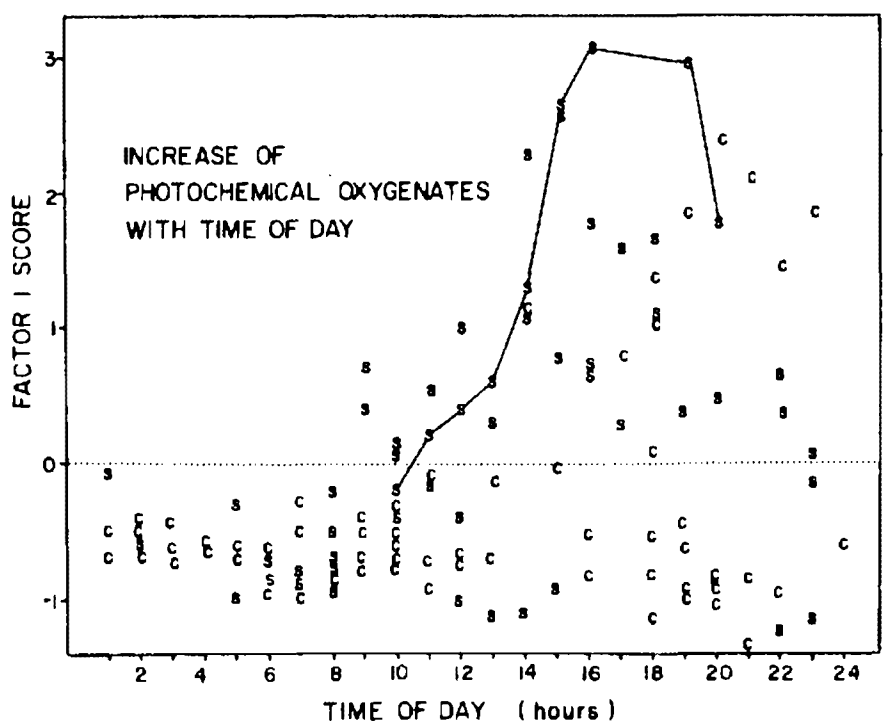

Figure 3. A large number of high Factor 1 scores during sunny days and low Factor 1 scores during the night and cloudy days (S=low cloud cover, C=high cloud cover). The line connects values during the course of one sunny day.

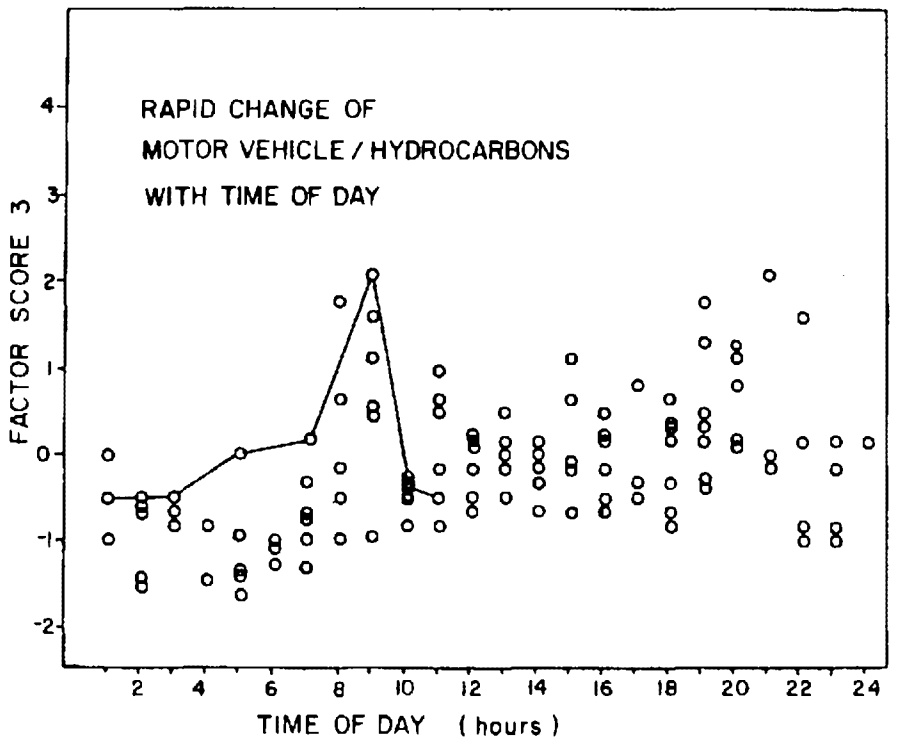

Figure 4. Rapid increase in Factor 3 scores during periods of heavy traffic volume (6:00 to 9:00 in the morning).

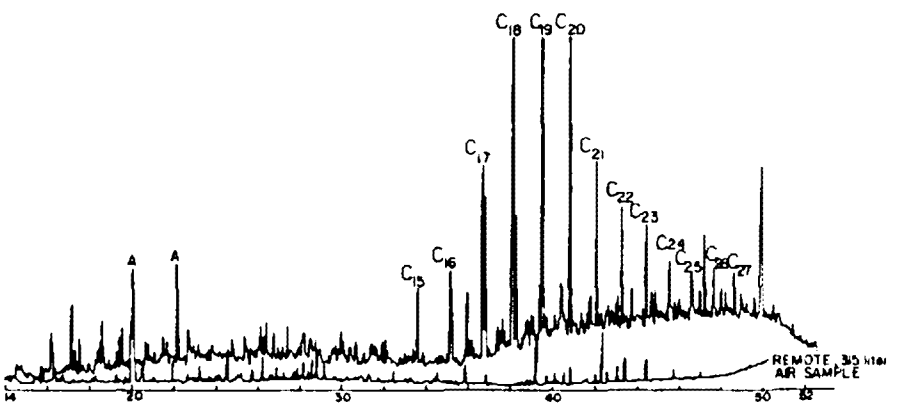

Figure 5. Hydrocarbons observed from particles collected in downtown Denver, Colorado, during peak traffic volume (top). Chromatogram from western Colorado, remote from urban sources (bottom).

RECEPTOR MODELING: A PROMISING ALTERNATIVE TO TRADITIONAL SOURCE APPORTIONMENT METHODS

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The traditional combination of source-emissions inventories and dispersion models for predicting ambient pollutant concentrations is not very accurate in a number of applications. An alternate method, receptor modeling, is becoming increasingly valuable as a complement to the traditional approach. Receptor modeling involves detailed analyses of particles and gases collected from ambient air and from sources important in the area in question. Contributions from the sources are identified on the basis of detailed composition patterns and other characteristics (e.g., particle morphology). Receptor modeling based on elemental compositions has been most used to determine sources of particles in urban areas. However, many sources are not well characterized by elemental patterns, especially sources that release mainly carbonaceous material. To detect emissions from these sources, investigators need to measure concentrations of some of the thousands of organic compounds in the gas or particle phases. Development of this approach has been hindered because of uncertainty regarding the fractions of various compounds that survive destruction by atmospheric reactions between the source and receptor. If stable tracers for the sources can be identified, either organic or inorganic, less stable species could be treated by a new model called "hybrid receptor modeling." The latter includes source-emissions, transformation and deposition treatments similar to those of traditional models, along with the use of tracer species of certain sources, as in receptor models. By use of tracers, one can eliminate many absolute uncertainties (e.g., dilution) common to dispersion modeling. The hybrid approach is now being used in attempts to provide an understanding of the sources, transformation and deposition of sulfur species related to acid-deposition problems.

Contributions of various sources to the atmospheric burden of total suspended particulate matter (TSP) or of certain species are commonly determined by a source-emissions inventory coupled with a dispersion model. Masses of materials released per unit time from the sources are measured or estimates are made based on the type of fuel used, the type of boilers or other process equipment, the pollution control devices, etc. These estimates or measurements are often quite inaccurate, usually being based on tests with new equipment, which deteriorates with use if not carefully maintained.

Even greater errors are probably introduced by the dispersion models, which work reasonably well in periods of steady winds in flat terrain, but break down seriously under conditions of calm and variable winds -- just the conditions under which the worst stagnations occur. In hilly terrain or in cities with tall buildings, dispersion models poorly approximate the complicated circulation patterns of the air.

Atmospheric scientists have developed a new approach to the problem of source apportionment: receptor models. Many parameters of ambient air are measured at a field site, the "receptor." Some of the parameters are characteristic of certain classes of sources. In the case of particles, for example, concentrations of forty or more elements and species are sometimes measured to identify the sources. Some elements have obvious connections with certain types of sources, e.g., most Pb and Br in U.S. cities arises from the combustion of leaded gasoline - a "tracer" which is, fortunately, rapidly disappearing in the U.S. After concentrations of forty or so species on ambient particles are measured, statistical methods are used to determine which elements come from each important type of source. A receptor model called "chemical mass balances" (CMBs) is often used, which assumes that the observed concentration pattern is a linear combination of concentration patterns of particles from the sources,[1] i.e.:

$$C_i = \sum_j m_j x_{ij}, \qquad (1)$$

where C_i is the concentration of element i in ambient material, m_j the mass of airborne material contributed by source j, and x_{ij} is the concentration of element i in material from source j. The source-composition terms, x_{ij}, are determined by analyzing particles collected from important sources. When the observed values of the Cs and xs are known, the unknown source strengths, m_j, are determined by a least-squares fit to the observed concentrations.

The CMB method has been used successfully to determine contributions of various types of sources to ambient TSP in several urban areas. For example, Kowalczyk *et al.*[2] resolved the concentration pattern of Washington, D.C. area particles into seven components: combustion of oil, coal and refuse, motor-vehicle emissions, sea salt, soil and limestone. Cooper *et al.*[3] performed a similar, but more extensive resolution of the Portland, OR atmosphere, performing separate CMBs for fine and coarse particles. Their resolution was apparently the first in which the results were considered reliable enough to be used for regulatory purposes, as the city determined from them that the optimal way in which to bring one area into compliance with the TSP standard was to control dust along roads that had heavy truck traffic. Recently, receptor models were mentioned in the Federal Register as a way for communities to devise methods for attainment of the proposed PM10 TSP standard. Although there are still many unanswered questions about receptor models, for many applications they are more reliable than the classical source-emissions/dispersion-model approach.

USE OF ORGANIC SPECIES

Research is continuing in an effort to improve receptor modeling. Some of the largest uncertainties involve sources that emit mainly carbonaceous particles, e.g., diesel engines and engines burning non-leaded gasoline, wood smoke, gas and oil furnaces, etc. To sort out these sources, it will be necessary to measure concentrations of various organic compounds. Analytical methods for organic compounds have improved so dramatically in recent years that the sensitivity and selectivity are available for measurement of many compounds that could serve as tracers for cetain sources. However, this field has been held back because it is not clear how long the organic compounds remain the same after release, as many are eventually degraded by photolysis or reactions with species such as O_3, NO, NO_2, NO_3 and ·OH radical.

The most studied class of organic compounds is the polynuclear aromatic hydrocarbons (PAHs). Even in this case, it is not clear how well the compounds survive in the atmosphere. Hites[4] measured concentrations of PAH compounds deposited in sediments of the Charles River in Boston years ago, but Friedlander observed losses of PAHs even close to highways in Los Angeles.[5]

In order to get beyond this problem, we should identify species that can be established as stable from the source to the receptor and measure concentrations of other species relative to the stable species, which could be an organic compound, but could be inorganic, a gas-phase species, certain particles identified microscopically, or any other conservative property. If no property associated with a particular source can be *a priori* established as conservative, one could release an inert tracer from the source, e.g., a non-commercial chlorofluoro compound.[6] The important point is that, once stable tracers are developed, one can use *ratios* of other species, rather than absolute concentrations, to observe changes. As has been demonstrated by Fehsenfeld *et al.*[7], if it is known that the only important sink for some compounds is reaction with ·OH radicals and rate constants for these reactions are known, one can use the decay rates to determine the important concentration values for ·OH radicals, a quantity that has eluded direct instrumental measurement at ground level for a decade despite several millions of dollars of support! Below I illustrate the value of the measurement of ratios of species as applied to the sources of acid deposited in the northeast U.S.

REGIONAL SCALE MODELING

The focus of receptor-modeling research involving inorganic species has shifted to regional scale questions such as those involving acid rain: what are the sources, and how far do emissions travel before converting to acids and being deposited? If emissions of S and N species are reduced, how will it affect the deposition of acids in regions of biological vulnerability? The weaknesses of classical source-based modeling on a regional scale are much more serious than those of the urban scale. Present day models, employing simple, first-order transformation of SO_2 to sulfate have been shown to be totally inadequate.[8] The Regional Acid Deposition Model (RADM), now under development at the National Center for Atmospheric Research (NCAR) for the National Acid Precipitation Assessment Program (NAPAP), will surely be much better, but it may be several years until it is considered reliable enough for making decisions regarding optimal control measures for acid rain. By contrast, regional scale receptor modeling, including an approach in between receptor and classical modeling, called "hybrid receptor modeling", shows promise of being able to answer some of these large questions reliably within the next couple of years.[9]

Elemental Signatures

One regional approach that has received much attention is that of Rahn and Lowenthal.[10,11] Their premise is that particles of certain large regions, which may be 100s of km on a side, become sufficiently well mixed before transport to receptors outside the region that they can be characterized by signatures made up of ratios of certain key tracer elements, in particular, by the ratios of concentrations of As, Zn, Sb, In and non-crustal (ncr) V and ncr-Mn to that of Se on airborne particles. In their model, eastern North America is divided into five regions: New England (NENG), central East Coast (CEC), southern Ontario (SONT), and upper (UMW) and lower Midwest (LMW). These signatures are strongly influenced by certain sources characteristic of those regions. For example, the CEC signature has a high ncr-V/Se ratio because of extensive use of oil along the East Coast. The SONT signature has a high In/Se ratio because of emissions from smelters in the Sudbury region. The LMW and UMW signatures differ because the former, representing the region around the Ohio River Valley, is largely dominated by emissions from coal-fired power plants, whereas the UMW, representing the more industrial areas of Chicago, Cleveland, Detroit, Pittsburgh, etc., have higher ratios of As, Zn, Sb and ncr-Mn.

Rahn and Lowenthal use their regional signatures to resolve the concentration patterns of these seven elements on airborne particles collected at sites such as Underhill, VT and Narragansett, RI, into contributions from the five source regions.[11] This approach has been criticized for several reasons, especially the fact that air masses arriving at these sites often travel through highly polluted areas whose additions to the air mass may "erase" the original signatures.[12] Rahn and Lowenthal's argument is, however, that even if new materials are added, e.g., by passage through the CEC region, the added material will carry the signature of its region and be resolved from the original signatures. It is not my purpose pursue that argument here. My student, Semra Tuncel, recently completed a re-analysis[13] of samples collected in the Ohio River Valley by Shaw and Paur and analyzed by them by using x-ray fluorescence (XRF).[14] By using instrumental neutron activation analysis (INAA), Tuncel measured the tracer elements recommended by Rahn and Lowenthal (except for In on some samples). Her results support some of the assumptions of Rahn and Lowenthal, e.g., except for Mn, concentration patterns in the Midwest do not differ strongly with the direction from which the air mass comes. Also, most of the ratios she observed fell between the LMW and UMW values recommended by Rahn and Lowenthal.

The more controversial aspect of Rahn and Lowenthal's approach is their determination of regression coefficients of particulate sulfate vs. the intensities of their regional signatures. Once they determine the regression coefficients, they resolve the pattern of each sample collected at, say, Underhill, VT, into the various regional contributions and multiply each contribution by the regression coefficient in order to apportion sulfate in the sample to various source regions. The result of this analysis is that, at Underhill, during the summer of 1982, 34% of the sulfate originated in the Northeast, 62% in the Midwest, and 4% from the Canadian smelter region. For the following winter, a similar analysis yielded 74% from the Northeast, 21% from the Midwest, and 5% from the Canadian smelter region.

These results are controversial, first because they disagree with much present thought that most sulfate in the Northeast is brought in from the heavy coal-burning region of the Midwest, the Ohio River Valley, in particular. My concern is not that the results disagree with popular thought, which isn't well substantiated, but with the model itself, which assumes that one can apportion the sources of sulfate in the same way as

regional signatures. The signatures are based on elements that are largely primary emissions from the sources. Most of the sulfate is secondary, i.e., it is formed from the primary emission, SO_2 gas, after a fairly long average time in the air, perhaps 10s of hrs. Prior to conversion, the SO_2 gas surely has different deposition properties, both wet and dry, than particles bearing the tracer elements. Even after conversion, there may be some differences, as the sulfate particles may have different size distributions and almost certainly have a different solubility, which will affect their behaviors in clouds and fogs. If rain falls on an air mass from the Midwest that is heading toward New England, does the rain bring down the same fraction of airborne sulfate and of trace elements? It may, but what about SO_2? The latter has a higher diffusion rate towards the droplets, but it may not dissolve very well in the droplet, especially if it is acidic. These are complex questions that cannot be answered with sufficient accuracy to reject the Rahn and Lowenthal hypothesis. On the other hand, these authors have not answered them to the satisfaction of the research community.

Hybrid Receptor Models

There is much confusion in the literature about the term "hybrid receptor models." I take it to mean that one combines some of meteorological aspects of traditional source-based models with some of the tracer aspects of receptor models. An important feature of such models is that one often works with ratios of species so that some of the most uncertain absolute parameters of classical models cancel out.

One promising approach is that of Samson el al., who calculate back-trajectories of air masses bearing various elements and species.[15] They assume that the contributing sources have a normal distribution about the trajectory, with a width that increases with distance. They first calculate contours of the potential mass transfer, i.e., the probability distribution of origin of airborne material arriving at the receptor site assuming uniform source strengths throughout the area. This might be considered a long range wind rose: for example, if most trajectories to a site come from the northwest, then the contours of potential mass transfer will have the highest values towards the northwest of the site. They then perform similar calculations in which the trajectory for each sampling period is weighted by the concentration of a certain species or a ratio of species. By comparison of the weighted and unweighted mass transfer function, they obtain a contour plot of the difference, the "implied transport bias." This separates the effect of wind-direction frequency from that of the concentrations when winds come from certain directions. For example, a simple "pollution rose" might show that most V comes to the site from the northwest, but this may simply be because the wind normally comes from that direction. Samson's method removes that effect and looks for the concentration when winds come from various areas to find out where the strongest source areas are regardless of wind frequency from that direction. Areas having positive biases in his contour plot for a given element, thus have the strongest sources.

At this point, his model is largely one-dimensional, mainly indicating the direction of strongest sources, but not necessarily their distances along those trajectories. The potentially unique aspect of his approach is that Samson has collected a great deal of precipitation data and tabulated it in a gridded format for successive time periods. Thus, it will be possible to couple the precipitation data with the back-trajectories to determine where rain cleaned material out of an air mass. This will be extremely valuable in indicating the distance scale for transport of sulfate to affected areas. Provision can also be made for inclusion of dry deposition

in his model, although that is probably of much less importance than wet deposition.

An important step towards the treatment of SO_2 conversion to sulfate and deposition of both species that avoids the absolute uncertainties of dispersion and deposition rates was taken by Lewis and Stevens, who investigated the mathematical basis of one form of hybrid receptor modeling.[16] Their model assumes that one measures concentrations of SO_2 and SO_4 relative to that of some species borne by particles from the plant. In setting up the model, they assumed that (1) dispersion, deposition and transformation of the three species (SO_2, SO_4 and fine primary particles) are linear or pseudo first-order processes, but may have complex dependences on time; (2) dispersion affects all three types of pollutants in an identical manner; (3) dry deposition is the only type of deposition which occurs; (4) deposition affects all fine particles in an identical manner, but may be different for SO_2; (5) secondary sulfate is produced only by homogeneous oxidation of SO_2.

Lewis and Stevens' mathematical treatment is fairly general, as it allows the conversion rate and deposition velocities to vary with time, which is to be expected. For example, the rate of SO_2 conversion is probably higher during daytime than at night. The value of their formulation is that the dispersion of both SO_2 and SO_4 and the deposition of SO_4 are handled by normalization to the concentration of fine primary particles from the SO_2 source. They made various assumptions about the time dependence of the conversion and deposition rates and, from this exercise, concluded that the errors are only about 10% or less if one assumes that they are equal to the time-averaged values.

As fine particles arise from many sources, it would be desirable to replace the fine particle mass concentration in the equations by the concentration of an element borne by the fine particles from coal combustion and no other source. The best candidate for such an element is Se.[16,17] In theory, if coal-fired power plants were the only significant source of Se (probably a good assumption in many areas), one could measure emission rates of SO_2, SO_4 and Se from the source and their concentrations at some downwind location and plug the values into the equations and solve them to obtain the conversion and deposition rates averaged over the travel time of the plume. The model is a useful first step towards the use of receptor-model methods to determine transformation and deposition rates, but it is over-simplified, especially the assumption that one can follow the plume from a large source for many hours to observe the changes. There are few areas of the world in which that is possible. Also, the neglect of in-cloud processes is a serious problem; however, one could test the approach by selecting periods of dominant high pressure systems during which there is little cloudiness or rain.

To examine the first problem in more detail, Gordon and Olmez performed calculations that crudely simulated an air mass moving up the Ohio River Valley and into New England.[18] They assumed that identical coal-fired plants were spaced at 50-km intervals over 1000 km and eliminated them for an additional 800 km. They assumed a ratio of Se/S = 0.00028 in the coal, and that 50% of the Se is released up the stack, of which 50% quickly becomes attached to particles, with the remainder staying in the gas phase. The atmosphere was assumed to be uniformly mixed up to 1.5 km and the wind speed, 10 km/hr. Selenium and sulfate particles were assumed to have the same deposition velocity, $\underline{v}_{g2}$, and SO_2 a larger value, $\underline{v}_{g1}$. Sulfur dioxide was also converted at a rate $\underline{k}_r$ = 1.0%/hr. Gordon and Olmez[18] also added a gas-phase tracer to the model, namely gas-phase B. In non-coastal areas, it seems to arise mainly from coal-fired plants. Fogg and

Rahn suggest that B, mainly as H_3BO_3, has deposition properties similar to those of SO_2, but no chemical reaction similar to SO_2 conversion is known for gas-phase B.[19] Thus, the addition of measurements and modeling of B/SO_2 ratios could add valuable additional constraints to hybrid receptor models. Fogg and Rahn used this approach to make rough estimates of SO_2 lifetimes (1-2 days) and oxidation rates (1-2%/hr) during transport from the Midwest to New England. Gordon and Olmez assumed the ratio of gas-phase B/SO_2 in stack emissions to be 0.00070 based on the results of Fogg and Rahn. Gas-phase B was assumed to have the same deposition velocity as SO_2, but no chemical decay. Calculations were performed, with $\underline{v}_{g1} = 2$ cm/sec and $\underline{v}_{g2} = 0.5$ cm/sec. As expected, just after each injection of fresh emissions, the particulate S/Se ratio drops because Se is added without new SO_4 until the new SO_2 has been converted to SO_4.

The predicted SO_2 concentration rises to 27 $\mu g/m^3$ at 500 km and remains almost constant to 1000 km, where no new SO_2 is added, and drops rapidly beyond that point. The sulfate concentration rises to about 19 $\mu g/m^3$ at 1000 km and continues to rise a bit, as SO_2 is further converted, to a maximum at 1100 km, before slowly dropping. The particulate Se concentration increases to about 3 ng/m^3 at 1000 km and slowly decreases to 1800 km. The particulate S/Se ratio asymtotically approaches about 2100 up to 1000 km and increases beyond that point because additional particulate S is formed, while no more Se is added, reaching a value of about 3100 at 1800 km. The parameters were not chosen to attempt an exact fit to a particular data set, but the predicted concentrations of species were fairly reasonable. The B/SO_2 ratio remains fairly constant at about 0.0007 up to 1000 km, then increases by a factor of about 2.5 by 1800 km, as SO_2 is removed faster than gas-phase B. The latter is in reasonable agreement with the findings of Fogg and Rahn.[19] The predictions were also in good agreement with measurements of gas-phase B and S and particulate B, S and Se in College Park, MD by Kitto and Anderson.[20]

Tuncel et al. tabulated S/Se ratios for particles observed at many locations.[17] The ratio is about 3000 at rural sites downwind, but outside of coal-burning areas. In the midst of the ORV, it is depressed to about 1700, in agreement with the model. In the midst of cities in which substantial coal is burned, the ratio is depressed to 1000 or less. Except for a few samples at Allegheny Mt. collected downwind from three power plants, Tuncel et al. did not see sudden drops in the S/Se ratio that one would expect to see occasionally in fresh plumes from coal-fired plants. A major flaw in the simple model is the assumption of uniform vertical concentration profiles, which will surely be a poor assumption just beyond a source. Most power plants have tall stacks, whereas, measurements are at ground level. The S/Se ratio will surely be strongly depressed near the plume centerline, but the effect will usually be washed out before the plume hits ground level. However, around cities, there are probably some ground level sources.

Recently I performed more detailed hybrid-receptor calculations in an attempt to fit Shaw and Paur's gas-phase and particulate S data for three stations in the Ohio River Valley.[14] Surprisingly, S concentrations do not increase strongly between the west station in Kentucky and the east station in Ohio. However, there was the possibility that high S levels occurred when air masses came back down the Valley from the east. Tuncel eliminated this possibility by determining back-trajectories for all samples and found essentially the same result when considering only air masses coming to the stations from the southwest.[13] Instead of assuming a constant SO_2 density vs. distance up the Valley, I put in estimates based on the SURE emissions inventory.[21] I could find no reasonable combination of parameters that could fit the observed levels at the west station without

grossly overpredicting them at the center and east stations. The difficulty is that there are very few SO_2 sources to the southwest of the west station closer than Texas. Possibly the observations could be fitted by including a more specific treatment of wet deposition. The lower frequency of rainfall in Texas relative to the Ohio River Valley may allow sulfur to survive transport from Texas to Kentucky more easily than transport up the Valley. Shaw and Paur's data are some of the most important to be fitted by models. No model should be considered reliable unless it can do so!

Although it is not exactly a hybrid model, a semi-empirical model by Fay et al.[22-24] is related to those discussed above. Their model is applicable only to long-term average data, e.g., yearly data. Horizontal movement from sources is governed by two terms, one for diffusion in all directions and a second represented by a net average windspeed and direction. The model also includes the usual parameters, e.g., mixing height, deposition velocities, etc. The model is a transfer function between a gridded source-emissions inventory and the airborne sulfate concentrations and wet deposition fluxes observed at many sites. Parameters are optimized to give the best fits to those observations. After the parameters are determined, the model can be used to apportion the sources of airborne sulfate or of sulfate in precipitation at a particular site to SO_2 emissions in various states.

The Fay et al. model yields results that are in general agreement with commonly held views, e.g., that only 8% of wet sulfate deposition at Whiteface Mt., NY orginates from the State of New York, whereas 11% comes from PA, 12% from OH, and 5% each from IN and WV. One result that relates to Shaw and Paur's data is their prediction that 9% of the airborne sulfate in St. Louis is transported from SO_2 sources in Texas.

CONCLUSIONS

Although most work on receptor modeling on a regional scale has been done during the last 5 years, progress has been very rapid. Already the results have reliability comparable with the best of the more expensive absolute, source-based models. In my view, receptor models are not yet reliable enough to be used for policy decisions. Some of the largest uncertainties involve vertical concentration profiles of the key species, about which we know very little. Airplane studies conducted in the SURE study involved measurement of profiles of SO_2 and b_{scat}.[22] Concentrations of SO_2 usually dropped strongly at the mixing height, but b_{scat} was more nearly uniform to somewhat higher altitudes. Assuming that b_{scat} is an indicator of sulfate particles, this result suggests that models that assume good mixing of all species up to the same mixing height are too simple, and that a lot of sulfate exists at higher altitudes than we normally assume. If we attempt to correct models for this and other effects, we must be careful that we don't make them so complicated that they approach the much more detailed source-based models. Perhaps we can avoid some of the pitfalls by continuing make heavy use of the ratios of species rather than just the absolute concentrations. These approaches, which are beginning to deal with transformations of sulfate during transport and with differing depositional properties of particles and gases, may well be equally useful in the treatment of organic species.

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PRECONCENTRATION AND ANALYSIS OF ATMOSPHERIC ORGANICS USING A CARBON HOLLOW TUBE - GAS CHROMATOGRAPHY SYSTEM

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A carbon surface deposited on the interior of glass tubing and heat treated allows preconcentration of a wide range of atmospheric organics. Thermal desorption at 270°C introduces analytes into a gas chromatograph. Tube capacity ranges from 0.4-2.6 umoles and is well correlated to vapor pressure. Compounds with boiling points ranging from 80-285°C have been successfully analyzed. The design of the hollow tube allows analyte size discrimination in accordance with the Gormley-Kennedy equation. Using this theory and experimental data, accurate diffusion coefficients have been determined.

Analysis of chemical patterns has many environmental applications. Such patterns have been recorded, and in some cases components were determined.

PRECONCENTRATION AND ANALYSIS OF ATMOSPHERIC ORGANICS USING A CARBON HOLLOW TUBE - GAS CHROMATOGRAPHY SYSTEM

INTRODUCTION

Atmospheric organic compounds have been analyzed by many methods - impingers (1,2), fiber glass or polyeurethane filters (2,3), charcoal (4-6), XAD's (7,8) Tenax (2,8-10), and metal chelates (11). Analysis methods are dominated by gas chromatography (GC)(2,4,5,8,12) GC-mass spectrometry (6,9,10) or high performance liquid chromatography (2,13). Analyte recoveries suitable for these analyses often cause complications. Many recoveries require lengthy extractions before analysis (5,9,10). Thermal desorption has been presented as an effective means of sample introduction for GC analysis (8,10,14). Nevertheless, analyte decomposition has been observed during adsorption/thermal desorption on Tenax (4,10) one of the most widely used collectors.

Interior coated hollow tubes have been as thermally reversible chemisorbers (15,16) for preconcentration of atmospheric nitrogen containing compounds. The carbon hollow tube was designed for atmospheric organic preconcentration. The thin carbon surface allows easy thermal desorption of the organic molecules, a fact which likely minimizes decomposition of trapped analytes. In addition, the rapid speed of desorption makes direct interfacing into a GC feasible without requiring an intermediate trapping step. The tubular design of this collector provides a high degree of separation of gases from particles based on the large difference in diffusion coefficients. Only gases have diffusion coefficients large enough to allow removal by hollow tubes. Particles 0.1 umeter diameter and larger have diffusion coefficients which are not large enough to allow efficient collisions with the hollow tube walls.

EXPERIMENTAL SECTION

TUBE PREPARATION AND COATING DEPTH

Carbon surfaces were deposited on the interior of 6 mm or 2 mm OD Vicor glass tubes. Tubes were first soaked in 10% aqueous NaOH for one hour, and then thoroughly rinsed with deionized water. After fire polishing the glass ends and flame drying the entire tube, the coating procedure began. Soot from the smoke of a benzene or toluene fire was drawn into the hollow tube. With helium passing through the tube, it was heated to 270°C for 30 minutes. Finally, one inch of coating was burned away from the tube ends.

Deterioration in the carbon surface became apparent only after one month of use. Spaces barren of the carbon surface began to appear. Analyte capacities and measured collection efficiencies decreased. At this point, the coating procedure was repeated from the surface deposition step. Carbon coating depths were estimated using the difference in mass of a tube before and after coating.

GC INTERFACE

The inlet of a Hewlett Packard - 3890 GC required modification to accommodate the hollow tubes. The septum and retaining nut were replaced with a system capable of holding the hollow tube, Figure 1. A 0.25 in. Swagelok tee was used to connect the tube with the new inlet in a verticle position and to allow a carrier gas bypass route.

The capillary column inlet utilized the same basic design as that for the packed column. Modification involved replacing the teflon O-ring with a septum containing a standard uL injection needle. The Swagelok nut and and teflon ferrule were replaced by an ultra torr fitting.

SAMPLE PREPARATION

Samples of test organics were prepared by use of a permeation system. Standards were 99% mole pure or redistilled over a range of not more than 1°C. The permeation devices were one of two types - a screw top vial with a 0.125 in. hole drilled in the top and a Teflon diaphragm inside the cap, or a Pasteur pipette with the large end sealed and the small end formed into a capillary. After addition of the standards, the permeators were placed in glass chambers and air was passed through the apparatus. Permeator masses were recorded until a constant permeation rate was achieved.

EXPERIMENTAL PROCEDURE

Hollow Tube Capacity. Hollow Tube capacity was determined using the design in Figure 2 and either a Direct Current Discharge (DCD) (17) or a Bendix NO_x Analyzer as a detector. The flow rate was less than 100 ml/min to insure highly efficient adsorption of analytes.

Molecular Stability Experiments. The stability of analytes undergoing adsorption/thermal desorption was studied using two tubes. Analytes were first adsorbed onto one tube and thermally desorbed into an analyzer. In a second experiment, the same amount of analyte was adsorbed onto one tube and desorbed onto a second tube. The second tube was then analyzed.

Calibration curve comparisons utilized GC responses of a component injected as a solution standard and of the same component adsorbed on a hollow tuve. The analytes tested were toluene, 1-decanol, hexadecane. A gas sampling rate of less than 100 ml/min was used.

Chromatography Effect. In the chromatography effect experiments, analytes from a permeation chamber were collected on a hollow tube, and analyzed directly as in the molecular stability experiments. Next, the compounds was collected on a tube and then exposed to 600 mL/min of clean breathing air prior to analysis. The duration of exposure to the air was varied during testing.

Diffusion Coefficients. Compounds from a permeation chamber were passed through a hollow tube pair. The quantity of analyte adsorbed on each tube was then determined by GC. Use of a computer program allowed calculation of diffusion coefficients according to the Gormley-Kennedy equation (28).

Organic Component GC Patterns. Using a single tube, organic components evolved from natural substances were preconcentrated from a permeation chamber. Car exhaust was sampled from the plume of a cold engine. Near ground samples were taken from a 10 L glass bell jar set on the ground. Ambient air, car exhaust, and ground air samples were taken at 200 ml/min.

GC Analysis. A Hewlett Packard - 3890 GC with a flame ionization detector (FID) was used. An HP-3390A Integrator and an HP-19400A Sampler/Event Controller Module, which controlled a 3 way Delta Solenoid Value (Fluorocarbon Inc.; Aneheim, CA.), were also used in combination with the GC. Separations were achieved using a 1 m x 0.125 in. stainless steel 5% OV-101 column with a carrier gas flow rate of 22-24 ml/min or using a 0.25 mm x 30 m SE-30 column with a flow rate of 1.0 mL/min.

For packed column analyses, samples were desorbed into the GC at 270°C for 2.5 min. For capillary separations, the desorption time was 10 min to allow an ample carrier gas volume to flush the tube during the desorption process.

RESULTS AND DISCUSSION

Analyte capacities ranged from 16-440 ug depending on the analyte (Table I). Capacity versus analyte vapor pressure was fit to an exponential curve. The resulting correlation coefficient was 0.90. This dependence illustrates the importance of analyte vapor pressure as a collection efficiency parameter.

The fact that the carbon surface degraded upon repeated use points to the possibility that species adsorbed on the surface may also decompose. Tests of compounds adsorbed onto a tube and desorbed for analysis showed no decompositon losses as indicated by the data in Table II. Analytes produce the same response whether desorbed from one tube into the detector or from one tube to a second tube then into the detector. The quantitative re-adsorption of components transferred from one tube to the next illustrates the retention of component integrity through the adsorption/thermal desorption process. If the analytes had fragmented, the products would likely have been too volatile to be readsorbed by the second tube.

In a simular experiment (Table II) benzene and nitrotoluene were collected on hollow tubes and analyzed by GC. Virtually identical GC retention times (+/- 0.05 min) and area responses were observed whether desorbed through 1 or 2 tubes. The combination of reproducible retention times and peak areas reinforces the assertion that compounds are unchanged in the adsorption/thermal desorption process.

The final stability study involved comparing calibration curves of injected samples to those of desorbed samples. Table III shows the regression analysis for integration verses analyte mass data. This experiment showed that polar and nonpolar analytes produce simular responses whether injected or adsorbed onto and then desorbed from carbon hollow tubes. Calibration curves derived from injected and desorbed standards were linear over the range 0-700 ng. The smallest samples of toluene, decanol, and hexadecane were 23.7, 2.84, 1.64 ng respectively.

A study of the extent to which various species chromatograph from the carbon surface at room temperature provided interesting results. Figure 2 depicts the movement of organics as air is passed through a loaded tube. The chromatograph effect seems to disappear above a boiling point of approximately 100°C. Cyclohexane had little quantitative retention as seen by the loss of analyte after only 150 mL. of air flow. Benzene and heptane retentions were a bit better. Toluene and nitrotoluene (not shown) were not moved after 40 L of air.

One useful application demonstrated for this method is the determination of diffusion coefficients. Gormley and Kennedy have described the adsorption of species, individual molecules or agglomerations. Their mathematical expression is:

$$C_1/C_0 = 0.819\exp(-3.6568\pi DLn/F)+0.097\exp(-22.3\pi DLn/F)+\ldots(28) \qquad [1]$$

Where

C_0 = analyte concentration entering hollow tube 1

C_n = concentration exiting hollow tube n
D = diffusion coefficient of the compound in question
L_n = length of tube n
F = flow rate

Defining S_n as the quantity of analyte retained by tube n,

$$S_1 = 1 - (C_1/C_0) \quad [2]$$

$$S_2 = (C_1 - (C_2/C_1)) \quad [3]$$

Iteration began by assuming a diffusion coefficient of 0.1 cm^2/sec. By varying this value, S_1/S_2 values calculated from eqs. 2 and 3 were adjusted to the experimental S_1/S_2 ratio.

Experimental diffusion coefficients were in good agreement with those calculated from physical properties using the Arnold method (Table IV)(18). Experimentally determined diffusion coefficients were within the error range of the theoretical values. The average standard deviation of experimental diffusion coefficients was +/- 12.1%, and the average absolute deviation between the experimental and theoretical calculations was +/- 6.91%. These data indicated collection in agreement with theoretical predictions.

Chemical patterns of volatile organics evolved from spices are shown in Figure 3. These chemical patterns are readily distinguished from one another. But better separation was desired to obtain more distinct patterns for sources of atmospheric organics. Capillary column separation was used to obtain the chromatograms in Figures 4 and 5. Well resolved spice patterns are shown in Figure 4. Near ground (0-0.5m), ambient air and car exhaust patterns are all shown in Figure 5. The car exhaust and near ground patterns contain all of the atmospheric organics found in ambient air.

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Table I

Hollow Tube Capacity

Compound	Capacities ug	Capacities umoles	Boiling Point °C	Vapor Pressure mm Hg @ 23°C	N
acetonitrile	16.38	0.397	81.6	68.2	1
benzene	31.1+/-2.2%	0.398+/-2.2%	80.1	61.6	2
toluene	78.5+/-6.1%	1.17 +/-6.1%	110.6	17.0	4
chlorobenzene	140 +/-2.8%	1.25 +/-2.8%	132	9.0	2
nitrobenzene	181 +/-2.4%	1.47 +/-2.4%	210.8	0.46	4
m-nitrotoluene	257 +/-10%	1.87 +/-10%	232.6	0.34	2
hexylamine	59.6+/-4.4%	0.589+/-4.4%	130	6.0	3
pyrrole	156 +/-1.7%	2.47 +/-1.7%	130	6.8	2
pyridine	181 +/-17%	2.30 +/-17%	115.5	14.5	4
nicotine	436 +/-9.9%	2.62 +/09.9%	242.3	0.20	3

Table II

Analyte Transfer

Compound	Desorptions prior to detection: single tube	tubel-> tube 2	%Recovery	N	Detector
1-butanol	96.0+- 2.9%	99.48+- 5.5%	103	3	DCD
2,4-pentanedione	55.3+- 7.0%	53.75+- 4.6%	97.2	2	DCD
chlorobenzene	25.5+- 9.5%	24.7 +-13.8%	97.2	5	DCD
pyridine	78.5	79.0 +-16.4%	101	3	NO_x
benzene	2.74	2.77	101	1	GC
nitrobenzene	18.7	18.2	97.4	1	GC

Table III

Calibration Curves

Compound	Delivery	Calibration Curves Slope	Intercept
toluene	injection	1.42+/-0.06	-4.03+/-1.3
	TD	1.26+/-0.13	4.47+/-8.2
1-decanol	injection	1.12+/-0.09	3.93+/-3.7
	TD	1.61+/-0.07	-18.3 +/-13
hexadecane	injection	1.08+/-0.08	0.30+/-0.05
	TD	1.16+/-0.05	1.46+/-1.16

Table IV

Diffusion Coefficients

Compound	Theoretical Value cm^2/sec	Experimental Value cm^2/sec	N
pyridine	0.09524	0.109+/03.85%	2
chlorobenzene	0.08146	0.0789+/-9.64%	3
toluene	0.08507	0.0802+/-1.50%	12
1,2-dichloroethane	0.09312	0.0931+/-32.9%	5
1,2-dibromoethane	0.08381	0.0744+/-12.8%	4

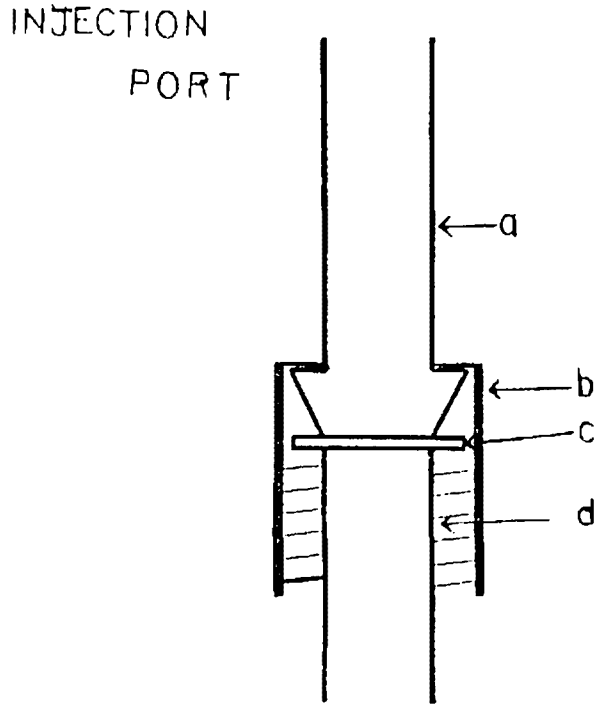

Figure 1. Modified injection port. a - port connector.
b - Swagelok nut. c - Teflon O-ring.
d- injection port inlet

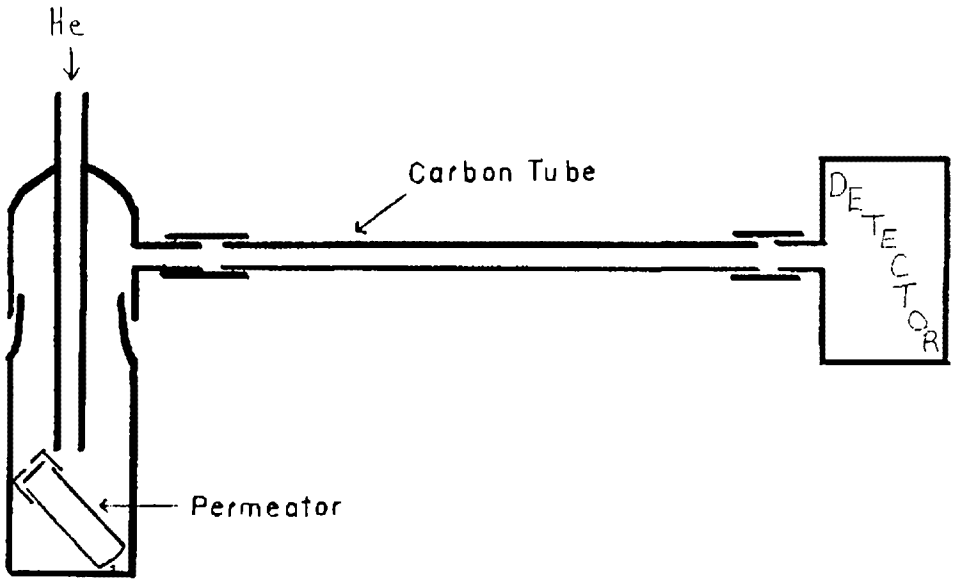

Figure 2. Capacity experimental design

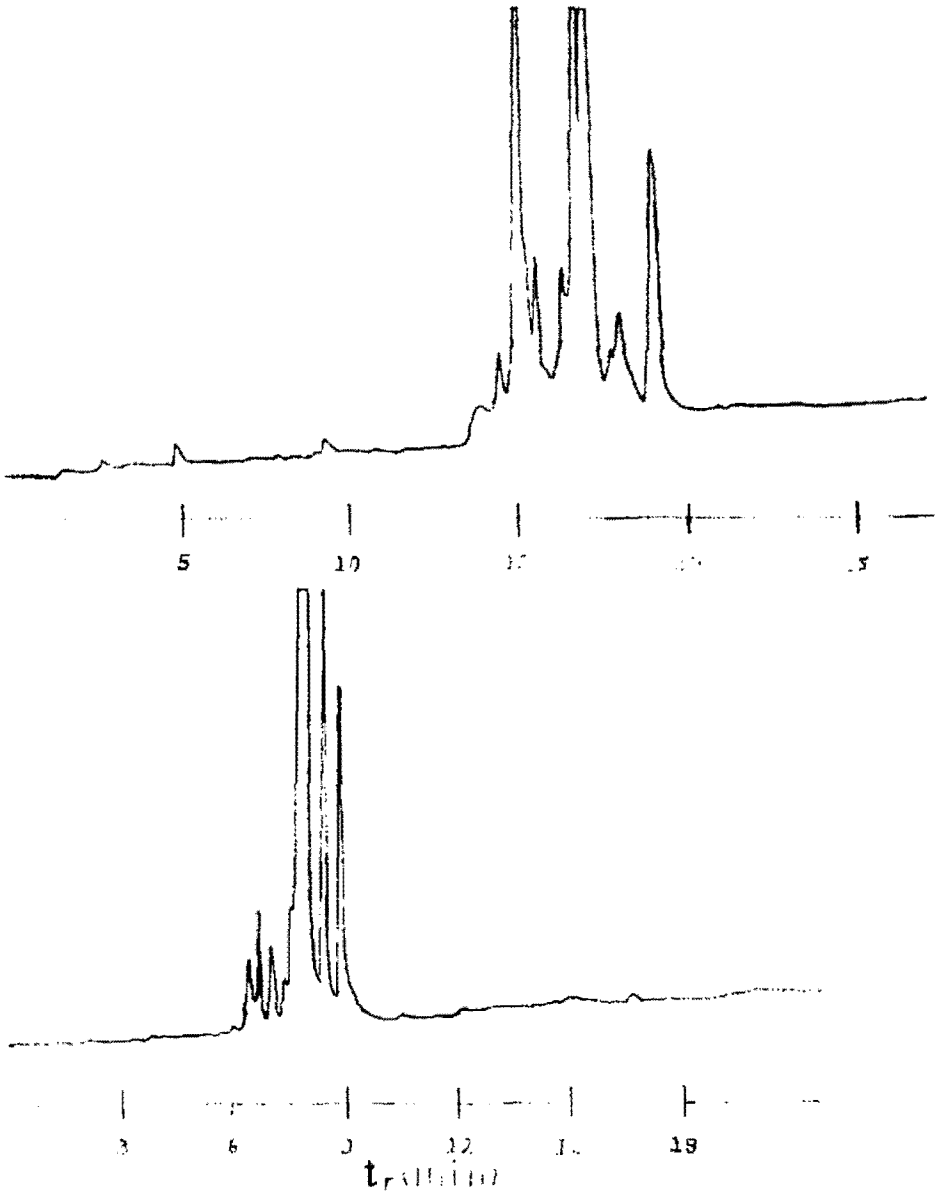

Figure 3. Chromatograms of spice effluents. Cinnamon, top. Nutmeg, bottom.

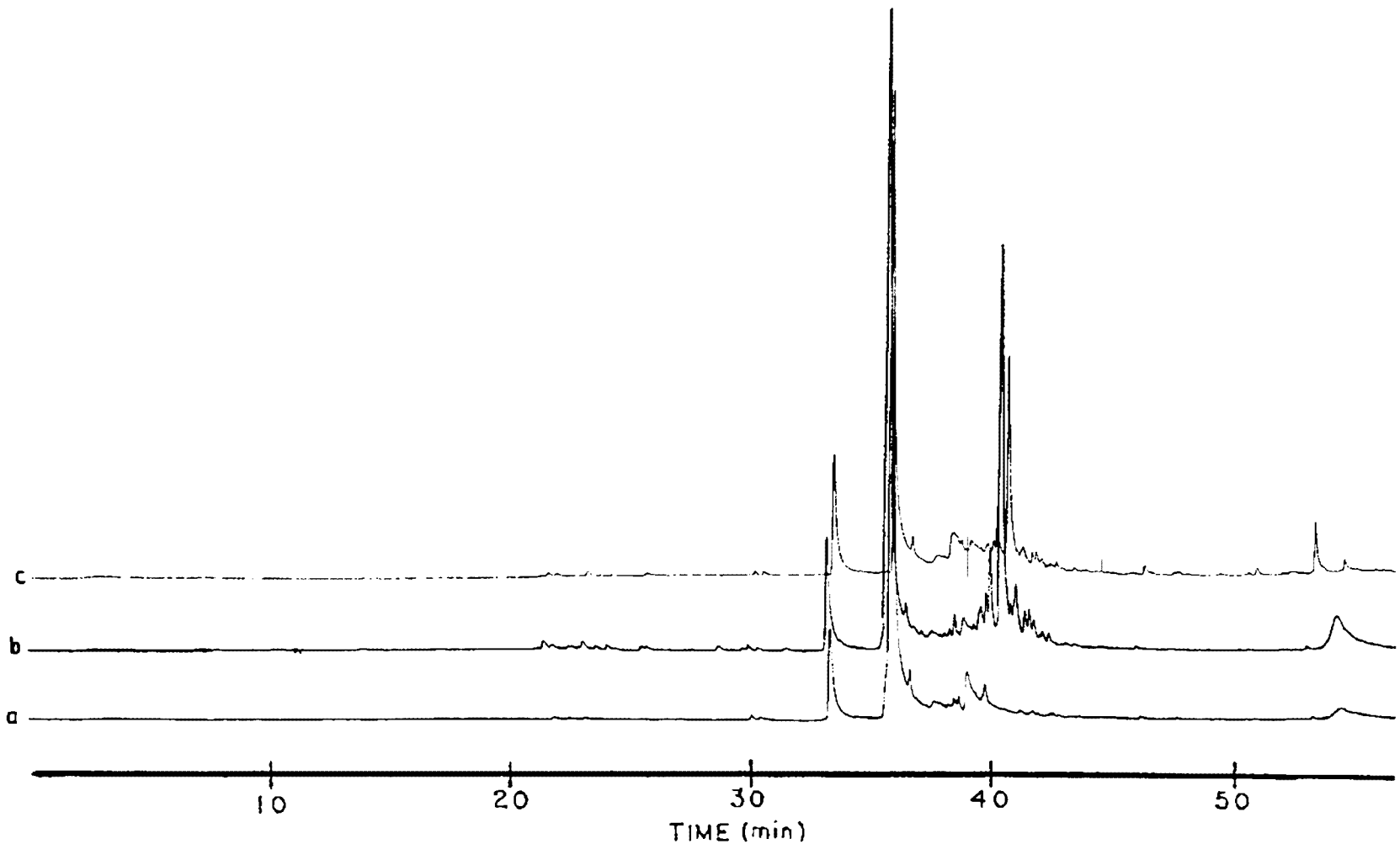

Figure 4. Capillary column chromatograms of spice effluents. a - Clove. b&c - Clove and ginger combination

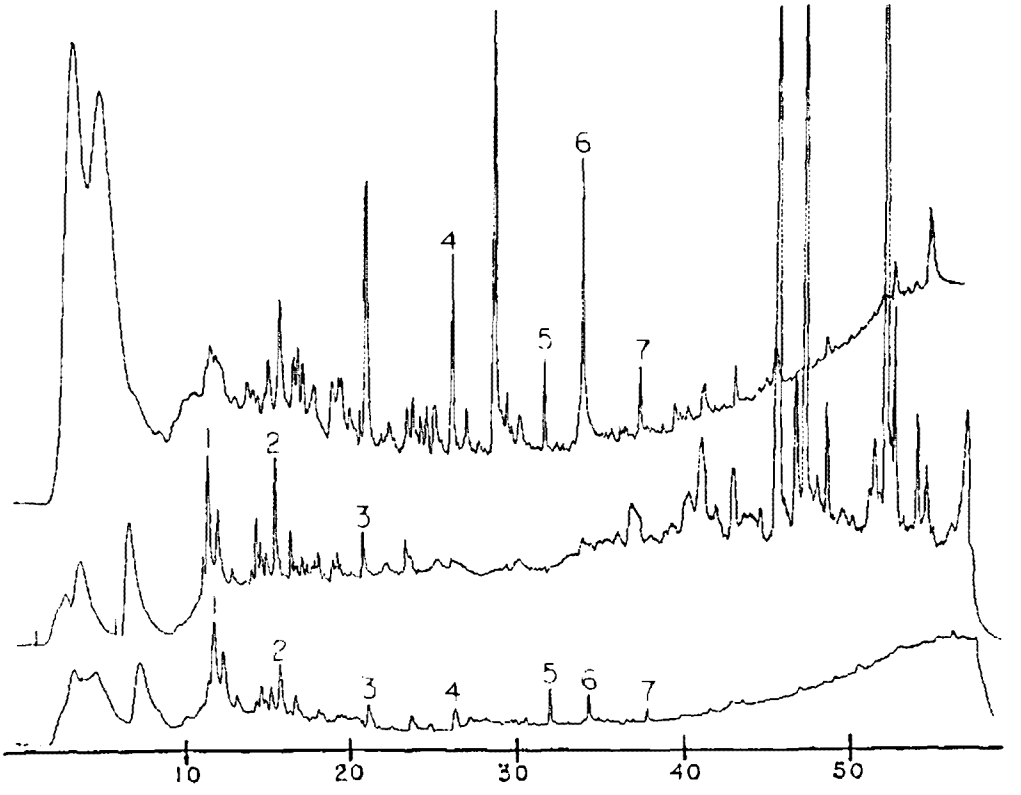

Figure 5. Components of ambient air pattern. Ambient air bottom. Car exhaust, center. Noncirculating near ground air, top. Numbered peaks designate the same retention times.

Analysis of Vinyl Chloride Monomer in Ambient Air by Gas Chromatography

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Delaware recognized the need to monitor ambient air levels of vinyl chloride because of repeated high-level emissions, and in April of 1984 started a program designed to locate potential problem areas of vinyl chloride emissions. A decision had to be made as to which of three methods to use; 1) GC/MS analysis of adsorbent tubes, 2) GC analysis of tedlar bags, or 3) GC analysis of ambient grab samples (glass bulbs).

It was decided that field samples would be taken using glass bulbs, and analysis would be done with a Photovac 10A10 Gas Chromatograph with a photoionization detector. This instrument is capable of measuring levels of vinyl chloride as low as 0.1 parts per billion. A procedure was developed to measure these ambient levels by direct injection of grab samples. A sampling protocol was established, and the program was instituted.

Delaware's program was the first application of direct measurement of ambient levels of vinyl chloride using the Photovac Gas Chromatograph in EPA Region III and has been functioning with very little problems since April of 1984. An initial problem was interferences with light hydrocarbons, but this was corrected by using a more appropriate column. Another problem was optimizing the sampling time for the grab sample. The technical assistance document entitled "Sampling and Analysis of Toxic Organic Compounds in Ambient Air" resolved this problem, and was helpful with other procedural techniques.

Analysis of Vinyl Chloride Monomer in Ambient Air by Gas Chromatography

Because vinyl chloride has been identified as a "carcinogen and a priority toxic pollutant" [1] and in addition, it is estimated that "4.6 million people are potentially exposed who live within five (5) miles of industrial sites at which environmental emissions could occur" [2], it has become necessary to measure the ambient air levels. There are three (3) basic methods for testing in ambient air: (1) Tenax or charcoal tube samples, which are taken over a given time period, and then thermally desorbed or chemically extracted for GC/MS analysis. This method is reliable, but sometimes requires placing pumps and tubes in public sight, thus presenting the possibility of vandalism. The sample is usually taken over a minimum of one (1) hour, so after the sampler is set-up, a wind shift could cause the sampler to be outside the area of the plume. (2) Tedlar bag samples can be used, but similar problems can occur. Also, an instrument that can detect vinyl chloride in the parts per billion (ppb) range is required. (3) Glass bulb samples which are instantaneous can be valuable in identifying problem areas. It also requires an instrument in the ppb range. All three methods are useful, and if used properly, can yield good results.

The State decided that the first aspect of monitoring for vinyl chloride should be the identification of potential problem areas and the best method for carrying out this phase of the program would be an instantaneous measurement using the glass bulb sampling technique.

Method Apparatus

The gas chromatograph used was a Photovac 10A10 Gas Chromatograph with a photo-ionization detector. This instrument has two (2) separate columns, each with its own injection port. The unit is manufactured to be portable so the columns are not temperature controlled. This is not a serious problem if the unit is used in a temperature controlled environment, however, for precise quantification, the unit should not be used in a field situation. It would only be acceptable for field use if identification and an estimated concentration were desired.

The unit should always have a constant flow of gas through the columns even when not in operation. This will minimize start-up time when the unit is needed. The carrier gas used is ultra-zero air, however, nitrogen or helium can be used. It is very important to never inject anything other than a gas sample into the instrument. A liquid sample would contaminate the columns to the extent that they would have to be removed and reconditioned. The column of choice is a 4 ft. x 1/8 inch teflon column packed with BHT on Carbopack. The manufacturer of the instrument has suggested it may also be possible to use a column packed with picric acid for vinyl chloride analysis. The use of either of these two columns will eliminate any interferences caused by light hydrocarbons during the analysis.

Standards

Standards are made by doing serial dilutions from a tank of vinyl chloride gas certified by the manufacturer. Four (4) standards are usually run at any given attenuation, and a best-fit line is calculated. No extrapolations are done beyond the highest standard or below the lowest standard.

Field Sampling

Samples are obtained in the field and returned to the laboratory for analysis. Because instantaneous samples are desired to identify problem locations, glass bulbs are utilized. 250-ml. bulbs with a pump drawing air at 5 L/min. are used for sample collection. It is recommended that the bulbs "have their volume replaced 5-10 times to insure that equilibrium has been obtained." [3] This allows for a sample time of 15-30 seconds.

The bulbs should be conditioned before using by removing the teflon stopcocks and placing in an oven at 250°C for twenty-four (24) hours and then flushed with zero air for one (1) hour. After this initial conditioning, bulbs used for sampling that contained only low levels of pollutants can be cleaned by flushing in a stream of zero air for one (1) to two (2) hours. Bulbs which contained high levels of pollutants should be cleaned by reconditioning.

After sampling, the bulbs should be either wrapped or placed in a container which will minimize the exposure to light. Also exposure to high temperatures should be avoided. The samples should then be run the same day. This will minimize any problems with pollutants escaping from the bulbs.

Sampling should take place downwind of the suspected source, and as close to the center of the plume as possible. An upwind sample should always be taken. Date, time, wind speed, wind direction, distance from source, locations, and applicable meteorological conditions recorded. A blank bulb should also be taken into the field, returned, and analyzed along with the field samples.

Sample Analysis

Samples are allowed to equilibrate to room temperature before the analysis is done. Due to the temperature differences between the outside air and the inside air, all samples should ideally be corrected to standard temperature and pressure. However, due to the nature of the sampling, these calculations could be avoided without greatly affecting the results of the analysis. A 1 ml. sample is taken out of the bulb using a gas tight syringe and injected into the appropriate column. All samples are analyzed, along with the blank and then the standards are analyzed. Peak area is measured using an electronic integrator and sample results are calculated from the standards' best fit line. The results from the blank bulb should be subtracted from all sample bulb results to yield the final sample results.

A gas flow of 10-15 ml/min. should be maintained through the column during testing. The flow should remain constant for all analyses but is is not critical to have identical flows on a day-to-day basis since standards will be run daily. Results are usually reported to the nearest 0.1 ppb.

Conclusions

The glass bulb sampling method proved very effective in determining instantaneous levels of vinyl chloride. Development work was then done for the measurement of benzene, p-dichlorobenzene, and tetrachloroethylene in air. This sampling method also proved effective for these compounds, and the glass bulb method is still in use in Delaware for the identification of toxic chemicals in air.

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EPA-600/X-83-025 - U.S. EPA

CONTINUOUS AMBIENT MONITORING OF VINYL CHLORIDE IN THE PART PER BILLION RANGE UTILIZING THE PHOTOVAC 10S GAS CHROMATOGRAPH

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A Photovac 10S gas chromatograph is currently being utilized in Delaware to continuously monitor ambient levels of vinyl chloride monomer in the part per billion range for emergency planning and response purposes. The instrument is strategically located in a populated area downwind of a large petrochemical complex that include two polyvinyl chloride manufacturing facilities. The GC functions as a first line detector in the event of a large release of vinyl chloride and automatically alerts emergency response personnel when a preset level of VC is exceeded.

A 50ppb alarm level of vinyl chloride has been programmed into the microprocessor. In the event this preset level of vinyl chloride is exceeded, a signal is sent to an autodialer which automatically dials a preset telephone number and sends a pre-recorded message. In Delaware, the Emergency Planning and Operations Division receives the telephone call and initiates appropriate follow-up according to the outlined emergency plan.

The Photovac 10S employs photoionization detection with part per billion resolution of vinyl chloride. The carrier gas utilized is ultra pure air which lends itself nicely to remote unattended operation. Automatic calibration utilizing a 100ppb certified vinyl chloride cylinder standard sets retention time and quantitative levels. The injection frequency is presently set at five minutes with calibration and ambient sampling alternating to provide proper quality assurance. An internal sampling pump draws in outside air through a Teflon sampling line and delivers the sample through gas sampling valves to a BHT on 40/60 Carbopack column.

With the addition of a communications package utilizing a RS232 output and telephone modem, actual concentrations and associated quality assurance information are provided to a remote printer for decision making purposes. The 10S70 has an impressive operating record with over 30,000 injections performed before maintenance was necessary.

CONTINUOUS AMBIENT MONITORING OF VINYL CHLORIDE IN THE PART PER BILLION RANGE UTILIZING THE PHOTOVAC 10S GAS CHROMATOGRAPH

Introduction

The presence in Delaware of a large petrochemical complex including polyvinyl chloride manufacturing facilities prompted the establishment of a continuous monitoring program for vinyl chloride monomer. The major concern of the Department of Natural Resources and Environmental Control was the potential for a large release of vinyl chloride to the atmosphere which would expose surrounding populated areas to a large dose committment. Of a secondary nature was the long term survey to determine ambient levels of vinyl chloride as a result of normal emissions from the plants in the range of 100-200 tons per year.

The greatest concern involved the town of Delaware City with a population of 1850 persons located approximately 3.5 miles southeast of the PVC facilities. The close proximity of the town to the facilities and the fact that it lies in a prevailing wind direction during a majority of the year was sufficient justification for establishing a continuous monitoring program. The "real time" data acquisition aspects of this operation could be easily integrated into Delaware's existing emergency operations plan providing for necessary response actions to protect the public.[1]

A survey of available gas chromatographic instrumentation was initiated which would meet the requirements of remote continuous operation in the part per billion resolution range and have output capability for alarm purposes. After considerable evaluation the Photovac Model 10S70 was selected since it met these basic requirements plus the ability to communicate over phone lines for remote surveillance purposes. The advantages of this type of instrument are quite obvious providing "real time" air toxic data at the emergency planners fingertips so that necessary response actions can take place.

An acceptable site for the gas chromatograph was established on the second floor of the Delaware City Fire Hall. This location met the recommended siting requirements outlined by the Environmental Protection Agency and was strategically located in the populated area directly downwind of the sources. The fire hall also met the state's requirements of a secure site with good accessibility. The second floor location was excellent in that it provided an intake line location away from obstructions with a clear view of the industrial complex.[2]

System Design

The 10S70 Model gas chromatograph is supplied with relay contacts which interface with an auto-dialer for call-up capability. A Metro Tel, Tel-Aid auto dialer was selected for use with the system. The Tel-Aid dialer has the advantage of programmed stacking of up to four telephone numbers in order of priority for automatic sequential call-up. The dialer is easy to program with a standard telephone number programming pad.

A Radio Shack CCR-81 computer cassette recorder was incorporated into the system for use in providing a pre-recorded message for administrative use. The message was recorded on an "endless loop cassette" to provide for repetitive no rewind capability. When the pre-set concentration of 50 parts per billion vinyl chloride is exceeded,a signal (relay contact closure from the 10S70) activates the autodialer. The dialer initiates a call to the first telephone number (by priority) programmed. When the party answers, the dialer activates the recorder containing the message "This is the Air and Waste Management Division. The 50 part per billion level of vinyl chloride has been exceeded at Delaware City. To disable message, depress and hold star button on your telephone".

If the called party does not answer, the dialer automatically sequences to and calls the next level number. The dialing sequence continues until a party answers and the call-up is deactivated. To deactivate the system, the answering party momentarily presses the "star" button on his receiver. A tone deactivates the dialer and places it in a stand-by configuration. The call-up sequence presently utilized in Delaware is designed to insure that the phone is answered and the information is relayed to appropriate personnel. In the call-up procedure, if DNREC personnel do not answer, the 911 emergency number is dialed, thus assuring receipt of the message. The alerting system is patterned after Delaware's comprehensive radiological emergency plan which was developed as a result of a multi-reactor nuclear power plant complex in the area.

Gas Chromatograph Operation

The 10S70 employs photoionization detection with 0.1 part per billion resolution of vinyl chloride utilizing a BHT on 40/60 Carbopack column. The carrier gas utilized is ultra zero ambient monitoring air (Scott Gas) which lends itself nicely to remote unattended operation. With a low demand rate, the type K air cylinder lasts approximately 6-8 weeks. Calibration is accomplished utilizing a certified vinyl chloride, in-air cylinder mixture (Scott Gas) in the concentration range of 100 ppb. Under the present calibration scheme, the stainless steel, type B cylinder lasts approximately three months. A calibration and sampling sequence alternating every five minutes is presently being utilized with the GC. This provides representative sampling and allows calibration adjustment of retention time for ambient temperature variation since the column is not temperature controlled. An internal sampling pump draws outside air through a Teflon sampling line to the sample loop.The pump is operated for 60 seconds in the vacuum mode to properly flush the sampling line and loop with outside ambient air.

The 10S70 is fully programmable with respect to those functions which are required for automatic operation. A particular analysis sequence can be programmed to continuously sample and analyze utilizing multi-function valve arrangements, calibration and sampling sequences, and reporting of data utilizing time weighted averages and maximum level exceedences for alarm purposes.

An overall quality assurance program to insure the integrity of data collected is an essential part of this sampling program. Along with the continuous calibration outlined previously, Delaware utilizes a cylinder containing an unknown quantity of vinyl chloride provided through the Research Triangle Institute. A cylinder containing an unknown quantity of vinyl chloride was analyzed recently within 0.6% of the actual concentration. In addition, daily visits by staff evaluate the operation of the system including retention times, calibration records, operating temperatures and other operating parameters.[3]

The operating performance of the 10S70 has been quite impressive with over 30,000 injections performed before maintenance was necessary. This represents a three month period of continuous operation. As indicated previously, minimal ambient temperature variability is not a problem with the GC since autocalibration is accomplished with every other injection.

The present configuration of the 10S70 includes an internal printer/plotter which provides a chromatogram trace plus operational parameters such as dates, compound names, retention times and peak area/concentration. A remote terminal is also operated in conjunction with the 10S70 utilizing the built-in RS-232 output and telephone modem. The terminal is located at the Department's New Castle Laboratory where it is utilized for remote surveillance of the GC to determine actual concentrations, data validity and proper operation without travelling to the site.

Because of the success in operating the 10S70 for continuous monitoring of vinyl chloride, there is interest in doing simultaneous analyses of other organics. The emphasis is on determining the ambient levels of both benzene and the chlorinated benzenes because of known emissions in the area. The 10S70 has the capability of this type of analysis. Calibration would be accomplished by exposing the 10S70 to a mix of these components at known levels from a cylinder. The State of Delaware is also having a portable monitoring van constructed which will house an additional 10S70 for mobile air toxic type sampling along with routine air quality monitoring. The mobile van approach lends itself nicely to emergency response and short term studies to establish ambient concentration levels under varying meterological conditions.

Data from the van will be transmitted via cellular phone in "real time" to the Department's DEC 11/23 computer for subsequent processing and storage. For emergency response purposes data may also be transmitted to any modem-coupled terminal in the state for decision making purposes.

A Real Life Scenario

On February 28, 1986 at 9:40 p.m. a process failure occurred at one of the PVC facilities located at the industrial complex northwest of Delaware City. A safety valve released approximately 50 pounds of vinyl chloride monomer to the atmosphere. With an accompanying 2-5 mph wind from the northwest, the vinyl chloride plume was detected at the Delaware City fire station at 10:19 p.m. with an initial concentration of 94 ppb. The incident lasted for approximately one hour with a maximum concentration of 117 ppb observed. The emergency call-up sequence worked flawlessly with the auto-dialer initiating a call to emergency operations which in turn called the DNREC staff chemist. The staff chemist proceeded to the site and through a series of quality assurance checks established that the data was indeed valid. The chemist then informed his supervisor and Emergency Operations so that appropriate action could be taken. In this instance the only action taken was notifying a group of citizens who had requested notice of values over 50ppb.

This incident proved the reliability of the 10S70 and the established call-up procedure as an effective tool in emergency planning and response operations.

Acknowledgement

The author wishes to express his appreciation to Robert R. French, Manager, Air Resources Section, for the helpful suggestions and comments. The author would also like to thank Jeffrey C. Rogers for his diligence in making this project a success.

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AMBIENT MONITORING FOR EIGHT TOXIC AIR POLLUTANTS AT THREE SITES IN PHILADELPHIA

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Abstract

This paper will present results of initial method development work and analytical data for a selected group of trace level ambient organic compounds present in Philadelphia's air.

The methodology employed centers on the use of a novel composite sorbent tube containing glass beads, tenax and ambersorb XE-340 in series to form a sample collection tube capable of retaining and satisfactorily desorbing a wider range of volatile hydrocarbons than would normally be possible with a similar tube containing tenax alone. The system has the added advantage of using a smaller sorbent tube with much less total sorbent material than is typical for a single component tenax tube. Subsequent analysis is by thermal desorption coupled with GC-FID/ECD and selected ion monitoring MS.

The compounds investigated include methylene chloride, chloroform, carbon tetrachloride, 1,2-dichlorethane, benzene, 1,2-dichloropropane, trichloroethylene and perchloroethylene. Ambient levels measured were generally in the 0.1 to 10 PPB range 24 hour average. This group of eight compounds is monitored every sixth day at three sites in Philadelphia as part of an ongoing ambient monitoring program for non-criteria pollutants. Procedures and monitoring results will be presented as well as the techniques used for tube preparation, storage, standard preparation and analysis, and quality assurance procedures.

AMBIENT MONITORING FOR EIGHT TOXIC AIR POLLUTANTS AT THREE SITES IN PHILADELPHIA

Introduction

In recent years, various porous polymer and carbonaceous adsorbents have been used extensively as a means of trapping a wide range of volatile organic pollutants for subsequent thermal desorption and analysis by GC or GC-MS (1-4). Most of these have been used singularly in glass or metal traps of various configurations. The most widely used adsorbent at present, tenax, has been used for sampling numerous compounds including many aromatic and volatile chlorinated pollutants (3). Tenax, however, has low breakthrough volumes for highly volatile compounds such as vinyl chloride and methylene chloride, necessitating the use of relatively large amounts of adsorbent (2 gms. or more) or an alternative trapping media. To overcome the limitations of tenax for the collection of vinyl chloride for example, spherocarb has been used; however, this material will not satisfactorily desorb other compounds, including aromatics.

An approach to the solution of the problems associated with single sorbent packed tubes in our laboratory has been to use a system based on a composite tube containing three adsorbent beds in series: glass beads, tenax and Ambersorb XE-340. With this system, many of the more volatile compounds that pass through the tenax layer are retained by the more adsorbent XE-340 layer which is considered to have similar adsorbent properties to that of charcoal while being relatively hydrophobic and unaffected by high humidity. With this configuration, the total weight of adsorbent and the size of the sampling tube can be kept small (250 mg. glass beads, 75 mg. tenax and 170 mg. Ambersorb XE-340) while maintaining high adsorption and desorption efficiency for a broad range of hydrocarbons. A diagram of the tube is presented in Figure 1.

The instrumentation, sample tube and basic method described in this paper have been used successfully over the last four years in the analysis of a number of organic pollutants in ambient air at the City of Philadelphia's Air Management Services Lab. The results presented here are for the period of January to December 1985, and are part of an ongoing study of the levels of eight specific pollutants at three sites in the Philadelphia area. The compounds under investigation are given in Table 1.

These compounds (except 1,2-DCP) were selected because they are among the 99 toxic air contaminants regulated by Air Management Regulation VI, the city's toxic air pollutant regulation. They are also in widespread, large volume use in Philadelphia and are detectable to sub-PPB levels in air when concentrated for analysis by GC or GC/MS. Additionally, they are compounds under investigation in a cooperative study with the EPA as part of the Integrated Environmental Management Program being conducted in Philadelphia, Baltimore and San Jose. Other compounds could have been included but are presently not of interest in our program.

To date, three monitoring sites are being used in the project: AMS Lab, N. E. Airport, and Defense Supply. These sites, shown on the city map in Figure 2, were selected to begin obtaining data for a data base that, when coupled with source emission information, will be useful in making preliminary estimates of Philadelphia's urban air quality as it pertains to these contaminants. These non-source oriented sites are existing state and local air monitoring stations, representative of large sections of the city. Other source-oriented sites, which would likely give higher average concentrations, have been used in Philadelphia, but are not part of this study.

Experimental

Sample Tube Preparation

The tenax-ambersorb sorbent tubes are designed to fit the desorption chamber of an Environchem Model 780 or 810 concentrator.* The tubes are reusable but prior to each use, reconditioning is necessary. Typically, this has been done in batches of approximately 10 tubes in an apparatus designed for this purpose (Figure 3). The apparatus consists of a manifold, metering valves and a series of heating jackets which heat each tube while helium backflushes the sorbent bed at a constant rate. Normally, a conditioning period of 1-2 hours at 250-300 ^{0} C with a helium flow of 50-70 ml/min is sufficient to reduce background contaminants to acceptably low levels. The tubes may also be conditioned overnight. After conditioning, each tube is spiked with an internal standard containing chlorobenzene and stored in teflon capped vials in a freezer until use.

Experiments performed to determine if storage time has an effect on background contaminant levels or sample recovery have indicated that for periods of up to one month, no significant sample deterioration or increase in background occurs.

The internal standard spiked onto the tubes before sampling functions as a quality assurance check on the sampling procedure. Poor recovery is indicative of sample loss due to breakthrough during sampling or problems associated with the sampling procedure or subsequent sample handling.

A "static dilution method" is used to prepare the chlorobenzene and other standards (5). Basically, this procedure involves preparation of a liquid standard in methanol and injection of an aliquot (25 ul) into an evacuated container of known volume as depicted in Figure 4. The container is allowed to come to atmospheric pressure, the syringe removed from the septum sealed cap, and the contents of the flask agitated until use. Aliquots (0.5 ml) of this gaseous mixture are withdrawn with a gas syringe and spiked onto the tenax layer of each tube. Typically, the amount of compound added to the sample tubes is calculated to be within the concentration range of the sample components of interest (1-10 PPB).

* Envirochem, Inc., Route 897, Kemblesville,PA 19347

Sample Collection Procedure

The basic sample collection apparatus is shown in Figure 5; it consists of a 1/4 inch I.D. swagelok union with teflon furrels, a particulate filter, a low flow metering valve and an AC diaphragm pump. At the beginning and end of each sampling period, relevant information is logged in on the sample data sheet; this includes start and stop time, ambient temperature, barometric pressure and comments. Initial and final flow measurements are obtained by placing a surrogate sampling tube attached to a bubble meter in line in place of the actual sample tube.

Generally, two independent parallel sample tubes, plus one site blank tube, are used per site. The two sample tubes are set at flow-rates such that the second tube samples approximately twice the volume of the first (i.e., 20 and 40 L). This procedure has been recommended in an EPA publication and is designed to provide a degree of quality assurance in that good precision between samples should exist if there are no sampling volume effects (6).

The "site blank" tube for each site originates from the same batch as the sample tubes and is used to determine residual background plus contaminant levels from normal conditioning and sample storage. It is not exposed but is transported to the site and analyzed with the two sample tubes.

Total sample volumes of 10 to 30 liters have been found to be necessary to obtain sufficient sample for detection limits in the range of 0.02 to 0.20 PPB (V/V) for most compounds of interest in ambient air. For a 24 hour sample, this corresponds to minimum sampling rates of 7 to 20 ml/min. Larger sample volumes improve detection limits for some compounds in the sample, but breakthrough occurs for the more volatile compounds above certain sample volumes. Preliminary tests in which two tubes were connected in series to sample volumes of 10, 30, 60 and 100 L over 24 hours have indicated that significant breakthrough of methylene chloride occurs at 60 liters and above. For these reasons, 40 liters was set as the upper sample limit to avoid breakthrough, and 20 liters as the lower limit to maintain sensitivity.

Sample Analysis

Samples returned to the lab are stored in a freezer at 0° C. As soon as possible, generally within 3 days, each tube is spiked with a "preanalysis"quality assurance standard consisting of hexafluorobenzene (HFB) in an identical manner to that used for the "pre-sampling" quality assurance standard (chlorobenzene). This standard is used to detect problems associated with the analysis procedure such as internal trap leaks(in the concentrator) or incomplete sample transfer.

At least one day before analysis of the samples, a tube is prepared for the external standard used to quantitate sample components. A liquid standard is prepared containing 500 ul of each of the 8 compounds monitored, plus the two quality assurance compounds, giving a total volume of 5.0 ml. The static dilution method is again used to prepare the gaseous standard for spiking.

An additional "blank" tube (standard blank) is also set aside from the same batch to account for possible background contamination of the standard tube. As was done with the quality assurance standards, the amount of each component spiked onto the external standard tube is calculated to be within the range anticipated for a typical sample. A 10.0 ul injection of the above standard into a 4 liter dilution container and a 0.5 ml (gas) spiking volume, for example, represents 1-1.5 PPB of each compound in a 40 liter sample (.1 to .2 ug).

When a set of samples is ready for analysis, the usual procedure is to analyze the tubes in the following order: Standard blank, external standard, site blank, low volume sample, high volume sample .Additional standards plus a "system blank" consisting of background attributable to the internal components of the Envirochem Concentrator are also analyzed as necessary. A typical 8 hour day's analysis schedule on an instrument usually consists of 6 to 8 tubes.

Analysis By GC-MSD

Approximately 25% of the 1985 samples were analyzed by an HP 5970 MSD System in the selected ion monitoring mode. The ions monitored are presented in Table II.

General instrument parameters for the Gas Chromatograph and MSD are presented in Table III.

For positive identification of a compound, each of the three ions must be present at the proper retention time and in the correct relative ratio. Quantitation is based on the summed area of the three ions.

Analysis By GC-FID/ECD

Roughly 75% of the samples were analyzed with an Envirochem Concentrator interfaced to an HP 5790 gas chromatograph, equipped with flame ionization and electron capture detectors. A post column splitter, as show in Figure 6, was used to split column flow between the two detectors with a 39 (FID) to 1 (ECD) split ratio. Other essential parameters are as presented in Table III.

Additional Quality Assurance Procedures

On a monthly basis, as an added check on the analytical procedure, a blank and two sample tubes containing all the compounds of interest are prepared by each analyst, using the static dilution procedure. The tubes are exchanged and treated as unknowns. In addition to following the same analytical procedure as used to quantitate actual samples, a full calibration curve for each compound is prepared to verify linearity at the concentration range for typical samples.

Results and Discussion

A statistical summary of the data for the AMS site, the site for which the largest number of samples was obtained, is given in Table IV. Arithmetic means for only the quantifiable results have been computed along with standard deviations and ranges. Assuming that the calculated mean values are roughly representative of the annual means, they can be compared to Philadelphia's air quality guidelines and EPA's upper-bound cancer risk levels. In our opinion, this shows that only benzene and 1,2-DCE are in sufficient concentration to be of interest at that site, being 10% and 3% respectively of the guideline and representing upper-bound risks of 51 and 125 per million respectively (assuming lifetime exposure at that concentration). Results at other sites might be different depending on nearby emission sources, and could be radically different for a source oriented site; e.g., very limited measurements near a pharmaceutical firm are approximately 35% of guideline and 378 per million risk for carbon tetrachloride (7).

Arithmetic means for AMS plus the remaining two sites are presented for comparison in Table V. Although there were fewer samples for the Defense and N.E. Airport sites due to their Fall 1985 start up dates, the same general relationship exists for this data as was evident for the AMS site data. Table VI summarizes the results obtained for the two internal standard compounds spiked onto the sample tubes. In general, satisfactory recoveries were obtained. Figure 7 is a graphical representation of the data from Table IV and serves to illustrate the relative concentration difference between compounds.

In summary, AMS site which is near a high traffic intersection in a predominently residential area, 1-2 miles from heavy industrial operations, contains the highest relative levels for the monitored pollutants. The N.E. Airport site, located in a comparatively suburban area of the city and away from traffic, contains the lowest levels. The monitoring system described has produced generally good precision and accuracy in the low or sub-PPB range for the pollutants monitored and at a total cost of $70-80,000, is affordable for many agencies.

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TABLE I. COMPOUNDS MONITORED

Methylene Chloride	(MECL)
Chloroform	(CHL)
1,2-Dichloroethane	(1,2-DCE)
Benzene	(BZ)
Carbon Tetrachloride	(C.TET)
1,2-Dichloropropane	(1,2-DCP)
Trichloroethylene	(TCE)
Perchloroethylene	(PCE)

TABLE II. SELECTED IONS MONITORED

Compound	Ions
Methylene Chloride	49, 84, 86
Chloroform	47, 83, 85
1,2-Dichloroethane	49, 62, 64
Benzene	50, 77, 78
Carbon Tetrachloride	117, 119, 121
Trichloroethylene	97, 130, 132
1,2-Dichloropropane	62, 63, 76
Perchloroethylene	131, 164, 166
Hexafluorobenzene	93, 117, 186
Chlorobenzene	77, 112, 114

TABLE III. GENERAL GC AND MSD INSTRUMENT PARAMETERS

Gas Chromatograph

Column

60 M, J & W DB-1, FSCOT, 0.32 mm, 1.0 um Film,
1.0 ml/min. He Flow

Temperature Program

Temp. 1: 35°C, Time 1:25 Min
Rate 1: 4°C/Min. to 105°C
Rate 2: 20°C/Min. to 150°C
Run Time: 44.7 Min.

MSD

Mode: Selected ion monitoring, EI
EM Voltage: 1800
Threshold: 10
Scan Delay: 9 Min.
Dwell Time: 400 Milli-sec.
Cycles/Sec.: 0.7
Other parameters set by "Autotune" Program
Column directly connected to source

TABLE IV. AMS SITE, STATISTICAL DATA FOR 1985, PPBV

AMS LAB SITE

	MECL	CHL	1,2-DCE	BENZ	C.TET	1,2-DCP	TCE	PCE
ARITH. MEAN	2.68	0.09	1.21	2.44	0.12	0.31	0.24	0.50
STD. DEV.	2.77	0.05	1.29	1.53	0.06	0.29	0.16	0.35
MAX. VAL.	13.90	0.32	7.36	9.16	0.35	0.78	0.69	1.56
MIN. VAL.	0.02	0.03	0.03	0.04	0.03	0.03	0.05	0.02
QUANT. SAMPLES*	81	70	71	87	73	8	78	90
PHILA. AQG (8)	2400	24	37	24	12	N/A	1200	1200
EPA RISK LEVEL (per million)	1.7	4.5	125	51	11	1	5.3	5.7

CONFIDENCE INTERVALS

COMPOUND	LOW VAL.	AVERAGE	HIGH VAL.	ADJ LOW	FACTOR	95% Z VALUE
MECL	-2.75	2.68	8.11	0.00	5.43	1.96
CHL	-0.01	0.09	0.19	0.00	0.10	
1,2-DCE	-1.32	1.21	3.74	0.00	2.53	
BENZ	-0.56	2.44	5.44	0.00	3.00	95% t Val. - 7 df
C. TET	.00	0.12	0.24	0.00	0.12	
1,2-DCP	0.07	0.31	0.55	0.07	0.24	2.37
TCE	-0.07	0.24	0.55	0.00	0.31	
PCE	-0.19	0.50	1.19	0.00	0.69	

TABLE V. COMPARISON OF ARITHMETIC MEANS

FOR NCP AIR MONITORING SITES (PPB)

	MECL	CHL	1,2-DCE	BENZ	C. TET	1,2-DCP	TCE	PCE
AMS SITE	2.68	0.09	1.21	2.44	0.12	0.31	0.24	0.50
DEFENSE	1.11	0.13	1.42	2.88	0.16	0.04	0.12	0.30
N/E AIRPORT	0.69	0.08	0.33	1.64	0.12	0.12	0.11	0.25

TABLE VI. COMPARISON OF MEAN % RECOVERY DATA BY SITE FOR

QUALITY ASSURANCE COMPOUNDS SPIKED ONTO SAMPLE TUBES*

	AMS SITE		DEFENSE		N/E AIRPORT SITE	
	CLBS	HFB	CLBZ	HFB	CLBZ	HFB
ARITHMETIC MEAN (%)	95	87	103	101	104	107
NUMBER OF SAMPLES	36	42	8	11	11	11
AVG. UG's SPIKED	0.138	0.200	0.136	0.204	0.137	0.204

*Chlorabenzene (CLBZ): Spiked before sampling
Hexafluorobenzene (HFB): Spiked after sampling

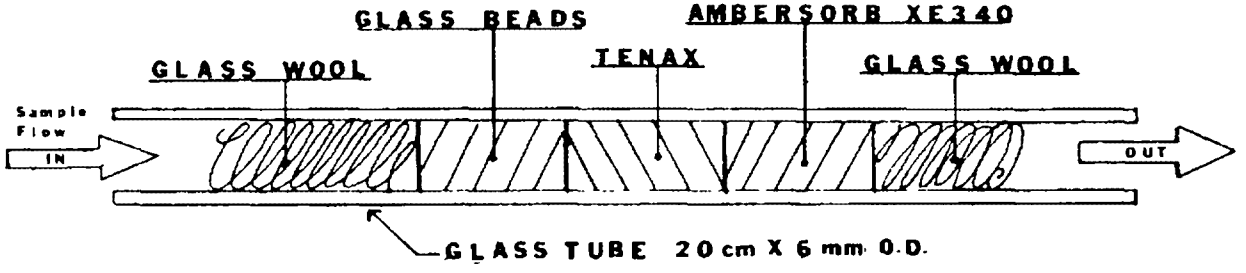
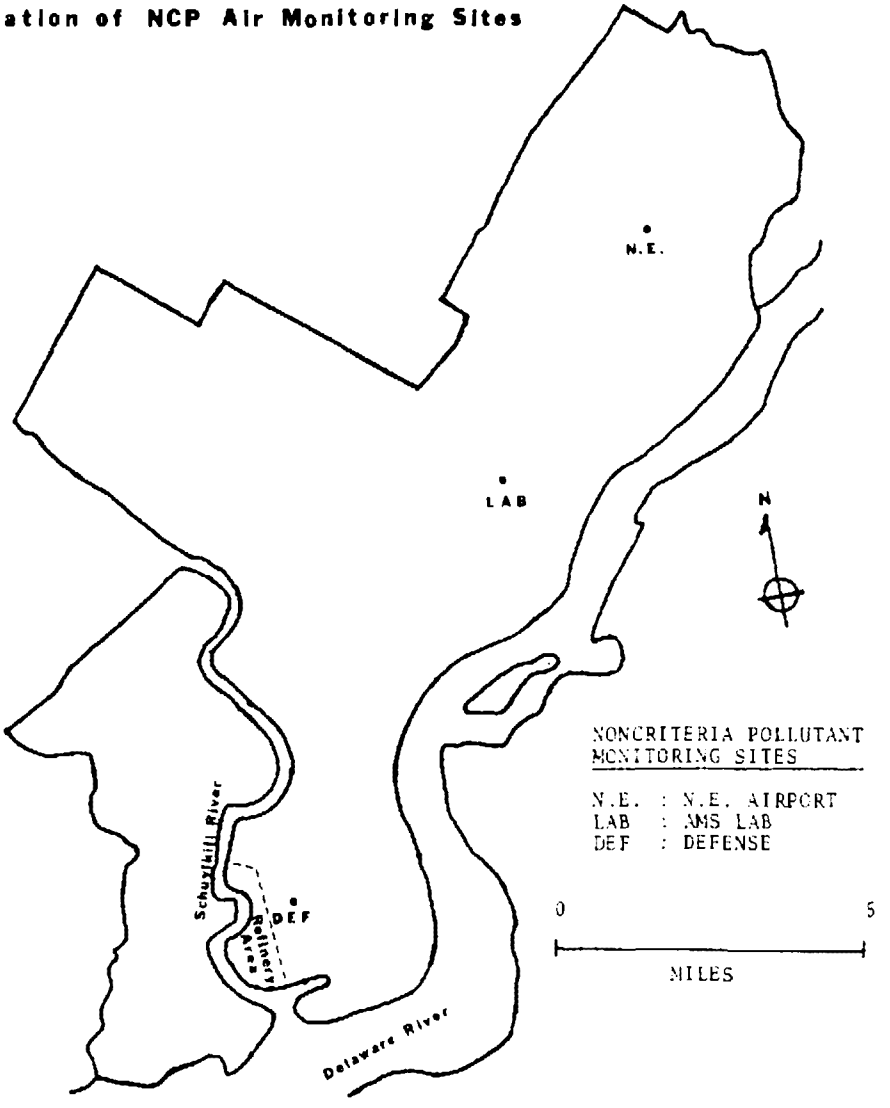


Figure 1. Envirochem Sorbent Tube.

Figure 2.

Map of Philadelphia Showing the Location of NCP Air Monitoring Sites



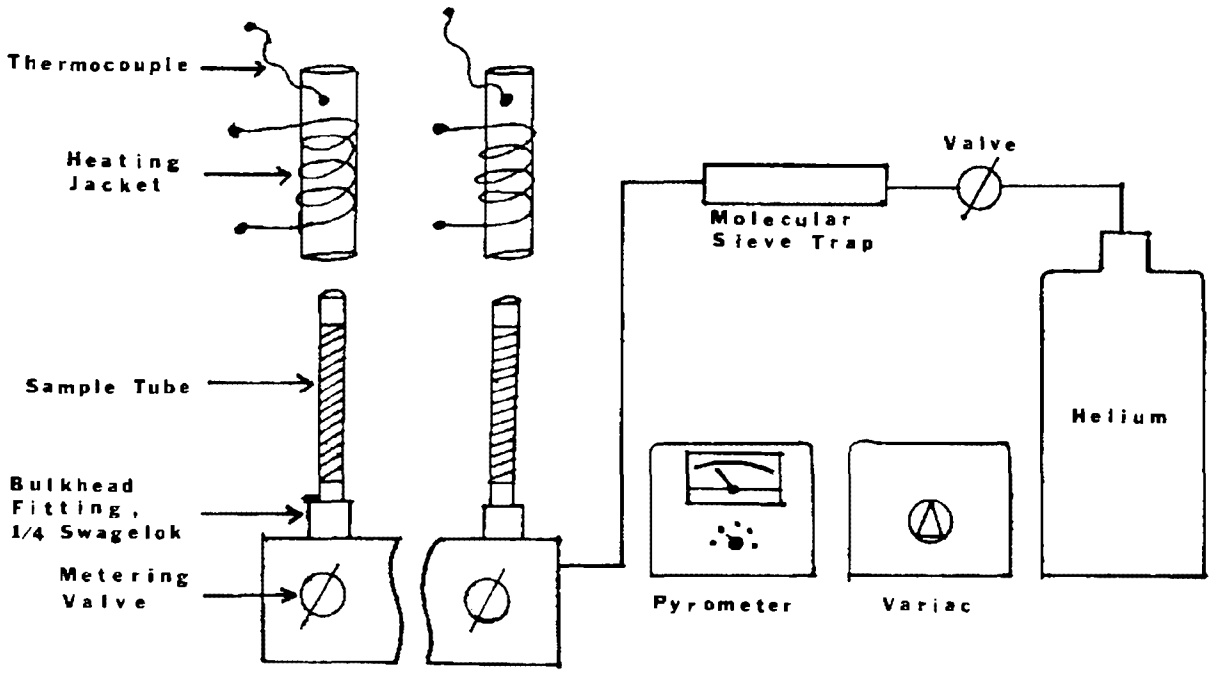


Figure 3. Multiple Sample Tube Thermal Conditoner.

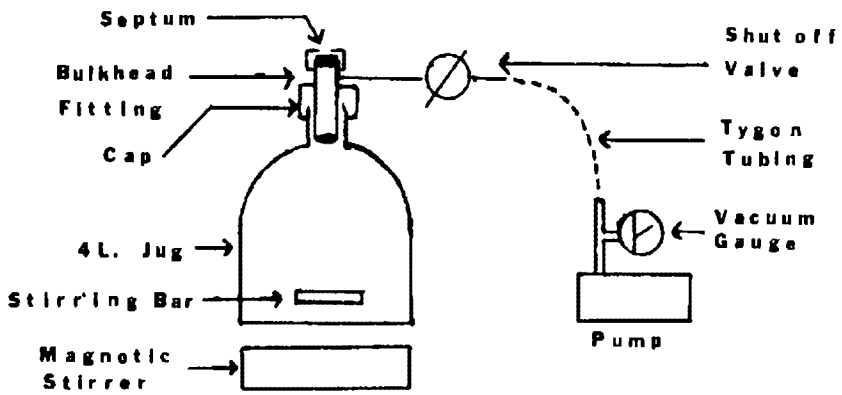


Figure 4. Static Dilution Apparatus.

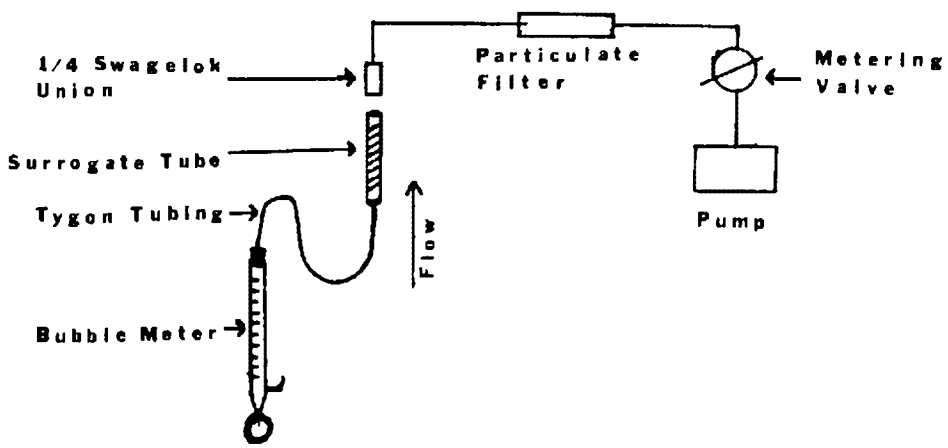


Figure 5. Sample Collection Apparatus.

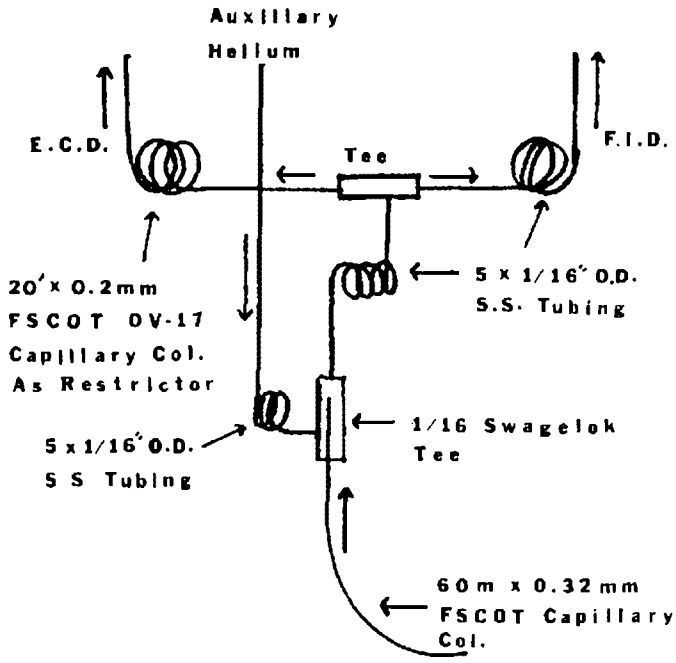


Figure 6. Column Effluent Splitter to E.C.D./F.I.D. Detectors.

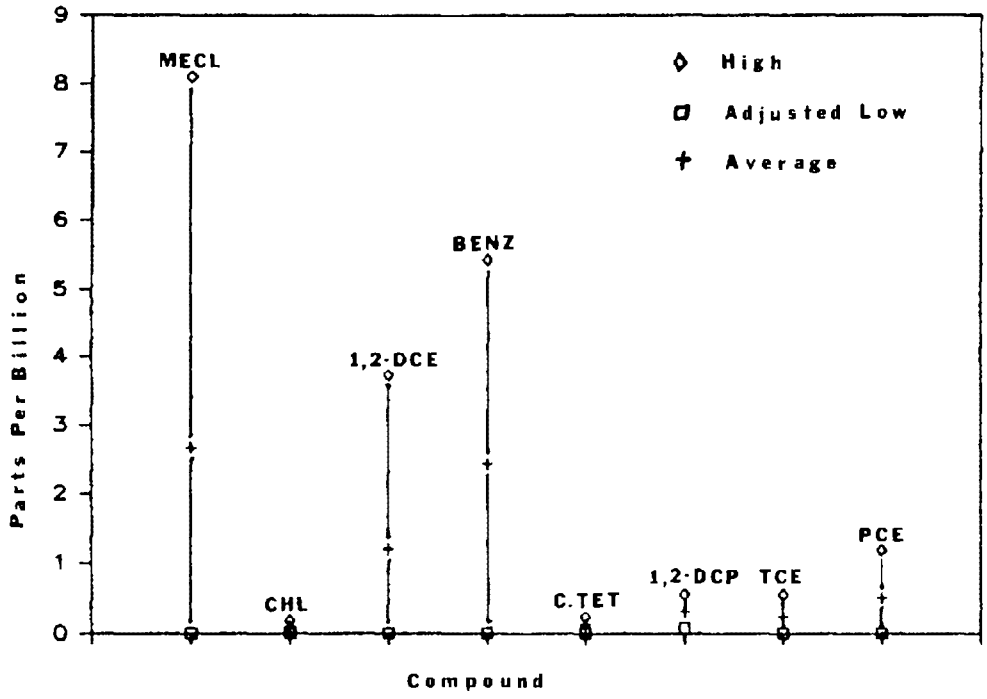
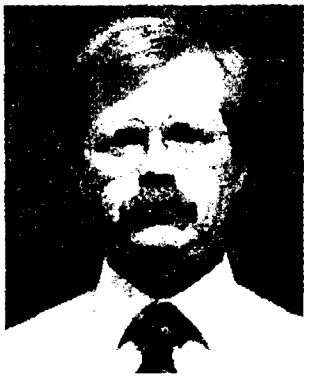


Figure 7. AMS Site, 1985 Data With 95% Confidence Intervals.

Industrial Emission Impacts in the New Jersey Environment: Results from a Study Near a Barrel and Pail Manufacturing Plant



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Abstract

Industrial emissions can have a significant impact on localized air quality in many urban areas. Many older urban/industrial areas contain manufacturing plants in close proximity to residential areas and which do not possess adequate air pollution control devices to minimize emissions. The present report summarizes the monitoring results obtained in the vicinity of a steel barrel and pail manufacturing plant in Jersey City, NJ. Local residents have complained of odors, headaches and nose bleeds from emissions from this plant. Although the surface coating materials utilized by the facility do not contain known carcinogens, these substances (xylenes, methylethylketone, acetone, butanol, etc.) are known to have relatively low odor thresholds. A sampling scheme was developed to obtain upwind, downwind and maximum impact data resulting from the emissions from this facility. All fixed site samples (4 hrs.) were collected on glass cartridges containing 1.1 gm Tenax-GC utilizing Nutech-221-1MC sampling pumps, while DuPont-Alpha-1 personal monitoring pumps were utilized to collect short-term (15 min.) peak levels of the selected substances. Cartridges were analyzed by thermal desorption into a HP 5995 GC/MS, equipped with a volatile organic column. The entire study was conducted utilizing a mobile laboratory (MMU) specially designed for thermal desorption - GC/MS analyses. Results from this monitoring effort indicate that levels of selected solvents measured in the community near the barrel and pail plant were not in excess of

published odor thresholds. However, it was clearly demonstrated that the manufacturing facility caused localized degradation of air quality.

INTRODUCTION - Volatile organic compounds (VOC) are thought to be of some environmental importance because of their role in: a) carcinogenesis, b) ozone formation, and c) smog aerosol formation (Harkov et al 1983, NAS 1977). In addition to these impact areas, VOC can be of localized significance as a nuisance (odor causing agent) and/or as an irritant if emitted by specific industrial sources. Some VOC that have particularly low odor threholds and also may cause a hypersensitive response in a portion of a population include: aldehydes, ketones and organic acids (Verschueren 1983, Keg et al 1977, Fay and Billings 1980). In the present context VOC are delimited as those substances with a vapor pressure greater than or equal to 0.02 psi.

Industrial impacts on localized VOC levels have been seldom reported in the technical literature (Sexton and Westberg 1980, Pellizari, 1982). Odor related VOC emission impacts also have been reported infrequently in the air pollution literature (Van Langenhose et al 1982). In New Jersey, studies have been conducted on the levels of selected VOC at urban and rural background locations (Harkov et al 1981, Harkov et al 1983, 1984) and most recently at site specific locations such as Superfund sites (Harkov et al 1985) and sewage treatment plants (Harkov et al 1986). Industrial based investigations of VOC in New Jersey have recently been initiated utilizing a mobile monitoring unit (MMU) (Haggert and Harkov, 1985). The present report contains results from an air quality investigation near a steel barrel and pail manufacturing facility in Jersey City, New Jersey. This facility has caused localized odor and irritant problems in the nearby neighborhood and grade school.

METHODS

Description of Facility - The barrel and pail manufacturing operations (VLCC) is located in a residential area in Jersey City, New Jersey (Figure 1). The plant fabricates and paints pails and barrels with a normal daily production rate of 3,500 and 15,000 respectively. Coatings are put on the products by VLCC using paint spray, lacquer spray and lithograph roller booths. The lithograph and part of the pail lines are vented to two separate exhaust incinerators. The VLCC facility is more than 100 years old and is currently updating equipment to comply with NJ VOC codes. Odors resulting from the facility can be detected as far as 2 km from the manufacturing site. Hudson Regional Health Commission (HRHC) has attributed typical irritation reactions (eye tearing, and headaches) in the residents living adjacent to the site and in children attending a nearby grade school to local odors. According to the records of the HCRHC the paint products utilized by VLCC contain at least the following solvents: acetone, methylethylketone, methylisobutylketone, butanol, ethanol, isopropanol, butylacetate, ektasolve, xylenes and toluene.

Sampling Design - All sampling took place during November 1985. Four permanent sampling sites were located at approximately 90° apart as indicated in Figure 1. All samples collected at these sites were for 4 hr. in duration and nine days of samples were collected simultaneously at each site. Site #5 was located within the school building. Short term (1½ hr.) and grab samples (15 min.) were collected on the same days as the fixed site samples to try to characterize transient, peak concentrations. A total of 11 grab and 6 short term samples were collected during this study. A meteorological station (wind speed and

direction, temperature) was installed on the roof (2nd story) of the church adjacent to VLCC.

Sample Collection and Analysis - Fixed site samples (4 hr.) were collected at a flow rate of 60 ml/min with Nutech-221-IMC air pumps equipped with 1.1 gm Tenax-GC (60/80 mesh) loaded glass cartridges. Grab samples (15 min.) were collected at a flow rate (1 L/min) utilizing identical cartridges as described above, but with DuPont-Alpha-1 personal monitoring pumps. Short term samples (1½ hr.) were collected at a flow of (200 ml/min) with the DuPont-Alpha-1 pumps.

All analyzes occurred in the MMU equipped with a Hewlett-Packard 5995 GC/MS. The MMU has been previously described by Haggert and Harkov (1985). Prior to thermal desorptions four internal standards were added to the cartridges (bromodichloromethane, 1-chloro-2-bromopropane, 4-bromofluoro- benzene, and 1,4- dichlorobutane). The Tenax-GC cartridges were then thermally desorbed at 225°C with a 25 ml/min He flow into a cryofocusing trap maintained at -148°C. The sample was heated, then injected onto a 60/80 mesh carbopack-B, 0.1% SP-1000 glass column (2.4M x 1/8" ID). Oven temperatures began at 40°C and were raised to 236°C at 14°C/min. The mass spectrometer scanned 35-320 amu. All cartridges were analyzed within 72 hours of sampling. Statistical analyses were carried out utilizing Statgraphics (STSC 1981).

Quality Assurance/Quality Control - During the course of this study a number of qa/qc steps were carried out. These procedures included the use of internal standards, calibration curves, field blanks, laboratory blanks, and tandem and duplicate cartridges. Prior to sampling, thermal flexing of the Tenax-GC resin was accomplished for all cartridges utilizing a triplicate 2 hour heating/cooling cycle followed by thermal desorption (Nutech 340-14). Precision estimates based on analysis of compounds on 5 duplicate cartridges were approximately ±24.3% at the 95% confidence interval. The minimum detection limits (MDL) were set at approximately three times the signal to noise ratio, while the minimum quantitation limits (MQL) were set at 2.5 times MDL. The MDL's varied from 0.07 ppbv (25°C, 760 mm) for toluene and ethylbenzene to 0.64 ppbv for ethanol. It should be noted that according to the Brown and Purnell (1979) report breakthrough was probably significant for acetone, ethanol and isopropanol. Breakthrough for these substances is estimated using tandem cartridges (N=4) to be on the order of 30%. It is thus reasonable to conclude that the levels for these three compounds are underestimated in this study.

Results - The monitoring information is presented on a site and upwind/downwind bases in Tables 1 and 2. Concentrations of perchloroethylene (perc) were also included in this study as an example of a ubiquitous urban VOC which was not utilized by VLCC. The highest VOC levels were generally recorded in grab samples, while location #2 had the most significant concentrations of the four fixed sites. Most VOC levels in the school were 50% or less than the nearby fixed site (#3) when ambient levels were significant (5-10 fold increase) as compared to periods when the plant impacts were small. Thus indoor/outdoor (I/O) ratios were nearly 1 during non-impact periods. However, the same compounds were identified in all samples within the school and in the adjacent communities. Downward samples were significantly elevated over upwind samples, particularly for ethanol, acetone, methylethylketone, ethylbenzene, and xylenes. The highest individual fixed site and short term samples are shown in Table 1.

Pairwise correlations (Table 3) indicate that most of the solvents thought to result from VLCC emissions are highly correlated (R _ 0.70), while none are related to perc. Factor analysis was carried out to identify those parameters which can explain the ambient data set and this effort resulted in a five-factor model (Table 4).

Discussion - Virtually all of the solvents reportedly utilized by VLCC and measured in the ambient air adjacent to the facility are known for their acute toxicity (Sax 1983). Levels of the twelve solvents measured during the present study were significantly below reported odor thresholds, although individual samples had total solvent concentrations above the odor thresholds of specific materials such as m-xylene (270 ppb_v) and isopropanol (130 ppb_v). Generally concentrations for selected VOC in grab samples were greater than fixed site samples, but were not more than 2 times the levels found at fixed sites. In spite of the levels of selected solvents found during this study, field personnel from the MMU experienced typical irritant responses when strong odors were detected off site, and near the plant boundaries. Because unknown organic compounds were not the focus of this study, it is uncertain whether high levels of other odorous materials were being emitted from VLCC. This issue is of particular concern for lightweight organics that are poorly trapped by the Tenax-GC adsorbent utilized in the present effort.

Many of the pollutants measured in the current study have been quantified in ambient air in urban portions of New Jersey. Levels of alkylbenzenes and perchloroethylene in the urban atmosphere of New Jersey have been recently reported (Harkov et al 1983, Harkov et al 1984). Both methylethylketone and methylisobutylketone were measured at a number of urban New Jersey sites during 1979, but were generally found at concentrations less than 0.01 ppbv (Harkov et al 1981). Utilizing ATEOS data as a comparison, significant increases over background VOC levels resulting from the facility were considered when VLCC/Newark ratios exceeded a factor of 3, which was the case for ethylbenzene and xylenes, but not for toluene and perc (Table 5). A comparison of upwind/downwind concentrations indicates that VLCC had significant impacts on localized air quality for ethanol, ektasolve, acetone, methylethylketone, ethylbenzene, xylenes and isopropanol when using a three-fold increase over background as the basis for this conclusion (Table 2). The failure to detect impacts on butylacetate and toluene levels from VLCC is probably a reflection of the lower level of use of these substances at this facility and the high background concentration of toluene in urban air. It should be noted that because of the high population and industrial density, it was expected that VOC levels in Jersey City would be slightly higher than in Newark and also that the shorter sampling times utilized in the present study would tend to produce somewhat higher levels than the 24 hour Newark samples.

The pairwise correlation matrix indicates that those substances utilized by VLCC were highly correlated, but not with perc which was not a solvent utilized at this facility (Table 4). While the pollutant levels for those substances were moderately correlated (R = 0.50) with position of sample collection (upwind/downwind), there was no such relationship for perc. This result is consistent with the observation that perc is a ubiquitous urban contaminant, but that VLCC is impacting localized air quality for a select group of solvents utilized in its internal processes.

Factor analysis was carried out to identify those issues which have the most impact on the correlation between the variables in the data set. Ideally, factor analysis should be carried out on large (_75 obs) data sets (Lioy et al, 1985) and the 57 observations from the current effort are great enough to draw some preliminary conclusions. A five factor model (Table 5) which explained about 94% of the variance in the model was produced from this data set. The first factor includes acetone, ethylbenzene, xylenes, isopropanol and butanol and is most likely related to a specific spray coating operation and the solvents associated with this process within VLCC. The second factor had high loadings of methylethylketone, methylisobutyl- ketone, and ektasolve, which are the main solvents utilized in the roller operations at VLCC. Both toluene and butylacetate were highly loaded on factor three which is probably related to the influence of background levels. Factor four has high loadings of perc and location which is indicative of the relative distance of the fixed and grab sites to the nearest dry cleaning operations on Fowler and Danforth Avenues. Finally, the fifth factor is related to upwind/downwind positions and was important for influencing the recorded concentrations.

By utilizing perc as a marker for ubiquitous urban VOC contaminants, it can be shown that VLCC clearly had an impact on localized air quality in this portion of Jersey City (Figures 2 and 3). The levels of perc near VLCC were: a) typical of urban concentrations (Singh et al 1981, 1982), b) not effected by wind direction, c) poorly correlated with the other VOC measures, and c) location of sample collection was the only variable in the data set which could partially explain the measured perc trends. The results for the ketones, alkylbenzenes and alcohols are directly opposed to those of perc and demonstrate that VLCC has a measurable impact on localized air quality.

As a final comment it is unclear whether the sample collection period of November 1985 corresponded with typical operations at VLCC. The plant personnel were aware of the presence of a sampling crew in the vicinity of the facility. Also, the HCRHC claimed that the odors were relatively mild during the present study compared to other periods during the past few years. For lack of better information, the data presented here in this report should be considered representative of off-site VOC impacts near VLCC.

Conclusions - Ambient VOC data was collected to document the impact of emissions from a steel barrel and pail manufacturing facility on localized air quality in Jersey City, New Jersey. This facility was shown to cause increases in selected VOC from 3 to 30 fold over background levels. These solvents corresponded to those utilized during coating operations at this facility. In spite of demonstrating the impact of this facility on localized air quality, odor thresholds reported in the literature for individual compounds were not exceeded in any samples. Whether other materials that were not measured during this study contribute to the localized odor and irritant problem is not known. However, these data indicate that for short periods of time total solvent concentrations can exceed odor thresholds for specific compounds.

Acknowledgements - The authors would like to thank the Hudson County Regional Health Commission, particularly Mr. John Demjanick and Mr. Gary Garetano, for assistance during this study. A special thanks to all the local citizens who provided site access for sample collection during this effort.

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Table 1 - Concentrations of Selected VOC near VLCC by site (ppb_v, X±STD)

POLLUTANT	1	2	3	4	5	6	Max.[c] 4/hr Sample	Peak Grab Sample
ethanol	15.2±19.1	10.3±8.0	4.4±4.4	10.1±20.8	4.7±4.3	25.3±27.6	60.7	NR[b]
isopropanol	9.5±7.7	18.9±15.8	9.9±8.1	10.9±14.6	11.6±7.5	33.9±38.3	45.6	110.0
butanol	10.5±11.0	15.4±11.3	7.3±6.2	10.3±11.4	5.9±3.0	24.6±19.1	37.3	62.8
acetone	9.3±11.4	14.8±10.3	5.5±5.4	9.2±13.4	5.[illegible]9	38.6±51.2	45.2	191.2
methylethyl-ketone	10.9±14.2	9.5±5.9	5.4±5.6	5.7±10.2	4.[illegible].0	29.4±23.0	33.7	90.4
methylisobutyl-ketone	1.3±1.4	1.4±0.6	1.4±0.7	1.1±1.5	0.8±4.0	3.2±2	4.5	6.8
butylacetate	1.4.±1.1	1.7±.08	1.4±0.6	2.6±2.1	0.8±0.2	1.2±1.2	4.8	6.4
ektasolve[a]	2.7±4.7	2.2±1.9	1.2±2.8	1.7±3.8	1.5±2.1	8.8±7.7	13.3	26.7
toluene	8.1±7.6	8.7±4.7	5.3±2.9	5.5±4.4	5.7±1.8	12.4±6.6	21.8	24.1
ethylbenzene	6.2±7.7	7.2±6.6	4.0±4.7	2.9±4.9	2.1±2.0	10.1±8.1	16.7	33.1
m-xylene	10.9±17.4	12.0±16.0	3.8±8.0	5.7±13.8	4.8±5.1	31.1±24.2	42.5	89.5
o&p-xylene	9.4±12.2	9.8±16.8	4.9±6.5	4.1±8.9	3.2±2.7	18.0±12.8	27.5	48.3
perchloro-ethylene	0.8±.07	0.9±.08	1.0±.0.8	1.1±1.4	0.9±0.5	0.7±0.9	4.5	2.6
N[d]	11	10	10	9	6	11		
DESCRIPTION	Danforth Ave.	Greenville Ave.	Lembeck Dr.	Sullivan Dr.	School (indoor)	Grab		

a- Ektasolve = ethyleneglycol monopropylether
b- NR = Offscale
c- Max. = highest value in 40 samples
d- N = includes duplicates

Table 2 - Comparison of Upwind and Downwind Concentrations at VLCC (ppb_v, $\bar{X}$±STD)

	UPWIND	DOWNWIND	RATIO (D/U)
ethanol	1.7±3.	23.0±23.4	13.5
acetone	4.9±4.	28.1±35.6	5.7
methyethylketone	2.7±2.5	23.0±18.0	8.5
methylisobutylketone	0.9±.07	2.5±1.7	2.8
butylacetate	2.0±2.8	1.8±1.0	0.9
ektasolve	0.2±0.4	6.7±6.1	33.5
ethylbenzene	0.6±1.0	10.0±6.7	16.7
toluene	5.1±2.9	11.9±6.3	2.3
m-xylene	0.9±0.9	26.0±20.4	28.9
o,p-xylene	0.9±1.0	16.3±11.5	18.1
butanol	6.5±5.3	22.1±15.2	3.4
isopropanol	6.0±7.0	26.7±27.7	4.5
perchloroethylene	0.9±0.8	0.8±0.7	0.9
N	13	25	

Table 3 - Pairwise Correlations for Selected VOC at VLCC

	ETOH	ACE	MEK	ETBZ	MXYL	PROP	PERC	LOC	POS
ETOH[a]	1	0.84	0.71	0.77	0.80	0.54	-0.18	-0.29	0.39
ACE		1	0.84	0.82	0.85	0.73	-0.29	-0.31	0.47
MEK			1	0.65	0.69	0.34	-0.28	-0.34	0.48
ETBZ				1	0.99	0.70	-0.42	-0.39	0.58
MXYL					1	0.71	-0.38	-0.36	0.61
PROP						1	-0.05	-0.11	0.39
PERC							1	0.60	-0.22
LOC								1	0.06
POS									1

a- ETOH - Ethanol
ACE - Acetone
MEK - Methylethylketone
ETBZ - Ethylbenzene
PROP - Isopropanol
PERE - Perchloroethylene
LOC - Location
POS - Position

Table 4 - Final Factor Analysis Solution for VOC from VLCC[a]

	Factor Loadings[b]				
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
ETOH	0.60				
ACE	0.75				
MEK		0.79			
MIBK		0.97			
BUTACE			0.89		
ETBZ	0.76				
TOL			0.71		
MXYL	0.76				
OPXYL	0.77				
PROP	0.97				
BUT	0.87				
PERC				0.91	
EKTA		0.84			
POS					0.86
LOC				0.82	

a- Principal Factor Analysis (PFA) was conducted on Stagraphics (1981) utilizing listwise deletion and varimax rotation.
b- Factor loadings greater than or equal to 0.60 are shown.

Table 5 - Comparision of Selected VOC Levels at VLCC and Newark (ppb_v)

	Newark - Winter 1982[a]	Ratios (VLCC/Newark)
perchloroethylene	0.46	1.8
ethylbenzene	0.51	12.4
o,m,p-xylenes[b]	2.23	10.9
toluene	4.93	1.4

a- From - Harkov et al (1984)
b- o,m,p-xylenes are combined due to the different isomeric separations on packed and capilliary columns utilized in both studies

Figure 1.

Sampling Sites Around VLCC

Jersey City, New Jersey

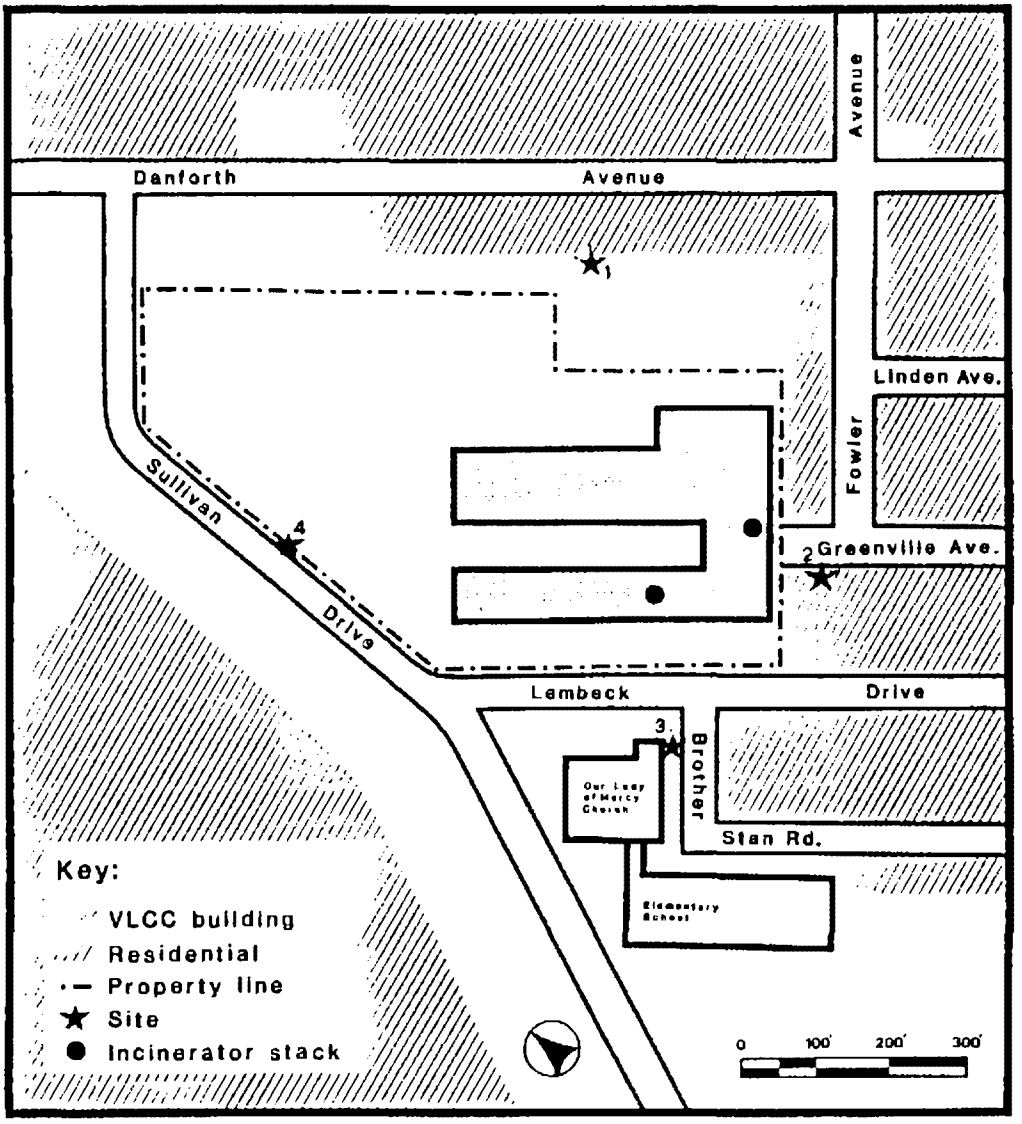
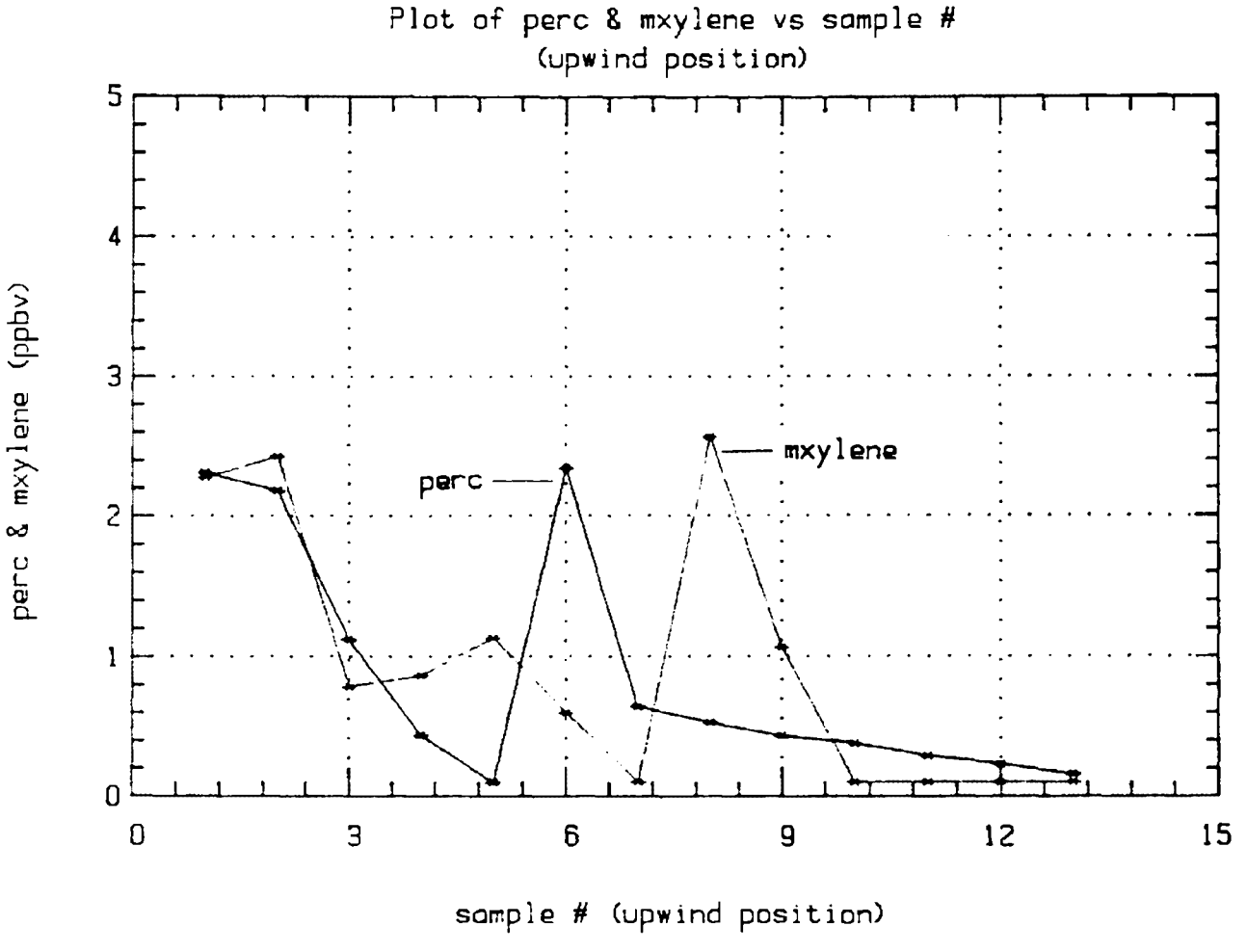
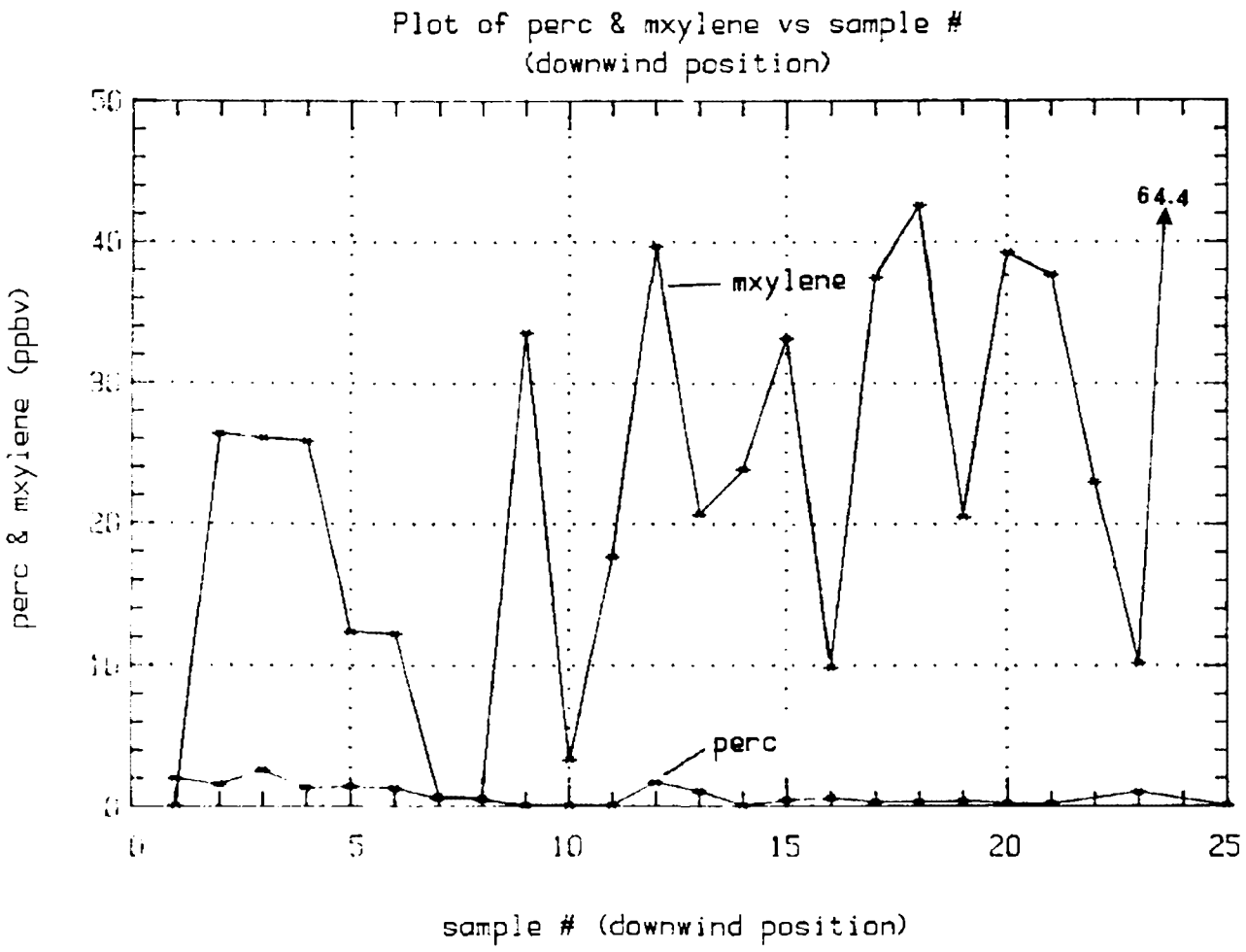


Figure 2

Upwind concentrations trends for m-xylene and perchloroethylene.



Downwind concentrations trends for m-xylene and perchloethylene.



IMPLEMENTING A QUALITY ASSURANCE PROGRAM FOR SAMPLING AND ANALYSIS OF AMBIENT AIR TOXICS COMPOUNDS

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The California statewide ambient toxic air monitoring program was established to obtain ambient toxic data for selected compounds. The toxic air monitoring network consists of 20 sites statewide with ambient samples taken on selected days. Samples are collected in Tedlar bags, by filtration, and with solid sorbent tubes. The bags are analyzed for aromatic and halogenated hydrocarbons, the filters for heavy metals and the tubes for various organics, e.g., pesticides.

In developing and implementing the statewide ambient toxic quality assurance program, emphasis was placed on a cooperative approach between the participating sampling, laboratory and quality assurance staff. The staff believes that this is the best way to obtain prompt, coordinated action on a multiplicity of quality assurance elements, namely: developing an overall project outline, selecting specific workplan items, documenting laboratory quality control procedures, encouraging interlaboratory activities, and conducting performance tests.

Of particular interest are the results of the performance tests. In this activity the laboratories are challenged with ppb-levels of benzene and halogenated hydrocarbons. The results of performance tests at four laboratories are presented.

Progress towards developing and certifying low ppb-level working standards for laboratory use, the start of a control sample program and the development of new instruments are also reported.

IMPLEMENTING A QUALITY ASSURANCE PROGRAM FOR SAMPLING AND ANALYSIS OF AMBIENT AIR TOXIC COMPOUNDS

Introduction

The California Air Resources Board (ARB) is required by state legislation to identify and then control toxic air contaminants.[1] The contaminants identified to date and those currently in the identification process are presented in Table I.

As part of the ARB's overall control program, the staff has established an ambient air monitoring network to provide the data necessary to characterize population exposure to toxic contaminants and monitor trends. The network currently consists of 20 sites located throughout California.[2] Each site is located at an existing state or local criteria pollutant air monitoring station which is configured in accordance with siting procedures outlined in the Code of Federal Regulations, Title 40, Part 58, Appendices D and E for manual sampling methods. Two samples per month are collected at each site. Volatile organic ambient air samples are collected in 30-liter Tedlar bags over an integrated 24-hour period with samplers specially designed by the Board's staff to minimize sample degradation problems. Once the sample is collected, the Teldar bag is shipped via courier to the appropriate laboratory. The analysis is completed within 24 hours of the sampling end time. The laboratory staffs are using gas chromatographic procedures for quantitating and gas chromatograph/mass spectrometry procedures for confirming the amount and identity of the volatile organic compounds.

An interim quality assurance plan has been prepared and partially implemented to help ensure and document the reliability of the airborne toxic contaminant data collected from the ambient network. A major goal is to avoid some of the historical problems.[3,4] The plan includes the essential elements that are usually considered by any group conducting ambient air monitoring for regulatory purposes.[5] The implementation to date is focused on:

- assessing the current state of analytical capabilities within the four laboratories reporting or planning to report ambient toxics data within California,
- documenting possible analytical variability associated with the respective analysis of known standards, and
- developing a framework within which the quality control and quality assessment functions can cooperatively and successfully operate.

The full implementation of the plan will lead to the establishment of a quality assurance program for the assessment of all the data submitted for regulatory use. An overview of our quality assurance structure is shown in Figure 1. As indicated, the term quality assurance is used as the overall term. Quality control includes field, laboratory and data activities. Quality assessment includes performance check and audit activities.

The variety of activities implied in Figure 1 are usually assigned to different staff sections within a given management division. Since more than four interagency divisions are involved in this program, the

coordination aspects alone are somewhat complex. In view of the newness of the program, technical measurement problems at ppb-ppt concentrations, lack of low-concentration gas standards, etc., the reader may foresee the selective nature of the first-year effort, all of which is not reported here.

This report is about the start of a program and the implementation of selected initial elements aimed at producing precise and accurate data for the regulatory process.

Performance Check Program

One key element (Figure 1) selected for action was performance checks. The performance check activity was started in the fall of 1984 and continued into 1986. The program was designed to allow the laboratory staffs an opportunity to challenge their analytical instruments with the reference gases and concentrations shown in Tables II-IV. The data in Tables II and III illustrate the challenges that were made possible by the availability of cylinders of compressed gas containing ppb-concentrations of various toxic substances from the Environmental Protection Agency's (EPA) Environmental Monitoring Systems Laboratory (EMSL) and the Research Triangle Institute (RTI). The challenges illustrated in Table IV were based on ARB compressed gas cylinders certified by the National Bureau of Standards (NBS). The cylinders were systematically made available to the two ARB laboratories already engaged in ambient sampling and analysis of toxic substances in the ambient air and to two regional district laboratories. The program was aimed at these four air pollution control laboratories because they were involved in or about to be involved in analyzing ambient air concentrations of toxic substances. The two district laboratories are those operated by the South Coast Air Quality Management District and the Bay Area Air Quality Management District. The two ARB laboratories are those operated by the Haagen-Smit Laboratory Division and the Aerometric Data Division.

The specific objectives of the performance check element include:

- developing protocol on a cooperative basis that would also serve as a guide for the conduct of future audits,
- providing the laboratories with a systematic measure of their analytical capabilities based on their analysis of high quality, relatively low concentration compressed gas mixtures with an assigned concentration,
- providing a baseline of the analytical capabilities at an early stage in the program against which to measure future progress, and
- providing a vehicle to encourage realistic interagency working arrangements between the individual laboratory quality control staffs, the central quality assurance staff and the appropriate staffs of EMSL, RTI, and NBS.

The results of three "low" concentration checks are presented in Table II. The data indicate that 80% of the determinations were generally within ± 2 ppb of the assigned reference value. The results of two "high" concentration checks are presented in Table III. The fact that only one laboratory analyzed for ethylene dibromide (EDB) and ethylene dichloride (EDC) confirms the staffs stated lack of interest in conducting checks at concentrations well above the range that the

instruments, procedures and staff are normally required to work. For example, the mean ambient concentration for EDB is somewhat less than .01 ppb. Hence the challenge concentrations, 17 (Table II) and 196 ppb (Table III) are approximately 2,000 and 20,000 times greater than the mean ambient concentrations. The challenge concentrations and the mean ambient concentrations are given for each compound in both tables. A check in March 1986 using an EPA cylinder showed the average check vs assigned concentrations to be 10 vs 9 ppb for EDC and EDB.

The results of the benzene performance checks, which were conducted in 1985, are presented in Table IV. The five cylinders used in these checks were manufactured by a commercial vendor to ARB specifications and two of the cylinders were assayed by NBS. Assigned concentrations were developed for two other cylinders by reference to the cylinders certified by NBS. The average check vs assigned concentrations reported for the four cylinders were in close agreement: 3.4 vs 3.4, 5.4 vs 4.9, 7.5 vs 7.6 and 8.9 vs 8.2 ppb, respectively.

Control Sample Program

The control sample program was selected for implementation in early 1986. In this program we are trying to:

- provide an immediate practical focus for developing precision and accuracy data, and
- provide a framework for developing a coherent statewide data base that will have direct and documented linkage to NBS standards.

As an initial step in documenting acceptable error levels in the analysis of volatile organic compounds in ambient air, an EPA Group I cylinder was provided to the participating laboratories. The protocol calls for the laboratory staffs to analyze the control cylinder following every tenth sample analysis. The protocol also calls for the submittal of the plotted data within 60 days to the quality assurance staff in normal Shewhart control chart format. In addition, the average of all measurements and standard deviations are to be presented. The laboratories are now participating in this program. The cylinder being used contains low and known ppb concentrations of chloroform, benzene, perchloroethylene, carbon tetrachloride and vinyl chloride.

Results

The air pollution control agency laboratories participated in the performance check program, to varying degrees. As discussed above, there was not much interest in conducting checks against high concentration cylinders when daily demands called for determining some of the compound concentrations at levels just above the limit of detection. Then, too, there were a number of work crises associated with workload and new procedure developments. Notwithstanding, it appears that the level of participation in the overall program in October 1985 was nearly double that of October 1984.

Laboratory participation is also reflected in the appointment of laboratory quality control officers and development of documented quality control procedures. Additionally, for example, the elements to be used in the laboratory standard operation procedures (Appendix A) have been defined.

New Developments

Two new developments in the ambient air toxic program concern standards and sampling instruments.

Most staff members involved in ambient monitoring for toxic substances reached early agreement about the need for analytical gas standards. Laboratory staffs have developed or purchased such standards to the extent possible. Under ordinary circumstances, it is not a quality assurance staff function to provide the laboratories with analytical standards. However, since low-concentration NBS standards for volatile organics were not yet available, it was decided that this would initially be a staff function. From the overall quality assurance view it appears most desirable to use NBS standards. Hence, we have had considerable discussion with a number of NBS staff about its development of such standards. In recent discussions[6] it has become evident that 5 ppb NBS traceable standards in compressed gas cylinders may be available later this year. At this time it appears that the cylinders will contain about 30 ft^3 mix of the following gases: benzene, chloroform, carbon tetrachloride, trichloroethylene, perchloroethylene, methylene chloride and 1,2-dichloroethane. The ARB staff has expressed strong written support for the NBS program and its intention to purchase standards as soon as NBS sets its specifications and prices.

Early in the monitoring program, the instrument staff developed and built a prototype ambient air sample collection system for Tedlar bag sampling over an integrated 24-hour period. Specifications were subsequently prepared and a contract awarded to an instrument manufacturer thereby providing commercial availability. This has worked well for measuring a number of volatile organic compounds. However, as more varied sampling requirements have appeared (e.g., pesticides and aerosols) an additional approach to sampling has been taken. This approach provides for efficient and reliable sampling at several different flow rates using a multiplicity of independent sample collection media (filters, sorbent tubes, etc.). As a result, the performance requirements of an eight component toxics sampler have been specified by the instrument staff. It is now in the procurement phase.

Conclusions and Summary

The performance check program was initiated in October 1984 and has been successfully operated since then. Participation in the program has more than doubled and accuracy has improved. The compressed gas cylinders used have been provided by EMSL at Research Triangle Park, North Carolina, through RTI. The protocol developed for the check program will serve as a guide for future audits. Data obtained from the checks provide an early baseline of analytical capabilities which can be used to help measure future progress.

A control sample program has been initiated. When fully implemented it should provide each laboratory with adequate and defensible analytical precision data. The compressed gas cylinders used in these initial control sample checks were provided by EMSL.

All the participants agreed that standards are a key part of a successful program. The laboratory staffs have worked hard to obtain and use improved gas standards, but readily available low-ppb NBS

materials are still needed. Discussion with NBS indicate that traceable standards at 5 ppb may be available later this year in 30 ft^3 cylinders containing benzene, chloroform, carbon tetrachloride, trichloroethylene, perchloroethylene, methylene chloride and 1,2-dichloroethane. We think NBS reference gases are vital to produce accurate data.

ARB's instrument staff has developed sampling equipment which is currently being used in the ambient air monitoring program. Specifications have been developed to handle the more varied sampling requirements for an increasing variety of toxic compounds. Purchase orders for new multi-filter media instruments are in the procurement phase.

In addition, the participants have cooperatively established protocols, defined basic analytical methods, conducted interlaboratory comparisons, appointed quality control officers, and documented quality control procedures. The four laboratories are operated by two regional and two state air pollution control agencies, namely:

- The South Coast Air Quality Management District, El Monte,
- The Bay Area Air Quality Management District, San Francisco,
- ARB Haagen-Smit Laboratory Division, El Monte, and
- ARB Aerometric Data Division, Sacramento.

Some of the essential elements of the program are in place and the cooperative approach has worked well. The next elements we plan to focus on include: providing NBS gas standards to all the laboratories engaged in ambient sampling of toxics for control purposes, upgrading the sampling network instrumentation, conducting audits, improving the data screening process, developing and testing standard operating procedures for a new group of contaminants, and completing more studies on sample stability and contamination.

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4. "Problems in Air Quality Monitoring System Affect Data Reliability," U.S. General Accounting Office, GAO/CED-82-101, 1982.

5. "Quality Assurance Handbook for Air Pollution Measurement Systems," Vol. I, Sections 1.3 and 1.4, U.S. Environmental Protection Agency, EPA-600/9-76-005, 1984.

6. W. L. Zielinski, National Bureau of Standards, Washington, D.C., personal communications, 1986.

Table I. Current status of compounds.

Identified and now in control process	Now in identification process
Benzene	Dioxins
Ethylene dibromide	Inorganic arsenic
Ethylene dichloride	Carbon tetrachloride
Hexavalent chromium	Vinyl chloride
Asbestos	Ethylene oxide
	Perchloroethylene
	Cadmium
	Methylene chloride

Table II. Statewide performance checks at low concentrations, two or more laboratories; a) EPA assigned concentration, b) 1985 data, c) data from one laboratory.

October 1985

Compound	Mean conc. (ppb)	Assigned[a] conc. (ppb)	Mean conc. (ppb)	Assigned[a] conc. (ppb)	Mean[b] ambient conc. (ppb)
Chloroform	4	4	37	37	.08
Benzene	11	12	18	20	2.8
Perchloroethylene	15	14	11	10	.65
Carbon tetrachloride	17	15	11	10	.14

January 1985

Compound	Mean conc. (ppb)	Assigned[a] conc. (ppb)	Mean[b] ambient conc. (ppb)
Trichloroethylene	16	15	.38
Ethylene dichloride	23[c]	15	.06
Ethylene dibromide	19[c]	17	.01
Methyl chloroform	19	15	1.9

Table III. Statewide performance checks at "high" concentrations, two or more laboratories; a) EPA assigned concentration, b) 1985 data, c) data from one laboratory.

October 1984

Compound	Mean conc. (ppb)	Assigned[a] conc. (ppb)	Mean[b] ambient conc. (ppb)
Chloroform	157	129	.08
Benzene	162	146	2.8
Perchloroethylene	171	136	.65
Carbon tetrachloride	146	132	.14

January 1985

Compound	Mean conc. (ppb)	Assigned[a] conc. (ppb)	Mean[b] ambient conc. (ppb)
Trichloroethylene	184	145	.38
Ethylene dichloride	150[c]	157	.06
Ethylene dibromide	320[c]	196	.01

Table IV. Benzene performance checks, 1985; a) nominal concentrations are as requested from vendor, b) assigned concentrations based on standardization against NBS values, c) number "N" of reported values.

Nominal[a] Conc. (ppb)	Assigned[b] Conc. (ppb)	NBS	N[c]	Mean Conc. (ppb)	Low (ppb)	High (ppb)
4	3.4		9	3.4	2.8	4.3
5	4.9	4.9	19	5.4	4.0	6.9
8	7.6		9	7.5	6.0	9.7
9	8.2	8.2	14	8.9	7.3	11.0
16	None		9	18.4	16.0	21.0

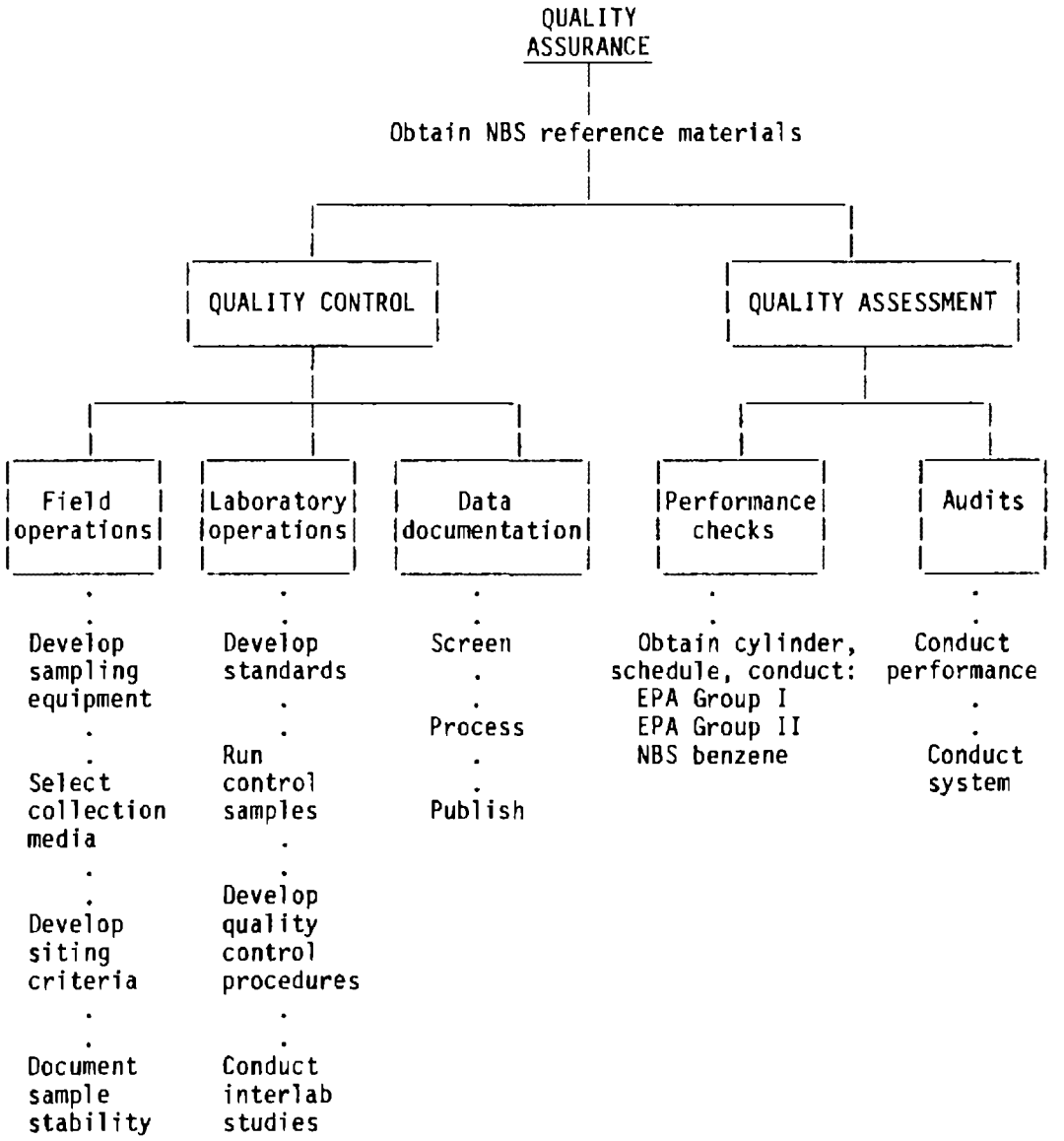

Figure 1. Quality assurance for ambient air toxic substances monitoring program.

Appendix A. Elements to be included in laboratory standard operating procedures for air analysis.

I. Scope

A. Description of scope and limits of elements to be analyzed.
B. Documents and references upon which method is based.
C. Definitions of any special terms must be given.

II. Summary

A. General description of sampling and analytical procedure. Enough information should be included for an experienced analyst to readily recognize the principles of operation.

III. Interferences and limitations

A. Comments made here should cover both analytical and sampling problems, known and potential.

IV. Apparatus

A. Instrumentation: As specific a description as possible. Any modifications or improvements of the basic system must have an accompanying schematic.
B. Auxiliary apparatus: Give description of function and operating conditions. Give description of sampling equipment if the equipment is specific to this method. For example, "Vacuum pump, Acme Model 62, capable of maintaining a 1 CFM air flow at 10" vacuum.

V. Reagents and materials

A. Give a list of all reagents used and specify purity/grade.
B. Describe preparation of any special reagents for analysis and sampling.
C. Specify composition, preparation, and concentrations of stock, intermediate, and working standards.
D. Describe in detail any necessary safety precautions for handling and disposition of chemicals.

VI. Procedures

A. Field sampling techniques

1. Refer to appropriate Field Sampling S.O.P. for exact details of sampling, chain of custody and sample identification procedures.
2. Describe equipment used and provide schematic.
3. List sampling conditions: materials, flow rates, etc.
4. Describe any potential problems and limitations, with means of controlling such problems.
5. Give calculation methods for sample volumes, flow rates, times, etc.
6. Describe any methods used to split samples for other types of analyses, if necessary.

B. Laboratory sample preparation/pretreatment techniques

1. Describe or refer to the appropriate section of the Laboratory Quality Control Manual for a description of a protocol for sample log-in procedures, including document control and sample examination for damage. Any possible hazards due to toxic or flammable chemicals must be clearly identified. Any sample storage requirements, such as immediate refrigeration or protection for light must be noted.
2. Describe any methods used for preconcentration, dilution clean-up filtration, extraction, etc., after the sample is received from the field.

C. Analysis

1. Describe as clearly as possible the exact instrument configuration and set-up techniques. In the case of chromatographic analysis, a special section should be indented giving a concise, but complete list of columns, flow rates, temperatures, detectors, amplifier ranges and attenuations, sample volumes, etc.
2. Describe analysis blank and calibration procedure with associated limits on precision and accuracy. Describe analysis of control samples and limits of the resulting data. Describe steps taken in an "out-of-control" situation. Specify the format and location of recorded calibration and control sample data.
3. Describe sample analysis. Description must include an example of expected data (for example, a sample chromatogram with all components of interest labeled).
4. Give calculation procedures for results. Describe data recording and data submittal.

VII. Performance criteria

A. Describe frequency of duplicate analyses, spikes, field blanks, and acceptable limits of each.
B. Describe frequency of multiple standard analyses to check method linearity and detection limit.
C. If confirmatory method is used, refer to specific S.O.P.

VIII. Method sensitivity, precision, and accuracy

A. A table describing linearity (correlation coefficients), accuracy (method bias), precision (standard deviations at all levels analyzed), and detection limits (with method of calculations) is necessary.
B. Data on sampling efficiencies, break through volumes, stability, and desorption efficiencies must be included, if appropriate.
C. Data on storage stability and conditions for samples and standards.
D. References to quality assurance information derived from published and/or interlaboratory sources must be included, if available.

NMOC CONCENTRATIONS MEASURED ALOFT

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Characterization of NMOC levels in transported air masses is currently of interest in terms of oxidant production and the formation of acidic species in the atmosphere. Instrumented aircraft have been used to obtain NMOC data in background air masses advected into several urban areas in the United States. Measurements were made during the morning hours in the layer above the surface inversion (~1000 ft.) and below the usual afternoon mixing height (~4000 ft.). Special emphasis was placed on measurement of individual hydrocarbon and carbonyl compounds.

Mean hydrocarbon concentrations for the various cities ranged from about 10 to 50 ppbC with individual samples varying from less than 5 to approximately 90 ppbC. Aldehydes generally contributed less than 10% of the total NMOC measured. There do not appear to be any strong correlations between NMOC levels aloft and other chemical and physical parameters.

NMOC CONCENTRATIONS MEASURED ALOFT

Introduction

Nonmethane hydrocarbon concentrations in the layer above a morning surface inversion and below the afternoon mixing level are of interest because oxidant precursors in this layer mix with urban plumes following breakup of the surface inversion. Most photochemical models that are designed for regulatory purposes incorporate oxidant precursors from aloft. Recent modelling studies have indicated that control requirements are quite sensitive to the nonmethane hydrocarbon input from aloft.[1] Therefore, it is important that hydrocarbon concentrations in this layer be defined.

Hydrocarbon concentrations aloft have been determined in several oxidant field study programs. While in most of these special studies hydrocarbon samples were collected primarily in urban plumes, there were always some samples obtained above the surface inversion during the morning hours. During the summer of 1985, a field measurement program was initiated with the primary objective being to define NMOC levels transported into urban areas from aloft during the morning hours. Studies were conducted in the vicinity of Dallas, Houston, Tulsa, Atlanta and Birmingham. In this paper we will summarize the types and concentrations of organic species measured aloft. Relationships between the organics and other pollutant and meteorological parameters will be described as well.

Data Sources

The nonmethane hydrocarbon data utilized herein were obtained in airborne sampling programs conducted during the period from 1978 through 1985. Table I provides a listing of the cities near which airborne hydrocarbon measurements have been made. This table also indicates which research organizations collected and analyzed the samples. Washington State University, Brookhaven National Laboratory, Battelle Columbus Laboratories, Battelle Pacific Northwest Laboratories and EPA-Las Vegas, each participated in one or more of the sampling programs. Samples for NMOC analysis were collected in rigid metal containers. The sampling period in each locality coincided with the oxidant season in that region.

Sample Selection

Since the objective of this work was to characterize nonmethane hydrocarbon concentrations in the layer above a morning surface inversion and below the usual afternoon mixing level, sample selection criteria was based primarily on collection time and altitude. All samples that were collected during the morning hours before 10 am at altitudes between 1000 ft and 5000 ft above the surface were considered acceptable in the initially screening.

Following the selection of appropriate samples based on time and altitude, the nonmethane hydrocarbon totals were visually examined for each sample in all cities. When the total nonmethane concentration exceeded 60 ppbC, additional information was sought which could be used to verify that the sample had been collected above the morning surface inversion. Ozone concentrations at the time of hydrocarbon sample collection provided a good indicator of mixing heights. A few samples were removed from the data base because hydrocarbon concentrations were abnormally high and ozone levels were very low (<20 ppb). This condition was judged to be characteristic of pollutant conditions in the surface layer below a low level inversion. When available, temperature soundings were examined to verify that samples were collected above the morning surface inversion.

Hydrocarbon Sampling and Analysis

Only a brief summary of the hydrocarbon sampling and analysis techniques will be provided here. Full details of the procedures utilized by the various research groups can be found in the references listed in Table I. Sample collection generally involved transferring air from a ram-air manifold inside the aircraft to the collection container. Rigid metal containers were filled to a positive pressure by inserting a pump between the aircraft's inlet manifold and the metal canister. All hydrocarbon concentration data reported herein were determined by gas chromatographic methods which provided individual species identification. The total hydrocarbon levels were then calculated by summing the concentrations of the individual species that were reported to be present. These analyses were performed using gas chromatographs equipped with flame ionization detectors. Each research group used a cryogenic step to concentrate the organics, two or three column systems in order to obtain adequate hydrocarbon resolution, and computerized data acquisition systems for signal processing.

Results and Discussion

There were 97 samples identified in the field studies prior to 1985 that appeared to be useful for characterizing NMHC levels aloft. This data base included samples from Atlanta-1981, Baltimore-1980, Boston-1980, Houston-1978, Milwaukee-1981, New York-1980, Philadelphia-1979 and Washington, DC-1980. The mean NMHC concentration calculated for each of the eight cities is listed in Table II. Average concentrations ranged from 21.6 ppbC aloft near Atlanta to 47.0 ppbC in the vicinity of Baltimore. In general, cities located in the northeast corridor between Washington, DC and New York City exhibited higher average hydrocarbon levels aloft than cities in other sections of the U.S. For example, the Washington, DC-Baltimore-Philadelphia-New York City average was 40.5 ppbC while the combined average for Atlanta, Boston, Houston and Milwaukee was 25.8 ppbC.

The mean nonmethane hydrocarbon concentration for all cities combined was 35.4 ppbC with a coefficient of variance of approximately 55%. Paraffinic species were by far the major type of hydrocarbons present in samples collected aloft. Saturated compounds comprised approximately 76% of the identified hydrocarbons while the mean aromatic contribution was about 16% and the olefins averaged 8%. The mean paraffin concentration for all cities was 20.0 ppbC. The aromatic mean was 4.3 ppbC and the olefin mean equalled 1.8 ppbC. These data are summarized in Table III.

Hydrocarbon concentrations measured aloft in the vicinity of the eight cities listed in Table II ranged from 10.0 to 89.6 ppbC. Since this represents a difference of almost an order of magnitude, it was of interest to see if there were obvious correlations between hydrocarbon levels aloft and other physical or chemical parameters. In a few specific cases it was possible to examine the relationship between hydrocarbon levels aloft and such factors as wind direction, emission input along back trajectories and surface ozone readings. The Baltimore and New York areas were selected for examining these types of correlations because the comprehensive data base acquired during the 1980 NECRMP and NEROS programs provided the necessary meteorological and pollutant information.

Wind directions over the nine hour period prior to sample collection were determined for each sampling day in Baltimore and New York City. The back trajectories were based on winds averaged over altitudes of 500 to 1500 m. Three hour intervals were utilized in plotting the back trajectories

from each city. Figures 1 and 2 summarize the relationship between hydrocarbon levels aloft and wind directions for Baltimore and New York, respectively. As shown in the center of Figure 1, the mean nonmethane hydrocarbon concentration for 21 samples collected over Baltimore was 47.0 ppbC. Fourteen of the 21 samples were collected with wind trajectories originating in the northwest quadrant. The average hydrocarbon concentration in these cases was 50 ppbC. When winds were out of the southwest quadrant, the mean hydrocarbon level was 41 ppbC. This corresponds to less than a 20% difference which is about the same as the accuracy of the hydrocarbon measurement methodology. Therefore, it appears that hydrocarbon levels aloft in the vicinity of Baltimore are essentially the same in air masses transported into the region from the two westerly quadrants. In the New York City area, there appears to be some dependence of hydrocarbon levels on wind direction. As shown in Figure 2, when winds were out of the southwest quadrant hydrocarbon levels aloft averaged 55 ppbC. This compares to a mean hydrocarbon concentration of 36 ppbC when winds were from the northwest. A logical explanation for this observation is that under a southwesterly wind regime New York City is near the end of the highly populated eastern corridor. Consequently, air masses advected into the New York City area from the southwest should be more polluted than those entering from the northwest or moving onshore from the southeast.

Field studies during the summer of 1985 were designed specifically to measure NMOC levels advected into urban areas from aloft during the early morning hours. The aircraft flew arcs upwind of the urban area at two different altitudes above the surface inversion but below the normal afternoon mixing height. An attempt was made to expand the NMOC measurements to include carbonyl compounds and PAN. The quality of the PAN data is questionable so will not be discussed. Carbonyl compounds were trapped by passing air through adsorbant cartridges impregnated with dinitrophenylhydrazine. The hydrazones that formed were analyzed using HPLC. Table IV provides average NMHC and aldehyde concentrations measured aloft over the five cities studied in 1985. Formaldehyde and acetaldehyde levels in Houston, Atlanta and Birmingham were generally below the detection limit of the analytical procedure, while in Dallas and Tulsa, these two carbonyl compounds accounted for approximately 10% of the NMOC present.

A positive correlation was generally observed between NMHC and aldehyde concentrations. For example, hydrocarbon levels aloft over Dallas on the morning of July 6, 1985 averaged 20 ppbC with a corresponding mean aldehyde concentration of about 2 ppb. On July 14, Dallas NMHC levels were down to about 2 ppbC and the aldehyde concentrations ranged from below the detection limit (~0.1 ppb) up to 0.7 ppb.

The 1985 studies made it possible to examine the variability in hydrocarbon concentrations aloft during the morning hours since sampling arcs were flown at different distances and altitudes upwind of the urban area. Generally, one or more samples were collected along each of three upwind arcs. Figure 3 graphically illustrates the daily variations in hydrocarbon levels observed in Houston. The solid circles in Figure 3 represent measured NMHC levels in individual samples. The vertical lines connect maximum and minimum levels each day. On most days, the high NMHC measurement exceed the low value by at least a factor of two and on several occasions by as much as a factor of ten. As can be seen in Figure 3, on days when the NMHC concentration range was large, one sample exhibited a much higher hydrocarbon level than the others. The reason for this anomalous behavior is not immediately obvious. The high readings showed no consistent correlation with altitude or distance from the city.

Summary

Characterization of NMOC concentrations in transported air masses is currently of interest because organic species are known to contribute to oxidant formation. In addition, hydrocarbons and their oxidation products have been implicated in the production of acidic species in the atmosphere. Hydrocarbons can directly contribute to acidity through their conversion to organic acids (e.g. formic acid) and/or indirectly by promoting the conversion of SO_2 to sulfate. The airborne measurements described herein provide new knowledge concerning NMOC concentrations typically found in background air masses.

Acknowledgments

Funds for this research work were furnished by the U.S. Environmental Protection Agency, Research Triangle Park, NC and the Radian Corp., Austin, TX.

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TABLE I. AIRBORNE HYDROCARBON MONITORING PROGRAMS

City	Sample Collection	Sample Analysis	Sampling Period	Reference
Atlanta	WSU	WSU	July 1981, Aug. 1985	2,4
Baltimore	WSU/BNL	WSU	July-Aug. 1980	3
Birmingham	WSU	WSU	Aug. 1985	3
Boston	BCL	BCL	July-Aug. 1980	3
Dallas	WSU	WSU	July 1985	4
Houston	WSU	WSU	Sept. 1978, Aug. 1985	5,8
Milwaukee	WSU	WSU	Aug. 1981	6
New York	PNL	WSU	July-Aug. 1980	3
Philadelphia	EPA-LV	WSU	July-Aug. 1979	7
Tulsa	WSU	WSU	July 1985	4
Washington, DC	EPA-LV	WSU	July-Aug. 1980	3

WSU: Washington State University
BNL: Brookhaven National Laboratory
BCL: Battelle Columbus Laboratories
PNL: Battelle Pacific Northwest Laboratories
EPA-LV: EPA-Las Vegas (Northrup Services)

TABLE II. MEAN NMHC CONCENTRATIONS (ppbC) MEASURED IN VARIOUS URBAN AREAS PRIOR TO 1985

CITY	ALOFT
ATLANTA	21.6
BALTIMORE	47.0
BOSTON	21.7
HOUSTON	32.7
MILWAUKEE	27.1
NEW YORK	44.5
PHILADELPHIA	23.3
WASHINGTON, DC	38.1

TABLE III. SUMMARY STATISTICS FOR HYDROCARBON DATA COLLECTED ALOFT PRIOR TO 1985

	Mean	Standard Deviation	Coeff. Variance	Min. Value	Max. Value
NMHC (ppbC)	35.4	19.4	54.9	10.0	89.6
Paraffin (ppbC)	20.0	12.3	61.6	3.5	73.0
(%)	76	13	17	28	96
Aromatic (ppbC)	4.3	4.2	98.5	0.3	28.5
(%)	16	10	64	3.6	60
Olefin (ppbc)	1.8	2.0	111	0	11.0
(%)	8.1	8.9	110	0	35

TABLE IV. MEAN NMOC CONCENTRATIONS DETERMINED DURING 1985 FIELD STUDIES

CITY	NMHC (ppbC)	FORM (ppb)	ACET (ppb)
HOUSTON	20.0	<0.5	<0.2
DALLAS	17.6	1.7	0.2
TULSA	34.6	3.5	0.9
ATLANTA	24.9	<0.7	<0.3
BIRMINGHAM	10.6	<0.7	<0.3

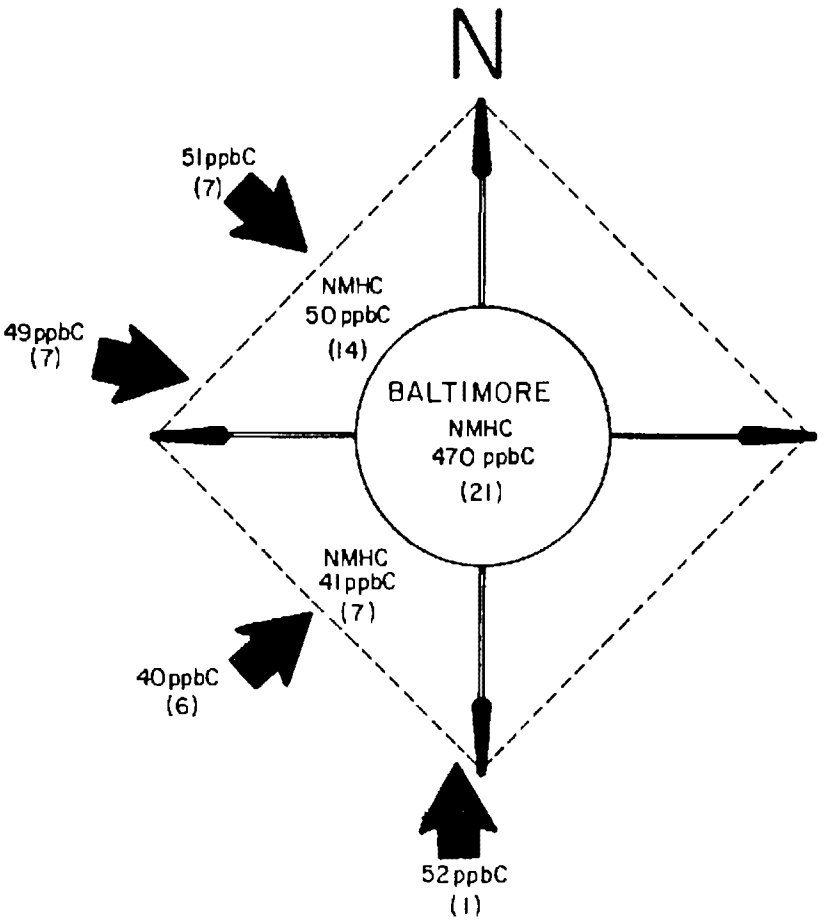

Figure 1. Diagram showing relationship between hydrocarbon levels measured aloft over Baltimore and wind direction.

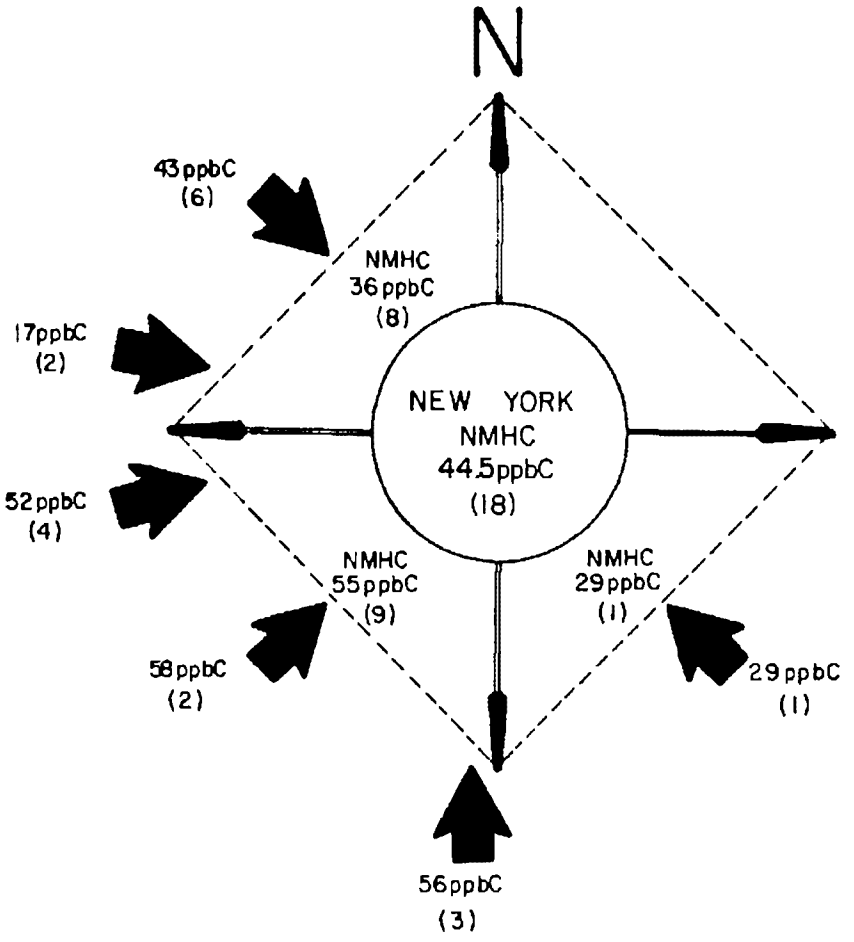

Figure 2. Diagram showing relationship between hydrocarbon levels measured aloft over New York City and wind direction.

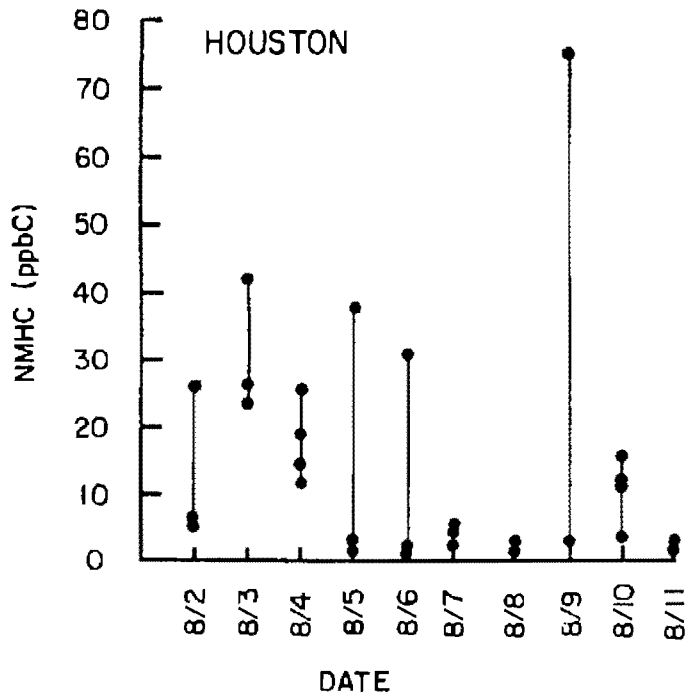

Figure 3. Variability in daily NMHC concentrations observed in Houston during August 1985.

FIELD APPLICABILITY AND PRECESSION OF A WHOLE-AIR SAMPLING METHOD FOR AMBIENT AIR VOLATILE ORGANIC COMPOUND DETERMINATION

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ABSTRACT

Toxic substances can enter the atmosphere through continuous emission at relatively low concentration levels. Characterization of such emissions is difficult. A method of sampling volatile organic compounds from a continuous point source using stainless steel spheres as whole-air samplers is described. Laboratory analysis using cryogenic focusing and gas chromatography allows assessment of the samples.

The method was tested at a gasoline loading station for a pipeline company. Five of the spheres were located downwind of the source in the plume centerline; one sampler was located upwind of the source to collect background concentrations. The compounds chosen for analysis were isopentane, n-pentane, n-hexane, benzene, isooctane, and n-heptane because of their prevalence in the emissions from the source type. Concentrations of selected compounds varied from 57.1 ppm to less than 0.01 ppm depending on the compound itself, location of the sampler relative to the source, and meteorological conditions.

At two downwind sample points, co-located samplers were used to assess the precision of the sampling system. Co-located sampler data showed differences in compound concentrations ranging from 2.8 percent to 17.9 percent. Most variations, however, fell in the 5 percent to 10 percent range.

Results showed that the stainless steel spheres performed well in the field. In comparison with other available ambient air volatile organic samplers, the system described in this study has many advantages, including ease of operation, a wider range of applicability to various organic compounds, and more versatility in actual field monitoring configurations.

Field Applicability and Precession of a Whole-Air Sampling Method for Ambient Air Volatile Organic Compound Determination

BACKGROUND

Continuous, low level emission of volatile organic compounds may cause chronic health effects to various parts of a population. These types of emissions could be produced by certain industrial source classes. Characterization of compounds present in such a situation is difficult at best, but the necessity for emission safeguards can only be justified once ambient air concentration levels are assessed. Unfortunately, no standard procedure for doing so has been developed to date. In 1984, the U.S. Environmental Protection Agency completed a report entitled "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air" (NTIS #EPA-600/4-84-041). This document describes five techniques applicable to the monitoring of volatile organic compounds. All but one of the methods (cryogenic trapping) are somewhat specific to a certain group of volatile compounds.

Field testing of these possible methods is limited. The most extensive work was performed by Riggins (EPA-600/4-83-027), who collected field data using the five methods and evaluated their applicability for use with various volatile compounds, but this work was not intended to compare the relative performance of each method at a co-located site. Other data that exist on the five methods discussed in the compendium document are Krost - Tenax^R GC (1982), Pellizzari - Tenax^R GC (1979), Kebbekus - Tenax^R GC, molecular sieve (1982), Walling - Tenax^R GC, molecular sieve (1982), Holdren - cryogenic (1984), Lewis - organochlorine pesticides (1982 and 1980), Bjorkland - organochlorine pesticides (1970), and Grosjean - aldehydes and ketones (1980).

The most recent field study of hazardous organic chemicals in the ambient atmosphere was done by Singh, et al. (1983). Concentrations of forty-four organic chemicals (many were bacterial mutagens or suspected carcinogens) were measured in ten USA cities over a nine to eleven day period using a gas chromatograph-equipped mobile laboratory. Results indicate that average concentrations of the measured species ranged from 0-20 ppb.

Of the five techniques developed to date, only the cryogenic trapping and GC/FID or ECD analysis has more than narrow applicability. It is capable of detecting volatile, nonpolar organics having boiling points in the range of -10 to +200°C. The major disadvantage to this technique is its requirement for cryogenic gas chromatographic measurements in the field, thereby permitting only single point concentration assessments of a volatile compound from the suspected source; simultaneous mapping of the plume cannot be done.

An alternative technique, or compatible add-on technique, is needed to make the cryogenic trapping method more versatile. One approach is the development of a secondary collection system capable of storage and transportion of the sample(s) to a stationary cryogenic gas chromatograph. In this study, such a procedure is explored by collecting volatile organic compounds from a bulk petroleum transfer facility near Topeka, KS using stainless steel spheres. Five spheres were located downwind, and one upwind, of the source. At two of the downwind sampling points, co-located samplers were used to check the precision of the system. The samples were then transported to the laboratory for analysis on a cryogenic gas chromatograph. Laboratory procedures for analyzing the samples were based

on McClenny's work (Pleil, et. al. 1984 & Holden, et. al. 1985). General laboratory use of cryofocusing gas chromatography is reviewed by Brettell et. al. (1985) and Wampler et. al. (1985).

DESCRIPTION OF METHODS

Field Sampling

Stainless steel spheres (Demaray Scientific Instrument Ltd., Model 0647, 6.0 liter) equipped with Whitey Microvalves were used to collect volatile organic compounds emitted from a bulk gasoline transfer station (Williams Pipeline Company, Wakarusa, Kansas). The collection spheres were evacuated in the laboratory before placement in the field. To insure that no carryover of compounds between different tests occurred, the spheres were evacuated to 60 microns of mercury vacuum using a Welch Duo Seal vacuum pump (Model 1402R); they were then flushed for three minutes and pressurized to 30 psi with hydrocarbon-free air supplied by Linde Corporation (NBS traceable). After the spheres had set for approximately one hour, they were prepared for field sampling by evacuating to 60 microns of mercury vacuum using the same pump. A Hastings vacuum gauge (Model DV-6) was used to measure the 60 micron value.

The Whitey microvalves (Model SS-21RS2) were calibrated in the laboratory using a certified bubble meter. During the calibration procedure, the spheres were treated in the same manner as if they were being used for field sampling. Microvalve settings were determined to allow a 100-105 mℓ/min initial flow rate.

Each of the spheres was transported to the field site for a sampling run. They were attached to two-meter high fence posts which had been driven at three arithmetically or geometrically-spaced sample points. At two points, co-located samplers were installed to check the precision of the sampling system. One sample was always located upwind of the source to evaluate background levels of the selected volatile compounds. Before each sampling period began, a hand level was used to ensure that the five downwind samplers were at the same approximate height above the ground.

A portable meteorological station was monitored to provide an accurate picture of wind speed, wind direction, relative humidity and atmospheric temperature during each sample run. The temperature and windspeed were taken at two and six meters above the ground. Wind direction and relative humidity were also recorded at two meters above the ground. Data from the meteorological station were used in aligning the downwind sample points on the plume centerline which corresponded to the direction of the prevailing wind (see Figure 1), and in determining atmospheric conditions for future use in computer dispersion modeling.

Each of the microvalve settings was checked for proper readings before a test. The three downwind sample points were chosen such that the sampler locations were within ± 10° of the plume centerline at the initiation of a test. This criterion was met using triangulation techniques as illustrated in Figure 1. Values were adjusted until they matched the calculated values corresponding to a direct centerline alignment. A subsequent check of meteorological data suggested that we were successful in sampler location using this approach.

After all the prestart steps had been rechecked, the main valves adjoining pre-set microvalves on the spheres were opened and sample collection began. In all cases, there was less than a one minute delay between the first valve opening and the last based upon stopwatch observations.

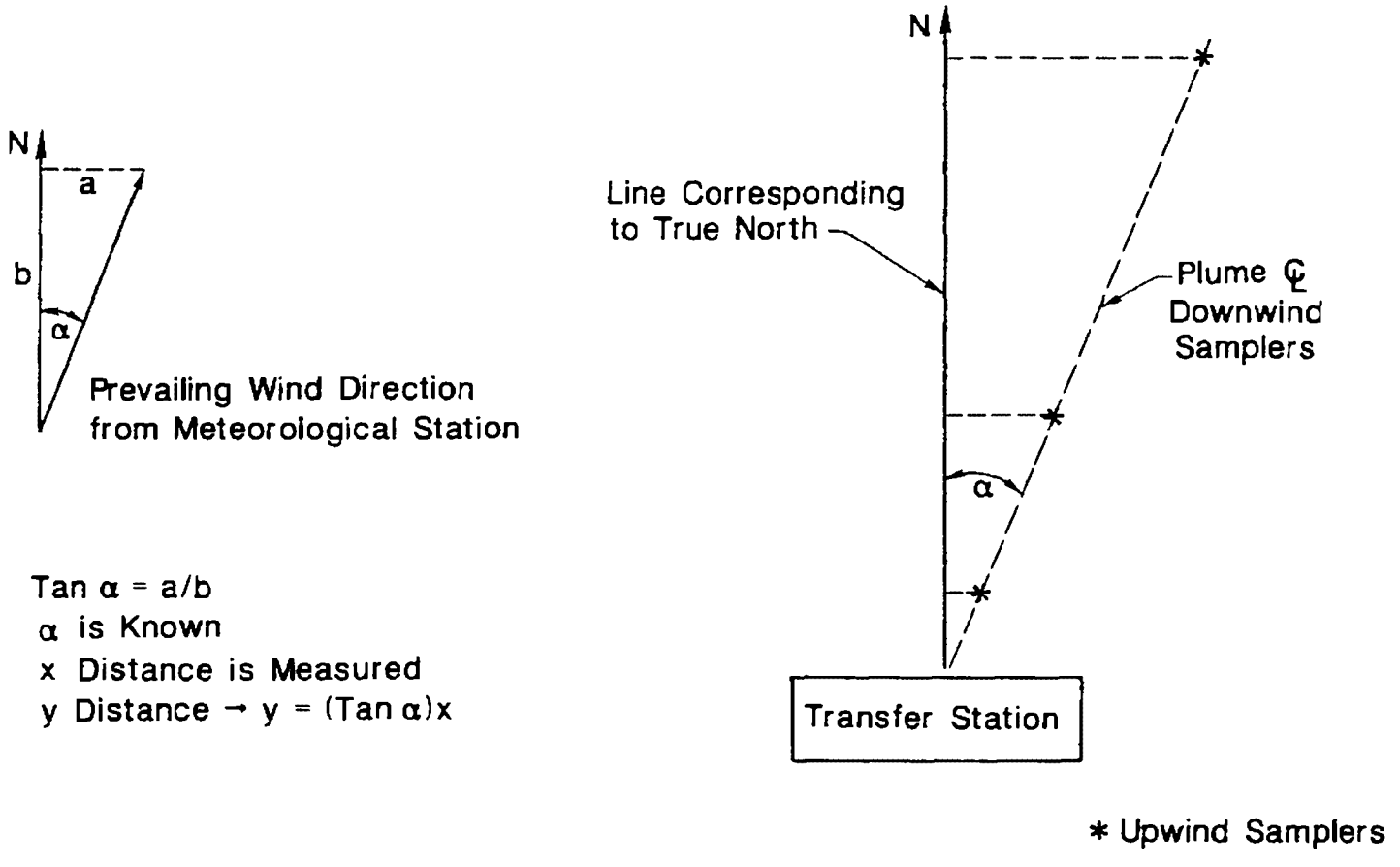

Figure 1 - Illustration of Sampler Placement

William's Pipeline Co. allowed access to the on-site product flow computer system to determine the amount of liquid product transferred during any sample period.

At the end of the test, the main valve and microvalves on each sphere were closed, again within a one minute period. The sample collection spheres were then removed from the field site and transported to the laboratory for analysis.

The total setup time for a test (including meteorological equipment) using a two person crew was thirty-five minutes. If the meteorological station was not deployed, samplers were in place in less than fifteen minutes after reaching the site. Takedown time with the meteorological equipment required twenty-five minutes. The six samplers without the meteorological equipment could be removed from the site in less than fifteen minutes. Total time for an actual sixty minute test averaged a little less than two total hours with meteorological equipment setup.

Laboratory Analysis

The samples were analyzed with a Nutech cryogenic sampling system and a Hewlett-Packard 5880A gas chromatograph. A flame ionization detector was used for all samples. A detailed description of the laboratory procedures and gas chromatography variables is not presented here; the reader is referred to Holden et. al. (1985), Pliel et. al. (1984) and Tripp (1984).

A volume of approximately four liters was collected in each of the six-liter spheres. The volume was determined using Figure 2. By plotting the flowrate through the Whitey microvalves versus time, a curve was generated for each valve system (i.e., stainless steel sphere and Whitey microvalve). Graphical integration of the area under this curve yielded an approximate volume collected for each microvalve of four liters. For example, for microvalve number 4:

Initial flowrate = 114.9 ml/min.

Final flowrate = 29.9 ml/min.

Elapsed time = 60 min.

$$\frac{114.9 \text{ ml/min.} + 29.9 \text{ ml/min.}}{2} \times 60 \text{ min.} = 4334. \text{ ml}$$

A vacuum was required to remove the samples from the spheres. To avoid contamination of the samples, a metal bellows pump was chosen for this task.

The 28-minute sampling and analysis cycle allowed for a maximum of 18.5 minutes of sample collection per cycle. To ensure that only pure sample was circulated through the cryogenic trap, the flow from the sampler to the sampling manifold was maintained at a value higher than the 25 cc/min flow into the cryogenic sampling system. If the flow was maintained in the 35-40 cc/min range, samples could be drawn from the sampler for approximately 100 minutes, sufficient for four samples at 18.5 minutes of sample collection each.

To maintain the flow from the sampler in the 35-40 cc/min range, both a Whitey microvalve and a mass flow controller were placed in the sampling system between the metal bellows pump and the sampling manifold. The mass flow controller was set at 40 cc/min, and the opening of the microvalve was constantly monitored and adjusted to maintain a reading slightly less than

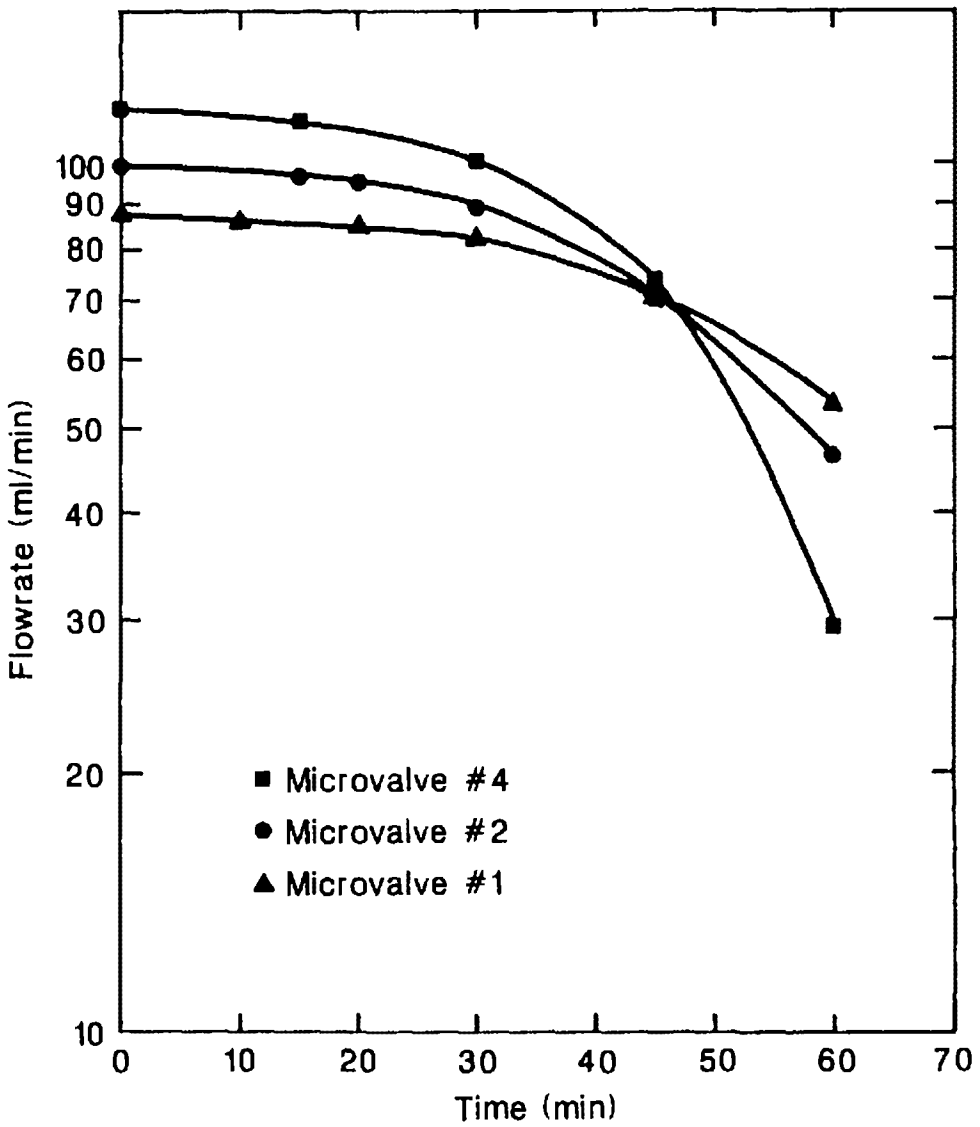

Figure 2 - Sampler Flowrate Versus Time For Whitey Microvalves

40 cc/min. Flow from the sampler was started by opening its top valve approximately 1.5 minutes before the start of the sample collection period of the first of four samples taken from each sampler. Flow was stopped by closing the same valve at the end of the sample collection period. The same procedure was used for the remaining samples, with the exception that the flow was started only 30 seconds prior to the start of the sample collection period.

Each time a change was made from one sampler to the next, the entire sampling system was flushed with hydrocarbon-free air. In most cases, the first of the four analyses of each sample resulted in a slightly lower concentration than the others. Thus, there is not absolute confidence that the 1.5 minutes of sample flow prior to the start of the sample collection period is sufficient to fill the lines and the sampling manifold with pure sample. In order to achieve this confidence, either a higher flow rate must be used, or the first sample should be discarded.

The gas chromatograph was calibrated using a mixture of gases provided by Scott Specialty Gases,Inc. This mixture contains NBS-traceable concentrations of all of the desired compounds except n-heptane. In order to obtain a known concentration of n-heptane, a portion of the pure compound (in the liquid state) was placed in a diffusion tube, which provided a constant release of vapor at constant temperature. The n-heptane was released from the diffusion tube into a closed system, through which hydrocarbon-free air was passed at a known rate, which was controlled by a mass flow controller. However, because the mass flow controller was found to yield readings approximately 10% lower than the actual flow (as measured by a bubble flowmeter), a correction factor was introduced. This flow was mixed with that from the cylinder containing the other five compounds (also measured with a bubble flowmeter) and introduced into the sampling manifold. The diffusion rate of n-heptane was obtained by weighing the diffusion tube several times, with about a week between each of the weighings. Knowing this diffusion rate, the concentrations of the compounds in the calibration mixture (as furnished by Scott), the flow through the diffusion system, and the flow from the cylinder containing the calibration mixture, the exact concentrations in the sampling manifold could be calculated.

A calibration method involving the use of diffusion tubes for all the analyzed compounds was also used during the course of the study. Comparisons of the diffusion tube method and compressed calibration gases indicate a maximum concentration difference between the two methods of seven percent. Most of the concentration differences ranged from two percent to four percent. Due to their high volatility rate in the 20-25°C range, the diffusion rates of isopentane and n-pentane are variable with slight temperature changes. Therefore, a system capable of holding a constant temperature (± 0.5°C) several degrees below room temperature (i.e. 10°C) is necessary.

The performance of the gas chromatograph used in this study is limited to concentrations above 0.01 ppm for the compounds under consideration and the type of laboratory protocol followed during the analysis phase. Characteristics of the gas chromatograph and manufacturer's specifications indicated that the instrument was capable of parts per billion determination of volatiles with a ±5 percent maximum variation. However, simultaneous dual column runs of the samples and calibration compounds were required to achieve the necessary precision in this low concentration range. Time limitations on this study and the expected high concentrations of the chosen volatiles emitted from the site precluded the need for this type of laboratory protocol for this series of sample runs.

TABLE 1

TEST #1

August 2, 1985, 9:33 a.m., CDT-10:32 a.m. CDT, ~7/10 cloud cover

Temperature (2m): 67-70°F — Avg. wind speed (2m) - 6.0 mph

Temperature (6m): 68°F — Avg. wind speed (6m) - 7.5 mph

Net flow, Regular - 16,064 gal — Avg. wind direction - 105°

Net flow, Unleaded - 20,748 gal

Location of Samplers	Concentrations (ppm) Isopentane	n-Pentane	n-Hexane	Benzene	Isooctane	n-Heptane
70m downwind	4.6	2.5	0.22	0.15	0.12	0.044
	4.9	2.7	0.24	0.17	0.13	0.046
45m downwind	10.3	6.1	0.49	0.32	0.26	0.094
	11.2	6.6	0.54	0.36	0.29	0.10
45m downwind (colocated)	10.8	6.4	0.51	0.34	0.27	0.10
	11.2	6.6	0.54	0.36	0.29	0.11
30m downwind	18.0	10.6	0.86	0.56	0.45	0.16
	17.5	10.8	0.88	0.59	0.47	0.17
30m downwind (colocated)	18.2	10.6	0.86	0.57	0.45	0.17
	17.0	10.5	0.90	0.60	0.47	0.18

TEST #2

August 8, 1985, 8:52 a.m., CDT-9:53 a.m. CDT, scattered clouds

Temperature (2m): 73-80°F — Avg. wind speed (2m) - 6.1 mph

Temperature (6m): 76-78°F — Avg. wind speed (6m) - 7.8 mph

Net flow, Regular - 11,995 gal. — Avg. wind direction - 140°

Net flow, Unleaded - 20,704 gal.

Location of Samplers	Concentrations (ppm) Isopentane	n-Pentane	n-Hexane	Benzene	Isooctane	n-Heptane
Upwind	0.11	0.016	0.015	0.025	0.008	0.006
	0.11	0.012	0.015	0.023	0.006	0.008
80m downwind	0.28	0.13	0.017	0.025	0.007	0.007
	0.32	0.15	0.021	0.023	0.008	0.006
52m downwind	1.7	0.88	0.084	0.057	0.037	0.015
	2.0	0.89	0.097	0.071	0.042	0.021
52m downwind (colocated)	1.8	0.83	0.090	0.064	0.042	0.016
	1.9	0.86	0.091	0.067	0.044	0.017
28m downwind	7.2	3.3	0.46	0.26	0.17	0.061
	7.7	3.9	0.48	0.27	0.18	0.066
28m downwind (colocated)	7.0	3.2	0.35	0.25	0.16	0.057
	7.3	3.4	0.36	0.26	0.17	0.057

TABLE 2

TEST #3

August 16, 1985, 9:43 a.m., CDT-10:42 a.m. CDT, fog lifting at start, changed to scattered clouds

Temperature (2m): 72-77°F — Avg. wind speed (2m) - 3.8 mph

Temperature (6m): 72-77°F — Avg. wind speed (6m) - 2.9 mph

Net flow, Regular - 19,984 gal — Avg. wind direction - 145°

Net flow, Unleaded - 30,700 gal

Location of Samplers	Concentrations (ppm) Isopentane	n-Pentane	n-Hexane	Benzene	Isooctane	n-Heptane
Upwind	0.024	0.014	0.010	0.018	0.025	0.002
	0.025	0.014	0.010	0.017	0.026	0.002
50m downwind	6.2	3.2	0.31	0.20	0.12	0.047
	6.4	3.6	0.32	0.21	0.13	0.051
35m downwind	10.1	5.6	0.50	0.32	0.20	0.078
	10.8	6.1	0.54	0.35	0.23	0.087
35m downwind (colocated)	10.6	5.8	0.52	0.34	0.21	0.083
	10.9	6.0	0.53	0.35	0.22	0.086
15m downwind	52.0	24.6	2.6	1.6	1.0	0.36
	57.1	26.5	2.4	1.8	1.1	0.42
15m downwind (colocated)	55.9	25.7	2.8	1.8	1.1	0.42
	57.6	27.0	2.4	1.8	1.1	0.44

TEST #4

August 20, 1985, 9:28 a.m., CDT-10:28 a.m. CDT, cloudy, occasional drizzle

Temperature (2m): 62-63°F — Avg. wind speed (2m) - 3.5 mph

Net flow, Regular - 12,353 gal — Avg. wind direction - 110°

Net flow, Unleaded - 9,321 gal

Location of Samplers	Concentrations (ppm) Isopentane	n-Pentane	n-Hexane	Benzene	Isooctane	n-Heptane
Upwind	0.016	0.018	0.019	0.029	0.008	0.013
	0.014	0.016	0.018	0.025	0.006	0.012
50m downwind	6.7	2.9	0.33	0.26	0.10	0.062
	6.2	2.7	0.31	0.25	0.10	0.060
35m downwind	10.5	4.4	0.52	0.42	0.16	0.10
	10.4	4.3	0.52	0.42	0.17	0.10
35m downwind (colocated)	9.6	4.0	0.47	0.39	0.15	0.094
	10.4	4.4	0.52	0.42	0.17	0.10
15m downwind	31.8	12.0	1.6	1.3	0.55	0.28
	34.1	12.7	1.7	1.4	0.60	0.32
15m downwind (colocated)	33.3	12.6	1.6	1.4	0.67	0.30

TABLE 3

TEST #5

August 26, 1985, 9:23 a.m., CDT-10:08 a.m. clear

Temperature (2m): 66-69°F
Temperature (6m): 67-68°F
Net flow, Regular - 19,315 gal
Net flow, Unleaded - 11,473 gal

Avg. wind speed (2m) - 1.6 mph
Avg. wind speed (6m) - 4.0 mph
Avg. wind direction - 310°

Concentrations (ppm)

Location of Samplers	Isopentane	n-Pentane	n-Hexane	Benzene	Isooctane	n-Heptane
Upwind	0.061	0.026	0.013	0.013	0.005	0.004
	0.063	0.027	0.011	0.010	0.004	0.003
113m downwind	0.006	0.004	0.005	0.009	0.017	0.002
	0.007	0.005	0.007	0.011	0.015	0.002
113m downwind (colocated)	0.003	0.002	0.002	0.003	0.001	0.001
	0.005	0.003	0.003	0.004	0.001	0.001
50m downwind	0.015	0.014	0.012	0.022	0.005	0.005
	0.011	0.009	0.010	0.017	0.004	0.004
50m downwind (colocated)	0.011	0.008	0.005	0.008	0.002	0.002
	0.014	0.009	0.006	0.009	0.002	0.002
25m downwind	0.031	0.017	0.004	0.005	0.003	0.001
	0.045	0.021	0.006	0.008	0.004	0.002

TEST #6

August 29, 1985, 4:11 p.m., CDT-4:56 p.m., partly cloudy, brief showers

Temperature (6m): 88-89°F

Avg. wind speed (2m) - 5.4 mph
Avg. wind speed (6m) - 4.0 mph
Avg. wind direction - 200°

Net flow, Regular - 12,814 gal
Net flow, Unleaded - 13,083 gal

Concentrations (ppm)

Location of Samplers	Isopentane	n-Pentane	n-Hexane	Benzene	Isooctane	n-Heptane
Upwind	0.065	0.011	0.014	0.023	0.010	0.005
	0.073	0.011	0.015	0.023	0.010	0.005
52m downwind	3.2	1.8	0.15	0.11	0.080	0.031
	2.9	1.7	0.15	0.10	0.090	0.029
26m downwind	6.8	3.7	0.31	0.21	0.16	0.060
	6.6	3.5	0.31	0.21	0.15	0.058
26m downwind (colocated)	6.4	3.7	0.29	0.19	0.14	0.055
	6.6	3.6	0.30	0.20	0.15	0.056
13m downwind	12.6	7.3	0.67	0.38	0.30	0.11
	13.0	7.4	0.69	0.40	0.31	0.12

TABLE 4

TEST #7

September 5, 1985, 2:30 p.m., CDT-3:15 a.m.,CDT, Clear

Temperature (6m): 93-94°F — Avg. wind speed (2m)-11.3 mph

Net flow, Regular - 7,816 gal — Avg. wind speed (6m)-15.0 mph

Net flow, Unleaded - 13,405 gal — Avg. wind direction - 310°

Location of Samplers	Concentrations (ppm) Isopentane	n-Pentane	n-Hexane	Benzene	Isooctane	n-Heptane
Upwind	0.012	0.011	0.009	0.016	0.005	0.004
	0.012	0.010	0.008	0.013	0.004	0.004
64m downwind	2.1	0.92	0.11	0.073	0.045	0.022
32 downwind	4.5	1.8	0.22	0.15	0.084	0.044
	4.7	2.0	0.23	0.16	0.089	0.047
32m downwind (colocated)	4.8	2.0	0.23	0.16	0.090	0.048
16m ground	9.5	3.8	0.43	0.29	0.18	0.088
	11.5	4.6	0.54	0.37	0.22	0.112
16m-2m high	10.6	4.2	0.49	0.34	0.21	0.10
	10.8	4.3	0.50	0.35	0.21	0.11

DESCRIPTION OF FINDINGS

Field Data

Six volatile organic compounds were chosen for evaluation in this study. These were isopentane, n-pentane, n-hexane, benzene, isooctane, and n-heptane. The choice of these compounds was based on a report by the U.S. Environmental Protection Agency (PB83-256206, EPA-450/3-80-038B), which shows these to be the primary volatile components of regular and unleaded gasoline.

Tables 1-4 describe the actual field data collected during each test.The tables also contain information on weather conditions and sampler location. A "co-located" designation simply means that two samplers simultaneously monitored at that point. As shown in the tables, meteorological conditions varied considerably for each test run. Position (distance from the source) of the samplers were governed by the meteorological conditions as well as limitations on how close to the source a sampler could be placed. In general, safety limitations restricted sampler placement to at least thirteen meters from the source. Stable meteorological conditions (i.e., light surface winds and isothermal or an inversion profile) dictated that the downwind samplers be placed closer to the source in order to remain in the plume centerline. Unstable atmospheric conditions (i.e., moderate to high wind speeds and lapse profiles) resulted in the downwind samplers being located farther away from the source.[1]

[1]Due to a large shift in wind direction approximately ten minutes into Test 5, the concentration values do not represent those along the centerline.

TABLE 5

SUMMARY OF CO-LOCATED SAMPLER DATA

Test No.	Concentrations (ppm) Isopentane	n-Pentane	n-Hexane	Benzene	Isooctane	n-Heptane
1-A	10.3	6.1	0.49	0.32	0.26	0.094
	11.2	6.6	0.54	0.36	0.29	0.10
	10.8	6.4	0.51	0.34	0.27	0.10
	11.2	6.6	0.54	0.36	0.29	0.11
1-B	18.0	10.6	0.86	0.56	0.45	0.16
	17.5	10.8	0.88	0.59	0.47	0.17
	18.2	10.6	0.86	0.57	0.45	0.17
	17.0	10.5	0.90	0.60	0.47	0.18
2-A	1.7	0.88	0.084	0.057	0.037	0.015
	2.0	0.89	0.097	0.071	0.042	0.021
	1.8	0.83	0.090	0.064	0.042	0.016
	1.9	0.86	0.091	0.067	0.044	0.017
2-B	7.2	3.3	0.46	0.26	0.17	0.061
	7.7	3.9	0.48	0.27	0.18	0.066
	7.0	3.2	0.35	0.25	0.16	0.057
	7.3	3.4	0.36	0.26	0.17	0.057
3-A	10.1	5.6	0.50	0.32	0.20	0.078
	10.8	6.1	0.54	0.35	0.23	0.087
	10.6	5.8	0.52	0.34	0.21	0.083
	10.9	6.0	0.53	0.35	0.22	0.086
3-B	52.0	24.6	2.6	1.6	1.0	0.38
	57.1	26.5	2.4	1.8	1.1	0.42
	55.9	25.7	2.8	1.8	1.1	0.42
	57.6	27.0	2.4	1.8	1.1	0.44
4-A	10.5	4.4	0.52	0.42	0.16	0.10
	10.4	4.3	0.52	0.42	0.17	0.10
	9.6	4.0	0.47	0.39	0.15	0.094
	10.4	4.4	0.52	0.42	0.17	0.10

TABLE 5
(continued)

Test No.	Concentrations (ppm) Isopentane	n-Pentane	n-Hexane	Benzene	Isooctane	n-Heptane
4-B	31.8	12.0	1.6	1.3	0.55	0.28
	34.1	12.7	1.7	1.4	0.60	0.32
	33.3	12.6	1.6	1.4	0.67	0.30
5-A	0.006	0.004	0.005	0.009	0.017	0.002
	0.007	0.005	0.007	0.011	0.015	0.002
	0.003	0.002	0.002	0.003	0.001	0.001
	0.005	0.003	0.003	0.004	0.001	0.001
5-B	0.015	0.014	0.012	0.022	0.005	0.005
	0.011	0.009	0.010	0.017	0.004	0.004
	0.011	0.008	0.005	0.008	0.002	0.002
	0.014	0.009	0.006	0.009	0.002	0.002
6-A	6.8	3.7	0.31	0.21	0.16	0.060
	6.6	3.5	0.31	0.21	0.15	0.058
	6.4	3.7	0.29	0.19	0.14	0.055
	6.6	3.6	0.30	0.20	0.15	0.056
7-A	4.5	1.8	0.22	0.15	0.084	0.044
	4.7	2.0	0.23	0.16	0.089	0.047
	4.8	2.0	0.23	0.16	0.090	0.048

TABLE 6

SELECTED CO-LOCATED SAMPLER DATA
ISOPENTANE

Test No.	Concentration (ppm)	Percent Difference (%)
1-A	10.3	
	11.2	
	10.8	
	11.2	8.0
1-B	18.0	
	17.5	
	18.2	
	17.0	5.6
2-B	7.2	
	7.7	
	7.0	
	7.3	9.1
3-A	10.1	
	10.8	
	10.6	
	10.9	7.3
3-B	52.0	
	57.1	
	55.9	
	57.6	9.7
4-A	10.5	
	10.4	
	9.6	
	10.4	8.6
4-B	31.8	
	34.1	
	33.0	6.7
6-A	6.8	
	6.6	
	6.4	
	6.6	5.9
7-A	4.5	
	4.7	
	4.8	6.2

TABLE 7

SELECTED CO-LOCATED SAMPLER DATA
BENZENE

Test No.	Concentration (ppm)	Percent Difference (%)
1-B	0.56	
	0.59	
	0.57	
	0.60	6.7
3-B	1.6	
	1.8	
	1.8	
	1.8	11.1
4-B	1.3	
	1.4	
	1.4	7.1
7-1	0.15	
	0.16	
	0.16	6.2

SELECTED CO-LOCATED SAMPLER DATA
n-HEXANE

Test No.	Concentration (ppm)	Percent Difference (%)
1-B	0.86	
	0.88	
	0.86	
	0.90	4.4
3-B	2.6	
	2.4	
	2.8	
	2.4	14.3
4-B	1.6	
	1.7	
	1.6	5.9
7-1	0.22	
	0.23	
	0.23	4.3

Co-located Sampler Data

Two samplers were located side by side at the same height at two downwind sample points in order to determine sampler precision. Co-located samplers were treated in exactly the same manner as the other spheres, but represent two distinct samples because they were not connected to a common sampler manifold. Tables 5-7 summarize the results of the co-located sampler data.

The data indicate excellent correlation among samplers. In the selected data cases, the difference in co-located volatile compound concentrations was less than eighteen percent for co-located samplers. Results presented in the tables show that most of the differences ranged between five and ten percent.

CONCLUSIONS

The following conclusions appear warranted based on the data:

1) The stainless steel spheres with microvalves are good sample collection vessels for field use: they are easy to prepare for field tests; require no maintenance in the field; are easily transported to and from the field; and can be adjusted for varying sample collection times.

2) The cryogenic gas chromatograph with flame ionization detector is compatible with the field samples collected in this study. If the procedures used herein are followed, reliable data can be generated.

3) Co-located sampler data show that the precision between samplers is very good. The difference in co-located sampler data ranges between 2.8 percent to 17.9 percent, although most variations lie between 5 percent and 10 percent.

4) Data indicate that the downwind centerline of the plume concentrations of isopentane, n-pentane, n-hexane, benzene, isooctane, and n-heptane vary from 57.1 ppm to less than 0.01 ppm for sampler distances from the source between 13 m and 80 m, respectively. These concentrations are also dependent on meteorological conditions.

5) Visual observations of the source indicate that the volatile emission fraction settles close to the emission point and is resuspended by ambient air flow to form a plume. Modeling techniques will have to take this point into account.

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CANISTER-BASED VOC SAMPLERS

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ABSTRACT

Canister-based sampling units for volatile organic compounds are a viable alternative to sampling onto adsorbent-packed cartridges. Units for sampling periods of from one minute to one week (periodic sampling) have been assembled and tested. Side-by-side field evaluation of weatherized, ambient air samplers show ± 5.1% percentage difference at low and fractional ppbv levels; a sequential sampler has been used to document VOC variability in laboratory air.

INTRODUCTION

Canister-based sampling systems for toxic volatile organic compounds (VOCs) have been developed by EMSL, US EPA as a possible alternative to collection on solid sorbents. The most frequently used solid sorbent, Tenax GC, has been shown empirically to give results that are difficult to interpret.[1,2] Use of the canister-based sampling systems for toxic VOCs has evolved as an extension of the use of canisters for halocarbon[3] and hydrocarbon analysis[4], primarily with canisters treated by the proprietary process of SUMMA® polishing. The SUMMA® process is available on license from Molectrics Corp.[5] Demaray Scientific Corp[6] and Biospherics[7] supply most of the SUMMA® polished canisters currently in use for collection of VOCs. Canisters have been used in a number of applications prior to which some storage stability data were obtained for the specific compounds of interest. Reference to these previous studies, and the documentation of storage stability for a group of eighteen VOCs performed by Northrop Services, Inc. are now available[8] as a result of the EPA-sponsored development program.

Additional storage stability studies have recently been completed by an EPA contractor, Battelle Columbus Laboratories, and are available on a limited basis.[9] Initial studies with the canisters have included a survey of VOCs in indoor air[10] and comparison studies of VOC sampling procedures.[11,12] A related application[13] has been the use of canisters as a sampling and storage medium for a national program to document the nonmethane organic compound concentration (as ppbC) for the purpose of SIP (state implementation plans) revision. This program has been effective in establishing the reliability of methods for shipping the canisters from the sampling locations to a central analytical laboratory, as well as being a successful monitoring program. Various canister-based sampling configurations have been evaluated by the EMSL, EPA to achieve time-averaged continuous (or periodic, integrative) sampling and to obtain short-term samples for survey or temporal variability studies. This paper gives a description of the sampling systems and of representative results.

DESCRIPTION AND SELECTED RESULTS FOR CANISTER-BASED SAMPLING SYSTEMS

Advantages/Disadvantages Relative to Solid Sorbent Cartridges

The canister-based samplers have the following advantages as compared to solid sorbent cartridges:

1. Canister pressure can be used as an indicator of correct sampler operation.
2. No thermal desorption is required.
3. Multiple analyses can be performed from a canister.
4. Artifact problems related to the storage of enhanced trace gas concentrations, to thermal decomposition of the sorbent, to memory effects in the sorbent and to the effect of thermal desorption on the target compound concentration are not present.
5. The operator of the system need not be present at the beginning and end of the sampling run, i.e., to cap the sorbent.
6. The sample concentrations can be easily diluted if concentrations are too high.
7. The evacuated canisters can be used for sampling without need for electricity.

The canister-based samplers have the following disadvantages as compared to solid sorbent cartridges:

1. The sample is stored after passage through a sampling train, each component of which (filter, pump, valve) must be clean. Solid sorbent tubes are usually the first element in the sampling train.
2. Air leaks in system elements upstream of the canister are a potential source of error.
3. A limited sample volume (approximately 15 liters) at ~24 psig can be stored in canisters of easily manageable size (6 liters).
4. Because of the limited prior use of the canister-based samplers for toxic VOCs, some uncertainty remains with respect to potential problems.

Continuous Samplers for Obtaining Time-Averaged Concentrations The weatherized sampler currently in use in EPA field studies is shown schematically in Figure 1. This sampler is designed for limited temperature control of the inlet line and the interior of the sampler housing. Components have been selected for proven reliability and not for cost or size. These components are listed in Table 1 along with corresponding alternate components that

have either a cost or size advantage. The alternate components are being tested for possible updating of the sampler design. The sampling train for the current EPA sampler is patterned after that used for NMOC sampling[13] except that a Tylan model FC-260 flow controller is used instead of a hypodermic needle flow restrictor. The flow controller was required to maintain flow rates at 10 sccm over 24 hour periods during which the canister is filled from vacuum to 24 psig to collect about 15 liters of whole air sample.

A number of preliminary ambient air tests have been performed in preparation for the first field application of the sampler. A code to the evaluation tests is provided as Table 2. Samplers were numbered one through five. Sampling locations were either on the roof of the Environmental Research Center Annex Building or in the Northrop Services analytical laboratory. Results from these tests for a set of target compounds are given in Tables 3 and 4. Additional compounds are listed in Table 5. The results of comparison of samplers are given in nominal parts-per-billion (ppbv). These concentration values are only approximate. The average value of percentage differences for tests 1-4 involving paired samplers #1 and #2 and test 5 involving paired samplers #3 and #4, is ± 5.1% as calculated by taking the difference between two nominally identical analysis results, dividing by their sum and multiplying by 100%; excluding the o-xylene result of test #1, this difference is ±3.5%. As noted in Table 2, evaluation test #6 was not a legitimate side-by-side test and is not included in the averages. This may explain the large percentage difference for the estimation of o-xylene in test #6. With respect to side-by-side ambient air tests involving the target compounds, the tests show agreement within 0.3 ppbv for concentrations of 5 ppbv or less and agreement of ± 15% for higher concentrations, except for o-xylene. Aside from the target compounds, some specific contamination was noted in samplers #3, #4, and #5. Sampler #4 gave consistently high Freon 113 concentration levels of 3-4 ppbv above the concentrations from samplers #3 and #5; #3 sampler gave a Freon 11 concentration of approximately 1 ppbv above the others; and #5 gave consistently high relative values for an unidentified hydrocarbon. In summary, the initial comparison tests indicated general agreement among samplers for the target compounds but there was also evidence that better quality control procedures should be implemented during assembly of sampler components.

Sampler components like those listed in Table 1 can be used to fabricate canister-based systems with sampling periods from approximately 1 min up to 24 hours. For shorter time intervals less stringent performance requirements are placed on the sampler components, and smaller pumps and/or less expensive flow restrictors (e.g., hypodermic needles) can be used. For sufficiently short collection periods of less than approximately 2 hours, the evacuated 6-L canisters can be used without a pump to obtain a rough time-weighted average sample. Flow profiles for a 500 sccm Tylan mass flow controller and for a hypodermic needle (30 gauge) restrictor are shown in Figure 2. The advantage of the hypodermic needle is that no electrical power is required; this would be advantageous for taking samples on buses, cars, airplanes, etc. On the other hand, the controller provides a more constant flow rate over the sampling period.

The sampler configuration shown in this section is similar to that in use by other groups. Of particular interest is the work done by Rasmussen[14] on sampler design. One difference from the design shown in Figure 1 is the order of components. A pump is used to pressurize a backpressure regulator which vents a large portion of a high throughput while maintaining a constant pressure upstream of a flow rate restrictor that leads into the canister.

Samplers for Obtaining Time-Weighted (Periodic, Integrative) Average Concentrations - New versions of the canister-based sampling system are required to meet EMSL's need for special studies. A pending indoor air survey study for VOCs will require a sampler to cover a full week, thereby simulating the major repetitive activity pattern to which occupants are exposed. A tentative sampling design is shown in Figure 3. This unit will operate in a periodic integrative mode, taking a limited duration sample during each increment of time, e.g., every hour. The representativeness of the sample will depend on the temporal variability of the various VOC sources. For this reason such a sampler may not be the one actually selected for the study. As indicated in Figure 3a, the sampler design includes a filter element, on-off valve, electric timer, flow restrictor and 6-Liter canister. Two restrictors have been used to test the design over simulated week-long sampling periods. In the first test a hypodermic needle restrictor was used. The inlet configuration was the same as in a recent NMOC sampler design.[13] The valve was opened for 15 s during each of 168 time increments (simulating 168 hourly samples per week). A gradual 18% decrease in peak flow rate was noted (See Figure 3b) and a total volume of approximately 3.5 liters was sampled. Similarly, a Whitey micrometering valve (SS-21R32) was set for 17.5 sccm and operated for 168 times with 1 min. sampling durations. A 23% decrease in flow rate was noted (See Figure 3c) while approximately 3.5 liters was sampled. In both cases, the final canister pressure is approximately 0.5 atmospheres. To the extent that the restrictor acts as a critical orifice, the sample flow rate should be constant until the pressure drop across the orifice approaches 0.5 atomospheres. One set of components for this system are identified by underlining in Table 1 (See footnote). The anticipated approximate cost of such a unit is less than $1000.

Samplers for Temporal Variability Studies - A commercially available sampler using a set of twelve SUMMA® polished stainless steel syringes (150 ml) has been modified for ease of analysis. The unit, manufactured by Demaray Scientific, is made as a sequential sampler. Along with controls for setting sample period and duration, it can now be returned to the analysis laboratory with the syringe units in place and be used to exhaust the individual syringes, one at a time, into a sample line leading into the analytical instrument. Signals provided by the GC, such as the external valve control outputs available on a HP5880, trigger the motor drive in reverse. The action of the drive allows the syringe exhaust port to open and gradually releases the contents of the syringe into a manifold through which zero air is passing. The contents are then passed through a reduced temperature trap to be concentrated prior to analysis.[15] Preliminary tests of the storage stability of a set of target compounds show that a number of the higher molecular weight compounds are either not efficiently stored or are not efficiently transferred from the syringes through the manifold to the analytical system. This ambiguity is still under study. Results of the evaluation tests are shown in Table 6. Two tests were performed by filling six syringes with a known mixture of eighteen VOCs in humidified zero air. Individual component concentrations were in the 2-4 ppbv range. The value of concentration averaged over the six syringes was compared to a direct analysis of the sample mixture. The results show the percentage difference calculated as a difference divided by a sum, multiplied by 100%. In general, the heavier compounds do not store as well as in the 6-liter SUMMA® polished canisters but, as noted earlier, the cause may not be the storage characteristics of the syringes. The remaining test of ambient air data shows the percentage difference between six paired samples of a direct analysis and of syringe samples taken simultaneously and analyzed 24 hours later. Concentrations are quite low in most cases

(< 5 ppbv), and show lower concentrations in the syringe sample in all but 9 of the 86 individual comparisons (not shown) that lead to the percentage differences in the ambient air test. Analysis of data show that better comparisons occur for the higher concentrations indicating that system precision is important. The result of one indoor air temporal variability study sequence is shown in Figure 4. The concentration variations are indicative of early morning changes in air ventilation rates as air handling equipment is turned on. Dichloromethane and chloroform are decreasing in concentration while Freon 11 and Freon 113 are increasing in concentration.

CONCLUSION

Initial results for canister-based samplers are encouraging in that side-by-side tests of weatherized samplers generally show small percentage differences at low ppbv concentration levels. The samplers can be configured to provide samples collected over collection periods of from one minute to one day by sampling continuously, with extension to one week if periodic sampling is used. For short duration sampling the vacuum of the canister can be used to establish a sampling rate so that no electricity is required. Sequential samplers using stainless steel syringes with SUMMA® polished surfaces show an apparent loss on storage of certain compounds, an observation which is being investigated further.

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Table 1. List of Canister-Based Sampler Components

Component	Identification	Supplier
1. Sample canister	6 Liter stainless steel sampling canisters, SUMMA® passivated Model 0647	Demaray Scientific Instruments, Inc. S.E. 1122 Latah St. Pullman, WA 99163 (509) 332-8577
2. Vacuum/pressure	Model 63-3704	Matheson PO Box 136 Morrow, GA 30260 (404) 961-7891
3. Chromatographic grade stainless steel tubing	Cat. #8125	Alltech Associates Deerfield, IL
4. Metal bellows pump	Model MB-151	Metal Bellows Corporation 1075 Providence Highway Sharon, MA 02067
4a* Stainless steel diaphragm pump	Model FC-1121-35	Biospherics Research Corp. 1121 N.W. Donelson Road Hillsboro, OR
5. Magnalatch solenoid valve	V52RAM 1100	Skinner Valve New Britain, CT
6. Control Timer	Model 7008-00	Paragon Electric Company, Inc. 606 Parkway Blvd. PO Box 28 Two Rivers, WI 54201
6a* Chrontrol timer	Model CD-4 FZ	Lindburg Enterprises, Inc. San Diego, CA
7. Electronic Flow Controller	Model FC-260, 0-100 sccm range with read-out box, Model RO-14	Tylan Corporation 19220 S. Normandie Avenue Torrance, CA 90502 (213) 532-3420

Table 1. List of Canister-Based Sampler Components
(continued)

Component	Identification	Supplier
7a* Whitey micrometer valve	Model SS-21R32	Whitey Co. Highland Hts., OH
8. Inlet Line Heater Control	Model 6102-J-0/300°F "Socket Mount" Controller	Omega Engineering Inc. Omega Drive, Box 4047 Stamford, CT 06906-0047 (203) 359-1660
9. Enclosure Heater	Watlow, Part 04010080	Watlow Co., PO Box 250 Pfafftown, NC (919) 922-3993)
10. Enclosure Fan	EG&G Rotron Model SUZA1	EG&G Rotron Woodstock, NY
11. Enclosure Heater Thermostat	Model 3455-RC-0100-0222 Open on Rise Sensor Switch	Elmwood Sensors, Inc. 500 Narragansett Park Dr. Pawtucket, RI 02861 (407) 727-1300
12. Enclosure Fan Thermostat	Model 3455-RC-0100-0244 Close on Rise Sensor Switch	Elmwood Sensors, Inc. 500 Narragansett Park Dr. Pawtucket, RI 02861 (407) 727-1300
13. Inline Filter	SS-2FT7-7 Nupro "F" Series	Nupro Company 4800 E. 345th St. Willoughby, OH 44094
14. 2 Micron Filter Elements for Inline Filter	SS-2F-K4-2	Nupro Company 4800 E. 345th St. Willoughby, OH 44094
15. Elapsed Time Meter	Type 6364 P/N 10082	Conrac, Cramer Division Old Saybrook, CN
16. Max-Min Thermometer	P/N 9327H30 Thomas Scientific	Brooklyn Thermometer Co., Inc.

* Alternate Components
__ Components for Periodic, Integrative Sampler

Table 2. Code to Evaluation Tests on Canister-Based Samplers

1. Side by side comparison of Samplers #1 and #2 on the roof of the ERC Annex building. Sampling period of 24 hours.

2. Same as 1.

3. Same as 1.

4. Sample audit material simulation test -- EPA Group III cpds. Samplers #1 and #2.

5. Side by side comparison of Samplers #3 and #4 in Northrop Services Laboratory. Sampling period of 24 hours.

6. Same as 1, however, Sampler #1 was sampling with a loose connector inside box, resulting in a sample of box air.

7. Side by side sampling of humidified zero air through the sampler system for Samplers #1 and #2. No canisters involved. Real time sample taken at the canister position using the analytical system.

8. Three sequential tests for contamination of Sampler #5 by sampling humidified zero air after passage through the sampler. Real time test as in Code 7 test.

9. Same as 7 again for Samplers #1 and #2.

10. Side by side comparison of Samplers #3, #4, and #5 on the roof of the ERC Annex building. Sampling period of 24 hours.

11. Repeat of Test 10.

12. Repeat of Test 10.

13. Repeat of Test 10.

Table 3 - Results of GC-MS Analysis During Evaluation Tests -- Values Given in PPBV Based on Working Standards. See Table 2 for Type of Test.

COMPOUND	TEST # 1	2	3	4	5	6	7	8	9
Vinyl Chloride						-,0.7	-,0.2		
1,1 Dichloroethene				9.0,9.0			-,0.2	0.2,0.3	
Methylene Chloride	2.9,2.6	0.7,0.8	3.9,3.9		65.5,67.5	1.6,1.5			
Chloroform			0.1,0.1						
1,2 Dichloroethane									
1,2 Dibromoethane									
1,1,1 Trichloroethane	0.6,0.5	0.3,0.3	1.0,1.0		0.8,0.7				
Benzene	1.6,1.4	0.5,0.4	1.5,1.5			0.7,0.6			
Tetrachloromethane	0.1,0.1	0.1,0.1	0.1,0.1		0.1,0.1	0.1,0.1			
Trichloroethene					0.2,0.1				
Toluene	8.0,7.6	0.8,0.9	2.6,2.3	7.8,9.8	1.9,1.9	1.2,1.0	0.1,0.2	0.1,0.2,0.2	
Tetrachloroethene	0.5,0.5	-- --	0.1,0.1		0.1,0.1	0.1,0.1			0.1,0.1
Chlorobenzene				8.5,11.0					
o-Xylene	2.0,4.2	0.1,0.1	0.6,0.5		0.3,0.3	1.1,0.2			

* Test #6 was not performed properly (see Table 2)

Table 4. Results of GC-MS Analysis During Evaluation Tests. Values Given in PPBV Based on Working Standards. Ambient Air Side-By-Side Sampling of Samplers 3,4,5. See Table 2 for Type of Test.

COMPOUND	TEST # 10	11	12	13
Vinyl Chloride	1.1,0.9,0.9		0.7,0.5,0.4	
1,1 Dichloro-ethene				
Methylene Chloride				2.4,2.5,2.8
Chloroform	0.03,0.03,0.02	0.1,0.0,0.0	0.1,0.1,0.1	
1,2 Dichloro-ethane				
1,2 Dibromo-ethane				
1,1,1 Trichloro-ethane				0.5,0.4,0.4
Benzene	0.7,0.7,0.7	0.4,0.5,0.5	0.5,0.6,0.5	0.7,0.7,0.7
Tetrachloro-methane	0.1,0.1,0.1	0.1,0.2,0.1	0.1,0.1,0.1	0.1,0.1,0.1
Trichloro-ethene				
Toluene	1.0,1.1,1.1	0.4,0.4,0.4	0.7,0.8,0.7	1.3,1.4,1.5
Tetrachloro-ethene	0.1,0.1,0.1	0.0,0.0,0.1	0.1,0.0,0.1	0.2,0.2,0.2
o-Xylene	0.2,0.2,0.2	0.1,0.1,0.1	0.2,0.1,0.2	0.2,0.3,0.3

Table 5. Results of GC-MS Analysis for Additional Compounds During Evaluation Tests. Values Given in PPBV Based on Working Standards. See Table 2 for Type of Test

COMPOUND	TEST # 1	2	3	5	10	12	13
Ethylbenzene	1.1,1.1		0.4,0.4	0.2,0.2			
Styrene	--		0.1,0.2				
m,p Xylene	3.6,3.5	0.3,0.4	1.3,1.3	0.7,0.7	0.4,0.4 0.4	0.3,0.3 0.3	0.5,0.5 0.6
4-Ethyltoluene	--	--	0.2,0.2	0.2,0.2			
1,3,5-Methylbenzene	0.6,0.9		0.3,0.2				
1,2,4-Methylbenzene	2.7,2.6	0.2,0.2	0.9,0.9	0.4,0.4	0.3,0.3 0.3	0.2,0.2 0.2	
Hexachlorobutadiene		0.2,0.2					0.1,0.1 0.1

Table 6. Evaluation Results Comparing Analysis from Sequential Syringe and Direct Analysis

COMPOUND	Mixture with Zero Air #1*	Mixture with Zero Air #2*	Ambient Air
1,2 Dichloroethene	-1.1%	10.2%	--
Freon 113	-2.2%	1.8%	--
Chloroform	1.5	0.2%	--
1,2 Dichloroethane	-10.0	12.2	--
1,1,1 Trichloroethane	1.7	0.6	-19.9
Benzene	-1.1	-5.7	-9.4
Tetrachloromethane	-7.2	-0.9	-7.8
Trichloroethene	1.6	-1.2	-18.7
cis-Dichloropropene	-3.2	--	--
trans-Dichloropropene	-8.7	--	--
Toluene	7.2	6.6	-17.7
1,2 Dibromoethane	-7.0	-9.9	--
Tetrachloroethene	-0.9	-5.7	-12.9
Chlorobenzene	-10.9	-20.1	--
o-Xylene	-9.1	-9.2	-18.7
Benzylchloride	-24.3	-26.6	--
Hexachlorobutadiene	-5.6	-12.6	--
F-12	15.4	2.2	-6.7
Methylene Chloride	--	--	-4.1

* (-) Control > Average Syringe

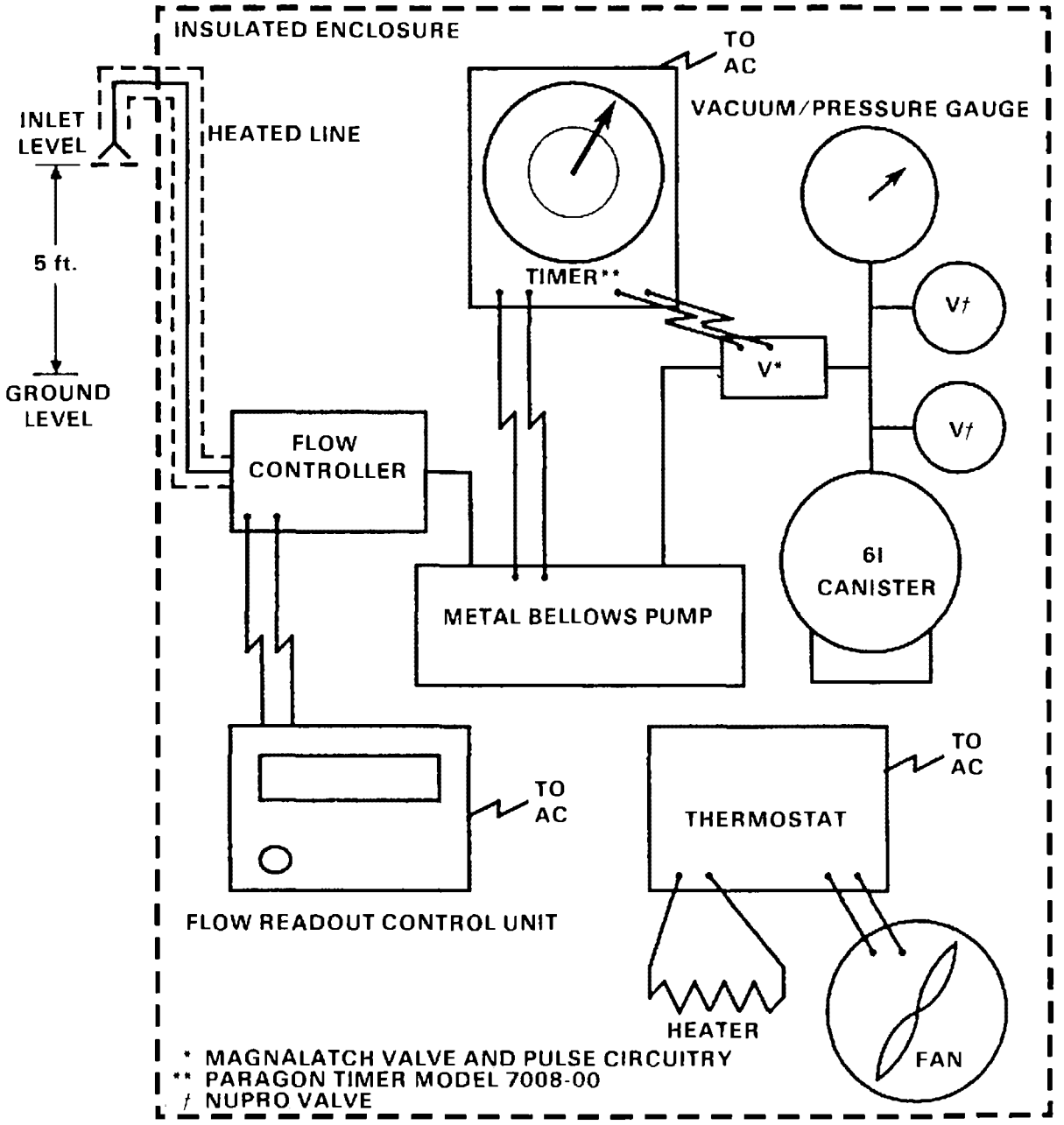


Figure 1. Schematic of Canister Sampler

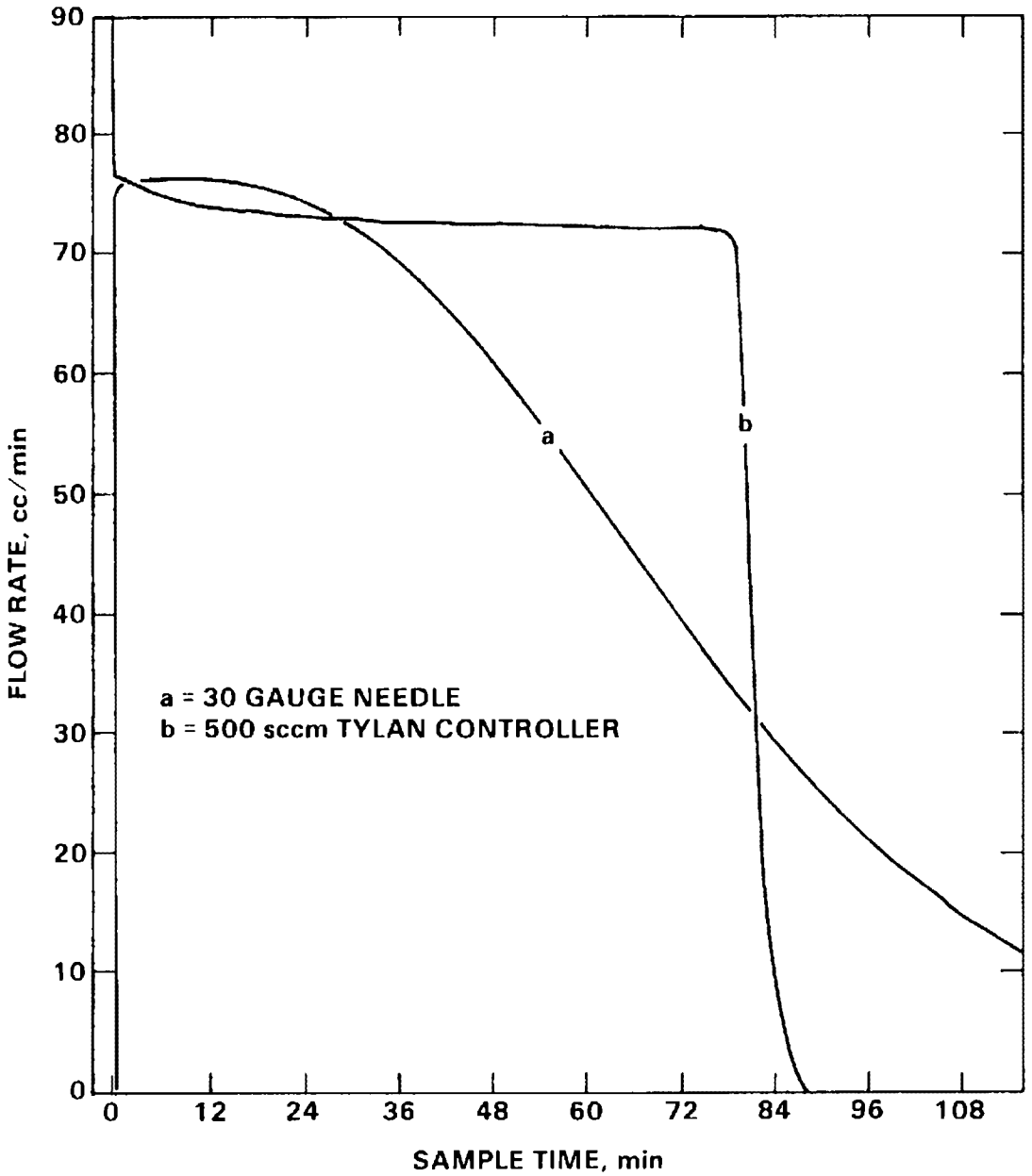
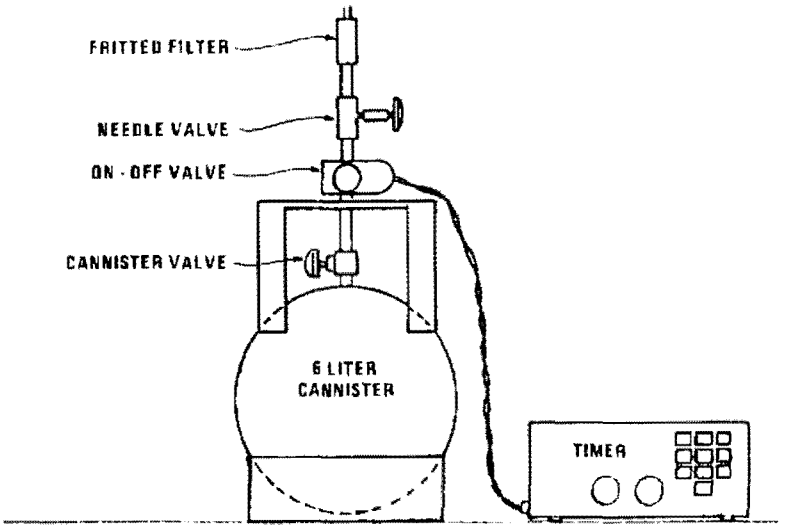
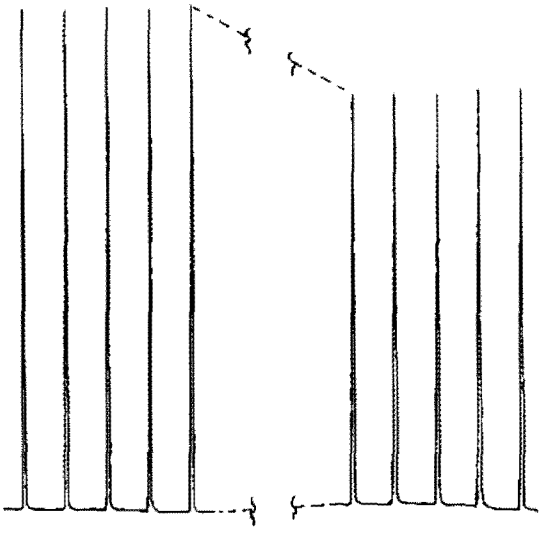


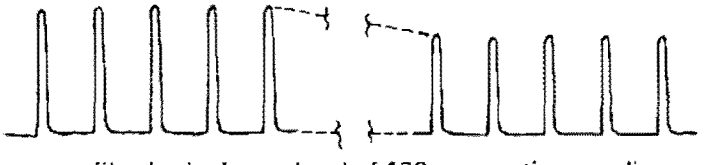
Figure 2. Flow rate profiles versus sampling duration for evacuated cannister with restrictors only.



(a) Sampler schematic.



(b) Flow rate profile - beginning and end of 168 consecutive sampling events, each 15 seconds duration.



(c) Flow rate profile - beginning and end of 168 consecutive sampling events, each one minute duration.

Figure 3. Periodic, integrative-type sampler approach.

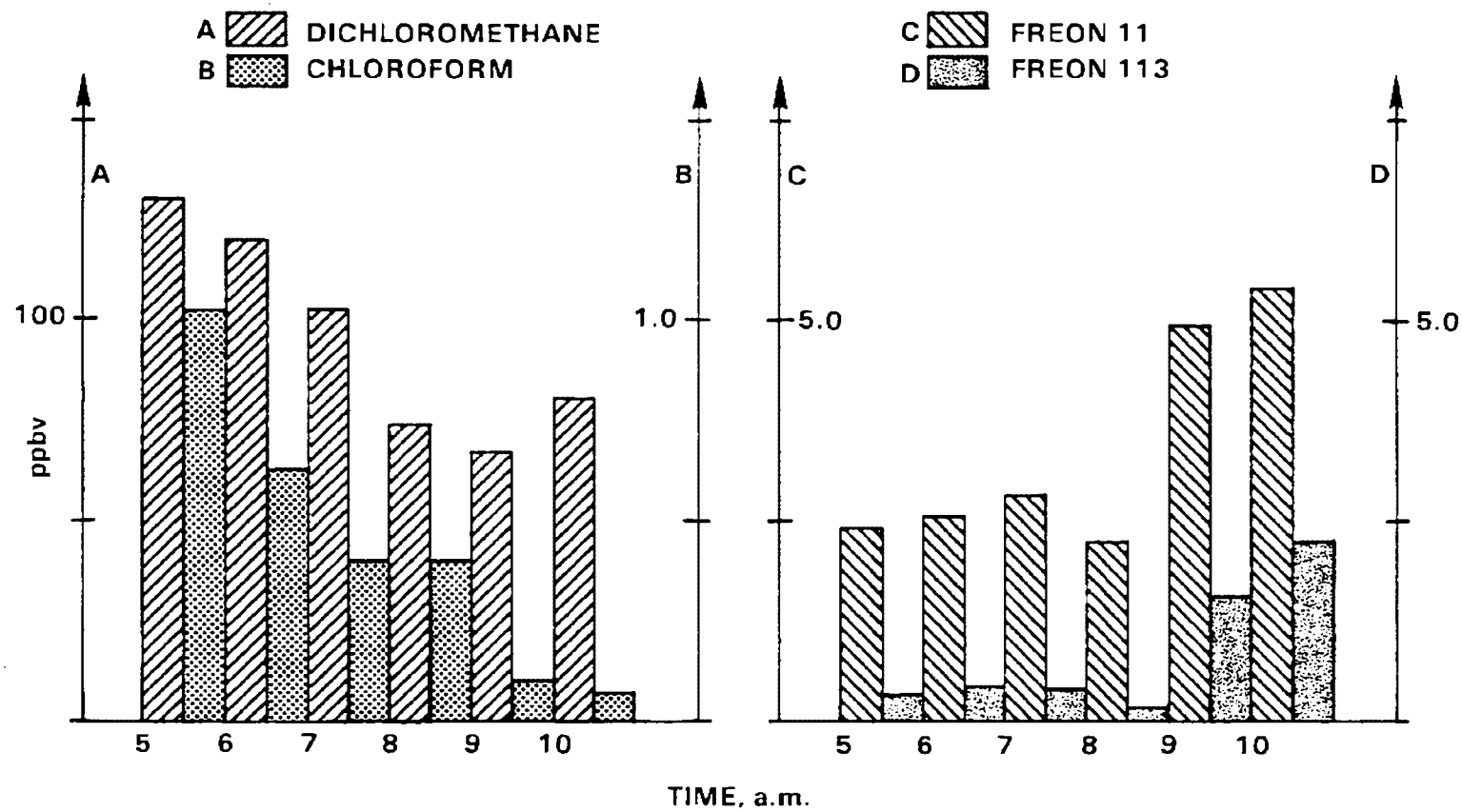


Figure 4. Variations in VOCs in lab air using sequential sampler.

COMPARISON OF 0600-0900 AM HYDROCARBON COMPOSITIONS OBTAINED FROM 29 CITIES

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Abstract

Mean nonmethane organic carbon (NMOC) compound concentrations are presented for 0600-0900 samples collected at 29 urban areas during the summer period of 1984 and 1985. Considerable differences are observed in those areas that have different volatile organic compound emissions. Ranges of benzene and toluene concentrations are presented for the 29 urban areas. It appears that variation in the observed concentration range is more evident for toluene than benzene. This observation suggests that there may be more discrete sources for toluene than benzene.

Introduction

A sampling program for nonmethane organic carbon (NMOC) compounds and the nitrogen oxides (NO_x) during the 0600 to 0900 period was conducted at several urban areas throughout the United States during 1984 and 1985. The purpose of the study was to obtain NMOC and NO_x information needed to prepare State Implementation Plans for ozone control strategies. Actually the cities participating in the study were identified in the Federal Register (1) as non-attainment areas for the National Ambient Air Quality Standard (NAAQS) for ozone. The 0600 to 0900 sampling period was selected to correspond with the guidance for the use of the Empirical Kinetic Modeling Approach (EKMA) for photochemical ozone control (2). According to the EKMA guidance, only 0600-0900 AM measurements of NMOC and NO_x are required at one representative central urban site location in the area to be modeled. There is also guidance for urban site location in terms of representing the general NMOC and NO_x emission patterns for the modeled area (3). Ideally, because of EKMA site selection requirements, the NMOC composition measured in the 29 urban sites reported here should represent all stationary and mobile sources in these areas.

NMOC determinations at the 29 urban sites were obtained from 3 hour integrated canister samples collected during the 0600-0900 AM period. The air sample canisters were shipped to a central laboratory facility located at Research Triangle Park, NC for total NMOC analysis using a cryogenic preconcentration FID approach (4). The measurement approach removed air and methane from the air sample permitting direct determination of NMOC. This approach was selected based upon the unreliable and inaccurate performance of continuous NMOC analyzers (5,6,7) typically used for these measurements.

Approximately 10 to 20% of the air samples were analyzed by detailed gas chromatographic procedures. Although the intent of the GC analyses was for quality assurance (QA) of the preconcentration total NMOC-FID approach, the detailed NMOC results are extremely useful for the evaluation and comparison of the NMOC compositions in these 29 urban areas located at diverse geographic areas of the United States. Some of the cities sampled have major industrial activities located within the urban area. Other cities have predominately vehicular NMOC emissions. Consequently large variation in NMOC compositions are expected among the 29 cities studied. Sampling during the 0600 to 0900 AM period provides only a limited period to compare NMOC composition. However, this time frame represents a period of active NMOC emissions and poor meteorological ventilation conditions. As a result, highest levels of NMOC concentration for these urban areas most likely occur during the 0600 to 0900 period.

The purpose of this paper is to compare NMOC compositions among the 29 cities to determine similarities and differences. Ranges for benzene and toluene are presented for the 29 sites since these compounds are under investigation as suspected toxic compounds.

Experimental

The sample collection device and analysis system used for the 1984 and 1985 studies have been published elsewhere (4). The publication contains detailed information concerning the sample canisters, the sample

collection device, the modified GC-FID system and the preconcentration procedure. Actually the preconcentration direct FID (PDFID) system described in this publication is similar to the ambient air GC-FID procedure without the GC column. The approximate 500 cc volume of ambient air trapped in the preconcentration system improves the sensitivity of FID system to measure ambient air NMOC concentration below 100 ppbC.

Details of the GC system (8) and the preconcentration procedure (9) have been published elsewhere. GC column conditions including flowrate and temperature programming conditions were identical for both the 1984 and 1985 studies. These conditions were unchanged between studies in order to directly compare 1984 and 1985 sample results. The column used was a 60 m x 0.32 mm i.d. DB-1 fused silica column (J & W Scientific, Cordova, CA). The helium carrier gas flowrate was maintained at 2-3 cm^3/min. The column temperature conditions consisted of an initial 1 min hold at -50°C followed by temperature programming at 8°C/min to a final temperature of 200°C with a final hold time of 5 min. Calibration of the individual compound peaks were performed with a National Bureau of Standards (NBS) 2.84 ppm propane in air Standards Reference Material (SRM) No. 1665b cylinder. A single response factor was used to determine all GC peak concentration. This approach has been determined to be valid for most hydrocarbon compounds (10). Canister samples were analyzed on the GC system generally within 2 to 4 days after collection.

At least one sample from each of the 29 urban areas was re-analyzed with chemical stripper columns (11, 12). A 4" x 1/2" stainless steel column packed with Ag_2SO_4 - H_2SO_4 on firebrick was used to remove all aromatic peaks except benzene which is approximately 60% removed. A 4" X 1/2" stainless steel column packed with $HgSO_4$ - H_2SO_4 on firebrick was used to remove all olefins peaks from the air sample.

Results and Discussion

The availability of detailed NMOC composition for 29 cities for the same calendar time period using the same GC analytical procedure is quite unique. In the past comparison of organic compositions in various cities consisted of using any available data collected over multi-year time periods determined by quite different GC analytical procedures. Such an approach can present serious problems when comparing complex chromatographic results such as those found in urban ambient air situations. This is particularly true for the comparison of the unidentified GC peaks observed in all chromatographic analyses of urban ambient air. The use of a single GC system, with air samples collected over a relatively short time span, presents a unique opportunity for the comparison of NMOC composition in these 29 cities. For the first time comparison among urban areas for unidentified compounds can be made with some reasonable degree of accuracy.

The 29 urban sites studies are listed in Table I. Those cities sampled in both 1984 and 1985 studies are identified with an asterisks to the left of the name. Eleven sites were sampled both years with 7 of these sites located in the State of Texas. The sites were assigned a different site number in the two studies. These site numbers are only important for following figures in which data results for the urban sites are unidentified by these numbers. As can be observed a large diversity of urban areas were sampled. These included cities with large industrial

sources, such as those in southeast Texas, to urban areas in which vehicular sources predominatee, such as Washington, DC and Boston, MA.

Two criteria were used to select samples for GC speciation analysis. First, the selected samples for all sites were equally distributed over the entire sampling period. An attempt was made to select an equivalent number of Monday, Tuesday, Wednesday, Thursday, and Friday samples to avoid possible day-of-week bias. Second, samples collected at sites that experienced afternoon ozone which exceeded 0.12 ppm were selected. It was anticipated that the GC analyses for high ozone days would be particularly useful to the States for their modeling studies. The latter criteria may result in a biased high average NMOC concentration for the GC samples at these sites since usually high precursor concentrations are observed on days of high afternoon photochemical ozone levels. However, NMOC emission patterns are expected to be somewhat consistent on a day to day basis. Consequently NMOC composition should not be significantly different on these high ozone days.

Figures 1 and 2 show a comparison of mean NMOC concentration by site for all samples analyzed with the PDFID procedure with those selected for detailed GC analysis. The general comparability between the two measurement procedures is quite reasonable for both the 1984 (Figure 1) and 1985 (Figure 2) studies. Perhaps the three sites demonstrating the most significant disagreement are site 1 (Akron, OH), Site 7 (Clute, TX) and site 14 (Miami, FL) all investigated during the 1984 study (Figure 1). The mean NMOC concentrations obtained by the GC procedure for sites 1 and 14 (Figure 1) are approximately 50% lower than the means measured by the PDFID procedure for all samples. The GC mean for site 7 (Clute, TX) is approximately 40% higher than that measured for all collected samples with the PDFID procedure. There appears to be little explanation for these significant variations. Samples were pre-selected by the same criteria as the other 19 sites. Also no samples were selected at these sites due to high ozone observations. Only three samples were analyzed by GC procedures at site 14 (Miami, FL) during the study period. Obviously the GC mean at that site is not representative of the NMOC mean concentration.

The comparison of GC with PDFID means for all sites sampled during the 1985 program (Figure 2) are much improved over the 1984 study. This is primarily due to the greater number of GC analyses performed at each site during 1985 program. The two sites that show significant disagreement are the Philadelphia sites 13 and 14. The GC means are approximately 25% higher than the PDFID means. For these two sites during the 1985 study pre-selection sample bias may be a legitimate explanation. Several samples were analyzed as the result of high afternoon ozone levels observed in the Philadelphia area.

Year to year comparisons of NMOC mean concentrations can be made for 11 sites common to both the 1984 and 1985 studies by reviewing the data in Figures 1 and 2. The only city showing a significant change was Beaumont, Texas. In 1985 the mean NMOC concentrate of 1.9 ppmC is nearly double the 1.0 ppm mean measured in 1984. None of the other 10 common sites

showed such significant changes. It is doubtful that meteorological changes over the one year period can explain such a significant increase. It is more likely that the NMOC emission levels were increased at the Beaumont site during 1985.

The number of GC peaks observed at the sites during both years ranged from about 100 on low NMOC concentration days to more than 240 peaks on the higher NMOC concentration days. Currently 65 of the GC peaks have been identified and verified by retention time location of pure hydrocarbon compounds. More than 175 peaks remain unidentified. In an effort to determine the nature of these peaks, collected samples were re-analyzed using stripper columns selective for the removal of olefin and aromatic compounds. Using this approach an assignment of the unidentified peaks as paraffinic, olefinic, and aromatic could be made. At least one pair of stripper column analyses were performed for each urban site studied during the 1984 and 1985 programs. No surprises were experienced with comparison of stripper column results from site to site. Each unidentified GC peak for all the urban site seemed to be the same type of hydrocarbon compound. Using the hydrocarbon classification assignments determined from the stripper column, total paraffin, olefin, and aromatic percent compositions were determined for each site. These percents of hydrocarbon compositions are shown in Figures 3 and 4.

In both Figures 3 and 4, it is apparent that paraffins are the most abundant species of hydrocarbon at all sites ranging from 50 to 60% of the total NMOC. Aromatic hydrocarbons are typically the next most abundant hydrocarbon type ranging from 20 to 30% of total NMOC. Olefins are the least abundant class of hydrocarbon observed ranging from 15 to 20% of total NMOC. This general composition breakdown, however, is not observed at the industrial-urban sites located on the southeast coast of Texas. At site 7 (Clute, TX) during the 1984 study (Figure 3) the percent olefin level was higher than percent aromatic. Similar observations were made for Clute (Site 5) during the 1985 study (Figure 4). Site 1 (Beaumont, TX) showed a more abundant level of olefin than aromatic composition during the 1985 study (Figure 4). In both the 1984 study (Figure 3) and the 1985 study (Figure 4) equally abundant levels of olefins and aromatics were observed at the Orange, TX and Texas City, TX sites. It is obvious that the petrochemical industries in these areas have a significant impact on the NMOC composition. The hydrocarbon composition in the urban areas investigated in both studies appear to be quite similar. This is not surprising since vehicular sources are expected to comprise the largest percentage of NMOC emissions in these areas.

The availability of detailed hydrocarbon compositional information for these 29 urban areas provides a wealth of information to compare NMOC emission sources affecting these areas. Mobile and industrial sources typically have fingerprints or hydrocarbon patterns that discriminate the NMOC composition. Also the availability of individual species information enables one to compare concentration levels in these different areas. This is particularly important when these individual NMOC compounds are suspected as toxic pollutants such as benzene and toluene.

In Figures 5 and 6 are plotted mean, median, high and low concentrations for benzene and toluene observed during the 1984 study. In Figure 5 the range between high and low concentrations are not very large and are

perhaps the result of meteorological differences between these two sample days. Consequently the sources of benzene are suggested to be relatively consistent during the 0600-0900 AM period. The ranges between high and low at site 3 (Birmingham, AL), site 6 (Chattanooga, TN), and site 12 (Indianapolis, IN) are quite different and suggest that large discrete benzene sources affect these sites. These periodic high values significantly affect the mean concentration. This is observed by the comparison of the mean with the median concentration. In Figure 6 large ranges between high and low concentration are observed at more sites for toluene. This would suggest that there are discrete sources of toluene periodically affecting more of the urban areas. This is not unexpected since toluene is a very common organic compound used as a solvent and in many manufacturing processes.

Similar benzene and toluene observations can be made for the 1985 study (Figures 7 and 8). Again the range between high and low concentration at several sites is perhaps a result of meteorological variations. Periodic discrete sources of benzene are most evident at site 1 (Beaumont, TX), Site 17 (St. Louis, MO), and Site 18 (Texas City, TX). Again, more discrete periodic sources of toluene are evident in the range of high and low concentrations (Figure 8).

Conclusion and Summary

The availability of detailed hydrocarbon compositional information for 29 urban areas sampled during the 0600-0900 AM period for two summer periods and analyzed on one detailed GC system is unique. This data base allows one to compare NMOC composition for a variety of urban areas that have significantly different NMOC emission source patterns. Using one GC system allows the comparison of unidentified compound peaks between cities. In 1986 an additional 7 cities will be added to the list of 29. These cities include Denver, CO, Salt Lake City, UT, New York City, Chicago, Hartford, CT, Bridgeport, CT, and Tulsa, OK. Consequently these comparisons will be even more extensive.

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Table I. Urban Sites Sampled for Detailed NMOC Measurements During the 1984 and 1985 Studies

Site ID	1984 Site Number	1985 Site Number
Akron, OH	1	--
Atlanta, GA	2	--
Birmingham, AL	3	--
* Beaumont, TX	4	1
Boston, MA	--	2
Baton Rouge, LA	--	3
Charlotte, NC	5	--
Chattanooga, TN	6	--
Cincinnati, OH	8	--
Cleveland, OH	--	4
* Clute, TX	7	5
* Dallas, TX	9	6
* El Paso, TX	10	7
* Fort Worth, TX	11	8
Houston, TX	--	9
Indianapolis, IN	12	--
* Kansas City, MO	13	10
Lake Charles, LA	--	11
Miami, FL	14	--
Memphis, TN	15	--
* Orange, TX	16	12
* Philadelphia, PA (1)	17	13
Philadelphia, PA (2)	--	14
Portland, ME	--	15
* Richmond, VA	18	16
St. Louis, MO	--	17
* Texas City, TX	19	18
Wilkes-Barre, PA	20	--
* Washington, DC	21	19
West Palm Beach, FL	22	--

*Sampled in both 1984 and 1985 studies

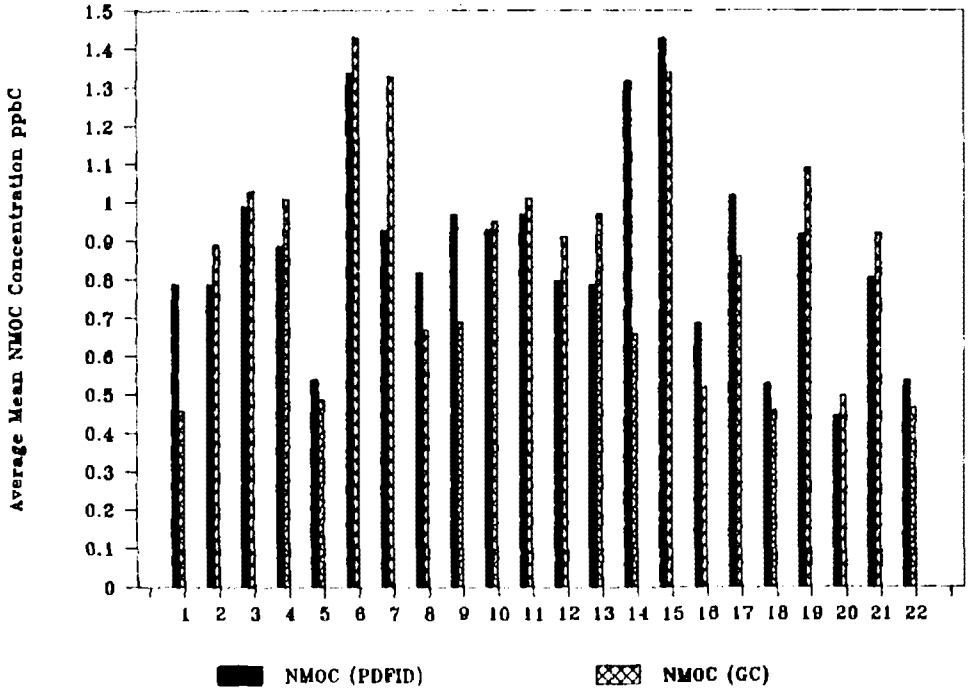

Figure 1. Comparison of average mean concentrations obtained with the PDFID and GC procedures for cities participating in the 1984 twenty-two cities NMOC study.

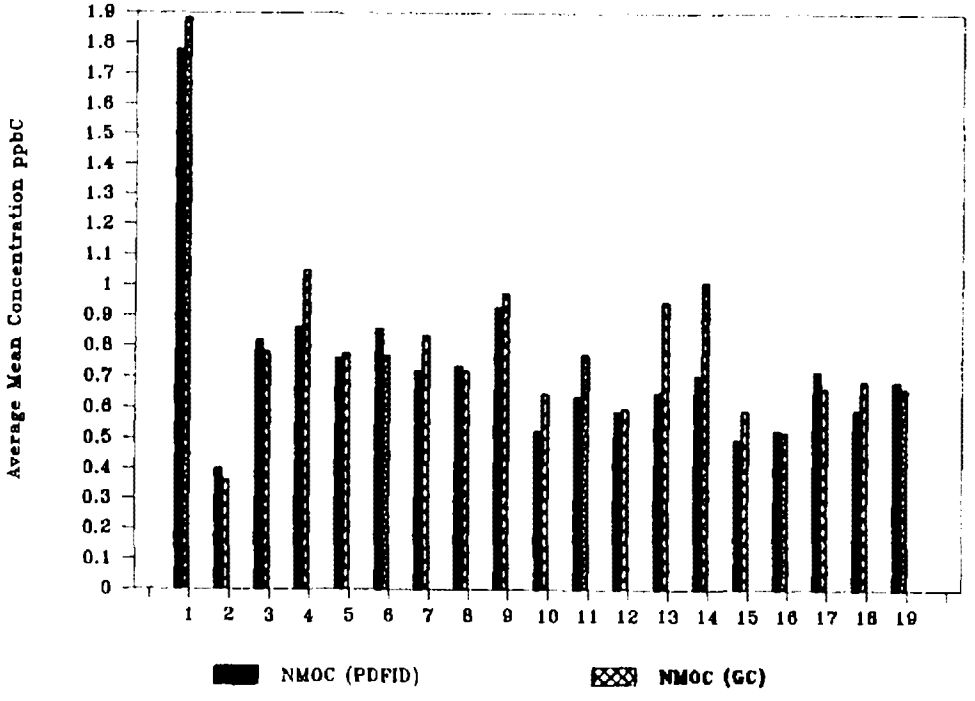

Figure 2. Comparison of average mean concentration obtained with the PDFID and GC procedures for cities participating in the 1985 nineteen cities NMOC study.

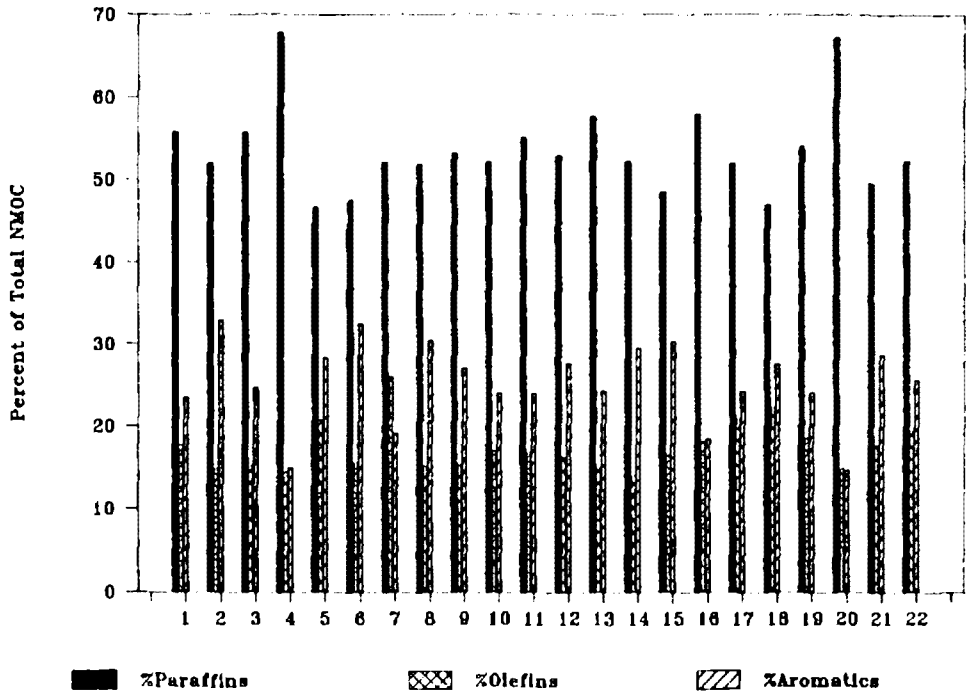

Figure 3. Percentage paraffins, olefins, and aromatics composition for the cities participating in the 1984 twenty-two cities NMOC study.

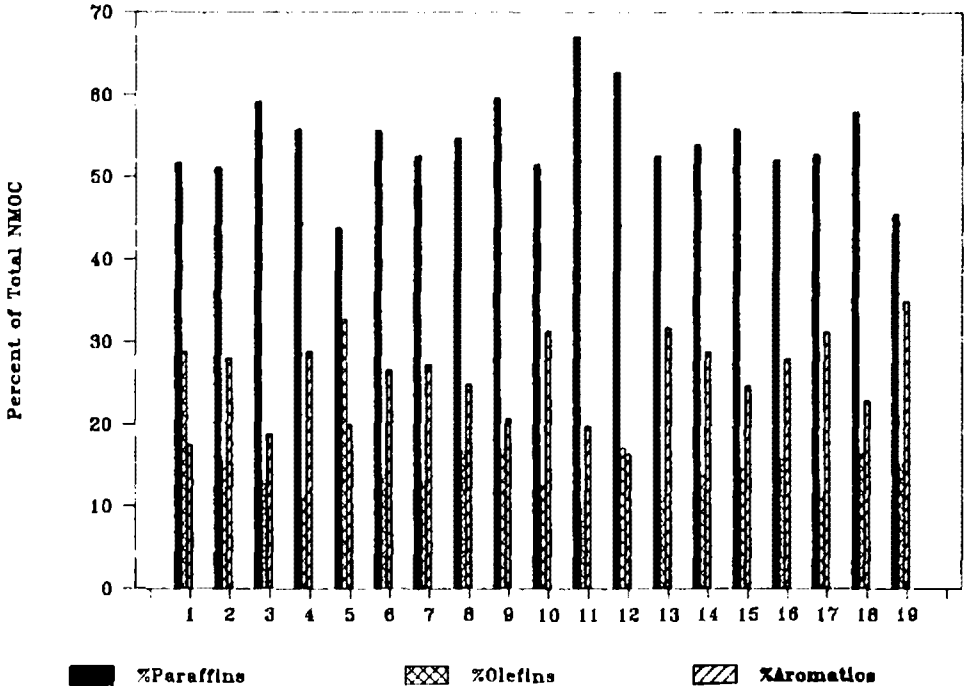

Figure 4. Percentage paraffins, olefins, and aromatics composition for the cities participating in the 1985 nineteen cities NMOC study.

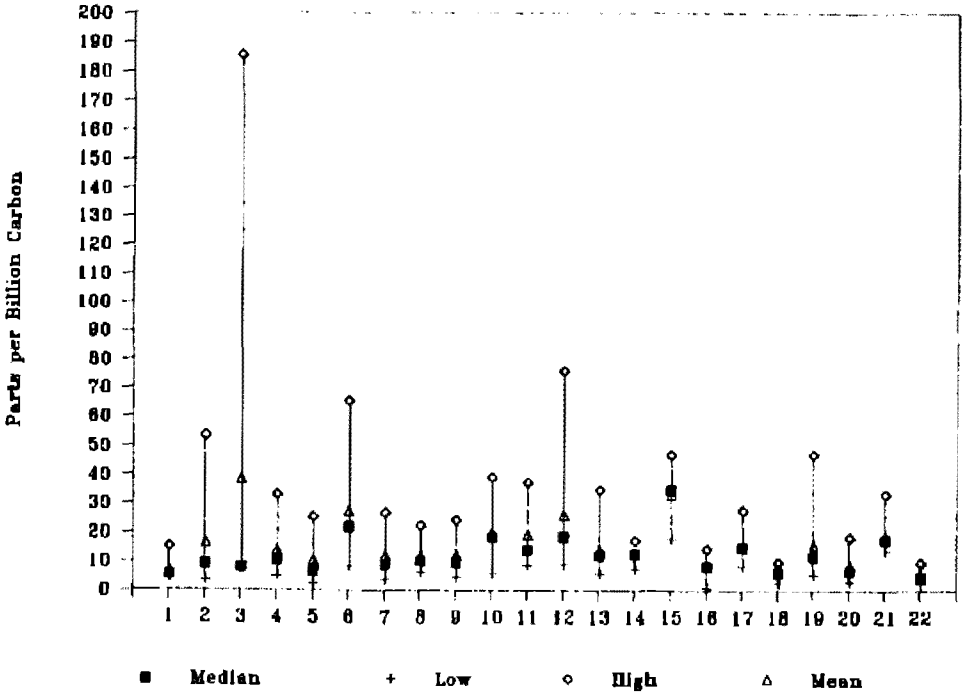

Figure 5. Mean, median, high and low concentrations of benzene observed at each city participating in the 1984 twenty-two cities NMOC study.

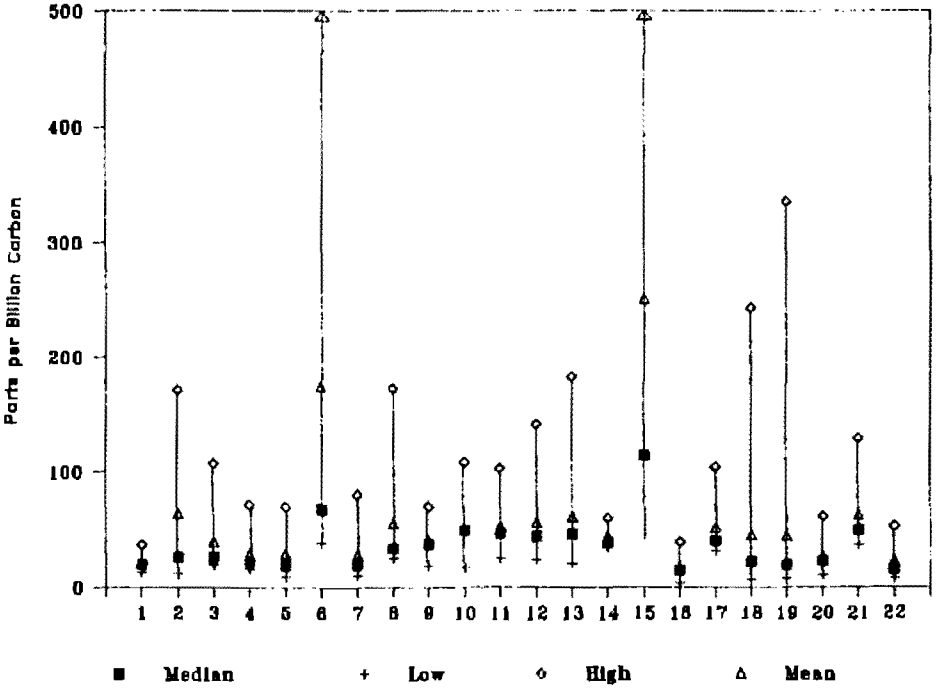

Figure 6. Mean, median, high and low concentrations of toluene observed at each city participating in the 1984 twenty-two cities NMOC study.

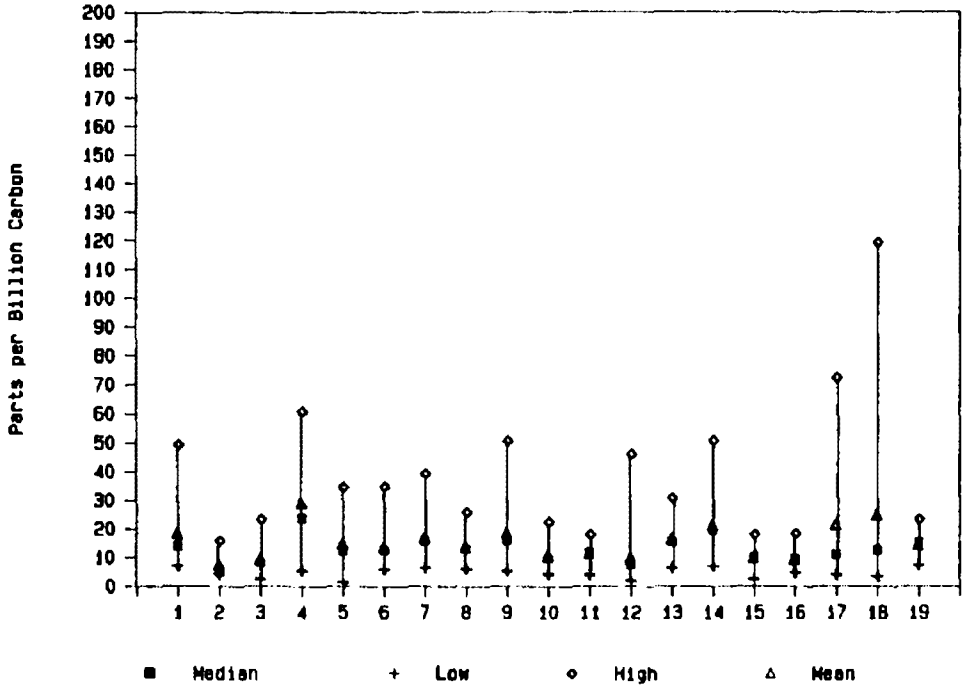

Figure 7. Mean, median, high and low concentrations of benzene observed at each city participating in the 1985 nineteen cities NMOC study.

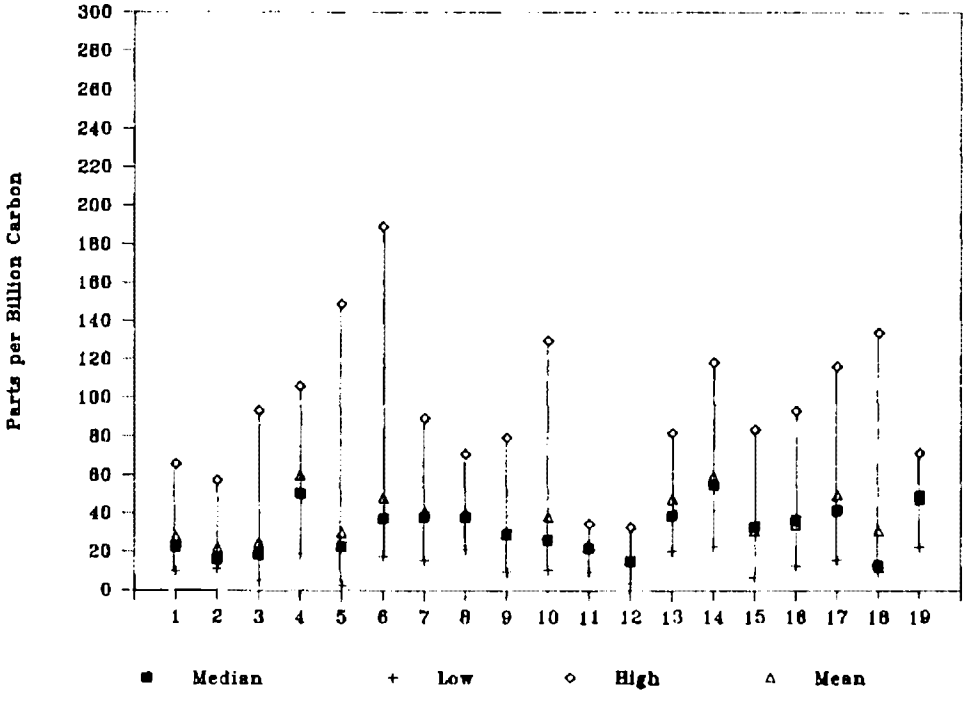

Figure 8. Mean, median, high and low concentrations of toluene observed at each city participating in the 1985 nineteen cities NMOC study.

AN AIR SAMPLING SYSTEM FOR MEASUREMENT OF AMBIENT ORGANIC COMPOUNDS

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A system for automatic collection, transport, and temporary storage of ambient air samples to be analyzed for concentrations of organic compounds has been devised and extensively tested. The air sample collection apparatus, which is designed for unattended sample collection at a remote site, includes a metal bellows pump, critical orifice flow control, a timer to start and stop sample collection, a noncontaminating solenoid valve, and a special sample storage container. The system is specifically designed to collect uniformly integrated air samples over a predetermined time period.

The integrated air samples obtained by the system are pressurized to approximately one atmosphere gauge pressure and stored in electropolished, six-liter stainless steel canisters for transport and subsequent analysis. Total nonmethane organic compound (NMOC) analyses and speciated organic compound data indicated that most atmospheric organic compounds are stable when stored in such treated canisters for periods of up to two weeks.

Following sample analysis, the canisters were readily cleaned for reuse by repeated evacuation and flushing with cleaned, dried air. The canisters are rugged and can be shipped repeatedly in special aluminum shipping cases. The efficacy of the canisters and the entire collection system was proven in field testing involving about 3,000 air samples collected at 31 sites in various parts of the United States during 1984 and 1985.

Introduction

In developing appropriate strategies to achieve compliance with applicable ambient air quality standards for ozone it is necessary to know ambient concentrations of precursor organic compounds and downwind concentrations of ozone.[1,2] Some photochemical dispersion models[1] require detailed organic species data obtained by multicomponent gas chromatographic analysis of air samples.[2,3] The simpler Empirical Kinetic Modeling Approach (EKMA)[1] requires total average NMOC concentration data, sampled from 6 A.M. to 9 A.M. daily.

The 1984 and 1985 NMOC Sampling and Analysis Program, described elsewhere,[5] was carried out to acquire and to validate data for modeling estimates of hydrocarbon control requirements to be used in State Implementation Plans (SIP's) for control of ozone in the participating localities. The program also afforded an excellent opportunity further to study the performance and merit of the Cryogenic Preconcentration, Direct Flame Ionization Detection (PDFID) method,[4] and further to compare the simpler PDFID method with the Gas Chromatographic, Direct Flame Ionization Detection (GCFID) method.[6] The results of the 1984 and 1985 NMOC Sampling and Analysis Program and the comparisons made of the sampling and analysis methods are presented in another paper.[5]

The purpose of this paper is to describe the sampling equipment and procedures used in the 1984 and 1985 NMOC Sampling and Analysis Program and to present the methods and results used to test and validate that equipment.

Sampling Equipment Considerations

Collecting of valid ambient air samples is a critical aspect of any air monitoring project, particularly when the samples will be stored and transported before analysis.

The air sampling equipment used in this study was designed specifically for the NMOC Program. However, the equipment and procedures described here are also likely to be suitable for sampling ambient air for determining concentrations of many specific organic compounds. Ambient air samples were taken at 31 sites in the Gulf Coast States, Midwestern, and Eastern United States and shipped by air freight to Research Triangle Park, NC for analysis. Samples were usually analyzed the next day, except that Friday samples were analyzed the following Monday. The time period between sampling and initial analysis was never longer than 72 hours.

Primary concerns regarding the sampling equipment were to verify that (1) the equipment did not contaminate the air sample collected, (2) the NMOC concentration of the collected air sample was stable during the storage period between collection and analysis, and (3) there was no significant carryover from previously collected samples, i.e., the canisters could be adequately cleaned and reused.

Field Sampling Apparatus

The sampling system for the collection of integrated field samples is shown in Figure 1. The sample intake port was an inverted glass funnel connected to 1/4-inch (6mm) outside diameter (o.d.) chromatographic grade stainless steel tubing. The optional auxiliary pump was used with long inlet lines (over 4m) to ventilate the inlet line and to ensure that the air at the stainless steel tee was representative of the ambient air at the intake. Sample lines leading from the tee to the sample canisters were 1/8-inch (3mm) (o.d.) chromatographic grade stainless steel tubing. A fritted stainless steel filter rated at 2μm pore size trapped particulate matter in the ambient air sample and protected the critical orifice.

Flow control over the three-hour sampling period, from 6 A.M. to 9 A.M., was effected primarily by the critical orifice downstream of the filter. The orifice was sized so that in the three-hour sampling period, the pressure in the sample canisters was raised from vacuum to about 15 psi (100 kPa) gauge pressure. When duplicate samples were taken, two canisters were connected to the sampling system simultaneously. For those samples, the critical orifice used for single canisters was replaced with a larger orifice having twice the flow rate so as to fill two canisters in three hours.

The main pump, a stainless steel bellows pump (Metal Bellows Corp., Model MB151) was capable of maintaining sufficient vacuum on its intake to sustain a critical pressure drop across the orifice, while pressurizing the canister.[4] Both critical orifices for single and duplicate samples and the pump were tested, prior to field installation, to verify that the flow rate through the pump was essentially constant over the three-hour sampling period. This flow control method also minimized internal heating of the pump, which could contaminate the sample air.

A solenoid latching valve was installed in the 1/8-inch (3mm) sample line downstream of the MB151 pump, and connected to the timer. The timer was set to turn on the two pumps and open the solenoid latching valve at 6 A.M., and to turn the pumps off and close the valve at 9 A.M. The stainless steel solenoid latching valve, with Viton® seats, provided a positive closure to the canister, so that when the valve was closed, no vacuum was lost before sampling and no sample air was lost after sampling. A special electrical circuit was installed in the timer to provide current pulses to the solenoid to open and close it. Unlike conventional solenoid valves the latching valve required no continuous current to keep it open during the sample period. This prevented heating of the valve during sampling, which could possibly cause outgassing from the valve or its seat, and contaminate the sample.

After the sample was collected, the site operator manually closed the valves on the sample canister(s) before disconnecting the canister(s) from

the sampling assembly. The site operator measured the canister pressure by connecting the canister to a pressure gauge, and opening the canister valve momentarily. The operator then reclosed the valve and disconnected the pressure gauge before preparing the canister for shipment to the Research Triangle Park (RTP) laboratory for NMOC analysis.

The sample containers were 6-liter spherical stainless steel canisters (Demarey Scientific Instruments, Ltd., Pullman, WA) with stainless steel bellows valves (Nupro Co., Willoughby, OH). A small stainless steel base was welded to the bottom of each canister, and a stainless steel valve guard was welded at the top to protect the valve from damage in shipment and handling. A Swagelok® fitting was welded into the sample port of the canister. The manufacturer electropolished the internal canister surfaces, using the Summa® process (U.S. Patent No. 764462), to passivate adsorption sites. Similarly processed canisters were used by Oliver,[7] et al., in their study on the storage stability of volatile organic compounds in ambient air. Canisters were shipped in aluminum shipping containers designed to hold two canisters.

Installation And Operation Of The Sampling Equipment

The field sampling apparatus was housed in an air conditioned facility. The sample intake point, the inverted glass funnel in Figure 1, was located outside the building about 7.6 meters above ground level. A checklist of steps was used to verify the correct operation of the sampling equipment and its proper assembly. The final step involved training the site operator, who would connect and disconnect the sample canisters daily, Monday through Friday. The daily routine of the site operator included checking the operation of the sampling equipment assembly, checking the timer settings, changing canisters, filling out field sampling forms, packing the canisters along with the field sampling forms for shipment, and calling Radian's Research Triangle Park Laboratory if unanticipated problems were encountered.

Canister Cleanup Apparatus

Canisters were cleaned in preparation for another sample by first evacuating the canisters to a pressure of 5mm Hg absolute (667 Pa), followed by pressurizing the canisters to 40 pounds per square inch gauge (psig) pressure (276 kPa), with cleaned, dried air. This cycle was repeated three times. Tests indicated that carryover of NMOC from one sample to the next averaged less than 0.10%.

Figure 2 shows the apparatus used to clean up to 12 sample canisters at a time. An oil-free compressor with a 45-liter reservoir provided a source of air for the system. The oil-free compressor assured a minimum of hydrocarbon contamination. The compressor reservoir was drained of condensed water each morning. A coalescing filter provided water mist and other particulate removal

down to a 5-micron particle size. Permeation dryers (Perma-Pure, Oceanport, NJ) removed water vapor such that moisture indicators downstream of the permeation dryers never showed any detectable moisture in the cleaned air.

The air was then passed through catalytic oxidizers (MSA Model B) to destroy any hydrocarbons. One-micron inline filters were attached to the outlets of the oxidizers. A single-stage gas regulator controlled the air flow rate to the canisters as well as the final canister pressure. The flow was measured by a rotameter installed in the dry air line. A shutoff valve was installed between the rotameter and the manifold where the canisters were connected for cleanup.

A bellows valve installed in the line between each canister manifold and the vacuum pump regulated access of vacuum to the manifold. The cryogenic trap between the manifold and the vacuum pump prevented any back diffusion of hydrocarbons from the vacuum pump into the cleanup system or the canisters.

Canister Cleanup Procedure

After NMOC analyses were completed, six canisters were connected to each manifold shown in Figure 2. The valve on each canister was opened, with the shutoff valves and the bellows valves closed. The vacuum pump was started and one of the bellows valves was opened, drawing a vacuum on the canisters connected to the corresponding manifold. After reaching 5mm Hg absolute pressure (667 Pa), the vacuum was maintained on the six canisters connected to the vacuum manifold for 15 minutes. The bellows valve was then closed and the cleaned, dried air was introduced into the evacuated canisters until the pressure reached 40 psig (276 kPa). The canisters were filled from the clean air system at the rate of 7.0 L/min, a flowrate specified by the manufacturer as the highest flowrate at which the catalytic oxidizers would handle elimination of hydrocarbons with a minimum 99.7% efficiency.

When the first manifold had completed the evacuation phase and was being pressurized, the second manifold was then exposed to the vacuum by opening the bellows valve. After 15 minutes of exposing the second manifold and canisters to <5mm Hg absolute pressure, the second manifold was isolated from the vacuum and connected to the clean air. The first manifold of canisters was then taken through a second cycle of evacuation and pressurization. Each bank of six canisters was subjected to three cleanup cycles.

In the third cycle, after the canisters had been pressurized to 40 psig (276 kPa), the canister on each manifold that had contained the highest NMOC concentration sample prior to cleanup was selected for cleanup testing. It was removed from the manifold under pressure and analyzed for its NMOC content, which averaged 1.5 parts per billion carbon (ppbC). If the analysis measured less than 2.5 ppbC then all six canisters on the manifold were considered to be clean. The canister that had been removed from the manifold for cleanup

testing was reconnected to the manifold and all six canisters were evacuated to <5mm Hg absolute pressure the fourth and final time. They were kept at that pressure for 10 to 15 minutes, after which time, the canister valves were closed, and the canisters were disconnected from the manifold and packed into the shipping containers.

In the 1985 NMOC Program, all the canisters cleaned by the procedure described above met the 2.5 ppbC criterion for cleanness after three cleaning cycles. Per cent carryover was defined as the percentage of the NMOC contained in an ambient air sample that remained after the canister was cleaned via the cleanup procedure. Measured per cent carryover ranged from 1.16% to 0%, with an average percent carryover of 0.10%. The overall average carryover was probably less than 0.10% because the canisters were evacuated a fourth time after the per cent carryover had been measured.

Sample Degradation Studies

Important aspects of the 1985 NMOC study were (1) to investigate the effect of the length of the storage time on the NMOC concentrations of an ambient air sample in the sample canisters, and (2) to determine whether the NMOC concentration was affected by the pressure of the sample in the canister at the time of analysis. Two studies were done:

1. Radian selected 26 canisters at random during the summer program for a sample degradation study. NMOC measurements were made on each canister by the PDFID method seven days after the initial analysis. On the 14th day after the initial analysis, one or more analyses were done until the pressure in the canister fell below 5 psig (34.5 kPa).

2. Four canisters were selected from among the site samples for sample degradation studies by the GCFID method. These studies were conducted in the U.S. Environmental Protection Agency's Atmospheric Sciences Research laboratory (EPA-ASRL). Seven days after the initial analysis, the samples were reanalyzed. On the 14th day after the initial analysis, the sample was analyzed three times.

Data for the Radian sample degradation study are given in Table 1; similar data are given for the EPA-ASRL study in Table 2. Sample ID numbers in Tables 1 and 2 were those assigned by Radian for each ambient air site sample as it was prepared for analysis. The pressures recorded in the Tables are the absolute canister pressures measured before each analysis. For each sample, 2 to 5 sets of pressures and NMOC values are given. The first pressure and NMOC value are the results from the first analysis. The second pressure and NMOC value for each sample are the results for the second analysis done seven days after the initial analysis. The rest of the pressures and NMOC values for each group are the results for the 14th day after the initial analysis.

To detect a possible change of the NMOC measured concentration upon storage in the sample canisters for the two-week period after the initial analysis, the hypothesis that the mean of the second through the fifth (or 6th) NMOC concentration determination was equal to the first NMOC concentration in each data set was tested.[8] Two data sets, Sample ID Nos. 1399 and 1739, in Table 1 and one data set, Sample ID No. 2135, from Table 2 show the NMOC mean after the first analysis to be different from the initial NMOC value at the 5% level of significance. In the first two cases, the final NMOC mean was less than the initial value, and in the third case, the EPA-ASRL results, showed the final mean to be greater than the initial value.

To look for a pressure-related effect, correlation coefficients for the linear relation of pressure as the independent variable, versus NMOC concentration, were calculated for each data set. Four out of the 26 data sets in the Radian study (Table 1) showed a correlation coefficient significantly greater than zero at the 5 percent level of significance.[8] None of the EPA-ASRL sample data sets (Table 2) showed a significant correlation coefficient for the linear relation of pressure vs. NMOC. In Table 1, Sample ID Nos. 1486, 1738, 2129, 2150 showed significant correlation coefficients. It should be noted for that Sample ID Nos. 1486, 2129, and 2150, NMOC values "increased" 4.3%, 11.8%, and 4.3%, respectively while for Sample ID No. 1738, the NMOC value "decreased" 2.8%. It is also to be noted that in the linear correlation with from 3 to 6 total data sets, the correlation is not a robust or definitive measure because two degrees of freedom are taken by the constants in the linear correlation. The amount of increase or decrease of NMOC with decreasing pressure is within the repeated error measurement of 10.5%,[5] with the exception of Sample ID 2129. This means that there is a significant probability that the successively increasing (or decreasing) NMOC values could have occurred due to random variation.

The final point to be made is that the Sample ID Nos. found to have NMOC values differing significantly from the initial value were different from the Sample Nos. showing significant linear correlation coefficients with respect to pressure.

There was no well defined increasing or decreasing trend in the NMOC concentration versus pressure or time after initial analysis. For the few cases that had a discernable trend the results were conflicting and small, i.e., within the average error for the method. It was therefore concluded that there was no significant NMOC concentration change (1) when the canister pressure was decreased, and (2) when the ambient air samples were stored in the canisters for a two-week period after the initial analysis. These results also supported the assumption that there was no change in the NMOC concentration between the time of sampling and the time of analysis.

Conclusions

The automated sampling system described, reliably collected integrated ambient air samples suitable for NMOC or species analysis. The canisters used in this study were rugged and utilitarian for collecting, storing, and shipping air samples. The sample cleanup procedure was reliable and effectively reduced average sample carryover to less than 0.10% from one sample to the next. No significant NMOC concentration changes were related to storage of the sample for up to 14 days, or related to pressure of the sample air in the canister.

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TABLE 1. SAMPLE DEGRADATION STUDY, RADIAN RESULTS

Sample ID No.	Pressure, psia[a]	NMOC, ppmC	Sample ID No.	Pressure, psia[a]	NMOC, ppmC	Sample ID No.	Pressure, psia[a]	NMOC, ppmC
1642	33.7	0.440	1874	37.2	2.274	2363	32.7	0.840
	28.7	0.420		32.7	2.302		27.7	0.938
	26.7	0.362		25.2	2.317		22.7	0.807
	29.7	0.386		22.7	2.289		16.7	0.932
1486[b]	33.2	0.966	1318	32.7	0.154	2129[b]	39.7	1.565
	28.7	0.985		26.7	0.178		32.7	1.579
	24.7	0.990		22.7	0.202		27.2	1.687
	19.7	1.008		19.2	0.179		18.7	1.750
1399[c]	32.7	0.984	1768	41.7	2.500	1470	33.7	0.965
	25.7	0.425		34.7	2.472		26.7	1.050
	19.7	0.426		30.2	2.590		22.2	1.014
				22.2	2.513		17.7	0.990
1875	37.2	2.284	1848	33.2	1.557	1324	31.7	0.177
	31.7	2.257		27.7	1.544		24.7	0.167
	27.7	1.469		23.7	1.532		20.7	0.168
	18.7	2.076		17.7	1.579		17.7	0.209
2305	31.7	1.084	2360	32.7	0.412	1738[b]	31.7	0.675
	28.2	1.110		25.2	0.324		27.7	0.663
	21.2	1.189		19.7	0.399		22.7	0.656
1302	31.7	0.413	2635	18.7	0.651	1739[d]	32.7	0.695
	27.7	0.399		31.2	1.071		26.7	0.676
	23.2	0.447		27.7	0.959		22.7	0.678
	19.7	0.455		19.7	0.947		16.7	0.671
1847	33.7	0.460	1093	47.7	1.170	2203	33.7	0.852
	29.7	0.449		38.7	1.151		28.7	0.825
	26.2	0.458		31.7	1.180		24.2	0.934
	22.7	0.438		23.7	1.100		23.7	0.882
	20.7	0.438		19.7	1.134		18.7	0.795
2150[b]	32.7	0.862	2322	26.7	0.208	1124	34.2	2.115
	25.7	0.873		25.7	0.187		26.7	2.055
	17.7	0.889		20.7	0.230		16.7	1.780
1000	47.7	1.076	2103	28.7	0.984			
	40.7	1.089		17.7	0.929			
	29.7	1.168						
	25.7	1.041						
	21.7	1.099						
	17.7	1.131						

[a]Pressure reported here is lb/in^2 absolute pressure. Multiply by 6.894757 to convert to kPa.

[b]There was a correlation of pressure and NMOC concentration at the 0.05 level of significance.

[c]The mean of the last two NMOC values is significantly less than the first NMOC value at the 5% level of significance.

[d]The mean of the last three NMOC values is significantly less than the first NMOC value at the 5% level of significance.

TABLE 2. SAMPLE DEGRADATION STUDY, EPA-ASRL RESULTS

Sample ID No.	Pressure, psia[a]	NMOC, ppmC	Sample ID No.	Pressure, psia[a]	NMOC, ppmC
2461	24.0	0.895	2151	25.5	0.815
	23.7	0.890		21.8	0.839
	22.2	0.931		18.7	0.802
	20.7	0.897		16.7	0.808
	16.7	0.884		16.2	0.834
2135[b]	25.0	0.919	2323	21.2	0.204
	23.2	0.981		20.2	0.204
	22.2	0.984		19.2	0.174
	16.7	1.003		16.7	0.173
	16.2	0.984		15.2	0.171

[a]Pressure reported here is lb/in^2 absolute pressure. Multiply by 6.894757 to convert to kPa.

[b]The mean of the last 4 NMOC values is significantly greater than the first NMOC value at the 5% level of significance.

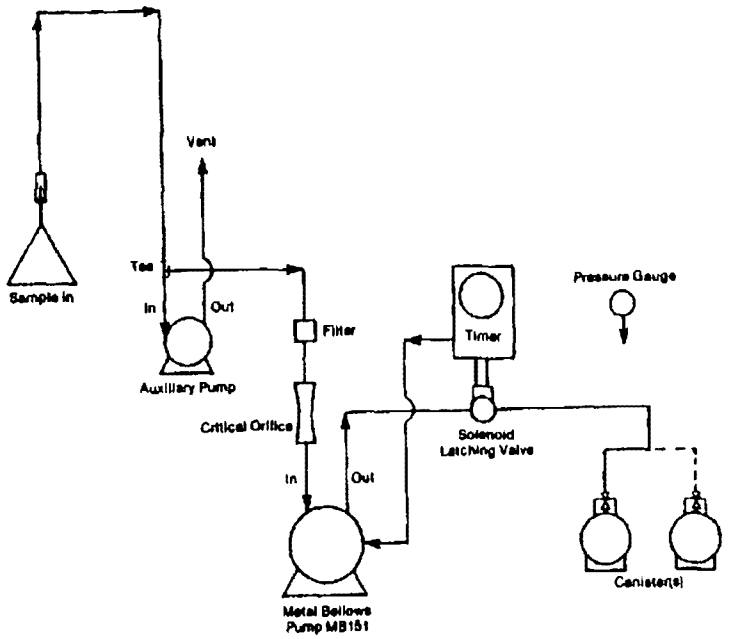

Figure 1. Sampling system for collecting integrated ambient air samples.

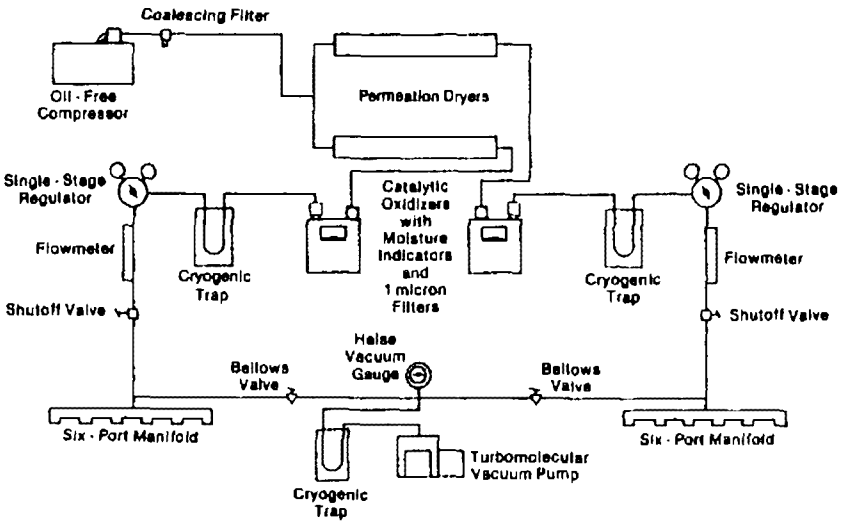

Figure 2. Canister cleanup apparatus.

1984 AND 1985 NONMETHANE ORGANIC COMPOUND SAMPLING AND ANALYSIS PROGRAM

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A Cryogenic Preconcentration Direct Flame Ionization Detection (PDFID) method was used to measure nonmethane organic compound (NMOC) concentrations in about 3000 samples of ambient air from 31 locations in 14 States and the District of Columbia during the Summers of 1984 and 1985. Air samples under pressure where shipped air freight in electropolished stainless steel containers and analyzed the next day, or the following Monday for Friday samples. Analyses were done at Radian Corporation's Research Triangle Park (NC) Laboratory on two dual-channel PDFID instruments. A number of the samples were also analyzed on the U. S. Environmental Protection Agency's PDFID instrument in their Quality Assurance Division (EPA-QAD) laboratory, and by a Gas Chromatographic Flame Ionization Detection (GCFID) instrument in EPA's Atmospheric Sciences Research Laboratory (EPA-ASRL).

Repeated analyses of 155 of the field samples gave an average absolute precision of 10.5% for the four Radian Channels. Audit sample analyses, using propane concentration standards, showed that Radian NMOC concentrations averaged 3.6% higher than the Research Triangle Institute's GCFID results, that EPA-QAD NMOC concentrations averaged 3.9% higher than RTI's, and that EPA-ASRL's results averaged 6.10% higher than RTI's.

Local ambient air samples were collected weekly and analyzed on each Radian Channel, and on both EPA instruments. There was a 0.72% NMOC concentration difference between Radian Channels, and a 5.6% within-laboratory coefficient of variation. The EPA-QAD NMOC concentrations averaged 8.9% higher than the Radian results, and there was a 7.7% between-laboratory coefficient of variation. The EPA-ASRL, GCFID method gave NMOC values averaging 2.5% lower than the Radian results.

NMOC concentrations for the combined 1985 data were reported in parts per million carbon (ppmC) by volume, were lognormally distributed, ranged from 0.05 to 5.27 ppmC, and averaged 0.75 ppmC.

The study has provided an extensive data base of NMOC concentrations, and has shown the PDFID method of analysis to be precise, accurate, and cost effective relative to the GCFID method of analysis.

Introduction

Photochemical dispersion models[1,2] describe quantitative relationships between ambient concentrations of smog precursor organic compounds and subsequent downwind concentrations of ozone. The models are used to determine the degree of control of organic compound concentrations in air required to meet applicable ambient air quality standards for ozone. Measurement of NMOC concentrations in ambient air is required for the models. The Gas Chromatographic, Flame Ionization Detection (GCFID) method has been one of the most accurate and widely used methods for determination of the NMOC concentration in air.[3]

A Preconcentration Direct Flame Ionization Detection (PDFIC) method was developed and used in 1984 and 1985 NMOC studies to measure NMOC concentrations in ambient air. The PDFID method is faster, simpler, and less costly to operate than the GCFID speciation method of NMOC analysis. The purpose of the NMOC studies was to assist the States in achieving the National Ambient Air Standard for ozone by 1987. These studies also afforded an excellent opportunity further to refine the PDFID method, to build a NMOC data base at several key sampling sites in the United States, to test and validate the equipment used, to determine the precision and accuracy of the sampling and analysis, and to compare the simpler PDFID method with the GCFID method.

The purposes of this paper are to discuss quality assurance procedures used to test and validate the sampling and analysis techniques, to describe the NMOC data characteristics, and to indicate the results of a quantitative comparison between the PDFID method and the GCFID method. A description of the sampling equipment and the procedures used to test and validate that equipment are given elsewhere.[5]

The experience and data of the 1984 study were used to refine the experimental design for the 1985 study. The results described below refer primarily to the data obtained in the 1985 study.

Experimental Design

Photochemical smog and haze occur more frequently in the summer months and the phenomenon is related to the NMOC and NO_x content of ambient air. The objective of the 1984 and 1985 NMOC studies was to obtain NMOC concentration measurements during the 6 A.M. to 9 A.M. time period on days when the ozone concentration was most likely to be the highest. These data can then be used to develop NMOC control plans based on the Empirical Kinetic Modeling Approach (EKMA).[1] All of monitoring sites chosen were in metropolitan areas, and several were located near petrochemical facilities.

Integrated, 3-hour, ambient air samples were scheduled to be taken during the Summer of 1985 at 19 sites from 6 A.M. to 9 A.M., Monday through Friday, except on holidays. Sampling was scheduled from early June through

September for most of the sites. The number of sample days scheduled for the various sites ranged from 44 to 88.

The determination of precision and accuracy was an important part of the 1984 and 1985 NMOC studies. Repeated analyses of some samples provided measures of analytical precision, while analysis of duplicate samples collected simultaneously once every two weeks at each site gave overall sampling and analysis precision results.

Electropolished, cleaned stainless steel canisters, under vacuum, were shipped via air freight from Radian's Research Triangle Park (RTP) Laboratory to each site. After sampling was completed, the canisters, filled with ambient air to about 15 psig (103 kPa), were returned via air freight to Radian's RTP Laboratory for NMOC Analysis the next day (or Monday for Friday samples).

Each day the first two samples analyzed were reanalyzed on another of the Radian analytical channels. These repeat measurements provided one measure of the within-Radian laboratory precision among the four Radian Channels (Channels A, B, C, and D). Another within-Radian precision was obtained from the analysis of the local ambient samples discussed below. Two samples daily, after being analyzed by Radian, were reanalyzed by the PDFID method in the EPA-QAD Laboratory. Four samples daily, after analysis by Radian, were reanalyzed by the GCFID method in the EPA-ASRL.

Each week, duplicate ambient air samples were collected in Raleigh, NC and analyzed by both EPA instruments, and by each of Radian's four channels. This series of duplicate ambient air samples was the most direct comparison of each channel's precision and accuracy relative to each other channel, since each channel analyzed the same sample twice, counting the duplicate sample. One of the duplicate local ambient samples was analyzed first by the Radian laboratory and the other duplicate was analyzed first by the EPA-QAD and ASRL laboratories. The purposes of this procedure was to test whether the order of analysis by a particular laboratory showed any detectable bias in the measured NMOC values.

Accuracy was monitored on four days each week on the Radian channels by in-house quality control propane-in-air samples. On Mondays, Tuesdays, Thursdays, and Fridays, a mixture of propane (0.03 to 9 ppmC) in air was analyzed by each Radian channel. Two external propane samples having different propane concentrations, were used as the primary basis for determining bias or accuracy for the four Radian PDFID channels, the EPA-QAD PDFID channel, and the EPA-ASRL GCFID channel. The Research Triangle Institute's Center for Environmental Studies was chosen as the reference laboratory in providing a basis for determining accuracy, or bias. Analysis of the audit samples by RTI was done by the GCFID gas speciation method, the same method used by EPA-ASRL.

Analytical Technique

The PDFID method for measuring the NMOC compounds in ambient air is described by the EPA.[4] The Radian PDFID instruments utilized a modified Hewlett-Packard, Model HP-5880, dual-FID chromatograph, along with the auxiliary equipment shown in Figure 1. The 6-port value was installed in an auxiliary heated zone, and the sample trap itself was located inside the chromatograph's column oven. Figure 1 shows the valve setting for introducing a constant volume of sample from the canister into the cryogenic sample trap, which was cooled with liquid argon. Once the sample had been trapped, the 6-port valve setting was changed to bring the carrier gas (He) through the sample trap into the FID, the liquid argon was removed, and the chromatograph's oven door was closed. The chromatograph's automatic program then assumed control of raising the oven temperature, at a preset rate, which released the trapped sample to the FID.

The daily calibration procedure began with an initial zero (blank) reading, followed by determination of a calibration factor, using propane of a known concentration. At the end of the day, a zero reading and calibration factor were again determined, and the calibration factor drift for that day was calculated. The initial calibration factor determined each day was used to calculate NMOC concentrations for the day. The acceptance criterion for the calibration factor measured at the end of the day was that if the largest NMOC value measured for the day changed in the third significant figure to the right of the decimal point, using the afternoon calibration factor, all NMOC values calculated for that day would be adjusted, using an average calibration factor for the day. This kind of a adjustment was never needed in the 1985 NMOC program.

The zero response was determined by averaging the peak area responses in area counts from two analyses of cleaned, dried air. An oil-free compressor provided source air for the clean air system. The air was filtered and permeation dryers removed water vapor. Catalytic oxidizers destroyed any hydrocarbons contained in the air. Zero readings averaged less than 1.0 ppbC, mornings and afternoons. Calibration factor drifts ranged from -11.7 to +7.7 percent, averaging +0.2% drift. The average of the absolute values of the calibration factor drift was 1.6%.

NMOC Data

The 1985 NMOC data are presented in Figure 2 as a stem-and-leaf plot,[6] along with statistics for the entire data set. The plot is a frequency histogram (rotated 90^0) which plots the NMOC concentrations, sorted from the smallest to the largest, and truncated to the nearest hundredth ppmC. The stems are the numbers to the left of the vertical open space and the leaves are to the right. As indicated on the graph, the smallest NMOC value is 0.045

ppmC, truncated to 0.04, and is shown at the top of the plot as "0 4" in the first stem and leaf. The second stem and leaf (or row) of the plot shows "0 799", which describes the next three largest of the sorted NMOC values to be 0.07, 0.09, and 0.09. The maximum NMOC value in the 1985 study was 5.267 ppmC, shown as "52 6" at the bottom of graph as the last stem and leaf. The M shown in the vertical open space locates the stem and leaf containing the median, which is 0.603 ppmC for this data set. The "H's" in the stem-and-leaf plot locate the stems and leaves containing the upper and lower hinges, which are the NMOC values dividing each half of the sorted data into quartiles.

Figure 2 suggests that the overall NMOC data approximately fit a log-normal frequency distribution. Additional tests confirmed this hypothesis. The mean NMOC value given in Figure 2 is the arithmetic mean and is 0.755 ppmC. For the lognormal distribution[7] the mean, α, equals $\exp(\mu+\sigma^2/2)$, where μ is the mean of the logarithm (to the base e) of NMOC values and σ is the standard deviation of the logarithm of NMOC values. For the 1985 NMOC data set, $\alpha = 0.753$ ppmC.

The NMOC data from each of the 19 sites in the 1985 study also appeared to be lognormally distributed, but because the number of data points per site ranged form 48 to 93, the conclusion was less well defined than for the combined NMOC concentration data for all sites. Mean values, assuming a lognormal NMOC distribution for each site, ranged from 0.401 to 1.781 ppmC. Arithmetic means ranged from 0.398 to 1.769 ppmC. The NMOC data from each site were shown to be random variables, i.e., not autocorrelated.

Quality Assurance Results

Completeness of sampling and analysis for the 19 sites of the 1985 NMOC study ranged form 86.1% to 102.2%, averaging 95.8% overall. Completeness was defined as the per cent of the total scheduled samples (regular daily samples plus duplicate samples) that were successfully taken and analyzed. Three sites showed per cent completeness values greater than 100%, which resulted because one or more extra samples were taken on scheduled holidays.

Analytical precision was determined by repeat analyses of 155 samples. Per cent differences between the second and the first analysis averaged +0.49%. The average of the absolute values of the per cent differences was 10.5%, with a standard deviation of 13.4%. The analytical precision reported here included the variability both between Radian channels and within Radian channels.

Overall precision, including both sampling and analysis variability, was determined by repeated analyses of 131 duplicate samples simultaneously collected in two identical canisters. The per cent differences for Radian's analyses of both duplicates averaged 1.69%. The average of the absolute values of the per cent difference between duplicates was 12.4%, and their standard deviation was 17.3%.

Accuracy was monitored with four internal propane standards per week analyzed by each Radian channel. Average per cent differences between the calculated and the measured NMOC concentrations of the internal propane standards ranged from -3.29% to +2.06% among the Radian channels. The overall per cent difference for the four Radian channels was -0.69%.

External audit samples having propane concentrations of about 3 ppmC and 9 ppmC, respectively, were analyzed three times each by the four Radian channels, the EPA-QAD PDFID instrument, and the EPA-ASRL GCFID speciation instrument. The average bias of the Radian results was +3.00%; EPA-QAD bias averaged +3.88%; and EPA-ASRL bias averaged +6.00%, all relative to the RTI results.

Canister cleanup studies[5] established that there was little carry-over of NMOC from one sample to the next. Twenty-six sample degradation studies[5] by Radian and four by EPA-ASRL showed than NMOC samples from the field sites did not change significantly in NMOC concentration over a 14-day period of storage in the sample canisters after the initial analysis.

Comparisons of Radian PDFID NMOC analyses with EPA-ASRL GCFID NMOC analyses and with the EPA-QAD PDFID NMOC analyses are given in terms of orthogonal regression statistics in Tables 1 and 2 and Figures 3 and 4. Figure 3 compares the NMOC values determined by EPA-QAD PDFID channel with the Radian NMOC results for the same site samples. Figure 4 gives a similar comparison for the EPA-ASRL and the Radian NMOC measurements. Table 1 compares the orthogonal regression statistics for the two curves. For Radian--EPA-ASRL results the slope is closer to 1.000 than the Radian--EPA-QAD results. The comparison of the regression results is further illustrated in Table 2. Using the slopes and intercepts from Table 1, EPA-QAD and EPA-ASRL NMOC predicted values are calculated at 3 arbitiarily selected Radian NMOC values which cover most of the range of NMOC values measured in the 1985 NMOC study. It is seen that the EPA-QAD NMOC values are less than the Radian NMOC values above 0.5 ppmC (because the slope of the regression line is about 0.942). For the EPA-ASRL--Radian comparison, above 0.5 ppmC, the EPA-ASRL NMOC results are only slightly higher.

Additional definition of the comparisons between and within laboratories for the PDFID method, and the comparisons between methods for the PDFID and the GCFID methods is given in Tables 3, 4, and 5, and Figures 5 and 6. During the period of June through September 1985, duplicate local ambient air samples were taken weekly and analyzed by each Radian channel, by the EPA-QAD PDFID instrument, and by the EPA-ASRL GCFID instrument. Tables 3 and 4 show comparisons made between each channel pair that analyzed each duplicate local ambient air sample. Table 3 shows the results for the duplicate analyzed first by the Radian Channels, and Table 4 shows the results for the duplicate analyzed first by the EPA channels. The mean difference refers to the average of the NMOC differences determined by the first-named channel of the

pair and the second-named channel, i.e., ($NMOC_{Rad\ A}$ - $NMOC_{Rad\ B}$) for the first row in the table. The third column refers to the standard deviation of the differences and the 4th column gives the number of comparisons.

Table 3 shows the overall Radian-to-Radian, within-laboratory average differences to be +0.0106 ppmC. The between Radian-laboratory and EPA-QAD-laboratory differences average +0.0567 ppmC. The comparison between Radian laboratory results and the EPA-ASRL results are between-NMOC-method comparisons and are shown in Table 3 to average 0.00365 ppmC. Table 4 shows similar results for the duplicate local ambient sample that was first analyzed by the EPA Laboratories, followed by analysis in the Radian laboratory.

These results are shown graphically in another way in Figures 5 and 6. In these figures, the mean ppmC differences are plotted for each channel pair, along with the 95% confidence intervals on the means. For the most part, the comparison show mean differences not significantly different from zero. Visual observation, confirmed by an analysis of variance, shows no significant difference between the duplicate local ambient sample results. There was likewise no difference between the duplicate sample NMOC results that could be attributed to the order of analysis. The between-laboratory results for the Radian--EPA-QAD PDFID determinations show the EPA-QAD results to average significantly less than the Radian results, while the EPA-ASRL NMOC results are slightly higher than the Radian channel averages. These mean differences are summarized in Table 5, which show the Radian within-laboratory differences to average less than 1.0%. The EPA-QAD NMOC determinations averaged about 8.0% lower than the Radian NMOC results, while the EPA-ASRL GCFID speciation method results averaged 1.6% higher than the Radian PDFID NMOC measurements.

Conclusions

The results of the 1985 NMOC study show the PDFID method to have a bias which averaged less than +4% with respect to propane standards using RTI's NMOC measurements by the GCFID method as reference values. The overall absolute values of the sampling and analysis precision averaged 12.4%, and the absolute values of the analytical precision averaged 10.5%. The PDFID method was shown to compare favorably with the GCFID speciation method, giving NMOC values which averaged only 2% lower than the GCFID speciation method, well within the precision of either method.

The PDFID method of measuring NMOC concentration is accurate, precise, and cost effective relative to the GCFID speciation method, and should become the method of choice.

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TABLE 1. COMPARISON OF RADIAN AND EPA ANALYSES; ORTHOGONAL REGRESSION PARAMETERS

EPA Channel	Slope	Intercept	n	Correlation Coefficient
QAD	+0.941771	+0.066219	128	0.927851
ASRL	+1.008515	-0.008069	281	0.948292

TABLE 2. COMPARISON OF PER CENT DIFFERENCES OF RADIAN AND EPA NMOC ANALYSES AT THREE CONCENTRATIONS.

Radian PPMC	QAD PPMC	ASRL PPMC	EPA-QAD % Diff.	EPA-ASRL % Diff.
0.5	0.53710	0.49619	+7.42	-0.76
1.2	1.19634	1.20215	-0.31	+0.18
5.5	5.24596	5.53876	-4.62	+0.70

TABLE 3. LOCAL AMBIENT SAMPLE RESULTS, FIRST ANALYSIS BY RADIAN.

Channel Pair	Mean[a] Difference ppmC	Standard Deviation	Number
Radian A-Radian B	0.0178	0.0381	12
Radian A-Radian C	0.0057	0.0351	12
Radian A-Radian D	0.0279	0.0376	12
Radian B-Radian C	-0.0122	0.0615	12
Radian B-Radian D	0.0101	0.0545	12
Radian C-Radian D	0.0223	0.0398	12
Average or Pooled Value	0.0106	0.0325	72
Radian A--(EPA-QAD)	0.0704	0.0829	8
Radian B--(EPA-QAD)	0.0481	0.0605	8
Radian C--(EPA-QAD)	0.0675	0.1069	8
Radian D--(EPA-QAD)	0.0408	0.0994	8
Average or Pooled Value	0.0567	0.0891	32
Radian A--(EPA-ASRL)	-0.0017	0.0570	9
Radian B--(EPA-ASRL)	0.0100	0.0726	9
Radian C--(EPA-ASRL)	0.0159	0.1034	8
Radian D--(EPA-ASRL)	-0.0096	0.1232	9
Average or Pooled Value	0.00365	0.09323	35

[a]The mean difference is the average NMOC difference between the first channel of the pair and the second channel, e.g., for the first row it refers to the difference between the Radian Channel A NMOC value and Radian Channel B NMOC value, = $(NMOC_{Rad\ A} - NMOC_{Rad\ B})$.

TABLE 4. LOCAL AMBIENT SAMPLE ANALYSIS RESULTS, FIRST ANALYSIS BY EPA LABORATORIES

Channel Pair	Mean[a] Difference ppmC	Standard Deviation	Number
1st Analysis by EPA Laboratories			
Radian A-Radian B	-0.0123	0.0465	11
Radian A-Radian C	-0.0074	0.0410	11
Radian A-Radian D	-0.0047	0.0458	11
Radian B-Radian C	0.0072	0.0618	12
Radian B-Radian D	0.0112	0.0297	12
Radian C-Radian D	0.0040	0.0665	12
Average or Pooled Value	+0.00006	0.0503	69
Radian A--(EPA-QAD)	0.0628	0.0915	10
Radian B--(EPA-QAD)	0.0684	0.1031	10
Radian C--(EPA-QAD)	0.0670	0.1248	10
Radian D--(EPA-QAD)	0.0604	0.0949	10
Average or Pooled Value	+0.0646	0.1044	40
Radian A--(EPA-ASRL)	-0.0325	0.0809	10
Radian B--(EPA-ASRL)	-0.0254	0.0657	11
Radian C--(EPA-ASRL)	-0.0237	0.1047	10
Radian D--(EPA-ASRL)	-0.0279	0.0755	10
Average or Pooled Value	-0.02745	0.0830	31

[a]The mean difference is the average NMOC difference between the first channel of the pair and the second channel, e.g., for the first row it refers to the difference between the Radian Channel A NMOC value and Radian Channel B NMOC value, = $(NMOC_{Rad\ A} - NMOC_{Rad\ B})$.

TABLE 5. COMPARISON OF LABORATORIES AND NMOC METHODS

Channels	NMOC Method	Mean[a] Difference ppmC	Mean[b] Per Cent Difference
Radian--Radian	PDFID	0.0053	+0.7%
Radian--EPA-QAD	PDFID	0.0606	+8.0%
Radian--EPA-ASRL	GCFID	-0.0118	-1.6%

[a]Estimated using 0.75 ppmC as the mean NMOC value.

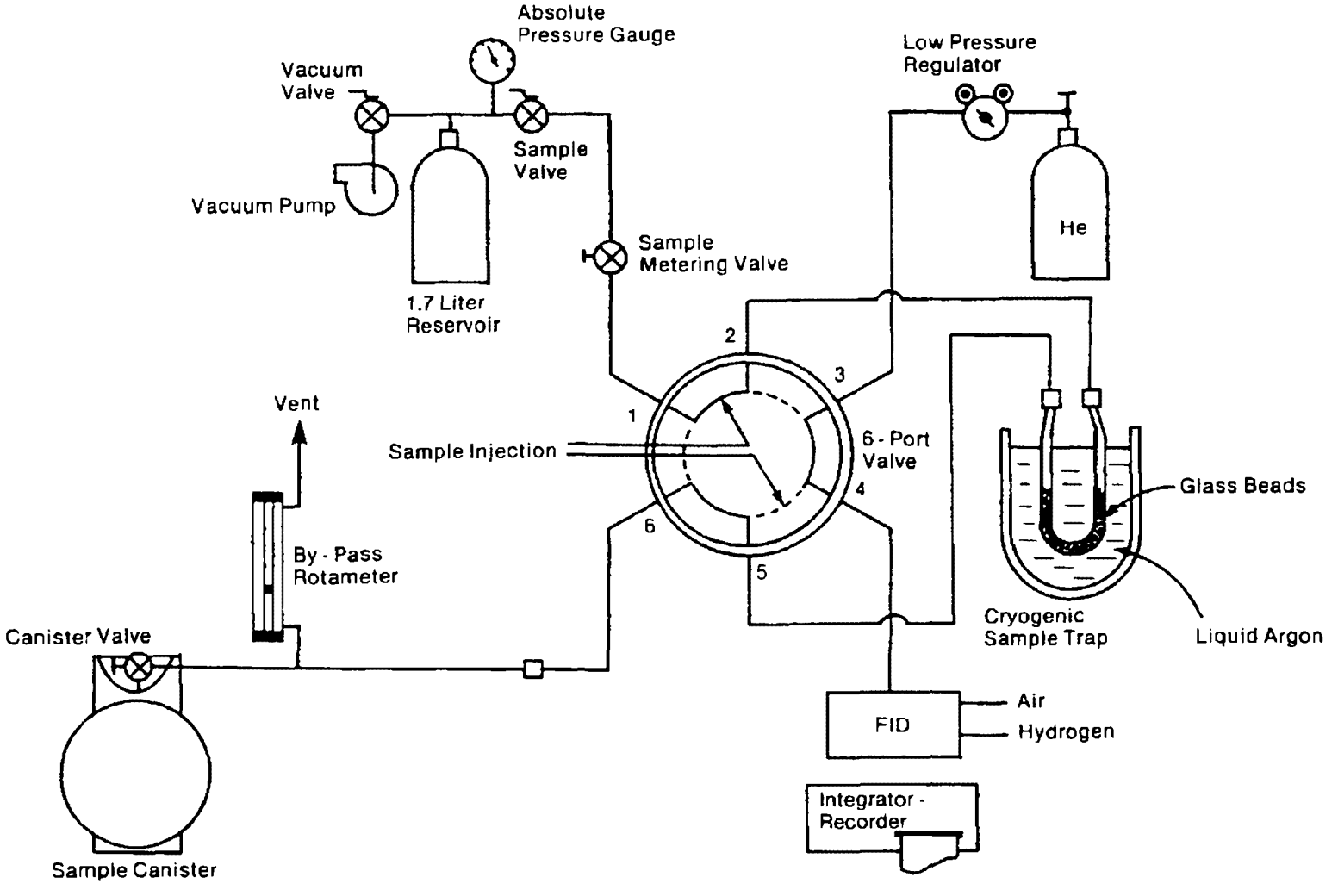


Figure 1. Schematic diagram of system for analysis of total nonmethane hydrocarbons by cryogenic preconcentration and flame ionization detection.

Smallest value at top of plot is : 0.045 ppmC

```
0     4
0     799
1     00111 12222 23333 34444 4
1     55566 66666 66677 77777 77777 88899 999
2     00000 00011 11111 11111 11122 22222 22333 33333 33333 44444 44444 44
2     55555 55555 55566 66666 66666 67777 77777 77777 77888 88888 88888 88899 99999 99999
3     00000 01111 11111 11111 11122 22222 22222 22223 33333 33333 33333 33333 44444 44444 44444 44444 4
3     55555 55555 55555 55556 66666 66666 66666 66667 77777 77777 77777 77777 78888 88888 88888 89999 99999 99999 999
4   H 00000 00000 00000 00000 00011 11111 11111 11111 12222 22222 22222 22222 22222 22222 22222 33333 33333 33333 34444 44444 44444 44444 44444 444
4     55555 55555 55555 55666 66666 66666 77777 77777 77777 77777 77777 88888 88888 88888 88899 99999 99999 99999 99999 99999 99
5     00000 00000 00000 00111 11111 11111 11111 12222 22222 22222 22223 33333 33333 33333 33444 44444 4444
5     55555 55555 55555 66666 66666 66666 66677 77777 77777 77777 77788 88888 88888 89999 99999 99
6   M 00000 00000 01111 11111 11111 22222 22222 23333 33333 33333 44444 44444 44444 444
6     55555 55555 55555 56666 66666 66666 66777 77777 78888 88888 88888 89999 99999 9999
7     00000 00000 00000 11111 11111 11111 11111 11112 22222 22222 23333 33333 33333 33334 44444 44444 44
7     55555 55555 55666 66666 66666 66777 77777 78888 88999 99999 99999 9
8     00000 00111 11122 22222 22233 33333 33344 44444 44
8     55555 55555 56666 77778 88899 99998 99
9   H 00000 00011 11111 11122 22233 33333 33344 44444 444
9     55555 55556 66666 66677 77777 77888 89999 99
10    00111 11112 22222 33333 33444 444
10    55555 55566 66666 66677 77778 88899 99999 9
11    00111 12222 22233 33344
11    55677 88999 9
12    00001 11122 22222 344
12    55566 66667 77777 77778 8899
13    00011 12222 23334 4444
13    55555 66667 78888 9
14    01111 22333 34444
14    678
15    00011 22233 44444
15    55667 788
16    00012 233
16    67777 88
17    00123
17    33566 778
18    00123 35566 678
19    01113 34457 889
20    01125 79
21    11235 67
22    22467 789
23    46778
24    12589
25    25568 9
26    468
27    0467
28    6
29    379
30    56
31    7
32    08
33    4
36    8
37    7
52    6
```

	NMOC,ppmC
N OF CASES	1500
MINIMUM	0.045
MAXIMUM	5.267
MEAN	0.755
MEDIAN	0.603
STANDARD DEV	0.541
SKEWNESS	2.166
KURTOSIS	7.232

Figure 2. Stem-and-leaf plot of NMOC data.

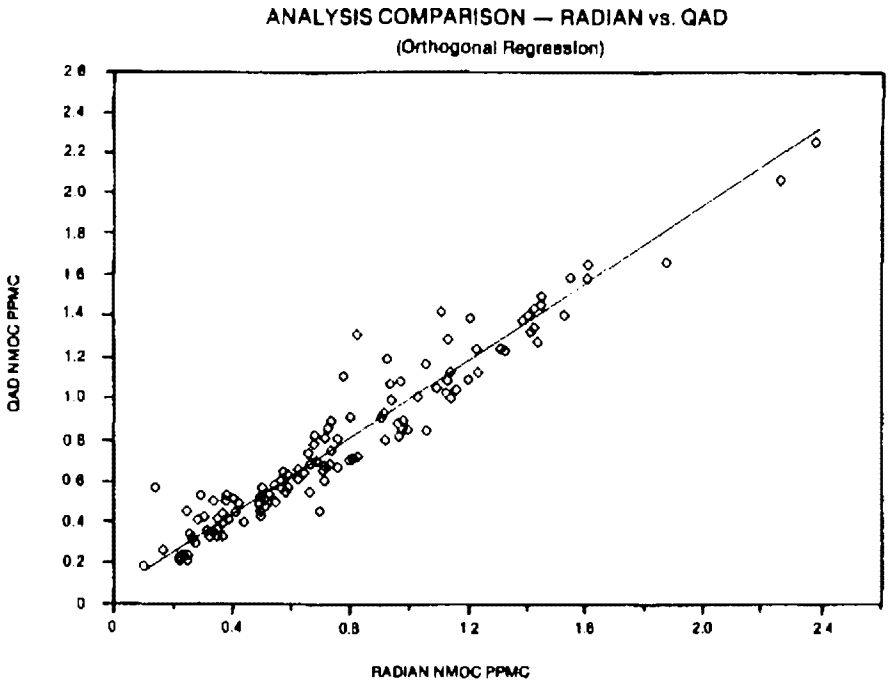


Figure 3. Comparison of Radian PDFID analyses with EPA-Quality Assurance Division PDFID results.

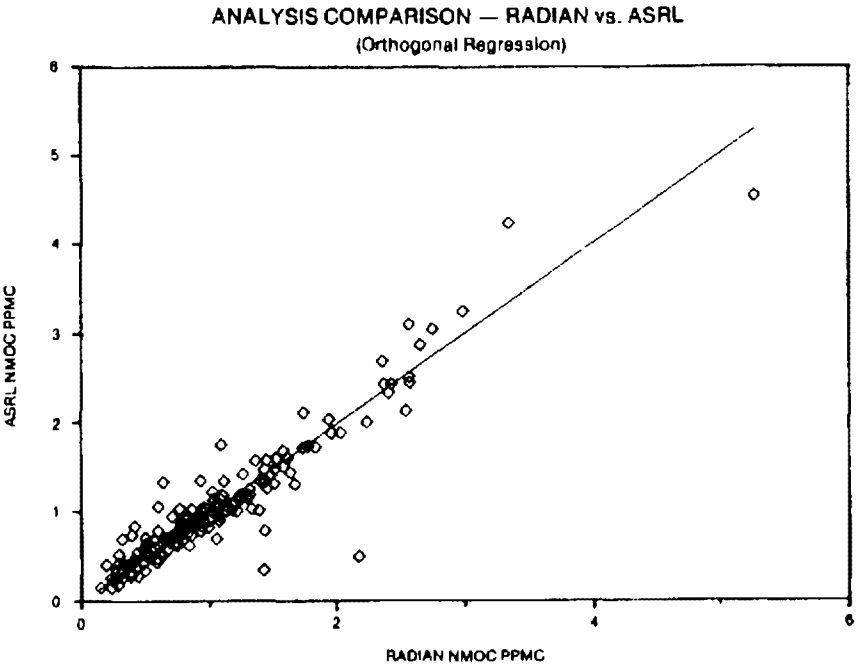
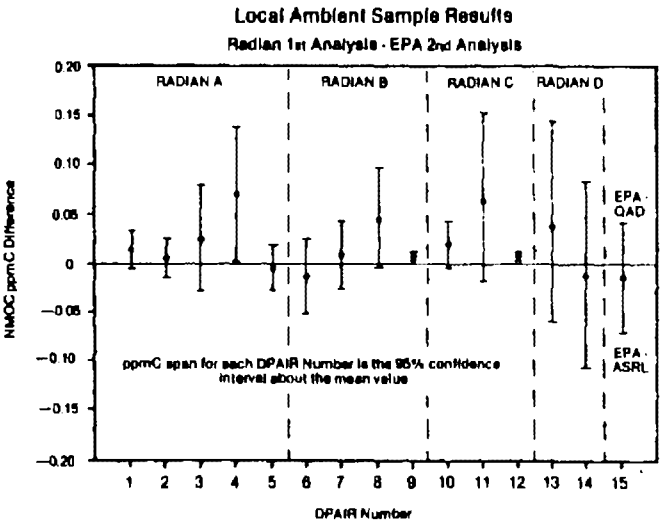
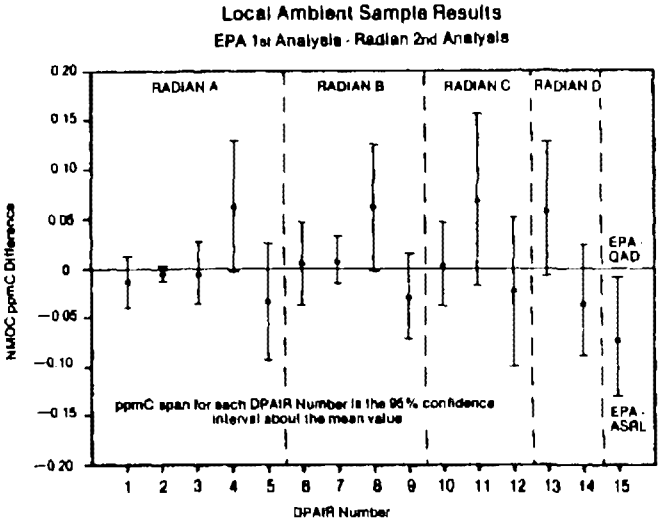


Figure 4. Comparison of Radian PDFID analysis with EPA-Atmospheric Sciences Research Laboratory GCFID results.



DPAIR NUMBER	CHANNEL PAIR
1	RADIAN - A - RADIAN - B
2	RADIAN - A - RADIAN - C
3	RADIAN - A - RADIAN - D
4	RADIAN - A - EPA - QAD
5	RADIAN - A - EPA - ASRL
6	RADIAN - B - RADIAN - C
7	RADIAN - B - RADIAN - D
8	RADIAN - B - EPA - QAD
9	RADIAN - B - EPA - ASRL
10	RADIAN - C - RADIAN - D
11	RADIAN - C - EPA - QAD
12	RADIAN - C - EPA - ASRL
13	RADIAN - D - EPA - QAD
14	RADIAN - D - EPA - ASRL
15	EPA - QAD - EPA - ASRL

Figure 5. Round robin analyses, first analyses by Radian.



DPAIR NUMBER	CHANNEL PAIR
1	RADIAN - A - RADIAN - B
2	RADIAN - A - RADIAN - C
3	RADIAN - A - RADIAN - D
4	RADIAN - A - EPA - QAD
5	RADIAN - A - EPA - ASRL
6	RADIAN - B - RADIAN - C
7	RADIAN - B - RADIAN - D
8	RADIAN - B - EPA - QAD
9	RADIAN - B - EPA - ASRL
10	RADIAN - C - RADIAN - D
11	RADIAN - C - EPA - QAD
12	RADIAN - C - EPA - ASRL
13	RADIAN - D - EPA - QAD
14	RADIAN - D - EPA - ASRL
15	EPA - QAD - EPA - ASRL

Figure 6. Round robin analyses, first analyses by EPA.

SELF SERVICE STATION VEHICLE REFUELING EXPOSURE STUDY

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Abstract

A four-day, ten vehicle study was conducted to quantify the concentration and composition of gasoline vapor at five fixed distances from a single island refueling point during February 1985, in Raleigh, N.C. Liquid and vapor grab samples were collected to identify and quantify the specific components of a commercial unleaded regular gasoline and associated refueling vapors. This study also provided information as to the potential individual exposure during self-service refueling operations. Vapor samples were collected in evacuated six-liter stainless steel canisters at five fixed distances from the vehicle refueling intake point. The sampling was conducted under three different wind directions relative to the vehicle intake point. Meteorological data (wind speed, wind direction, temperature, and relative humidity) was collected at the study site during all sampling periods.

Vapor samples were analyzed by both cryogenic preconcentration direct flame ionization (PD-FID) and by gas chromatography/flame ionization detection (GC-FID) for total non-methane organic carbon. Analysis by GC-FID also provided a detailed hydrocarbon profile (82 compounds) for all liquid samples and vapor samples greater than 20 parts per million as carbon (ppm C).

Introduction

On August 8, 1984, EPA announced in the Federal Register the availability of a document prepared by the Office of Air Quality Planning and Standards (OAQPS) describing the risk analysis and control options for gasoline vapors[1]. This document indicated that although there are several sources of public exposure to gasoline vapors, eighty percent of the estimated cancer incidence was due to exposure during self-service refueling of motor vehicles. Estimates of typical exposure during self-service refueling were made from a limited amount of data taken from a report prepared by Clayton Environmental Consultants (CEC) for the American Petroleum Institute (API)[2]. Unfortunately, the Clayton report did not describe many of the key variables that could influence exposure (e.g. distance from the pump nozzle to the breathing zone of the exposed person, wind speed, wind direction). A limited amount of data was also available from the City of Philadelphia[3]. The City of Philadelphia's data indicated that such variables can account for orders of magnitude changes in exposure.

OAQPS requested assistance from the Environmental Monitoring Systems Laboratory (EMSL) at Research Triangle Park in an effort to expand the limited data base which describes the exposure to and composition of gasoline vapor concentrations associated with self-service refuelings. EMSL and OAQPS jointly developed a limited four-day study design based on what could be reasonably accomplished by EMSL with in-house personnel and equipment resources, and utilizing analytical support from the Atmospheric Sciences Research Laboratory (ASRL).

The principal objectives of this study were: (1) to quantify the concentration and composition of gasoline vapor at fixed distances from the refueling point, and (2) to identify and quantify the specific components of commercial unleaded regular gasoline in a vapor and liquid phase.

Experimental Methods

A. Site. EMSL obtained the use of the North Carolina Department of Administration Motor Fleet Management Garage on Blue Ridge Road, Raleigh, N. C. as the study site. This location was selected because it contains a single pump island, refuels with only unleaded regular gasoline and contains a large pool of available vehicles requiring daily refuelings. A "study" vehicle was defined as one that requires refueling from the right or left rear side, uses unleaded regular gasoline, and is a sedan design. The vehicles used in this study were either Plymouth Reliant "K" (Model Year 1981-83) or Mercury Zephyer (Model Year 1980).

Meteorological monitoring was conducted during all sampling periods with a mechanical weather station (Model 1076 Meteorology Research, Inc. (MRI)). The MRI station was used to collect data on wind speed,wind direction, and temperature. Relative humidity data was obtained by the use of a psychrometer (Model 566 Bendix Environmental Science Division). The MRI station was located forty feet from the pump island and the measurements were obtained at an elevation of six feet above ground level. The separation distance (40 feet) from the pump island was necessary to obtain an adequate indication of wind speed and direction without being influenced by the garage or pump island facilities.

B. Sampling Approach. Sampling was limited to periods when the wind speed was no greater than twelve miles per hour (12 mph), the ambient temperature was above freezing (0° Centigrade) and no forecasted precipitation. During the four days of sampling all vehicles were obtained from the vehicle pool located at the Motor Fleet Garage. These vehicles had been parked in

the lot at least overnight and were selected based on refueling intake point location and indicated volume of gasoline in the tank reservoir by the gasoline gauge. Only vehicles with an indicated gasoline volume of $\leq$ one fourth tank were selected for use in the study. As a result of the overnight parking all vehicle gasoline tank temperatures approximated the ambient temperature.

Three types of gasoline samples were collected during each sample day. They were vapor, liquid, and bulk liquid samples. Vapor samples were collected in evacuated six-liter stainless steel canisters at five fixed distances from the vehicle refueling intake point during a ninety second refueling period (Figure 1). A daily background vapor sample was collected in the breathing zone "A" (BZA) position prior to the commencement of any other sampling. Immediately following the collection of the background sample the temperature of the vehicle tank reservoir was obtained by removing the gas tank cap and inserting a temperature probe (Model 5650 Digital Thermometer, Markson Scientific, Inc.) into the tank reservoir.

The fixed distance vapor grab sampling was conducted under three different wind directions relative to the vehicle intake point. They were parallel, perpendicular, and reverse parallel (Figure 2).

Liquid samples and bulk liquid samples were collected from the pump nozzle immediately following the refueling operations on the last study vehicle for each sample day. Two types of liquid samples were necessary due to differing analytical techniques and laboratories involved in their analysis. Liquid samples were collected in four milliliter glass conical reaction vials with twin septum mininert® caps (Wheaton Inc. and Dynatech Inc.) and stored on ice for the return trip to the laboratory. These samples were collected and analyzed to provide a detailed hydrocarbon profile of the study site gasoline. Bulk liquid samples (aproximately 0.8 gal.) were collected in a stainless steel can and also stored on ice for the return trip to laboratory. Bulk liquid samples were collected and analyzed to monitor the gasoline's Reid vapor pressure (RVP). Upon return to the laboratory and until analyzed the bulk liquid samples were stored at 5°C and the liquid samples at -10°C. The study site was supplied with fuel under contract to the State of North Carolina from Texaco, Inc. On the 1st and 19th of February 1985, the station was supplied with fuel (approximately 8850 gallons on each occasion).

C. Sample Collection. Specific sampling points were selected perpendicular to the vehicle's refueling intake point. These points are defined below and can be located on Figure 1. Emission Point (EP): located at a distance of six inches from the refueling intake point and at the same elevation above ground level. Breathing Zone Point A and B (BZA and BZB): located at a distance of two feet from the refueling intake point and at an elevation of five feet above ground level. The breathing zone position was selected as the approximate location of an individual during a refueling operation. These samples were simultaneously collected (for duplicate analyses) through a common intake connected by six inches of stainless steel tubing. Profile Sampling Points (PS5, PS7, and PS9): located at distances of five, seven and nine feet from the refueling intake point and at an elevation of five feet above ground level. Utilizing a perpendicular orientation of the sampling support frame to the vehicle intake point, sampling was conducted under three different wind orientations. A parallel wind configuration was defined as a wind blowing from the direction of the fuel intake point and along the axis of the vapor sampling frame. A perpendicular wind configuration was defined as a wind blowing across the axis of the vapor sampling frame. A reverse parallel wind configuration was a wind blowing toward the fuel intake point and along the axis of the vapor sampling

frame. Four refueling operations were conducted under a parallel and perpendicular wind configuration and two refueling operations under a reverse parallel wind configuration. During each of the refueling operations an individual held the pump nozzle in place during the ninety second period in order to regulate the pump rate and to minimize spills. The position occupied by the attendant during the refueling operation was adjacent to the sampling apparatus and such that it minimized the blocking of the air flow around the emission point.

The six-liter canisters used in this study were manufactured by Demaray Scientific Instruments, Ltd., Pullman, WA. These canisters contain an electropolished interior (Summa® treatment) and were equipped with a leak free shutoff valve (Nupro® Model SS4H). The attachment position on the sampling frame was equipped with a two liter per minute stainless steel critical orifice (Model XX5000020, Millipore Corp.) to maintain a constant flow rate during sampling. The orifice was attached to a stainless steel Whitney® toggle valve to facilitate the manual opening and closing of the canister valve during sampling. Prior to use in the field all canisters were leak tested by pressurization to thirty-five pounds per square inch absolute (35psia) with zero air. Following leak testing all canisters were cleaned and assigned sample numbers. The canisters in groups of five were cleaned by attachment to a metal vacuum manifold and evacuated for a four hour period. A cryogenically-cooled trap of liquid Argon was placed in the vacuum line to eliminate the possibility of back-diffusion of hydrocarbons or oil from the vacuum pump. Following the evacuation procedure twenty percent of the canisters were pressurized to 35 psia with zero-grade compressed air passed through the liquid Argon cryogenic trap. The pressurized canister was then analyzed on a preconcentration direct flame ionization detection (PD-FID) system for a check on the background total nonmethane organic carbon (NMOC). The maximum allowable background level of total NMOC established for this study was no greater than 0.01 parts per million as carbon (ppm C). In the event this standard was not achieved, all canisters in the group were re-evacuated for an additional four hours and re-analyzed. All canisters used in this study were cleaned with the above procedure and met the established standard.

After field sampling and upon return to the laboratory the canisters containing the vapor samples were attached to a pressure gauge and an ending pressure was recorded. The canisters were then pressurized to 35 psia with zero-grade air passed through a cryogenic cold trap. The difference in absolute pressures recorded from each canister enables the analyst to calcualte the Dilution Factor (DF) associated with each sample collected. This calculation is shown below:

$$DF = \frac{\text{Final Pressure psia}}{\text{Sample Pressure psia} - \text{Initial Pressure psia}} \quad \text{e.g.} \quad \frac{34.95 \text{ psia}}{(8.40-0.10)\text{psia}} = 4.21$$

The canister analytical concentration (ppm C) would then be multiplied by the dilution factor to determine the total NMOC concentration. D.F. x Analytical ppm C = Total NMOC concentration in parts per million as carbon (ppm C).

D. Sample Analysis. Total NMOC and speciated data was developed on all liquid samples and on as many vapor samples as possible. Two similar techniques were selected to provide an analytical comparison. Initially, all vapor samples were analyzed by cryogenic preconcentration direct flame ionization (PD-FID)[5,6] and then by gas chromatography/flame ionization detection (GC-FID)[4] if possible. Liquid samples were only analyzed by GC-FID. The bulk liquid samples were analyzed by the North Carolina Department of Agriculture, Standards Division, Fuels Laboratory located in Raleigh,

N.C. The chromatographic system precision required canister total NMOC concentrations greater than 5 ppm C, which with dilution equated to about 20 ppm C ambient concentrations.

Results

The parallel wind configuration based data is emphasized in the following discussion as illustrative of the higher concentrations observed in this study.

Table 1 summarizes the meteorlogical and gasoline volume data collected during the four-day study. Table 2 profiles the average NMOC concentration values for the four refuelings conducted under a parallel wind configuration and the expected benzene exposure reported as ppm C. Table 3 summarizes the levels of exposure to NMOC at the breathing zone position under the three wind configurations. Table 4A contrasts the composition of both the liquid fuel and vapor samples collected under a parallel wind configuration. Table 4B shows the breathing zone fraction greater than and equal to carbon number six for the gasoline and the refueling vapors.

Figures 3A and 3B graphically compare the detailed hydrocarbon compositions of the fuel and the vapor at the breathing zone position under a parallel wind. Percent aromatic, parrafin, and olefin compositions are also shown.

Conclusions.

The limited data collected in the short term study indicates that the level of exposures to NMOC during refueling operations is similiar to data reported in earlier studies.[2,3] The effect of wind direction shown by the significant drop in exposure at the breathing zone position may explain the differences reported in the City of Philadelphia Study. The detailed hydrocarbon composition data indicates that the exposure during refueling is predominately volatile C_4 & C_5 hydrocarbons.

The evaluated stainless canisters used in this study provided an extremely stable and safe storage container for the vapor samples collected in this study. The canister cleanup procedure used demonstrated that NMOC concentrations as high as 10,000 ppm C created no background contamination to the study canisters.

A copy the complete report containing detailed hydrocarbon and additional NMOC data from all five sampling points is available from the authors.

Acknowledgement

The authors wish to acknowledge the excellent analytical support provided by J. Duncan and W. Crews, Northrop Services, Inc., Research Triangle Park, N. C.

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TABLE 1. METEOROLOGICAL & GASOLINE VOLUME DATA

Sample Date	Wind Speed (mph)	Wind Direction	Relative Humidity (%)	Temp. (°C)	Sampling Configuration	Average Gasoline Volume Pumped (gal)
02/07	9.0	NE	41	4	Perpendicular	10.6
02/11	6.5	SW	30	13	Reverse Parallel	9.1
02/20	4.5	SE	69	14	Parallel	8.9
02/26	3.0	NE	77	16	Perpendicular	10.2

TABLE 2. AVERAGE EMISSIONS UNDER PARALLEL WIND CONDITION

	Total NMOC (ppm C)	benzene (ppm C)
EP	6,313 ± 1877	63 ± 21
BZA	110 ± 26	1.4 ± 0.4
BZB	108 ± 27	1.4 ± 0.5
PS5	47 ± 20	0.56 ± 0.3
PS7	36 ± 18	0.40 ± 0.3
PS9	24 ± 12	0.36 ± 0.2

TABLE 3. BREATHING ZONE CONCENTRATION AS FUNCTION OF WIND DIRECTION

Wind	NMOC (ppm C)
parallel (4.5 mph)	109 ± 27
perpendicular (9.0 mph)	9.2 ± 12.4
reverse parallel (6.5 mph)	0.33 ± 0.1

TABLE 4A. COMPOSITION OF BREATHING ZONE VAPORS

	Volume %				
	Aromatic	Benzene	Toluene	Olefinic	Paraffinic
Vapor	5.6	1.2	1.3	13.9	80.5
Fuel	48	2.0	7.3	7	45

TABLE 4B. BREATHING ZONE FRACTION $\geq C_6$

Vapor	.186
Fuel	.874

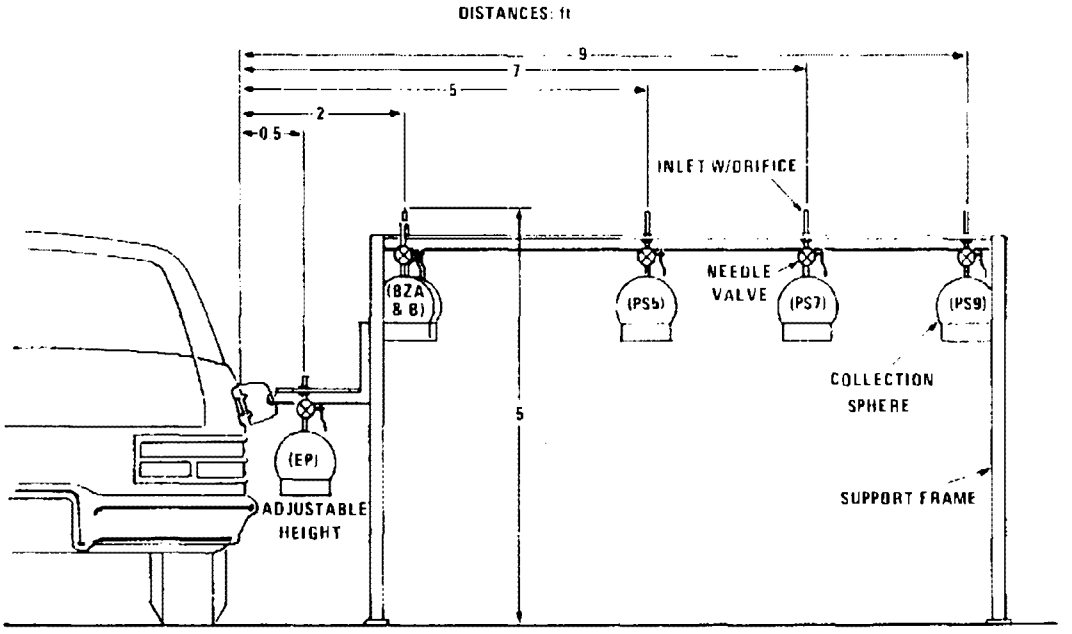

Figure 1. Selected sampling points.

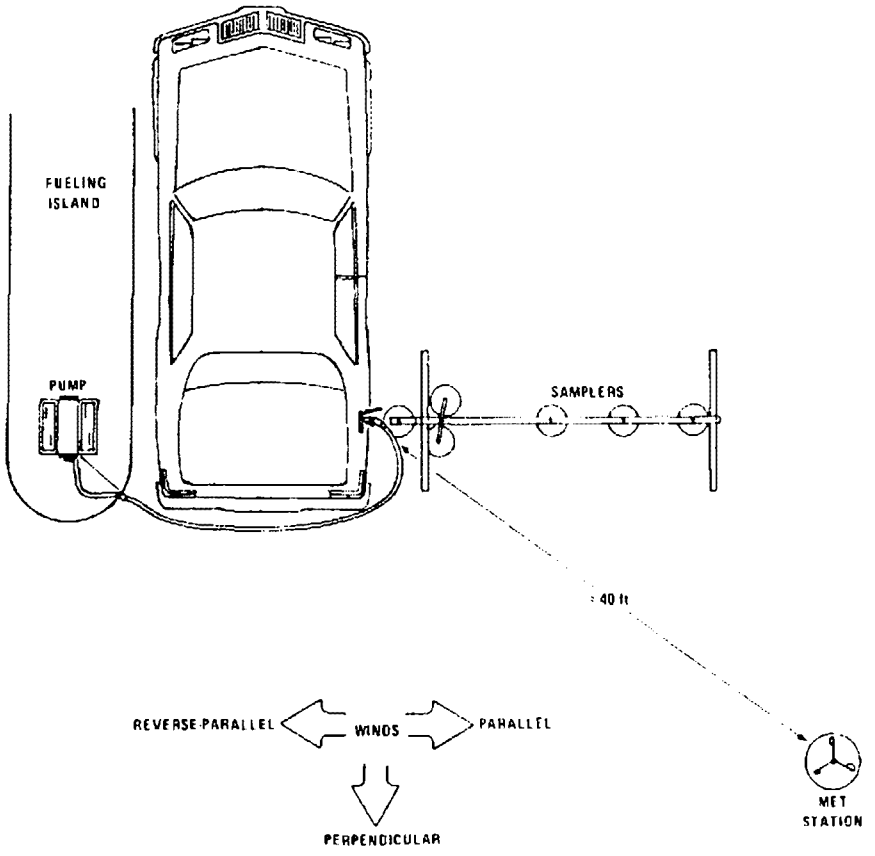

Figure 2. Wind directions during sampling.

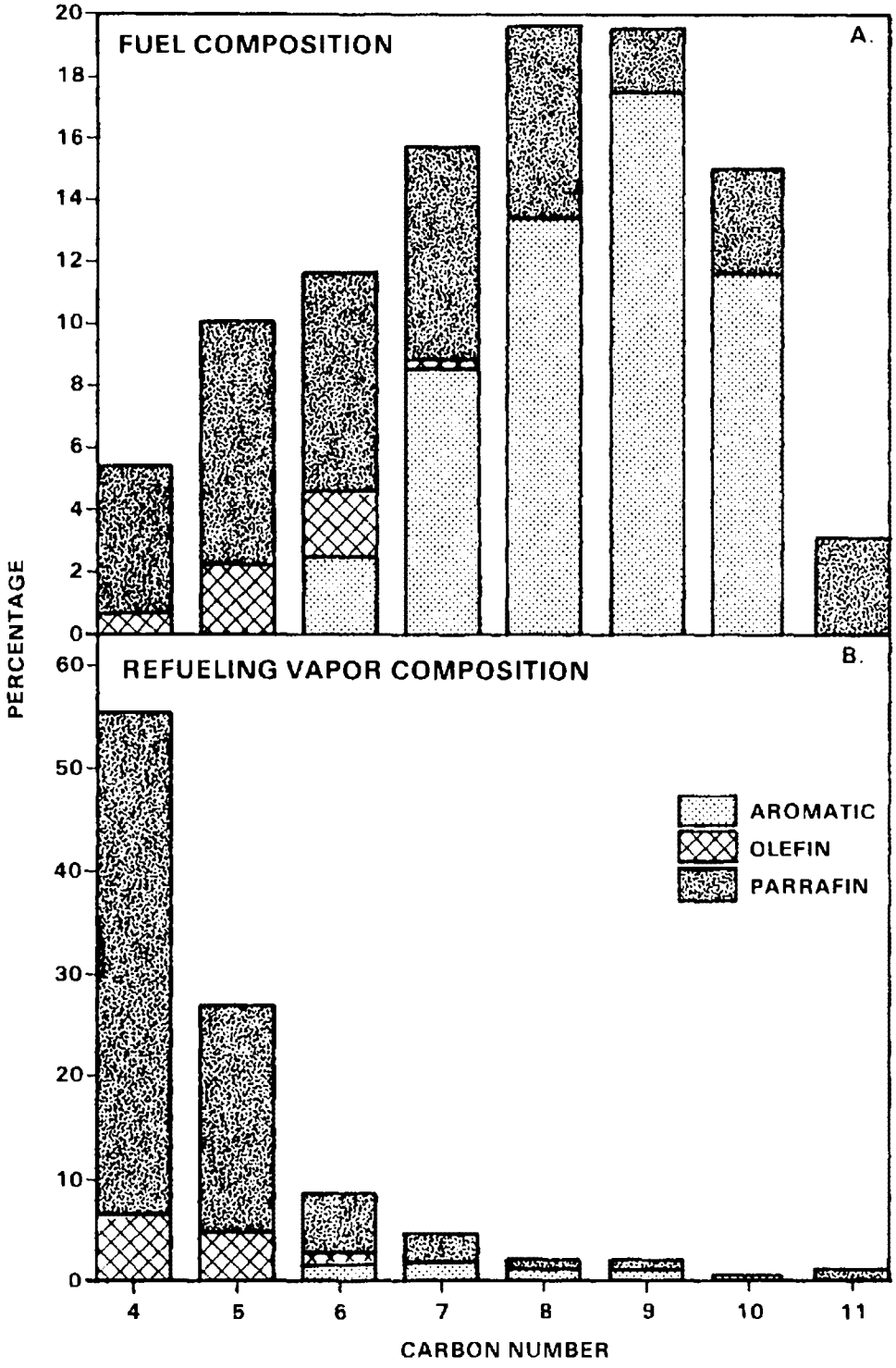

Figure 3. Fuel and vapor composition.

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PART 2 OF 2

COMPUTER ASSISTED INTERPRETATION OF GAS CHROMATOGRAPHY/MASS SPECTRAL DATA FROM COMPLEX MIXTURES

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The analytical method of choice for determining the composition of complex mixtures, as observed in the EPA's air quality monitoring program, is gas chromatography/mass spectrometry (GC/MS). With this method it is possible to observe very large numbers of components in a sample. The gas chromatography retention data and the mass spectral data contain information which can be used to identify the specific agents present in mixtures. A number of methods of pattern recognition are used in the interpretation of GC/MS data. In this report, these methods are reviewed. Also, methods are being developed at the University of Illinois at Chicago for interpretation of air quality monitoring data. These techniques involve the use of computational methods of pattern recognition for the interpretation of mass spectral data. As part of data interpretation, molecular modelling and computer graphics methods are used to develop parameters which can be used to predict the gas chromatographic retention data for analytes.

Pattern recognition, as applied to GC/MS data, is the process of comparing the spectra of unknown (test) compounds with those of known (training) compounds with the objective to identify the test compounds. Visual inspection of spectra by a trained mass spectrometrist is the most reliable method of pattern recognition but it is also the most inefficient and time consuming. With the large volumes of data generated by the air quality monitoring program, there are advantage to applying methods of artificial intelligence to the problem of mass spectral interpretation.

There are two general types of pattern recognition: 1) syntactic and 2) computational. In the former case, grammatical rules are applied to match test spectra with training data. In the latter

case mathematical functions are derived from the training data which describe the spectral differences between chemical classes or the variation in the data of specific classes. These rules are then used to identify test compounds. Syntactic methods of pattern recognition are extensively used in mass spectral interpretation and form the basis for searching algorithms (1). In order to be effective, syntatic methods require that very large data bases of reference spectra be available for searching and matching. Most data bases resident on mass spectrometers contain 30,000-60,000 spectra. Syntactic methods are most useful with instruments that are general purpose machines.

Computational methods have only recently been used in mass spectral interpretation (2,3). Such methods are generally applicable to cases in which the number of chemical types and substances of interest is small and limited. This could be the case in which a spectrometer is dedicated to a very specific task. Large data bases are not necessary here so it is possible to limit the reference data to those of specific interest. Computational methods have advantages in this case. Data can be transferred from the instrument to a small desk top computer where the necessary calculations and interpretation can be done thereby freeing the instrument for data acquisition.

Examples of computational methods of pattern recognition are class discrimination or hyperplane methods such as linear discriminant analysis (LDA), distance methods such as k-nearest neighbor (kNN), and class modelling methods such as SIMCA. In this work SIMCA and kNN methods are applied.

A typical gas chromatogram of an air quality field sample is given in Figure 1. This sample contains a large number of components, some of which are potential health hazards. Approximately 80 compounds are in this category and interpretation of the mass spectral data associated with the chromatogram involves determining the presence or absence of the toxic agents. The list of potentially toxic air pollutants has been published (3) and are given in Table I. These are low molecular weight aromatic hydrocarbons and halocarbons. Due to the structural similarity of the reference substances, this classification problem is particularly suited for computational pattern recognition.

The reference compounds were initially grouped into 3 classes by chemical type: 1) nonhalogenated aromatics, 2) chlorocarbons, and 3) bromo- and bromochlorocarbons. These classses are referred to as the training data. In addition two standards and tetrahydrofuran and dioxane were included as uncatagorized agents. The mass spectral data were obtained from the NIH/EPA library resident on the mass spectrometer.

The initial application of SIMCA to the mass spectral data for the training sets was of only limited success. It has been published that mass spectral ion intensity data is not appropriate for computational pattern recognition (4,5) and that the autocorrelation transform of the mass spectrum should be used. This tranform converts the ion intensities to frequency of loss of fragments as shown in Figure 2 which compares the mass spectrum of 1,2,3-trichloropropane. The high values of the transform at 35, 36, 37 and 38 indicate a high frequency of loss

of ^{35}Cl, ^{37}Cl and the corresponding hydrochlorides. The coefficient at 2 indicates the occurrence of peaks 2 mass units apart. The transform is typical of a chlorocarbon.

After transformation of the mass spectral data and applying SIMCA to the training sets, class models were derived for the three classes. These class models correctly classified 93% of the training set data. In order to be correctly classified, it was necessary that a reference compound be predicted to be a member of its class and a nonmember of the two other classes. With this significant classification outcome, it was decided to test the approach on calibration data used in the monitoring process.

SIMCA pattern recognition, being a class modelling method, can only identify compounds according to chemical class. In order to assign a structure to a compound it is necessary to use another method. Once a class assignment is obtained for an unknown the kNN method was used to determine the 3-nearest neighbors to the unknown in the appropriate training set. The kNN calculation was carried out on the autocorrelation spectra. This provided ranked possibilities for a structure assignment. To confirm a structure assignment, the normalized correlation coefficient was calculated for the unknown with its 3-nearest neighbors. This calculation was done on the mass spectral data, i.e. in mass intensity space. The normalized correlation coefficient is the cosine of the angle between the unknown and the reference vector. As the two vectors become identical the cosine of the angle between the two approaches 1. Therefore, correlation coefficients > 0.9 indicate that two spectra are very similar.

It is possible to observe compounds with very similar autocorrelation spectra but very different mass spectra. This would lead to an inconclusive assignment of structure in the first step of the classification procedure. Therefore, a feedback correction loop was necessary. If an inconclusive classification result is obtained from the correlation coefficient, the 3-nearest neighbors in the next closest class were calculated and the procedure continued. In most cases this will lead to the correct classification.

TABLE I

Compounds on the Air Quality Monitoring List

Compound	Class*	Name
1.	0	1-FLUOROTOLUENE (STANDARD)
2.	0	1-FLUORO-2-IODO BENZENE (STANDARD)
3.	1	1,4-DIMETHYLBENZENE
4.	1	1,3,5-TRIMETHYLBENZENE
5.	1	(1-METHYLETHYL) BENZENE
6.	1	BUTYL BENZENE
7.	1	1-METHYL-4-(1-METHYLETHYL) BENZENE
8.	2	1,2-DICHLOROBENZENE
9.	2	1,4-DICHLOROBENZENE
10.	2	1-CHLORO-2-METHYL BENZENE
11.	2	1-CHLORO-4-METHYL BENZENE
12.	2	1-ETHYENYL-4-CHLORO BENZENE
13.	2	1,1-DICHLOROETHANE
14.	2	1,1,1,2-TETRACHLORETHANE

15.	2	1,2,3-TRICHRLORPROPANE
16.	2	3-CHLORO-1-PROPENE
17.	2	2-CHLOROBUTANE
18.	2	1,3-DICHLOROBUTANE
19.	2	1,4-DICHLOROBUTANE
20.	2	1,4-DICHLORO-2-BUTENE (CIS)
21.	2	3,4-DICHLORO-1-BUTENE
22.	0	1,4-DIOXANE
23.	2	1-CHLORO-2,3-EPOXYPROPANE
24.	2	2-CHLOROETHOXYETHENE
25.	1	1-PHENYLETHANONE (ACETOPHENONE)
26.	1	BENZONITRILE
27.	1	BENZENE
28.	1	METHYLBENZENE (TOLUENE)
29.	1	1,2-DIMETHYLBENZENE
30.	1	1,3-DIMETHYLBENZENE
31.	1	ETHYLBENZENE
32.	1	ETHENYLBENZENE (STYRENE)
33.	2	CHLOROBENZENE
34.	3	BROMOBENZENE
35.	2	1,3-DICHLOROBENZENE
36.	2	1-CHLORO-3-METHYL BENZENE
37.	2	TRICHLOROMETHANE (CHLOROFORM)
38.	2	TETRACHLOROMETHANE (CARBON TETRA-CHLORIDE
39.	3	BROMOCHLOROMETHANE
40.	3	BROMOTRICHLOROMETHANE
41.	3	DIBROMOMETHANE
42.	3	TRIBROMOMETHANE
43.	2	1,2-DICHLOROETHANE
44.	2	1,1,1-TRICHLORETHANE
45.	2	1,1,2-TRICHLOROETHANE
46.	2	1,1,2,2-TETRACHLOROETHANE
47.	2	PENTACHLOROETHANE
48.	2	1,1-DICHLOROETHANE
49.	2	TRICHLOROETHANE
50.	2	TETRACHLOROETHANE
51.	3	BROMOETHANE
52.	3	1,2-DIBROMOETHANE
53.	2	1-CHLOROPROPANE
54.	2	2-CHLOROPROPANE
55.	2	1,2-DICHLOROPROPANE
56.	2	1,3-DICHLOROPROPANE
57.	3	1-BROMO-3-CHLOROPROPANE
58.	3	1,2-DIBROMOPROPANE
59.	2	2,3-DICHLOROBUTANE
60.	0	TETRAHYDROFURAN
61.	1	BENZALDEHYDE
62.	3	1-BROMO-2-CHLOROETHANE
63.	3	2,2-DIBROMOPROPANE
64.	3	2-BROMO-1-PROPENE
65.	3	2-BROMPROPANE
66.	3	3-BROMO-1-PROPENE
67.	3	1-BROMOPROPANE
68.	2	1-CHLOROBUTANE
69.	3	1-BROMO-2-CHLOROETHANE
70.	3	BROMODICHLOROMETHANE
71.	3	1-BROMOBUTANE
72.	2	2,2-DICHLOROBUTANE
73.	3	DIBROMOCHLOROMETHANE

74.	2	1,1,2-TRICHLOROPROPANE
75.	3	1,3-DIBROMOPROPANE
76.	2	1,1,1,2-TETRACHLORPROPANE
77.	2	1,2,2,3-TETRACHLOROPROPANE
78.	3	1,3-DIBROMOBUTANE
79.	2	1,1,2,3-TETRACHLOROPROPANE
80.	3	1,4-DIBROMOBUTANE

* Class 0 = standard; class 1 = nonhalogenated aromatic; class 2 = alkyl- or aryl chloride; class 3 = bromo- or bromochloro carbon

TABLE II

Summary of classification results

Sample	Correct/Total
85II025	28/35
85II052	25/26
85II072	14/18
Total	67/79 (85%)

A hierarchical classification scheme results which is shown in Figure 3. To test the approach, the scheme was applied to data used in the calibration of the air monitoring mass spectrometer. Since these data were obtained on a different instrument from the library data, this is a more difficult test.

A summary of the results is given in Table II. At this point the results are very good. It was not possible to achieve 100% correct classification results and to expect to do so would be unreasonable. The difficulties with the approach appear to be the result of assumptions made about the data. One difficulty arises from instrument variability. The reference data were obtained from the NIH/EPA library while the calibration data were obtained on the EPA monitoring instrument. It is very difficult to precisely reproduce the spectrum of a compound on a different instrument. Also, it is assumed that the unknown compounds are resolved and that the mass spectra are of the pure substance. In a number of cases, mass spectra of the unknowns contain ions from coeluting or otherwise contaminating compounds. An example is shown in Figure 4 in which the mass spectrum of 1,2-dibromoethane is compared with that of the same compound as observed in the calibration data. The calibration sample bears little resemblence to that of the reference and an identification in this case would be impossible. Even in view of these limitations it is felt that the approach can be used advantageously as an aid to mass spectral interpretation and efforts are underway to apply the technique to field data.

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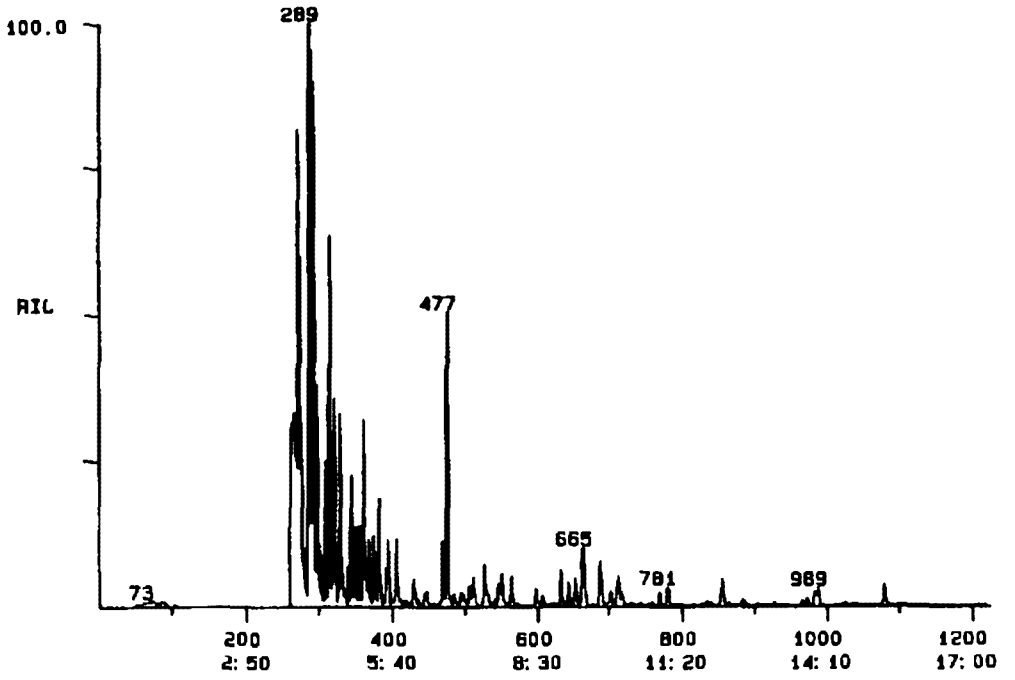

Figure 1. Reconstructed ion chromatogram of an air quality field sample.

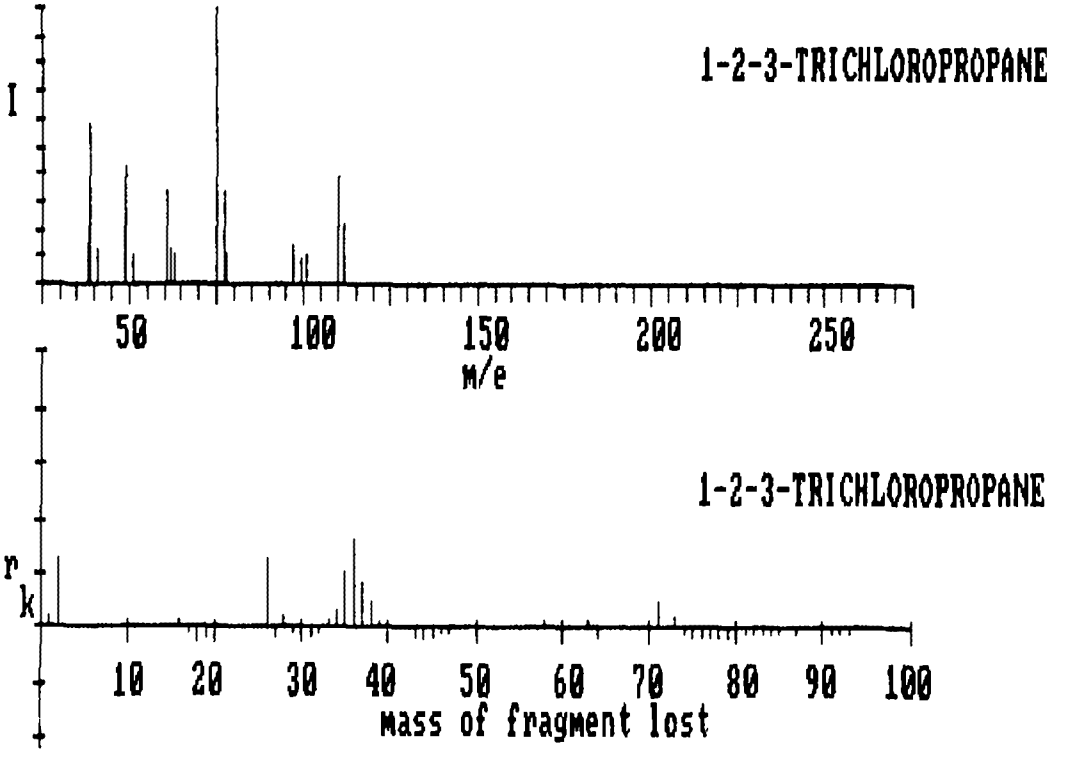

Figure 2. Mass and autocorrelation spectra of 1,2,3-trichloropropane.

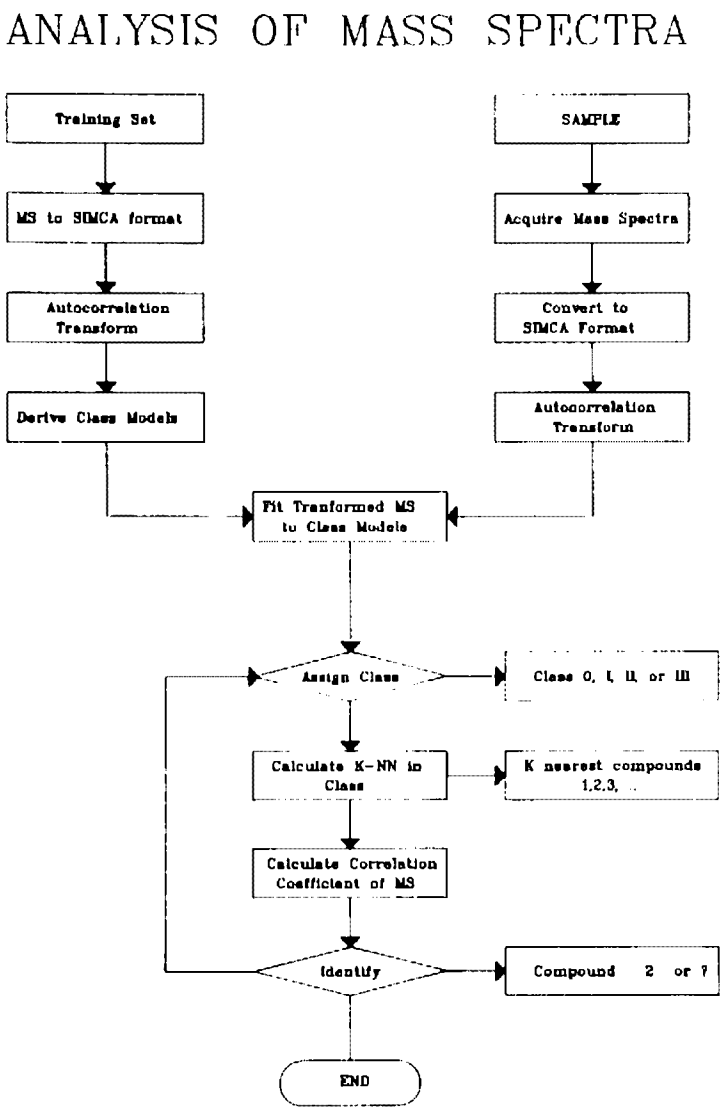

Figure 3. Flowchart of hierarchial classification scheme.

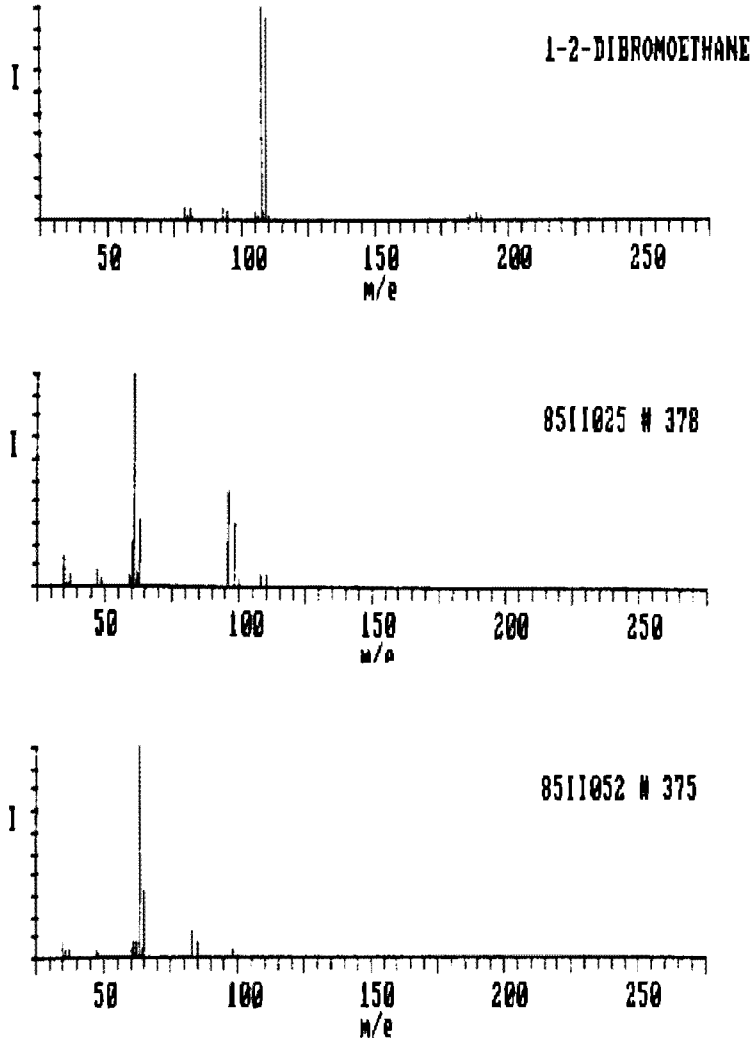

Figure 4. Library and calibration mass spectra of 1,2-dibromoethane.

APPLICATIONS OF INFORMATION THEORY AND PATTERN RECOGNITION TO GAS CHROMATOGRAPHY-MASS SPECTROMETRIC ANALYSIS OF TOXIC ORGANIC COMPOUNDS IN AMBIENT AIR

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The number of information channels contained in the gas chromatographic, mass spectrometric, and combined gas chromatography-mass spectrometric analysis of 78 toxic organic compounds has been determined. The toxic compounds are those routinely monitored in ambient air samples using Tenax collection and gas chromatography-mass spectrometric analysis. The Shannon information content of the binary encoded and full intensity mass spectra, of the gas chromatographic retention times, and of the combined gas chromatographic-mass spectrometric spectra of the 78 compounds has been calculated. The maximum binary information contents of the 35 channel gas chromatographic, 17 key channel mass spectral, and the 595 channel gas chromatographic-mass spectral methods were 6.4, 15.4, and <21.8 bits, respectively. The 17 masses with the highest binary information content with regard to the 78 compounds were used with SIMCA pattern recognition to determine four classes among the 78 compounds. These included aromatics without chlorine substitution, chloroaromatics, bromoalkanes and alkenes, and chloroalkanes and alkenes. Alkenes and alkanes with both chloro- and bromo substitution were classified as bromo compounds. The principal component models generally consisted of only one component per class, with five masses per class. However, the total alkene and alkane class had two components with twelve masses. Classification accuracy was 96% for the total aromatics and total alkanes and alkenes and 82% for the four subclasses. The pattern recognition study was performed on a commercially available microcomputer with a 64 k CPU. The information content of gas chromatography, mass spectrometry, and gas chromatography-mass spectrometry in general and with regard to this analytical problem is discussed.

APPLICATIONS OF INFORMATION THEORY AND PATTERN RECOGNITION TO GAS CHROMATOGRAPHY-MASS SPECTROMETRIC ANALYSIS OF TOXIC ORGANIC COMPOUNDS IN AMBIENT AIR

INTRODUCTION

At the present time the most commonly used analytical procedure for the determination of volatile organic compounds in ambient air is gas chromatography-mass spectrometry. This is due to its high selectivity, sensitivity, and applicability to a very large number of compounds. The present study is concerned with the development of methods for efficient extraction of information regarding chemical class identification from data obtained during routine gas chromatographic-mass spectrometric analyses. The pattern recognition techniques are empirical in nature and therefore do not require any expert knowledge regarding the mass spectra of the classes. The development of such methods would allow retrospective analysis of routine data files for determining the presence or absence of defined chemical classes of interest. The determination of the classes could be done on a small microcomputer without additional analytical costs and does not have to be confined to the compounds originally sought. Such information may be of interest in survey studies of health hazards and in preliminary scans of mass spectral data files before detailed interpretation is accomplished.

A set of 78 toxic organic compounds was chosen from those ca. 100 compounds presently routinely sought in ambient air samples. The set of 78 toxic compounds investigated contained primarily aromatic compounds, haloalkanes, and haloalkenes together with an additional four ethers and epoxides. Approximately 80% of these compounds contain chloro and/or bromo groups. All alkanes and alkenes contained at least one halogen. Shannon information theory and SIMCA pattern recognition were used. The Shannon information contents of the gas chromatographic, mass spectrometric, and the combined gas chromatography-mass spectrometric methods for the identification of the set of 78 compounds also were determined.

THEORETICAL BACKGROUND

Shannon Information Theory

The Shannon information content of a message (1) is related to the reduction in uncertainty gained by the receiver of the message. The information content will depend on the probability of occurrence of the symbols used, correlation between the symbols, encoding and decoding errors, and other uncertainties due to random errors. After chemical analysis the uncertainty with regard to the presence of certain species in the sample is reduced. Therefore the analysis produces a certain amount of Shannon information concerning the sample. In low resolution mass spectrometry the message is equated to the mass spectrum itself. The symbols are the intensities at a given unit mass channel. Neglecting errors, the information content per mass channel, I(j), is given by

$$I(j) = -\sum_{i=1}^{m} p_j(i) \log p_j(i)$$

where m is the number of discrete intensity values available for mass channel j. The probabilities of occurrence of a mass intensity, $p_j(i)$, are calculated over the entire set of reference spectra. The total information

content of a given mass spectrum is the sum of the information contents of the individual channels, if correlation between masses is neglected. Since correlation between masses is well known in mass spectra, this information content should be regarded as an upper limit to the true information content. This formula can also be used to calculate the informational contents of gas chromatography channels (retention time data) and of gas chromatography-mass spectral channels if the distribution of the data representations over the respective channels and compounds are known.

In the case of binary data the Shannon information content can be calculated from a simplified formula. For example with binary encoded spectra there are only two possibilities for the intensity of a mass peak, 1 or 0, corresponding to the presence or absence of the peak above a threshold level. Therefore the information content for mass channel j can be calculated from

$$I(j) = -p_j \log p_j - (1-p_j)\log (1-p_j).$$

Here p_j is the probability of a peak occurring at the mass channel j calculated over the set of mass spectra of the 78 compounds. In the case of the gas chromatography data the binary data corresponds to the presence or absence of a peak in a given channel. In the combined gas chromatography-mass spectral channels the binary data corresponds to the presence or absence of a compound-mass spectral peak in that channel. If the logarithm used is to the base two, then the information content is expressed in bits. The maximum information content per channel for the binary case is one bit and occurs at a probability of 0.5. Nonoccupied channels and those with probabilities of 1.0 contribute no information content.

SIMCA Pattern Recognition

The SIMCA (Soft Independent Modeling of Class Analogy) pattern recognition techniques were developed by Wold and coworkers and have been described in the literature (2,3). The statistical pattern recognition techniques are based on disjoint principal component models for classification of objects. The SIMCA class models are bilinear projection models obtained by decomposing the class data matrix (X) into a score matrix (T) (n x F), a loading matrix (P) (F x p) and a residual matrix (E) (2).

$$(X) = 1 \cdot \bar{x} + (T)\ (P) + (E) \qquad (1)$$

The row vector $\bar{x}$ is composed of all the averages of the variables in the class data matrix. The n x F score matrix (T) describes the projection of the n object points down on the F dimensional hyperplane defined by the F x p loading matrix (P). The residual matrix (E) contains that part of the data matrix due to measurement and modeling errors. If the residuals in (E) are small compared with the variation in (X), then the model is a good representation of (X). When F is two or three, the columns in the score matrix (T) can be plotted against each other to get two dimensional pictures of the objects in hyperspace (measurement space). The modeling power, i.e. the reduction of variance, for a given variable can be used as a measure of its relevance to the class model. Judicious use of the variable loadings and modeling powers obtained in preliminary analyses of the data allows one to polish the model and remove variables which are not significant to the class.

The number of principal components determined and retained for a particular class model is an important consideration. Within the SIMCA

procedures the process of cross validation (4) is used to determine the number of statistically significant principal components for a given class. In this process subsets of the training set of objects are used to fit a class model with one principal component. The objects not used in determining this class model are then fitted to the model, and the sum of squared residuals for the withheld objects is calculated. This is repeated until all of the objects in the training set have been withheld from the model fitting. The overall sum of squared residuals is then calculated for all the withheld objects for this particular model. The entire process is repeated with a class model containing an additional principal component. Addition of principal components to the model is continued until comparison of the sums of squared residuals for the previous and present model show no improvement. Generally, if the number of principal components for a given class model is much smaller than the number of either objects or variables for the class; then the model will be statistically stable.

Once the class models have been determined, objects are classified by fitting their data to the various class models. A standard deviation for each model is calculated from the residuals. This represents a class tolerance level around the principal component model in measurement space. The standard deviations for the objects are calculated from the residuals, and the objects are classified based upon their distances from the class models.

EXPERIMENTAL

Data Set

The low resolution mass spectra of the 78 compounds were obtained from the EPA-NIH Mass Spectral Library on an INCOS data system. A typical spectrum contained approximately 16 peaks. The range of mass/charge ratios was from 35 to 256 with 151 different peaks occurring in the total set. For the full intensity data the intensities were scaled to give a maximum of one for the base peak. The data were also binary encoded by assigning an intensity of one to any peak over the threshold level, which was 1% of the base peak intensity. A list of individual compounds in the set is given in Table I. The retention times were determined on a 50 meter, open tubular, SE 30 wall coated column relative to perfluorotoluene and 1-fluoro-2-iodobenzene internal standards.

Hardware and Software

In this study an Osborne 1 microcomputer (Z80A) with a CP/M operating system and 64 k memory was used. This amount of memory is sufficient to handle a data matrix of size 50 objects by 50 variables. The SIMCA 3B software package was obtained from Principal Data Components, Columbia, Mo.

Data Analysis

The information content of the 151 different nonzero intensity mass channels was calculated from the distribution of the binary encoded mass spectra of the set of 78 compounds using the formulas given above. The full intensity mass spectra of the data set were encoded into ten discrete levels above the threshold level, and the information content for the mass channels also was calculated using this distribution. No correction was made to account for encoding errors or for correlation between mass channels. In the case of the gas chromatography analysis, the width of a channel was determined from the reproducibility (three standard deviations = ca. 0.35 min.) of the relative retention times. The total number of channels was

calculated from the channel width and the time spread from the first and last compounds eluted. The binary information content of the retention times was calculated from their distribution over these channels. The number of combined gas chromatographic-mass spectral channels was limited by using only the 17 most informative mass channels and combining these with the gas chromatographic channels as determined previously. The binary information content of the distribution of the compound occurrence-mass spectral peaks over these channels was then calculated. Since no corrections were made for correlation or for residual errors, the calculated information contents should represent upper limits to the true values.

The class modeling and object classification were performed with the SIMCA 3B software. The data were preprocessed by binary encoding of only those 17 mass channels selected after calculation of the Shannon information content. All data were class scaled. The training sets for each of the classes were selected after investigating the inherent structure of the data set. All objects in a given class were used for the training sets, except for bromobenzene which was only used in the total aromatic training set. The numbers of compounds used in the training sets for the classes were 23 for total aromatics; 51 for total alkanes and alkenes; 8 for chloroaromatics; 14 for nonhaloaromatics; 21 for bromo-alkanes and -alkenes; and 30 for chloroalkanes and -alkenes. Cross validation was used to determine the minimum number of statistically significant components for each class model. Variables with modeling powers less than 0.18 for the principal component models were deleted in the initial stages of the refinement of the class models.

RESULTS AND DISCUSSION

Pattern Recognition of Classes from Mass Spectra

The binary encoded mass spectra of the 78 compounds yielded information contents per channel of 0.10 to 1.00 bit with the higher information at mass channels below 107. Of the channels from 107 and below, 70% had 0.5 bit or greater information. Of the channels greater than 107, only 7.4% had 0.5 bit or greater information content. The information content for the full intensity spectra of the 78 compounds ranged from 0.10 to 2.29 bit with no channels above 107 exceeding 1.02 bit. In general the information contents of the binary and full intensity mass spectra show a linear correlation up to a binary information content of ca. 0.9 bit. Even in the case of the higher information channels there is good qualitative agreement as shown in Table II where the 17 mass channels with the highest binary spectral information content are compared with those from the full intensity spectra.

Table II also contains the information content of the same masses evaluated for a set of 9600 binary mass spectra (5). Comparison of the information content of these 17 mass channels for the binary spectra of the 78 compounds with those found for the set of 9600 compounds also shows a good correlation. The 17 highest information mass channels for the set of 78 compounds yielded 0.80 to 1.00 bit with a median of 0.92 bit, while the same mass channels with the set of 9600 compounds gave 0.62 to 1.00 bit with a median of 0.91 bit. These channels have the highest information content, i.e. greater than 0.80 bit, for the binary encoded spectra with the exception of channel 39, which is not listed. This latter mass channel was not used since it is one of the most frequently occurring peaks in mass spectrometry (6). Thus it is clear that this set

of 17 most "informative" mass channels contains very much information not only with regard to the set of 78 compounds but also with regard to the much larger set of 9600 compounds.

It is well known that the information in a complete mass spectrum is highly redundant and that compressed binary encoded spectra retain a large portion of the information present in the complete spectrum (5,7,8). To solve the present pattern recognition problem on a microcomputer, the number of mass channels considered was reduced from 151 to the 17 channels listed in Table II. This set of binary encoded, 17 mass channel spectra, which will be designated hereafter as the compressed spectra, was used as the trial set of variables in the pattern recognition classification of the 78 compounds. The use of the compressed set of binary spectra caused nine pairs and one trio of compounds to have identical mass spectral representations.

The inherent structure of the data should determine the nature of the classes and not some preconceived scheme based on chemical training or intuition. For a preliminary overview of the data a two dimensional principal component plot of the 17 mass, full intensity data was constructed. Only 49 of the 78 compounds were considered in this plot due to limitations of the SIMCA program used. However, the compounds selected included representatives of all apparent chemical classes in the set. There was no class separation of any type visually apparent in the resulting plot. This result was not unexpected since it has been pointed out in previous studies (9,10) that untransformed mass spectral data should not be used for pattern recognition studies. An examination of the binary encoded, 17 mass data for the same 49 compounds in a two dimensional principal component plot gave the results shown in Figure 1. It is apparent from this plot that there is some basic separation of the compounds into at least three classes and probably four. In the lower right corner is a bromo substituted group of alkanes/alkenes including bromochloro substituted alkanes/alkenes. In the lower left corner is a group of nonhalogenated aromatic compounds. At the top center is a group of chloroalkanes/alkenes. Lying between and partially overlapping the latter two groups is a group of chloroaromatics.

It is clear that the compressed set of data contains enough information for useful classification of the 78 compounds. We have chosen to use two general classes: aromatics with 23 compounds and alkanes/alkenes with 51 compounds. For further detailed classification four subclasses were used: nonhalogenated aromatics with 14 compounds; chloroaromatics with 8 compounds; chloroalkanes/alkenes with 30 compounds; and bromoalkanes/alkenes with 21 compounds. The seven alkanes/alkenes with both chloro and bromo substituents were found during initial calculations to fit with the bromo alkaenes. The additional four compounds, the three ethers and one epoxide, were withheld from the training sets and used as test objects.

With the use of the variable modeling power and the compressed set of 17 mass spectra, it was found that only five masses were required for each refined class model except for the total alkanes/alkenes class. In the total alkanes/alkenes case 12 masses were required. The use of cross validation resulted in the refined models having only one principal component per model except for the total alkanes/alkenes model which had two. The model parameters including loadings are given in Reference 11. The unexplained variance ranged from a low of 19% for the chloroaromatic model to a high of 47% for the chloroalkane/alkene model. The residual standard deviations, which are a measure of the spatial extent of the models, ranged from 0.49 for the chloroaromatic model to 0.77 for the chloroalkane/alkene model.

After the class models were determined, the entire set of compressed spectra of the 78 compounds was run through all of the six models to determine classification accuracy. Compounds were considered as members of the class to which they were closest. In the case of the two major classes, aromatics and alkanes/alkenes; the training set accuracy was 91 and 98%, respectively, with an overall accuracy of 96%. Only 1 and 3% of the 74 compounds were incorrectly classified as members of the two classes. All of the four test set compounds, which do not properly belong to any of the classes, were classified as alkanes/alkenes, which is correct when interpreted as "not aromatic".

In the case of the four subclasses: nonhaloaromatics, chloroaromatics, bromoalkanes/alkenes, and chloroalkanes/alkenes; the training set accuracy was 79, 87, 86, and 80%, respectively. The overall accuracy was 82%. The number of compounds misidentified as members of the four classes were 3, 4, 3, and 8%, respectively. In this case bromobenzene was added to the four test set compounds. The two chlorosubstituted alkane/alkene type compounds were correctly classified. Bromobenzene was classified as a chloroaromatic which is the most suitable of the four possible classes. The two cyclic alkane ethers were classified as bromoalkane/alkenes, which if regarded as "alkane/alkene, but not chloroalkane/alkene", is correct within the available models.

It was also possible to construct a class model for chlorinated alkane/alkenes based upon the number of chloro groups present in a compound. A single principal component model using the five masses - 63, 65, 75, 77, 91- was found to be statistically valid for the class of mono- and dichloroalkane/alkenes, which did not include compounds substituted with both chloro and bromo groups. This model gave an unexplained variance of 42% for the 16 training set compounds with a residual standard deviation of 0.73. The loadings of the principal component were ca. 0.4-0.5 with mass 63 and 65 having negative loadings. The training set accuracy was only 62%, but the overall accuracy for 78 compounds was 91%. Only two compounds, both monochloromonobromoalkanes/alkenes, were misidentified as members of this class.

Information Content of Analytical Methods

The relative retention times of the 78 compounds on the SE-30 column and their reproducibility resulted in 45 discrete gas chromatography channels for this problem. No compounds were eluted in ten of these channels, so there were only 35 nonzero channels to consider. Since there were less than one-half as many channels as compounds, complete separation (one compound per channel) was not achieved with this column. Of the 35 channels 8.5% contained five compound peaks in each; 5.7% had four compound peaks; 17% had three compound peaks; 37% had two compound peaks; and 31% had only one compound peak. The zero-filled channels contribute no information content. The maximum information content of the 35 gas chromatography channels was 6.41 bits, which was obtained by summing the individual channel information contents.

In the case of the mass spectral channels only the 17 channels used in the pattern recognition study were considered in order to keep the calculations at a manageable size. The largest correlation coefficient among these mass channels was 0.75 between masses 81 and 93, and only four pairs of masses had correlation coefficients greater than 0.5. The maximum information content of these 17 mass spectral channels was 15.4 bits.

One would expect the number of channels available for the combined gas chromatography-mass spectral method to be the product of the two individual methods, i.e. 45 x 17 = 765. This is illustrated in Figure 2, where N =45 and M =17. The shaded areas are zero-filled channels. However, due to the ten zero-filled gas chromatography channels there is a general loss of 170 combined channels, leaving 595 channels. The maximum information content of the combined method can not exceed the sum of the information contents of the individual methods and can not be less than the smaller of the two methods. Therefore the maximum information content of the combined methods is less than 21.8 bits and, with much less certainty, greater than 6.4 bits.

The number of channels, the information contents for the three methods, and the maximum and actual number of compounds distinguishable are summarized in Table III. The maximum number of compounds distinguishable was calculated by using the maximum bits of information as a power of two to obtain the maximum number of different spectral representations. The actual number of compounds distinguished is the average number which is found to be different in a given method. Even though the theoretical maximum number of compounds which can be distinguished is 78 for gas chromatography to ca. four million for gas chromatography; the actual number is much less and only amounts to 76 for the combined gas chromatography-mass spectrometry method. Correlation and uncertainties remaining after analysis account for much of the difference, but some of the difference is due to excess capacity which is not relevant to this particular analysis problem.

CONCLUSIONS

Shannon information theory has been used in this study for selection of relevant variables in SIMCA pattern recognition studies of mass spectral data and as a quantitative measure of maximum information content of analytical methods for a specific problem. In the pattern recognition study of the 78 toxic compounds 151 different mass channels were compressed into 16 which were actually used in the different class models. The major classes found were nonhaloaromatic, chloroaromatic, bromoalkane/alkene, and chloroalkane/alkene compounds. A subclass of alkanes/alkenes containing one or two chlorosubstituents was also found. In all models except the all alkane/alkene model only one principal component containing five masses was found to be statistically significant. The accuracy was 96% for alkane/alkene vs. aromatic classification and 82% for classification into the four groups.

SIMCA pattern recognition is an empirical classification technique and does not require particular spectroscopic expertise for its application. Its successful application to the present problem on a microcomputer with limited memory should demonstrate to chemists the availability and power of the technique and the large amount of useful information in the low resolution mass spectra.

The numbers of channels and information content for a given method should not be confused with those relevant to the solution of a particular problem. As has been shown here the amount of maximum information for a given analytical method may be very large, but all of the capacity of the method may not be applicable to a specific analytical problem.

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TABLE I. COMPOUNDS INCLUDED IN THIS STUDY

1. p-xylene
2. 1,3,5-trimethylbenzene
3. isopropylbenzene
4. n-butylbenzene
5. 1-methyl-4-isopropylbenzene
6. o-dichlorobenzene
7. p-dichlorobenzene
8. 1-chloro-2-methylbenzene
9. 1-chloro-4-methylbenzene
10. p-chlorostyrene
11. 1,1-dichloroethane
12. 1,1,1,2-tetrachloroethane
13. 1,2,3-trichloropropane
14. 3-chloropropene
15. 2-chlorobutane
16. 1,3-dichlorobutane
17. 1,4-dichlorobutane
18. 1,4-dichloro-2-butene (cis)
19. 3,4-dichlorobutene
20. 1,4-dioxane
21. 1-chloro-2,3-epoxypropane
22. 2-chloroethoxyethene
23. acetophenone
24. benzonitrile
25. benzene
26. toluene
27. o-xylene
28. m-xylene
29. ethylbenzene
30. styrene
31. chlorobenzene
32. bromobenzene
33. m-dichlorobenzene
34. 1-chloro-3-methylbenzene
35. chloroform
36. carbon tetrachloride
37. bromochloromethane
38. bromotrichloromethane
39. dibromomethane
40. bromoform
41. 1,2-dichloroethane
42. 1,1,1-trichloroethane
43. 1,1,2-trichloroethane
44. 1,1,2,2-tetrachloroethane
45. pentachloroethane
46. 1,1-dichloroethene
47. trichloroethene
48. tetrachloroethene
49. bromoethane
50. 1,2-dibromoethane
51. 1-chloropropane
52. 2-chloropropane
53. 1,2-dichloropropane
54. 1,3-dichloropropane
55. 1-bromo-3-chloropropane
56. 1,2-dibromopropane
57. 2,3-dichlorobutane
58. tetrahydrofuran
59. benzaldehyde
60. 1-bromo-1-chloroethane
61. 2,2-dibromopropane
62. 2-bromopropene
63. 2-bromopropane
64. 3-bromopropene
65. 1-bromopropane
66. 1-chlorobutane
67. 1-bromo-2-chloroethane
68. bromodichloromethane
69. 1-bromobutane
70. 2,2-dichlorobutane
71. dibromochloromethane
72. 1,1,2-trichloropropane
73. 1,3-dibromopropane
74. 1,1,1,2-tetrachloropropane
75. 1,2,2,3-tetrachloropropane
76. 1,3-dibromobutane
77. 1,1,2,3-tetrachloropropane
78. 1,4-dibromobutane

TABLE II. 17 KEY MASSES WITH HIGHEST INFORMATION CONTENT FOR 78 TOXIC COMPOUNDS

MASS	INFORMATION CONTENT BINARY[a]	FULL[b] (BITS)	9600[c]	MASS	INFORMATION CONTENT BINARY	FULL (BITS)	9600
41	0.92	1.92	0.90	77	0.94	1.75	1.00
49	0.98	1.68	0.62	78	0.84	1.31	0.93
50	0.84	1.18	0.98	79	0.96	1.27	0.97
51	0.99	1.78	1.00	81	0.80	1.02	0.91
61	0.82	1.36	0.75	91	0.92	1.47	0.96
62	0.95	1.61	0.81	93	0.87	1.22	0.83
63	1.00	1.95	0.97	95	0.90	1.39	0.83
65	0.92	1.35	0.98	107	0.82	1.08	0.74
75	0.89	1.42	0.89				

a. Binary spectra of 78 compounds.
b. Full intensity spectra of 78 compounds.
c. Binary spectra of 9600 compounds, Reference 5.

TABLE III. GC, MS, GC-MS INFORMATION CONTENT FOR 78 COMPOUNDS USING 17 KEY MASSES

METHOD	CHANNELS TOTAL	NONZERO	MAXIMUM I (BIT)	CMPDS DISTINGUISHABLE MAXIMUM[a]	ACTUAL[b]
GC	45	35	6.4	78	27
MS	17	17	15.4	43000	60
GC-MS	765	595	< 21.8	< 3700000	76

a. The number obtained by raising two to the power of maximum I.
b. The number of different compounds actually distinguished by the method.

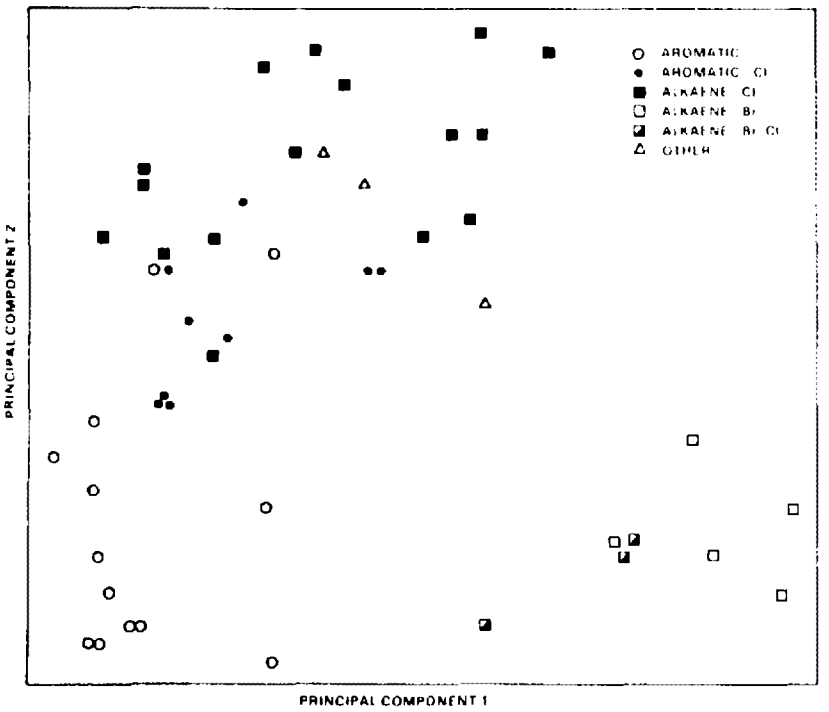

Figure 1. Principal component plot of 17 key mass spectra.

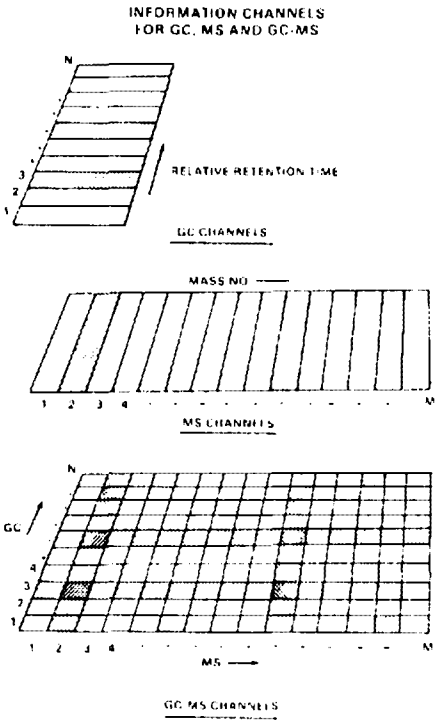

Figure 2. Combination of GC and MS channels.

USING THREE DIMENSIONAL GRAPHICS TO VISUALIZE MULTIVARIATE SCIENTIFIC DATA

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The two dimensional plot is unquestionably the most commonplace graphics tool of the scientist. Yet in dealing with problems often involving high dimensionality, more sophisticated representations (such as 3D) are only infrequently used.

In the work reported here, several real-world examples are used to illustrate the wide variety and the resultant interpretive potential possible through the use of three dimensional graphics. These examples are a study of climate data and of air pollution monitoring. Among the variety of 3D plots presented are discrete point plots; mesh-like surface plots showing either theoretical or empirical model behavior; and combinations of points and surfaces. Some of the many techniques available to enhance the utility of such graphics are shown.

USING THREE DIMENSIONAL GRAPHICS
TO VISUALIZE MULTIVARIATE SCIENTIFIC DATA

Climate Data Example

A better understanding of climate would yield many obvious practical benefits.[1] In a continuing study at the Lawrence Livermore National Laboratory of the possible climatic effects of greenhouse gases [2], particularly carbon dioxide, a large number of historical temperature records have been examined. To determine and isolate possible statistically significant changes in these climate records, "noise" inherent in these data must be characterized. Here, this noise will be estimated as the standard deviation of surface temperature (σ(T)), measured at a specific point over some extended time period. Because climatic changes of various types may be occurring, this estimate may, include multiple effects: eg. volcanic eruptions and even changes due to slow increases due to greenhouse gases. In more detailed studies, we may have to be more selective in our definition of "noise."

In the example given here we will examine the spatial distribution of the estimated σ(T) of monthly temperatures measured over the past century over the North American (NA) mainland. The data record used is one of the most complete gridded sets available.[3] We wish to examine the variation of the estimated standard deviation of temperature as a function of: (1) latitude, (2) longitude, and (3) month of the year.

In the following discussion a variety of 3D plotting techniques will be used to illustrate how these data can be graphically presented to better facilitate understanding. From these examples, it is hoped that the reader will gain a better appreciation for both the promise and the difficulties which arise in graphically showing abstract data using three dimensions.

Before showing these results using three dimensional plots, let us examine a simple, more conventional, two dimensional representation of the January distribution of σ(T) (Figure 1). Here, the numerical values for σ(T), in °C, are shown next to their spatial positions. These σ estimates are made using 100 successive January mean temperatures over the period: 1881–1980, placed on a regular $5^\circ \times 10^\circ$ grid.[3] Another common 2D representation is the contour plot, routinely produced by many software packages.

There are several very practical advantages to such plots. They are easily generated using widely available software, and one can certainly infer many of the important characteristics of the data from them. Because of the emphasis here on 3D plots, one should definitely not infer that plots such as Figure 1 are outmoded or, of little value! On the contrary, the contention here is that in conjunction with any and all such 2D representations, the three dimensional plot can convey a richer, deeper, and generally more profound understanding of the data.

Figure 2 shows these same data in a simple three dimensional plot with the vertical axis indicating the rms value of January temperatures and the lower plane, the geographical location over NA. In this first 3D representation, The points are drawn using two dimensional symbols. This representation is ambiguous since the relative positions of the points are difficult to sense, and consequently the plot is not readily interpretable. In the following series of plots, a variety of visual enhancements are used to illustrate a number of techniques that can substantially increase the utility of such plots.

Merely connecting the points in space with their location on the base plane results in a significant improvement in our ability to interpret these data (Figure 3). The locations of the points are now much clearer, and we can see immediately that the January σ(T)

increases markedly as we move away from the equator. Our understanding is further enhanced if the data points are shown as shaded three dimensional cubes and their locations on the base plane are further accented using tilted projections, as in Figure 4.

Probably the most significant improvement in our understanding of these data is achieved by changing our viewpoint relative to the data, as is shown in the four subplots of Figure 5. Here, we have "walked" around the scene and tilted it to show more clearly various aspects of the data. The increase in January temperature variability with latitude is particularly apparent, but now we can better sense another aspect of the variation, the increase in $\sigma(T)$ as we move inland, away from the moderating effects of the ocean, the continentality effect.

We have examined the variability of temperature for only the month of January. How does it change for different months of the year? Specifically, how does it vary between summer and winter over North America? Figure 6 shows the analagous plots for July seen from the same viewpoints and drawn with identical scaling to those of January (Figure 5). The striking difference between summer and winter is immediately evident. Both the increase of $\sigma(T)$ with latitude and with continentality have moderated considerably, and in July there is much less variability than in January.

In an attempt to quantify these spatial distributions for computational purposes, quadratic surfaces (in terms of latitude and longitude) were separately fit to these data for each month. The surface for January is shown in Figure 7. Both the quadratic surface (derived by linear least squares) and the actual data points are shown. Points above the surface are shown as open cubes, those below are shaded. Four different views of this surface (without the data points) are plotted in Figure 8. These points provide a better sense of the bowed nature of the surface. Finally, Figure 9 contrasts the January and July surfaces using superposition. The dramatic difference in $\sigma(T)$ between the two months is immediately evident. A capability for graphics software editing such as that used in Figure 9 is of great value in effectively manipulating such graphics.

At this juncture, it is worthwhile to emphasize several practical considerations. The necessity for real-time or near-real-time viewing of these plots should be apparent. The software producing such plots should ideally provide the user with considerable flexibility in the choice of options excercised, and these must be available in a "user-friendly" framework. The choice of the "best" viewpoint and the "best" combination of features to include is often both subjective and data dependent, and thus cannot generally be made, a priori. The challenge of three dimensional plotting is *judiciously* choosing from the wide range of enhancements available to facilitate our ability to derive informaion from such plots.

Spatial distributions of chemical pollutants

A second example, drawn from our air quality studies illustrates another application of three dimensional plotting. With virtually the same software used to generate the previous plots, other types of spatial distributions can be represented. The numerical results of computer simulation models can be directly used with such software to generate 3D plots showing the geographical distribution of a variety of variables: (1) terrain, (2) concentrations of various chemical species, (3) winds or mass fluxes. By combining a series of such "snapshots," at different times, all viewed from the same perspective and drawn with the same scaling, the evolution of different variables can be graphically followed in time.

In a numerical simulation of air pollution over the San Francisco Bay Area,[4] the concentrations of a variety of chemical species were calculated as a function of geographical

position (x, y) and of time. In this example, hourly concentrations were available for each of five species at 400 grid points over the San Francisco Bay Area. From the model, mass flux vectors at each grid point were also calculated as a function of time. The challenge is to represent these variables graphically in a manner that is both accurate and interpretable by both the specialist and the non-scientist.

Using a Gaussian random number generator to calculate displacements from each of the central grid points (in all three dimensions), a cloud of hundreds of discrete points can be generated that is spatially centered in 3D about each grid point. If, for a given species, the number of points comprising each cloud is made proportional to the concentration of that species at that gridpoint, a plot can be developed in which the spatial density of points is proportional to the calculated concentrations. By appropriately choosing the spreading parameters of the pollutant cloud (ie, the standard deviations of the displacements), a faithful rendition of the model predictions can be obtained. The use of contrasting colors in highlighting important features, for example, the coastline and the Bay, can be extremely valuable. The vertical exaggeration of terrain and of the cloud positioning can be interactively modified by the user until a meaningful representation is achieved. Coordinate axes and grids can be included if more quantitative locations are required.

Note that, in this case, both the vertical positioning and the vertical scaling of the pollution cloud are arbitrary. Here, the central vertical level chosen for each point corresponds to the terrain height at the grid point. This offset from the lower terrain was necessary because the graphics software that was available did not have a hidden line removal capability when drawing the cloud points. Thus, to avoid confusion, particularly when overprinting with color, this vertical offset was used.

As with the earlier examples, there are a wide variety of modifications that can be used to facilitate the interpretation of these graphics. Among these are: different viewpoints, cloud dispersion characteristics, offsets, scaling, colors, numbers of points, and connectors between surfaces. To facilitate the process of generation, the graphics software should provide the user with many "knobs and switches" that can be interactively manipulated to achieve the desired result. Since each application is likely to call for different characteristics, even within the same project, such user controls are virtually essential in providing the flexibility which is generally required. Equally vital is the capability for real-time or near-real-time viewing of any graphics generated.

Figure 10 shows the model prediction of the early morning (8 AM) distribution of ozone over the Bay Area. To aid in spatially locating "hot spots" of concentration for any species plotted, the software locates and then connects with the terrain, the desired N-highest grid point concentrations. These locations may be further highlighted using contrasting colors in both the cloud and on the projections to the lower surface. In Figure 10 this has been done for the 10 highest concentrations. Alternatively, it might be useful to highlight only specific locations, for example, to connect only those grid points over San Francisco.

Figure 11, shows additional snapshots of the ozone concentration, at three hour intervals. The increase in ozone during the day and the movement of the peak concentrations to the South Bay are evident. To facilitate these intercomparisons for the viewer, all plots should be drawn from the same perspective using the same scaling factors, particularly the proportionality factor relating the number of cloud points to concentration.

Once again, the choice of viewpoint can be important with such graphics. By rotating the perspective and viewing at a lower angle, a different sense of the distribution can be achieved (Figure 12). A continuous rotation capability would be highly desirable, but

the computing requirements needed in generating many thousands of 3D points in real time would tax most computing systems.

Many other refinements of these plots are possible, dictated by the desired application. More than a single chemical species can be followed by generating multiple point clouds at separate vertical levels (Figure 13). If the depiction of the wind field is important, wind vectors might also be included at other vertical positions (Figure 14). Particle trajectories, from point of origin to the time shown might also prove valuable. Software flexibility is essential since it is usually unlikely that all desired features would have been foreseen at the outset. Care in the application of these methods is also important since the user may be saturated by too much information appearing on a plot.

CONCLUSIONS

A variety of examples showing the practical utility of 3D plots in meteorological and pollution applications has been presented. Such graphics can be of great value in providing a more profound understanding of the results of experimental measurements or of model calculations, particularly to a broader non-scientific audience.

Today, computer technology is literally exploding before our very eyes. The area of computer graphics is achieving particularly impressive growth. Under such circumstances, it may be dangerous to predict the future, but I believe it can be safely said that we will be seeing far more routine use of three dimensional techniques as both increasing software and hardware availability place such tools in the hands of the working scientist/engineer.

Acknowledgment

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

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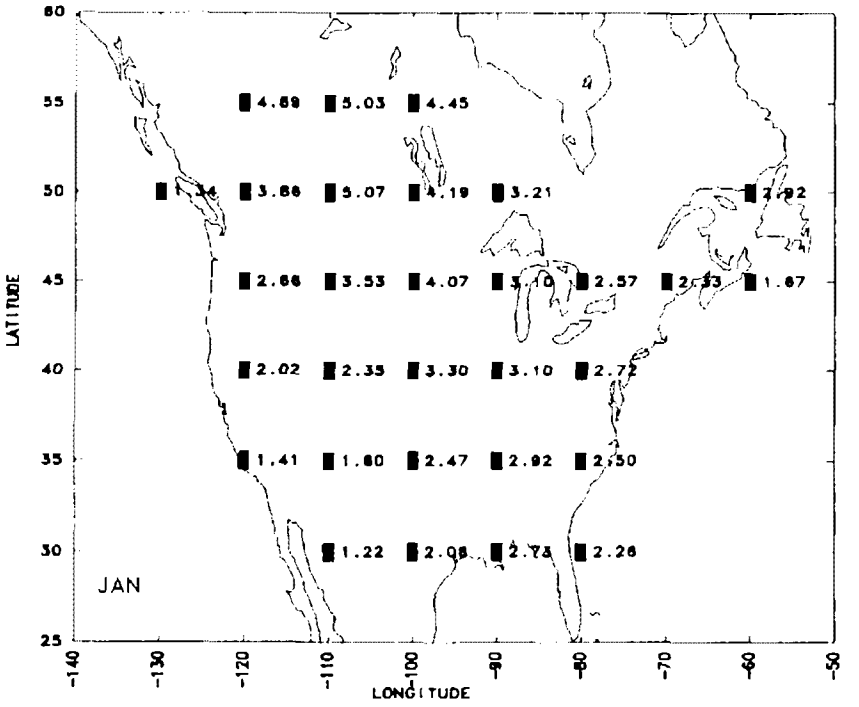

Figure 1. Spatial distribution of σ(T) for January over North America. (NA)

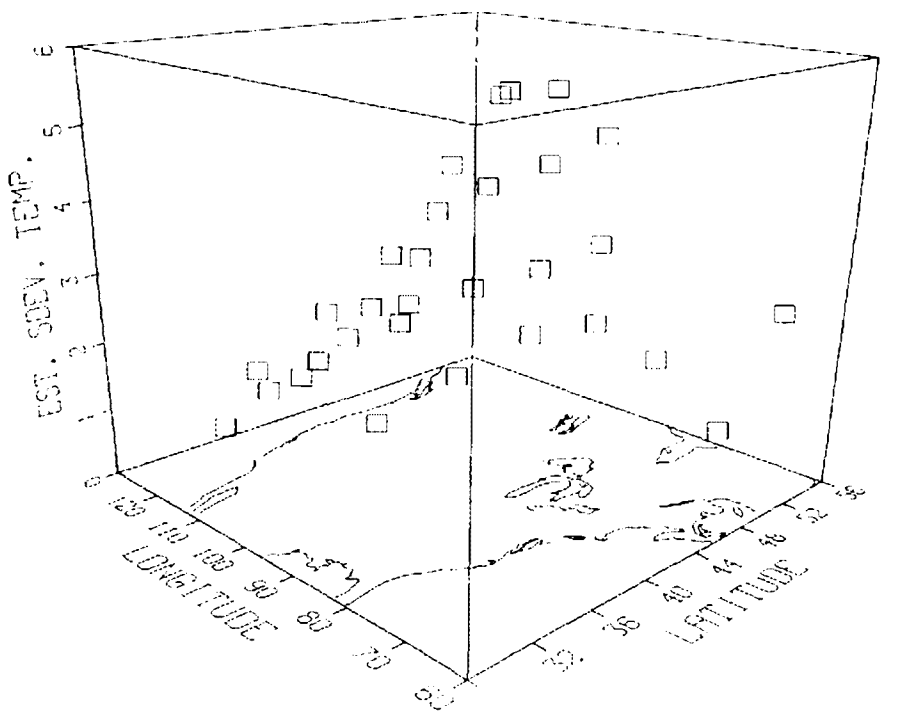

Figure 2. 3D distribution of σ(T) for January over NA using two dimensional symbols.

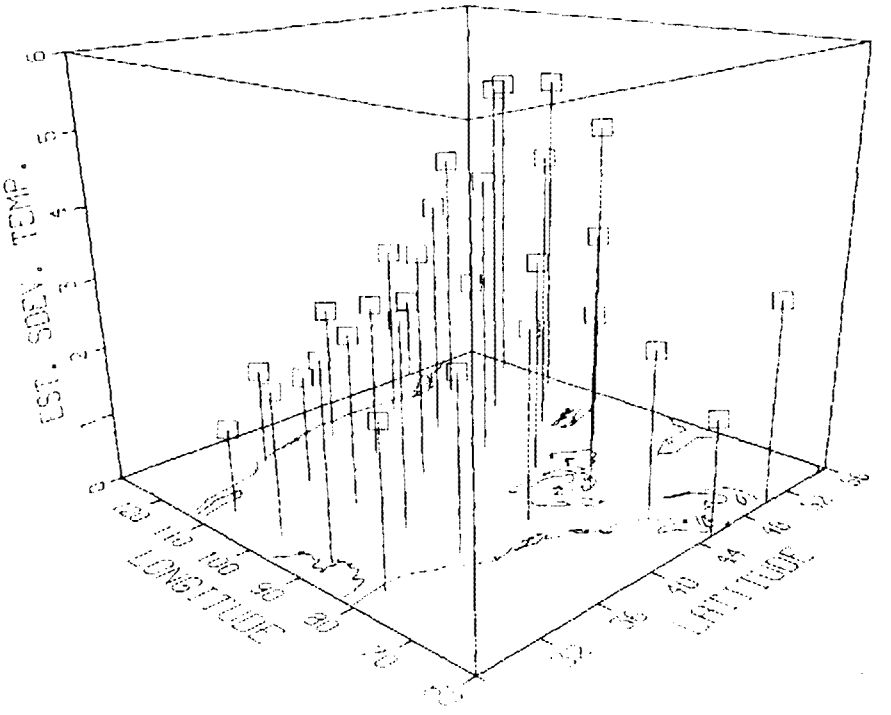

Figure 3. 3D distribution of $\sigma(T)$ for January over NA with 2D symbols and connectors to the lower surface.

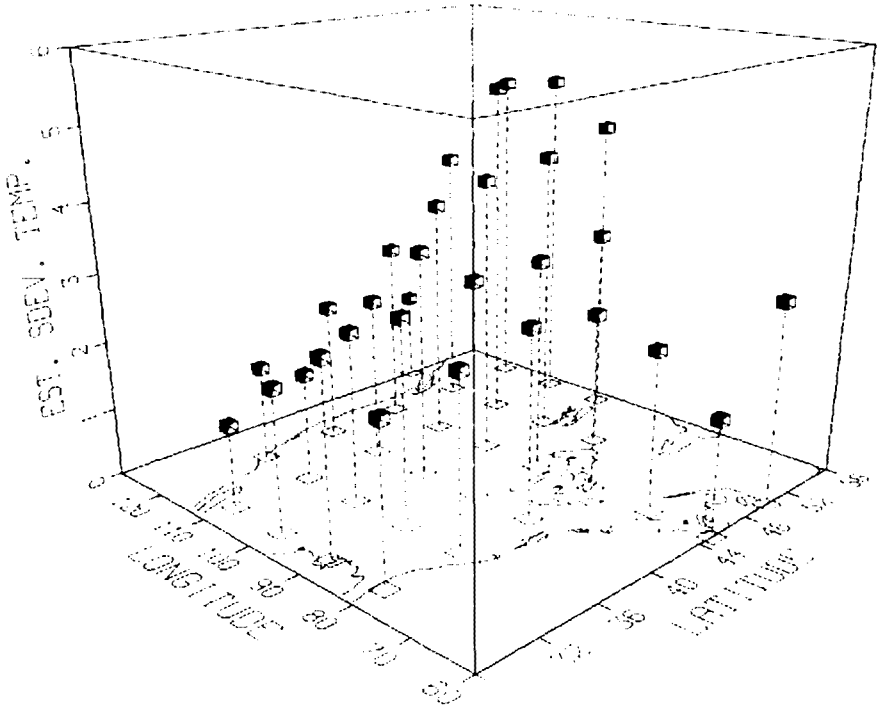

Figure 4. 3D distribution of $\sigma(T)$ for January over NA with 3D cubes used to locate points and their projections shown on base plane.

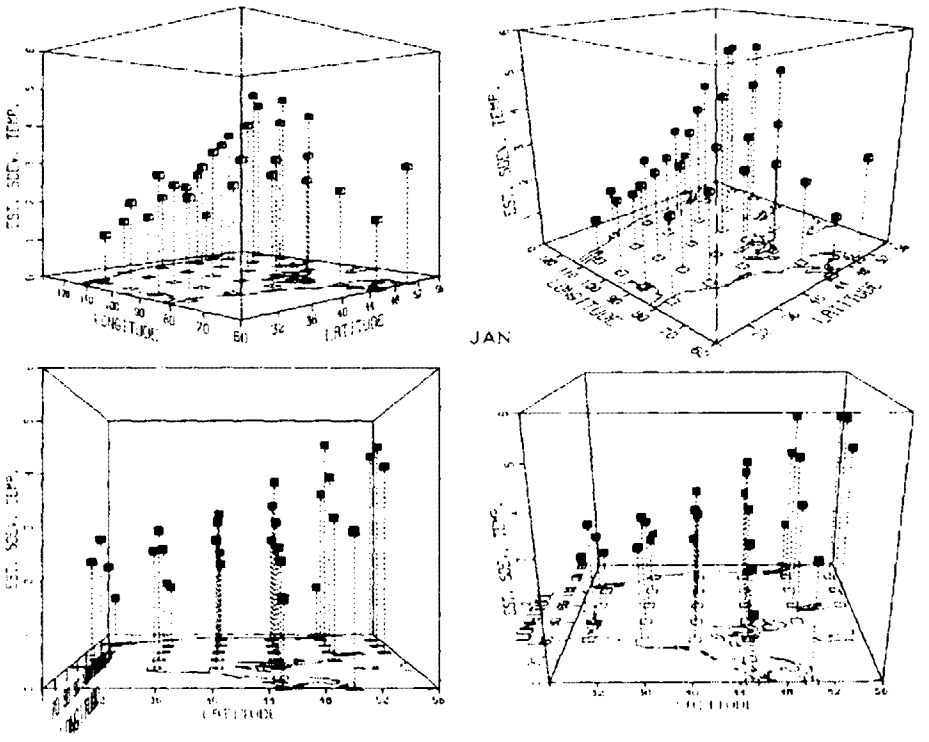

Figure 5. Four views of σ(T) for January over NA.

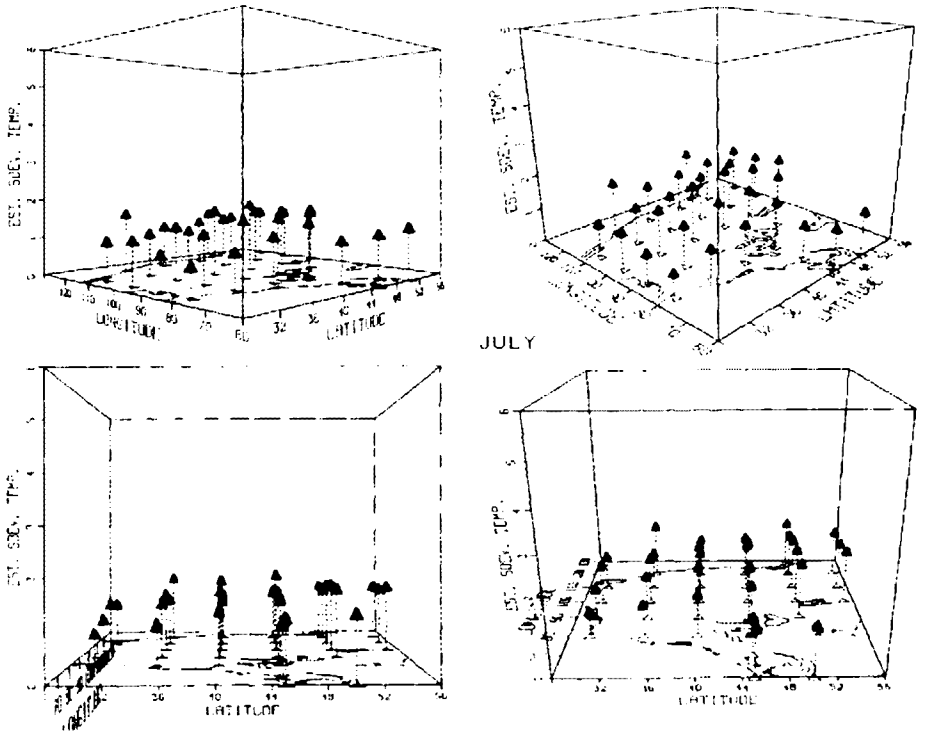

Figure 6. Four views of σ(T) for July over NA.

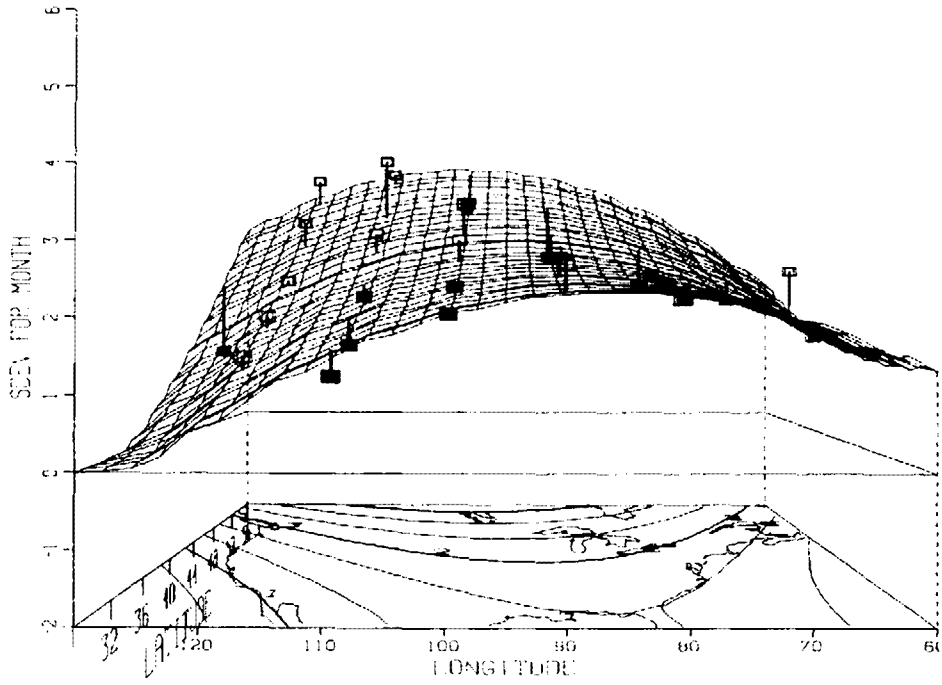

Figure 7. Quadratic surface fit to January $\sigma(T)$ data for NA, including original data points.

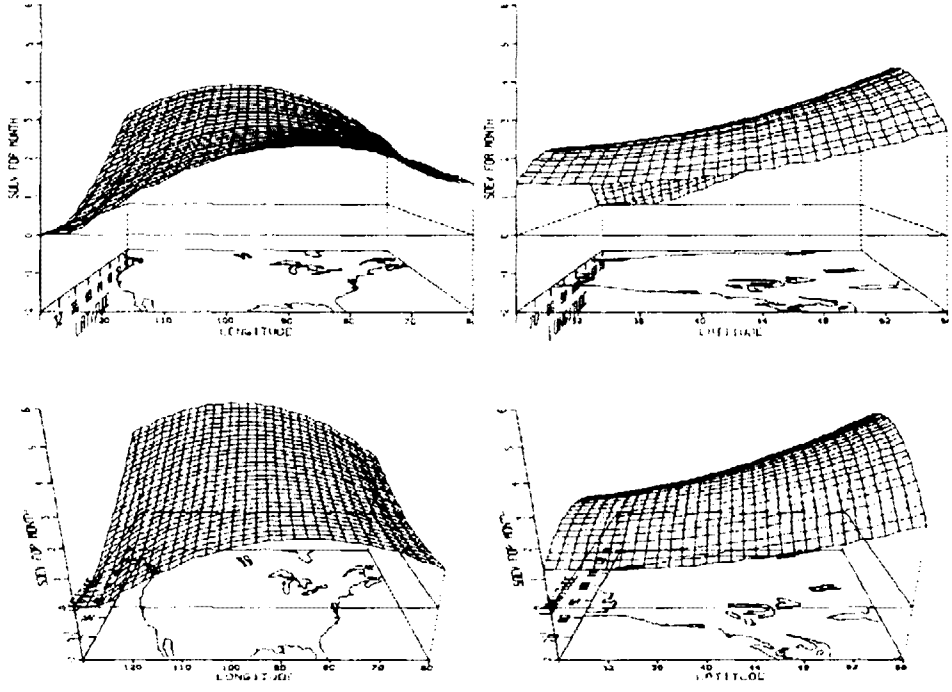

Figure 8. Four views of January quadratic surface for $\sigma(T)$.

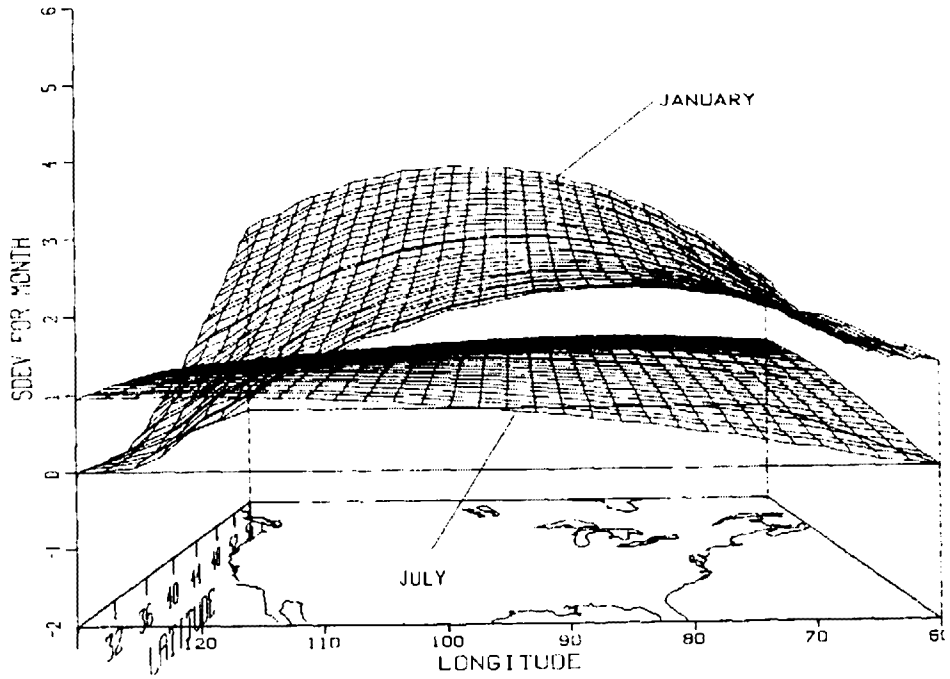

Figure 9. Superimpose $\sigma(T)$ surfaces for January and July.

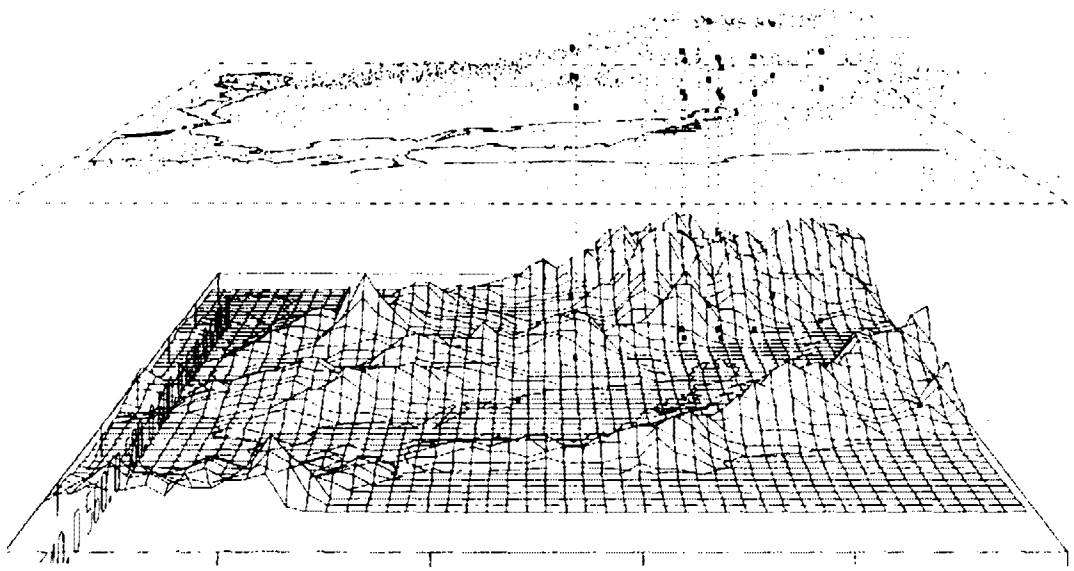

Figure 10. Early morning distribution of ozone over the San Francisco Bay Area terrain. Ten highest concentration grid points are highlighted.

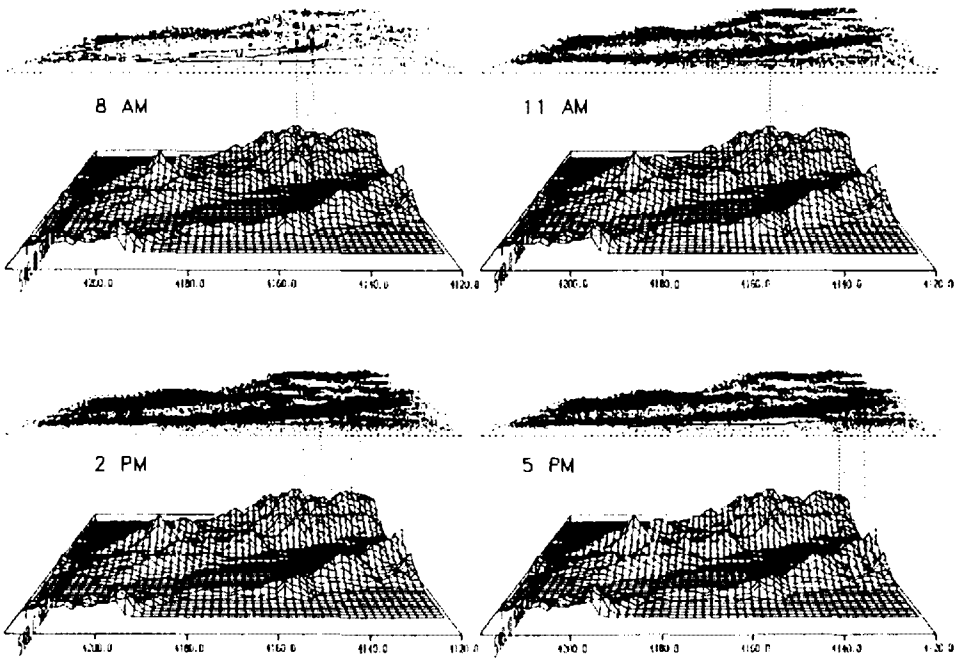

Figure 11. Ozone distribution over the San Francisco Bay Area at different times.

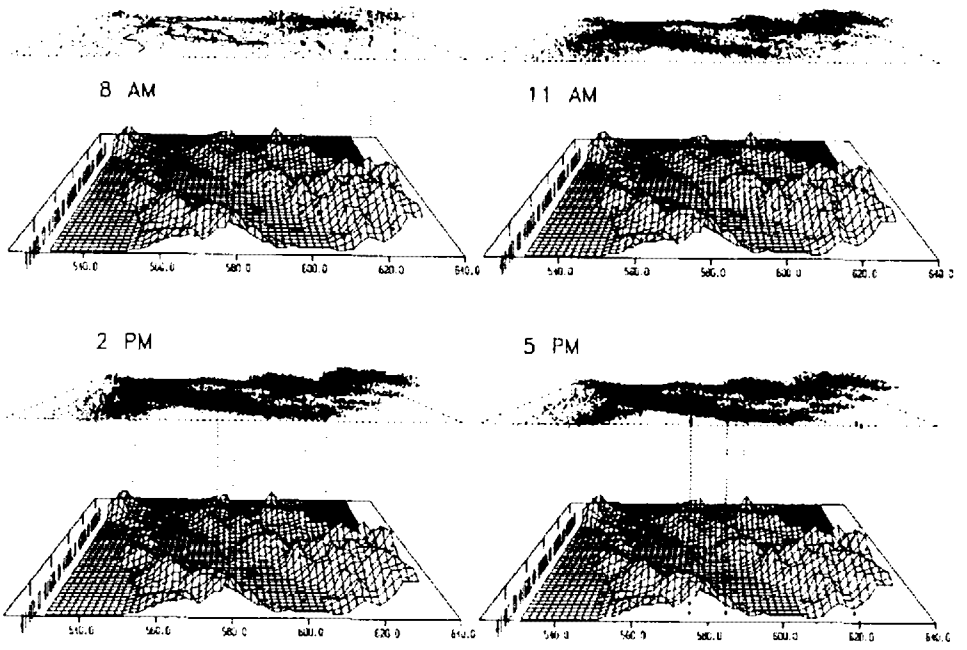

Figure 12. Ozone distribution over the San Francisco Bay Area, second viewpoint.

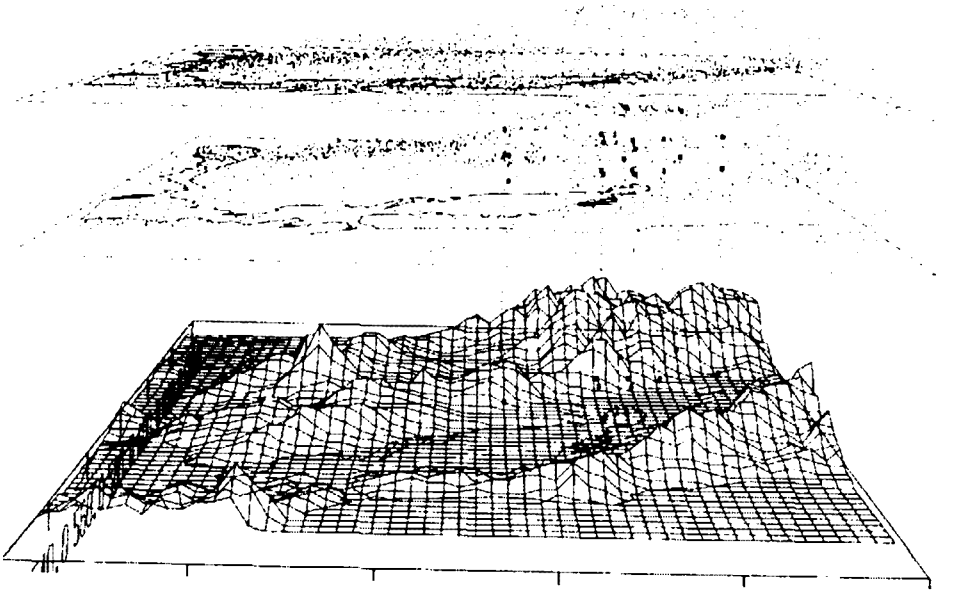

Figure 13. Concentrations of both ozone (top layer) and NO_2 (middle layer) over the Bay Area.

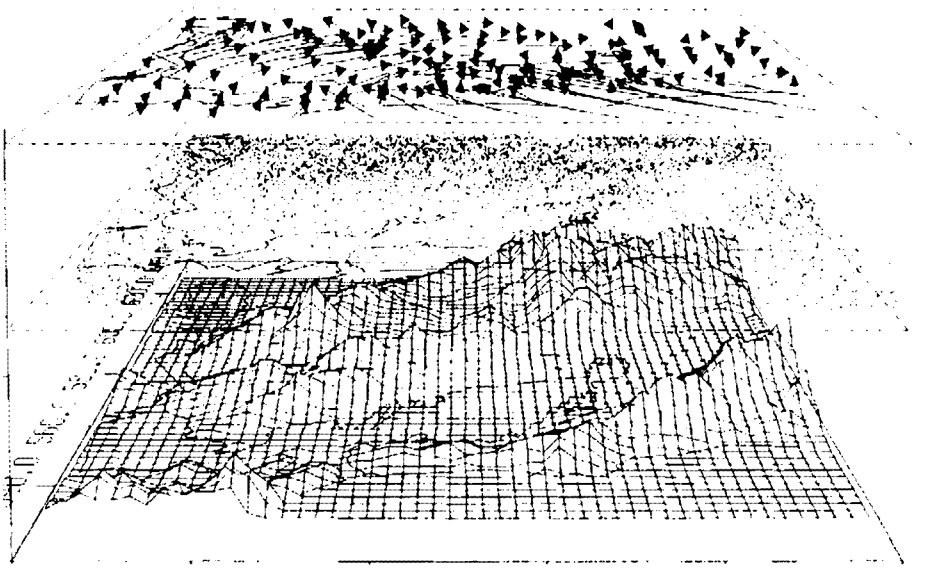

Figure 14. Ozone concentration cloud and mass flux vectors.

SOURCE-RECEPTOR ANALYSIS OF VOLATILE HYDROCARBONS COLLECTED IN NEW JERSERY

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A Chemical Mass Balance (CMB) receptor model for total non-methane hydrocarbon concentration (NMHC) was developed based on ambient measurements of 24 volatile hydrocarbons collected at two sites in New Jersery. The CMB model was used to quantify the contributions from petroleum refineries, gasoline vapors, vehicle exhaust, paint solvents and petrochemical industries to ambient NMHC. A total of 135 one-hour integrated air samples collected at 0600 and 0800 EDT during July and August were selected for this study. The CMB equation was solved using a weighted least squares procedure. Source profiles (mass fractions of the individual 24 hydrocarbons in the emissions from each modeled source category) were developed from published data.

For the 8 AM samples collected at Linden and Newark, N.J., the average contributions to ambient NMHC (defined as the sum of the 24 individual hydrocarbons) were: 92 and 47 $\mu g/m^3$ from refineries, respectively; 83 and 45 $\mu g/m^3$ from gasoline vapor; 29 and 7 $\mu g/m^3$ from petrochemical industries; 49 and 50 $\mu g/m^3$ from vehicle exhaust; 26 and 23 $\mu g/m^3$ from paint solvents; and 77 and 51 $\mu g/m^3$ from other sources. A validation of the CMB predictions for point source contributions showed the results to be consistent with source geometry and wind direction relationships. For the early morning samples analyzed in this study, hydrocarbon reactivity does not have a significant effect on the CMB predictions.

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[a]This study was performed by M. Klevs as a graduate student at IIT and does not reflect the policy of the EPA.

SOURCE-RECEPTOR ANALYSIS OF VOLATILE HYDROCARBONS COLLECTED IN NEW JERSEY

Introduction

Increasing attention is being paid to the chemistry of organic compounds in the atmosphere. In addition to their toxic and in some cases carcinogenic effects, many of these materials play an important role in the photochemistry of air pollution. Any regulatory strategy aimed at controlling the problems associated with organic pollutants will require a better understanding of their emission sources as well as the relationship between emissions and ambient air quality.

Air dispersion models are a widely used tool for relating the emission of a pollutant to its ambient air concentration. Conceptually, these models follow the dispersion of pollutants as they travel downwind. Great uncertainties in our understanding of the emissions from the sources of organic pollution, however, makes applying these models to defining source-receptor relationships for organic materials extremely difficult. An alternate approach using receptor oriented models has been developed to predict source-air quality relationship.[1] In contrast to dispersion models, receptor models start with a measurement of air quality and by using a variety of mathematical techniques, predict the relative contribution of each of the major sources of a pollutant (such as inhalable particulate matter or total non-methane hydrocarbon, NMHC) from measurements of the composition of the pollutant at a receptor site.

One type of receptor model is the chemical mass balance (CMB) or source reconciliation model.[2,3] The CMB requires that the chemical composition of the pollutant be known in the emissions from each source category affecting the air quality at a receptor, and that the chemical composition of a source, or source fingerprint, be stable to the point where it can be quantitatively identified at the receptor. CMB models have been applied to and validated for particulate matter in a variety of locations.[2,4,5] The method has also been applied in a more limited form to fit 6 sources of total hydrocarbons from 9 chemical components in Los Angeles[6] and 5 sources from 15 components in Sydney, Australia[7]. A recent study in Tokyo, Japan used 18 individual hydrocarbon components to resolve 4 sources of NMHC.[8,13]

This paper reports on a study of the application of the CMB to NMHC data collected at Newark and Linden, New Jersey in July and August of 1980.[9] In this study, 24 individual hydrocarbons were used to quantify the contributions from petroleum refineries, gasoline storage facilities, petrochemical industries, vehicle exhaust and paint solvents to ambient NMHC concentrations.[10]

Experimental

Data Set. The data for this project were taken from the Northeast Corridor Regional Modeling Project (NECRMP). For the two receptor sites selected, Newark represents a high traffic density, city center location and Linden represents an industrial location. Note, however, that the two receptor sites are located 16 km apart

and many of the major NMHC sources would be expected to impact both receptors. A map of the area with the locations of the two receptor sites and major NMHC sources is shown in figure 1. One hour integrated air samples were collected at 0600 and 0800 EDT and a total of 135 samples analyzed for the concentration of 24 hydrocarbons were selected for this study. NMHC was defined as the sum of the 24 individual hydrocarbons. Details of the sampling, analysis and quality control procedures have been previously published.[9]

CMB Model. The general equation of the CMB receptor model is:

$$Y = Z\ B + E \qquad (1)$$

where Y is a vector of i molecular concentrations, $\mu g/m^3$, measured at the receptor; Z is the pollution source molecular composition matrix of i components for each of j sources, g of i/ g of NMHC from source j; B is a vector of j source coefficients, μg of NMHC from source j/m^3; and E is a vector of i errors. The values of B, therefore, represent the contributions to the NMHC at the receptor from the source categories.

Equation 1 was solved using the weighted least squares procedure (WLS) for each of the 135 air samples evaluated.[2] The WLS analysis adjusts for unequal variances among the residuals by normalizing the errors (vector E) by the variance of the measurements. The standard deviation (σ) of each measurement was calculated as the product of the molecular concentration and coefficient of variation (CV) of the analytical technique. A conservative estimate of the CV for the NECRMP species data of 0.15 was used for this study. The weight is then the inverse of the square of the measurement σ.

The only restriction on the solutions of Equation 1 was that the source coefficients had to be > 0. For each run, sources with negative coefficients were dropped from the model, the remaining non-negative coefficients re-calculated using the reduced model, and the coefficient for the eliminated source assumed to be zero. The prediction of negative source coefficients did not cause a significant problem with this data set.

Source Characterization. Five source categories were selected for the CMB analysis. These categories were chosen because they represent major sources of NHMC in the study area and reasonable estimates of their fingerprints could be developed. It should be noted, however, that some major categories were not included (e.g printing solvents and pharmaceutical manufacturing). It was not expected or desirable, therefore that the predicted NMHC (ΣB_j) add up to the measured NMHC. 2,8

The source compositions are shown in Table I. The petroleum refinery fingerprint was derived from a study of the air concentrations of hydrocarbon species downwind of an oil refinery.[11] The gas vapor fingerprint is based on vapors from a composite sample of summer blend gasoline at 23°C.[12] The petrochemical fingerprint is based on 36 monthly measurements near a polyethylene plant in Japan.[13] Vehicle exhaust is based on the emissions of four different models of cars burning three separate fuel mixtures.[14] The paint solvent fingerprint is based on air samples down-wind of a large automative painting plant.[15]

Reactivity. A basic assumption of the CMB form of receptor model is that the fingerprint from a particular source remain unchanged from the time of emission to collection. While this assumption allows for overall decay and deposition, selective decay of components before collection could distort the finger-print. Because various hydrocarbons have different reaction rates, the time between emission and collection of the NMHC should be less than the time interval which would allow significant relative changes in concentration due to reactivity. If this is not true, significant changes in the fingerprints could lead to invalid predictions. The extent to which this occurs was evaluated by considering hydrocarbon reactivity in the analysis. The hydroxyl radical reaction rate constant, k_{OH} was used to quantify hydrocarbon reactivity, and the six most reactive materials (m-and p-ethyltoluene, o-ethyltoluene, m-,p-and o-xylene, propylene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene) were removed to form a reduced data set. CMB predictions with the reduced data were developed to test for the effect of selective decay.

Results

Table II shows the average concentrations of the chemical species selected for the CMB analysis. Included on the table are the average NMHC concentrations and the reaction rate constants of the organics with the hydroxyl radical. Table III lists the average of the source coefficients predicted for each hydrocarbon sample for the 6 and 8 AM samples from Linden and Newark. There were a total of 33 valid 6 AM and 8 AM samples from Linden and 35 6 AM and 34 8 AM samples from Newark. The results shown for 24 components represent a summary of solutions with all the hydrocarbons selected contributing to the model. The 18 components solution represents CMB predictions without considering the six most reactive materials. For most samples, the sum of the source predictions was less than the measured NMHC. Given the number significant sources of VOC not included in the model, this result was expected. For each sample, the unexplained fraction which represents the unmodeled sources was calculated as the difference between the measured NMHC and CMB predictions (ΣB_j). The unexplained fraction is also shown on Table III.

Discussion

The results summarized on Table III are generally consistent with receptor site characteristics. Linden, which was considered the more industrial site, has significantly higher average contributions from petroleum refineries, gasoline vapor, petrochemical, paint solvents and unexplained. Looking at the results as average percent contributions, vehicles represent 14% and 19% of the 8 AM NHMC at the Linden receptor based on the 24 component and 18 component solutions, respectively. On the other hand, Newark, considered a city-center site is more dominated by vehicle exhaust with about 22 and 23% of the NMHC at 8 AM for the 24 and 18 component solutions, respectively.

Hydrocarbon reactivity has a subtle effect on the CMB predictions. Examining Table I, the 6 most reactive materials are m-p-ethyltoluene, o-ethyltoluene, 1,3,5 trimethylbenzene, m-p-o-xylene, 1,2,4-trimethylbenzene, and propylene. Because of their reaction rate constants, these materials are preferentially

removed from the atmosphere. This could result in disproportionately lower ambient concentrations for these selected materials. However, Table III does not show a significant difference between the 24 and 18 component solutions (i.e. the difference in average source coefficient between the two solution sets was always less than 5.3% of the measured NMHC). Table IV shows the correlations between the 24 component solutions and the 18 component solutions. The high correlations on this table show that both solution sets predict the same day to day variation in source contributions. It appears, therefore, that for early morning samples, even in the summer, hydrocarbon reactivity does not have a significant effect on the CMB predictions.

The coefficient of determination (R^2) of a multiple regression model is the square of the correlation between measured hydrocarbon concentration and predicted hydrocarbon concentration. It is, therefore, a measure of overall quality of fit of a regression model. Table V summarizes R^2 of the individual solutions for the 24 and 18 component CMB models. This table shows generally higher R^2 (or lower errors) for the 18 component solutions and, therefore, that the 18 component source profiles are more representative of the hydrocarbon patterns measured at the receptor sites than the 24 component profiles. Given the more homogeneous atmospheric life-times of the 18 component materials, this result is expected.

The distributions of the daily CMB predictions of NMHC from the individual sources were compared with each other. It is interesting to note that most of the correlation coefficients between daily CMB source predictions are low ($r < 0.5$). This suggests that the model is responding to the complex variation in daily source contributions and resulting hydrocarbon patterns rather than simply loading all sources in proportion to the total hydrocarbon concentration.

Figure 1 shows the location of the major hydrocarbon point sources with respect to the receptor monitoring sites. Because these sources are not homogeneous throughout the study area, variations in source impact predictions with wind direction are expected. Table VI shows the source coefficients averaged by wind quartile for the combined 6 AM and 8 AM results for the 24 component solutions. A number of points are worth noting. There is a clear relationship between the location of gasoline storage facilities and gas vapor source predictions. For example, there are three major storage facilities SE of the Newark receptor site. As shown on Table VI, gas vapor predictions are highest for SE winds. The location of gasoline storage NE and SE of the Linden site is also shown on Table VI as increased source contributions from these wind sectors.

The same relationship between source location and CMB prediction is seen for paint operations. The three major paint sources are located NE of the Linden receptor and E and SE of the Newark receptor. The averages on Table VI are consistent with this geometry. Petrochemical sources are all south of the Newark receptor and surround the Linden site. Again Table VI shows results that are reasonably consistent with this source pattern. However, the relationship between source location and CMB predictions for refineries is less clear. With a major refinery point source east of the Newark site, the Newark predictions of

major contributions from the SE is not unreasonable. On the other hand, the prediction of significant refinery contributions from the SE of Linden do not agree with source location.

One should be cautious in interpreting the wind direction information. Given its proximity to the ocean, the area is frequently influenced by sea breezes on summer mornings. The wind direction information used for this analysis was collected at the Newark airport, and may not, therefore, be representative of the actual air flow at the receptors during the morning sampling periods. A more sophisticated validation procedure using plume trajectories could not, therefore, be applied. [2,13]

Conclusions

1. The average prediction of source contributions for the two receptor sites are consistent with the general characteristics of the sites.

2. Despite the consistently higher R^2 for the 18 component solutions, there was very little difference in source fraction explained between the 18 and 24 component solution sets. Both solutions represent the same daily variation in source-receptor relationships and predict the same average source contributions.

3. In general, the CMB predictions for point source contributions to the NMHC at both receptor sites are consistent with source geometry and wind direction relationships. For gasoline storage facilities, paint operations, petrochemical, and to a lesser extent, refineries, winds from the areas where point sources are present show higher contributions from the sources compared to winds from other directions. These relationships appear to represent specific source-receptor relationships rather than generally higher predictions across all source categories resulting from higher receptor NMHC.

Acknowledgments

We would like to thank Harold G. Richter of the USEPA Office of Air Quality Planning and Standards for his generous assistance in providing the NECRMP species data. We also thank Bill Oliver of Systems Applications Inc. for the update to the VOC species manual and Barry Bolka of Region V EPA for the emission inventory.

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Table I Hydrocarbon Source Fingerprints

Component	Weight %				
	Refinery	Gasoline Vapor	Petro-Chemical	Vehicle Exhaust	Paint
ethane	1.88	.26	3.0	5.03	-[a]
ethylene	.52	-	50.0	10.08	-
acetylene	.01	-	1.8	2.32	-
propane	11.57	2.50	4.3	2.24	-
propylene	.56	-	3.9	2.06	-
i-butane	5.16	14.65	2.6	1.58	-
n-butane	20.29	34.21	5.5	11.94	-
i-pentane	21.67	32.09	4.0	12.52	-
n-pentane	8.55	10.28	2.8	-	-
2-methylpentane	8.78	-	1.5	3.12	.71
3-methylpentane	5.28	2.34	1.1	1.56	.59
n-hexane	4.55	1.83	4.3	1.02	1.13
benzene	1.63	.76	3.4	8.54	-
n-heptane	2.19	.27	.0	1.07	9.14
toluene	4.02	.55	7.7	22.28	70.68
n-octane	-	.02	.0	.89	5.46
ethylbenzene	.60	.04	1.6	1.84	5.99
p,m,o-xylene	2.32	.14	2.5	7.23	.25
n-nonane	.11	.01	-	.44	-
n-propylbenzene	-	-	-	.68	.71
m,p-ethyltoluene	.16	-	-	-	2.25
1,3,5-trimethylbenzene	.00	.00	-	-	.77
o-ethyltoluene	.11	.02	-	-	.65
1,2,4-trimethylbenzene	.05	.02	-	3.54	1.66
	100.00	100.00	100.0	100.00	100.00

[a]Not measured, however, assumed to be zero for CMB calculations.

Table II Average Concentration and Reactivity for Selected Hydrocarbons

Component	Average Concentration, $\mu g/m^3$				kOH[a]
	Linden		Newark		
	6 AM	8AM	6AM	8AM	
ethane	50.8	16.4	14.1	11.2	1.7×10^{11}
ethylene	19.2	17.8	6.3	7.3	4.9×10^{12}
acetylene	5.4	6.5	6.2	7.4	4.1×10^{11}
propane	34.4	22.4	11.5	10.1	1.1×10^{12}
propylene	6.2	8.2	6.3	5.6	1.5×10^{13}
i-butane	33.9	21.8	10.7	11.8	1.6×10^{12}
n-butane	59.3	49.9	21.8	25.3	2.0×10^{12}
i-pentane	68.0	52.5	25.2	29.8	2.1×10^{12}
n-pentane	50.0	28.9	11.0	13.3	3.0×10^{12}
2-methylpentane	20.1	13.6	7.4	7.7	3.0×10^{12}
3-methylpentane	12.5	8.7	4.9	5.0	4.1×10^{12}
n-hexane	14.8	13.4	5.3	5.7	3.5×10^{12}
benzene	9.1	9.0	5.2	6.0	8.5×10^{11}
n-heptane	5.3	5.1	2.9	3.8	3.7×10^{12}
toluene	38.0	37.9	23.3	29.5	3.7×10^{12}
n-octane	2.6	1.9	1.1	1.5	4.9×10^{12}
ethylbenzene	6.8	6.3	5.3	5.5	4.9×10^{12}
p,m,o-xylene	18.6	17.2	14.3	17.4	1.3×10^{13}[b]
n-nonane	1.5	1.5	1.3	1.7	4.3×10^{12}
n-propylbenzene	1.7	1.5	1.2	1.0	5.8×10^{12}
m,p-ethyltoluene	5.8	5.5	4.4	5.5	1.8×10^{13}[c]
1,3,5-trimethylbenzene	1.2	1.2	1.2	1.3	5.2×10^{13}
o-ethyltoluene	7.1	6.4	5.7	6.4	1.3×10^{13}
1,2,4-trimethylbenzene	2.7	2.9	2.5	2.8	3.5×10^{13}
NMHC	475.0	357.2	199.1	222.6	

[a] cm^3/mole·sec; from reference 16.
[b] m-xylene
[c] m-ethyltoluene

Table III Summary of CMB Results.

		Source Coefficient, $\mu g/m^3$			
	Number of	6 AM		8 AM	
LINDEN	Components	Average(σ)	Range	Average(σ)	Range
Refinery	24	141 (233)	0 - 1310	92 (71)	0 - 356
	18	124 (202)	0 - 1150	80 (65)	0 - 325
Gas Vapor	24	152 (350)	0 - 1680	83 (122)	0 - 616
	18	171 (373)	7 - 1870	90 (122)	7 - 617
Petrochemical	24	29 (32)	0 - 96	29 (31)	0 - 150
	18	24 (31)	0 - 101	21 (19)	0 - 66
Vehicle	24	62 (49)	0 - 252	49 (32)	0 - 96
	18	79 (98)	0 - 550	68 (61)	0 - 275
Paint	24	22 (24)	0 - 100	26 (43)	0 - 245
	18	17 (20)	0 - 84	20 (36)	0 - 212
Unexplained	24	65 (283)	-1370 - 508	77 (77)	-42 - 291
	18	56 (276)	-1400 - 314	79 (71)	11 - 323
NEWARK		Average(σ)	Range	Average(σ)	Range
Refinery	24	52 (71)	0 - 406	47 (40)	0 - 193
	18	50 (65)	0 - 368	44 (38)	0 - 187
Gas Vapor	24	33 (36)	0 - 149	45 (45)	8 - 222
	18	35 (36)	0 - 149	47 (45)	9 - 222
Petrochemical	24	6 (10)	0 - 34	7 (10)	0 - 53
	18	5 (8)	0 - 26	5 (9)	0 - 48
Vehicle	24	38 (40)	0 - 187	50 (42)	0 - 143
	18	43 (50)	0 - 253	52 (45)	0 - 148
Paint	24	16 (20)	0 - 90	23 (23)	0 - 94
	18	13 (17)	0 - 68	19 (20)	0 - 84
Unexplained	24	54 (38)	11 - 188	51 (38)	16 - 181
	18	53 (40)	13 - 195	55 (41)	21 - 202

Table IV Correlations Between the 24 and 18 Component Solutions

	Linden		Newark	
Source	6 AM	8 AM	6 AM	8 AM
Gas Vapor	0.99	0.97	0.99	0.99
Refinery	0.99	0.97	0.99	0.99
Petrochemical	0.87	0.89	0.94	0.96
Vehicle exhaust	0.91	0.62	0.97	0.97
Paint	0.86	0.98	0.97	0.99

Table V Summary of the Coefficient of Determination for the 24 and 18 Component Solutions

Site	Hour	Number of Components	Median	Min	Max
Linden	6	24	0.745	0.047	0.801
		18	0.826	0.334	0.941
	8	24	0.741	0.255	0.821
		18	0.842	0.304	0.906
Newark	6	24	0.706	0.183	0.770
		18	0.814	0.228	0.883
	8	24	0.721	0.321	0.778
		18	0.838	0.343	0.884

Table VI Source Coefficients Averaged by Wind Quartile

	Average Source Coefficient[a] ($\mu g/m^3$) by Wind Quartile				
LINDEN	NE	SE	SW	NW	ALL DIRECTIONS
Refinery	80	201	104	96	117
Gas Vapor	121	312	59	44	118
Petrochemical	18	31	31	36	29
Vehicle exhaust	43	63	58	54	55
Paint	38	21	18	24	24
NEWARK					
Refinery	50	79	41	36	49
Gas Vapor	35	62	30	37	39
Petrochemical	4	7	9	4	6
Vehicle Exhaust	51	66	38	29	44
Paint	26	27	14	18	20

[a] 24 chemical solutions

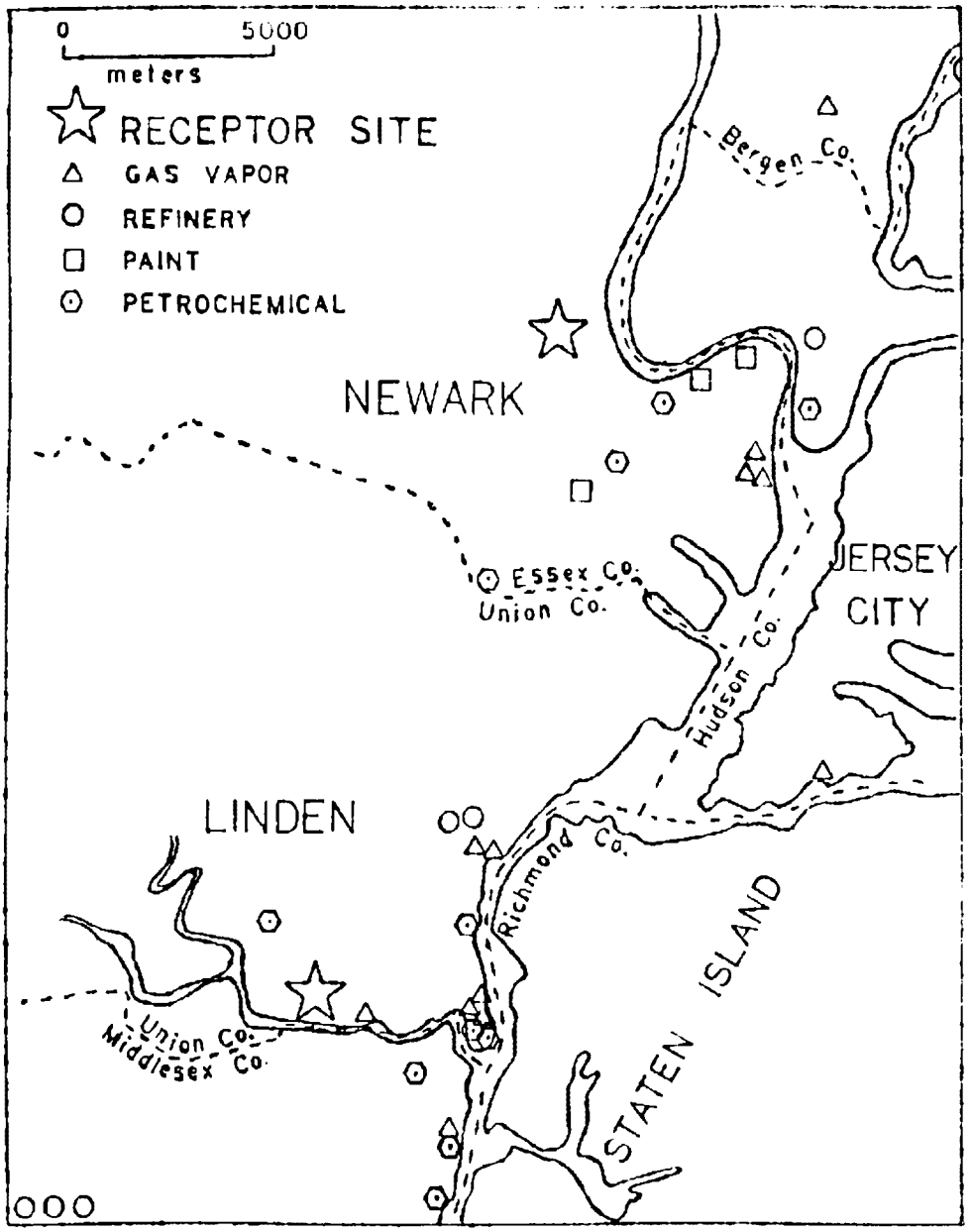

Figure 1. Locations of receptor sites and VOC sources.

ESTIMATING SPECIFIC SOURCE EXPOSURES TO TOXIC AIR POLLUTANTS

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The evaluation of the extent to which a chemical, or a class of chemicals, presents a health hazard to the public relies on an accurate assessment of human exposure to that chemical. To control emissions of toxic substances effectively, the source of exposure must be identified. Exposure models have been developed which assess total exposure from all sources to a chemical. Source-receptor models can identify source contributions to the concentration of a chemical in an individual environment. A Source Exposure Model (SEM) is developed here which combines both types of models to give estimates of human exposure to chemicals from specific source categories. The SEM combines the Chemical Mass Balance receptor model with a discreet form of exposure model, and provides an assessment of the fraction of total chemical exposure due to various source types.

A simplified form of the SEM is applied in a small residential community to assess atmospheric exposure to fine particles and benzo(a)pyrene indoors and outdoors from both automobiles and woodburning stoves. Atmospheric tracers are used to estimate source contributions.

ESTIMATING SPECIFIC SOURCE EXPOSURES TO TOXIC AIR POLLUTANTS

INTRODUCTION

A human exposure model and a source-receptor model are combined to form a Source Exposure Model (SEM) which can be used to estimate human exposure to specific source categories. This type of information is useful in targeting source categories for regulatory efforts.

Personal exposure information may be obtained by the use of personal monitoring equipment which is worn on the individual, or by estimation of exposure through theoretical models using concentration information from fixed monitoring sites in many different environments, together with activity profiles of the movements of the individual in and out of those environments. The exposure of an individual to a pollutant is a measure of pollutant concentration available to the body, while the dose is the actual quantity that enters the body. Exposure calculations are used to estimate dosages.

METHODOLOGY

The total exposure is the product of the concentration of pollutant times the length of exposure. Since the length of exposure in a microenvironment may vary from a few minutes to many hours, the concentration information must be representative of the concentration over the particular period of individual exposure. The average integrated exposure to a pollutant, E, of an individual may be calculated by summing over the time periods t_k spent in each microenvironment k that the person encounters during a day[1]:

$$E = \sum_k c_k t_k , \qquad (1)$$

where C_k is the concentration of the pollutant in the microenvironment k during period t_k. For the integrated exposure to be truly representative of the dosage received, the measured concentration must be determined specifically for each period t_k. In fixed site monitoring, a sampling period should be chosen over which concentration fluctuations are small and therefore the measured concentration is representative of the exposure within the period. For example, concentration of inhalable particulate material averaged over 24 hours may underestimate a short 1 hour exposure by a factor of 2 to 3. Nephelometry readings may be examined for periods of maximum acceptable concentration fluctuation and used to determine the sampling period of the fine particulate material or gases related to the fine particles.[2]

In the Source Exposure Model (SEM), the average individual exposure to a pollutant from source j over period i, E_{ji} is:

$$E_{ji} = 1/n_i \sum_k S_{jik}\, ti_k, \qquad (2)$$

where t_{ik} is the number of hours spent in microenvironment k during period i, S_{jik} is the contribution of source j to the pollutant in microenvironment k during period i as determined by the CMB and n_i is the number of hours in each period i. In the application of the

SEM presented here, the sampling period is 4 hours ($n_i = 4$). For non-continuous sampling, the sampling period is generally equal to or greater than the minimum activity profile period to assure that it is representative of the exposure concentration ($n_i \geq t_{ik}$ minimum). A typical minimum activity profile period is one hour since 1) detailed activity dairies over time periods shorter than one hour are difficult to maintain, and 2) sampling periods for toxic pollutants of less than one hour are often not practical both for analytical and economic reasons.

Where unique tracer characterizations may be found to represent a source of interest, the jth source contribution during period i in the kth microenvironment, S_{jik}, is:

$$S_{jik} = \alpha_{jk} C_{Tik}, \tag{3}$$

where α_{jk} is the ratio of the pollutant concentration to the tracer T concentration in source j in microenvironment k, and C_{Tik} is the concentration of the tracer T during period i in microenvironment k. The average individual exposure to source j during period i then becomes:

$$E_{ji} = 1/n_i \sum_k \alpha_{jk} C_{Tik} t_{ik}. \tag{4}$$

If α is invariant with k, it may be removed from the summation. In this case, the exposure to a pollutant from source j may be directly ascertained with the use of personal exposure badges over any time period, and

$$E_j = \alpha_j C_T. \tag{5}$$

The daily average individual exposure for person type p, with person type being defined as a category of individuals with similar activity diaries (e.g. office worker), to the pollutant from source j, $E(D)_{pj}$, is:

$$E(D)_{pj} = 1/24 \sum_i n_i E_{ji}, \tag{6}$$

The daily weighted population exposure to the pollutant from source j, P, is:

$$P_j = \sum_p f_p E_{pj}, \tag{7}$$

where f_p is the fraction of person type p in the population. A weighing factor may also be included here to represent relative risk to varying types within the population, e.g. the very young, sick or elderly. An annual weighted population exposure may also be calculated in a similar manner. The weighted population exposure may be used in risk assessment models to determine if regulatory control should be initiated on a particular source of a pollutant.

MODEL APPLICATION

A simplified form of the SEM was applied to assess source exposures to automobiles and residential woodburning in a small community near Portland, Oregon. Through the use of gaseous tracers in a receptor model, these two sources have previously been determined to be the major wintertime contributors to fine particulate pollution in the

residential neighborhoods of this community[3].

The contribution from automobiles and wood stoves to the ambient, outdoor fine particle and benzo(a)pyrene (BaP) concentrations were estimated by applying a two component Chemical Mass Balance Model.

The gases methyl chloride (CH_3Cl) and carbon monoxide (CO) were used as surrogate tracers for these sources. Methyl chloride has been shown to be a unique tracer for wood combustion in residential neighbor hoods [2-4]. Both woodburning and automobiles contribute to the local carbon monoxide concentrations. The value for α (woodburning) in equation (3) and (4) was experimentally determined for the ambient outdoor environment [5]. The value for α (automobiles) was taken from calculations based on the local traffic mix [6].

Typical indoor concentrations of woodsmoke in homes where there is wood being burned were estimated from previous studies [7,8]. The concentrations vary widely between the individual homes and fluctuate greatly over the day. The highest concentrations occur during the stoking of the fire, as indicated by spikes in the CO concentrations. An average indoor concentration of woodsmoke during periods of woodburning is 20 $\mu g/m^3$. A survey has shown that of those who burn wood (56 percent of the population in this community do), 23 percent of wood stove burners burn all day on the weekdays and 44 percent burn all day on the weekends [9]. The simplifying assumption is made that there is no infiltration of particulate material from outdoors into homes.

Source exposures are estimated for two categories of people: an office worker and a person who spends most of the day at home, such as a homemaker or elderly person. The activity patterns for these two types are taken from studies of population mobility [10]. It is assumed that the employed person (office worker) spends one hour in the morning and evening period outdoor in transit to and from work and one hour during the lunch period in the outdoor environment. The transit mode and outdoor environment are considered to be the same. The unemployed person spends two hours in the afternoon in transit and in outdoor activities.

The contribution of woodburning to the fine particle concentration, S_{jik} to which a person in each category is exposed during each period, t_{ik}, is shown in Table 1 and Table 2 for persons living in woodburning households (WB), and non-woodburning households (NWB). The daily average exposures, E(D), for each category, are calculated using equation (6) and shown in the tables. For the employed person, the average daily exposure to woodsmoke is 13 $\mu g/m^3$ for the individual in the woodburning home. The corresponding concentration for the unemployed person is 18 $\mu g/m^3$ in the woodburning home and 1 $\mu g/m^3$ in the non-woodburning home. Despite the higher concentrations in the outdoor ambient air, the indoor exposures dominate the total dosage of woodsmoke that an individual receives over the day. A similar calculation for the average daily exposure to auto exhaust gives a value of 1 $\mu g/m^3$ for both the employed and unemployed. Assuming 60 percent of the population can be classified as employed and 40 percent as "at home", the weighted population exposures, P_j from equation (7), to fine particles from woodsmoke and auto exhuast are 9 $\mu g/m^3$ and 1 $\mu g/m^3$ respectively.

The source exposure model may be applied to calculate exposures to

toxic compounds from specific sources, if the ratio of the compound to the tracer, α, in that source is known. Such a calculation has been carried out for exposure to benzo(a)pyrene (BaP). The ratio for BaP to methyl chloride in woodsmoke is calculated from the ratio of fine particles to methyl chloride used above and a value for the ratio of BaP to fine particles of about 0.06 percent [11,12]. An estimate for the value of. about 0.001 percent for BaP to fine particles in auto exhaust is from the literature [13]. The weighted population exposure to BaP from woodburning and auto exhaust is 5 ng/m^3 and .01 ng/m^3 respectively. The weighted population exposures to fine particles and BaP from woodburning and from automobiles is shown in Table 3.

The weighted population exposure may be used in risk assessment models to calculate the contribution to health risk of toxic chemicals from specific sources. This type of assessment is useful for targeting sources for regulatory control. The weighted population exposure to BaP calculated above, for example, may be converted to an average daily intake of BaP using a value for daily air inhalation of 19 m^3/day [14]. The average wintertime daily intake of BaP is calculated to be 100 ng/m^3 from woodsmoke and 0.2 ng from auto exhaust. This is compared with a recommended daily intake of 48 ng. A comparison of BaP intake from other sources is shown in Table 4.

This simple application illustrates the use of the Source Exposure Model to evaluate the health hazard of toxic chemicals in the environment. A more thorough application of the model may include many more chemicals, chemical sources, people types, microenvironments, transport mechanisms between microenvironments, and risk factors. With the increasing awareness that many chemical exposures occur in environments other than that of the outdoor ambient air, this type of model should find increasing applicability in the assessment of public health hazards from toxic chemicals.

Acknowledgments

This work was supported in part by the U.S. Environmental Protection Agency. Additional support was provided by the Biospherics Research Corp. and the Andarz Co.

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TABLE 1. DAILY INTEGRATED EXPOSURE TO WOODSMOKE FOR PERSONS EMPLOYED INDOORS IN OFFICE BUILDINGS

Microenvironment (ME) (# hours spent in ME in period 1,2,3,4)		S_{jik} Concentration of Fine Particles from Woodburning μg/m³ Period 1 6-10am		Period 2 10am-6pm		Period 3 6pm-2 am		Period 4 2-6am	
ni		4		8		8		4	
		WB*	NWB	WB	NWB	WB	NWB	WB	NWB
k	t_{ik} (i = 1,2,3,4)								
Home	(2,0,7,4)	20	0	20	0	20	0	10	0
Work	(1,7,0,0)	0	0	0	0	0	0	0	0
Street	(1,1,1,0)	29	29	19	19	42	42	24	24
Average for Period E_{ji}		17	7	2	2	23	5	10	0
Total Daily Average: E(D)		WB Household				13 μg/m³			
		NWB Household				4 μg/m³			

TABLE 2. DAILY INTEGRATED EXPOSURE TO WOODSMOKE FOR PERSONS WHO SPEND MOST OF THE DAY IN THE HOUSE

Microenvironment (ME) (# hours spent in ME in period 1,2,3,4)		S_{jik} Concentration of Fine Particles from Woodburning μg/m³ Period 1 6-10am		Period 2 10am-6pm		Period 3 6pm-2am		Period 4 2-6am	
ni		4		8		8		4	
		WB*	NW	WB	NWB	WB	NWB	WB	NWB
k	t_{ik} (i = 1,2,3,4)								
Home	(4,6,8,4)	20	0	20	0	20	0	20	0
Street	(0,2,0,0)	29	29	19	19	42	42	24	24
Average for Period E_{ji}		20	0	20	2	20	0	10	0
Total Daily Average; E(D)		WB Household			18 μg/m³				
		NWB Household			1 μg/m³				

*WB means woodburning household and NWB means non-woodburning household

TABLE 3. POPULATION WEIGHTED SOURCE EXPOSURES TO FINE PARTICLES AND BENZO(a)PYRENE FROM WOODBURNING AND AUTO EXHAUST IN A RESIDENTIAL NEIGHBORHOOD DURING THE WINTER

	Woodburning	Auto Exhaust
Fine Particles $\mu g/m^3$	9	1
Benzo(a)pyrene ng/m^3	5	.01

TABLE 4. AVERAGE DAILY EXPOSURE TO BaP FROM WOODSTOVES AND AUTOMOBILES, CALCULATED WITH THE SOURCE EXPOSURE MODEL COMPARED WITH ALLOWABLE DAILY INTAKE AND EXPOSURE FORM OTHER SOURCES [15].

	Daily BaP Intake
Allowable Daily Intake	48 ng
Woodstoves	100 ng
Automobiles	0.2 ng
Food	160 - 1600 ng
Smoking	400 ng

PERFORMANCE AND RESULTS OF THE ANNULAR DENUDER SYSTEM IN THE SAMPLING AND ANALYSIS OF AMBIENT AIR NEAR LOS ANGELES

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Airborne gaseous and particulate chemical species contribute to acid deposition. Among them are gaseous nitric acid (HNO_3), nitrous acid (HNO_2) ammonia (NH_3), and sulfur dioxide (SO_2); and particulate nitrate (NO_3^-), sulfate (SO_4^{2-}), and ammonium (NH_4^+). Accurate measurements of the atmospheric concentrations of these chemicals are needed to facilitate an understanding of the important chemical and physical processes that lead to acid deposition.

Although commercially available instrumentation is available to monitor some of these pollutants, the sensitivity is frequently inadequate at concentrations typical of nonurban sites. As a result, researchers have devised several approaches to determine the ambient levels of these pollutants. A methods' intercomparison study was conducted from September 11 to 19, 1985 on the Pomona College Campus at Claremont, California near Los Angeles. Approximately 20 different research groups participated, using various state-of-the-art methods for sampling and analyzing ambient air. This paper describes the performance of the annular denuder system (ADS) and presents results collected using the system during this study.

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Introduction

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Experimental

The ADS was developed by the Istituto Inquinamento Atmosferico of the Consiglio Nazionale delle Ricerche (CNR) of Rome (Italy). As illustrated in Figure 1, the ADS is a denuder-filter pack assembly for the simultaneous collection of atmospheric trace gases (i.e., HNO_3, HNO_2, SO_2, and NH_3) and fine particles (i.e., NO_3^-, SO_4^{2-}, and NH_4^+). Two denuder-filter pack sampling trains are contained in a weatherproof box. Air enters the ADS at 15 lpm through a Teflon cyclone (2.5 μm cut size) and flows through a Teflon manifold sequentially into one of the two denuder-filter pack sampling trains. Sampled air contacts only Teflon surfaces or the coated glass surfaces of the denuder tubes. The components of each train are assembled with threaded rings and connectors. In each train, air passes through: two Na_2CO_3-coated, 22 cm-long annular denuders (AD) to collect HNO_3, HNO_2, and SO_2; one citric acid-coated, 13 cm-long AD to collect NH_3; a 47 mm diameter Teflon 2 μm pore size filter to collect fine particles (NO_3^-, SO_4^{2-}, and NH_4^+); a 47 mm diameter 1 μm pore size nylon filter to collect nitrate volatilized as HNO_3 from the Teflon filter; a citric acid-coated 13 cm-long AD to collect ammonium volatilized as NH_3 from the Teflon filter; and a microprocessor-controlled air sampler.

In each annular denuder, air is drawn under laminar flow conditions through the annular space between two concentric glass cylinders coated with a chemical appropriate for retention of the trace gas of interest. The walls of the denuder are etched so that the surface area available for chemical coating is increased. As the sample stream passes through the annular space, the gaseous species travel by molecular diffusion from the bulk gas to the reactive surface and are collected. The collection efficiency of an annular denuder depends on the air flow rate, the tube length, and on the inner and outer tube diameters. At equivalent tube lengths and outer tube diameters, larger sampling rates are achievable with annular denuders than with open tube denuders (1). The capacity of the denuder is in the milligram range (2).

The denuder removes reactive gaseous molecules from air samples. Particles are collected on back-up filters, minimizing artifact formation from gas-particle interactions on the filter surface. Diffusional and inertial deposition of particles at the denuder inlet has been shown to be negligible (1,2). The transit time of air through the denuder is short (< 0.1 sec); this retards the reestablishment of a gas-particle equilibrium that is appreciably different from that existing in the sampled atmosphere (3).

Samples collected with denuders and with filters were extracted in virgin Nalgene containers with distilled water and subsequently analyzed. The extract solutions were analyzed for NO_3^- and SO_4^{2-} by ion chromatography, and for NO_2^- and NH_4^+ by colorimetry (4,5). Other substances deposited on the denuder may give rise to the formation of the same ions: for example, the sorption of NO_2 and PAN on an Na_2CO_3-coated denuder produces nitrite, which interferes with the measurement of HNO_2; deposition of particulate matter containing sulfates nitrate interferes with the measurement of SO_2 and HNO_3 (2,6). The collection of the interfering species is small (1-3 percent). By placing two denuders in series, the amount collected on the first one will be approximately equal to that found on the second one, which can be used to correct data obtained from the analysis of the first denuder. The use of two denuders in series then permits the simultaneous analysis of several acidic compounds over a wide range of gas-to-particle analyte ratios.

The filter extractions and the bulk of the chemical analyses were performed by Global Geochemistry of Canoga Park, California. The denuder extract volume was 10 mL, and the filter extract volume was 20 mL. The units on the species concentrations in the liquid extract solutions are reported in μg/mL. By combining the liquid species concentration, the extract volume, and the sampled air volume, an ambient air species concentration may be computed and expressed in $\mu g/m^3$.

The air sampler, specifically developed for the ADS, consists of a membrane pump and a microprocessor. The measurement of the flow rate is achieved by measuring the pressure drop, the temperature across a downstream orifice, and atmospheric pressure by means of suitable electronic transducers. Data are sent to the microprocessor, which corrects the flow rate to normal temperature and pressure (20°C and 760 mm Hg). By integration of the flow rate, the volume of air which has been sampled is obtained. The microprocessor adjusts a valve to achieve a constant inlet flow rate regardless of temperature, air pressure, and the pressure drop across the filter pack.

In the current study, two ADS's were used for collocated sampling. The sampling flow rate was 15 lpm. Two types of sampling periods were used. Short duration samples were collected for the following periods: 0000-0600; 0800-1200; 1200-1600; 1600-2000; and 2000-0000 PDT. Long duration samples were collected from 0800 to 2000 and from 2000 to 0600 PDT. This arrangement permits comparison of the sum of two or three short duration samples with the corresponding long duration sample. In the current study, one ADS was used to collect short duration samples, while the second was used simultaneously to collect either short or long duration collocated samples.

Performance

Several measures were taken to assure that the data collected with the ADS were of both high and known quality. Results of these studies are highlighted in the following paragraphs.

Analytical Quality Control

Quality control (QC) solutions for NH_4^+, NO_2^-, NO_3^-, and SO_4^{2-} were prepared independently of the routine calibration standards and analyzed daily to determine if the analytical results were biased. The concentrations of these QC samples were chosen to be representative of those found in the authentic environmental samples. The concentration of each species found was compared with the amount expected, and a percent recovery was determined. These results may be used to infer 95 percent confidence intervals for the species recoveries ($\bar{x} \pm 2s$, where $n \approx 85$): 100 ± 2.7 % for NH_4^+; 98 ± 9.9% for NO_2^-; 102 ± 8.2 % for NO_3^-, and 102 ± 3.7% for SO_4^{2-}. These findings show quantitative recovery with very good precision and suggest that there was no bias in the analyses.

Replicate Analyses

Samples collected on each day of the study were selected for replicate analyses to provide estimates of analytical precision. Between 22 and 33 paired comparisons were considered for NH_4^+, NO_2^-, NO_3^- and SO_4^{2-}. For each pair of data, a mean and a coefficient of variation ($CV = 100s/\bar{x}$) were computed. The average of the individual CV's is 6 percent or less for each species.

The individual data were ordered by mean concentration, and average CV's were determined for the upper and lower concentration quartiles for each species. Comparison of these results shows no appreciable difference for NH_4^+. In contrast, the remaining species, NO_2^-, NO_3^-, and SO_4^{2-}, exhibit more relative variability at the low concentrations than at the high concentration.

Concentrations were identified below which the relative variability showed appreciable increases. These liquid concentrations, referred to as critical concentrations, are 0.20 μg NO_2^-/mL, 0.15 μg NO_3^-/mL, and 0.10 μg SO_4^{2-} mL. When only replicate analyses above these arbitrary levels are considered, the average CV's are near 1.0 percent. Ammonium within the concentration range considered did not show an increase in relative variability with decreased concentration and displayed an average CV of less than 2 percent.

Blanks

Both laboratory and field blanks were prepared and analyzed to identify sources and assess the magnitude of contamination. Laboratory blanks were prepared using the coated denuders or filters and were extracted and analyzed in the usual manner. In this case, however, the sampling components were not loaded into the sampler box. Field blanks were prepared in the usual manner: sampling components prepared, loaded into the sampler box, taken to the field, connected to the flow module with zero flow rate for one sampling period, and returned to the laboratory for disassembly, extraction, and analysis.

The ratio of field to laboratory mean blank concentration was examined for each species. This ratio is high for the gaseous species, HNO_2, HNO_3, SO_2, and NH_3, ranging from 2 to 17. It is near unity for the species determined from filter extracts, NH_4^+, NO_3^-, and SO_4^{2-}. This suggests that the operations associated with loading the sampling components and handling/exposing the sampler box provide opportunity for more contamination of gas sampling components than of particle sampling components.

Individual field blank data showed no discernable trends from day to day. As a result, the mean field blank concentrations were determined and used to correct the computed concentrations for each of the reported species. In most cases, this contamination does not appear to be severe since, in general, the equivalent atmospheric concentrations corresponding to the mean field blanks are appreciably less than 0.5 μg/m3.

Ammonia Contamination

During the course of the study, prompt analysis of samples permitted timely examination of results. Although the field blanks showed no evidence of NH_3 contamination, examination of actual field data revealed variable, and sometimes suspiciously high, NH_3 concentrations. Subsequent tests during the field study suggested contamination from a source within the sampling box. Later tests confirmed that the interior foam insulation does release ammonia. This resulted in the invalidation of most of the ammonia data.

Quality Assurance Filters

Independently prepared quality assurance (QA) filters were extracted and analyzed to assess the precision and accuracy associated with nitrate and sulfate recovery from Teflon and nylon filters. Known amounts of KNO_3 and K_2SO_4 from gravimetrically prepared stock solutions were deposited on 47 mm diameter, 1 μm pore size Teflon and nylon membrane filters. For both the Teflon and the nylon filters, each of three 3-filter sets was loaded at a different analyte level. A loading precision of 0.3 percent is claimed.

Prompt extraction and analysis of these QA samples permitted early detection of an apparent species instability at low loading levels on nylon filters. As a result, the study was repeated with a second allocation of 18 spiked filters. The CV's for analyses of three identically loaded filters show good precision (5 percent or less) for both nitrate and sulfate on Teflon filters at each of the three loading levels. This good precision is seen only at the medium and high loading levels for nylon filters, with considerable variability at the lowest loading level. Quantitative recoveries at each of the three loading levels were found for both nitrate and sulfate from Teflon filters. Low recoveries for nitrate and sulfate were found on nylon filters. This bias is largest (50 to 60 percent) at the low loading and decreases (to 2 to 18 percent) at the high loading. These results indicate that no bias is associated with Teflon filter extraction and analysis for nitrates and sulfates. An appreciable bias is indicated for the extraction and analysis of nitrates and sulfates from nylon filters. The implications of these findings are: increased confidence in the accuracy of the particulate nitrate and sulfate data from Teflon filter extracts; and expectation that since volatile nitrate data (based on nylon filter results) are subject to a low bias, they represent a lower bound estimate of the true values.

Equivalent Atmospheric Levels

Using the critical NO_2^-, NO_3^- and SO_4^{2-} concentrations, extraction volumes, and the extremes of sampled air volumes, estimates of equivalent atmospheric levels (EAL's) for good analytical precision were made. These results, shown in Table I, suggest that in the current study, the relative variability associated with analytical precision should be negligible at EAL's above approximately 0.5 $\mu g/m^3$. The fraction of data above this level is also shown for each species. These results suggest that most of the HNO_2, HNO_3, SO_2, and SO_4^{2-} particulate data are relatively free from analytical imprecision. It is likely, however, that much of the NO_3^- particulate data are not of such quality.

Interlaboratory Comparisons

Authentic field samples were selected and analyzed by the regular analytical laboratory and then reanalyzed by two other laboratories to provide bases for interlaboratory evaluation of the quality of the analytical results. During the first week of September 1985, before the start of the current study, the ADS was used on the RTI campus to sample ambient air. The resulting samples were analyzed in the RTI laboratory, and three sets were taken to Los Angeles for reanalysis by the laboratory that would be performing the routine

analyses. The results of these analyses are given in Table II under the heading, "RTI/Regular Laboratory." For each data pair, a mean, standard deviation, and coefficient of variation were computed. The tabulated results summarize these findings by providing the mean of the individual CV's ($\overline{CV}$), the number of pairs of data considered, and a qualitative indication of whether the second measurement exceeded the first. Comparisons were made only for those cases where both paired data points were nonzero; in a few cases, subjectively identified outliers were omitted from consideration. Usually, the outliers were at low concentrations, below those identified earlier as critical concentrations.

The results for the RTI/Regular Laboratory comparison show good interlaboratory agreement. Except for SO_4^{2-}, results of the second analysis were generally smaller than the first.

At the conclusion of the field study, after initial analysis by the regular analytical laboratory, six sets of field samples were selected and returned to RTI for reanalysis. The results are presented in Table II under the heading "Regular Laboratory/RTI," using the previously described analytical format. In this case, the interlaboratory agreement is good. The second measurement exceeded the first for NH_4^+ and SO_4^{2-}, but not for NO_2^- and NO_3^-.

Three sets of samples were selected and sent to Rome, Italy for reanalysis in the CNR laboratory. These results are presented in Table II under the heading, "Regular Laboratory/CNR." The interlaboratory agreement in this case is also good for NO_2^-, NO_3^-, and SO_4^{2-}, and the second measurement for each species exceeded the first.

Since the duration between the first and second analysis for the interlaboratory comparisons was at least a week, an aging study was conducted with analyses performed by the regular laboratory. In this study, three sets of samples were selected from those collected on the second day of the field study. After their initial analysis, they were stored under refrigeration and reanalyzed 8 days later with the last batch of field samples. Results of this study are presented under the heading, "Aging," in Table II. The comparison in this case has $\overline{CV}$'s ranging from 1 to 7 percent. The second measurement exceeds the first for SO_4^{2-} and NH_4^+ but not for NO_2^- and NO_3^-.

Overall, the interlaboratory comparisons show good agreement for each species. The results generally agree to within 20 percent or less. The species concentrations show evidence of aging influences, as indicated by the comparison of the mean magnitudes of the first and second analyses. In each of four cases, the sulfate concentration increased with time, while ammonium increased in two of three cases. Both nitrite and nitrate levels decreased in three of four cases.

Collocated Samples

On selected days during the study, collocated sampling was performed. Two types of sampling strategies were followed. The first strategy involved operating two identical samplers side by side over the same 4- or 6-hour sampling period. There were 17 cases using this approach. Results of this study are summarized in Table III for each of the test species. A coefficient of variation was computed for each data pair. The tabulated results give the number of cases where both paired data points were nonzero (n) and the mean of the individual CV's ($\overline{CV}$).

In general, the collocated samples were in good agreement with $\overline{CV}$'s of 20 percent or less. The best comparisons were found for SO_4^{2-} and SO_2, where agreement was better than 10 percent. Nitrous acid, NH_3, NH_4^+ (particulate), and HNO_3 exhibit comparisons showing agreement of 10 to 20 percent. Agreement was poorest for NO_3^- (total), NO_3^- (particulate), and NO_3^- (volatile): 20 to 25 percent. Subjective inspection of the data also revealed apparent outliers. After elimination of apparent outliers, the comparisons improved and showed agreement of 15 percent or better.

Inspection of collocated results gives an indication of the precision associated with sampling and analysis using the ADS. Based on previously discussed results, the precision of analysis only should be 1 to 2 percent, except for the particulate and volatile NO_3^-, where the analysis precision should not exceed 9 percent. Examination of the $\overline{CV}$'s for the side-by-side collocated samples, in light of the analytical precision estimates, suggests that most of the variability of ADS results is associated with sampling operations rather than chemical analysis.

Since 100 percent of the collocated results for SO_2 and SO_4^{2-} are at concentrations above EAL's, the analytical precision should be better than 1 percent. After eliminating apparent outliers from consideration among side-by-side collocated samples, the sampling and analytical precision for SO_2 and SO_4^{2-} is 6.7 and 6.1 percent. The resulting relative variability associated with ADS sampling of SO_2 and SO_4^{2-} should be slightly less but still between 6 and 7 percent. If SO_2 and SO_4^{2-} may be considered stable, representative gas and particulate species that are not subject to interferences, then the sampling variability for these species may be indicative of the best sampling precision to be expected for the ADS when operated for 4- to 6-hour sampling periods. As a result, a best case relative variability of 6 to 7 percent may be associated with sampling operations for gases and particules using the ADS in its current configuration.

The second collocated sampling strategy involved using one sampler to collect a long duration (10- or 12-hour) sample and using additional samplers to collect short duration (4- and/or 6-hour) samples simultaneously with the long duration sampler. The 10-hour sample was a nighttime sample (2000 to 0600), while the 12-hour sample was a daytime sample (0800 to 2000). Volume-weighted average concentrations were computed using the individual short duration samples to compare with the long duration samples, and CV's were computed for each data pair. Ratios of weighted average to long duration results were also determined for each data pair. These results are presented in Table III as means of the individual CV's ($\overline{CV}$) and as mean ratios ($\overline{Ratio}$). These mean ratios are tabulated for all the paired results.

The volume-weighted average concentrations from the short duration samples are in good agreement with the concentrations from the longer duration samples. The tabulated $\overline{CV}$'s show agreement of better than 10 percent for NH_3, SO_4^{2-}, SO_2, and HNO_2; better than 20 percent for HNO_3, NH_4^+, and NO_3^- (total); and above 20 percent for volatile and particulate NO_3^-. The $\overline{CV}$'s from the volume-weighted comparisons are also in good agreement with those for the side-by-side samples.

Except for particulate and volatile NO_3^-, the weighted averages agree well, with the long duration samples having overall mean ratios of 0.92 to 1.19. This suggests that collection efficiencies for most species are comparable for 4- to 6-hour and 10- to 12-hour samples.

Results

The ambient concentrations of gaseous HNO_3, HNO_2, and SO_2, and fine particle NO_3^-, NH_4^+, and SO_4^{2-} near Los Angeles were determined using the ADS. The range, mean, and median concentrations for each species over the duration of the study are shown below.

Mean and Concentration Range ($\mu g/m^3$) of Species Determined in Ambient Air Near Los Angeles Using the ADS

Gas	Mean	Median	Range	Particle	Mean	Median	Range
HNO_3	4.8	2.0	0.2 to 32	NO_3^-	3.3	1.9	0.0 to 19
HNO_2	3.4	2.8	1.0 to 9	NH_4^+	1.0	0.7	0.3 to 5
SO_2	3.2	3.1	0.6 to 10	SO_4^{2-}	2.4	2.0	0.8 to 7

Concentration trend profiles for each species were prepared from the results of short duration samples. A representative profile is shown in Figure 2; this trend profile is for nitric acid. In this diagram, points representing the 4- to 6-hour average concentrations were connected to permit the trend to be distinguished easily. The diurnal behavior showing daytime accumulation and nighttime depletion is consistent with the concept of HNO_3 being generated photochemically during the day with nocturnal surface deposition.

Conclusions

The performance of the ADS for the determination of HNO_2, HNO_3, NH_3, SO_2, and fine particle NO_3^-, SO_4^{2-}, and NH_4^+, has been evaluated using the results of a field study conducted near Los Angeles. Most of the variability of ADS results is associated with sampling rather than analytical operations. The best-case relative variability associated with gas and particle sampling using the ADS for 4- to 6-hour sampling periods is between 6 and 7 percent. For the species under consideration, except for fine particle nitrates, the collection efficiencies are comparable for 4- to 6-hour and 10- to 12-hour samples. Statistics summarizing the ambient concentrations of each species are given, and an 8-day concentration profile for HNO_3 is presented, which illustrates a pattern typical of species in the atmosphere having a photochemical source and a surface deposition sink.

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TABLE I. ESTIMATES OF THE EQUIVALENT ATMOSPHERIC LEVELS (EAL's) CORRESPONDING TO GOOD ANALYTICAL PRECISION

Sampler Component	1st and 2nd Denuder			Teflon Filter		Nylon Filter
Species	NO_2^-	NO_3^-	SO_4^{2-}	NO_3^-	SO_4^{2-}	NO_3^-
$EAL_{3.3}$ ($\mu g/m^3$)[a]	0.61	0.46	0.30	0.68	0.53	0.80
EAL_{10} ($\mu g/m^3$)	0.21	0.15	0.10	0.22	0.17	0.26
Fraction >0.5 ($\mu g/m^3$)[b]	1.00	0.77	1.00	0.53	1.00	0.63

[a]EAL - equivalent atmospheric concentration, computed using the critical concentrations for good analytical precision, the extraction volumes, and the extremes of sampled air volumes, 3.3 and 10 m^3.

[b]Fraction of the atmospheric concentration data exceeding 0.5 $\mu g/m^3$.

TABLE II. INTERLABORATORY COMPARISONS

Comparison	NH_4^+	NO_2^-	NO_3^-	SO_4^{2-}
RTI/Regular Laboratory				
$\overline{CV}$, %	22.7	15.4	19.8	4.2
n	6	6	5(2)[a]	7(2)
2nd > 1st?	no	no	no	yes
Regular Laboratory/RTI				
$\overline{CV}$, %	4.3	16.8	5.0	3.5
n	9(1)	7(2)	16(6)	11(2)
2nd > 1st?	yes	no	no	yes
Regular Laboratory/CNR				
$\overline{CV}$, %	---	21.8	8.3	5.5
n	---	6	11	6
2nd > 1st?	---	yes	yes	yes
Aging				
$\overline{CV}$, %	4.0	2.8	5.0	6.7
n	7	8	8(3)	6(2)
2nd > 1st?	yes	no	no	yes

[a]Parentheses contain the number of outliers not considered in the compiled statistics.

TABLE III. COMPARISON OF COLLOCATED SAMPLING RESULTS

	HNO_2	HNO_3	SO_2	NH_3	SO_4^{2-}*	NO_3^-*	NO_3^-**	NO_3^-***	NH_4^+*
Side-by-Side Samples Pairs of Nonzero Data									
n	13	17	17	5	17	14	12	17	17
$\overline{CV}$	12.6	17.0	9.2	15.1	6.9	24.2	24.9	20.9	15.4
Weighted Average Versus Long Duration Samples									
n	5	6	6	2	7	7	6	7	7
$\overline{CV}$	8.8	15.1	8.7	1.6	6.1	32.4	28.6	19.9	15.9
$\overline{Ratio}$	1.09	1.19	1.00	1.00	0.93	1.41	1.50	1.19	0.92

*Particulate

**Volatile

***Total

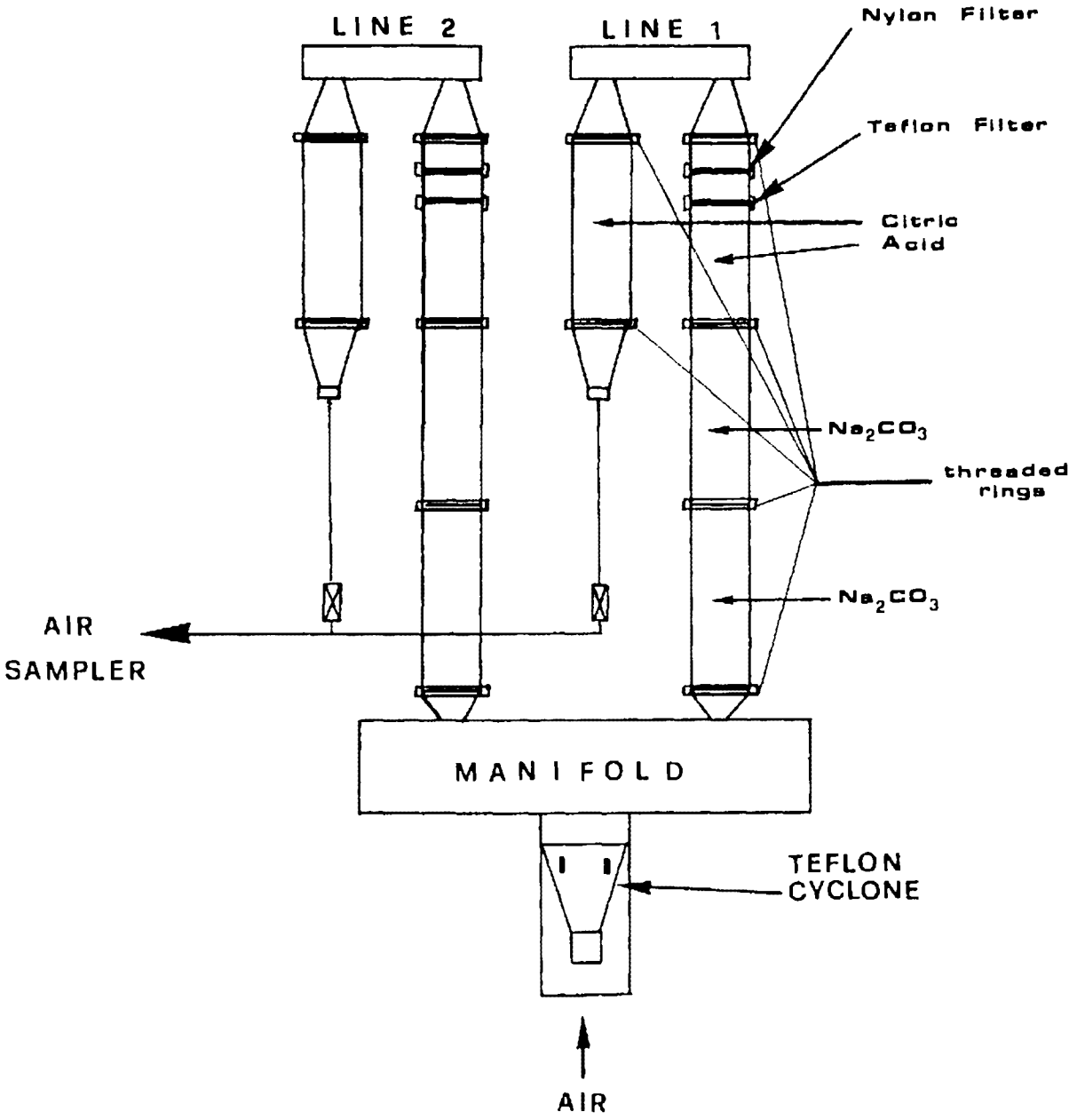

Figure 1. Annular denuder system.

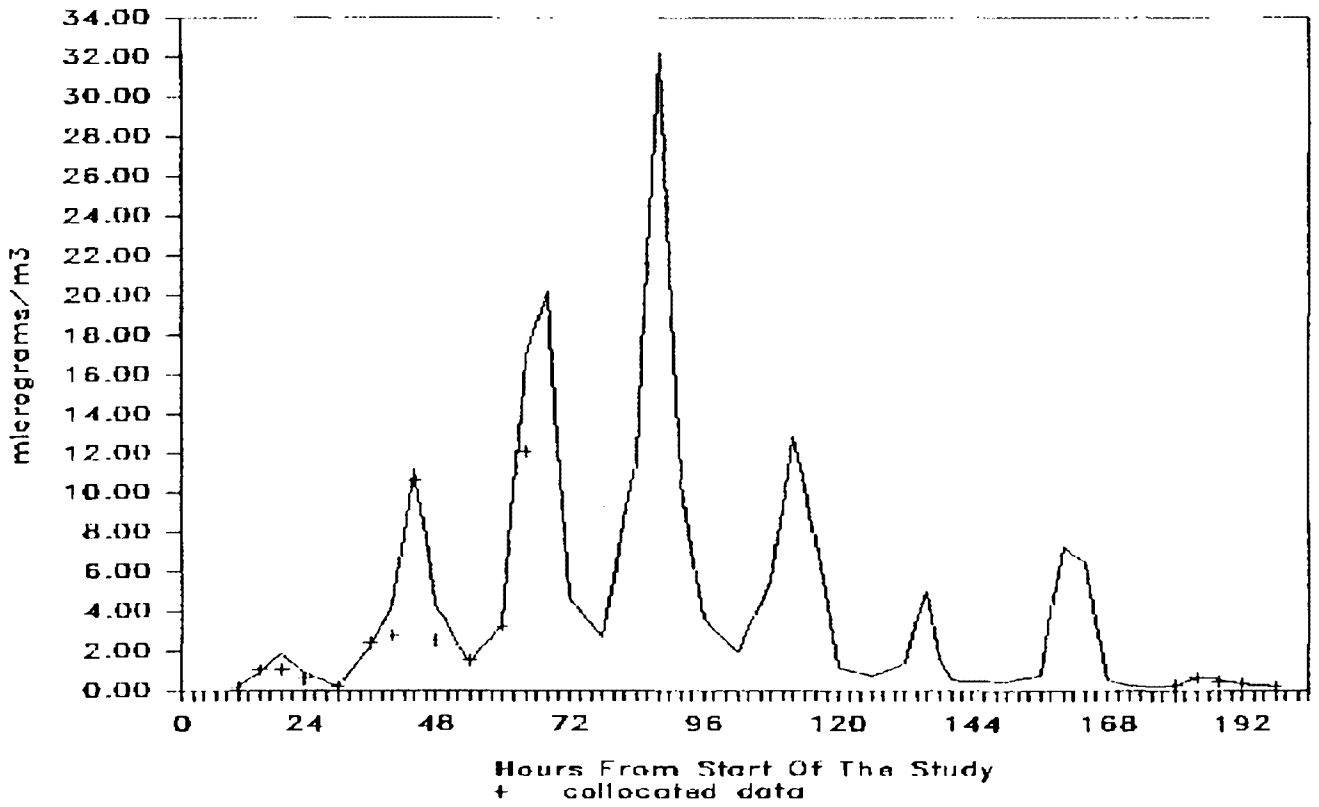

Figure 2. Nitric acid concentration profile near Los Angeles from 0000 PDT September 11 through 0600 PDT September 19, 1985.

A SIMPLIFIED TEM ANALYSIS METHOD FOR ASBESTOS ABATEMENT PROJECTS

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Recently the Office of Toxic Substances, U.S. Environmental Protection Agency, revised the document "Guidance for Controlling Friable Asbestos-Containing Materials in Buildings" with the 1985 edition entitled, "Guidance for Controlling Asbestos-Containing Materials in Buildings" (EPA 560/5-85-024, June 1985).

Air monitoring has a well-defined role in determining when an abatement project is completed. The transmission electron microscopy (TEM) method, although technically superior, has cost, turnaround time, and instrument availability as disadvantages when compared to the Phase Contrast Microscopy (PCM) method with its inherent limitations.

This paper condenses the TEM method that was developed to cover a broad spectrum of asbestos analysis problem situations. That method has been streamlined within the abatement requirements of the 1985 edition. Data necessary for clearance standards are collected, while extraneous information is not.

The applications of the simplified method plus changes such as filter size, carbon coating, counting criteria, and scheduling are presented. Data and results obtained are also shown. Although the method still will not compare in time and cost with the PCM method, the gap has been reduced and thus provides a better option for prospective abatement work.

A SIMPLIFIED TEM ANALYSIS METHOD FOR ASBESTOS ABATEMENT PROJECTS

Introduction

Asbestos is a generic term applied to several commercially useful fibrous silicate minerals and categorized as chrysotile asbestos and amphibole asbestos. The unique properties of asbestos, such as heat resistance, strength, chemical resistance, and morphology led to its extensive use in the construction industry. Sprayed-on troweled-on asbestos-containing materials were commonly used in fireproofing and insulation of the structural components of a building. Asbestos was also incorporated in pipe and boiler room insulation, floor tiles, and decorative wall coverings.

The potential for injury by respiratory exposure to asbestos fibers has been well documented. Asbestosis, lung cancer, and mesothelioma (an incurable cancer of the pleura) have been attributed to asbestos inhalation and the numbers of these cases have been increasing yearly. The latency period for these asbestos-related diseases has been projected at 20 to 40 years, which makes it difficult to assess dose-response relationships, threshold values, or size/shape effects.

Since the U.S. Environmental Protection Agency (EPA) banned the use of asbestos-containing material (ACM) in these construction activities, the problem remained as to what to do with the ACM already in place. The EPA established a Technical Assistance Program (TAP) to provide technical expertise on how to identify and control ACM. The presence of asbestos in schools, public-access buildings, and commercial buildings required identification (location) and its condition (risk). Guidance documents were prepared and distributed in 1979--Orange Book,[1] in 1983--Blue Book,[2] and 1985--Purple Book,[3] which incorporated state-of-the-art results from numerous EPA sponsored studies.

A high risk situation contains deteriorating asbestos designated friable (when dry, could be easily crumbled, pulverized, or reduced to powder by hand pressure) in a location where many individuals would congregate for extended periods of time. Since children have the greatest potential for long term exposure, schools were the first choice objective in asbestos abatement. Building tenants and occupants were also in the risk group.

In asbestos abatement, the owner or manager has already surveyed his building and is aware of the presence, condition, and relative quantity of ACM. The building owners or managers, in considering the health and welfare of their occupants, are also aware of possible legal consequences and public reaction. At present there are four options for the responsible owner/manager. These are:

1. remove the ACM
2. encapsulate the ACM
3. enclose the ACM
4. establish a sound operation and maintenance plan.

The guidance documents provide to the owner/manager a course of action for controlling the ACM.

Asbestos abatement is a growing industry, with a concurrent increase in rules and regulations at the Federal and State levels. The Occupational Safety and Health Administration (OSHA) maintains responsibility for activities inside the enclosed abatement workplace. The EPA responsibility resides outside of the enclosure, checking for asbestos leakage and most important, whether the clean-up of asbestos in the enclosed air space is adequate for removal of the enclosure barriers without release of additional asbestos to the environment. State agencies responsible for asbestos abatement usually incorporate Federal rules, regulations, and guidelines into their regulatory procedures, thus enlarging the area of enforcement.

The EPA presented its latest findings in the 1985 document entitled, "Guidance for Controlling Asbestos-Containing Materials in Buildings," the so-called Purple Book.[3] In this document, release of the abatement contractor is based on visual inspection and air testing to determine that the source of asbestos fiber release has been controlled and the asbestos generated during the abatement activity is below a designated level of acceptance.

Three microscopic methods are used in airborne asbestos analysis. These are phase contrast microscopy (PCM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

The TEM method is the state of the art in identifying and quantifying the asbestos concentration levels in ambient air. It gives the most complete information on airborne asbestos since it can detect the extremely small and thin fibers as well as distinguish asbestos from other fibers. However, it has the reputation of being expensive ($200 to $600 per sample) and time-consuming (two- to seven-day turnaround), and the instrumentation is not widely available.

This presentation is made to show that in air testing for asbestos abatement projects, the recommended, comprehensive TEM analysis method developed under contract to EPA can be simplified. Using the guidelines of the Purple Book and without any sacrifice of quality, the method will result in a less costly and time-consuming analysis. The increased use of TEM analysis should result in a corresponding increase in the number of TEMs.

Method Development

Background

The EPA sponsored an in-depth study of various electron microscopy procedures that resulted in the provisional methodology manual, "Electron Microscope Measurement of Airborne Asbestos Concentrations."[4] Limitations in the provisional method resulted in a follow-up study and the development of a refined transmission electron microscope method for the determination of asbestos in the ambient environment. The refined method, "Methodology for the Measurement of Airborne Asbestos by Electron Microscopy,"[5] incorporates the basic concept of the provisional methodology as one of its protocols. However, both methods are referenced in the Purple Book for air testing for abatement clearance.

The refined methodology is divided into three levels of data acquisition. Level I is a relatively rapid procedure and provides information on

fiber number, size distribution, visual selected area electron diffraction (SAED) pattern, and a calculated mass concentration. Level II adds elementary chemical analysis for individual fibrous structures, and Level III confirms asbestos identification by quantitative electron diffraction pattern analysis.

To meet the objectives of the method's development, emphasis was placed on eliminating non-essential parts of the Level I analysis, incorporating time-saving features of data acquisition and reduction, and changing to a smaller filter size in the air sampling equipment.

Non-Essential Features

The first feature eliminated was the size measurement of the individual fibrous structures. Measurement required positioning of the structure relative to concentric circles of known radius, taking length and width estimates, and finally repositioning back to its original location in order to continue traversing across the grid opening. The writing of lengths and widths onto the data sheet also added to the time factor. Once voice-activated input to a computer is perfected, this feature may be added back to the method.

The second feature to be eliminated was the transfer of data into the computer for a computerized printout of the results. The computer generates calculated mass of individual fibers, aspect ratios, average dimensions, etc. However, according to the Purple Book, only the number of fibers per cc is of importance, and it is used to compare inside and outside levels of the enclosed abatement area. Therefore, the data sheet can be simplified without concern for computer input requirements.

The third feature to be eliminated was the cumulative fibrous structure classification, since in asbestos abatement clearance testing the concentration levels inside the enclosure are monitored during the workday with phase contrast microscopy. Asbestos levels are minimal when clean-up is completed.

Time-Saving Features

The data sheet for the electron microscopist has been redesigned. All pertinent information that was included in the Level I data sheet, computer printout, and report form were incorporated into the abatement data sheet that would be filled in and calculated by hand. The results themselves would then be reported directly to the requestor of the analysis (asbestos project manager); the data sheet would be kept on file.

Change to 25 mm Filter Size

The TEM methods have in the past recommended the 47 mm and 37 mm filter sizes. A change to the 25 mm size results in several time and cost savings.

1. A smaller sampling volume would be required for the same detection limit, or a lower detection limit would be attained for the same sampling volume, as shown in Table 1.
2. With the use of a smaller size filter, more filters can be carbon-coated at one time.

3. The cost of 25 mm filters is less than half that of the 37 mm size. The possibility of a box of filters being contaminated exists, and replacement costs would not be as great. The other filter cassette components would be correspondingly lower in cost. Although field samples and field blanks would be supplied by the asbestos project manager, each laboratory has to prepare its own laboratory blanks.

Results (Simplified Method)

This simplified TEM asbestos analysis method is specifically designed for air testing in an asbestos abatement project and includes the following steps:

1. The 25 mm, 0.4 μm polycarbonate filters in a box are spot checked for asbestos contamination prior to use of the remainder.
2. The three-piece filter cassettes are loaded on a clean bench. A support pad is placed into the cassette base, then a 5.0 μm pore size cellulose ester backing filter is placed on the support pad. Finally, a clean 0.4 μm polycarbonate filter with the shiny side up is placed on the backing filter. The cassette assembly is pressed tightly together to hold the filters in place and prevent leaks from the sides of the cassette. An added precaution is to use a plastic tape to seal the sides. The assembly is then placed in a plastic bag to keep it dust-free until needed.
3. A known volume of air is passed through the polycarbonate filter to obtain approximately 5 to 10 μg of particulates per cm^2 of filter surface. Knowledge of the particulate loading of the source of make-up air into the abatement enclosure will aid in the selection of the sampling volume.
4. Periodic flow rate checks are made with a calibrated flow meter.
5. Upon completion of sampling, the cassette is removed while upright, placed carefully into a plastic bag, and placed in the carry case and hand-carried back to the laboratory.
6. The filter is carbon-coated while still in the cassette by removing only the top lid.
7. The particulates are transferred to an electron microscope (EM) grid using a refined Jaffe Wick Washer.
8. The EM grid is examined under low magnification (250X and 1000X), followed by high magnification search and analysis (20,000X or approximately 16,000X on the fluorescent screen).
9. A known area (measured grid opening) is scanned and the fibrous structures (fibers, bundles, clusters, and matrices) are identified as to asbestos, ambiguous, or non-asbestos; length measured for categorization; and counted. No distinction is made between chrysotile and amphibole asbestos.
10. The observations are recorded for 10 grid openings on the data sheet. For better statistics, another 10 grid openings in a second grid from the same filter may be examined. Figure 1 is an example of a completed data sheet.

Since rates per hour vary between personnel, a standard of comparison may be the analytical time necessary to complete a filter analysis. Previously, a Level I analysis took 3 to 4 hr per sample. With the new method it takes 2 to 2-1/2 hr to complete an analysis.

Thus, for an abatement clearance test, if samples arrive by 3:00 P.M., carbon coating and grid transfer is started before 5:00 P.M. The next morning by 9:00 A.M., samples could be examined in the electron microscope. Results could be telephoned out to the job site 40 hr after receipt of the samples.

Conclusions

A simplified TEM analysis method for asbestos abatement projects is described. The important data necessary for proper evaluation of the airborne levels of asbestos in the abatement enclosure are obtained while eliminating extraneous information. An actual time period of 2 to 2-1/2 hr per sample is estimated for performing the analysis. However, because of grid transfer time, a total of 40 hr is necessary to approve or disapprove contractor clearance.

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TABLE I. DETECTION LIMITS

1.0	Filter Size	25 mm	37 mm
2.0	Effective Filtration Area	3.8 cm^2	8.55 cm^2
3.0	Average Area of Grid Opening (75 μm per side)	.00005625 cm^2	.00005625 cm^2
4.0	Number of Grid Openings	10	10
5.0	Sampling Volume--Detection Limit	3000--2.25 fibers/ liter	3000--5.07 fibers/ liter
6.0	Sampling Volume--Detection Limit	2000--3.38 fibers/ liter	2000--7.6 fibers/ liter
7.0	Sampling Volume--Detection Limit	1332--5.07 fibers/ liter	--

TEM ASBESTOS ABATEMENT ANALYSIS REPORT

Sample I.D. C701-275 | Date Analyzed 1/16/86 | Grid Box Misc. #23
IITRI I.D. C08820-C701 | Accl. Voltage 100 kV | Grid Location B2 + B3
Date Sample Received 1/15/86 | Beam Current 100 μA | Volume Sampled 2520 liters
Filter Type 25 mm Nuclepore | EM Magnification 20,000X | Method of Sampling Aggressive
Filtration Area (cm^2) 3.8 | Fluor. Screen Magnif. 1 μ = 16 mm
Description of Location Northeast corner of enclosure | Results 0.017 asbestos structures per cc

Grid Opening	Chrysotile and Amphibole Asbestos							Ambiguous	Non-Asbestos
	Fibers			Bundles		Clusters	Matrix		
	< 1 μ	1 to 5 μ	> 5 μ	< 5 μ	> 5 μ				
1 0 / 0									
2 / 0		1 1							
3 / 0					1				1
4 0 / 0									
5 / 15		1 1							
6 0 / 16		1					1	1	1
7 / 0		1							
8 / 0	1 1	1							
9 / 19	1	1		1				1	
10 / 0									1
TOTALS	3	8	0	1	1	0	1	2	3
Per Filter Area	9186	24,496	BDL*	3062	3062	BDL*	3062	6124	9186
No. per Liter	3.65	9.72	—	1.22	1.22	—	1.22	2.43	3.65
No. per cc	.004	.01	—	.001	.001	—	.001	.002	.004

*BDL = Below detection level | Detection Limit 1215 asbestos structures per m^3
Area of G.O.--Start 63 x 63 @ 1000X - 64 x 64 | Area of G.O.--End 63 x 63 @ 1000X - 61 x 62
20 (No. of G.O.s Examined) x .00006205 (Avg Area of G.O., cm^2) = .001241 (Total Area Examined, cm^2)
EM Description of Sample Medium loading; opaque spheres and combustion aerosol

Figure 1. An example of a completed data sheet.

A NEAR REAL-TIME INSTRUMENT FOR MONITORING TOTAL, COMBUSTIBLE, AND ASH PARTICULATE FROM INCINERATORS

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The basic concept of the tapered element oscillating microbalance instrumentation as it has been previously applied to realtime particulate measurements is described. A new instrumental form is then described which subjects samples of collected particulate to a high-temperature oxidation step that yields total, oxidizable, and ash residue mass data for a 15-minute instrument cycle time. This unit is fully automatic and has been demonstrated for near-realtime characterization of the carbon content of flyash from a coal-burning power plant. Applications of this measurement technique for combustion control research and emission monitoring characterization at waste incinerators are discussed.

A NEAR REAL-TIME INSTRUMENT FOR MONITORING TOTAL, COMBUSTIBLE, AND ASH PARTICULATE FROM INCINERATORS

Introduction

Background

Particulate mass is a common surrogate parameter for detailed emission species for a wide variety of regulatory, research, and combustion control purposes. Particulate weight as obtained by conventional filter techniques necessarily yields a single average datum per filter, this after a post-experiment gravimetric analysis. The measurement needs of emission characterization research, combustion process control, and continuous emissions monitoring (CEM), are not always well-served by this historic particulate sampling approach, even though it occupies a central position for regulatory compliance determination. Over the years various techniques have been proposed to bring particulate measurement into the "on-line" category of process measurement. These usually suffer from the problem that some additional surrogate property, such as opacity, is introduced in place of mass, with the correlation to mass then depending on non-mass related particulate properties. This dilemma represents an acute problem if the realtime measurement is to serve the dual purposes of characterization and compliance testing.

This paper is not a general survey of realtime instrumentation concepts or their current status; it is rather an introduction to one emerging technique for realtime measurement of collected mass on a filter substrate. Here, a mass sensitive instrument is brought to the particle sampling point and a large number of realtime mass determinations are provided while particulate collects on a single filter. The mass measurement is accomplished by a proprietary concept wherein the particulate collection filter sits atop a hollow tapered tube which oscillates in a lateral plane while sample flow passes through the filter and out through the center of this tapered element. The frequency of oscillation for the tapered element is analogous to a common tuning fork, in that the frequency is uniquely related to the oscillating mass. This patented tapered element oscillating microbalance (produced exclusively by Rupperecht and Patashnick Company, Inc. under the trade name TEOM®) technology has been the subject of numerous demonstration projects applied to a wide range of particulate measurement conditions. These include ambient air[1], underground mine air[2], fire research, turbine exhaust, diesel emissions[3,4,5,6], stack testing from stationary combustion sources[7,8], and is also being prepared for particle measurement in space. From this early phase of prototype TEOM instrumentation one can anticipate a subsequent phase wherein the TEOM concept will gain a wider acceptance, where several applications will become instrumentally routine. Identification of clear measurement goals will thus become significant in directing these developments, since the question is not "Can one measure particulate mass in realtime," but rather "To what end will the demonstrated capability be applied?"

This paper describes a prototype TEOM instrument constructed for the goal of monitoring not only total particulate mass, but also the mass fraction removed by heating to ≈ 800°C in air. Through repeated programmed time-cycle instrument steps of collection, oxidation, and ash

removal, this instrument operated on a near-realtime basis. This TEOM instrument thus provides near-realtime data indicating total, "combustible", and ash residue data from an experimental test in a coal-burning power-plant.

The array of regulatory, research, and combustion control needs facing the expected large scale introduction of waste incinerators makes this TEOM concept a logical candidate for some of these purposes. Potential uses for the data generated by the TEOM would include: more efficient operation of the combustion and flue gas cleanup equipment, a refined correlation parameter for chemical species studies, and a useful CEM parameter to insure regulatory compliance and public acceptance. However, since the near-realtime partitioning of total particulate mass into combustible and ash residue fractions remains to be applied to a combustion source burning the variety of fuel/feed components typical of waste incineration, these applications are deserving of demonstration research study.

TEOM Concept

A schematic of the TEOM concept for particle mass measurement is shown in Figure 1. Particle laden gas passes through the filter and down through the hollow tapered element to mass flow control components, not shown. Mass measurement during this sampling process is achieved by detection of a change in oscillation frequency of the tapered element/filter/particulate composite. The following steps described how these oscillations are established and detected; referenced to Figure 1.

1) A constant DC electric field is set up between the field plates.
2) An image of the tapered element is projected on a phototransistor by the illumination provided by a light emitting diode (LED).
3) The mechanical oscillation of the tapered element produces an AC voltage at the phototransistor.
4) This AC voltage is amplified and fed back through a conductive path on the tapered element. This voltage then interacts with the DC electric field and maintains the oscillation of the element at its resonant frequency.
5) The frequency of oscillation is determined by a counter/timer interfaced to an electronic control and data processing module.

When an increment of particulate mass, δm, has accumulated on the oscillating filter, the frequency of oscillation changes (decreases) according to:

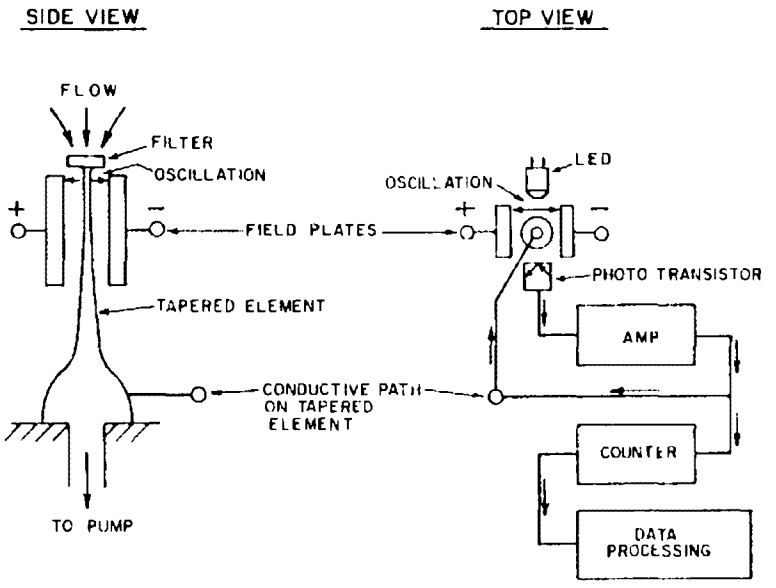
$$\delta m = K_o \left(f_1^{-2} - f_o^{-2}\right) \qquad (1)$$

where δm = deposited mass on filter

K_o = calibration constant

f_o = frequency before addition of mass, δm

f_1 = frequency after mass addition, δm



Typical Tapered Element Oscillating Microbalance (TEOM®) Configuration

Figure 1

By proper dimensioning of the tapered element the sensitivity of the mass/frequency relationship can be selected according to the measurement application. TEOM instruments have been built that span the range of sensitivity from picograms to grams. Previous work by the authors has explored calibration techniques[6] and found the inherent linearity sufficient to enable single point calibration capable of ±1% accuracy over a wide range of mass additions. In Equation 1, K_o represents a constant based on the physics of an a harmonic oscillator, and in practice the TEOM unit conforms to this description sufficiently well that K_o can be treated as a constant for incremental mass additions to a clean filter as well as final mass additions to a dirty filter. Thus, a frequency comparison between any two times in a long series of data acqusition points provides an accurate mass differential on the filter corresponding to these times.

A TEOM Instrument for Measuring Carbon in Flyash

Background

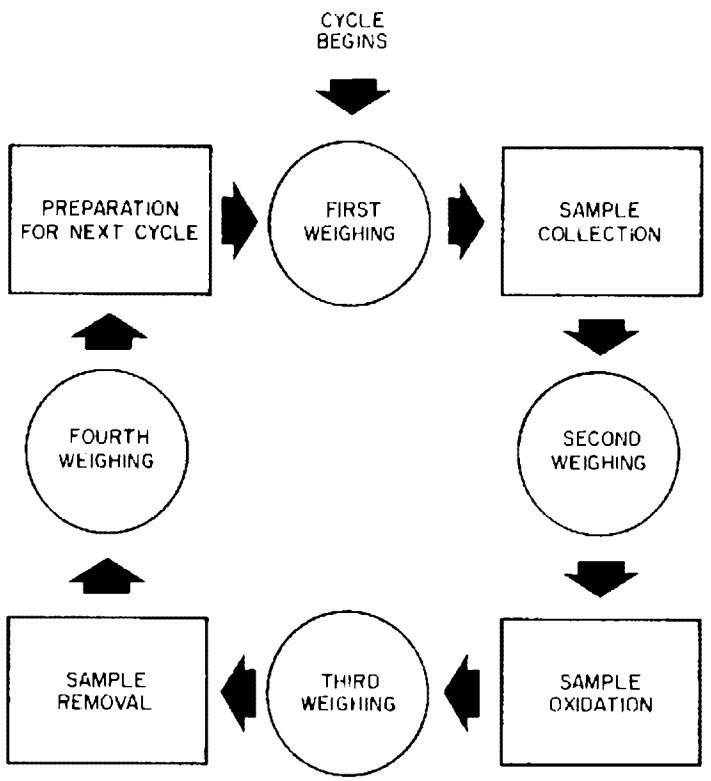
A common characteristic of flyash used by plant operators for combustion evaluation is the Loss-On-Ignition test (LOI) to determine the carbon (combustible, or oxidizable) content of flyash. This is a laboratory analysis test providing retrospective data on the plant, whereas the TEOM instrument to accomplish this particulate characterization is automatic, and performs the analysis on a 15-minute time cycle basis with immediate graphic reporting of results.

Mode of Operation

This instrument uses a ceramic filter placed on the tapered element, with three different sequential instrument functions performed on the ceramic filter. Particulate sample is first collected, then heated to drive off the oxidizable portion of the collected sample, and finally the ceramic filter is cleaned to remove the non-oxidizable portion of the particle sample. A mass determination is recorded between each of these steps from which results are obtained for total particulate, loss of combustible particulate, ash residue, and clean-up efficiency. The sequence of functional steps in a complete instrument cycle is shown in Figure 2.

Key Instrument Features

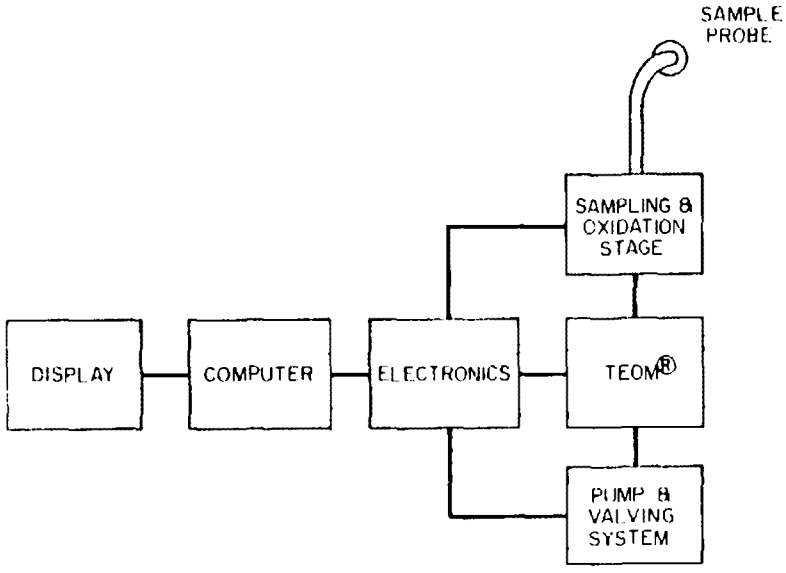
The key features that describe this instrument are briefly outlined below, although numerous critical details such as flow control, computer software, graphic display options, and automatic fault diagnosis are omitted for this conceptual presentation.



TEOM® CARBON CONCENTRATON MONITOR INSTRUMENT CYCLE

Figure 2

Instrument Sub-System Schematic. Figure 3 is a block diagram showing the various sub-systems and their functional relationships. A desk top computer controls all sequencing of the instrument operations and displays results and error messages. The computer, which can be located remotely from the measurement system, is interfaced with an electronics module that 1) controls and extracts mass data from the TEOM frequency signals, 2) controls the moveable stage and heated sample probe to the stack, and 3) controls the pumping and valving systems to achieve the various functions previously described. Figure 4 schematically shows



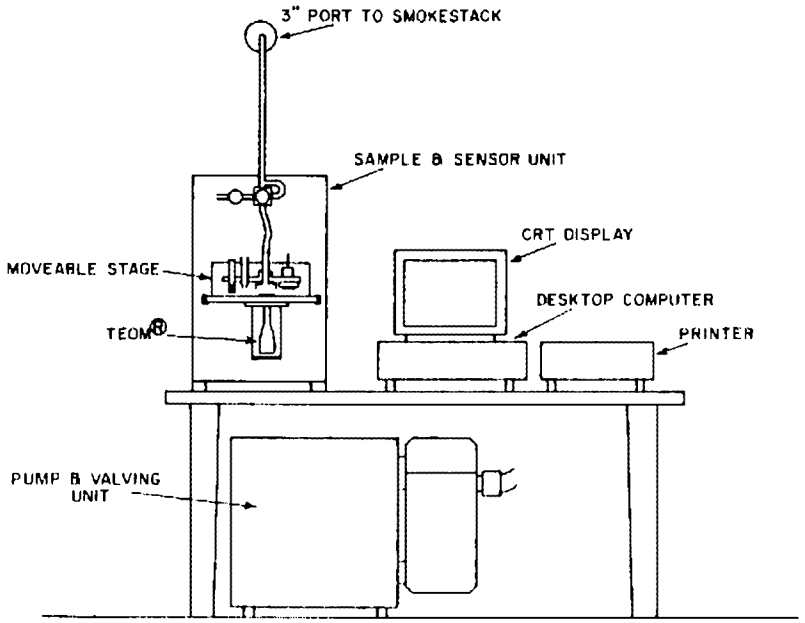
CARBON MONITOR SUB-SYSTEMS

Figure 3

these subsystems as they were configured for operation with the computer/printer situated next to the sampling, sensing, and flow control elements.

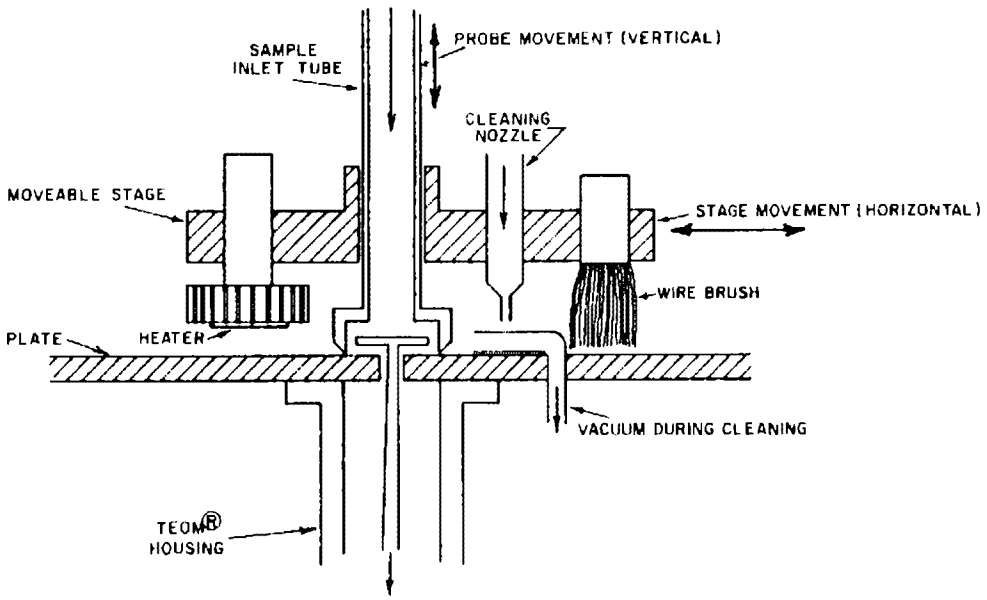
Movable Stage Design. The functions of particulate collection, heating, and ash residue clean-up were all incorporated into a movable stage assembly as shown schematically in Figure 5. The movable stage provides precise location in both the lateral and vertical directions under instrument computer control. The TEOM and ceramic filter assembly are fixed below this moveable stage.

Operation Cycle. The sequence of instrument operations that constitute a complete measurement cycle was previously shown in block diagram form as Figure 2. With the unloaded filter in position for sampling, a frequency determination is made to start the cycle. Sample



SCHEMATIC OF SYSTEM COMPONENTS

Figure 4



THE MOVEABLE STAGE IN SAMPLING MODE

Figure 5

collection then follows for either a prescribed time interval or particulate mass loading on the filter, after which a second frequency determination is obtained yielding the total mass collected. The heating element is then moved into position and the sample temperature is raised to approximately 800°C for a few minutes. A second frequency measurement is recorded after cool-down. The computer monitors TEOM frequency and stability before final mass determinations to insure that filter mass loadings are not changing when readings are taken.

Sample removal then proceeds with the moveable stage positioned to direct the air nozzle over the filter. Compressed air is then back flushed through the tapered element and ceramic filter while vacuum draws the dislodged residue away from the sensing area. Simultaneously, compressed air is directed through the nozzle to aid the cleaning process. Nozzle flow is stopped while the back flush flow continues, and the stage moves back and forth to cause a wire brush to wipe across the filter to complete the cleaning process.

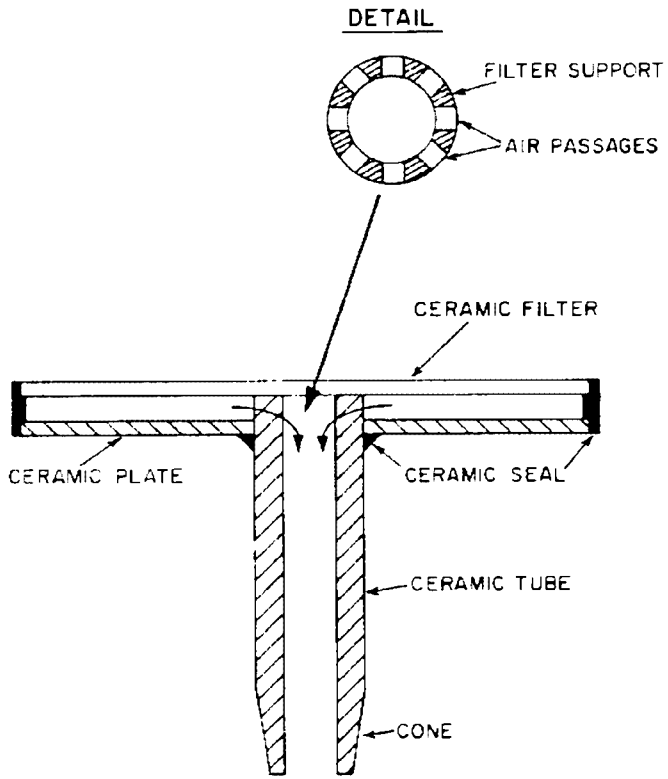
The stage then moves back to the sampling position, and the frequency of the cleaned filter recorded to determine both the efficiency of particulate removal for the current instrument cycle and the baseline filter mass for the next cycle. The entire instrument cycle was, for this application, set to 15 minutes.

Ceramic Filter. A new ceramic filter, shown in Figure 6, was designed for the TEOM instrument so that a high-temperature oxidation period would not damage the filter during the LOI tests. The porous ceramic filter for particulate collection is supported and sealed by solid ceramic elements, with the ceramic stem of the filter tapered to fit the oscillating tapered element. This filter was designed to have both low mass, which increases the mass sensitivity of the final TEOM instrument; as well as low thermal mass, which aided in optimizing the cycle time required for heat-up and cool-down.

The filter is removable from the tapered element, allowing filter exchange as needed. In this application the filter was not changed but was automatically cleaned as part of the event cycle, as described below.

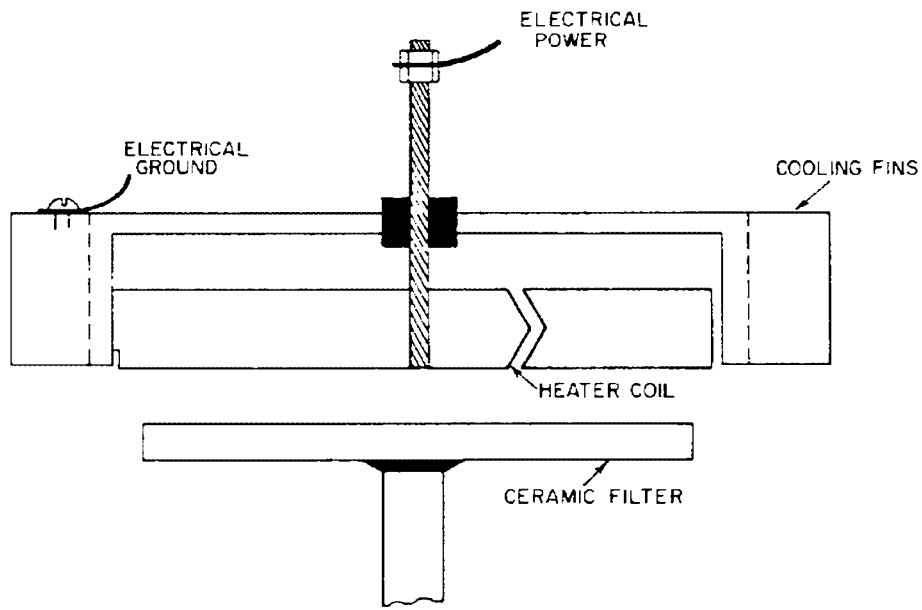
Heater Design. Particulate collected on the ceramic filter was heated by a spiral-wound nichrome ribbon that forms a disc-shaped element, shown schematically in Figure 7. Height of the heater element above the ceramic filter is adjustable, and is set to provide rapid heat-up of the particulate sample when the heater is powered. A thermocouple positioned on the ceramic filter indicated a steady 800°C temperature after one minute of heater operation. From previous LOI test characterizations of flyash this heating level was considered ideal.

Flow Control. Throughout the entire cycle of instrument operation several flow conditions are demanded, including sample flow through the TEOM filter, reverse flow through the heated stack sample probe prior to reestablishment of sample flow, reverse flow through the TEOM ceramic filter after ash determination to clean the ash from the filter, nozzle flow directed at the face of the ceramic filter during the clean-up segment, and also vacuum flow to collect the dislodged ash particles during this clean-up phase.



CERAMIC FILTER DESIGN

Figure 6



HEATER ELEMENT OVER FILTER

Figure 7

Results

Laboratory Tests

Flyash samples with carbon content ranging from 2.3% to 12.2% as determined by standard LOI techniques were used to test the TEOM instrument. Each flyash sample was desiccated and then aspirated into the instrument, which then cycled through the steps as previously described. The nominal loading of total particulate for these tests was program set to be 35mg. The average difference between the LOI valves and those obtained by the TEOM instrument was 0.5% by weight. Since no errors of determination were available for the laboratory LOI values, this result is a comparative and not an absolute value.

Determination of LOI valves at low carbon content is more demanding than at higher levels since the subtraction of two large numbers (before and after oxidation) to yield an accurate weight loss of small magnitude increases the influence of any other sampling or measurement errors. The flyash sample with 2.3% carbon as determined by the standard LOI method was tested seven times by the TEOM instrument with the a 2.38 ± 0.19 (C.V. = 8%) result for these runs.

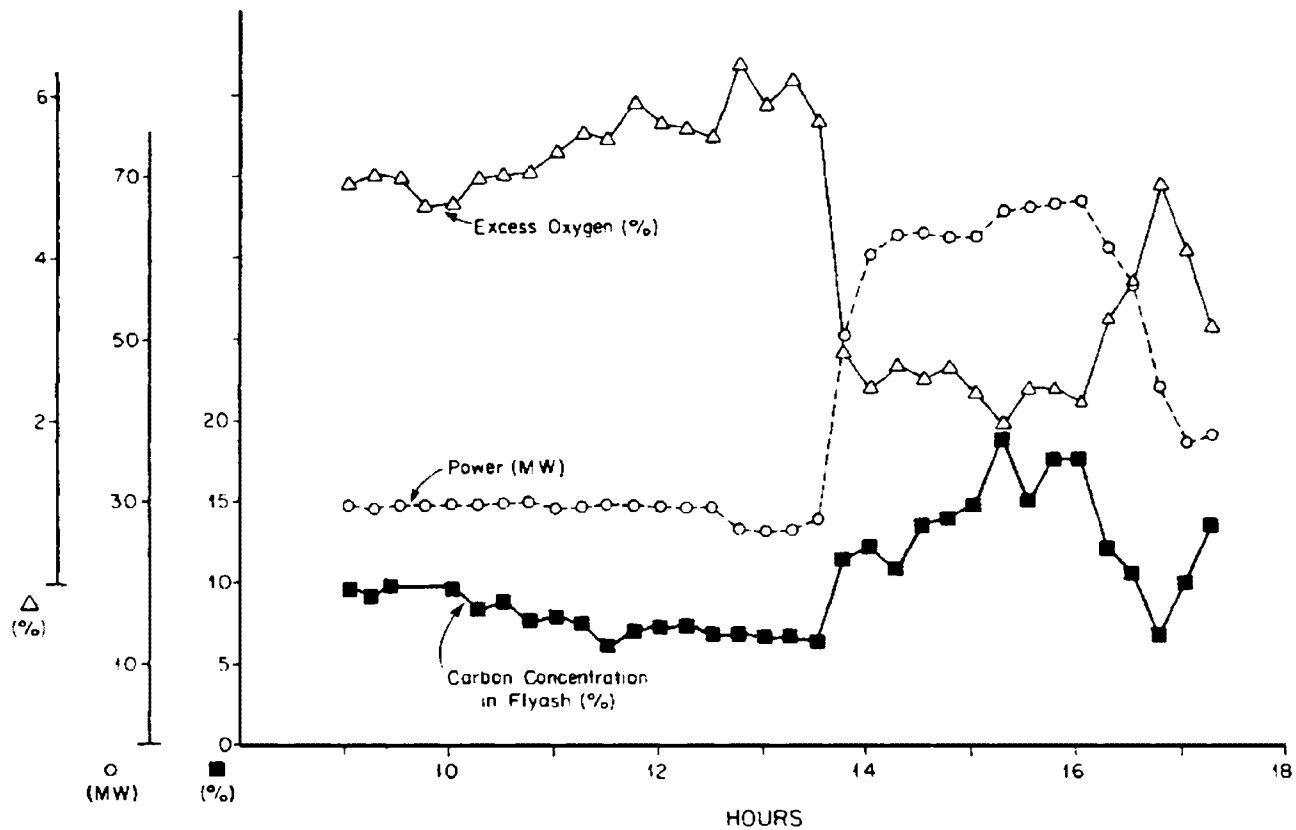
The removal efficiency of particulate from the ceramic filter between sampling runs averaged 98.7% for these seven runs. Obviously if the filter slowly loads up with material that is not removed, it will increase in pressure drop and require a new filter. Both the laboratory and stack tests with flyash exhibited very high removal efficiencies which permit fairly long periods of instrument operation. If filter plugging is a problem encountered in further application testing, the ceramic filters could be mass produced as a replaceable instrument item.

Stack Tests

The TEOM instrument was used for stack-test evaluation at a coal-burning power plant. The cycle time was set to 15 minutes. Figure 8 shows the results from 12 hours of operation, with the flyash carbon concentration displayed in parallel with power output of the plant and excess oxygen. Changes in flyash character as determined in near-realtime by the TEOM are evident in concert with plant operation adjustments.

Discussion

A new instrumental method capable of providing near-realtime particulate, oxidizable fraction, and ash residue has been demonstrated for application to coal-burning power plants. Extension of this prototype instrument to characterization of particulate emissions for waste incineration may require further instrument modifications since the particulate source is more complex and varied, but these can reasonably be anticipated to be solvable given the existing work. The ultimate use or value of such data will not really be evident until some representative data are first obtained. As compared to combustion monitoring through standard gas analysis, particulate and particulate break-down data should provide results more directly related to the species of emission concern.



FLYASH CARBON CONCENTRATION RESULTS FROM A COAL-BURNING POWER PLANT

Figure 8

Given the proto-type nature of the present TEOM instrument, these studies should at present be viewed as research topics by which to advance both the applicability of the technique and the understanding of incinerator emissions. Beyond those goals, the TEOM instrumental technique presented would appear to have significant long-term potential for CEM use to insure that incinerator facilities are routinely operated in accordance with permit specifications.

Acknowledgements

Funding for the TEOM Carbon Concentration Monitor project was provided by the Empire State Electric Energy Research Corporation and the New York State Energy and Research Development Authority.

The authors thank Linda Stuart for manuscript preparation and Gary Lanphear for cartographic contributions.

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AMBIENT ATMOSPHERIC CONCENTRATIONS OF TOXIC METAL AND TOXIC ORGANIC SPECIES IN NEW YORK STATE URBAN ENVIRONMENTS

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The New York State Department of Environmental Conservation, in cooperation with the NYS Department of Health's Wadsworth Center for Laboratories and Research, has initiated the Toxic Air Monitoring (TAM) project to monitor air toxics on a routine basis and for determining the background concentrations in selected urban environments across the state.

Ambient atmospheric measurements for seven toxic metal species (Cd, Cr, Mn, Ni, Pb, V, and Zn) and four classes of toxic organic species (phthalates, hexachlorocyclohexanes, polychlorinated biphenyls, and benzo[a]pyrene) at ten sites in urban areas of New York State indicated that ambient concentrations were lower than the concentrations currently used as the New York State acceptable ambient levels (AAL).

Vanadium at Poughkeepsie and lead at Hempstead (Long Island) exhibited the highest ambient mean concentration to AAL ratios. Statistical estimates of the upper limit of the annual means for these two highest data sets were 0.51 AAL and 0.38 AAL respectively. The means of the data sets (21 to 27 samples taken over one year periods) were typically 0.05 AAL to 0.25 AAL for Pb and V and below 0.05 AAL for the other metal species monitored. Organic species were not observed at concentrations above 0.025 AAL with the exception of benzo[a]pyrene, which was frequently observed in the 0.015 AAL to 0.15 AAL range.

In addition, the first unambiguous measurement of dioxins and furans in ambient air in the U. S. was conducted at two sites in New York State and results indicate no immediate or acute health concerns. However, the existing database is very limited and more monitoring data is needed to form better conclusions.

AMBIENT ATMOSPHERIC CONCENTRATIONS OF TOXIC METAL AND TOXIC ORGANIC SPECIES IN NEW YORK STATE URBAN ENVIRONMENTS

Introduction

This work was undertaken as a part of the New York State Department of Environmental Conservation's Toxic Air Monitoring (TAM) program. The purpose of the TAM program is to provide, for the first time, long-term systematic collection and analysis of selected toxic air contaminants at sites located statewide. Previous studies have been short-term source oriented and not sufficiently developed and funded to adequately identify atmospheric toxics or to detect temporal and spatial variations of contaminant concentrations. Additionally, the minimum detection level was not always low enough in previous studies to adequately measure the background concentrations of toxic contaminants.

The contaminants chosen for this study were selected primarily because of their interest within the Department and because only minimal research effort would be required for an expeditious start of the program. Funding levels also limited the scope of the study.

Measured values were compared to acceptable ambient levels (AAL)* obtained, except where noted, from "Air Guide-1," a publication of the New York State Department of Environmental Conservation which serves as a guideline document for the control of toxic ambient air contaminants[1]. The AAL values for measured species are presented in Table I.

The Division of Air Resources (Department of Environmental Conservation) was responsible for the selection and operation of sample sites and the collection of all ambient samples. All analytical chemistry to determine concentrations of the selected toxic contaminants in samples was performed by the Wadsworth Center of the Division of Laboratories and Research (Department of Health).

Study Sites

The Toxics Air Monitoring sites were selected to provide measurements representative of urban, industrialized, residential, and background areas. Personnel from the Department of Environmental Conservation were responsible for the selection and establishment of the sampling sites. Some of the study sites were continuous air monitoring stations (CAMS) which are part of the Division of Air Resources' air monitoring network. Other sites were stations that are also in the total suspended particulate (TSP) monitoring network or in use for special studies. The Lake Placid site was specifically selected for this study to provide background measurement data.

The use of existing CAMS and TSP sites maximized the information available with minimal expense. CAMS personnel were employed to operate the organic toxics sampling equipment and TSP filter samplers. The TAM study sites and sampling periods are presented in Table II and described in detail below. Some sites remain currently active in the TAM program.

*Acceptable Ambient Levels (AALs) in New York State are defined by: NYS Department of Environmental Conservation, "NYS Air Guide-1, Guidelines for the Control of Toxic Ambient Air Contaminant, 1985-86." A calculated AAL value (such as TLV/300) is used when a contaminant specific AAL analysis based on health effect criteria is not available.

° The Poughkeepsie site is located in the western portion of the city next to the Hudson River, in an urban area close to Columbus School. The site is a continuous monitoring station for SO_2, O_3, and meteorological parameters, and is operated by Department personnel.

° The Buffalo site is located on the roof of Public School 66 at Parkside and Tacoma Avenue in the central part of Buffalo. It is primarily a residential area, downwind of industry located along the Niagara River. The site is operated by Department personnel.

° The Lake Placid site is located on the roof of the Lake Placid arena, 216 Main Street. The village is situated in the north central portion of the Adirondack Mountains. The site is operated by Department personnel.

° The Rochester site is on Farmington Road in eastern Rochester. The site is a continuous monitoring station for SO_2, O_3, CO, and meteorological parameters and is operated by Department personnel.

° The Hempstead site is at Eisenhower Park and Merrick Avenue in eastern Nassau County. This is a continuous monitoring station for SO_2, CO, NO_x, and meteorological parameters operated by County personnel.

° The Niagara Falls site is at 63rd Street and Girard Avenue, in the southeastern part of the city. The site is a continuous monitoring station for SO_2, O_3, CO, and meteorological parameters, operated by Department personnel.

° The Syracuse site is located on the roof of Lakeland Elementary School, on Bury Drive in the western portion of Syracuse. This TSP site is operated by State personnel.

° The Rensselaer site is on Riverside Drive at the southeastern part of the city, on the eastern side of the Hudson River. This is a continuous monitoring station for O_3 and meteorological parameters operated by Department personnel.

° The Greenpoint site is on the roof of the Sewage Treatment Plant at 301 Greenpoint Avenue in northern Brooklyn. This station is located in an industrial area and continuously monitors for SO_2. The station is operated by Department personnel.

° The Susan Wagner site is located in Staten Island at the Susan Wagner High School at 50 Brielle Avenue. This is a residential location. The station also monitors continuously for SO_2, O_3, and meteorological parameters under the operation of Department personnel.

° The Travis site is located on the roof of Public School No. 26 at 4108 Victory Boulevard in Staten island. This is a residential location. This TSP site is operated by Department personnel.

Procedures and Methods

Toxic Metal Species

Toxic metal species are found in particulate form in ambient air. To determine the selected metal species concentrations, particulate samples were collected on glass fiber filter paper. Filter paper manufactured by Schleicher and Schuell or by Whatman were used during the January to March 1982 study period. Following this initial period, only Whatman

filters were used. Samples were collected using the standard high volume air sampling unit (General Metal Works) used throughout the TSP network. Air samples were collected over 24 hour periods, from midnight to midnight.

After air sample collection, the filters were first weighed to obtain TSP data for each site and then subjected to chemical analysis to determine concentrations of toxic metal species. Portions of the filters were subjected to a heated nitric acid extraction procedure using 15 ml of 3 molar nitric acid. Distilled, deionized water was added to the acid solution (after cooling) to bring the volume to 40 ml. The sample solution was shaken and centrifuged and the supernatant liquid transferred to plastic vials. The samples were then analyzed by atomic absorption sectrophotometry. During the 1982 portion of the project, flame atomic absorption spectrophotometry (FAAS) was the analytical method employed for lead, zinc, and copper species. FAAS was also used to determine cadmium, chromium, and nickel concentrations for January through March 1982 samples. The latter species, however, were determined by graphite furnace atomic absorption spectrophotometry (GFAAS) for the remainder of 1982. During the 1983-84 phase of the project, samples were first analyzed for toxic metal species by FAAS and sample extracts below predetermined concentrations were further analyzed by the more sensitive GFAAS technique.

Analytical determination of copper species was discontinued at the end of 1982 due to suspected contamination of samples from electrical arcing in the high volume sampler blowers which draw air through the filters. Copper data are, therefore, not reported here in view of the possible sample contamination. Vanadium and manganese were added to the 1983-84 phase of the project, primarily to serve as tracer species data for the acid rain program.

Toxic Organic Species

Toxic organic species may exist in gas phase or particulate forms in the ambient atmosphere. Many organic species may be collected on a suitable sorbent material contained in a cartridge through which ambient air is drawn. An organic solvent extraction of the collected species, followed by chemical analysis of the resultant extract, determines the concentrations of the toxic organics in the ambient atmosphere.

In this study polychlorinated biphenyls (PCB), hexachlorocyclohexanes (BHC), and phthalate species were selected as toxic organics to be determined in ambient air samples by collection on sorbent media. An additional toxic organic, benzo[a]pyrene (BaP), was determined using TSP filter samples.

Sorbent cartridges (0.75 x 5 inch glass tubes) containing activated Florisil (7-8 grams, 60-100 mesh, held in place by glass wool end plugs) were attached to ollless vacuum pumps by Tygon tubing. A total of 17 to 20 cubic meters of air was drawn through the cartridge at a constant rate over a 24 hour period for each sample.

Following sample collection, the sorbent was eluted with a 1:1 hexane:ether mixture (100 ml) and the eluate (contalning collected PCBs, BHCs, and phthalates) concentrated to about 1 ml. The concentrate was rechromatographed on a column (1 x 30 cm) packed with 3% deactivated Florisil (10 g). Two 100 ml fractions were collected. The first fraction was eluted with 6% ether in hexane and contained the PCBs and BHCs.

Phthalates were collected in the second fraction which was eluted with 20% ether in hexane. Both fractions were concentrated to 1 ml and transferred to vials for analysis by gas chromatography (GC).

Analysis was performed by electron capture (EC) detection on a Hewlett Packard 5840 gas chromatograph equipped with an SE-54 capillary column (60m) using hydrogen carrier gas and argon/methane makeup gas. Following a one minute initial hold, the column oven was temperature programmed from 80°C to 260°C at a rate of 5°C/min with a 15 minute final hold. The injector and EC detector temperatures were 225°C and 310°C, respectively.

BaP analysis was performed on one TSP sample per month, using the same filter sample which was analyzed for toxic metals, provided sufficient sample remained after the metal analysis. Otherwise, another filter collected during the same month was used. Fifty percent of the TSP filter was extracted with benzene and the extract concentrated to 1 ml. The concentrate was chromatographed on a 3% deactivated silica gel column (1 x 30 cm, 35-70 mesh, 10 g) in hexane. Elution with 25 ml hexane was followed by a 60 ml, 6:4 hexane:methylene chloride elution. The first fraction was discarded and the second fraction concentrated to 1 ml then transferred to vials for automatic injection to a GC for analysis by flame ionization detection (FID).

A Hewlett Packard 5880 GC-FID instrument was equipped with an SE-30 capillary column (30m) for BaP analysis. The column oven was temperature programmed from 80°C to 275°C at 10°C/min with a 20 minute final hold. Injection port and FID temperatures were 225°C and 280°C, respectively. Helium was used as both carrier and makeup gas.

Field Sampling

TSP filters were collected according to Federal Reference Methods[2,3] which address such necessary issues as flow rate calibration, total volume air sample calculation, and sample handling and transport to analytical laboratory facilities. Detailed information on the TSP network procedures may be found in the Division of Air Resources Annual Report[4].

Air flow measurements were performed on the Florisil cartridges before and after sampling. The average flow was used to calculate the total air volume sampled. During 1982 and 1983, additional flow measurements taken at the sample sites were found to be within 8.4% of the average flow calculations.

Filter and cartridge samples were collected over 24 hour periods (midnight to midnight) on a 6 day schedule from January through March 1982 and generally on a 12 day cycle thereafter. Site operators were responsible for ensuring proper sample identification, recording flow related equipment measurements, preparing clean filters and cartridges for the succeeding sampling period, and forwarding collected samples by mail to project analytical staff.

Quality Assurance

Quality control measures for toxic metals included reagent and filter blank analyses, spiked sample recovery determinations from clean and sampled filters, and duplicate analysis of filter aliquots.

Quality control for BaP included recovery analysis from spiked glass fiber filters and recovery analysis from the 3% deactivated silica gel column. Spiked Florisil cartridge tests were performed for PCBs, BHCs, and phthalates. In addition, blank (clean) filter and Florisil cartridge analyses were also performed.

Assurance testing was undertaken to insure against organic breakthrough in the Florisil cartridge and also to establish analytical procedures which unambiguously separated BHCs and phthalates into separate elution fractions. The procedures previously described accomplished the latter by rechromatographing the Florisil sampling cartridge eluate into two fractions on a second Florisil column. This procedure was necessary because BHCs were potentially more mobile in the cartridge and consequently may have been partitioned into either or both fractions of a simple two stage elution of the sampling cartridge.

Results

Toxic Metals

The 1982-84 TAM study collected nearly 400 TSP filters at the 11 sites given in Table II. The 1982 sites were located in western and central New York and in the upper Hudson Valley. The 1983-84 sites were lower Hudson Valley and metropolitan New York City locations. The background Lake Placid site was operative in both periods of the study.

Five toxic metal species were determined throughout the study (cadmium, Cd; chromium, Cr; nickel, Ni; lead, Pb; and zinc, Zn). In 1983-84 two additional metal species were added (vanadium, V; and manganese, Mn). In the 1982 phase, 20 to 24 measurements (24 hour samples) were available at each site for Pb and Ni. For the other metal species, several samples yielded less than detectable levels during the first three months of the project. Also, during this period Zn was not included in the analysis of some samples. For the remainder of 1982 significant improvement in the minimum detectable levels (MDL) for Cd and Cr provided greater sensitivity for these species. However, only 9 to 11 samples using improved analytical procedures with lower MDLs were available at several sites for some species.

Ambient concentrations of toxic metals at each site are expressed as ratios relative to the acceptable ambient level (AAL). This normalization simplifies presentation and discussion of the data. Typical ambient concentrations are less than one-tenth or one-twentieth of the AAL (0.1 AAL or 0.05 AAL). In some cases, however, maximum observations (single samples) may exceed 0.5 AAL. Figures 1-3 present the maximum and mean (arithmetic) concentrations as AAL ratios for each toxic metal species measured at each site. The 1982 Lake Placid results are not presented, as the data for measured species yielded similar mean and generally lower maximum concentration values relative to the 1983-84 results at that site.

With regard to maximum values, it is important to note that a single sample which approximates or exceeds the AAL concentration does not necessarily indicate a danger to public health. The AAL values for each toxic species are generally derived from the occupational health and safety exposure regulations and include a large margin of safety (typically a factor of about 300). Thus, an ambient concentration equal to the AAL would, in most cases, be approximately 1/300 the maximum acceptable concentration in the work environment. Furthermore, the AAL is

established as an annual mean concentration. For this reason the mean concentrations relative to the AAL are important while maxima must be considered relative to short duration exposure criteria. Maxima are given as AAL ratios for convenience in data presentation.

In order to facilitate representation of data in which AAL ratios may encompass two to three orders of magnitude, a logarithmic rather than linear scale is used in Figures 1-3. The study means at each site were below the AAL for each toxic metal species. There were, however, two individual measurements which exceeded the AAL value. An ambient concentration of 1.6 AAL for V was determined from one Poughkeepsie sample and an ambient concentration of 1.1 AAL for Pb was determined from one Hempstead sample.

Lead and V were the metal species which were most consistently observed at the highest AAL ratios. In addition to the Hempstead maximum noted above, maximum Pb concentrations were 0.19 to 0.56 AAL at urban sites and 0.17 at the Lake Placid background site. In addition to the Poughkeepsie maximum for V, other urban site maxima ranged from 0.27 to 0.42 AAL and a maximum of 0.10 AAL was observed at Lake Placid.

Mean normalized ratios for Pb ranged from approximately 0.08 AAL at Lake Placid and Syracuse to 0.30 AAL at Hempstead. Vanadium study means were 0.02 AAL at Lake Placid, 0.07 AAL at Niagara Falls, and, at the remaining 1983-84 sites, ranged from 0.10 AAL at Hempstead to 0.35 AAL at Poughkeepsie. No other study means exceeded 0.10 AAL for any metal species at any site, and only Cr at Greenpoint (0.06 AAL) exceeded 0.05 AAL.

Relatively high maximum observations for Cd and Cr, 0.16 to 0.42 AAL, were observed at Hempstead, Greenpoint, Travis, and the background Lake Placid site. An unusually high Zn maximum, 0.79 AAL, was found in one sample at Hempstead. This single observation was nearly an order of magnitude greater than the next highest Zn concentration reported in the study. Similarly, a rather high Mn maximum, 0.24 AAL, for one sample at Niagara Falls was more than five times greater than the next highest observation at that site and nearly two orders of magnitude greater than the highest maximum at the other sites.

Figures 1-3 demonstrate that the toxic metal data are sometimes characterized by maxima several times to an order of magnitude greater than the mean value. One possible explanation for such observations is that a specific toxic metal source may occasionally impact the receptor site directly. This study did not, however, attempt to identify any specific toxic metal sources.

Cadmium and Cr maxima were frequently much greater than mean values while Pb maxima were less than a factor of 3 greater than the mean at seven of the 11 sites and less than four times the mean at all sites. The relatively narrow distribution of Pb concentrations at all sites may be expected, given automotive emissions as the primary source. Automotive emissions are likely to be more uniformly distributed both temporally and spatially than other species.

Statistical Considerations

The annual mean is the average of the ambient concentrations for each day of the year. However, everyday sampling was not performed in this

study and is not the norm for most studies. Everyday sampling is generally available only for the gaseous criteria pollutants (ozone, sulfur dioxide, carbon monoxide, and oxides of nitrogen) through the continuous air monitoring system. Toxic metal samples were obtained on a 12 day schedule; however, the schedule could not always be maintained so that sets of only 21 to 27 data points (less for some data in 1982) were available to compute the study means.

Statistical methods permit the estimation of population means on the basis of the individual sample values from small data sets. Statistical analysis using the "bootstrap" resampling technique[5] determined the 95% confidence upper limit of the annual mean AAL ratio for the two highest toxic metal study means: V at Poughkeepsie, 0.35 AAL; and Pb at Hempstead, 0.30 AAL. The results are given in Table III.

Since Table III is for the highest AAL ratios, there is a high degree of confidence that the annual mean for measured toxic metal species is less than one-half the AAL at all study sites. Much lower annual means, 0.01 to 0.1 AAL, are indicated at most sites for all species except Pb and V. It should be noted, however, that the data sets exhibit considerable scatter, as evidenced by the high relative standard deviation values.

Comparison with Historical Data

Toxic metal ambient concentration data from previous studies may be compared to TAM data. Toxic metal data has been obtained nationwide for over a decade by the Environmental Protection Agency's National Air Sampling Network (NASN). NASN samples were collected using a biweekly random schedule (26 samples per year) in 1970-71 and a 12 day sampling schedule in 1972-74[6]. Quarterly means and annual means were reported for six toxic metal species common to TAM. A New York State DEC study[7] for six study sites in Buffalo and a background site at Angola during 1978-79 also provided data for six toxic metal species. A quantized presentation of the means and maxima for these studies may be found in Figures 4 and 5, providing a historical perspective on nominal urban ambient concentrations for toxic metal species. It is cautioned that sites are not necessarily the same, although located in the same city. Differences in analytical procedures may also bias comparisons. Nonetheless, the data would appear to indicate an improving picture for Pb and V, the species with the highest AAL ratios. Furthermore, for other metals, the historical and present indications are that mean concentrations are typically less than 0.1 AAL and maxima above 0.5 AAL are not frequent.

Figures 4 and 5 present the maxima and means as AAL ratios, segregated by general site geographical location within New York State. The presentation of individual metal concentrations within a discrete AAL ratio regime is given for comparative convenience and does not represent relative relationships within the regime.

For both maxima and means, Pb and V are the toxic metal species which have been observed at the highest AAL ratios. Comparisons may best be made for those sites which were the same in both the TAM study and NASN studies (Niagara Falls, Rochester, Syracuse, and Albany-Rensselaer). In all cases, the Pb concentrations are lower, most dramatically at Syracuse and Albany-Rensselaer, in 1982-84 relative to 1970-74. Vanadium data was not available for all sites and several different sites were employed in the New York City metropolitan area, making V trends more difficult to discern. Nonetheless, it would appear that somewhat lower V maxima and means have been observed in the New York City area in 1983-84 relative to the NASN data of over a decade ago.

Toxic Organic Species

Phthalates. The extracts from the Florisil cartridges were analyzed for eight phthalate species: dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DIBP), dibutyl phthalate (DBP), butylbenzyl phthalate (BBP), diisooctyl phthalate (DIOP), diphenyl phthalate (DPP), and dioctyl phthalate (DOP). Of these species, DPP and DOP were never observed at atmospheric concentrations above a 5 nanogram/m^3 minimum detectable level (MDL) for 368 cartridge samples at the 11 sites over the three year study period. DMP was detected in excess of a 3 ng/m^3 atmospheric concentration MDL in less than 3% of the samples (highest measurement 31 ng/m^3). Of the remaining five phthalate species, DIOP and DIBP were most frequently detected; however, maximum concentrations (303 and 130 ng/m^3 respectively) were very low relative to the established 16700 ng/m^3 AAL. Furthermore, these measurements were complicated by the fact the DIOP and DIBP were potentially system contaminants (from plastic components of the system and tubing) and significant amounts were measured in analytical blanks, necessitating correction by blank subtraction for ambient sample concentration calculations. Thus, there is the possibility of incorrectly attributing to the atmosphere quantities of DIOP and DIBP which were collection system interferences.

The maximum total phthalate atmospheric concentration (sum of the eight phthalate species) determined in this study was less than 400 ng/m^3, or less than 3% of the AAL. Average concentrations at each site were less than 0.6% of the AAL. In the event that interferences were significant, the actual ambient concentrations would be less than cited above. Thus phthalate species appear to be well below the currently established AAL concentration values.

BHCs (hexachlorocyclohexanes). The AAL concentration for BHCs (1670 ng/m^3) is an order of magnitude less than the phthalate AAL. The BHC species measured in this study represent four of eight known BHC stereoisomers[8,9]. All isomers were detected at very low ambient atmospheric concentrations (less than 10 ng/m^3) and very infrequently above 1 ng/m^3 in the case of the β, γ and δ isomers (2.2%, 1.4%, and 1.1% of 368 cartridge samples). The α isomer was found at ambient concentrations in excess of 1 ng/m^3 in 31% of the samples. This observation is interesting in that the γ isomer is the only one of the BHC isomers which is biologically active and is solely responsible for the insecticidal properties of BHC commercial products[8,9]. Lindane is 99% pure γ isomer, but other commercial products may be mixtures of BHC isomers[9,10]. Thus the relative frequencies of observation at detectable levels of the α and γ isomers suggest BHC sources other than Lindane in the environment, or chemical mechanisms which would account for observed concentrations.

Total BHC concentrations in the study environments did not exceed 1% of the AAL in any single sample and yearly average concentrations were estimated to be on the order of 0.1% of the AAL or lower.

PCBs (polychlorinated biphenyls). Florisil cartridge air samples were analyzed for four PCB species (Aroclors 1016, 1254, 1221, and 1260). Of 368 samples, none were found to exceed the 1 ng/m^3 atmospheric concentration MDL for Aroclor 1260 and only one sample was found to exceed this concentration for Aroclor 1221. Aroclors 1016 and 1254 were found to exceed this level in 24% and 22% of the samples, respectively.

The highest total PCB concentration measured was approximately 13 ng/m^3, less than 1% of the AAL (1670 ng/m^3). Annual averages were estimated to be on the order of 0.2% of the AAL or lower.

BaP (benzo[a]pyrene). Atmospheric BaP concentrations were determined by analysis of particulate filters. In 1982, samples were analyzed on a nominal one month basis (10 to 12 samples at each site). In 1983-84, between 9 and 16 samples were available from each site. The AAL concentration for BaP is 33 ng/m^3. The maximum ambient concentrations determined were 2.2, 2.1, and 4.5 ng/m^3 in 1982, 1983, and 1984, respectively, while typical concentrations were less than 1 ng/m^3. The maxima were approximately 7% to 14% of the AAL while annual averages may be estimated at 2% of the AAL or lower.

Dioxins and Furans. One year studies were conducted at Niagara Falls and Hempstead, Long Island, to determine ambient atmospheric concentrations of dioxins and furans. Sample collection was performed by NYSDEC and chemical analysis by gas chromatography - mass spectrometry (GC-MS) was accomplished by the Wadsworth Center for Laboratories and Research of the NYS Department of Health. The results were evaluated by NYSDEC and the Division of Environmental Health Assessment of the NYSDOH. The study results are available in detail from the NYSDEC[1]. In summary, the data represent the first unambiguous measurement of these species in ambient air in the U. S.; however, evaluation of the data did not indicate any acute or immediate health hazard.

Twelve samples were obtained at Niagara Falls and four samples contained quantifiable amounts of furans. Three samples were found to have non-quantifiable traces of furan species. The remaining five samples did not yield detectable levels of furans. The measurable quantities, calculated as ambient air concentrations, ranged from 1.0 to 13.6 pg/m^3 (picograms/m^3) with three samples in the 1.0 to 1.3 pg/m^3 range. Only one of the twelve samples contained a quantifiable amount of dioxin, 1.2 pg/m^3 (expressed as an ambient air concentration). At the Hempstead site, all samples resulted in below detectable concentrations of dioxins and furans.

A statistical analysis of the furan data at Niagara Falls using the "bootstrap" resampling technique[6] was performed by NYSDEC to give a 95% confidence interval for the annual mean furan concentration. The upper bound of the annual mean was approximately 4 pg/m^3.

Seasonal Variation

Ambient organic measurements (PCBs, BHCs and phthalates) were grouped by three month periods, and the average ambient measurement for each quarter determined to provide insight on seasonal variation in the data. The average ambient organic measurements in each quarter at each site are given in Figure 6. For PCBs and BHCs, the maxima appear primarily during the third quarter. The seasonal variation for total phthalate species is much less pronounced; however, 5 of 11 sites observed maximum average measurements in the third quarter and 4 sites observed maximum average measurements in the fourth quarter. In four of the six cases when the third quarter average measurement was not the seasonal maximum, the third quarter average measurement was 50% or more of the maximum.

These results must be considered preliminary and additional statistical evaluation of the small data sets involved is required. It would appear that certain factors (chemical use or meteorology, for instance) associated with the third quarter may induce relatively higher ambient organic concentrations.

Conclusions

* For ten sites representative of urban New York communities, there is a high degree of confidence that the mean ambient air concentrations of seven toxic metal species, phthalates, BHCs, PCBs, and BaP do not exceed the established AAL concentrations.

* At Niagara Falls, the detected ambient air concentrations of dioxins and furans do not pose immediate or acute health hazards, based on the limited avaialble data. Sampling during the same period at Hempstead did not detect the presence of dioxins or furans.

* Pb and V are the toxic metal species observed in the highest concentrations relative to the AAL. Historical data indicates a decline in both maxima and mean concentrations for these species.

* The mean ambient concentrations of Cd, Mn, Ni and Zn have been consistently below 0.05 AAL at sites similar to TAM sites and were also below 0.05 AAL at all TAM sites.

* TAM data and historical data indicate mean ambient concentrations of Cr have declined from the 0.05 to 0.25 AAL range to below 0.05 AAL at the TAM and similar sites with the exception of Greenpoint (Brooklyn) where the estimated 1983-84 mean concentration was 0.06 AAL.

* Mean phthalate, BHC, and PCB ambient concentrations were estimated to be less than 0.01 AAL at all TAM sites. The mean BaP ambient concentrations were estimated to be less than 0.03 AAL at all TAM sites.

Acknowledgements

The authors wish to thank Dr. J.Y. "Mike" Ku, NYSDEC, Division of Air Resources, for providing the bootstrap statistical analysis for toxic metals data. Additionally, the authors gratefully acknowledge the assistance of NYSDEC staff members Carol Clas, Linda Stuart and Stephanie Liddle in preparing the graphics and the typewritten copy for this manuscript.

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TABLE I

TOXIC AIR MONITORING CONTAMINANTS AND AAL VALUES

Pollutant	AAL* (nanograms/m^3)	Major Emission Source (s)	Health Effect
Cadmium	167	Ore processing, plating operations, pigment manufacturing	Potential human carcinogen
Chromium	167	Iron, steel, and non-ferrous alloy production, chrome plating, pigment production	Human carcinogen
Copper	4000	The manufacture of bronzes, brass, copper alloys, electrical conductors, etc.	Low toxicity. Soluble salts as copper sulfate are irritants to skin and mucous membranes.
Nickel	3300	Iron and steel alloy production, combustion of coal and fuel oil	Potential human carcinogen
Lead	1500	Automotive vehicles, battery manufacturing, non-ferrous foundries	Organic Pb compounds may cause permanent brain damage, colic anemia and changes in bone marrow.
Zinc	16700	Ore processing, galvanizing	Zinc is relatively non-toxic orally. Inhalation of zinc oxide fume causes "Metal Fume Fever". Carcinogenesis is contradictory.
Vanadium **	167	By-product of ore processing, combustion of coal and fuel oil	Respiratory effects, gastro-intestinal, kidney injury, nervous disorders
Manganese **	16700	Smelting and refining of iron ore, combustion of coal and fuel oil	Potential mutagen, respiratory effects
Benzo[a]pyrene	33	Coke plants, combustion of coal, oil and wood	Human carcinogen
Polychlorinated biphenyls (PCBs)	1670	Electrical applications, plasticizers, hydraulic fluids, etc.	Potential human carcinogen
Hexachloro-cyclohexanes (BHCs)	1670	Insecticides - Lindane is also used as a therapeutic agent in veterinary medicine	Carcinogenic in animals; neurotoxic effects in humans. Cirrhosis and carcinogenicity in humans require further evaluation.
Phthalate compounds	16700	The manufacture, fabrication, and use of plastics	In general are slightly toxic. May cause eye, skin and mucous membranes irritation.

* Acceptable Ambient Level, from guideline document Air Guide-1 (1983-1984) published by NYS Department of Environmental Conservation

** Preliminary AAL values - not yet published.

TABLE II
TOXIC AIR MONITORING SITES AND SAMPLING PERIODS

	Site	Location Type	Sampling Period
Western New York Sites	Buffalo	Residential	1/82-12/82
	Niagara Falls	Industrial/Residential	1/82-12/82
	Rochester	Urban	1/82-12/82
Central New York Site	Syracuse	Urban	1/82-12/82
Hudson River Valley Sites	Rensselaer	Urban/Industrial	1/82-12/82
	Poughkeepsie	Residential	6/83-7/84
Metropolitan New York City Sites	Greenpoint (Brooklyn)	Industrial	6/83-7/84
	Susan Wagner (Staten Is.)	Residential	6/83-7/84
	Travis (Staten Is.)	Residential	6/83-7/84
	Hempstead (Long Is.)	Urban	6/83-7/84
Rural, Background	Lake Placid	Background	1/82-12/82 6/83-7/84

TABLE III
STATISTICAL DATA FOR HIGHEST METAL AAL RATIO OBSERVATIONS

Toxic Metal	Site	Number of Samples	Study Mean (AAL Ratio)	Study SD	95% Confidence Level Estimate of Annual Mean to AAL Ratio Upper Limit
V	Poughkeepsie	25	0.35	0.36	0.51
Pb	Hempstead	27	0.30	0.20	0.38

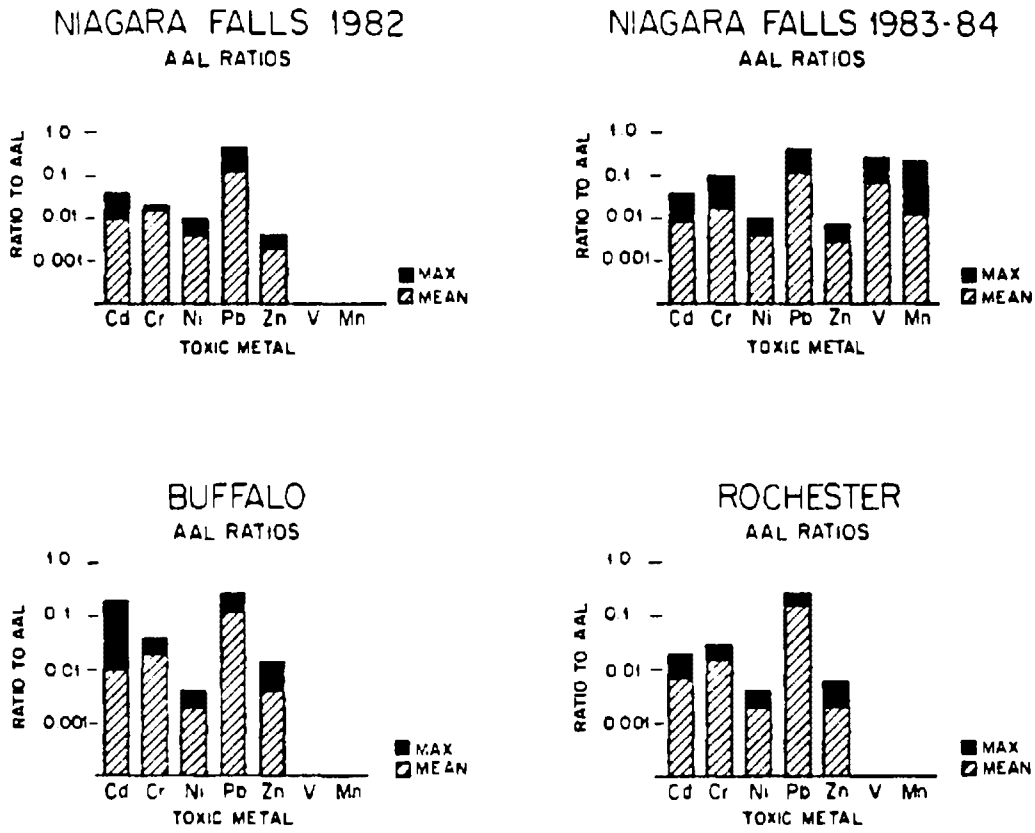


Figure 1. Maximum and mean ambient concentration to AAL ratios for toxic metal species at western New York sites.

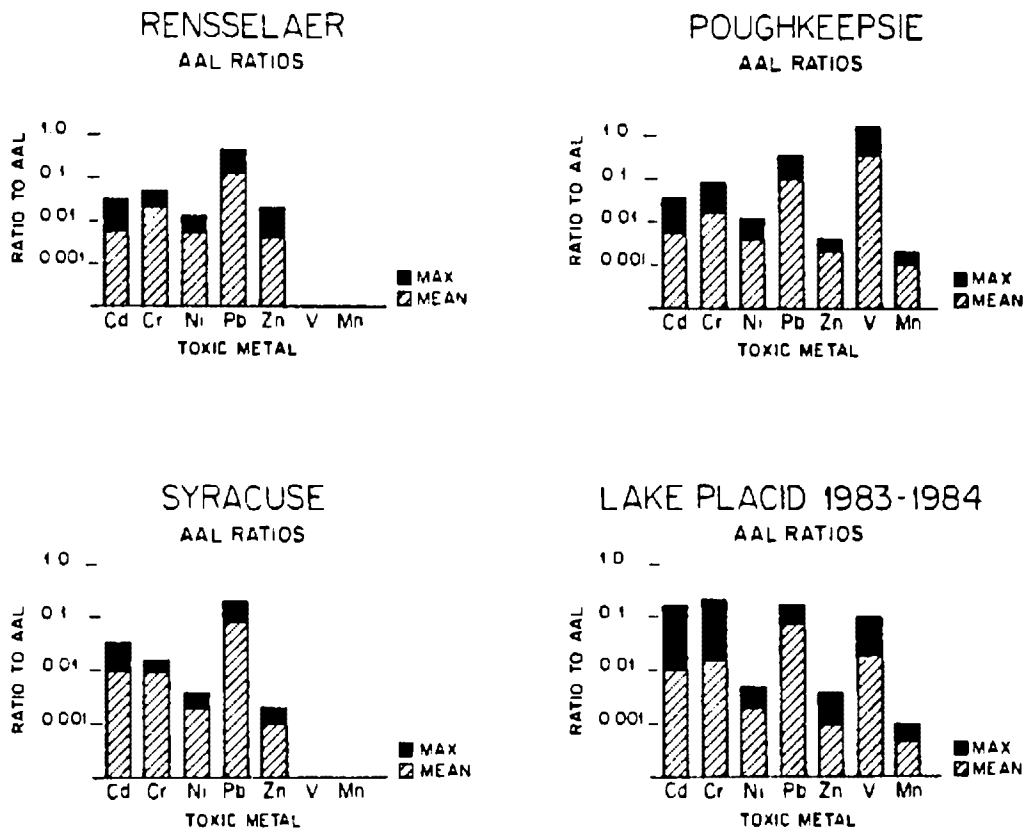


Figure 2. Maximum and mean ambient concentration to AAL ratios for toxic metal species at study sites in the upper and lower Hudson Valley regions (Rensselaer and Poughkeepsie), the central New York region (Syracuse), and the Adirondack Mountain region (Lake Placid).

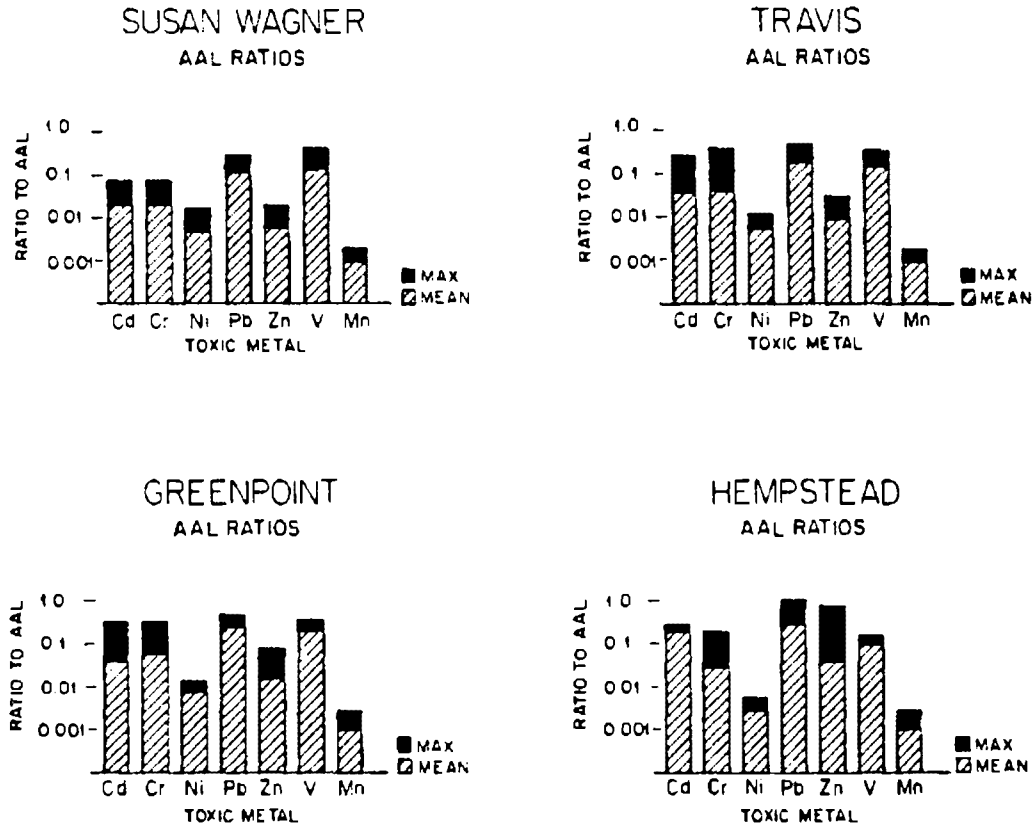
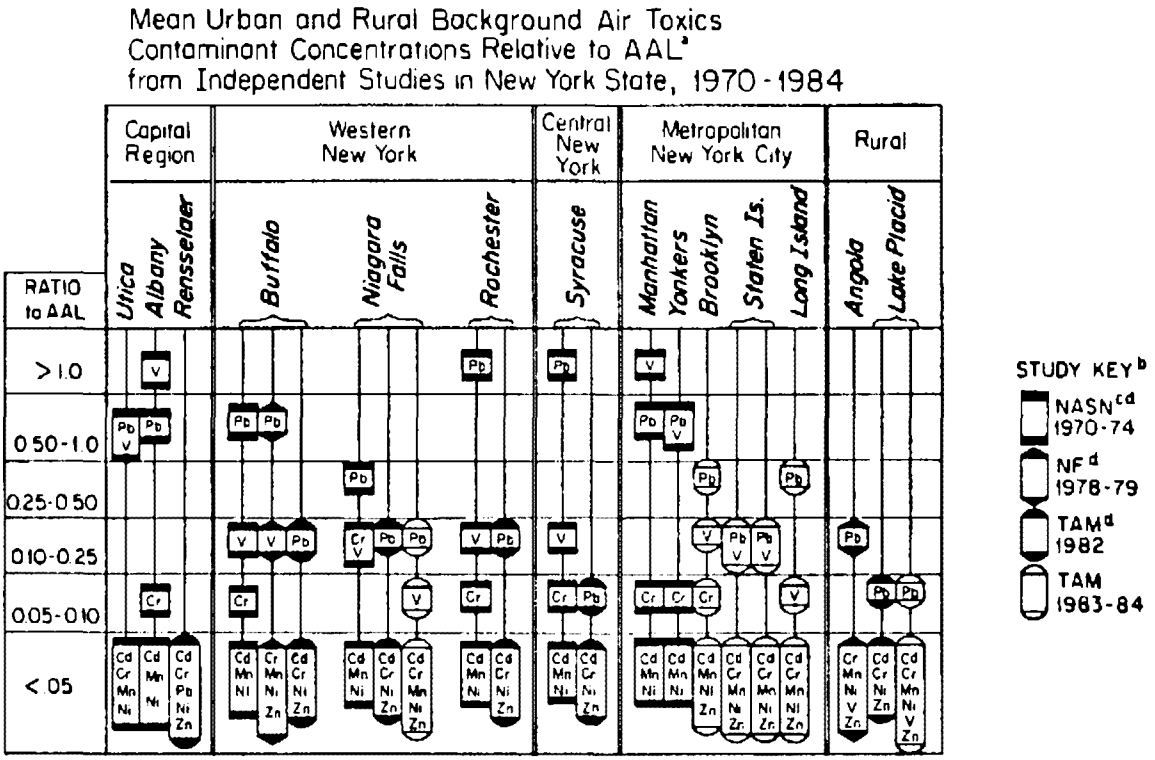
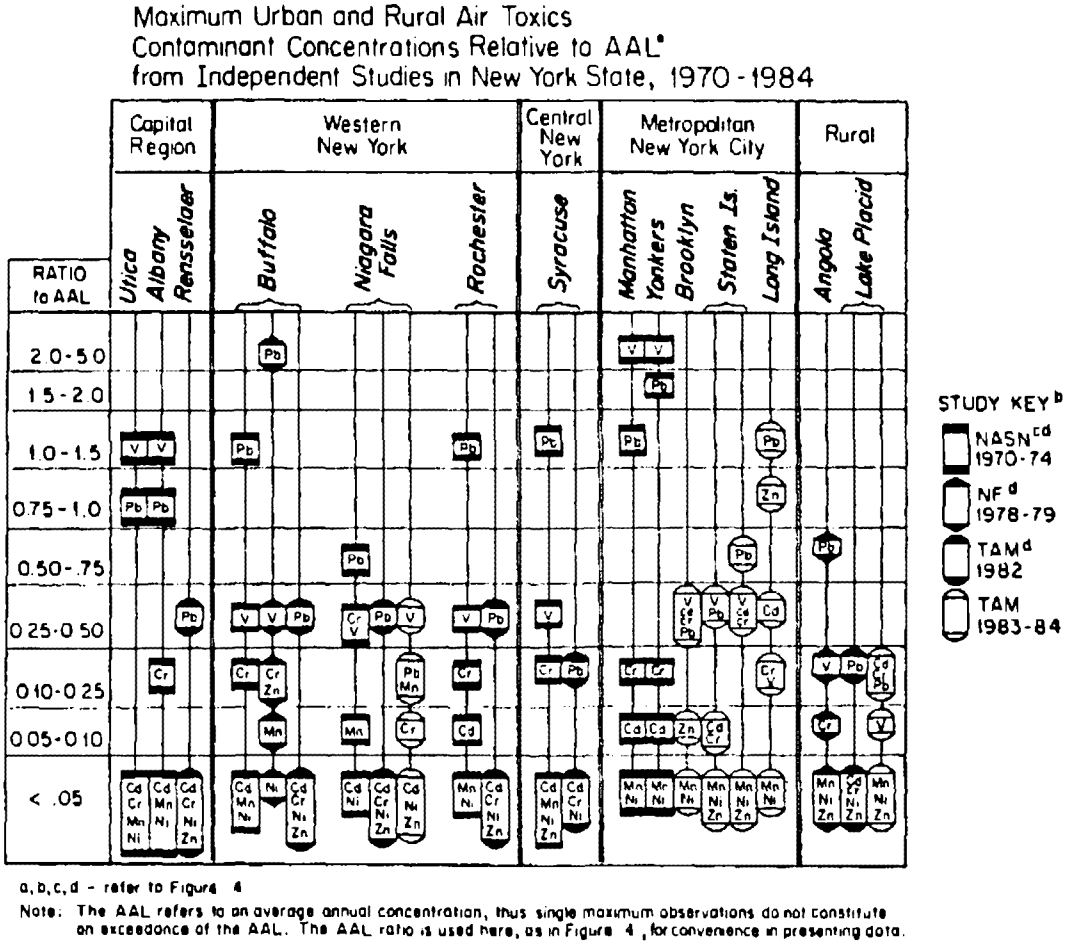


Figure 3. Maximum and mean ambient concentration to AAL ratios for toxic metal species at study sites in the New York City metropolitan region.



a - AAL Acceptable Ambient Level for toxic air contaminant (NYS).
b - NASN = National Air Sampling Network (EPA), EPA-600/4-76-041.
NF = Particulate Source Contributions in the Niagara Frontier (NYSDEC, Kolak, et al.), EPA-902/4-79-006.
TAM = Toxic Air Monitoring (NYSDEC), this study.
c - NASN values presented are highest reported annual mean in 1970-74 period.
d - Zn not measured in NASN Study
Cd not measured in NF Study
Mn and V not measured in TAM-1982 Study

Figure 4. Historical comparison of mean toxic metal AAL ratios in several geographic regions of New York.



a, b, c, d - refer to Figure 4

Note: The AAL refers to an average annual concentration, thus single maximum observations do not constitute an exceedance of the AAL. The AAL ratio is used here, as in Figure 4, for convenience in presenting data.

Figure 5. Historical comparison of maximum toxic metal AAL ratios in several geographic regions of New York.

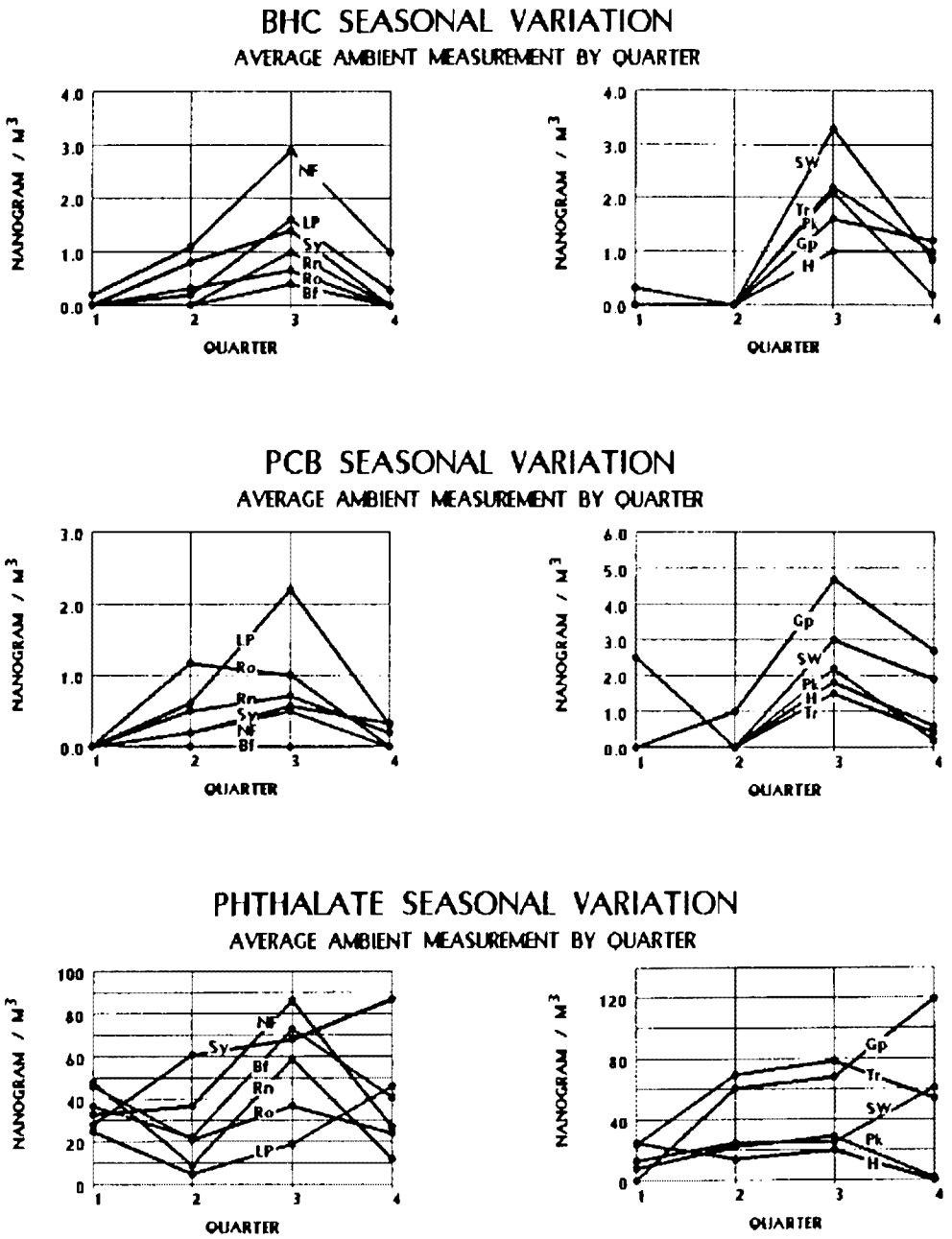


Figure 6. Seasonal variation, estimated by average quarterly ambient measurements, for BHCs, PCBs, and phthalates at TAM study sites : NF=Niagara Falls, Bf=Buffalo, Ro=Rochester, Sy=Syracuse, Rn=Rensselaer, LP=Lake Placid, SW=Susan Wagner, Tr=Travis, Gp=Greenpoint, H=Hempstead, Pk=Poughkeepsie.

A CONTINUOUS ISOKINETIC GAS/MIST SAMPLER FOR FLUE STREAM EXTRACTIVE ANALYSIS

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A special-purpose stream sampler is required for the automated and continuous extractive analysis of saturated mist-laden flue gas streams. Isokinetic sampling is essential for those applications in which the analyte molecules are miscible in or otherwise associated with the mist droplets. Essentially, continuous isokinetic sampling is accomplished over a 30- to 60-ft/sec flue stream velocity range by a heated sampling probe through which a large sample (~50 to 100 liter/min) is pumped solely by the flue stream dynamic pressure and returned directly to the flue. The probe geometry and dimensions are configured to permit the probe pressure losses experienced by the sample stream to vary in proportion to the flue stream dynamic pressure, i.e., flue stream velocity, to maintain an isokinetic condition at the probe entrance. As the sample flows through the probe, it is heated, and the mist droplets are vaporized by the energy from the probe wall, which is maintained at 340°F. Near the probe exit and prior to return of the sample stream to the flue, a second probe extracts continuously a small fraction (~1 to 2 per cent) of the sample stream for further processing, if required, and subsequent analysis. Because the analyte and water molecules at the heated probe exit exist in gas phase, isokinetic sample extraction is not required for operation of the second probe. Efficient sample transport through the heated probe is attained by vaporization of the mist droplets and liquid phase altogether, which precludes the formation of absorbing wetted-wall surfaces.

A CONTINUOUS ISOKINETIC GAS/MIST SAMPLER FOR FLUE STREAM EXTRACTIVE ANALYSIS

Introduction

Flue gas monitoring of waste incinerator systems for hazardous and toxic emissions imposes two major requirements on the overall analytical process not associated normally with source monitoring systems:[1] (1) an analyzer lower detection limit at sub-ppm to sub-ppb or lower levels[2,3] and (2) relatively high molecular detection specificity.[4,5] Because of the detection response requirements, extractive analytical techniques are used in most applications. Cross-stack, in situ, and remote analyses usually do not possess the sensitivity or zero-span stability to attain the lower detection limit required and do not accommodate dynamic calibration methods well.

However, attendant to extractive analysis are sample stream conditioning and processing (particulate filtering, dilution, heating, etc.).[1,6-9] Additional requirements arise for applications in which the analyte species is above its dew point in the flue stream but miscible in a liquid medium, such as mist, that the flue stream may carry or in liquid films attached to solid surfaces.

For most mist-laden flue streams, a substantial fraction of miscible analyte molecules can be dissolved in individual mist droplets. Thus, for those applications, two additional constraints are imposed on the extractive sampling process: (1) it is imperative to perform the sampling isokinetically within the flue to obtain a sample stream representative of the larger mist droplets (>0.5 μm)* carried by the flue stream[10-13] and (2) the sample stream must be transported to the analyzer or detector module in a fashion that eliminates entirely the deposition of mist droplets on any conduit walls or surfaces. An accumulation of mist on surfaces can eventually transform the external sample stream conduit into an absorbing wetted-wall column that will deplete the gas stream of miscible analyte molecules[14,15] prior to its arrival at the analyzer.

Waste Incineration Effluent

A typical incineration system was examined that included a downstream in-line water quench tower, a venturi scrubber, a packed-bed scrubber, a mist eliminator assembly, and a forced-draft flue. The average flue gas temperature is 170°F and gas velocity varies from 30 to 60 ft/sec. It is saturated with water vapor and can carry a mist load of 10^{-2} to 10^{-3} mass-liquid/mass-gas. A significant mist load is present despite mist elimination in-line equipment.[16]

The resultant liquid mass loading and its dispersion as a mist is sufficient to absorb a large fraction of the miscible analyte molecules into solution and cause a significant positive or negative interferent response in the analytical process. An engineering analysis shows that the rate of mass transfer of miscible analyte molecules from gas phase to

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*English and metric units are used throughout this document for the convenience of the reader.

individual droplets over the residence time of the incinerator effluent in the flue is sufficient to scrub efficiently the flue gas of analyte molecules.[17-19] Thus, isokinetic sampling for extractive analysis of the incineration system effluent is very likely required to obtain a representative extractive sample of the miscible analyte molecules.

Isokinetic Gas/Mist Sampling System

All extractive sampling systems must operate under various environmental and flue conditions. In each case, constraints are established by sampling requirements that are defined by the analyte molecules, the flue and its effluent properties over a range of operating conditions, the interface constraints of the sample probe/collector in the flue stream, and the analyzer interface constraints.

The unique and most severe system requirements are those related to simultaneous gas and mist collection under isokinetic conditions. In addition, it is imperative to transport the sample to the analyzer in the gas phase entirely without mist deposition on the sample conduit walls. This constraint arises primarily from analytical considerations, as well as from system reliability and low maintenance considerations.[1,6,8,20]

Figure 1 is a functional illustration of the isokinetic gas/mist sampling system. It comprises two subsystems: (1) the effluent probe and sample processor, operating inside the flue, and (2) the sample transport network and processor, operating outside the flue.

A special-purpose effluent probe and sample processor was designed to perform the isokinetic sampling and processing within the flue. It is called VapaTrog for brevity. It is a 2-stage sampling probe comprising a heated and insulated tube that is oriented longitudinally in the flue, as shown in Figure 2. Effluent enters the heated tube at a velocity near that of the free stream (i.e., isokinetically). As the effluent sample stream flows through the tube, it is heated, and the mist droplets are vaporized. The effluent sample stream continues out the heated tube and is returned directly to the flue. Upstream of the tube exit, approximately 1 to 2 per cent of the effluent stream is bled off by the bleed stream probe, which is at a slightly reduced pressure. The bleed stream is transported through heated lines that pass through the flue wall to the sample transport network and processor and subsequently to the analyzer. It is important to note that only the flue effluent stream is sampled isokinetically. There is no need for isokinetic sampling at the bleed stream probe because, at this station in the heated tube, the effluent sample stream does not contain mist droplets; these have been vaporized. Thus, to minimize the ingestion of solid aerosols, the bleed stream probe is oriented to the flue stream as shown by Figure 2 to force the gas to negotiate a 180-degree turn (i.e., to sample nonisokinetically).

VapaTrog performs the isokinetic sampling function entirely by passive means, i.e., the effluent probe itself is self-adjusting to a varying flue gas velocity without active assistance from downstream valves, pumps, etc. This action is possible because of VapaTrog's pneumatic configuration, whereby an effluent sample stream passes through a tube and is returned directly to the flue. The effluent sample stream is thus pumped solely through the heated tube by the flue stream dynamic pressure. Its flow rate varies in proportion to the flue stream dynamic pressure.

The isokinetic condition exists when the effluent sample stream velocity at the probe entrance plane is equal to the flue gas free stream velocity.[13] For isokinetic flow, the effluent sample stream is described by:

$$W_v = k\rho_f V_f A_i \tag{1}$$

where W_v = effluent sample stream flow rate through the heated tube, lb/sec;

k = isokinetic factor proportional to the probe inlet to free stream gas velocity ratio, dimensionless;

ρ_f = flue gas density, lb/ft^3;

V_f = flue gas velocity, ft/sec; and

A_i = tube inlet area, ft^2.

For isokinetic sampling, k = 1.00.

To obtain the effluent sample stream flow rate described by Eq. (1), a combination of the tube dimensions and geometry and the inlet area are designed such that the pressure loss incurred by the effluent sample stream in flowing through the tube is equal to the total pressure difference available from the tube entrance to its exit. The total pressure difference established aerodynamically is proportional to the dynamic pressure as follows:

$$(\Delta P)_v = (1 + C_b)\ q_f \tag{2}$$

where $(\Delta P)_v$ = maximum aerodynamic pressure difference available from the tube entrance to exit, lb/ft^2;

C_b = base pressure coefficient at tube exit, dimensionless; and

q_f = flue gas dynamic pressure, lb/ft^2.

The total pressure loss experienced by the effluent sample stream in traversing the length of the tube is the sum of entrance, expansion, contraction, frictional, and exit losses. For entrance and exit sections designed for low pressure losses, the sum of entrance, exit, expansion, and contraction losses can be minimized to less than 2 per cent of the total pressure loss. VapaTrog was designed such that the effluent sample stream operating pressure drop is mainly frictional, as shown below:

$$(\Delta P)_t = 4f\ (L/D)\ q_v \tag{3}$$

where $(\Delta P)_t$ = total or frictional pressure loss of effluent sample stream in traversing the length of the tube, lb/ft^2;

f = effluent stream Fanning friction factor, dimensionless;

L = tube length, ft;

D = tube inside diameter, ft; and

q_v = effluent sample stream dynamic pressure, lb/ft^2.

Because the effluent sample stream frictional pressure loss, $(\Delta P)_t$, is equal to the maximum aerodynamic pressure difference available from tube entrance to exit, $(\Delta P)_v$, a combination of Eqs. (1), (2), and (3) is reduced to:

$$A_i = \frac{1}{k} \left[\frac{\pi^2 (\rho_v/\rho_f) \ (1 + C_b)}{64 f \ (L/D^5)} \right]^{1/2} \tag{4}$$

where k = 1.00 for the isokinetic condition and

ρ_v = average gas density of the effluent sample stream in the tube, lb/ft^3.

Note that flue gas velocity, V_f, drops out of the relationship and k is independent of V_f.

It is certain that variations in ρ_v, ρ_f, and f arise over the range of flue conditions encountered, and these variations will produce corresponding variations in the isokinetic sampling as described by Eq. (4). For example, the flue gas temperature will vary from 160 to 180°F, and the effluent sample stream flow rate will vary from 50 to 100 liter/min, as determined from the flue gas velocity range and Eq. (1). Temperature changes affect primarily the gas density terms in Eq. (4). There is also negligible change to the effluent sample stream Reynolds number arising from changes to the gas viscosity with temperature. A ±1 per cent deviation from isokinetic sampling is ascribed at a 170°F temperature level and to a ±10°F variation in the flue and heated tube.

Pneumatic effects on f in Eq. (4) are more difficult to predict analytically. It is estimated that the Reynolds number of the effluent sample stream will be 2300 and 4600 at flue gas velocities of 30 and 60 ft/sec, respectively. At these levels, the effluent sample stream flow is in the transition region between laminar and turbulent flow modes. By a tenuous interpolation of the Fanning friction, f, curve[21] in the transition region, f may vary from 0.0085 to 0.0095, to produce a ±2 per cent variation. The total maximum departure from isokinetic sampling is estimated to be ±3 per cent for the flue conditions described earlier.

Vapatrog Design

A prototype VapaTrog unit was designed and fabricated for test and evaluation. Figure 3 illustrates its basic functional elements, geometry, and configuration. The dimensional specifications are established primarily by the maximum total flow rate requirement of the effluent sample stream and the heating load constraint defined by the sample stream heat capacity and mist loading. Inlet area is defined by Eq. (4); the heated tube length and diameter are constrained by Eqs. (3) and (4). To ensure that the effluent bleed stream does not interfere significantly in processing the effluent sample stream the bleed stream is maintained at a flow rate level sufficient to supply the analyzer interface requirements and not exceed 2 per cent of the effluent sample stream at any time. For example, an analyzer interface requiring a 1-liter/min minimum bleed stream flow rate will constrain the minimum effluent sample flow rate of 50 liter/min at any operating and flue condition.

The heated tube dimensions must be compatible with the thermal and pneumatic constraints imposed functionally by the VapaTrog performance requirements. A combination of heat transfer surface area and convective film coefficient must be developed to provide a heat flux of sufficient magnitude to heat the effluent sample stream to 340 °F and to vaporize the mist droplets the stream carries. Yet the combination of heated tube length and diameter must also provide the means to limit the effluent sample stream flow rate to incur the pressure drop prescribed by Eq. (3).

VapaTrog comprises a two-concentric-tube assembly 56 in. long with its annular gap sealed at each end: a nose cone seals the front end, and a base plate seals the rear end. The outer surface of the inner tube, i.e., the heated tube, is surrounded over nearly its entire length by two 500-W wrap-around heaters, a layer of thermal insulation, and finally, the outer tube, 4 in. in diameter. The nose cone is interfaced mechanically with the inner and outer tubes.

Test and Evaluation

The VapaTrog test and evaluation was focused primarily on two objectives: (1) establish and demonstrate the aerodynamic characteristics of VapaTrog regarding isokinetic sampling performance over a 30 to 60 ft/sec flue gas velocity range and (2) define VapaTrog performance regarding its mist collection and processing characteristics.

In both cases, a fully instrumented vertical wind tunnel[22] was used to simulate the flue and flue stream. All aspects of the flue were simulated, with the exception of gas temperature and composition. The VapaTrog unit was suspended longitudinally in the wind tunnel, with the inlet facing downward and opposed to the wind direction.

The aerodynamic characterization was performed by a quantitative examination of the mass conservation relationship at the VapaTrog inlet and exit. At the inlet, the flow rate entering VapaTrog is described by Eq. (1). The wind tunnel gas stream and properties and VapaTrog gas sample stream and properties were measured over wind tunnel gas velocities from 30 to 60 ft/sec. By mass conservation at the VapaTrog inlet (Eq. (1)) and at the exit (denoted by the subscript, x), the inlet isokinetic

factor, k, is related to the measured parameters of the experiment as described below:

$$k = \frac{A_x \rho_x V_x}{A_i \rho_f V_f} \tag{5}$$

where ρ_x = the average gas density of the effluent sample stream at the heated tube exit, lb/ft^3;

V_x = the average velocity of the effluent sample stream at the heated tube exit, ft/sec; and

A_x = cross sectional flow area at the heated tube exit, ft^2.

Eq. (5) describes how well VapaTrog is operating isokinetically. For absolute isokinetic sampling, k = 1.00. Deviations of k from 1.00 are its departure from isokinetic sampling. Wind tunnel free-stream density was determined from static temperature and pressure measurements, and velocity was obtained from the free-stream dynamic pressure. Five individual dynamic pressure measurements were made in the VapaTrog heated tube for all operating conditions to construct the exit velocity profile[23,24] and obtain an average exit velocity, V_x.

The dynamic pressure measurements were reduced to velocity data at each radial position for each VapaTrog inlet over 30 to 60 ft/sec wind tunnel stream velocity, as shown in Figure 4. With these data and the wind tunnel free-stream measurements, Eq. (5) was evaluated to assess the isokinetic sampling performance of VapaTrog.

Mist Collection and Processing

The VapaTrog mist collection and processing evaluation was performed in a vertical wind tunnel subsequent to the aerodynamic evaluation. The evaluation comprised operation of the wind tunnel and mist generator and measurement of the wind tunnel free-stream parameters, mist droplet population density, and droplet size distribution. In addition, the VapaTrog unit was equipped with a bleed stream probe and line of 1/8-in.-OD bare TFE tubing immersed approximately 4 in. into the heated tube exit and insulated thermally thereafter.

The effectiveness of VapaTrog to collect a representative sample of flue gas and mist is a function of the VapaTrog isokinetic sampling and its efficiency in vaporizing the mist droplets carried by the effluent sample stream. A mass conservation relationship is used to assess VapaTrog's mist collection and processing characteristics. It relates the water entering VapaTrog as liquid and vapor to the total water content of the bleed stream.

Gas and mist are sampled continuously by VapaTrog over a given time increment, and the tunnel gas mist loading is measured at the VapaTrog inlet by a droplet-counting anemometer. Simultaneously, the bleed probe and line transport a 1000-ml/min stream of effluent sample to an assembly of three containers in series immersed in an ice bath and subsequently to

a flow meter. The liquid water collected at 0°C is the water vapor that condenses out of a water-saturated stream at 0°C. The mass of liquid water collected in the ice bath is equal to the water vapor entering the ice bath less the water vapor leaving the ice bath saturated at 0°C. The mist loading of the wind tunnel is obtained from these parameters as shown by Eq. (6):

$$W = \frac{V_l \rho_l + (W_{H_2O})_{0°} (\Delta t) Q_B \rho_r}{Q_B \rho_r (\Delta t)} - W_{H_2O} \tag{6}$$

where V_l = liquid water volume collected at 32 °F, cm^3;

ρ_l = liquid water density at 32 °F, g/cm^3;

W = tunnel air mist loading, mass liquid water/mass air;

(Δt) = collection time interval, min;

ρ_r = room or tunnel air density, g/cm^3;

Q_B = bleed stream flow rate measured downstream of the collection bath, ml/min; and

$(W_{H_2O})_{0°}$ = saturated air specific humidity at 32 °F, mass water vapor/mass dry air.

An indirect but important measure of the VapaTrog k is obtained from a comparison of the mist loading calculated from Eq. (6) with the mist collection test parameters and the mist loading measured at the VapaTrog inlet. This approach represents independent verification of the isokinetic sampling action because nonaerodynamic parameters are used in the execution of Eq. (6).

Results

The mist collection test and evaluation results are summarized in Tables I and II. Figure 4 illustrates the reduced aerodynamic data. All final data reduction was executed by Eqs. (5) and (6) for the aerodynamic and mist collection characteristics, respectively.

Aerodynamic Characteristics

The primary objective of the VapaTrog aerodynamic test and evaluation was to define experimentally the isokinetic sampling factor, k, over the range of flue gas conditions described earlier. However, only the more important conditions affecting k were simulated. Operational data were obtained at ambient conditions as a function of wind tunnel air velocity and VapaTrog inlet diameter as listed in Table I. In addition, supplementary data were obtained to augment design information and to support the validity of Eq. (4).

Aerodynamic data were recorded for the 0.440-, 0.423-, and 0.405-in. inlet diameter over 20 to 48°F and 29.30- to 30.21-in. Hg ambient

temperature and pressure ranges, respectively. Ambient temperature variations for the 0.384-in. inlet diameter extended from 74 to 78°F. For practical reasons, the wind tunnel and VapaTrog were operated such that the pitot-tube position in the VapaTrog exit plane was maintained constant while the inlet diameter was varied. These measurements were performed over periods lasting several days with attendant changes in ambient temperature. Thus, normalization thermally of the VapaTrog performance as prescribed by Eq. (4) for a given inlet diameter cannot be discharged consistently to k. This limitation in the data reduction process results from the derivation of the local exit velocity of the VapaTrog effluent sample stream velocity profile and subsequent resolution of average exit effluent sample stream velocity (i.e., exit velocity profile data were derived from cross-plots of raw data of the local exit velocity measurements at different tunnel gas temperatures).

An examination of Table I data reveals that the VapaTrog sampling operation is described satisfactorily by Eq. (4). The isokinetic factor, k, is reasonably constant over the wind tunnel air velocity range scanned for each VapaTrog inlet diameter, regardless of its magnitude. In addition, the variation of k with A_i is shown by Table I. For the conditions of the test normalized to 35°F wind tunnel temperatures, k = 1.03 for A_i = 0.116 in.^{2} or a 0.384-in. inlet diameter.

For example, considering only the data for the 0.440-, 0.423-, and 0.405-in. diameters, the k variance from the average k for each inlet diameter extends from a ±0.7 per cent minimum to a ±3.2 per cent maximum at 0.440- and 0.405-in. inlet diameters (see Table I, notes), respectively. It is estimated from Eq. (4) that a maximum ±4 per cent variance in k may be ascribed to the changes in the ambient conditions experienced. Because of the experimental procedure by which the aerodynamic tests were performed, it is not possible to establish the direction of the thermal variance induced in k.

The thermal variance k for the 0.384-in. inlet diameter was minimized in a relative sense. In this case, ambient temperature variations ranged from 74 to 78°F, which account for less than a ±2 per cent variance after normalizing the data to 32°F. Yet the variance in k is ±5.8 per cent. An examination of the effects of variations in the Fanning friction factor, f, as prescribed by Eq. (4) indicates that variances of ±4.8 per cent can be induced in k. The friction factor, f, will vary from 0.0105 to 0.0085 for corresponding effluent sample stream Reynolds numbers of 3400 and 7200 as calculated from effluent sample stream average exit velocity measurement at 30 and 60 ft/sec wind tunnel air velocities, respectively. However, Eq. (4) describes the effect of f on k as proportional inversely with f. This is contrary to the data on k shown in Table I (i.e., k decreases with increases in wind tunnel air velocity).

Variations in the base pressure coefficient, C_b, of Eq. (4) were examined with varying effluent sample stream flow rates and wind tunnel air velocities. For solid disks and ellipsoids of revolution, however, the base drag coefficients over Reynolds numbers of 2000 and 500,000 are reasonably constant at 1.0 and 0.6, respectively.[25,26] On this basis, variations of C_b are minimal. To determine whether the effluent sample stream flow rate affects C_b as wind tunnel velocity varies, calculated estimates of C_b were obtained from the static pressure measurements of

Table I at the VapaTrog heated tube exit. The average C_b over a wind tunnel velocity range from 60 to 30 ft/sec was 0.430, +1.5 per cent, -3.8 per cent, without showing any trend with wind tunnel velocity. It is a small variation and does not affect k to any significance.

The preceding discussion on the effects of such parameters as ρf, C_b, and f on k suggests that some of the variance in k for the 0.384-in. inlet diameter is due to errors arising from experimental method, technique, or procedure.

Table I lists other aerodynamic data that substantiate the VapaTrog principle of operation and support the validity of the measurements. It is noted in all cases that the ratio of the average velocity to the centerline velocity is near the theoretical value for fully developed turbulent flow in a tube, 0.79.[24] The variance of the velocity ratio from the theoretical level as well as from the measured average is acceptable in all cases. The maximum velocity ratio occurs with the 0.384-in. inlet diameter. The largest variance in k also occurs for this dimension.

In addition to the performance data, verification of the VapaTrog sampling process principle of operation was obtained. The total and static pressure measurements listed in Table I at the VapaTrog exit plane show a reasonable consistency at each wind velocity regardless of variations in other operating and dimensional parameters. This condition correlates well with the notion that despite varying conditions, dimensions, and configuration, the VapaTrog effluent sample stream flow rate self-adjusts to a level that attains a given pressure drop proportional to the dynamic pressure of the flue gas. The maximum variance from the average exit total pressure is +2.5 per cent, -1.3 per cent at 50 ft/sec wind tunnel air velocity; the maximum variance from the average exit static pressure is +2.4 per cent, -3.6 per cent at 40 ft/sec wind tunnel air velocity. These data substantiate further the VapaTrog principle of operation.

Mist Collection and Processing Characteristics

The primary objective of the mist collection test and evaluation was to ascertain the quantity of mist sampled and processed by VapaTrog during operation in a mist-laden airstream. Also, an indirect measurement of the VapaTrog isokinetic sampling factor was obtained from a comparison of the liquid water collected in the ice bath to the mist load measured at the VapaTrog inlet. A 0.384-in. inlet diameter was used for all the mist collection tests. Mist was generated by a Sonotek ultrasonic mist generator. Measurements were made of the parameters comprising Eq. (6); subsequently, Eq. (6) was used to derive the tunnel mist gas load.

The time-weighted average mist load at the VapaTrog inlet varied from 2.25×10^{-3} to 4.07×10^{-3} as measured by the droplet-counting anemometer (KLD Associates Droplet Measuring Device). There was no detectable mist at the VapaTrog outlet over the entire mist load range. Thus, vaporization of the mist carried by the effluent sample stream appeared to be complete.

The mist loading, W, is calculated from the Table II summary of raw and reduced data produced by the tests. For exact isokinetic sampling ($k = 1.00$) and excluding experimental errors, the calculated mist loading, W_c, should compare exactly with the measured mist loading, W_m.

Three individual mist collection runs were taken over 275-, 336-, and 300-min intervals at corresponding wind tunnel air speeds of 39.2, 43.6, and 47.1 ft/sec, respectively. Although the test conditions including mist loading were reasonably similar, an examination of Table II reveals that a large discrepancy was attained between the calculated and measured mist loadings for two of the three test runs. This discrepancy is inexplicable without consideration of experimental errors and the effects of unanticipated sampling malfunctions at the VapaTrog inlet.

The most probable experimental error arises from the instabilities in the mist generation process and the limitations of mist loading measuring equipment at the VapaTrog inlet. As described, these circumstances led to a measured mist load comprising a time-weighted-average over the entire run time interval. In this regard, it is significant that run 2 yielded the mist load comparison minimum discrepancy (+11.4 per cent), and runs 1 and 3 yielded +39.9 per cent and +47.4 per cent discrepancies, respectively. The measured mist load for run 2 is based on 34 individual readings over a 336-min time interval while those of runs 1 and 3 are based on 16 and 15 readings over 275- and 300-min time intervals, respectively. The implication is that the measured time-weighted-average mist loading for run 2 is more accurate than those of runs 1 and 3 because approximately twice as many readings were made.

It is also significant that the mist load comparison discrepancy is positive for each run (i.e., it appears that more water is entering the VapaTrog inlet than is carried by the effluent sample streams entering isokinetically). Table I shows the isokinetic factor for the 0.384-in. VapaTrog inlet to be 1.02 and 1.08 at 40 and 30 ft/sec, respectively. The effect of these isokinetic factors on ingesting additional mist particles is minimal. Only the smaller particles (<5 μm diameter) will be ingested by VapaTrog in greater proportion than they exist in the mist population at the VapaTrog inlet. The average mist droplet diameter was near 36 to 39 μm, and the total volume per cent of mist comprising droplets less the 5 μm is less than 0.1 per cent.

A more plausible explanation for additional liquid water entering VapaTrog arises from a combination of effects descried during the testing. At low wind tunnel air speeds (~50 ft/sec), mist droplets collect on the nose cone surface. Evidently, the nose cone average temperature must be higher than 150°F to evaporate the liquid water collecting on the nose cone surface. Eventually, a sufficient number of the droplets attached to the nose cone coalesce, developing into a liquid film. The film enlarges until it forms a relatively thick toroid attached to discontinuities on the nose cone surface (e.g., edges, grooves, joins, etc.) where gas flow separation occurs. Also, if the mist load is high and the wind tunnel air speed is low, this toroid of liquid can attach itself to the sharp edge of the VapaTrog inlet. As the toroid enlarges, it becomes unstable and oscillates vigorously in the wind tunnel airstream until it detaches from the nose cone and is carried away in the form of a few large droplets. There are times that a part of the liquid toroid is

ingested directly into the VapaTrog heated tube. In this event, more liquid water is entering the VapaTrog inlet than predicted from the aerodynamic circumstances and mist population characteristics. It is very probable that this effect accounts for a significant part of the positive discrepancy between the calculated and measured mist loads.

In this regard, it may be of significance that the per cent discrepancy between calculated and measured mist load increases with the measured mist load as shown by Table II. In other words, these data substantiate the likelihood that liquid water from liquid film attached to the nose cone is ingested by the VapaTrog inlet at higher mist loading.

Discussion

VapaTrog is a continuous gas/mist sampling and sample conditioning probe that operates isokinetically in a completely passive manner (i.e., the effluent stream velocity at the VapaTrog inlet will self-adjust with flue gas velocity without manual or automated operation of downstream valves, vacuum pumps, or feedback devices). The wind tunnel test and evaluation of the VapaTrog design provided confirmation of its isokinetic sampling performance and its mist processing capabilities. More specifically:

- The VapaTrog performance and operation regarding its isokinetic sampling action as described by Eqs. (1) and (4) were verified by the relatively small response of the isokinetic sampling factor, k, with wind tunnel or flue gas velocity, V_f.

- The VapaTrog unit possesses sufficient thermal and heat transfer capacity to heat the effluent sample stream from 32°F to 340°F and to vaporize a water load of at least 6×10^{-3}.

- Eq. (4) was verified because both k and A_i were shown to be relatively independent of V_f.

- Eq. (4) can be used to design a VapaTrog unit, design modifications, scale changes, and establish its operational limitations for different applications and conditions than tested in the wind tunnel.

- It is essential that the VapaTrog nose cone outer surface be smooth or otherwise free of discontinuities that cause flow separation and subsequent water film growth and eventual ingestion by VapaTrog. For identical reasons, it is important that the VapaTrog nose cone be maintained at temperatures above 212°F.

Acknowledgements

The authors thank the Aerodynamics Research and Concepts Assistance Branch of the U.S. Army Chemical Research and Development Center, Aberdeen Proving Ground, Maryland, for use of the vertical wind tunnel and attendant facilities in the aerodynamic and water mist collection experiments. Successful completion of this work was due to a large

measure to the expert advice and support of Miles Miller and his staff, Joseph Huerta, John Molnar, and Owen Smith. Their contributions are appreciated greatly.

The authors also thank Susan Hendrickson of Germantown, Maryland, for managing the preparation of this manuscript.

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Table I. VapaTrog Aerodynamic Characteristics

The reduced data listed was obtained over 20°F to 48°F and 29.30- to 30.21-in. Hg ambient temperature and pressure conditions except for the 0.384-in. inlet diameter data, which were taken at 74°F to 78°F ambient temperature. All exit velocity data were corrected for pitot-tube blockage. The reduced data listed below for the 0.384-in. inlet diameter were normalized from 70°F to 35°F ambient conditions per Eq. (4).

Operating Parameter	Values at Each Wind Tunnel Velocity (ft/sec)					Notes
	60	50	40	35	30	
At Inlet Diameter: 0.440 in.						
Isokinetic factor	0.831	0.838	0.832	0.842	0.836	1. k variance from average k +0.7 per cent, -0.6 per cent
Average isokinetic factor		0.836 (+ 0.006, -0.005)				
Exit centerline velocity (ft/sec)	52.2	44.0	35.0	30.5	27.0	2. Average/centerline velocity ratio variance +2.2 per cent, -3.6 per cent
Exit average velocity (ft/sec)	40.9	34.4	27.3	24.2	20.3	
Average velocity/centerline velocity ratio	0.786	0.781	0.779	0.795	0.750	
Exit total pressure at centerline (in. H_2O)*	2.25	1.61	1.00	-	0.63	3. k assumed to operate at 35°F
Exit static pressure at centerline (in. H_2O)*	1.97	1.35	0.80	-	0.49	
At Inlet Diameter: 0.423 in.						
Isokinetic factor	0.871	0.886	0.880	0.897	0.918	1. k variance from average k +3.2 per cent, -2.1 per cent
Average isokinetic factor		0.890 (+ 0.028 -0.019)				
Exit centerline velocity (ft/sec)	51.0	43.0	34.5	30.0	26.0	
Exit average velocity (ft/sec)	36.6	33.6	26.7	23.8	20.6	2. Average/centerline velocity ratio variance +1.3 per cent, -1.4 per cent
Average velocity/centerline velocity ratio	0.771	0.781	0.774	0.792	0.792	
Exit total pressure at centerline (in. H_2O)*	2.25	1.55	0.97	-	0.63	
Exit static pressure at centerline (in. H_2O)*	1.95	1.35	0.84	-	0.47	3. k assumed to operate at 35°F
At Inlet Diameter: 0.405 in.						
Isokinetic factor	0.906	0.923	0.928	0.921	0.953	1. k variance from average k, +2.2 per cent, -2.9 per cent
Average isokinetic factor		0.926 (+ 0.020 -0.027)				
Exit centerline velocity (ft/sec)	48.5	41.5	34.0	31.0	27.5	
Exit average velocity (ft/sec)	37.8	32.1	25.8	22.4	19.6	2. Average/centerline velocity ratio variance ±4.0 per cent
Average velocity/centerline velocity ratio	0.78	0.77	0.76	0.72	0.72	
Exit total pressure at centerline (in. H_2O)*	2.23	1.55	0.99	-	0.61	
Exit static pressure at centerline (in. H_2O)*	1.97	1.35	0.85	-	0.47	3. k assumed to operate at 35°F
At Inlet Diameter: 0.384 in.						
Isokinetic factor	0.97	1.01	1.02	1.05	1.08	1. k variance from average k, +4.9 per cent, -5.8 per cent
Average isokinetic factor		1.03 (+ 0.05, -0.06)				
Exit centerline velocity (ft/sec)	43.0	38.0	33.0	30.5	27.5	
Exit average velocity (ft/sec)	34.8	30.2	24.5	21.5	19.5	2. Average/centerline velocity ratio variance +6.7 per cent, -5.3 per cent
Average velocity/centerline velocity ratio	0.80	0.78	0.75	0.71	0.71	
Exit total pressure at centerline (in. H_2O)*		(not measured)				
Exit static pressure at centerline (in. H_2O)*		(not measured)				3. k normalized to 35°F per Eq. (4)

*The maximum variance of exit total and static gauge pressure from the average at a given wind tunnel air velocity is +2.8 per cent, -3.6 per cent.

Table II. VapaTrog Mist Collection and Processing

Eq. (6) was used to calculate the average mist loading with $\rho_v = 1.16 \times 10^{-3}$ g/ml, $\rho_l = 1$ g/ml, and $(W_{H_2O})_0^* = 3.3 \times 10^{-3}$. The air specific humidity was defined from dry and wet bulb temperatures. A 0.384-in. diameter inlet was used in these experiments.

Parameter	Run Number 1	2	3
Wind tunnel air velocity (ft/sec)	39.2	43.6	47.1
Mist loading measurements over Δt	16	36	15
Nose cone average temperature (°F)	147 to 109	160 to 130	160 to 130
Mist droplet average diameter (μm)	36	35	39
Collection time—Δt (min)	275	336	300
Bleed flow rate—Q_B (ml/min)	1070	1150	1110
Liquid water collected—V_l (ml)	5.45	6.50	6.15
Air specific humidity—W_{H_2O}	1.582×10^{-2}	1.582×10^{-2}	1.374×10^{-2}
Calculated average mist loading—W_c	4.1×10^{-3}	2.5×10^{-3}	6.0×10^{-3}
Measured time weighted average mist loading—W_m	2.93×10^{-3}	2.25×10^{-3}	4.07×10^{-3}
Percent discrepancy between W_c and W_m	+39.9	+11.4	+47.4

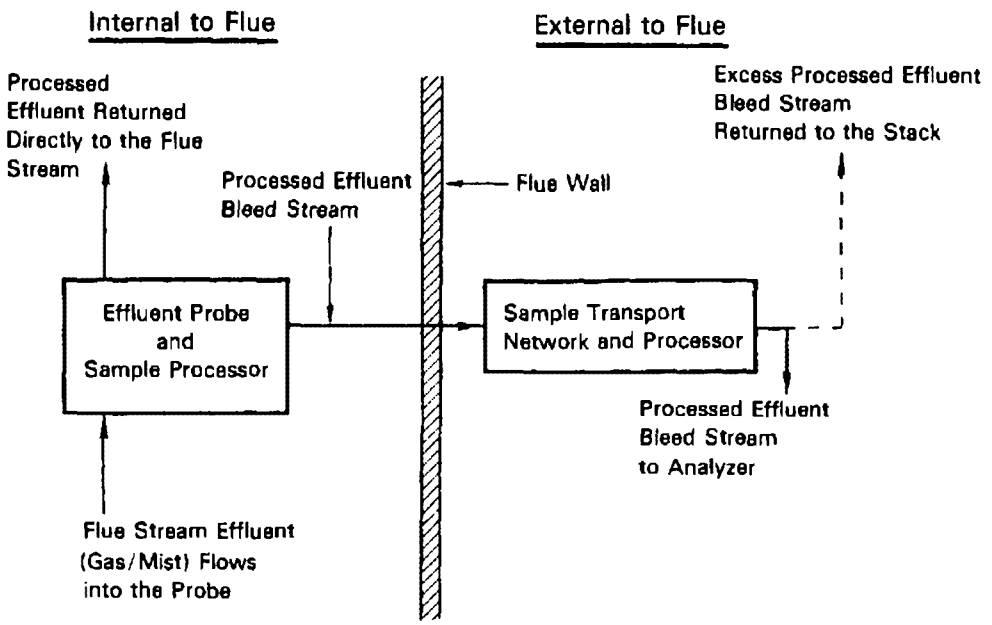

Figure 1. Isokinetic gas/mist sampler.

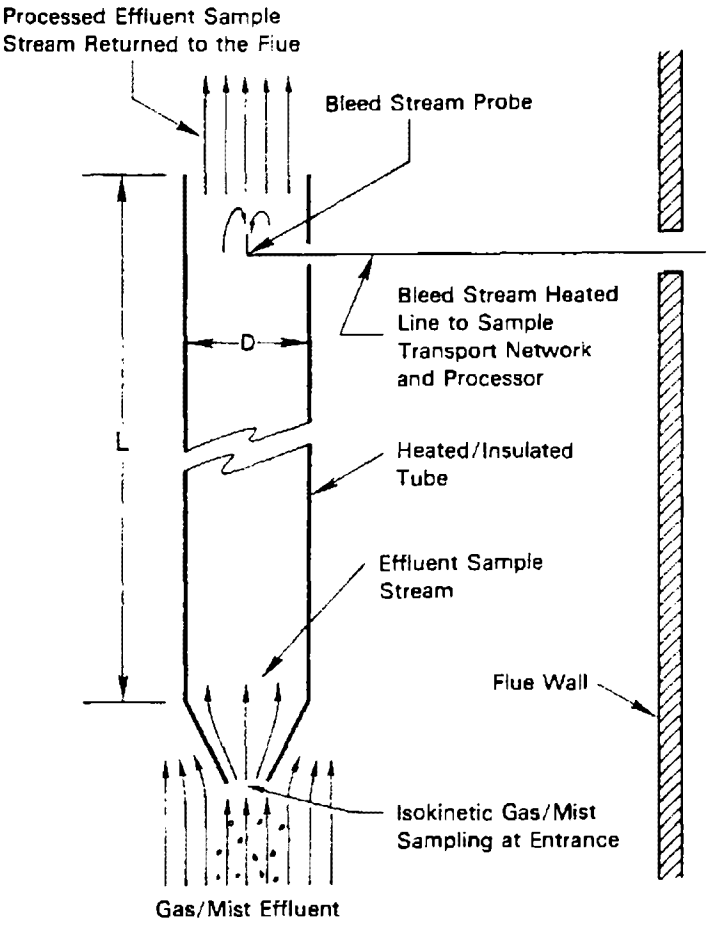

Figure 2. VapaTrog (effluent probe and sample processor).

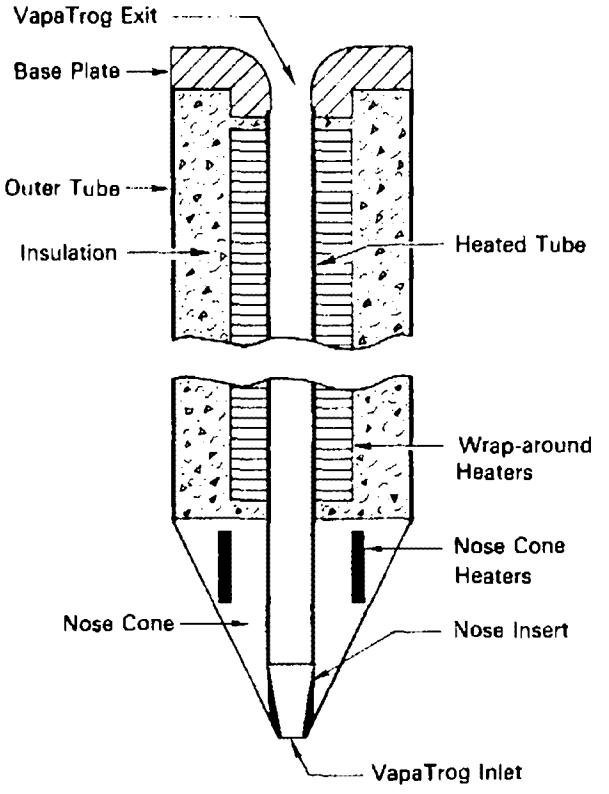

Figure 3. VapaTrog probe.

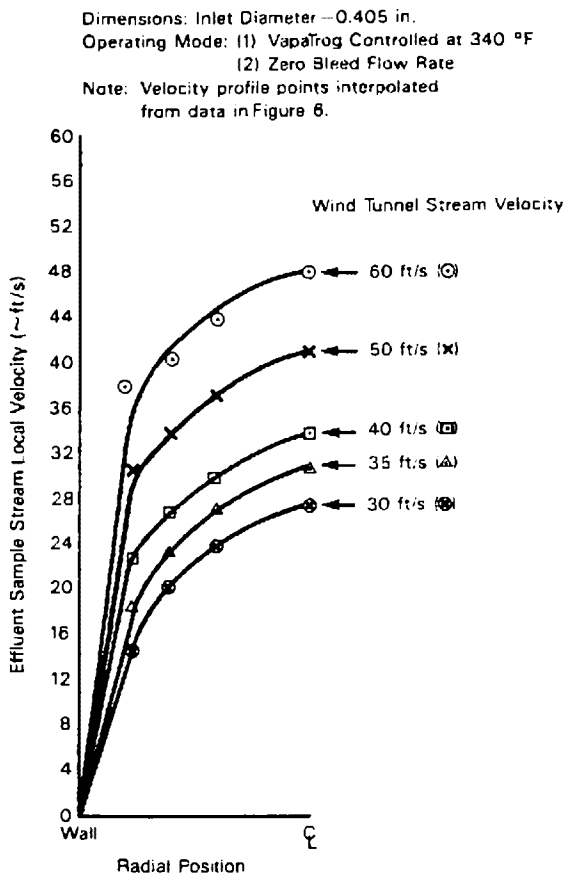

Figure 4. Effluent sample stream exit velocity profile.

DEFINING AMBIENT IMPACT OF VOLATILE ORGANIC COMPOUNDS EMITTED FROM AN AUTOMOBILE ASSEMBLY FACILITY

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General Motors (GM) organized a five-day analysis of ambient concentrations of twenty-one volatile organic compounds near a high-capacity automobile assembly facility applying low-solvent coatings. A consultant was retained to perform on-site measurements using a mobile TAGA® 6000 tandem mass spectrometer. In addition to providing quantitative results for twenty-one target compounds, all organic materials were identified. Ambient air monitoring was conducted in the late summer and early fall of 1985. GM received preliminary data in mid-March, 1986. This paper describes project objectives, monitoring strategy and data analysis techniques. Project results are not included, due to the late arrival of preliminary data and the need for further analysis. However, it was found that the minimum detection limit of the TAGA® 6000, as used in this study, was generally not low enough to enable a comparison of ambient concentrations with fractional occupational limits. This project was a first attempt at applying an emerging technology to better understand the ambient impact of VOC's emitted from a large automobile assembly plant applying low-solvent coatings.

DEFINING AMBIENT IMPACT OF VOLATILE ORGANIC COMPOUNDS EMITTED FROM AN AUTOMOBILE ASSEMBLY FACILITY

Introduction

Within the past five years, regulatory agencies and the general public have shown an increasing concern over the industrial emission of toxic air pollutants. This concern is evident by the introduction of bills to revise the Clean Air Act, articles in leading national newspapers and numerous government research projects.[1] In addition, many state and local agencies either have developed, or are now developing, air toxics regulatory programs apart from federal activities[2]. As such, General Motors (GM) has intensified its long-standing efforts in evaluating and reducing the impact of potentially hazardous air pollutants resulting from the operation of its products and facilities. GM has elected to participate in further analyses of potentially hazardous stationary source emissions in order to 1) contribute in a positive fashion to the formation of reasonable and effective air toxics regulations, and 2) identify and correct as a responsible citizen any potential problems resulting from current plant emissions.

In mid-1984, GM decided to examine further the ambient impact of specific volatile organic compounds (VOC) emitted from an automobile assembly center, as some of these compounds, such as toluene, were, and still are, under review as potentially harmful to humans[3]. Stringent federal surface coating requirements designed to attain the national ambient air quality standard for ozone have necessitated the use of low-solvent coatings at most GM assembly centers. However, few comprehensive studies have measured the ambient impact of specific VOC's emitted from facilities applying these coatings.

A reference facility for this ambient monitoring study was selected based upon several factors. First, the surface coating operations had to be representative of those in current and near-future GM vehicle assembly centers. Second, no variances in production should be anticipated during the scheduled monitoring period. Next, the area surrounding the plant had to contain numerous public streets to facilitate monitoring with the proposed mobile analytical laboratory. Finally, some prior measurements of ambient VOC concentrations should be available from the site in order to check project results. The selected facility, one of GM's highest volume vehicle assembly operations, continues to be in compliance with all applicable air pollution regulations.

Project Tasks

Six tasks were identified to guarantee that the project results would satisfy the objectives of the Corporate air toxics strategy as described above. These are:

1) Determine known hazardous, high-usage VOC's from production operations; (These, and other organics selected by the consultant, would be target compounds for which quantitative ambient results were desired. This step was required to calibrate proposed mobile analytical equipment, and for identification of production material constituents.)

2) Measure ground level concentrations of all target compounds in the community near the automobile assembly facility under various meteorological conditions;

3) Identify all organic materials in detected plumes; (Quantification of these compounds could be performed in later studies.)

4) Calculate annualized concentrations for identified target compounds using maximum short-term average levels and meteorological scaling factors;

5) Compare annualized concentrations to fractions of occupational threshold limit values and cancer assessment group values, and

6) Compare peak concentrations to documented threshold odor levels.

Selection of Target Compounds

Three criteria were evaluated in order to select target compounds for this study: emission rate, priority ratio and expert opinion. A prior GM study identified the usage of production materials containing VOC's. From this internal study, and a thorough review of vendor supplied material safety data sheets, it was possible to rank the known VOC emitted by the facility according to maximum potential emission rate. Next, a priority ratio was developed for each compound by dividing the maximum potential emission rate by its respective Threshold Limit Value (TLV) set by the American Conference of Governmental Industrial Hygienists. This ratio reflects both maximum potential emission rate and a degree of toxicity. A high priority-ratio qualified the compound for further review. If no TLV existed for a compound, then an arbitrary high value was assigned in order to calculate that specific compound's priority ratio. Typically, this high TLV value created a low priority ratio. This practice was deemed justifiable, in the absence of a better method, because it was felt that if the compound was a widely used toxic material, then it would likely have an assigned TLV. The last criteria used in selecting target compounds was the advice of Dr. Pat Beattie of GM Toxic Materials Control Activity, and Dr. Kay Jones of Roy F. Weston, Inc.. These individuals recommended additional compounds on the basis of other air toxics studies and the unique compound identification characteristics of the proposed mobile analytical equipment. Table I identifies the selected target compounds.

Mobile Analytical Laboratory

Roy F. Weston, Inc. and their subcontractor York Research Consultants, Inc. were retained to conduct the ambient monitoring. The monitoring equipment consisted of a TAGA® 6000 tandem mass spectrometer (MS/MS) mounted in a 33-foot modified Bluebird motorhome. The TAGA® 6000 system has the ability to analyze complex gaseous mixtures for individual components without prior entrapment of sample. This feature enabled the mobile analytical laboratory to conduct real-time monitoring over a large geographic region near the plant. Further, the mobile analytical laboratory was able to locate plume centerlines quickly and obtain maximum time-averaged concentrations of detected target compounds.

The existing conventional methodologies for the detection of low levels of organics in ambient air require that the compounds be adsorbed onto a

substrate over a finite period of time. The substrate is then taken for analysis in an off-site laboratory, where the compounds are either thermally desorbed or solvent eluted from the substrate and analyzed by GC or GC/MS. The conventional monitoring techniques suffer from several drawbacks. Extensive sampling using a network of monitoring locations is necessary to quantify maximum ambient levels of organic compounds. Results are obtained several days or weeks after the sampling is performed. Also, temporary fluctuations cannot be identified, as the results are always time-averaged over the duration of the sampling period. Uncertainties are also introduced in the desorption process.[4] These difficulties are minimized or eliminated by employing a mobile tandem mass spectrometer.

Tandem mass spectrometry emerged as an analytical tool in the early 1980's and several reports are available which describe the system and its development.[5] While the intent of this paper is to discuss the ambient monitoring strategy, it is important to note some of the limitations of the TAGA® 6000 system in this application. Interferences are possible in the measurement of some target compounds. For example, except through detailed study of the mass spectra, ethylbenzene cannot be distinguished from the xylenes. Likewise, methylene chloride cannot be distinguished from chloroform, and the aliphatics hexane and heptane cannot be distinguished from the corresponding olefins hexene and heptene.[6] Also, the detection limit of the TAGA® 6000 as used for this project was not as low as other methods currently accepted by the Environmental Protection Agency, such as the volatile organic sampling train (VOST).[7] Manual sampling techniques can achieve lower detection limits by increasing sampling time, while the minimum detection limit of the TAGA® 6000 is defined as three standard deviations above instrument noise.

Monitoring Procedures

Based on estimated project costs and the consultant's assurance that meaningful results could be obtained from five days of testing, the ambient monitoring was scheduled for August 29-30 and September 4-6, 1985. Nearly all monitoring was conducted during the hours in which the plant was operating at full capacity. During the first three days and the fifth day monitoring was conducted between the hours of 7:00 A.M. and 4:00 P.M. corresponding to first shift production operations. On the fourth day monitoring was initiated at 3:00 A.M. in effort to assess the ambient impact of methylene chloride and other organic compounds emitted from paintshop maintenance activities performed during the early morning hours.

Sampling was conducted both upwind and downwind of the assembly facility. One of the first operations performed each day was an upwind background scan. Background scans were conducted upwind of the facility in various rural locations, and the corresponding spectra were stored onboard electronically. Later, the background spectra were subtracted from the downwind spectra in order to identify unique components or those compounds present in higher concentrations than background levels.

The TAGA® 6000 was calibrated for each target compound at the beginning and end of each monitoring day using pure laboratory standards kept in the liquid phase in an onboard freezer. A known mass of the standard was injected at a precise rate into the constant flow of the ambient sampling stream. Calibration curves were generated by noting the corresponding rise in signal intensity from the known concentration of introduced sample.

The TAGA® 6000 was utilized for both mobile and stationary monitoring. Wind conditions dictated the major quadrant around the facility in which the mobile laboratory would begin monitoring. Wind speed, wind direction and other meteorological data were continuously collected at an on-site station. The mobile mode of operation was used first to locate specific geographic areas having the highest concentrations of target compounds. Later, the mobile laboratory was parked in these areas, and operated in the stationary mode. Sensitive receptors, such as schools and hospitals, were given priority as monitoring sites. While operating the TAGA® 6000 system in the stationary mode, fluctuations in plume concentration at individual locations were recorded. After examining these fluctuations over a ten minute interval, time-weighted average concentrations were calculated. The spectra from twenty-two mobile and twenty-one stationary runs was analyzed.

Data Analysis

The specific techniques used in the analysis of the raw data are critical to obtain meaningful project results. Time-weighted average concentrations can be calculated in several different ways and for varying periods of time. Use of different techniques and averaging periods may yield significantly different project results. For this analysis, ten-minute average concentrations of target compounds were calculated using recognized integration techniques.[8] A standard time-frame of ten minutes was selected, because this was typically the longest period for which conclusive measurements were recorded repeatedly over the five-day monitoring period. However, these ten-minute maximum concentrations do not accurately represent average maximum levels in the community over the course of a year. The maximum ten-minute concentrations were annualized using conservative scaling factors developed from EPA guidelines.[9] These annualized concentrations will be compared with acceptable ambient levels. Instantaneous peak levels of target compounds are relevant only in comparison to documented threshold odor concentrations.

A number of states and localities derive acceptable ambient concentrations for certain compounds by applying a safety factor to the corresponding occupational TLV. The most stringent safety factor in use in the United States applicable to most compounds is 1/420.[10] Annualized concentrations of target compounds will be compared to recommended levels calculated with this stringent safety factor. However, as shown in Table II, the minimum detection limits reported for many compounds during portions of this study were not low enough to permit a comparison of project results with fractional occupational limits.

Conclusions

The mobile, real-time analysis capabilities of the TAGA® 6000 permitted plume tracking and location of sites experiencing maximum ambient levels of detected target compounds. However, the minimum detection limit of the TAGA® 6000, as used in this study, was generally not low enough to enable a comparison of ambient concentrations with acceptable community health levels.

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Table I. Selected Target Compounds

1) acetone
2) 1,3-butadiene
3) n-butanol
4) n-butyl acetate
5) epichlorohydrin
6) 2-ethoxyethanol
7) 2-ethoxyethylacetate
8) ethyl acetate
9) heptane
10) hexane
11) isobutyl alcohol
12) methylene chloride
13) methyl ethyl ketone (MEK)
14) methyl isobutyl ketone (MIBK)
15) 2-propanol
16) styrene
17) toluene
18) tetrachlorethylene
19) 1,1,1-trichloroethane
20) vinyl chloride
21) xylene (o,m,p)

Table II. Range of TAGA® Detection Limits During Study vs. TLV/420

	Target Compound	Range of TAGA® 6000 Detection Limits (ppb)	TLV/420 (ppb)
1)	acetone	58-630	1,786
2)	1,3-butadiene	11-120	24
3)	n-butanol	38-1,100	119
4)	n-butyl acetate	140-9,500	357
5)	epichlorohydrin	5-69	5
6)	2-ethoxyethanol	not determined	12
7)	2-ethoxyethylacetate	not determined	12
8)	ethyl acetate	78-3,000	952
9)	heptane	54-2,900	952
10)	hexane	540-25,000	119
11)	isobutyl alcohol	not determined	119
12)	methylene chloride	1,400-4,800	238
13)	methyl ethyl ketone	34-630	476
14)	methyl isobutyl ketone	6-76	119
15)	2-propanol	not determined	476
16)	styrene	360-3,400	119
17)	toluene	28-1,900	238
18)	tetrachloroethylene	340-3,300	119
19)	1,1,1-trichloroethane	38-2,800	833
20)	vinyl chloride	25	12
21)	xylene (o,m,p)	5-79	238

QUALITY ASSURANCE FOR NON-ROUTINE AIR MEASUREMENT PROGRAMS: EPA's EXPERIENCE WITH THE NATIONAL DIOXIN STUDY

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ABSTRACT

In recent years, air measurement programs have become more and more sophisticated. For example, today it is not unusual for an industrial process emissions research program to require the use of a variety of stack and ambient air sampling trains and continuous emission monitors, the collection of numerous process and soil samples, the recording of voluminous amounts of process operating data, and the use of several complex analytical techniques, including gas chromatography/mass spectroscopy. As interest develops in the measurement of air toxics, air measurement programs have become further complicated by the use of non-routine methods. The net result of these complexities is often confusion over the appropriate use of equipment and procedures, resulting in the generation of poor, or at least unknown, data quality. A few organizations, including the U.S. Environmental Protection Agency (EPA), have addressed these problems through the implementation of a quality assurance strategy as part of the overall test plan. EPA's experience in implementing a quality assurance program for Tier 4 (Combustion Sources) of the National Dioxin Study is discussed. The study involved the measurement of dioxin (2,3,7,8-TCDD) and dioxin precursors (i.e., chlorophenols and chlorobenzenes) at thirteen emission sources, and analyses associated with these measurements. Lessons learned from the study and recommendations for the designers of future air toxics measurement programs are presented.

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Introduction

During the past several years an increasing need for quality assurance (QA) in environmental test programs involving air measurements has become evident. This need has resulted largely from the substantial number of measurements now made in many test programs, the use of contractors and subcontractors who are inexperienced with new and non-routine test methods, and the increasing necessity to defend test results before industry and the public, sometimes in litigation. Recently, as interest has developed in the measurement of toxic air pollutants, the need for QA has become even more important. This is due to: (1) the high costs associated with many air toxics measurement programs; (2) the complexity of the measurement and analytical methods; and (3) the importance of these measurements in establishing a potential health risk to the public. Unfortunately, as QA has become more important, it has also become more challenging to effectively implement.

QA, which involves a series of independent checks of test program procedures and documentation, is intended to help:

- Define the quality of data produced by the test program; and
- Assure that the quality of data produced is adequate to achieve the objectives of the test program.

The experience of the U.S. Environmental Protection Agency (EPA) in implementing a QA program for Tier 4 (Combustion Sources) of the National Dioxin Study is presented here. Since similar large-scale sampling and analysis programs involving toxic air pollutants will be performed in the future, it is hoped that EPA's Tier 4 experience will be useful to future investigators in planning their air toxics measurement programs.

Background

In 1984 EPA implemented a national strategy to study the nature and extent of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) contamination in the environment. The strategy, known as the National Dioxin Study, established seven categories (or Tiers) of investigation, ranging from the most probable contamination to the least. The category dealing with air emission sources, Tier 4, was defined as:

- Combustion sources such as the incineration of hazardous and municipal wastes, internal combustion engines, wood-burning stoves, and others.

The responsibility for investigating Tier 4 sources was assigned to the Air Management Technology Branch (AMTB) of EPA's Office of Air Quality Planning and Standards. AMTB's contractor for the Tier 4 sampling and analytical support activities was Radian Corporation of Research Triangle Park, North Carolina. Additionally, EPA's Troika Laboratories (i.e., the three dioxin analytical facilities at Research Triangle Park, North Carolina; Bay St. Louis, Mississippi; and Duluth, Minnesota) performed all of the analyses for chlorinated dioxins and furans. The Tier 4 activities performed by these two organizations, including the sampling and analytical techniques used, are summarized in Table 1. A total of thirteen emission sources were investigated during the study.

QA support for the study was provided by Research Triangle Institute

(RTI) of Research Triangle Park, North Carolina. RTI's responsibility was to independently evaluate the test procedures used in the study and to report its evaluation, with any recommendations, to AMTB. This effort resulted in three separate on-site evaluations of the test systems in use in the field, nineteen performance audits of the measurement and analytical equipment, eight reviews of various reports and documents, and a final report.[1] RTI's cost in performing these duties was approximately four percent of the total Tier 4 budget. Although AMTB personnel played a role in determining which tests, equipment, and documents should be evaluated, these individuals remained independent of the conclusions and recommendations presented by RTI.

In addition to RTI's QA support program, several other organizations also performed independent QA evaluations. For example, both Radian Corporation and the Troika Laboratories had their own QA and quality control (QC) programs in effect.[2,3] Additionally, EPA had its own observers present during all stack tests.

Elements of the QA Program

The Tier 4 QA program can be divided into three categories: QA Management, Internal QA/QC Operations, and External QA Evaluations. The first category, QA Management, consists of the set of requirements and procedures specified by EPA management. The second category, Internal QA/QC Operations, covers the responsibilities of Radian Corporation. The final category, External QA Evaluations, involves the audit and review activities performed primarily by RTI. Although the Troika Laboratories' internal QA/QC program is not discussed here, these Laboratories were evaluated as part of RTI's QA effort.

QA Management

As noted earlier, EPA's AMTB had overall responsibility for the Tier 4 study, including QA management. QA was recognized early in the program planning stage as a key factor in determining the overall success of the study. Therefore, it was determined that a multifaceted QA effort would be needed. The major program components that affected data quality were identified as the sampling activity conducted by Radian and the analytical activity which was the responsibility of EPA's Troika Laboratories. Both of these functions would have their own internal QC. Additionally, it was decided to have RTI, a completely independent QA contractor, provide an independent and unbiased assessment of the data quality generated under the study.

In addition to the QA contractor's oversight role, an on-site EPA representative was present at each source test site as a test observer. The EPA on-site observer was familiar with the sampling protocols and provided additional QA verification that field operations had followed the established protocols.

Major emphasis under the QA portion of this study was placed on the sampling activity. The primary reason for this emphasis was that Troika represented established laboratories which had considerable experience in the analysis of chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs), and which already had rigorous QA programs in place. In contrast, the sampling activity had to develop its own written sampling procedures, prepare a detailed QA Project Plan (QAPP), and refine these

procedures through experience gained in the field. Thus, greater QA emphasis was placed on the field sample phase of the study.

Data quality objectives can be established in one of two ways. One means of establishing these objectives involves an analysis of the parameters to be measured, an assessment of the allowable uncertainties in measuring these parameters, and the selection of appropriate methods to measure these parameters, based upon the established measurement criteria. The task of QA then becomes one of determining whether or not the data generated satisfies the specified quality objectives. The second approach to setting data quality objectives, and the one used in this study, involves the specification of a particular sampling and analytical methodology. Once the methodology has been specified, the task of QA is to determine whether the methodology was properly followed. Under this study, state-of-the-art methods were specified for both sampling and analysis to obtain results that deliver the highest level of data quality possible.

The remaining QA management functions were operational in nature. It was necessary to maintain an oversight responsibility to ensure that the various elements of the QA program functioned properly and were properly coordinated. For example, it was important to schedule a QA field audit of Radian's stack sampling program early in the study. Thus, if difficulties were identified, there would be ample time remaining in the program to implement corrective action. Also, future QA field audits could verify that proper corrective action had been taken.

Perhaps the most significant QA management responsibility involved the decision of how to resolve problems that affect data quality after the QA program has identified them. Each situation is unique. Two examples from this study will serve as illustrations. In the first example, the QA contractor, RTI, identified a problem in Radian's laboratory method for the analysis of low levels of chlorine in fuel oil audit samples. The problem was identified as an inappropriate analytical methodology for low level chlorine analysis. Radian elected to subcontract this analysis to another laboratory that had experience in analyzing these types of samples. In this example, the problem was identified, a remedy implemented; and all data reported achieved satisfactory data quality.

In the second example, the EPA Troika Laboratories' internal QA program identified a data set that did not meet their own internal data quality objectives. The QA management decision in this case was to report the data (even though data quality objectives were not satisfied), but to clearly identify in the report that this was the case. The reader of the report was cautioned that these data did not satisfy QA criteria and should be regarded as estimated values.

Internal QA/QC Operations

Radian's QA activities for the Tier 4 study centered around the preparation and implementation of a sound and comprehensive Quality Assurance Project Plan (QAPP). The need for good planning cannot be overemphasized with regard to assuring high quality data from any field sampling effort. In preparing the QAPP, special attention was given to the sampling effort and the need for this plan to be a working or reference document for field sampling personnel. The plan, therefore, provided specific details on the sampling, analysis, calibration, data reduction, and QA reporting activities to be conducted under the Tier 4 program. The

process of specifying these details led to invaluable communications between the technical and QA project teams within Radian, EPA, and RTI. Ultimately, a sound and comprehensive plan acceptable to all parties was developed. The QAPP, being a working document, was later modified as certain procedures were refined through experience gained in the field.

The QA/QC planning efforts for Tier 4 were supplemented by the preparation of site-specific test plans for each of the thirteen test sites. These plans provided details to the technical and QA project teams on the particular combustion process, the number and types of samples to be collected, and any special QA/QC considerations to be noted.

The Tier 4 QAPP emphasized: (1) adherence to prescribed sampling/analytical procedures; (2) careful documentation of sample collection and field analytical data; and (3) internal (but independent) systems and performance audits similar to those conducted by RTI. Standard QC procedures, such as equipment calibrations, leak checks, etc., were implemented for each of the sampling/analytical methods. Additional QC measures implemented to further ensure valid data and/or to provide a measure of data quality are summarized below.

Modified Method 5 (Dioxins). Extensive glassware pre-cleaning procedures and blank sample train collections were implemented for the Modified Method 5 sampling effort. The purpose of the pre-cleaning procedure was to minimize the potential for sample contamination with substances that may interfere with the dioxin analysis. Flue gas dioxin concentrations at the part-per-trillion level were targeted for the method.

Two types of sample train blanks were collected. One of the blanks (called a proof blank) was collected from a set of unused, pre-cleaned glassware to verify that the cleaning procedure was effective. The second blank was a site-specific sample train field blank. The field blank was obtained using a train that had previously been used to collect at least one actual sample from the test site. The field blank provided data on the effectiveness of the sample recovery procedures.

Continuous Monitoring. Specific acceptance criteria for continuous monitor calibrations were set forth in the QAPP to provide field personnel with a basis for accepting or rejecting calibration curves. All data, including calibration results, were collected and recorded using a microprocessor-based data acquisition system, thereby reducing the potential for errors from manual data reduction. Daily drift checks and QC gas analyses were also performed to provide a measure of data quality and to identify the need for instrument maintenance.

Process Sample Collection. The types of process samples collected for Tier 4 varied widely from liquids/slurries (e.g., scrubber blowdown and fuel oils) to sludges/solids (e.g., sewage sludge and wood chips). Methods used to sample these materials were detailed in the site-specific test plans and agreed to by all team members before testing was performed. Whenever feasible, these samples were collected from a moving stream as close as possible to the equipment being sampled. Duplicates for the process samples were analyzed to assess sampling/analytical precision.

Sample Custody. Since samples collected during the Tier 4 study were analyzed in several different laboratories, sample custody and handling was an important part of the field sampling effort. Key elements of the sample custody and handling procedures included the following:

- Preformatted data sheets for all sampling efforts.
- An informal daily log to document events.
- A unique alphanumeric identification number for samples from all sites.
- A "master" logbook to document all samples collected.
- Labels, custody seals, and chain-of-custody forms specific to Tier 4.
- Sample shipment letters prepared prior to leaving for the field.
- Packing and shipping procedures that minimized sample loss due to spillage or breakage.

Laboratory Analyses. Procedures for laboratory QA/QC consisted of laboratory blanks and duplicate analyses. In addition, blind audit samples were submitted to the laboratories to assess analytical accuracy.

External QA Evaluations

RTI's QA activities took the form of technical systems audits, performance evaluation audits, and documentation reviews. A technical systems audit is a qualitative, on-site evaluation of a measurement system. The objective of the technical systems audit is to assess and document the use of all:

- Test facilities and equipment.
- Recordkeeping and data validation procedures.
- Equipment operation, maintenance, and calibration procedures.
- Reporting requirements.
- QC operations.

In contrast to the technical systems audit, a performance evaluation audit involves a quantitative evaluation of the measurement system. Ordinarily, this type of evaluation requires the measurement or analysis of a certified or verified reference material having associated with it a known value or composition. The third RTI QA activity, documentation review, is simply the evaluation of pertinent test documentation (usually QA or test plans) against a standardized set of QA criteria. Each of RTI's QA activities are described in more detail below.

Technical systems audits were performed at three test sites. In preparing for these audits, RTI compiled a series of checklists covering every significant operation, calibration, and adjustment associated with each critical measurement. (The critical measurements included operation of the inlet, outlet, blank, and ambient Modified Method 5 sampling trains; operation of the HCl sampling train and continuous emission monitors; the collection of process samples; sample handling, transportation, and storage; and the collecton of soil samples.) Similar checklists were also prepared for Radian's laboratory operations. The questions contained on the check-

lists were based on a review of all applicable test methods and on the auditors' experience with those methods. The advantages of using checklists to perform technical systems audits are that they: (1) help guide the auditors in identifying what aspects of the testing to focus on; (2) help assure objectivity and completeness in the selection of questions to be asked on-site; and (3) provide thorough documentation of all critical test procedures and operations.

It was not practical to attempt to complete the entire series of checklists (i.e., eight checklists containing a total of 202 questions) during each of the three technical systems audits. Instead, the complete set was used only during the first audit, and abbreviated forms were used thereafter. (The abbreviated forms focused on recommendations made by RTI as a result of the first audit.) For each audit, the use of checklists was augmented with visual observations of critical test procedures and discussions with the test team leaders.

In preparing materials for use in RTI's performance evaluation audits, RTI followed, where appropriate and feasible, these procedures: (1) the most critical measurements and analyses were evaluated; (2) blind samples were submitted (i.e., samples indistinguishable from actual field samples); (3) the audit sample concentrations were certified or verified; (4) a portion of each sample was stored at RTI in case the integrity of the audit sample should be called into question at a later date; (5) the audit samples covered the range of concentrations expected to be encountered in the test program; (6) duplicate audit samples were submitted to check analytical precision; (7) the audit sample matrices were selected to be the same as or similar to those encountered in the field; and (8) the samples were submitted early enough in the test program to allow for procedural changes to be made without seriously compromising final results.

RTI's performance evaluation audits of analyses performed by Radian examined the following systems:

- <u>Analysis of chlorine in fuel oil</u>

  These analyses were evaluated by submitting to Radian a set of four (and later a second set of two) Number 2 fuel oil samples that had been spiked with methylene chloride. The concentrations of the spiked samples were verified at RTI using the same method later used by Radian.

- <u>Analysis of HCl train impinger water</u>

  These analyses were evaluated by submitting to Radian a set of two impinger water samples taken during a earlier test program. The concentrations of the samples were verified by RTI before analysis by Radian.

- <u>Dry gas meter calibrations</u>

  The calibrations of the sampling train dry gas meters were evaluated using a calibrated orifice supplied and certified by EPA.[4]

- <u>Computerized calculations</u>

  Radian used a computer to perform routine data calculations associated with operation of the sampling trains. This system was

evaluated by providing for input to the computer a set of hypothetical data for which the expected calculated results were known only to RTI.

The analysis of 2,3,7,8-TCDD by the Troika Laboratories was evaluated by submitting the following samples obtained from the National Bureau of Standards (NBS):

- NBS Urban Particulate (SRM 1648) and Urban Dust (SRM 1649)

  The concentrations of 2,3,7,8-TCDD in these samples had been verified earlier by DOW Chemical.[5,6]

- NBS Dioxin in Isooctane (SRM 1614), Two Samples

  These were preliminary samples made available to RTI by NBS. (This audit material has since been made available to the public.[7])

RTI's original intention was to prepare its own 2,3,7,8-TCDD audit materials and submit them as blind samples to Troika. However, when the costs associated with the preparation of these samples in a toxicological laboratory and the verification of the samples using sophisticated HRGC/HRMS techniques were considered, a decision was made to use an alternative approach. (The health risks associated with the preparation of the samples were also a factor in this decision.) The alternative approach was to submit directly to Troika, without modification, the NBS samples. The disadvantages of this approach are that: (1) the samples would not be blind; (2) Troika may have been able to guess the concentrations due to previous experience with similar samples (although the isooctane samples were not formally available to the public at that time, and Troika would not have known whether the dust samples had been spiked by RTI); and (3) the sample media were not the same as experience by the field samples (i.e., XAD-2 resin). Despite these shortcomings, it is believed that the Troika Laboratories made a good faith effort to analyze the samples without bias.

The third aspect of RTI's audit activities involved the review of documentation, primarily Radian's QAPP and several site-specific test plans. This review process was guided by the set of QA criteria specified in EPA's "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans" (QAMS-005/80), and by the experience of the auditors with the methods being evaluated. The QAMS-005/80 criteria are listed in Table 2.[8]

Assessment of the Tier 4 Program

Although data analysis will continue, it appears that the Tier 4 sampling effort was quite successful. Data quality objectives were generally achieved, sampling and analytical requirements were fulfilled, and little data were lost. Only a few test runs had to be repeated due to technical or procedural problems (e.g., a filter mounted backwards), and no series of testsonducted at a specific site had to be repeated due to deviations from program procedures. Thus, when judged by the quality of data produced, it appears that the QA/QC program was a success.

One outcome of the Tier 4 program was evidence, based on the use of audit samples, that the sampling and analytical procedures were performed

correctly. For example, the analytical results for 2,3,7,8-TCDD compared favorably to the expected results, as indicated below:

Sample Description	Expected Value	Reported Value[9]
SRM 1648	0.047 ppb	0.07 ppb
SRM 1649	0.0067 ppb	Not Detected (D.L. = 0.04 ppb)
SRM 1614 (#1)	98.3 ppb	99 ppb
SRM 1614 (#2)	98.3 ppb	100 ppb

In the only case where audit results were not achieving data quality objectives (i.e., the chlorine-in-fuel-oil analyses), the early use of audit samples allowed the implementation of an acceptable method without loss of data.

As discussed earlier, QC was also essential in producing the desired quality of data. In one case, the cleanup and analysis of a blank Modified Method 5 sampling train revealed that significant dioxin contamination had occurred. Apparently, the sampling glassware, which had been used earlier in the test program, had not been completely cleaned by the hexane and acetone rinses in use. Reasoning that dioxins were more soluble in methylene chloride than in hexane or acetone, a decision was made to switch to methylene chloride rinses for the dioxin sampling trains.[10] This decision was made early enough to avoid significant loss of data.

Despite the apparent success of the Tier 4 sampling program, there were several QA activities that could have been improved. For example, it would have been useful to provide more audit samples, such that the systems under evaluation could have been audited periodically throughout the entire study. Another area for improvement concerns the preparation of audit samples for the 2,3,7,8-TCDD analyses. Samples which were truly blank and which were prepared in a matrix similar to that of the field samples would have been preferable. Finally, it would have been useful to perform technical systems audits of every field sampling operation rather than the three of a possible thirteen actually evaluated. Nevertheless, given the cost and time constraints inherent in the study, we believe that the design of the QA program was appropriate.

Recommendations for Future Air Toxics Measurement Programs

It has been our experience that when sophisticated or non-routine sampling and analytical procedures are part of any air pollution study, the implementation of a well-planned QA program is essential. Such programs usually pay for themselves in reduced re-testing and loss of data, and provide thorough documentation for the quality of data produced. It is not unreasonable for up to twenty percent of the entire budget of an air pollution study to be devoted to QA.

A number of QA procedures which we have found useful in designing air

pollution studies, including the Tier 4 study, are listed below:

- Establish a budget for quality assurance from the very beginning of the test program.
- Develop the QA plan and test plan simultaneously.
- Define a QA official who is not part of the test team and who reports directly to management.
- Use the QA plan to establish data quality objectives as well as to anticipate and plan for any unexpected problems or delays.
- Be sure to allow sufficient time for laboratory work, especially where non-routine methods are in use or where difficult sample matrices are to be handled.
- Include the periodic use of audit materials for all critical measurements. Where materials to assess accuracy are not available, provide for a thorough technical systems audit of the system.
- Make liberal use of blanks (including blank trains) as well as duplicate and replicate analyses.
- Sample identification and tracking is very important. Make use of field, transportation, and laboratory custody sheets and log books.
- Consider performing an audit of data quality (i.e., an assessment of all data transfer and reduction steps) for studies generating large amounts of data.
- Do not overlook the importance of documentation for procedures used and conditions encountered during the study.

Summary

If judged by the quality of data produced, the Tier 4 QA program was successful. Not only were all procedures and conditions thoroughly documented, but also several potential problem areas were detected and corrected early enough in the test program to prevent serious loss of data. Additionally, the performance of each critical measurement system was assessed in terms of precision and accuracy. During future studies, QA could be improved by increasing the number of audit samples employed, providing more realistic 2,3,7,8-TCDD audit samples, and increasing the number of technical systems audits of field sampling operations. Nevertheless, despite the time and cost constraints inherent in the study, the QA program was efficient and cost-effective.

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TABLE 1. TIER 4 ACTIVITIES PERFORMED BY RADIAN CORPORATION AND THE TROIKA LABORATORIES

Activity	Procedure
RADIAN CORPORATION	
I. Stack Gas Sampling	
o Dioxins and Precursors	Modified Method 5 (MM5) Sampling Train
o HCl	HCl Train (Modified Method 5)
o CO, CO_2, O_2, NO_x, SO_2, THC	Continuous Emission Monitoring System
II. Ambient Air Sampling	
o Dioxins and Precursors	Ambient XAD Train
III. Collection of Process Samples and Data	
o Feed Materials and Supplementary Fuels	Grab Samples
o Ashes, Liquors, and Other By-Products	Grab Samples
o Process Data	Recorded by Hand From Control Room
IV. Soil Sampling	
o Dioxins and Precursors	Grab Samples
V. Analyses	
o Dioxin Precursors (i.e., Chlorophenols and Chlorobenzenes)	GC/MS
o HCl	Ion Chromatography
o Chlorine-in-Fuel Oil	Parr Bomb/Ion Chromatography
TROIKA LABORATORIES	
I. Analyses	
o Dioxins and Furans	HRGC/HRMS

TABLE 2. QUALITY ASSURANCE CRITERIA DERIVED FROM EPA'S QAMS-005/80 DOCUMENT

QA Category	Key Elements
I. Project Description	Project description Experimental design Intended use of acquired data Start and completion dates Appropriate diagrams, tables, and figures
II. Project Organization and Responsibility	Organization of project Line of authority Key individuals (including quality assurance official)
III. Quality Assurance Objectives for Measurement Data	Precision Accuracy Completeness Representativeness Comparability
IV. Sampling Procedures	Site selection Sampling procedures Description of containers for sample collection, preservation, transport, and storage Procedures to avoid sample contamination Sample preservation methods and holding times Procedures for recording sample history, sampling conditions, and analyses to be performed
V. Sample Custody Records	Preparation of reagents or supplies associated with sample Location and conditions where sample was taken Sample preservation methods Labeling Field tracking forms Field and laboratory sample custodians Laboratory custody log Laboratory handling, storage, and dispersement procedures

TABLE 2. QUALITY ASSURANCE CRITERIA DERIVED FROM EPA's QAMS-005/80 DOCUMENT (Continued)

QA Category	Key Elements
VI. Calibration Procedures	Description of, or reference to, calibration procedure Frequency of calibration Calibration standards, including sources and traceability procedures
VII. Analytical Procedures	Analytical procedure Appropriateness of method
VIII. Data Reduction, Validation, and Reporting	Data reduction scheme Equations to be used Validation procedures Identification/treatment of outliers
IX. Internal Quality Control Checks	Replicates, blanks Spiked and split samples Control charts, internal standards Zero and span gases, reagent checks Quality control samples Calibration standards and devices
X. Performance and Systems Audits	Schedule for audits Systems to be audited Sources of audit materials
XI. Procedures to Assess Data Precision, Accuracy, and Completeness	Central tendency and dispersion Measures of variability Significance tests, confidence limits Testing for outliers
XII. Preventive Maintenance	Schedule of maintenance tasks List of critical spare parts on hand
XIII. Corrective Action	Predetermined limits for data acceptability Procedures for corrective action Responsible individuals
XIV. Quality Assurance Reports to Management	Frequency of reporting Significant problems and recommended solutions

ALKALINITY TESTING OF HI-VOL FILTERS BY A NEW METHOD

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Hi-Vol filter alkalinity measurements are important in that the EPA has set upper limits on values for the filters because of an apparent correlation with artifact formation.

Reproducibility problems between the laboratories involved in making the measurements, using the method ASTM D 202[14], prompted a study into factors influencing observed alkalinity values.[13] On the basis of the results a new alkalinity testing procedure, which was simpler and more reproducible than ASTM D 202, was developed and was accepted by the EPA.

Introduction

High volume (Hi-Vol) air samplers are widely used by air pollution control agencies and industries to determine the concentration of total suspended particulate matter by collection on 8" x 10" Hi-Vol filters (typically composed of glass or quartz fibers).

Alkalinity measurement plays a useful role in the evaluation of Hi-Vol filter performance. It is signigicant in that alkaline sites on the filters have been shown to interact with acid gases such as SO_2, NO_x and HNO_3 forming artifact sulfate and nitrate on the filters.[1-12] Sulfates and nitrates of this type are indistinguishable from particulate sulfate and nitrate. In turn, the total weight of particulates, sulfate content and nitrate content determined would be falsely high. Alkalinity may not be the only factor involved in artifact formation on Hi-Vol filters,[11] but its measurement does provide relative guidelines for comparing filters of different lots and

materials as well as testing filters for compliance with EPA specifications.

Northrop Services began measuring the alkalinity of Hi-Vol filters for the EPA in order to assess and document the quality of filters being used nationwide. Investigation into the factors effecting observed alkalinity values was initiated as the result of reproducibility problems between the laboratories using the alkalinity testing procedure ASTM D 202.[14] ASTM D 202 was designed for measuring the total acidity or alkalinity of electrical insulating papers. A capsule summary of the procedure is as follows:

1. Extract a 1 gram sample in 100 ml of CO_2-free water, at 95-100°C, while pulping for 5 minutes using high speed agitation.
2. Vacuum filtration twice through a perforated porcelain disk, with the initial filtration forming a mat to remove all solids during the second filtration.
3. Titration of the hot extract to pH 7 either by pH meter or neutral red indicator.

The results of that study, presented previously,[13] led to the development of a simpler, more reproducible method to replace ASTM D 202. Also, the study served to help rationalize the differences observed between laboratories.

This report places emphasis on the NSI method itself, comparison of it with ASTM D 202, and verification of its precision and reproducibility.

Experimental

Filters: Whatman EPM 2000 glass and Whatman QMA quartz Hi-Vol filters were used for most tests. Samples weighed ~1 g with the exception of cases where sample size was deliberately varied.

Reagents: Certified NaOH and H_2SO_4 solutions were diluted quantitatively to make 0.005N NaOH and 0.0100N H_2SO_4 titrants, respectively. The pH meter was calibrated at pH 7 and 10 using color-coded pH buffer solutions.

Equipment: The original extraction apparatus consisted of a 250 ml Phillips Beaker, a mechanical stirrer with the stirrer shaft adapted with a single-holed stopper, and a boiling water bath. Extracts were filtered from the pulped filter through a Whatman 41 or 541 filter circle lining a heated 7 cm ID Buchner funnel. Extracts were titrated using an Amber Science Solution Analyzer No. 4503A with Broadley-James combination pH electrodes.

The final extraction apparatus consisted of a Phillips beaker resting directly on a stirring hot plate employing a 2" magnetic stirring bar. A glass, water-cooled, reflux condenser was fitted in the top of the Phillips beaker with a Meoprene or rubber stopper. Extracts were filtered and titrated as above with the exception that the funnel was not heated.

Results and Discussion

Portions of ASTM D 202, such as sample size and extraction volume, were retained in the NSI method. Other features were changed completely to reduce errors in observed alkalinity values and to improve reproducibility. Table I. provides a brief summary of the two methods.

The most dramatic difference between the two methods is extraction time. This modification was a direct result of extraction time studies carried out by NSI.[13] In the study numerous glass and quartz fiber filters were extracted at times ranging from 1 minute to 30 minutes. Extraction times both shorter and longer than 5 minutes shoed substantial differences, with quartz filters exhibiting a less pronounced effect. Table II summarizes the mean % differ-

ences for both filter types based on μeq/g. It is evident that at five minutes timing differences of a minute or more between analysts leads to measurable errors. Plots of alkalinity versus extraction time, Figure 1, were logarithmic. Examination of the change in alkalinity with time (i.e. slope), summarized in Table III, indicates that such errors can be greatly reduced at longer extraction times. At 15-30 minutes the change in alkalinity with time is small and timing differences become less significant.

For several reasons, high speed mechanical stirring with a hot water bath was replaced by lower speed magnetic stirring with a 2" stirring bar and direct heating on a hot plate/stirrer. To compare high speed and low speed stirring, a 1" long magnetic stirring bar was selected first. The net result for a set of glass filters was a difference in alkalinity of -9.6 ± 3.4% between extraction using magnetic stirring and high speed mechanical stirring. However, when a 2" stirring bar was substituted, the difference was -0.5 ± 4.0%. Thus, magnetic stirring simplified the alkalinity testing procedure without sacrificing agitation efficiency. An additional benefit of switching to magnetic stirring was the direct heating of the extraction vessel. Previously, extract temperatures were found to vary from 81 to 98°C at the end of the ASTM D 202 pulping and extraction period.[13] Such temperature, variations were attributed to differences in initial water temperature, poor heat transfer from the water bath to the extraction vessel and rapid evaporative cooling when room air was drawn into the extracting water by the high speed stirring. Direct heating of the extraction vessel is more efficient because the extracting water reboils within a few seconds after transfer into the vessel and boiling is maintained throughout the extraction period. A reflux condenser was added to prevent evaporation of water throughout the extraction.

The extraction volume was retained at 100 ml because the curve obtained from previous volume studies[13] had a slope predicting a negligible error at this and higher volumes. Also, inspection of the combined volume and time data showed that larger volumes increased the slope in the time dimension more than the reduction in the volume dimension.

Filter samples ranging in weight from 0.25 g to 1.50 g were extracted and the observed alkalinity values compared to the values obtained for 1.0 g samples of the same filters. Table IV summarizes the differences observed for both glass and quartz fiber filters. Normalized alkalinity, i.e. the alkalinity value determined for the test sample divided by the alkalinity value determined for the same filter at 1.00 g, was calculated in order to conveniently plot a large number of data points on a single graph and to convert the alkalinity data for glass and quartz filters into a form that allowed plotting of the data on the same set of axes (Figure 2). Both fitted curves were logarithmic. The equations obtained for the fitted curves were used to determine if small variations from 1.0 g caused significant variations in the observed alkalinity. In earlier routine analyses, sample weights had not varied by more than ±2%, which constituted an alkalinity variation of ±0.6% for both glass and quartz filters. In a worst case situation, where a ±10% variation in sample weight occured, the variation in alkalinity for glass filters was ±3.6% and for quartz filters ±3.0%. If filter samples are confined to a weight between 0.99 and 1.01 g, where the alkalinity variation is ±0.3%, errors resulting from sample size variations remain small. Thus, sample size was retained at ~1.0 g, but as a result of this evaluation, was restricted to a range of ±0.01 g. Cutting the filters into ½" x ½" squares provided small enough pieces to easily achieve these weight limits.

Recognizing that electrodes and pH meters are not universal, the contributions of three brands of electrodes and two pH meters to variations in alkalinity values were examined. Broadley-James combination electrodes were used for most pH measurements. For determination of reproducibility between

electrodes the Broadley-James electrode was compared with two other brands of combination electrodes. Comparison with a similarly priced Fisher Scientific combination electrode showed a difference of 0.3 ± 0.1% and comparison with a more expensive Corning X-EL combination electrode showed a difference of -1.9 ± 1.5%. Thus, differences between electrodes were relatively small. This is especially true for comparably priced electrodes. The Corning X-EL electrode does offer the advantage that a shorter stabilization time was required before taking a pH reading. Extracts from the same filters were analyzed using a Corning 125 pH meter and an Amber Science 4503A pH meter. The mean % difference found was 0.8 ± 1.4%. A difference of this magnitude was expected based on earlier pH meter calibration studies[13] where a difference of -0.8 ± 1.2% was observed for the alkalinities of filter extracts analyzed with the pH meter properly calibrated and with the meter purposely adjusted off by 0.5 pH units. Comparative laboratory studies[15] also confirmed that differences between pH meters was small.

In order to test the reproducibility of the NSI alkalinity testing procedure, interlaboratory and intralaboratory comparisons were made on a range of difference filters. Two analysts in the same laboratory analyzed the same set of filters with two completely difference sets of equipment and with both analysts using the same apparatus. Overall a mean difference between analysts of 1.0 ± 2.0% was observed. Also, no significant difference was observed between sets of equipment. The best previous intralaboratory comparison had been 3.0 ± 3.5%. Thus, for analysts in the same laboratory, reproducibility had been improved.

Collaborative alkalinity measurements[15] made on a series of Hi-Vol filters in the EPA Environmental Research Center (ERC) at Research Triangle Park, NC and in the State of California's Air and Industrial Hygiene Laboratory (AIHL) at Berkeley, CA provided the ultimate proof of the reproducibility and precision of the NSI alkalinity testing procedure. Previously, the AIHL had also been using a modified version of ASTM D 202 and attempts by NSI to reproduce their results had been unsuccessful. Table V compares the two methods. Six selected filters were analyzed once at Research Triangle Park and transported to California for repeated analysis. Six additional filters of various types were selected by the AIHL and analyzed four times at that laboratory by both procedures. To examine the reproducibility of the NSI method, the six filters analyzed in the AIHL by different analysts were compared and the six filters analyzed once in RTP and once in California were compared. Statistical analysis of the raw data, the % differences and the graphical representation in Figure 3 indicated no significant analyst bias for the AIHL ASTM method with 95% probability. A large degree of variability or imprecision observed with that method may have masked a small analyst bias. Analysis of data obtained with the NSI method indicates good reproducibility between analysts and laboratories. Combining statistical results gives a mean percent difference of 1.3 ± 2.5%, and Figure 4 has a correlation coefficient of 0.998 between analysts. For comparison of the new NSI and AIHL ASTM methods, the mean alkalinity values for 12 filters were plotted (Figure 5), and a linear relationship having a correlation coefficient of 0.985 was obtained. Exclusion of the very low alkalinity values did not improve the correlation. Alkalinity data obtained for a set of filters using NSI ASTM D 202 and the new NSI procedure was also plotted (Figure 6), and a linear relationship was derived which had a correlation coefficient of 0.936.

Conclusion

The new NSI alkalinity testing procedure[17] was recommended to and accepted by the U.S. Environmental Protection Agency to replace ASTM D 202. It is simpler, the equipment used more readily accessible, and the reproducibility of the method has been shown to be excellent between analysts in the same

laboratory and different laboratories. Also, the AIHL concluded that the NSI procedure can be substituted for their procedure without sacrificing previously obtained alkalinity-SO_2 retention correlations.[16] In addition the linear correlations obtained between the NSI method and the other procedures allows for relating previous data to current.

Acknowledgement

This work was supported by the U.S. Environmental Protection Agency under Contracts 68-02-4035 and CR806734. The contents do not necessarily reflect the views and policies of the EPA nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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TABLE I. Comparison of ASTM D 202 and NSI Alkalinity Testing Procedures

Parameter	Method	
	ASTM D202	NSI
Extraction vessel	250 ml wide mouth Erlenmeyer flask	250 ml Phillips beaker
Sample size	1g	1g ± 0.01 g
H_2O Extraction Volume, ml	100	100
Heating technique	Boiling water bath (sample temp, ca 95-100°C)	Hot plate, reflux condenser (sample temp. ca 100°C)
Extraction time, min	5.0	20.0
Mixer	Mechanical stirrer, high speed	Magnetic stirrer w/2" stir bar
Filtration procedure	Vacuum filtration twice through a Buchner funnel with or without filter paper	Vacuum filtration twice through a 7 cm ID unheated Buchner lined with Whatman 41 or 541 filter paper
Titration vessel	250 ml filter flask	250 ml filter flask
Endpoint	pH = 7.0 ± 0.1	pH = 7.00 ± 0.01
Endpoint determination	pH meter or neutral red indicator	pH meter

Table II. Alkalinity vs. Extraction Time at 100 ml

Extraction Time (minutes)	Mean % Difference from 5 min	
	Quartz	Glass
1.0	-10.4	-37.0
2.0	-4.3	-25.6
3.5	--	-8.2
6.5	--	5.5
10.0	2.1	15.3
15.0	14.6	39.3
20.0	16.4	38.4
30.0	16.3	74.3

Table III. Slope Change with Extraction Time

Extraction Time (minutes)	Slope (μeq/g)/min	
	Quartz	Glass
1.0	1.7	32.2
5.0	0.3	6.1
10.0	0.2	3.0
15.0	0.1	2.0
20.0	0.1	1.5
30.0	0.1	1.0

Table IV. Effect of Sample Size on Alkalinity

Sample Size (g)	Mean % Difference from 1.0 g	
	Quartz	Glass
0.25	-58.8	46.5
0.50	-13.3	20.5
1.00	0.0	0.0
1.50	-9.2	-11.5

Table V. General Description of AIHL and NSI Filter Alkalinity Procedures

Parameter	AIHL	NSI
Sample Container	250 mL Phillips Beaker	250 mL Phillips Beaker
H_2O Extraction Volume, mL	100	100
Heating Technique	Boiling water bath, no reflux condenser (sample temp. 80-87°C)	Hot plate*, relux condenser (sample temp. ca. 100°C)
Extraction Time, Min	5	20
Mixer	Polytron PCU-2-110 homogenizer at 70% full scale	Magnetic stirrer with 2" stirring bar
Filtration Equipment	9 cm I.D. steam-heated Buchner funnel, 500 mL filter flask	7 cm I.D. unheated Buchner funnel, 250 mL filter flask
Filtration Procedure	Twice through Whatman 41 or 541	Twice through Whatman 41 or 541
Titration Vessel	Original Phillips beaker after transfer of extract	250 mL filter flask (no transfer needed)
Titration Techniques	Potentiometric without temperature control or exclusion of atm. CO_2	Potentiometric without temperature control or exclusion of atm. CO_2
Endpoint	pH = 7.0 ± 0.2 after 1 min. equilibration (electrode stationary)	pH = 7.00 ± 0.01 after 5 min. equilibration (electrode stationary)

FIGURE 1

NORMALIZED ALKALINITY vs EXTRACTION TIME at 100ml

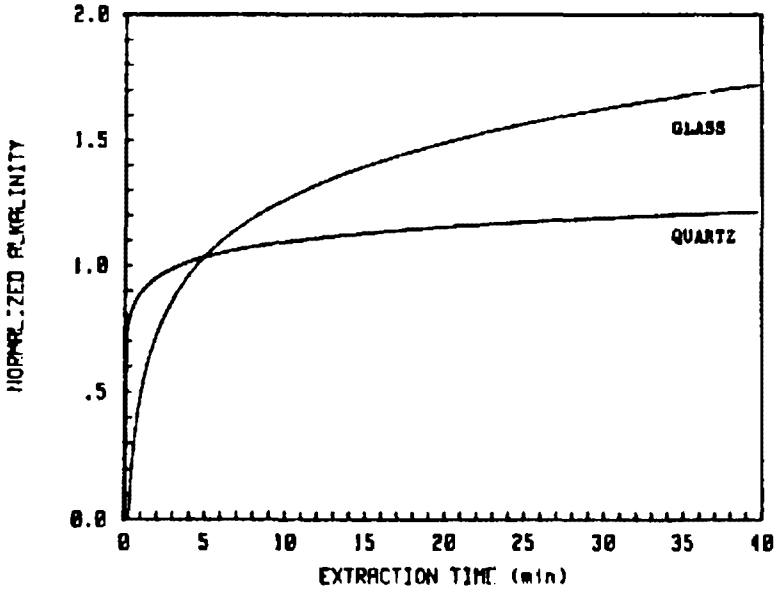


FIGURE 2

NORMALIZED ALKALINITY vs SAMPLE SIZE

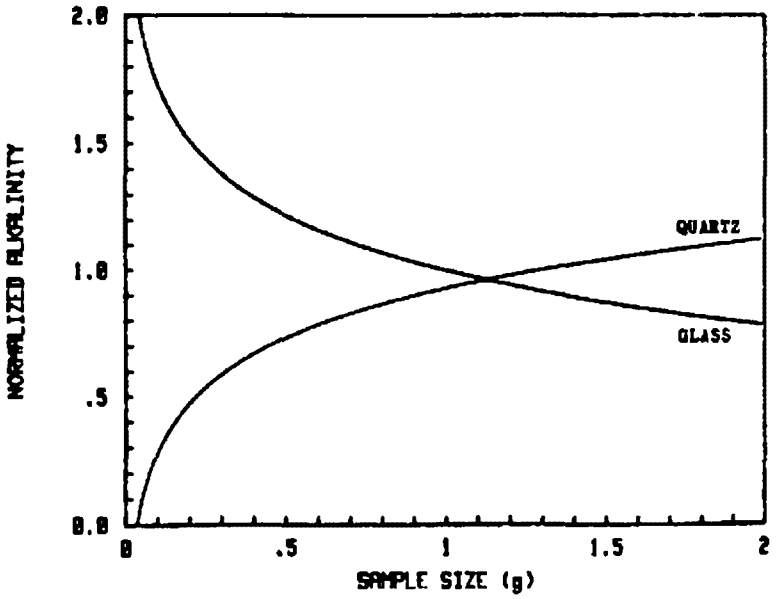


FIGURE 3

Analyst Bias With AIHL Method: Holland vs. Kothny

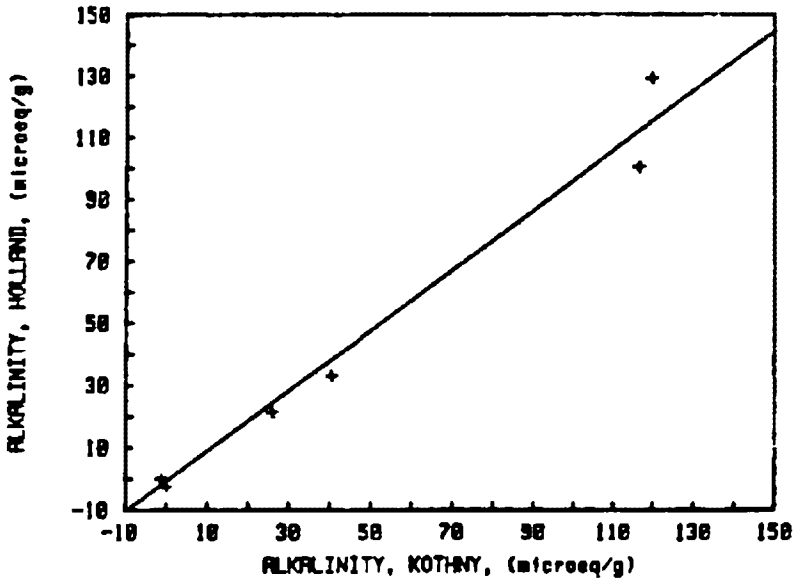


FIGURE 4

Analyst Bias with New Method

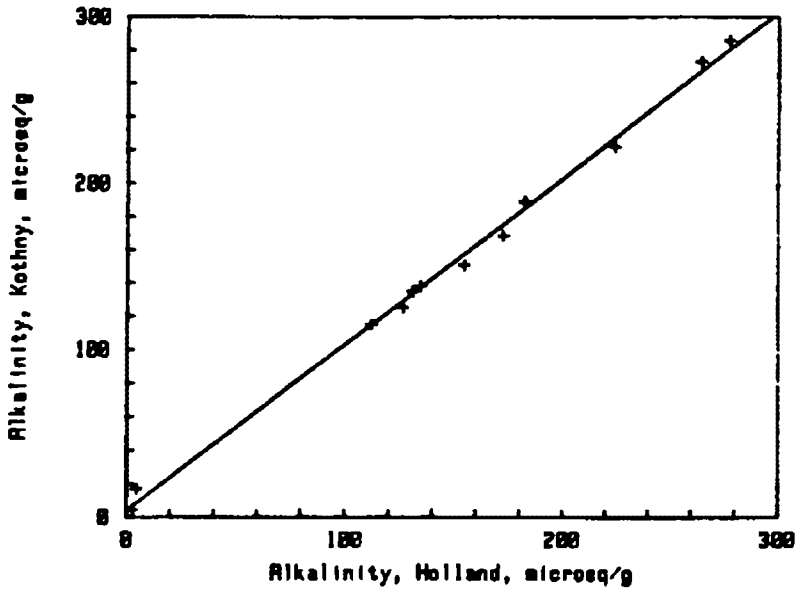


FIGURE 5

New Method vs. AIHL ASTM D202 Alkalinity

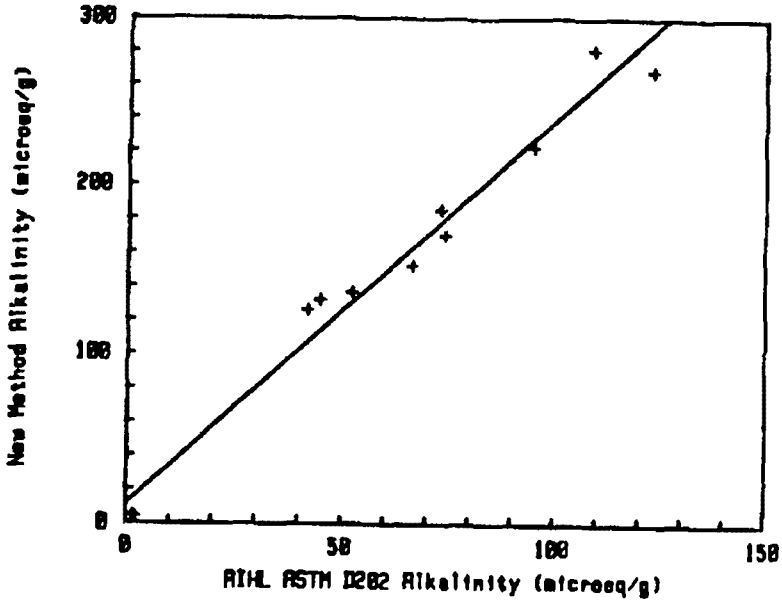
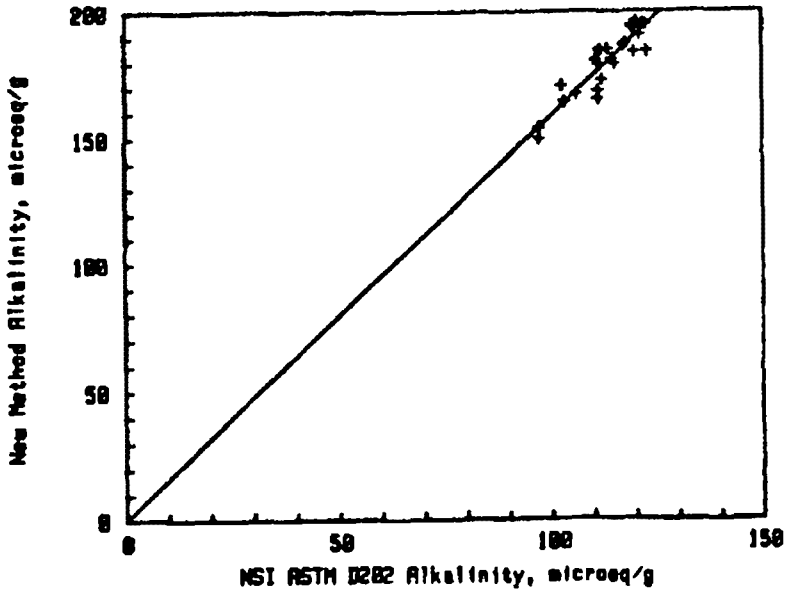


FIGURE 6

New Method vs. NSI ASTM D202 Alkalinity



PRECISION AND ACCURACY OF STATE AND LOCAL AGENCY AMBIENT AIR MONITORING DATA

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In accordance with federal regulations, state and local air pollution control agencies have been performing since January 1, 1981, special checks of their ambient air measurement systems to assess the precision and accuracy of the monitoring data. The measurement methods involved are those for total suspended particulate, nitrogen dioxide, sulfur dioxide, carbon monoxide, ozone, and lead.

The precisions of the measurement systems are estimated by some type of replicate measurement, including the use of collocated samplers. Accuracies of the measurement systems are estimated by measurement of, or comparison with, reference materials or devices. Because the variations of imprecision and inaccuracy tend to become proportional to pollution concentration levels with increasing concentrations, the assessments are expressed on a percentage basis.

State and local agencies submit their precision and accuracy assessments to the EPA. The EPA, in turn, produces annual reports summarizing and evaluating the data quality. Appreciable variation of data quality exists across the regions, states, and local agencies of the nation. Since 1981, some improvement in data quality has been evidenced. Whenever data users request monitoring data from the National Aerometric Data Bank, the users automatically receive precision and accuracy assessments of the corresponding air monitoring agencies. Planned revisions to the reporting procedure will require that the precision and accuracy assessments be identified to each individual monitoring site.

PRECISION AND ACCURACY OF STATE AND LOCAL AGENCY AMBIENT AIR MONITORING DATA

INTRODUCTION

While ambient air pollution measurements have been made for many years by state and local air pollution monitoring agencies, the establishment of the U.S. Environmental Protection Agency (EPA) in 1970 and the subsequent establishment of National Ambient Air Quality Standards has led to a considerable increase in the number of measurements made by the state and local agencies to monitor air quality. Measurements of the air pollutants for which standards exist (the so-called criteria pollutants) have been supplied to EPA's National Aerometric Data Bank (NADB) in Durham, NC. The EPA uses these data to track long-term trends in air quality, to measure the effectiveness of air pollution control activities, and to develop control strategies for the nation.

Although EPA had developed and issued a number of guidance documents recommending quality assurance practices, each state and local agency planned and implemented its own quality assurance programs. However, in 1979 the EPA issued regulations which required the quality assurance programs of the states to meet certain minimum requirements. The regulations also required that the states conduct or participate in two different audit programs to assess the quality of the routine monitoring data. The first was the performance of an internal-but-independent audit to assess the precision and accuracy of the measurement systems and to report the results to EPA. This program is called PARS, the Precision and Accuracy Reporting System.[1] The second was the participation by the states in an external EPA-conducted performance audit (PA) program.[2] A description of these two audit programs and a discussion of some of the results follow.

To provide a comparison of pollutant concentration levels used in the two audit programs with the concentrations specified in the National Ambient Air Quality Standards (NAAQS), the standards for the criteria pollutants currently are as follows:

Pollutant	Primary Standard, $\mu g/m^3$ (ppm)	
Total Suspended Particulate (TSP)		
Annual Average	75	
24-Hour Average	260	
Sulfur Dioxide (SO_2)		
Annual Average	80	(0.03)
24-Hour Average	365	(0.14)
Nitrogen Dioxide (NO_2)		
Annual Average	100	(0.05)
Carbon Monoxide (CO)		
8-Hour Average	10,000	(9)
1-Hour Average	40,000	(35)
Ozone (O_3)		
1-Hour Average	235	(0.12)
Lead (Pb)		
Quarterly Average	1.5	

METHOD: PARS

Federal regulations require that the states or subordinate districts within the states perform certain specified checks to assess the precision

and accuracy of their measurement systems. The precision checks are duplicate or repeated measurements made at ambient concentration levels. The concentration levels and frequencies of the checks are given in Tables I and II.

The accuracy checks are internal-but-independent accuracy audits made at specified concentration or flow levels. The audits of continuous analyzers are performed by challenging the analyzers with independently prepared calibration sources traceable to the National Bureau of Standards (NBS). The audits of the manual methods check the accuracy of only a portion of the total measurement method. For TSP, only the flow measurement portion is audited. For the SO_2 and NO_2 methods, only the analytical portion is audited. For Pb, the analytical portion is audited directly; however, the sampling is obtained by use of the TSP sampler, and thus assessments of both the flow and analytical portions of the method are available.

For the continuous methods and TSP, accuracy audits for each site must be performed at least once each year. Accuracy audits for the manual SO_2, NO_2, and Pb methods must be performed in the laboratory each analysis day.

The results of the precision and accuracy checks are expressed as percentage deviations of the observed values from expected or "known" values. Each state or subordinate district summarizes the results of its checks each calendar quarter and reports the results as 95 percent probability limits. The probability limits are calculated by the following expression.

$$\overline{D} \pm 1.96S$$

where $\overline{D}$ = the average of the percent differences

S = the standard deviation of the individual percent differences

1.96 = the standard deviate value corresponding to 95 percent probability, assuming a normal distribution

The standard deviation, S, of the percent differences is, in effect, the coefficient of variation for the measurement method at the concentration level involved. For precision, the standard deviation (or coefficient of variation) represents the within-instrument variability for the continuous and manual methods. For accuracy, the standard deviation (or coefficient of variation) represents the between-instrument variability (or biases) for continuous methods, and the within-laboratory variability of the particular portion of the manual method checked.

The audit results presented in this report are the average coefficients of variation of all the participating agencies in the nation.[3] Obviously, the results of about half of the agencies are better than the average and about half are worse.

Precision

The precisions of the various measurement methods, expressed as coefficients of variation, CV, (or relative standard deviation), for a recent year are listed below:

Manual Methods	CV, %	Continuous Methods	CV, %
SO_2	20.4	SO_2	5.9
NO_2	16.1	NO_2	6.6
TSP	6.4	O_3	4.8
Pb	7.9	CO	4.1

The variabilities of the manual methods are larger than for the continuous methods. However, these comparisons are not strictly valid because the precision checks for the continuous methods are made at the specified concentration levels (Table I) and the precisions of the manual methods are obtained from the results of collocated samplers (duplicate filter strips for Pb) at various ambient concentrations. Comparisons of greater validity could be made for the SO_2 and NO_2 methods if the results from the collocated samples were obtained at the same concentrations as those for the continuous methods. Nevertheless, the magnitude of the variabilities of the manual SO_2 and NO_2 methods are appreciable and provide justification to change to the continuous, but more expensive, methods.

Accuracy, Manual Methods

Figure 1 presents the accuracy results for the manual methods. The coefficient of variation for accuracy represents the variability of the accuracy audits across the monitoring agencies in the nation. As expected, the average of the CV's for all the agencies was very close to zero, and the variabilities of the accuracy audit results, expressed in percentage form, are larger at low concentration levels.

Components of Variability, Manual Methods

The manual methods are reasonably accurate; however, it is emphasized that only a portion of the total measurement system is being checked. The true accuracies of the manual methods cannot be any better than the precisions. Under the optimum but unrealistic assumption that the inaccuracies are the result of imprecision only, i.e., no average biases within agencies, it is interesting to compute the extent of variability that is unexplained by the accuracy audit results. Under the above assumption, the following relationship exists:

$$(CV)^2_{\substack{\text{precision,}\\ \text{total method}}} = (CV)^2_{\substack{\text{accuracy, (precision)}\\ \text{portion of method}}} + (CV)^2_{\substack{\text{unexplained}\\ \text{precision}}}$$

The following table presents the computed coefficients of variation unexplained by the accuracy audit results.

Manual Method	Total Method Precision CV, %	Portion of Method Accuracy (Level 1) CV, %	Variation Unexplained by Accuracy Audit CV, %
TSP	6.4	3.5 (flow)	5.4 (71% of Tot. Var.)
SO_2	20.4	5.5 (analytical)	19.6 (92% of Tot. Var.)
NO_2	16.1	3.8 (analytical)	15.6 (94% of Tot. Var.)
Pb	7.9	4.8 (analytical)	6.3 (64% of Tot. Var.)

The results for the TSP and NO_2 methods are presented in graph form in Figures 2 and 3. Similar charts could be drawn for the Pb and SO_2 methods. The sources of variability that contribute to the unexplained variability include the factors listed below.

Method	Possible Sources of Variability Unexplained by Accuracy Audit Results
TSP	Filter weighing, before and after exposure Filter conditioning for weighing, before and after exposure Loss of particulate or fibers from filter after pre-weighing Collection of particulate
SO_2, NO_2	Collection efficiency variation Loss of absorbing solution during sampling or in transport or handling prior to analysis Variation in flow rate measurement
Pb	Variation from strip-to-strip within a filter Loss of particulate in transport, handling, or cutting of strips Inaccurate cutting of filter strips

Because the manual SO_2 and NO_2 methods are being replaced by the continuous methods, it would not be worthwhile to investigate the source of variability for these methods. However, for the TSP and Pb methods, studies should be performed to determine the contributions of the various sources of variation, with the goal of reducing the total variability.

Because the Pb method involves the sampling method of the TSP method and a chemical analysis for Pb of the particulate collected, it is possible, as well as interesting to combine the estimates of variability. First, combining the accuracy audit results for the TSP flow audit (CV = 3.5%) and the accuracy audit results for the Pb analysis (CV = 4.8%) gives a resulting "total" coefficient of variability of 5.9% (Figure 4), in accordance with the following equation:

$$(CV)^2_{flow} + (CV)^2_{analysis} = (CV)^2_{combined}$$

$$(3.5)^2 + (4.8)^2 = (5.9)^2$$

However, it is noted that the 5.9% value is less than either of the coefficients of variation for precision of the Pb analysis (CV = 7.9%) or that of the TSP method (CV = 6.4%)! If it could be assumed that weighing portion of the TSP method is very small (i.e., negligible), then the CV for the TSP precision includes the error variations of flow rate, the variation in collection of Pb particulate from sampler to sampler, and possible loss of particulate from the filters in handling, all of which affect the Pb concentration. It is then considered appropriate to combine the two CV's to estimate the total imprecision of the Pb method. These variations are represented in Figure 5 and expressed by the following equation.

$$(CV)^2_{sampling} + (CV)^2_{analysis} = (CV)^2_{combined}$$

$$(6.4)^2 + (7.9)^2 = (10.2)^2$$

The CV of 10.2% for imprecision is nearly twice the CV of 5.9 for accuracy!! This can be explained by the following three factors:

1. the precision estimate for sampling is based on differences between real samples collected over a 24-hour period, whereas the accuracy estimate is based on an audit check of the flow measurement made only at a point in time,

2. the precision estimate for the chemical analysis is based on differences between duplicate strips from real particulate filter samples, whereas the accuracy estimate is based only on an analysis of an unexposed filter strip to which a synthetically prepared solution containing Pb has been added, and

3. the accuracy audits for both flow and chemical analysis may have been performed with more-than-routine care, whereas the routine flow measurements and particulate determinations for the collocated TSP samplers and the routine analysis of the duplicate filter strips were given only routine care.

In light of the three factors described above, the combined CV for Pb (10.2%) is probably a more realistic estimate than the 5.9%.

Accuracy, Continuous Methods

Figure 6 presents the results of the accuracy audits for the continuous methods. The results in terms of the coefficient of variability are plotted at the accuracy audit levels 1, 2, and 3. Note that the variabilities are higher at the lower concentrations, the same as for the manual methods, and that the variabilities tend to become constant at the higher levels.

Also shown in Figure 6 for comparison purposes are the precision results located at their approximate relative concentration level. Note that for CO, SO_2 and O_3 the values for precision fall closely in line with the curves for the accuracy results, indicating that practically all of the variability in accuracy is the result of imprecision. In other words, any errors of the calibration process are very small. Such is not the case, however, for the NO_2 method. As indicated on Figure 6, the expected variation of accuracy at the concentration level of the precision check is about 8.2%, compared to 6.6% for the precision variability.

Components of Variability, Continuous Methods

The following appropriate relationship for the NO_2 method gives an estimate of unexplained variability.

$$(CV)^2_{accuracy} = (CV)^2_{precision} + (CV)^2_{unexplained}$$

$$(8.2)^2 = (6.6)^2 + (CV)^2_{unexplained}$$

$$(CV)^2_{unexplained} = 23.7$$

$$CV_{unexplained} = 4.9$$

Thus, an unexplained variability of 4.9% may possibly be explained by variability in the calibration process. The calibration process for continuous NO_2 instruments is more complicated than for the CO, SO_2, and O_3 methods. It may be worthwhile to investigate the NO_2 calibration process to determine more precisely the cause of the additional variability. Appropriate modification of the calibration process may reduce some of the variability.

METHOD: PA

In 1972, the EPA's Environmental Monitoring Systems Laboratory (EMSL), located in Research Triangle Park, NC began a national performance audit program whereby blind samples are distributed to state and local air monitoring agencies and other interested participants for analysis. Performance audits for various pollutant measurement methods were commenced in the years indicated below.

Year	Pollutant Measurement Method
1972	Manual SO_2 (analytical portion)
	CO
1974	Manual NO_2 (analytical portion)
1975	NO_3^- and $SO_4^=$ in particulate (analytical portion)
1976	TSP (flow measurement portion)
1977	Pb in particulate (analytical portion)
1981	Continuous SO_2

As indicated, only the analytical portions of the Pb, NO_3^-, $SO_4^=$, manual SO_2, and manual NO_2 methods are audited. Only the flow measurement portion of the TSP method is audited. Audits for the continuous NO_2 and O_3 methods and for trace elements in particulate are planned for future implementation.

The audit materials for the manual SO_2 and NO_2 methods are freeze-dried materials of synthetically prepared solutions. The audit materials for the Pb, $SO_4^=$, and NO_3^- methods are unexposed filter strips containing known amounts of the particular chemicals. The audit devices for the flow measurement of the TSP method consist of a series of test plates containing various numbers of holes. Each plate has been calibrated against NBS-traceable flow standards.

The analyses for the audits for the manual SO_2 and NO_2 methods, and the Pb, NO_3^- and $SO_4^=$ methods are conducted at the state or local agency chemical laboratories since only the analytical portion of the methods is involved. However, the audits for the continuous methods are conducted at individual air monitoring sites.

Sample materials or devices are furnished at multiple levels (from three to six) to cover the range of values normally encountered in ambient monitoring. The materials or devices are characterized extensively by comparison with NBS or NBS-traceable standards to ensure that the "known" values have very small associated uncertainties.

The participating agencies report their results to EMSL for evaluation and analysis. The known, or true, values are then transmitted by EMSL to the agencies for their self-evaluation and for corrective action, if indicated by excessive deviations of their results from the known values.

EMSL analyzes and summarizes the results from all the participants and issues annual reports.[4] A part of the analysis consists of identifying

any outlier results, i.e., results that are grossly in error. Such results are eliminated to avoid an excessive effect upon the general pattern of results. The averages of all the participants' results are, in general, very close to the EPA known values. However, there is some appreciable variability among the reported agency results. The results of 1983 audits are presented in Figures 7 and 8.

RESULTS: PA

Manual Methods

Figure 7 presents the results of the performance audits for the manual methods. The results of the flow measurement audits for the TSP method are shown only at one level corresponding to the nominal flow rate of 50 cfm. The ranges of the concentration levels used in the other audits were:

	Minimum	Maximum
SO_2	48 $\mu g/m^3$	178 $\mu g/m^3$
NO_2	0.4 $\mu g/m^3$	0.9 $\mu g/m^3$
Pb	0.6 $\mu g/m^3$	7.5 $\mu g/m^3$
$SO_4^=$	1.2 $\mu g/m^3$	24 $\mu g/m^3$
NO_3^-	0.8 $\mu g/m^3$	14 $\mu g/m^3$

The general pattern of variabilities is similar to those previously shown -- higher CV's at low concentration levels with the CV's becoming nearly constant at high concentration levels.

The results for Pb analyses seem to be discontinuous between levels 3 and 4. A possible explanation is that at higher concentrations, the levels exceed the capacity of the instrument readout or the linear response region of the calibration curve, thereby requiring a dilution of the sample prior to analysis. This additional step in the analytical process increases the variability of the results.

Continuous Methods

Figure 8 presents the results for the continuous methods, CO and SO_2. Note that CO is audited at only three levels, whereas SO_2 is audited at five. The ranges of the concentrations were as follows:

	Minimum	Maximum
CO	6 ppm	44 ppm
SO_2	0.04 ppm	0.9 ppm

For the CO audits, three separate cylinders are used, each containing a different concentration. The gas from only one cylinder is used for each analysis. For the SO_2 audits, a zero gas and five concentration levels are employed through the use of a zero gas and one SO_2 cylinder equipped with three separate take-offs. The zero gas and each of the three take-offs are valved with a restricting orifice. The valves from the gas cylinder are numbered 1, 2, and 3 with valve 1 permitting the highest flow and valve 3, the least flow. The various concentrations are achieved as indicated below.

Approximate concentration level	Concentration level	Number of valve(s) open: Analyzers with 0-.5 ppm range	Number of valve(s) open: Analyzers with 0-1.0 ppm range
.75	5	---	1,2,3
.52	4	1	1
.27	3	2,3	2,3
.21	2	2	2
.07	1	3	3
zero		all three valves closed	all three valves closed

The flow rate for each restrictive orifice is individually calibrated with the corresponding valve in the open position.

The variability for CO decreases almost linearly, although previous audits revealed a pattern more similar to those of Figures 1, 6, and 7. The variability of the SO_2 audits are more nearly constant across audit levels. Note that the smooth curve through the points for levels 1, 2, and 4 give the expected pattern. The point for level 3 is somewhat above the line. The point for level 5 is farther from the line. These added variabilities are explained by the fact that for levels 1, 2, and 4, only one gas cylinder valve is open; for level 3, two valves are open; and for level 5, three valves are open. These added variabilities result from the variations in the calibrations of the flow rates for the additional restrictive orifices involved.

CONCLUSIONS

The precision and accuracy assessments of the internal-but-independent checks performed by the state and local agencies, and the results of the external audit results of the EPA performance audit program both provide valuable information concerning the quality of ambient air monitoring data collected by state and local agencies. The results of both programs show that the coefficients of variation (relative standard deviations) for all the pollutant measurement methods are higher at low concentrations and become more constant at higher concentrations.[5] Both programs reveal that the manual methods for NO_2 and SO_2 exhibit more variability (i.e., less precision and accuracy) than the corresponding continuous methods.

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TABLE I. REQUIREMENTS FOR PERFORMING PRECISION CHECKS

Parameter	Precision check level	Frequency
CO (continuous analyzer)	8 - 10 ppm	Once every 2 weeks
SO_2, NO_2, and O_3 (continuous analyzer)	0.08 - 0.10 ppm	Once every 2 weeks
TSP, SO_2, and NO_2 (manual)	Collocated samplers (Ambient concentration)	Once every 6 days
Pb	Duplicate filter strips (Ambient concentration)	Once every 6 days

TABLE II. CONCENTRATION LEVELS FOR CONDUCTING ACCURACY AUDITS

Parameter	Level 1	Level 2	Level 3	Level 4
SO_2, NO_2, O_3 (continuous)	0.03-0.08 ppm	0.15-0.20 ppm	0.35-0.45 ppm	0.80-0.90 ppm
CO	3-8 ppm	15-20 ppm	35-45 ppm	80-90 ppm
TSP (flow only)		1.13-1.70 m^3/min		
SO_2 (manual)*	0.013-0.020 ppm	0.033-0.040 ppm	0.053-0.059 ppm	
NO_2 (manual)*	0.018-0.028 ppm	0.046-0.055 ppm	0.074-0.083 ppm	
Pb**	0.6-1.8 $\mu g/m^3$	3.5-5.9 $\mu g/m^3$		

*Concentration levels corresponding to flow rates of .2 L/min
**Concentration levels corresponding to flow rates of 50 cfm.

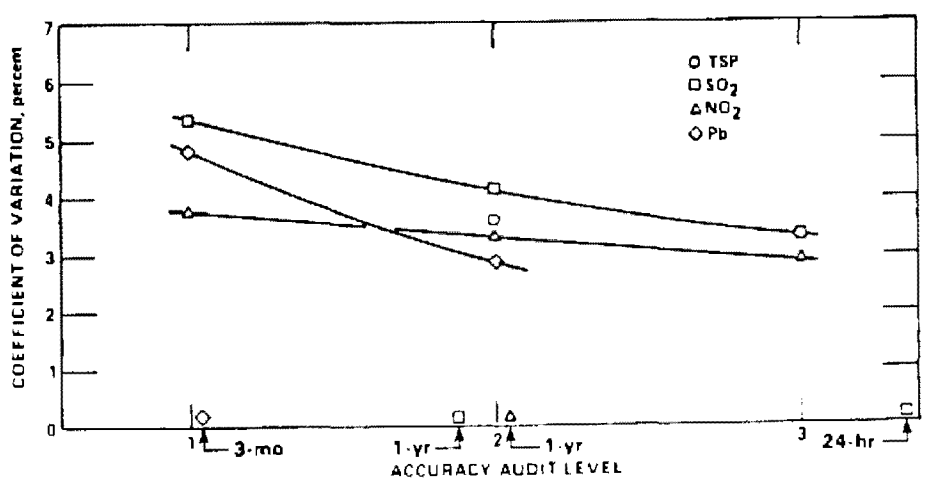

Figure 1. Accuracy audit results for manual methods for PARS.

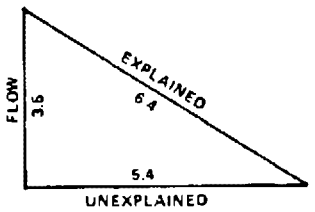

Figure 2. Components of variation for the TSP method.

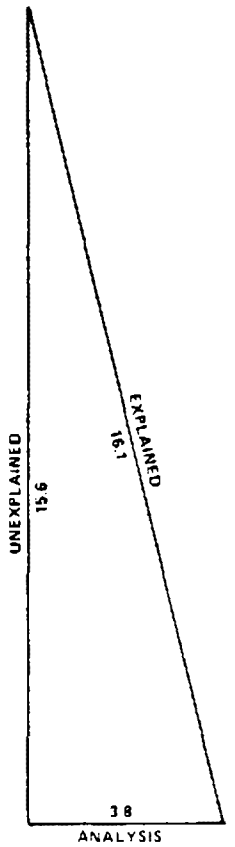

Figure 3. Components of variation for the manual NO_2 method.

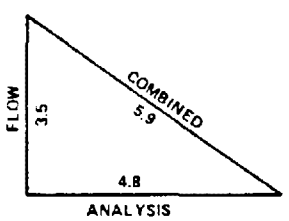

Figure 4. Components of variation for the accuracy of the Pb method.

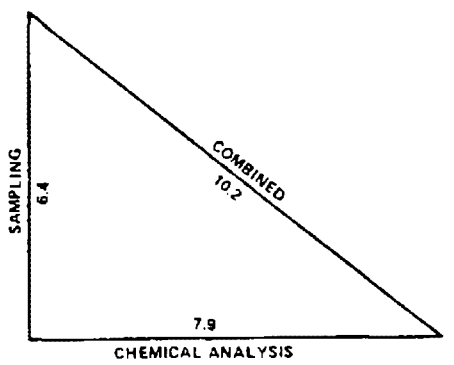

Figure 5. Components of variation for the precision of the Pb method.

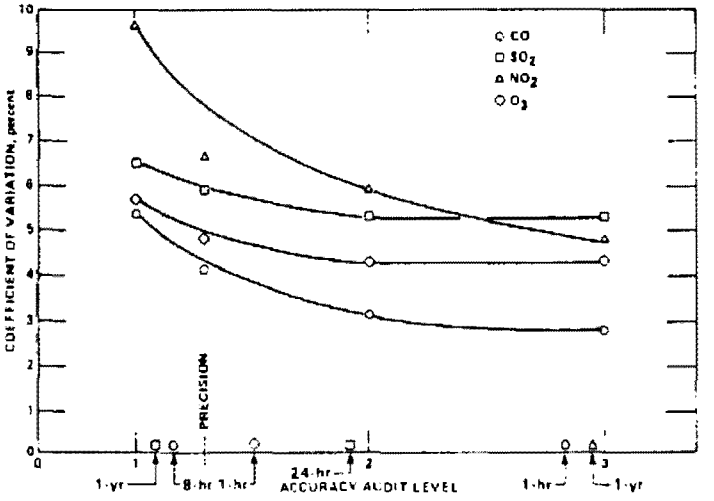

Figure 6. Accuracy audit (and precision) results for continuous methods for PARS.

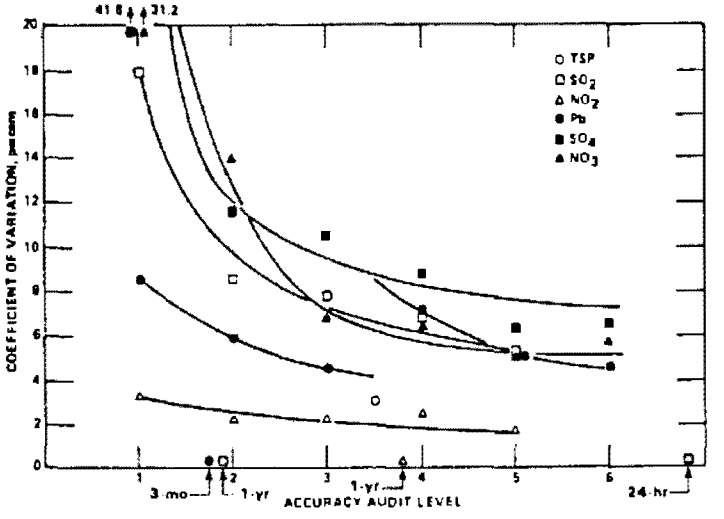

Figure 7. Performance audit results for manual methods for 1983.

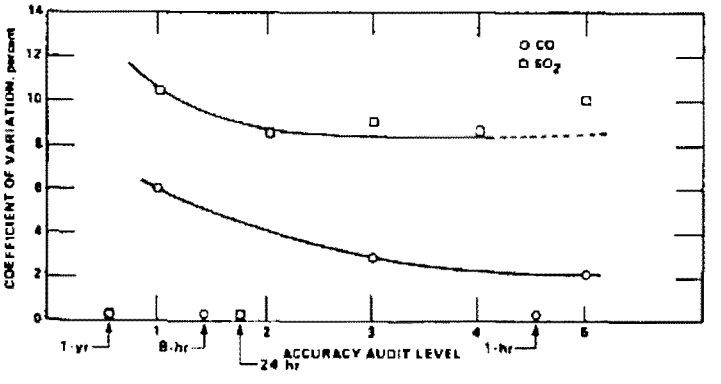

Figure 8. Performance audit results for continuous methods for 1983.

SOME NEW COST-EFFECTIVE APPROACHES FOR MEASURING ORGANICS ASSOCIATED WITH HAZARDOUS WASTES*

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A number of newer and often highly sensitive analytical techniques and field monitoring devices are described that have potential suitability for monitoring organic hazardous wastes. The focus is on devices and methods that are cost-effective and permit either direct measurements in the field or screening-type measurements on samples returned to the laboratory for analysis. Most of these methods are directed at categories of less volatile organic compounds. The results of some very preliminary field tests are given. Most promising were the results obtained for a wide variety of ground and surface waters screened spectroscopically using synchronous fluorescence.

*Research sponsored by the Division of Remedial Actions Projects, U.S. Department of Energy, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

Introduction

Land disposal facilities are subject to compliance with the 1981 Resource Conservation and Recovery Act (RCRA) groundwater monitoring requirements. The procedures for compliance are expensive. They typically involve general hydrological investigation and drilling of monitoring wells to obtain samples of groundwater. Chemical analysis using gas chromatography-mass spectroscopy (GCMS), which EPA favors for priority pollutants, costs about $1000 per set of analyses[1].

Methods for improving the cost-effectiveness of detecting contaminant plumes and screening groundwater for the presence of priority organic pollutants have an obvious attractiveness. Considerable activity has been reported recently for improving the detection and analytical capabilities for underground organic pollutants. A few noteworthy examples will be given below.

A fiber optic probe carrying UV light can be lowered down a test well[2]. Fluorescence is excited directly in the water from organics such as benzene and other aromatic compounds. This quick and relatively inexpensive, but non-compound selective, test procedure is claimed to be useful for determining whether more expensive laboratory tests are needed. Specific and sensitive analysis of volatile organics chlorides in groundwater has been accomplished by attachment of an optrode to the distal end of the fiber[3]. Part-per-million concentrations of volatile organic chlorides have been quantified in aqueous media.

A rather simple GC screening technique has been developed by EPA for analyzing volatile organic compounds (VOC) in collected samples of groundwater[4]. The technique involves partioning of VOC between water and air inside a small sample vial. A headspace sample of equilibrated air is withdrawn by a syringe inserted through a septum. The VOC are analyzed with a portable gas chromatograph equipped with a photoionization detector. This headspace technique for GC screening and quantification is complementary to the more accurate and informative EPA Method 624 that employs CGMS. It becomes especially cost-effective in situations where the accuracy and precision of the Method 624 is not required.

Other field devices have been developed for the collection and analysis of VOC in soil gases. One such technique measures emission rates from land surfaces using a hemispherical emission flux chamber placed at ground level[5]. The gaseous emissions are swept through an exit port. The VOC concentrations are monitored in real time with a portable total hydrocarbon analyzer or else discrete air samples are analyzed by GC for specific VOC.

Rods driven into the ground are used to sample soil gases at different depths up to 15 feet[6]. Soil air is withdrawn through the rod and subsequently analyzed for VOC, usually with a GC. For sampling at shallow depths, a device composed of a passive charcoal sorbent inside a test tube is buried below the surface and left for an extended period of time, usually 1 day[7]. After retrieval, the VOC are desorbed thermally and analyzed by GCMS. A plot of land can be contoured relatively inexpensively for VOC by laying out a grid of these devices all at the same time.

This presentation focuses on some alternative methods that have attractive potential for measuring organic compounds in soil, soil gas, and groundwater. The methods are described briefly and results from a preliminary field investigation are given.

Field Monitoring Devices

These are monitoring devices that can be operated in the field. Either they can provide real- or near real-time measurements of hazardous waste pollutants or else they are devices that sorb chemical pollutants for subsequent analysis.

Fluorescence Monitors

Two hand-carried devices have been developed at ORNL for measuring fluorescent contamination in the field.

Spill Spotter. A beam of UV light is shone through a telephoto lens at the object of interest[8]. The UV light is modulated at 1 KHz. Any returning fluorescence, at a frequency of 1 KHz, is demodulated and filtered. The signal output is used to drive an audio oscillator, the pitch of whose noise increases with increase in the fluorescence intensity. The recorded fluorescence intensity is distance independent over distances ranging from 0 cm to 80 cm when the illumination beam is focused 40 cm from the spotter. An accompanying battery pack is used for field work. Readings can be taken even in direct sunlight.

The spill spotter readings can be converted to benzo[a]pyrene (BaP) fluorescence equivalent units by reference to fluorescence from a standard of BaP embedded in a block of epoxy. Because fluorescence is often strongly quenched in real-life situations, the spill spotter is best suited to providing yes or no answers about the presence of fluorescing contamination. Two such applications are delineating the boundaries of surface contamination or measuring skin contamination on workers handling process oils at a coal-liquefaction plant[9].

Lightpipe Luminoscope. Fiberoptics direct ultraviolet light to a stethoscopic cap pressed against the surface of interest[10]. Induced fluorescence is returned along the bifurcated lightguide, processed and recorded either as an audio signal or meter reading. The principal intended use was measurement of skin contamination but, in principal, any solid surface can be examined. Liquid samples can also be spotted on filter paper and examined for fluorescing content with the luminoscope. If need be, this operation can be conducted in the field. Tar and oil can be detected typically at concentrations as low as 10 ng/cm^2 on filter paper. Above about 300 ng/cm^2, quenching effects reduce the intensity of the fluorescence and produce non-linearity of response. The lightpipe luminoscope is also being adapted as a small remote sensor for fluorescing contaminants in groundwater.

Derivative Ultraviolet Absorption Spectrometer (DUVAS)

This small (liftable) microprocessor-controlled spectrometer can be operated either with a gas cell for air monitoring[11] or a small quartz cell for measuring liquid samples. Within complex mixtures of compounds it is possible to selectively analyze specific compounds that have narrow absorption bands. This is possible because in the second-derivative mode, where one is measuring band curvature, the spectrometer response to narrow bands is enhanced while response to broad bands is reduced.

A functional prototype device produces a second-derivative signal by use of numerical methods in an integral microcomputer. Compared to an instrument based on wavelength modulation with detection of the second harmonic of the modulated frequency, an instrument using numerical derivatization considerably simplifies the optics, reduces the size, and improves the reliability of a portable DUVAS.

The DUVAS is suitable for measuring phenol and methyl-substituted phenols in water of variable turbidity[12]. A small flow-through cell and a small peristaltic pump can be employed if continuous monitoring of a water source is needed. Phenol can be measured directly at concentrations of 1 ppm and above. Sensitivity can be improved by extraction and concentration of the phenol in a solvent phase. But then one looses the direct capability for easy on-site measurements.

Passive Gas Sorption Monitors

Surface Emission Rate Monitor for Volatile Organic Compounds. This device is composed of a circular canister with one open face[13]. It is placed open face down on the ground during sampling. The sorbent of granular charcoal rests on a mesh screen. The amount of charcoal is sufficient to sorb all the volatile organic compounds that are emitted from the ground area enclosed by the container.

After the period of time for sampling is completed, the charcoal is removed, sealed in a small container, and returned to the laboratory. Analysis is conducted by solvent extraction of volatile organic compounds with carbon disulphide and gas chromatography with flame ionization and electron capture detectors.

Filter Paper Sorption Monitors. This simple device consists of a small disk of filter paper that is placed within a small holder. The filter paper is the vapor sorption element. During the period of time of sampling, the device is exposed to soil gases either underground or else within an open-ended small container set at ground level.

After exposure in the field, the device is returned to the laboratory inside a sealed container.

Analysis is conducted by the room-temperature-phosphorescence technique[14]. The filter paper is pretreated with a solution containing a heavy-atom salt that facilitate emission of phosphorescence at room temperature[15]. The reader is a standard spectrofluorimeter with a

phosphorescopic attachment. Only luminescing compounds are detected. These are usually in the class of compounds known as polynuclear aromatic hydrocarbons. These are compounds of intermediate or low volatility that can be detected in sub-ng amounts on the filter paper. It is anticipated in the future that some weakly or non-luminescing molecules will become amenable to sorption on silver or gold coated substrates and analysis by surface-enhanced Raman scattering[16]. The technique makes detection of several pesticides and herbicides a possibility. Detection of vapors of the insecticide Parathion is an example.

Laboratory Analysis of Water Samples

Synchronous Fluorescence (SF)

To use this technique, the excitation and emission monochromators of a fluorescence spectrometer are locked together at a fixed wavelength separation such that a spectrum can be scanned synchronously[17,18]. Samples of water, or other solvents that are UV transparent, are loaded into a small cuvette for the analyses of fluorescing analytes. The principal advantage of recording a fluorescence spectrum synchronously is that compound or groups selectivity is enhanced by spectral simplification. Considerable success has been achieved, especially in the ranking of a series of related environmental samples containing complex mixtures of aromatic compounds[19,20].

Room-Temperature Phosphorescence (RTP)

Often this technique is employed in conjunction with SF measurements since it provides information about luminescing constituents that is often complementary[20]. A few µL of water are spotted on filter paper pretreated with the salt of a heavy atom, such as lead acetate. The heavy atom serves to promote the conversion of singlet to triplet excited states from which phosphorescence can occur[15]. The small disk of filter paper is first dried and then inserted into a fluorescence spectrometer equipped with a phosphorescopic attachment. As with SF, RTP has already enjoyed successes in the ranking of a series of environmentally related samples[15,20].

Results and Discussion

A pilot study was initiated recently on the DOE reservation in Oak Ridge at a number of disposal sites for hazardous waste. Oils and degreasing solvents used in machine shop operations were the principal sources of contamination.

Surface Measurements

At an oil landfarm disposal area, luminescing constituents were sought with the spill spotter and RTP passive monitors. The spill spotter detected weak fluorescence in oily surface dirt. The fluorescence intensity was, however, weak and equivalent to only 0.3 ppm BaP. It is conceivable that the fluorescence was weak because of quenching caused by an overabundance of aromatic compounds. This possibility can be checked by adding a solvent to

the dirt to dilute the aromatic compounds and increase their ability to fluoresce strongly. Treatment of the dirt with solvent did not, however, increase the fluorescence induced by the spill spotter. The oily dirt must have been contaminated largely with non-fluorescing organic compounds. Neither did RTP filter paper monitors left at the site pick up measurable amounts of phosphorescing organic vapors. These devices were left overnight inside open-ended canisters placed upside down on the ground. This finding again points to low concentrations of high-boiling aromatics in the oily dirt.

The passive surface emission monitor for detecting volatile organics was left overnight on the ground at a number of different locations. At the oil landfarm area, several organics with a wide range of volatilities were detected. Analyses of water from wells drilled in this region have also shown VOC to be present in rather low concentrations. On the other hand, at a surface location downhill from an old solvent disposal area, a large number of VOC were detected in abundance including VOC identified tentatively as carbon tetrachloride, trichloroethylene, and tetrachloroethylene. Trichloroethylene and tetrachloroethylene were measured by GCMS in the well water at this location at concentrations of about 2 ppm and 17 ppm, respectively. These chlorinated hydrocarbons are resistant to biodegradation. A different admixture of VOC were measured on the banks of a oil retention pond. About 20 compounds with a wide range of volatilities were detected.

These minor successes open up the possibility of being able to use these passive monitors to measure rates of emission of VOC at ground level. Large numbers of these monitors could be dispersed at a site to provide contour maps of emission intensity and to enable estimates to be made of total release of VOC into the atmosphere.

Water Measurements

Samples of different well water and some surface waters were examined by the two techniques of derivative ultraviolet absorption spectroscopy and synchronous fluorescence.

Water from one well (designated GW15) located close to the inactive solvent disposal area was known to contain benzene at a concentration of about 100 ppm. Additionally this well water contained a host of other VOC at lower concentrations. The direct measurement in this well water of the UV-absorbing benzene was made using the DUVAS without any sample preparation or solvent extraction. The benzene concentration in the well water was 80 ppm. The ease with which the analysis was accomplished suggests that the DUVAS would be ideal for monitoring temporal fluctuations in benzene concentration at this particular location. Laboratory tests using cyclohexane to extract benzene from the aqueous phase point to a lower limit of detection of 0.1 ppm.

The results of synchronous fluorescence analysis of 1 ml samples of water were most encouraging. Fluorescence was detected synchronously in virtually all of the water samples that were collected from a wide variety of well and surface locations. These SF spectra are shown in Figures 1 and 2. The surface waters give mainly weakly structure a SF emission. The well waters on the hand produce SF emission with sufficient structure to indicate that specific compounds or groups of compounds should be identifiable and

quantifiable. Whether or not peak resolution happens to be possible, the water samples can be ranked according to their integrated SF. The ranking of this group of water samples according to integrated SF is listed in Table I. This ranking is made on the basis of arbitrary units of total fluorescence intensity. Alternately, by reference to a standard mixture of polynuclear aromatic (PNA) hydrocarbons of known concentrations, it would be possible to quantify the fluorescence of a particular sample in units of PNA equivalent concentration (ng/ml). The limit of detection for a fluorescent compound such as anthracene is about 0.1 ng/ml (0.1 ppb).

There is every reason to believe that SF screening of water samples will become a useful technique for quickly evaluating the overall quantity and nature of fluorescing constituents.

Summary

A number of new field monitoring devices and analytical screening techniques are described that have the potential for measuring and screening organic hazardous wastes in soil, soil gas, and water. The majority of these approaches are directed at the detection of categories of less volatile organic compounds, such as higher-boiling aromatics. These techniques will serve to complement a number of screening methods for VOC that have been developed by others. Some very preliminary field tests have been conducted using some of these new devises and analytical methods. The most promising method to date was SF screening as it was applied to a number of ground and surface waters.

Acknowledgements

Several other individuals played significant roles in the collection of field samples, conduct of laboratory analyses, and data treatment. In this regard, the efforts of G. H. Miller, D. L. Wilson, A. R. Hawthorne, and J. E. Mrochek are recognized and appreciated. The help of G. E. Kamp was invaluable in the organization of the field studies.

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TABLE I. INTEGRATED SYNCHRONOUS FLUORESCENCE INTENSITY FOR SAMPLES OF SURFACE AND WELL WATER NORMALIZED TO THE SYNCHRONOUS FLUORESCENCE INTENSITY OBTAINED FOR DRINKING WATER

Water sample	Integrated synchronous fluorescence normalized to drinking water	Ranking of samples according to fluorescing content
GW23	4.8	1
GW14	3.2	2
Puddle by Retention Pond No. 1	2.8	3
S-3 Pond	2.5	4
GW8	2.2	5
Retention Pond No. 1	2.2	6
GW15	1.9	7
Retention Pond No. 1 Run Off	1.6	8

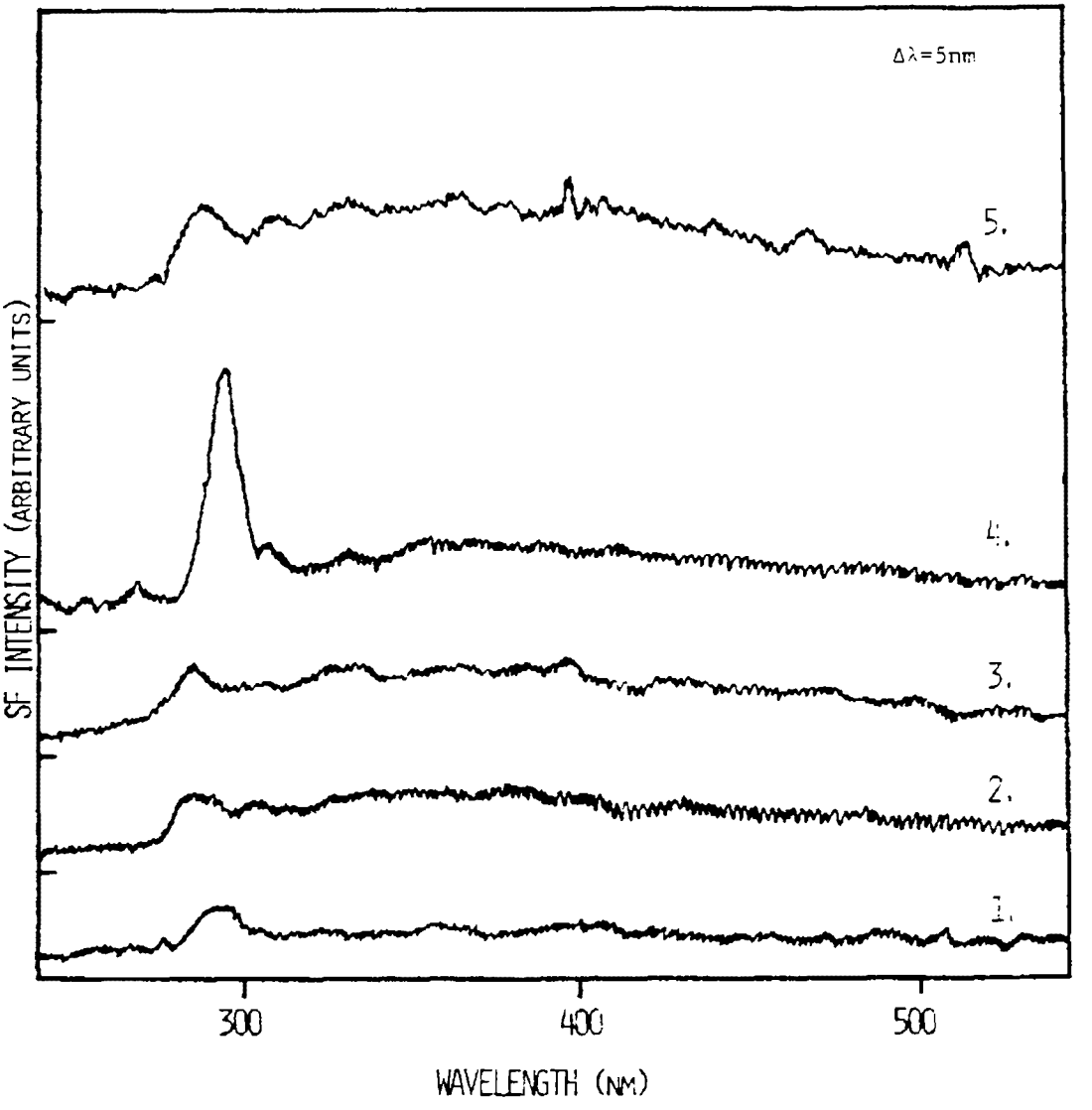

Figure 1. Synchronous fluorescence spectra for (1) drinking water, (2) run-off water from oil retention pond no. 1, (3) surface water from oil retention pond no. 1, (4) surface water from S-3 pond, and (5) puddle water on bank of oil retention pond no. 1. Wavelength separation (Δλ) between excitation and emission monochromators was 5nm.

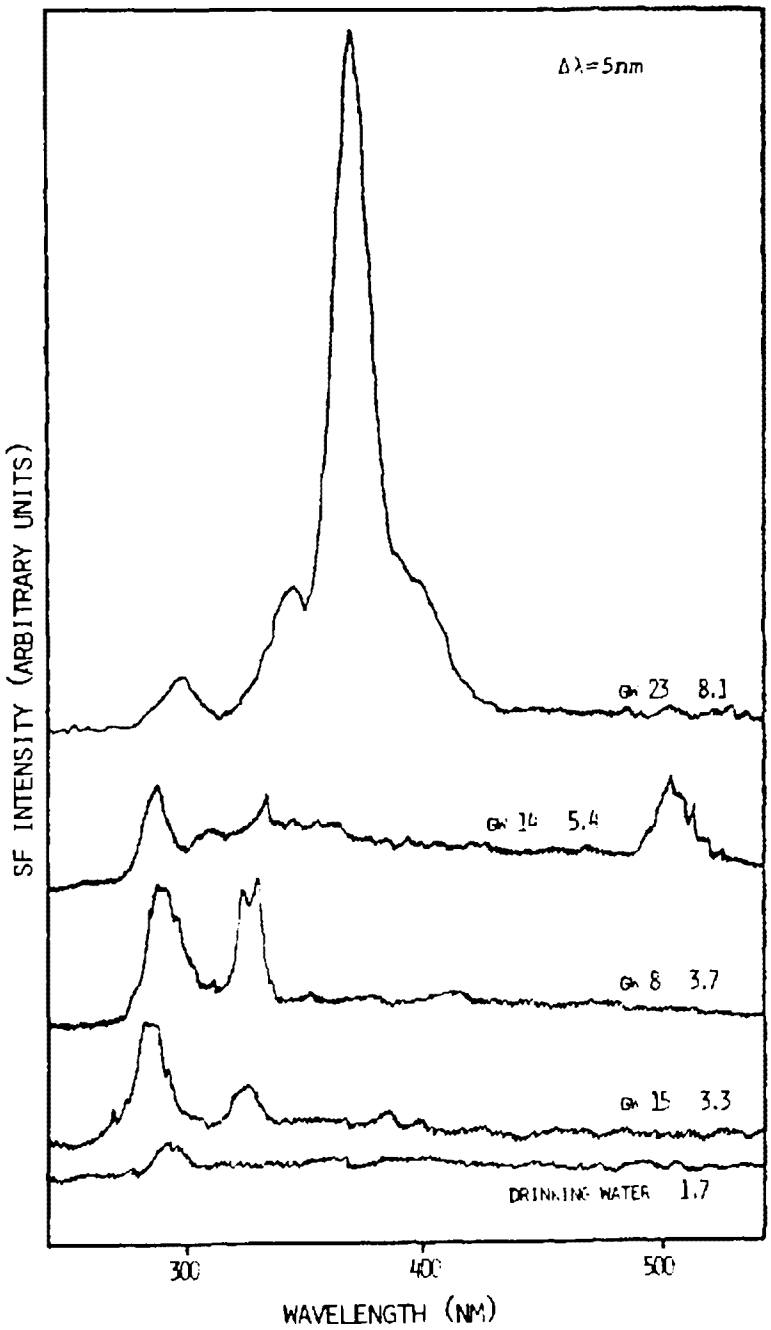

Figure 2. Synchronous fluorescence spectra (Δλ=5nm) for samples of well water close to an inactive solvent disposal area (GW14, GW15 samples), waste retention pond no. 2 (GW23 sample), and oil land-farm area (GW8). The values for integrated SF are noted in arbitrary units.

SURFACE-ENHANCED RAMAN SPECTROSCOPY: DETECTION OF HAZARDOUS CHEMICAL POLLUTANTS*

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Hazardous pollutants emitted from waste materials have toxicologically important chemical groups that can be characterized and detected by Raman spectroscopy. The conventional Raman technique, however, is often limited by its low sensitivity due to the inherently weak Raman cross section of organic chemicals. In this paper we report on a new detection technique based on the Surface-enhanced Raman Scattering (SERS) technique. The SERS effect is based on recent experimental observations, which have indicated enhancement of the Raman scattering efficiency by factors up to 10^6 when a compound is adsorbed on rough metallic (silver) surfaces having submicron protrusions. In this report we describe the development of the SERS technique as a new tool for monitoring hazardous chemical emissions.

Substrates developed in this laboratory consist of flexible materials such as filter paper and cellulosic membranes or rigid surfaces such as glass or quartz plates coated with submicron size polystyrene latex spheres. The microsphere-coated substrates are then covered with silver by vacuum evaporation. Another type of substrate consists of thermally etched quartz substrates having prolate SiO_2 posts coated with silver particles. The results for a variety of hazardous polycyclic compounds and multicomponent mixtures demonstrate the usefulness of this technique for detecting low-level toxic organic chemicals.

*Research jointly sponsored by the U.S. Department of the Army (Interagency Agreement No.'s DOE 40-1294-82/Army 3311-1450), and the Office of Health and Environmental Research, U.S. Department of Energy, under Contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

SURFACE-ENHANCED RAMAN SPECTROSCOPY: DETECTION OF HAZARDOUS CHEMICAL POLLUTANTS

INTRODUCTION

Hazardous pollutants emitted from energy-related technologies, chemical industries, or waste materials are of increasing public concern because of their potential adverse health effects. Many pollutants have chemical groups of toxicological importance that can be characterized and detected by Raman spectroscopy.

Raman spectroscopy, however, has not been widely used in trace organic detection, even though the information contained in a Raman spectrum is most valuable for chemical identification. One limitation of conventional Raman spectrosocpy is its low sensitivity that often requires the use of powerful and costly laser sources for excitation. However, a renewed interest has recently developed among Raman spectroscopists as a result of various observations that indicate enhancements in the Raman scattering efficiency by factors up to 10^6 when a compound is adsorbed on or near special metal surfaces[1]. These spectacular enhancement factors of the normally weak Raman scattering process help overcome the normally low sensitivity of Raman spectroscopy. The technique associated with this phenomenon is known as Surface-Enhanced Raman Scattering (SERS) spectroscopy. The Raman enhancement process is believed to result from a combination of several electromagnetic and chemical effects between the molecule and the surface[2,3].

In this communication we report the use of the SERS technique as a tool for monitoring compounds of environmental interest. An important class of environmental pollutants includes the polynuclear aromatic (PNA) compounds. The PNA compounds present a potential health hazard because some of these species are known to be carcinogenic in animal laboratory assays[4]. Extensive studies have been devoted to developing analytical techniques for the identification and quantification of PNA species in environmental samples such as air, soot, water, and soils[5]. In previous studies we have described the development of various luminescence techniques for trace analysis of PNA compounds in complex environmental samples[6,7]. In this study we describe the use of SERS for the characterization of a variety of important PNA air pollutants. Several examples of detection of PNA compounds commonly found in air particulates, such as anthracene, pyrene, and carbazole, illustrate the usefulness of the SERS technique using substrates developed in our laboratory[8-12]. The specificity of SERS for the analysis of complex mixtures is also illustrated in the characterization of a three-component sample containing benzo[a]pyrene, pyrene, and 1-nitropyrene. The potential of the SERS technique for air pollution detection is discussed.

EXPERIMENTAL SECTION

Apparatus

The instrumental system has been described in detail previously[8]. Only the salient features are given here. A high-resolution Raman spectrometer with double grating (SPEX, Model 1403) was used for SERS measurements. The excitation light sources were an argon ion laser (Spectra Physics, Model 164) and a krypton ion laser (Coherent, Model INNOVA 90K). The spectrometer

detector was a gallium arsenide photomultiplier (RCA, Model C31034) operated in the single-photon counting mode. Data storage and processing were performed on a SPEX Datamate DM1 Processor. All spectra were recorded with slit widths of 400 μm providing a 0.2-nm spectral resolution. A Vacuum Industries, Inc. plasma etcher using CHF_3 plasma was used for etching substrate surfaces. A quartz crystal thickness monitor (Kronos, Inc., Model QM-311) was used to measure the thickness of the silver layers on the substrates.

Chemicals and Reagents

Polynuclear aromatic compounds including anthracene, benzo[a]pyrene, carbazole, and 1-nitropyrene, were purchased in the purest grade commercially available. The solvent used was ethanol, spectroscopic grade (Aager Chemical).

Preparation of SERS-Active Substrates

We have investigated experimental procedures for producing SERS-active substrates that can be easily prepared and yet yield results with good sensitivity and reproducibility. Two practical approaches involve: (1) coating various solid surfaces first with submicron spheres and then depositing a layer of silver to produce a uniformly rough metal surface, and (2) etching a crystalline SiO_2 surface to produce submicron prolate posts which are also coated with silver. The detailed descriptions of these various SERS techniques have been given elsewhere[8-12]. Only the major features of the experimental conditions are provided here.

Substrates with Silver-Coated Spheres: A 200-μL volume of a suspension of 0.364-μm latex microspheres was applied to the surface of the substrate of interest (cellulose, quartz, or glass plate). The substrate was then placed on a spinning device (Headway Research, Inc.) and spun at 800-2000 rpm for 20 seconds. The solid substrates investigated in this work were filter paper and quartz microscope slides. The silver was deposited on the sphere-coated substrate in a vacuum evaporator at a rate of 1.5-2 nm/sec. The depth of silver deposited was 150-200 nm.

Silver-coated Prolate Posts: The preparation of SiO_2 prolate posts involves plasma etching of SiO_2 with a silver island film as an etch mask[6-8]. Since fused quartz etches much more slowly than thermally deposited quartz, a 500-nm layer of SiO_2 was thermally evaporated onto fused quartz at a rate of 0.1-0.2 $nm.s^{-1}$. The resulting crystalline quartz was annealed to the fused quartz for 45 minutes at ca 950°C. A 5-nm silver layer was then evaporated onto the thermal SiO_2 layer and the substrate was flash-heated for 20 seconds at ca. 500°C. This heating causes the thin silver layer to bead up into small globules which act as etch masks. The substrate was then etched for 30-60 minutes in a CHF_3 plasma to produce submicron prolate SiO_2 posts, which were then coated with an 80 nm silver layer at normal evaporation angle.

RESULTS AND DISCUSSION

SERS Detection of PNA Compounds

In most previous studies, SERS measurements were performed mainly for small compounds such as highly polarizable monocyclic molecules[1]. In this work we evaluate the SERS technique for a variety of PNA species. Figure 1 shows the SERS spectrum of anthracene adsorbed on a silver/quartz-post substrate. Anthracene was selected since this compound is an important species on the EPA Priority Pollutants List. Several major SERS peaks, at 1275, 1412, and 1564 cm^{-1} correspond to the normal Raman bands observed in polycrystalline anthracene at 1258, 1403, and 1556 cm^{-1}. These three Raman peaks were assigned to a_g symmetry, with the last two peaks attributed to totally symmetric C-C stretch modes. The SERS spectrum indicates also that several non-totally symmetric modes can be observed in the spectrum; these peaks are not prominent in the SERS spectrum, but are quite visible at the spectral frequencies 405, 1190, and 1477 cm^{-1}. These three peaks could be assigned to the b_{3g} Raman bands observed in anthracene at 394, 1185, and 1477 cm^{-1}.

Figure 2 shows the SERS spectrum of pyrene using the 647.1 nm laser emission line for excitation. Pyrene is also an important EPA Priority pollutant commonly found in air samples. The spectrum of pyrene was obtained using a prolate post substrate. The signal corresponds to the SERS emission from 7.2 ng of the pyrene sample spot illuminated by the laser beam. The SERS spectrum of pyrene exhibit a series of sharp peaks that could be assigned to a_g symmetry: The major peaks at 385, 785, 1038, 1180, 1220, 1235, 1380, 1490, 1540, and 1618 cm^{-1} have frequencies close to a_g symmetry bands observed in the Raman spectra of pyrene in solution at 408, 802, 1040, 1192, 1233, 1242, 1395, 1504, 1553, and 1632 cm^{-1}, respectively. In addition the SERS spectrum exhibit a peak at 1582 cm^{-1}, which has the spectral frequency close to the b_{3g} symmetry band at 1597 cm^{-1} observed in Raman spectra of pyrene in solution.

Figure 3 depicts the SERS spectrum of carbazole adsorbed onto another type of solid substrate (0.364-μm spheres on glass with a 2000 Å silver layer). Carbazole is an important nitrogen-heterocyclic compound often found in polluted airs and cigarette smoke emissions. In the SERS spectrum the peak at about 300 cm^{-1} is essentially the same as in the conventional Raman spectrum of solid carbazole (305 cm^{-1}), but the positions of the other enhanced peaks at 690, 996, and 1061 cm^{-1} are shifted considerably from the bulk carbazole peaks found at 435, 555, 746, 1015, and 1112 cm^{-1}. Some spectral changes are expected in SERS spectra relative to conventional Raman spectra and are indicative that the vibrations responsible for the shifted peaks are affected by adsorption onto the metal. It is expected that the spectral shifts will be greater in cases of chemisorption than in cases of simple adsorption. Figure 3 shows the 996 and 1061 cm^{-1} carbazole peaks from a 10 μL spot of 10^{-6} M solution. This represents only 1.7 ng of material. We have investigated the dependence of the SERS signal intensity upon the excitation wavelength using the two emission lines of the argon-ion laser at 4880 and 5145 Å. The 5145 Å excitation line produced a stronger SERS signal than did the 4880 Å line.

Characterization of Mixtures

A major advantage of Raman spectroscopy is the spectral selectivity of the technique for the analysis of complex mixtures because of the sharpness of the Raman emission peaks. Figure 4 illustrates this spectral selectivity for the SERS technique for the characterization of a synthetic mixture containing benzo[a]pyrene (BaP), 1-nitropyrene, and pyrene. We have selected these three PNA pollutants for several reasons. Benzo[a]pyrene is an important environmental air pollutant, which was found to induce cancer in animal bioassays[4,5]. Nitro-PNA compounds have also received intensive interest. These species are often produced in atmospheric reactions of PNA with NO_x or during incomplete combusion in automobile engines[13]. Nitro-PNA species have been detected in a variety of products including ambient particulates, diesel exhause emissions, and carbon black and xerographic toners. Recent studies have indicated that nitro-PNA compounds induce carcinogenic activity in rats. Special attention is devoted to the detection of 1-nitropyrene (1-NP), a potent direct-acting bacterial mutagen often found in light-duty diesel exhaust particulate extract. In a previous work, we described the use of SERS to detect nitro-compounds[11]. In this study we further illustrate the use of SERS to detect 1-NP in the presence of other PNA species. As shown in Figure 4 the SERS spectrum of the three-component mixture exhibit a series of sharp peaks that can be assigned to 1-NP, BaP, and pyrene. The results of spectral assignment are given in Table I. It is noteworthy that 1-NP can be easily differentiated from its parent compound, pyrene, by the SERS technique. The results in Table I show that each of the three compounds can be unambigously identified by several peaks. Recently we have successfully applied the SERS technique to detect subpicogram levels of organophosphorous pesticides and diesel particulate samples; the results of these studies will be reported elsewhere[14].

CONCLUSION

Much of the research in SERS has been devoted to achieving a fundamental understanding of the "giant Raman" enhancement. As the general features of the enhancement effects continue to emerge, SERS should also become a powerful tool for the analytical chemist. However, in spite of the great interest in fundamental research of the SERS phenomenon, there has been few reports on the analytical applications of this effect for trace organic analysis. Most of the basic studies reported in the literature mainly dealt with samples at concentrations between 10^{-1} and 10^{-3} M (i.e., well above the concentration range of interest to analytical spectroscopists). In general the SERS studies only involved specific surfaces, such as microscopically roughened electrodes, and dealt mainly with highly polarizable small monocyclic molecules, such as pyridine and its derivatives and a few ionic species. This study demonstrates the analytical usefulness of SERS for the detection of a variety of organic compounds using substrates that can be easily prepared for practical applications.

The SERS technique has several advantages for trace detection. The procedure requires only a small amount of sample for measurement. Usually a 3-μL sample is needed for the measurement. Therefore, the absolute detection limit for PNA compounds detected from a 10^{-6}M solutions is in the nanogram and subnanogram range. If we also take into account the fact that the laser beam illuminates an area 1/100 smaller than the actual sample spot, the actual

detection limits are only in the picogram range.

ACKNOWLEDGMENTS

These studies were carried out as applied development research within a collaborative project, with M. C. Buncick, T. L. Ferrell, T. A. Callcott, E. T. Arakawa, R. J. Warmack, and D. Bailey, sponsored by the U.S. Department of the Army (IAG 3311-1450) to study the fundamental physical mechanisms producing SERS. The quartz post substrates used in the studies were prepared with the technical assistance of P. Enlow and M. C. Buncick, which we gratefully acknowledge.

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Table I Spectral Identification of a Three-Component Mixture By Surface-Enhanced Raman Analysis

SERS Peaks In Mixture (cm^{-1})	SERS Peaks for Individual Compounds (cm^{-1})		
	Pyrene	B(a)P[1]	1-NP[2]
342	337		339
409	407		406
444			441*
465	462*		
481			479*
507			505*
530			529*
565	560*		
594	591		590
635			632*
720			719*
801	804		800
824			820*
893	890		890
921	917		916
1050		1045	1046
1074	1081*		
1127	1125	1127	1124
1176		1177*	
1194	1189		1190
1224	1220		1224
1240	1239	1249	1235
1277	1280		1278
1335	1328		
1350	1351	1348	
1385	1383	1382	1380
1420			1413*
1506	1501	1504	1500
1528			1524*
		1584*	
1607			1600*
1622	1625	1620	1615

[1]B(a)P = Benzo[a]pyrene
[2]1-NP = 1-Nitropyrene
* Spectral Position unique to each component

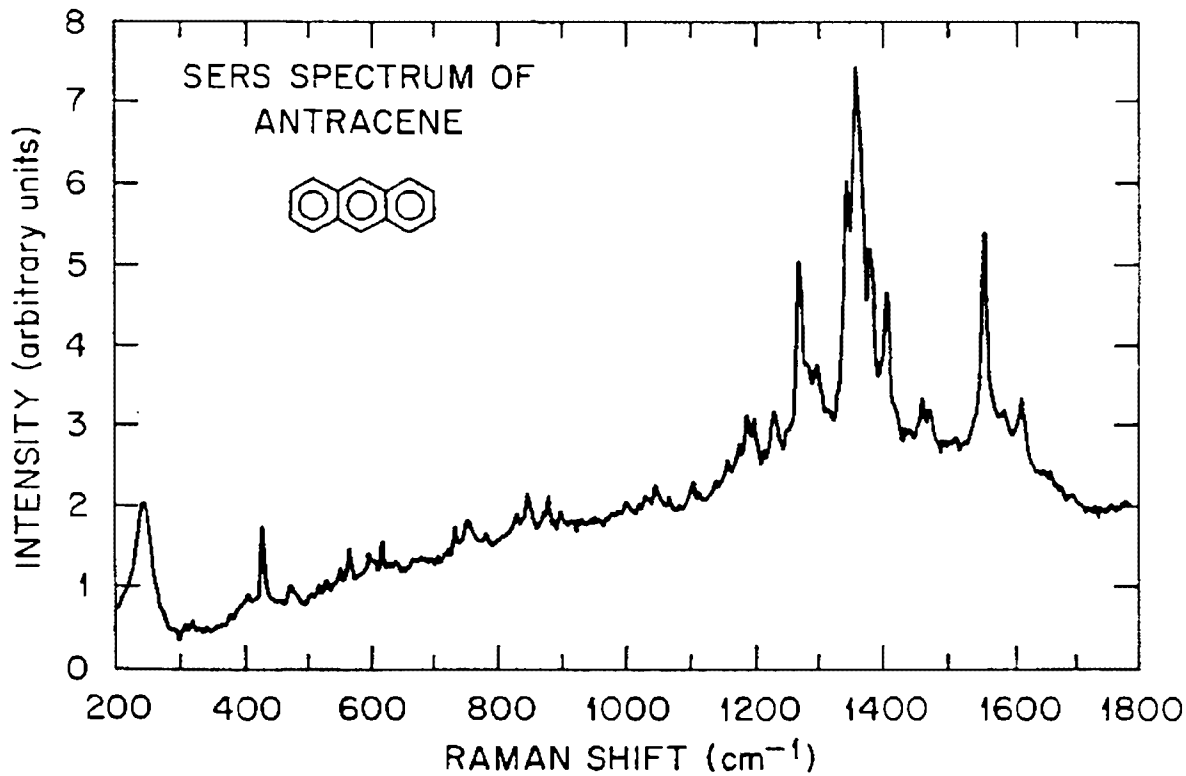

Figure 1: Surface-Enhanced Raman Spectrum of Anthracene on Quartz Post Substrate.

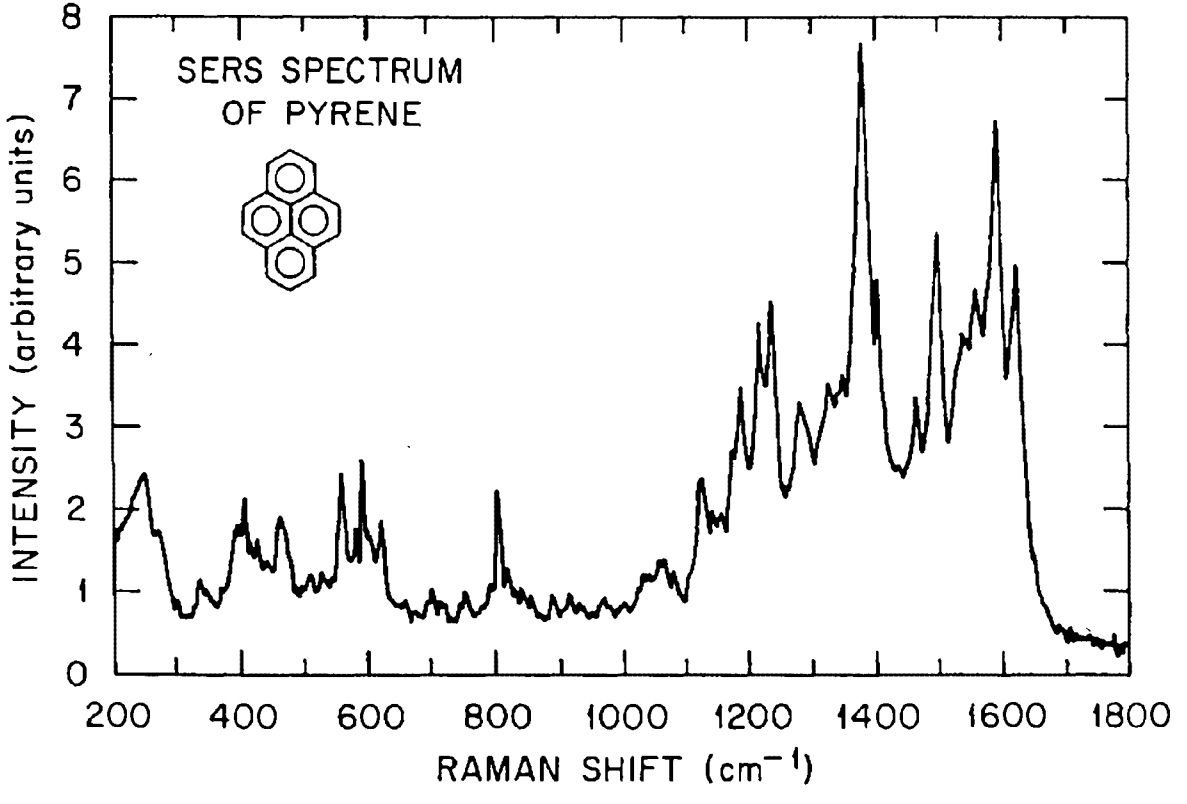

Figure 2: Surface-Enhanced Raman Spectrum of Pyrene on Quartz Post Substrate.

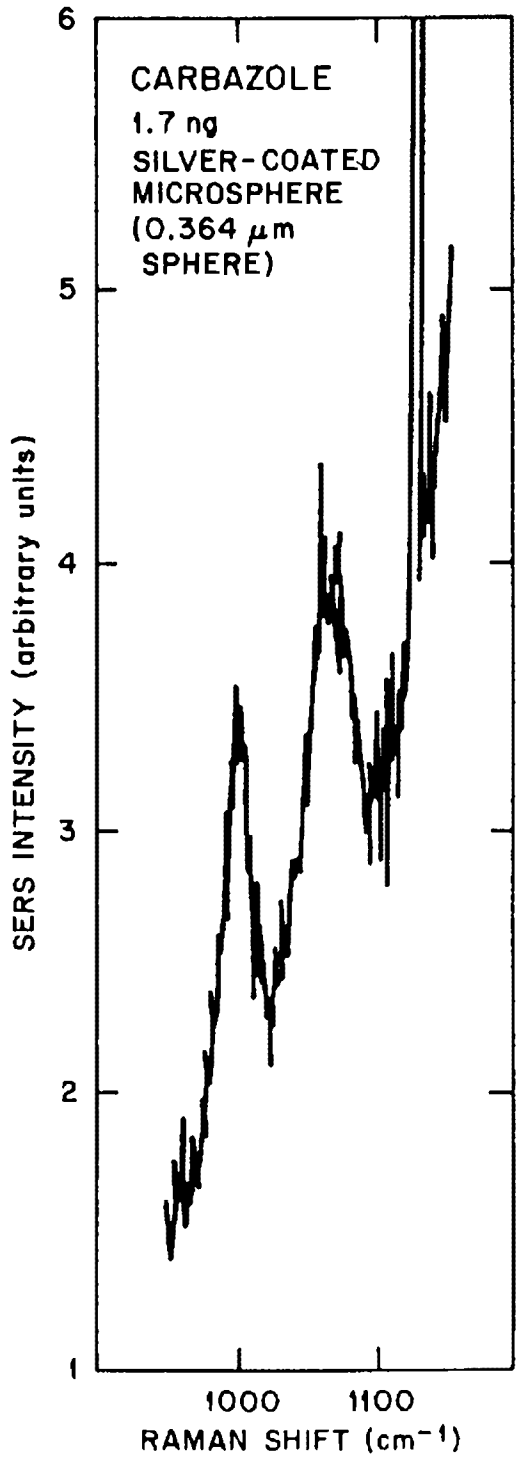

Figure 3: Surface-Enhanced Raman Spectrum of Carbazole on Silver-Sphere Paper Substrate.

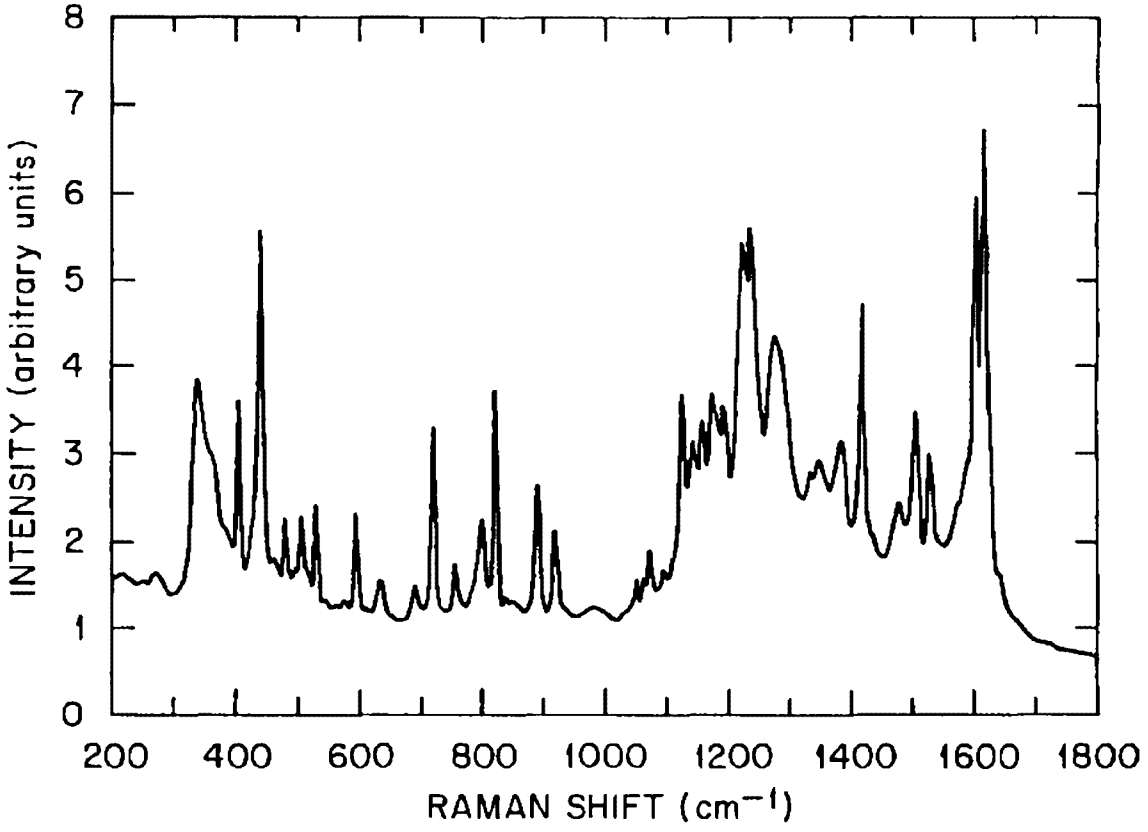

Figure 4: Analysis of a Complex Mixture by Surface-Enhanced Raman Spectroscopy.

A FLUX CHAMBER/SOLID SORBENT SAMPLING SYSTEM FOR VOLATILE ORGANIC AIR EMISSION MONITORING FROM HAZARDOUS WASTE LAND TREATMENT SYSTEMS: FIELD RESULTS

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A laboratory and field evaluation of a flux chamber/Tenax™ solid sorbent sampling system for the monitoring of volatile hazardous emissions from hazardous waste land treatment systems for air emission release rate (AERR) model verification is described. The laboratory phase involved the investigation of chamber interior pressure development and mixing conditions as a function of purge flow rate, Tenax™ and Tenax™/chamber compound collection and recovery efficiency, sampler manifold between-trap variability, and Tenax™ breakthrough volumes as a function of mass of contaminant collected. Field studies included the evaluation of field blanks, field spikes, sample breakthrough results, trap manifold variability, and temperature build-up within the chamber air space and soil below the sampler during sampling activities at an operating hazardous waste land treatment facility.

Laboratory results indicated that low purge flow rates ($\leq$1 l/min for flux chamber used in this study) are required to prevent pressure increases and subsequent emission suppression within the sampler unless a constant volume purge pump is incorporated into sampler design. Tenax™ breakthrough volumes were found to be a strong function of collected mass levels, with observed field breakthrough data generally agreeing with laboratory results. The under-prediction of breakthrough volumes for a number of compounds emphasizes the need for breakthrough traps in field sampling using Tenax™. Chamber air temperature increases were greatly moderated through the use of sampler shading, however, model and measured results indicate that 6.5 cm soil temperature, not chamber air temperature, should be used for emission rate modeling.

Finally, field breakthrough, blank and manifold variability data suggest that the flux chamber/Tenax™ system is best suited for use under high emission rate conditions, as experienced during field sampling activities following waste application, due to its susceptibility to background contamination.

A FLUX CHAMBER/SOLID SORBENT SAMPLING SYSTEM FOR VOLATILE ORGANIC AIR EMISSION MONITORING FROM HAZARDOUS WASTE LAND TREATMENT SYSTEMS: FIELD RESULTS

Introduction

The loss of volatile constituents from hazardous waste treatment, storage and disposal facilities has received increasing interest with the passage of the 1984 RCRA amendments that require EPA to promulgate air emission standards for such facilities within 30 months of the law's enactment. Volatile emissions from such facilities are of concern from the standpoint of potential health effects and the role these compounds may play in numerous photochemical reactions that take place in the lower atmosphere. For land treatment facilities, evaluation and quantification methods for volatile organic emissions are also necessary to provide a comprehensive approach to the determination of the ultimate land limiting constituent under a given set of soil/site/waste conditions.

The work described in this paper was undertaken to evaluate the applicability of a solid sorbent/isolation flux chamber sampling protocol that could be used for the quantification of specific volatile organic air emissions from soil surfaces following hazardous waste application. The sampling/concentration/analytical methodology was evaluated both on a laboratory and field scale at an active refinery land treatment facility to determine its operating limitations and performance characteristics.

Experimental Methods

Solid Sorbent Evaluation

Although established solid sorbent collection and concentration procedures for a wide range of volatile hazardous constituents are available from the USEPA[1] and the US Public Health Service[2], limited work has been reported on their use in hazardous waste land treatment emission measurements. Also, criticism has been leveled against solid sorbent concentration methods[3,4] as misuse of sampling procedures has occurred in the past with respect to quantification of sorbent collection, concentration, recovery and breakthrough efficiency for specific compounds of interest. When applying solid sorbent collection methods to air emission measurements from land treatment facilities, concern over compound retention, breakthrough volume and recovery efficiency becomes even more critical than in ambient air sampling due to the elevated levels of constituents released from the soil surface, especially immediately following waste application.

Charcoal and Tenax™ were considered as possible sorbents for use in the soil emission sampling system, however, consistent quantitative recovery of naphthalene from the charcoal at levels greater than 50% using carbon disulfide were not possible for mass injection levels from 15 to 1000 ug/tube. Similar difficulties have been reported for the recovery of aromatics from charcoal using a pentane solvent[5]. Because of the interest in monitoring naphthalene in subsequent laboratory and field studies, charcoal was not used in further sampling system analyses and will not be discussed further in this paper.

Tenax™ Sorbent Collection/Recovery and Breakthrough Evaluation. All Tenax™ sorbent traps used in laboratory compound collection/recovery studies were prepared according to EMSL/RTP[6] and Research Triangle Institute[7] standard operating procedures for the preparation of Tenax™ cartridges for volatile organic air contaminant sampling. Tenax™ sorbent traps consisted of 5 mm i.d., 10 cm long stainless steel tubing loosely packed in the interior 8 cm with 0.27 to 0.28 g of prepared Alltech Associates, Inc., 60/80 mesh Tenax™ GC solid sorbent material. Once packed, the traps were thermally desorbed for a minimum of 2 hours at 290°C to ensure the conditioning of column packing material and to minimize background organic levels in the cartridges. A single trap from a lot of 20 was checked for background contamination via thermal desorption/GC-FID analysis. A cartridge was rejected and a lot was reconditioned if background contamination was evident. Once the cartridge tested as clean, cartridges in the lot were placed in muffled Teflon lined screw capped culture tubes. The culture tubes were then placed in air tight metal containers and stored at 2 to 4°C until needed. All Tenax™ sorbent tubes used in field measurements were prepared as described

above, were individually checked and were rejected if background contamination was evident. Tubes used in the study were prepared no earlier than three weeks prior to their use to accommodate the recommended tube storage time of four weeks.

Tenax™ recovery data were collected utilizing EMSL/RTP[8] standard operating procedures for the spiking of Tenax™ cartridges with a known mass of an organic constituent utilizing the flash vaporization technique. A heated injector tube was maintained at approximately 300°C, and data were collected for compound mass injection levels ranging from 0.09 to 250 µg. Spikes for recovery/desorption efficiency experiments were prepared using a sample volume of 200 ml (purge flow of 40 ml/min, sample time of 5 min), the approximate breakthrough volume of methanol. Breakthrough analyses were conducted at sorbent tube temperatures of 19-23°C and 28-32°C using a purge flow rate of 200 ml/min, comparable to that used in laboratory and field emission measurements, for sample durations yielding sample volumes from 1 to 24 liters.

Analysis of the Tenax™ sorbent tubes was carried out using the Tekmar LSC-1 Liquid Sample Concentrator equipped with a modified trap oven to accommodate the 5mmx10 cm sorbent tubes using desorb and trap bake temperatures of 250°C and a desorb time of 4 minutes. Samples were desorbed into an HP 5880 Gas Chromatograph equipped with an FID detector . A 2 m long, 2 mm i.d. small bore glass column packed with SP-1200/1.75% Bentone 34 on 100/120 Supelcoport was used for peak separation and quantification. The following GC conditions were used throughout the study period:

Injector Temperature=250°C **Detector Temperature**=250°C
Carrier Flow=35 ml/min
Oven Temperature Program: Initial Temperature=35°C
Initial Time=4 minutes **Program Rate** 1=2°C/min to 60 °C, no hold time
Program Rate 2=10°C/minute to 165°C, 20 minute hold time.

Laboratory Isolation Flux Chamber Evaluation

The use of an enclosed chamber for the measurement of gases released from soil and plant surfaces has been practiced to some extent in the soil and biological sciences but has only been recently applied to the investigation of volatile hazardous emissions from land treatment facilities. An "emission isolation flux chamber" encloses a defined head space above a defined soil surface area to allow the collection and concentration of volatile organics emitted from a soil surface following waste application. An organic-free purge gas is introduced into the chamber at a known controlled rate to sweep volatile contaminants out of the chamber for collection/concentration by any means appropriate for the contaminants of interest. The flux chamber investigated in this study was a modification of a design developed for the USEPA Environmental Monitoring Laboratory, Las Vegas, NV, by Radian Corporation[9,10], and consisted of a 68.7 x 68.7 cm square exterior dimension (emission surface area= 4560 cm2), clear acrylic double-domed skylight modified for isolation flux sampling as shown in Figure 1. The acrylic double-dome interior was lined with opaque, adhesive Teflon tape to provide a non-adsorbing, non-reactive interior surface, and to prevent contamination of the sampling system via out-gassing from the chamber interior. Double-dome construction, as well as the opaque lining, were incorporated into sampler design in an effort to reduce the effects of incident radiation on heating within the chambers in field monitoring studies. Teflon was used for all bulk head fittings and purge gas inflow and outflow lines. Bulk head openings were provided for influent and effluent lines as well as for temperature and chamber interior pressure measurements. Flow calibration was carried out using a 1 liter bubble tube flow meter and a glass and Teflon micro-valve flow controller. Interior pressure measurements were determined by means of a Dwyer Magnehelic gauge reading ± 0.5 inches water full-scale.

Chamber Pressure Development/Mixing Studies. The flow regime within the flux chamber is of critical importance as component emission rate calculations are based on the assumption that emission measurements from the chamber effluent are representative of a completely-mixed chamber volume[9,10]. In addition, adequate flow and turbulence must be provided to assure no component concentration accumulation within the chamber that may

affect the component's flux from the soil surface into the lower atmosphere[11,12]. Counter to the desire for maximizing flow and turbulence within the flux chamber is the need to minimize positive pressure development within the chamber due to the potential for emission suppression and possible flux reversal during emission sampling. The impact of purge flow rate on chamber pressure development was evaluated through the monitoring of chamber interior pressure (with respect to ambient) indicated by the Dwyer Magnehelic as a function of purge flow determined at the chamber effluent port. The chamber was sealed air tight with a Teflon coated acrylic sheet, and pressure determinations were made over a range of purge flows from 1 to 10 l/min as suggested in Radian protocol[9,10].

Mixing within the flux chamber as a functionn of purge flow rate was evaluated using standard tracer techniques. The flash vaporization apparatus described above was placed up-stream of the flux chamber and was used to vaporize an acetone tracer. Chamber effluent acetone vapor concentrations were monitored us ng an AID portable GC equipped with a photoionization detector. Flow curves were evaluated utilizing standard procedures[13].

Flux Chamber/Sorbent Tube Collection/Recovery Evaluation. Contaminant collection and recovery efficiency for the combined flux chamber/solid sorbent sampling train was evaluated with the flux chamber configured as described above for the mixing studies, with a five position Tenax™ sorbent split-stream sampling system placed in the effluent line as indicated in Figure 1. The solid sorbent tubes (sampling and breakthrough traps) were connected to the chamber effluent line via a Teflon and glass constant flow, capillary manifold with all connections made via brass or stainless steel, Teflon lined Swagelok connectors. The effluent ends of the sorbent traps were connected to a second glass manifold to which a constant flow personal sampling pump, operated at 1000 ml/minute, was connected. Compound recovery data using the flux chamber/sorbent tube sampling train were collected in a manner identical to that explained above for the Tenax™ trap spike recovery experiments for compound mass levels ranging from 0.5 to 90 µg. Sampling continued for three theoretical chamber retention times to ensure representative sampling of the chamber volume. Sorbent traps were analyzed as described above, and individual trap data were pooled to indicate overall recovery efficiency, contaminant breakthrough, and collection variability between positions on the constant flow sampling manifold.

Field Isolation Flux Chamber Evaluation

Field sampling was carried out at an operating refinery land treatment facility at various time increments before waste application (BBT), before waste application following tilling (BAT), immediately following waste application (WBT), following an initial tilling (WAT), and following a second tilling (WST). Ambient air, chamber air, 0.6 cm soil and 6.5 cm soil temperature conditions were monitored with digital thermocouple thermometers during sampling, with and without isolation chamber shading, to ascertain heat build-up and its effect on measured emission rates.

Six isolation flux chamber/Tenax™ solid sorbent sampling systems shown in Figure 1 (less the heated injector tube) were transported to the full-scale facility in the summer of 1985 for field emission measurement and emission model validation studies. A constant volume, high capacity purge pump (2 to 6 l/min) was incorporated into sampler design to allow desireable high purge rate and short chamber residence times, while at the same time minimizing flux chamber interior pressure development and subsequent emission suppression. A three position constant flow capillary manifold was used in field sampling, and sample collection was carried out for a period of 5 to 15 minutes at a sample collection rate of 200 to 350 ml/trap depending upon the absolute sample time in relation to waste application. Sorbent tube breakthrough traps were utilized for all sampling events immediately following waste application, and at various other sampling times for quality control purposes.

Field sampler operation entailed the initial systematic random placement of the six sampling units in a 68.7 cm x 68.7 cm grid location within the approximate 6 m x 183 m application area. Once placed at a particular sampling location, all sampling during the study was conducted at the same relative position to preserve sample spatial identity. Both purge and sample pumps were calibrated on at least a daily basis using a bubble tube flow

meter. At the initiation of sampling, each flux chamber was placed in the appropriate location within the application area and was forced into the soil such that the Teflon lined acrylic dome rested on and sealed the soil surface. Purge gas and purge pump flow were initiated and continued for 15 minutes prior to sample collection to assure a representative atmosphere within the flux chamber during sampling. The sorbent trap manifold/sample pump system was opened to the chamber effluent line via a glass and Teflon valve, and the manifold pump was started, initiating a sampling event. Cold packs were placed over the Tenax™ tubes in an effort to reduce trap temperatures below the 30 to 38°C ambient temperatures which occurred during sampling.

Tenax™ sorbent tubes were randomly selected for use at the various sampling locations and sampling times during the field study. Following sampling, the traps were placed in culture tubes, and were maintained in air tight metal containers at 2 to 4°C at all times prior to final analysis as per methods described above. All field sorbent tube samples were analyzed within six weeks of collection. Field blanks were obtained by exposing sorbent tubes to ambient conditions for approximately 15 seconds (approximate time required for placement of tubes in sampling manifold) before being stored and processed as other samples for analysis.

Results

Laboratory Isolation Flux Chamber Evaluation

Pressure Development Results

As reviewed by Dupont[14], the development of pressure under the flux chamber during purging was found to be significant at purge flow rates as low as 1 l/min without an effluent sampling manifold. Pressure increased rapidly at purge flows greater than 1 l/min, reaching nearly 2 inches of water with respect to the outside of the chamber at a purge rate of 6 l/min. Because the Radian protocol recommends purge rates between 1 and 10 l/min[9,10], pressure increases should be quantified as a function of flow rate for the particular chamber being used in emission sampling. If a sealed sampling chamber is utilized, purge flows on the order of 1 to 1.5 l/min should be the upper purge flow limit unless a constant volume sampling pump downstream of the sampling chamber is used to provide a means of balancing chamber interior and ambient pressure.

Mixing Results

Because of the low flow rate necessary to minimize pressure build-up under the flux chamber, concern was raised regarding the mixing characteristics of the chamber at low purge rates. Complete-mix conditions are assumed within the sampling chamber when using chamber effluent concentrations for the estimate of surface flux rates, and flux chamber mixing results were used to test this assumption. Table I includes indicator retention time parameter and index data from mixing studies obtained from flow curves generated without internal mechanical mixing at purge flow rates ranging from 0.73 to 3.73 l/min. The decay portion of all flow curves observed did not vary more than 15% from corresponding theoretical complete-mix curves, meeting suggested Radian protocol for the use of flux chambers for soil surface emission measurements[10]. Mixing conditions within the sampling chamber are seen to be relatively insensitive to purge flow rate based on calculated retention time parameters and Morril Index values. No trend in dispersion with purge flow rate was evident from the mixing indices used, and these results indicate that the complete-mix assumption for flux chamber contents appears to be valid, even at flow rates as low as 0.73 l/min.

Solid Sorbent Recovery/Desorption Efficiency Results

Constituent mass recovery data from the Tenax™ and Tenax™/chamber recovery studies for the seven aromatic compounds of interest are discussed by Dupont14 and are summarized in Figure 2 along with field spike recovery data. Figure 2 indicates the mean and 95%

Confidence Intervals resulting for each compound for mass injection levels for Tenax™ alone of 0.1 to 250 µg/trap, for Tenax™/chamber recovery of 0.4 to 90 µg/trap, and for field blanks of 0.5 and 2 µg/trap. Tenax™ mean recovery efficiencies resulted in coefficients of variation under 10% for all compounds except naphthalene(C.V.=14.4%). Tenax™/chamber and spiked Tenax™ field trap data recovery represent a much wider range of variability than with the sorbent tubes used alone. The variability associated with the Tenax™/chamber studies is attributed to component losses within the sampling unit, sampling manifold between-tube variability, and purge flow/ sorbent tube/sampling flow variability during the sampling event in addition to analyses errors inherent in tube desorption and GC analysis. Field spike variability is associated with sample storage, transportation and analysis procedures, and is particularly apparent for benzene and naphthalene. Field recovery values were essentially identical to laboratory Tenax™ recovery data for the mid-range boiling point compounds, ethylbenzene to o-xylene, and are not significantly different (α=0.05) from laboratory recovery efficiencies for all compounds due to the large variability in field spike recovery data. Coefficients of variation were $\leq$ 30% except for benzene and naphthalene, which produced C. V. values of 38% and 69%, respectively.

Tenax™ Breakthrough Results

Results of laboratory breakthrough studies are shown in Table II and are expressed as sample volume in liters/0.28 g Tenax™ at a given compound mass level for 50% or 90% retention of the said mass on the first trap of two traps in series for a range of mass injection levels from 1.1 to 120 µg/tube at 19-23°C and 28-32°C. These values were generated from linear least-squares regressions of all collected breakthrough data for benzene and toluene which yielded regression coefficients greater than 0.870. All other compounds did not breakthrough in sufficient quantities to allow development of breakthrough volume predictor equations even with 120 µg injection masses and 24 l collection volumes. A number of references report data for breakthrough volume for benzene, toluene and ethylbenzene utilizing Tenax™ sorbent tubes[15,16] as indicated in Table II. Reported data do not adequately address the effect mass has on breakthrough volume. Under conditions of high volatile constituent mass loadings to the sorbent tubes, breakthrough volumes may be greatly overestimated based on current EPA sampling protocol[16].

Field breakthrough data shown in Table II were generated from linear and second order polynomial regression analyses, all of which were significant at the 95% confidence level. Field data represent a 1.34 l sample volume which resulted in total collected mass levels much higher than evaluated in laboratory studies for benzene (>900 µg) and toluene (>1550 µg). The loss of contaminants from breakthrough tubes was evident only for benzene at mass levels greater than 700 µg, at which point observed percent compound breakthrough decreased. Observed field breakthrough results for ethylbenzene, m- and o-xylene were under-predicted from laboratory data, with ethylbenzene exhibiting significant breakthrough (>30% at 120 µg collected) at a 1.34 l sample volume which was not observed in laboratory studies even at 31°C collection temperature.

From results of this study, for emission measurement sampling from land treatment sources for which $\geq$15 µg are to be expected during sampling, a 500 to 1000 ml sample collection volume is recommended to ensure minimum ($\leq$ 10%) breakthrough of the most volatile compounds being collected.

Field Blank Results

Blank sorbent tube data collected throughout the field study are presented in Table III. These data are divided into blanks collected before waste application and those collected following waste application due to the method of blank trap collection as described above. As others have indicated[4,5], occurrence of a number of very high levels of benzene and toluene occurred throughout the blank collection event. A number of these high blank values were attributed to GC analysis techniques which were corrected through post analysis temperature programming to rid the column/injector of high residual contaminant masses between samples. High benzene and toluene blank mass levels were traced to high level waste before tilling samples run just prior to these blank tubes, and these values

were not included in field data blank corrections. Blank correction values generally decreased as compound vapor pressure increased, and the levels increased during the waste application period before slowly falling to prewaste levels by the first tilling after waste application event.

Laboratory and Field Trap Manifold Variability

Laboratory manifold variability, expressed as the relative standard deviation (RSD) of collected mass within a manifold group, was found to range from 14 to 20% for all compounds investigated. Field data variability was much greater than laboratory data and appeared to be significantly affected by mass collection level. During sampling events when the highest mass of contaminants were being emitted, i.e., just following waste application, manifold variability approached those values observed in a controlled laboratory setting for all compounds (RSD=22 to 44%) except naphthalene (RSD=104%). Prior to waste application (RSD=83 to 140%) and after tilling (RSD=30 to 126%), sorbent tube characteristics and background contamination become significant for all compounds, requiring a strict QA/QC program to ensure adequately prepared and stored Tenax™ tubes.

Temperature Effects During Field Sampling

Temperature data collected during sampling events following waste tilling are shown in Figure 3. Significant temperature differentials, >40°C, with respect to ambient temperature were observed in flux chamber air during midday when the sampling units were not shaded. Shading using simple inclined plywood sheets was successful in reducing chamber air temperatures by 20 to 25°C during midday, significantly reducing air phase temperature gradients. Shading had a much smaller effect on soil temperatures as would be expected, producing only a 5 to 10°C reduction in 0.6 cm soil differentials, and only 1 to 2°C reductions at the 6.5 cm level with respect to field plot soils not covered with sampling chambers. Results of modeling activities correlating field data with Thibodeaux-Hwang land treatment emission model predictions[11] suggest that the 6.5 cm soil temperature depth is representative of mean soil temperatures occurring during waste volatilization. The use of temperature data at this depth for parameter temperature corrections has resulted in measured and predicted emission values consistently within a factor of 2 to 10 for most data collected during the field sampling described in this paper.

CONCLUSIONS

Based on the data and results presented above, the following conclusions were reached regarding flux chamber/solid sorbent sampling for soil surface emission measurements:

1. Tenax™ is recommended for land treatment emission sampling due to its effectiveness for the compounds of interest in this study and to its performance within the flux chamber sampling system.
2. The isolation flux chamber sampling system must be operated at low purge flow rates ($\leq$ 1 l/min for the 22.25 l chamber used in this study), if no purge pump is utilized, to limit excessive pressure build-up and potential emission suppression. At these low flow rates, complete-mix behavior is exhibited within the flux chamber, allowing for representative grab sampling of a uniform air space under the chamber.
3. Tenax™ breakthrough volumes were found to be a strong function of col-lected mass level as well as temperature. When using Tenax™ for source emission measurements, it is highly recommended that reported breakthrough volumes[15,16] be critically evaluated for the mass loading and operating conditions expected in laboratory and/or field emission measurement applications. It is further suggested that "in sampler" data should be collected to allow the quantification of specific "as used" collection and recovery efficiency values.
4. Field breakthrough data generally correlated with laboratory results, however, laboratory under-prediction of ethylbenzene, m- and o-xylene breakthrough volumes at low mass levels stresses the requirement for breakthrough traps when using Tenax™ for field sampling.

5. Flux chamber air temperature differentials were not observed to artificially affect emission rates and were found to be significantly reduced through the use of sampler shading. Measured emission rates appear to be predictable using parameter temperature corrections based on 6.5 cm soil depth data.

6. Results of field breakthrough, blank and manifold variability data suggest that the flux chamber/solid sorbent system is best suited for high emission rate conditions, i.e., immediately following land treatment waste application, but requires diligent QA/QC procedures to minimize background contamination to ensure representativeness during low emission rate events.

DISCLAIMER

Although the information in this paper has been funded in part by the US Environmental Protection Agency under Cooperative Agreement CR810999, it has not been subject to Agency peer review and does not necessarily reflect the views of the Agency, therefore no Agency endorsement should be inferred.

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Table I. Flux Chamber Mixing Retention Time Parameter Data

Flow Rate (ml/min)	Theoretical Retention Time T (min)	Ti (min)	Tm (min)	Ta (min)	Ti/T	Tm/T	Ta/T	T10 (min)	T90 (min)	Morril Index
732	30.4	1.28	6.67	30.44	0.04	0.22	1.00	7.51	83.89	11.17
732	30.4	0.55	5.65	14.91	0.02	0.19	0.49	3.82	30.65	8.02
1650	13.5	0.40	4.16	8.97	0.03	0.31	0.67	2.62	17.87	6.82
1650	13.5	0.24	2.00	8.35	0.02	0.15	0.62	2.16	17.07	7.90
2727	8.2	0.18	0.44	4.73	0.02	0.05	0.58	0.88	10.39	11.81
2727	8.2	0.10	0.19	4.61	0.01	0.02	0.56	0.60	10.69	17.82
2727	8.2	0.40	0.92	8.78	0.05	0.11	1.08	1.10	20.50	18.64
2727	8.2	0.14	0.49	4.68	0.02	0.06	0.57	0.54	10.92	20.22
3726	6.0	0.30	0.46	3.78	0.05	0.08	0.63	0.66	8.42	12.76
3726	6.0	0.10	0.19	3.04	0.02	0.03	0.51	0.52	6.82	13.12
3726	6.0	0.40	0.68	4.12	0.07	0.11	0.69	0.76	9.35	12.30
3726	6.0	0.45	0.86	7.30	0.08	0.14	1.22	1.06	16.98	16.02

- Ti = Time to initial tracer detection
- Tm = Time to peak concentration of tracer
- Ta = Time to centroid of area = average retention time
- T10 = Time to 10% area under tracer curve
- T90 = Time to 90% area under tracer curve
- Morril Dispersion Index = T90/T10

Table II. Tenax™ Sorbent Tube Breakthrough Volumes as a Function of Temperature and Mass Injection Level

28-32°C (19-23°C) Laboratory Tenax Breakthrough Volumes (l) for a Given Percent Recovery on First Trap of Two Trap Series

	Mass Level	Benzene	Toluene	Ethylbenzene	p-Xylene	m-Xylene	o-Xylene	Naphthalene
[Literature	32°C(21°C)]†	3.4(6.9)	15.5(31.2)	43.8(88.2)				
	120.0 µg							
	90%	0.28(0.20)	0.20(5.1)	11.3(25.0)	12.1(32.6)	11.0(25.6)	12.8(21.0)	>>24(>>24)
	50%	0.60(3.2)	2.50(14.7)	22.2(110.6)	22.5(150.0)	24.1(115.1)	25.4(91.8)	>>24(>>24)
	60.0 µg							
	90%	0.71(1.9)	0.22(>24)	14.3(>>24)	14.9(>>24)	15.2(>>24)	14.9(>>24)	>>24(>>24)
	50%	1.8(4.9)	6.0(>>24)	24.9(>>24)	25.4(>>24)	27.1(>>24)	28.6(>>24)	>>24(>>24)
		8.5-15.0 µg	**10-15.3 µg**	**9.7 µg**	**13.4 µg**	**29.8 µg**	**11.2 µg**	**18.0 µg**
	90%	1.2(3.0)	17.4(25.4)	>>24(>>24)	>>24(>>24)	>>24(>>24)	>>24(>>24)	>>24(>>24)
	50%	3.5(7.8)	33.2(49.5)	>>24(>>24)	>>24(>>24)	>>24(>>24)	>>24(>>24)	>>24(>>24)
		1.8-2.0 µg	**2.2 µg**	**1.1 µg**	**1.8 µg**	**4.2 µg**	**1.9 µg**	**2.4 µg**
	90%	4.5(5.3)	19.2(>>24)	>>24(>>24)	>>24(>>24)	>>24(>>24)	>>24(>>24)	>>24(>>24)
	50%	13.7(28.1)	40.4(>>24)	>>24(>>24)	>>24(>>24)	>>24(>>24)	>>24(>>24)	>>24(>>24)

Field Percent Tenax Breakthrough Data for Ambient Temperature=25.4-31.4 °C , Trap Temperature=20°C

Mass Level (µg)	% Breakthrough Benzene	Toluene	Ethylbenzene	p-Xylene	m-Xylene	o-Xylene	Naphthalene
1600	--	49	--	--	--	--	--
1000	70	18	--	--	--	--	--
700	74	9	--	--	--	-	--
450	51	4	--	--	--	--	--
200	29	3	--	--	17	--	--
120	21	3	33	--	11		-
60	16	3	11	0	7	14	--
15	12	4	3	0	5	3	0

† Breakthrough volumes shown are those reported by Reference 15 representing a 50% mass breakthrough.

Table III Field blank data summary

	Sample	MASS RECOVEREY (µg) Benzene	Toluene	Ethylbenzene	p Xylene	m Xylene	o Xylene	Naphthalene	COMMENTS
Background	BBT1B	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	BBT1B SB	0.30	0.00	0.04	0.00	0.04	0.03	0.15	
	BAT1E	3.70	0.90	0.00	0.00	0.00	0.00	0.00	
	BAT2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	MEAN	**1.00**	**0.23**	**0.01**	**0.00**	**0.01**	**0.01**	**0.04**	
	ST. DEV	**1.81**	**0.45**	**0.02**	**0.00**	**0.02**	**0.02**	**0.08**	
Waste Before Tilling	WBT2A	0.28	0.04	0.00	0.00	0.00	0.00	0.00	
	WBT3E SB	0.49	0.22	0.14	0.00	0.00	0.00	0.00	
	WBT4B	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	WBT4C	0.16	0.02	0.00	0.00	0.00	0.00	0.00	
	WBT2F	41.55	9.11	0.04	0.06	0.10	0.00	0.00	High Mass
	WBT3C	16.37	7.41	0.26	0.05	0.33	0.06	0.00	Sorbent Tube
	WBT5E	41.30	15.96	0.05	0.06	0.27	0.06	0.00	Preceeding
	WBT6B	3.40	0.99	0.01	0.10	0.12	0.04	0.02	These GC Runs
Not IncludingProblem Traps	**MEAN**	**0.23**	**0.07**	**0.04**	**0.00**	**0.00**	**0.00**	**0.00**	
	ST. DEV	**0.21**	**0.10**	**0.07**	**0.00**	**0.00**	**0.00**	**0.00**	
Waste After Tilling	WAT2E	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	WAT5B	0.01	0.00	0.00	0.00	0.00	0.00	0.02	
	WA16B	2.59	0.81	0.04	0.01	0.03	0.02	0.00	
	WAT6E	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	WA17F	0.63	1.14	0.00	0.01	0.04	0.01	0.01	
	WAT8B	5.77	2.16	0.15	0.00	0.10	0.07	0.00	
	WAT8F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	MEAN	**1.29**	**0.59**	**0.03**	**0.00**	**0.02**	**0.01**	**0.00**	
	ST. DEV	**2.19**	**0.84**	**0.06**	**0.00**	**0.04**	**0.03**	**0.01**	
Waste After 2nd Tilling	WST1A	0.00	0.00	0.06	0.00	0.23	0.04	0.00	
	WST1D	0.45	0.12	0.00	0.00	0.01	0.01	0.01	
	WST2A	0.14	0.00	0.00	0.00	0.01	0.00	0.09	
	MEAN	**0.20**	**0.04**	**0.02**	**0.00**	**0.08**	**0.02**	**0.03**	
	ST. DEV	**0.23**	**0.07**	**0.03**	**0.00**	**0.13**	**0.02**	**0.05**	

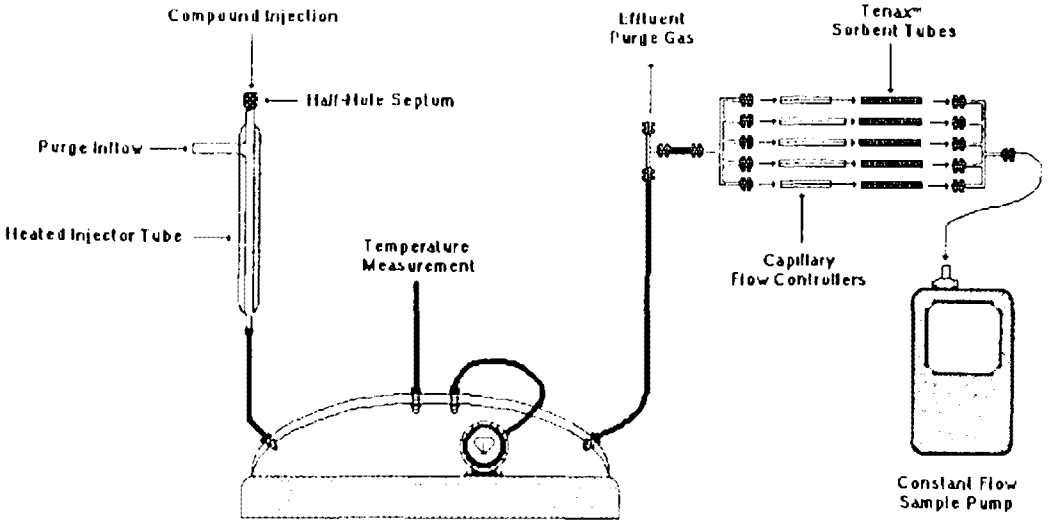

Figure 1 Flash vaporization/flux chamber/solid sorbent tube sampling system

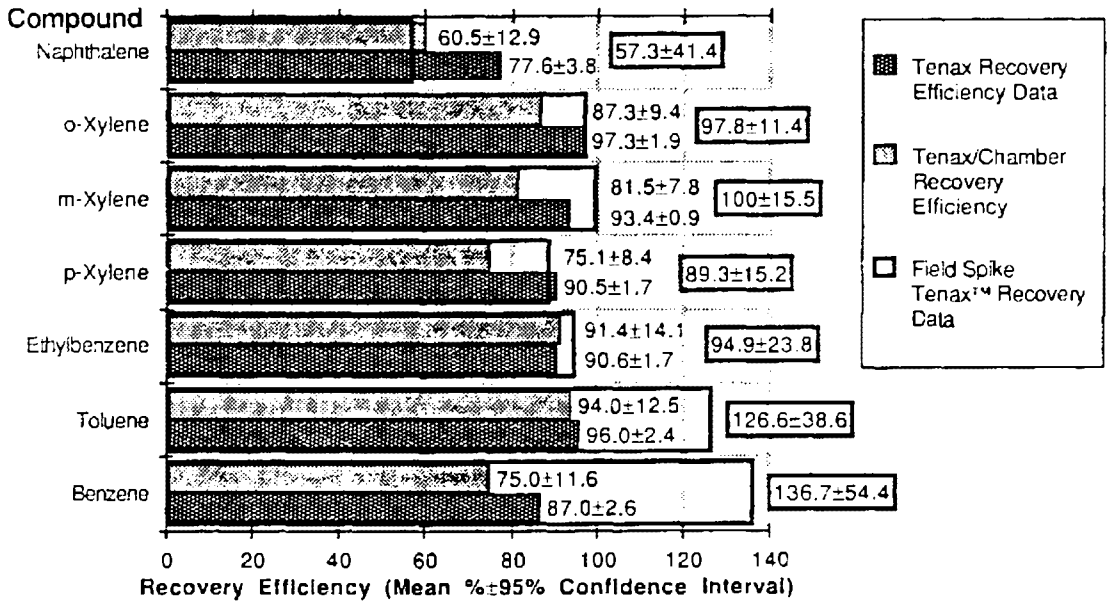

Figure 2. Laboratory and field Tenax™ recovery efficiency data

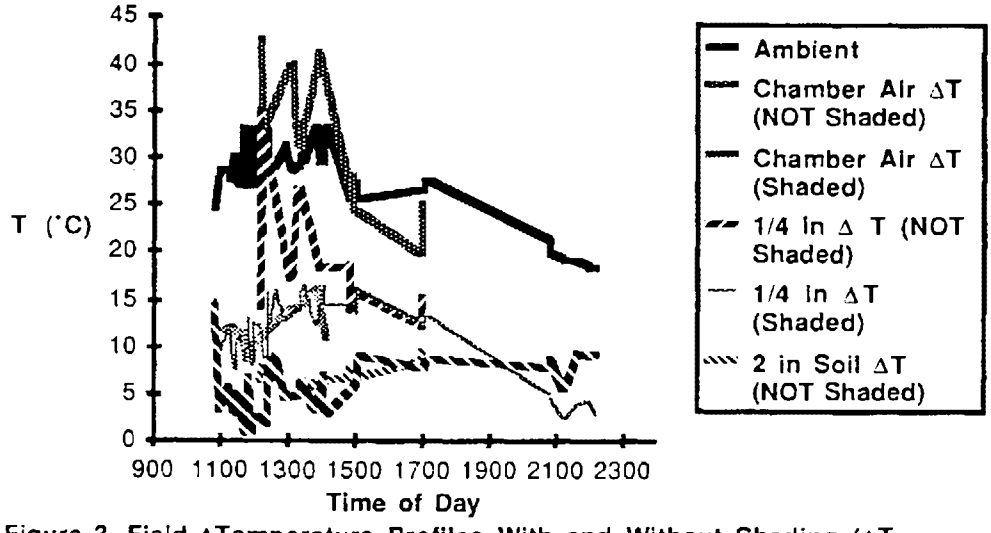

Figure 3. Field ΔTemperature Profiles With and Without Shading (ΔT based on values at start of chamber purge)

APPLICATION OF CAPILLARY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY TO THE VOLATILE ORGANIC SAMPLING TRAIN (VOST) ASSAY TO FACILITATE CHARACTERIZATION OF PRODUCTS OF INCOMPLETE COMBUSTION

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The extensive characterization of Products of Incomplete Combustion in Volatile Organic sampling train samples is greatly facilitated by improving the chromatographic resolution producing quality mass spectra that are easier to characterize. Cryotrapping and the substitution of a wide bore, thick film, fused silica capillary column for the packed column (6′ x 1/8", 1% SP-1000 on Carbopack B) now required is the easiest and most economical improvement.

This procedure desorbs the contents of a Tenax® or Tenax®/charcoal cartridge through a purge and trap apparatus and onto a sorbent trap. This sorbent trap is desorbed onto a nickel trap that is cooled with liquid nitrogen to approximately -198°C and rapidly heated to approximately 225°C. Approximately 2 mL/min of carrier gas sweeps the contents into a wide bore, thick film, DB-5 fused silica capillary column that is programmed and eluting compounds are detected by mass spectrometry. Further experiments are scheduled to evaluate the reproducibility of measurements obtained with the capillary system, a well as compound recovery. If reproducibility and recovery are acceptable, a field test is scheduled for spring.

INTRODUCTION

Background

The environmental scientific community is interested in the characterization of Products of Incomplete Combustion (PICs) in stack emissions. The current Volatile Organic Sampling Train (VOST) methodology[1] analyzes samples of stack gases that are acquired on Tenax and/or Tenax/charcoal cartridges. The cartridges are analyzed by thermal desorption with a subsequent purge through water, concentration of organics on a sorbent trap, and then introduction into a gas chromatograph/mass spectrometer (GC/MS) system as outlined in EPA Method 624. The analytical separation performed on the GC employs an 1/8 in x 6 ft column packed with 1% SP-1000 on Carbopack B. If the sample is not extremely complex and the level of products of combustion (POCs) does not saturate the mass spectrometer (MS) detector, then the quantitative analysis of the principal organic hazardous constituents (POHCs) is straightforward and a qualitative analysis of non-target compounds may be performed on chromatographically resolved peaks with an acceptable level of confidence. If the sample is complex and the level of POHCs nears saturation of the MS detector, then the high level of background may interfere with the compound identification. A PIC peak may easily coelute with the POHC compound because a packed column chromatographic peak is typically very broad (20-45 seconds). Identification is complicated when peaks coelute. The extensive use of background subtraction for PIC identification, by manual interpretation or by computerized library search, is time consuming and requires considerable experience and skill. Improvement of the analytical process by upgrading the chromatographic resolution would produce a better quality mass spectrum and a higher level of confidence in their identification. The use of a capillary column would provide this higher chromatographic resolution. The narrow peaks (typically 8-14 seconds) would decrease the chances of compound coelution and improve the level of confidence in compound identification. The capillary column is also capable of a shorter analysis time while retaining a sample capacity as high as ~500 ng on column.

Objectives

The objective of this program was to develop a working method of introducing a VOST sample to a capillary GC column in order to improve the chromatographic resolution and thus to facilitate characterization of PICs. Analytical precision and recovery had to be verified with any alteration of the VOST methodology and they could not be sacrificed for the additional chromatographic resolution.

EXPERIMENTAL METHODS

We approached this assignment with a two-part plan. The initial development was performed on a gas chromatograph/flame ionization detector (GC/FID) to keep costs at a minimum while experimenting with the assembly of the apparatus, program times on the Purge and Trap Concentrator (P-T) and temperature programs. The second portion was performed by GC/MS as described in the VOST protocol with the technology developed on the GC/FID.

GC/FID

The GC/FID portion of the program was performed using a Tekmar LSC-2 concentrator, a Nutech 320 Cryotrap/Nutech 320 Controller, a Varian 3700 GC equipped with a FID, and a Varian CDS 401 Data System. The LSC-2 is a P-T unit equipped with a "trap" column that may contain Tenax®, Carbopack®, SP-2100, charcoal, or some combination of these sorbents. The effluent of the trap is directed into the Nutech 320 Cryotrap via a heated stainless steel transfer line.

The Nutech 320 Cryotrap includes a six-port valve containing a stainless steel nickel-coated trap loop (SSNCTL). The 320 has a cooling cycle controlled by bleeding liquid nitrogen (LN) into a reservoir surrounding the SSNCTL and has a heating cycle controlled by a Nutech 340 Temperature Controller that pulse heats the SSNCTL from -198°C to ~240°C in ~1 minute. The Nutech 320 is operated by setting the valve to the Desorb position and freezing the SSNCTL to -198°C, while the LSC-2 is desorbed with the effluent being passed into the Nutech 320 and through the SSNCTL where all compounds will freeze, venting only N_2 carrier gas to the atmosphere. When the LSC-2 has finished the desorption cycle, the Nutech 320 valve is switched to the Sample position and the trap is pulse heated to 240°C by activating the Nutech 340 Temperature Controller. The heated SSNCTL volatilizes the trapped compounds which are swept to the column head via a diverted GC carrier gas.

The DB-5 thick film, 0.32 mm x 30 m fused silica capillary column receives the organic compounds vaporized from the Nutech 320 through a stainless steel transfer line via a zero dead volume fitting. A DB-5 was selected for the program because it is a nonpolar, bonded silicone phase that is very resistant to solvent, has an operating range of -60°C to 320°C, high resolution capability and its 0.32 mm I.D. x 30 m length allows a carrier flow rate to maximize resolution while minimizing analysis time. The thick film (1.0 um) is excellent for highly volatile compound analyses, exhibits maximum sample capacity and raises the elution temperature of compounds for maximum separation and retention of low boiling compounds. The effluent end of the capillary column is connected to the FID of the Varian 3700 Model GC.

The Varian 3700 GC/FID was operated with the injection port heated to 220°C and the detector to 300°C. All analytical data were recorded by the Varian CDS-401 Data System which plots the chromatogram and integrates the chromatographic peak areas.

GC/MS

The Tekmar LSC-2 and the Nutech 320 were transferred to the GC/MS Laboratory upon completion of the development work on the GC/FID and connected to a Finnigan 4500 GC/MS. The capillary column was connected to the Nutech 320 as before but the other end was inserted directly into the MS source. The GC/MS system is controlled by an INCOS Data System which is used to record and process data. A summary diagram of this system is shown in Figure 1.

RESULTS

Initial experiments optimizing the the analytical conditions using GC/FID, yielded well resolved chromatographic peaks of reproducible areas with linearity over the range of calibration.

Purge and Trap Apparatus

The P-T apparatus was connected to the cryotrap by a heated transfer line and fitted with a Method 624 trap (Tenax®/SP-2100/silica gel). The purge time was 11 minutes, trap desorb time 3 min at 180°C, and trap bakeout time 12 min at 200°C. The initial GC analyses failed to produce good analytical results so the purge time and trap desorb times were adjusted. Although moisture did not efficiently block the cryotrap, it was of sufficient quantity to extinguish the FID. The trap was replaced with an all-Tenax trap in an attempt to alleviate the problem. The purge time was tested as low as 5 minutes which did not purge compounds from the water and as high as 22 minutes which did not improve compound recovery. Increasing the trap desorb time to 5 minutes increased signal level by 1.5-2 times, but when desorb time was increased to 7 minutes or 10 minutes the signal level did not increase.

A "dry purge"[2] cycle was also tested. A "dry purge" is a technique performed after the carrier gas has passed through a purging vessel containing 5 ml H_2O for 11 minutes. The carrier gas is then diverted past the purging vessel and directly onto the LSC-2 trap. The dry purge eliminates the possibility of trapping excess moisture from the purging vessel on the LSC-2 trap and helps to remove any moisture already sorbed by the LSC-2 trap. The dry purge cycle had no effect on the signal of the compounds for this portion of the experiment. The final parameters were:

Purge Time:	11 min.	40 ml/min	ambient temperature
Desorb Time:	5 min.	1.5 ml/min	180°C

Gas Chromatography

The GC program was selected to allow analysis to begin at room temperature. The initial temperature of the GC oven was set at 35°C and held for 3 minutes, then programmed to 225°C at 8°C min^{-1} and held at 225°C for 15 min. Varying the initial hold times from 1 minute to 5 minutes did not improve peak shape or resolution. Changing the ramp rate to 6°C/min reduced the peak resolution and lengthened retention times but a ramp rate of 10°C/min did not improve the chromatography. The final program was:

Initial Temperature	35°C for 3 min
Ramp rate	8°C min^{-1}
Final Temperature	225°C for 15 min
Injector Temperature	200°C
FID Temperature	300°C
Flow Rate	1.5 mL/min

GC/FID Results

Precision and linearity of the method described above, when tested with a mixture of benzene, toluene, ethylbenzene, o-xylene, m-xylene, and p-xylene, suggest that transfer of the system to the GC/MS was feasible. This may be seen in the coefficient of variation in Table I and by correlation coefficient in Table II.

Gas Chromatography/Mass Spectrometry

The purge and trap/cryotrap apparatus was fitted to the GC/MS and operated under conditions identical to those used for the GC/FID analyses. A series of experiments was conducted to determine the best analytical trap composition and the best P-T methodology. Table III outlines a summary of these experiments and their results. The best trap composition is 10% charcoal and 90% Carbotrap by weight. Carbotrap is graphitized carbon black with a particle size distribution of 20/40 mesh and is very hydrophobic. The dry purge of seven minutes removes most of the moisture sorbed by the charcoal and allows maximum sensitivity of all Method 624 compounds including gases (Figure 2).

The analytical parameters for optimal analytical performance is as follows:

Sample Cartridge Desorb	
Temperature	180°C
Time	11 min.
Purge and Trap	
Purge Time:	11 minutes
Dry Purge Time:	6 minutes
Purge Flow:	40 mL/min (@20 psi head pressure)
Purge/Desorb Temp.:	25°C/180°C
Desorb Time:	3 minutes
Cryotrap	
Sample Temp.:	-198°C
Desorb Temp.:	225°C
GC/MS	
Injector Temp.:	225°C
Transfer Oven Temp.:	225°C
MS Manifold Temp.:	100°C
Ion Source Temp.:	150°C
Scan Rate:	1.0 sec/scan from 35 AMU to 265 AMU
GC Oven Program	
Initial:	35°C 3 minutes
Program:	8°C/minute
Final:	220°C 5 minutes

CONCLUSIONS

The purge and trap/cryotrap/capillary column/MS system is workable, and would require a minimum of capital and time to add to the presently accepted VOST methodology. The cryotrap used for this task was manually operated but there are semi-automatic and automatic traps commercially available to simplify the analytical procedure. Use of a cryotrap added a few minutes to the initial portion of the analysis, but the capillary column required approximately twenty minutes less per analysis than the SP-1000 packed column (Figure 3, Figure 4). The peak resolution of the capillary column made the identification of compounds easier with less chance of coelution and misidentification.

The capillary will also allow a qualitative examination of compounds that elute beyond the VOST range of interest ($< 30^{o}C$ and $> 100^{o}C$). Semi-VOST compounds (b.p. $> 100^{o}C$) for example will elute from the capillary column that would never elute from the SP-1000 packed column. This finite elution time of compounds with boiling points $> 100^{o}C$ may help to screen VOST samples for compounds that may be present in an accompanying Semi-VOST or Source Assessment Sampling System (SASS) type test; the only restriction being what compounds are sorbed and desorbed by Tenax and charcoal.

Further method development is underway to maximize the sensitivity of this procedure. This will include studying dry purge efficiencies and minimum detection limits. A field test is scheduled for June, 1986 to collect samples to evaluate the capillary-VOST method with incinerator emission samples.

ACKNOWLEDGMENTS

This study was supported by the U.S, Environmental Protection Agency, Environmental Monitoring Systems Laboratory (EPA-EMSL) under contract no. 68-02-4119.

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1. Earl M. Hansen, "Protocol for the Collection and Analysis of Volatile POHCs Using VOST," EPA Report 600/7-78-054, March 1978.

2. Eric Johnson, Finnigan Corp., Sunnyvale, CA, private communication (1986).

3. Earl M. Hansen, "Protocol for the Collection and Analysis of Volatile POHCs Using VOST," EPA Report 600/7-78-054, March 1978.

4. Ibid, Section 3.1.

TABLE I. PRECISION OF COMPOUNDS (THREE INJECTIONS BY GC/FID (100 ng each compound)

Compound	Average Raw Area Counts	Standard Deviation	Coefficient of Variation
Benzene	29382	2686	9.1
Toluene	32602	1525	4.7
Ethylbenzene	31700	155	0.5
m- and p-Xylene*	64930	263	0.4
o-Xylene	33727	887	2.6

*These compounds co-elute.

TABLE II. LINEARITY OF COMPOUNDS (THREE POINT CURVE) BY GC/FID

Compound	Correlation Coefficient
Benzene	.9993
Toluene	.9962
Ethylbenzene	.9879
m- and p-Xylene*	.9931
o-Xylene	.9893

*These compounds co-elute.

Table III. ANALYTICAL TRAP EXPERIMENTS

Trap Composition	Result
Tenax®	High moisture - no compounds of b.p. 30°C
Tenax® with dry purge	Poor chromatography detector
Tenax®/Charcoal	High moisture
Tenax®/Charcoal with dry purge	Poor chromatography
Tenax®/Charcoal with dry purge	High moisture; poor chromatography
Carbotrap®/Tenax®	No compounds at b.p. 30°C detected
Carbotrap	No compounds at b.p. 30°C detected
Tenax®/SP-2100/SP-1000	Two of four compounds at b.p. 30°C detected
65% Carbotrap/35% Charcoal	High moisture
90% Carbotrap/10% Charcoal with 5 minute dry purge	- all compounds detected - good chromatography - low moisture

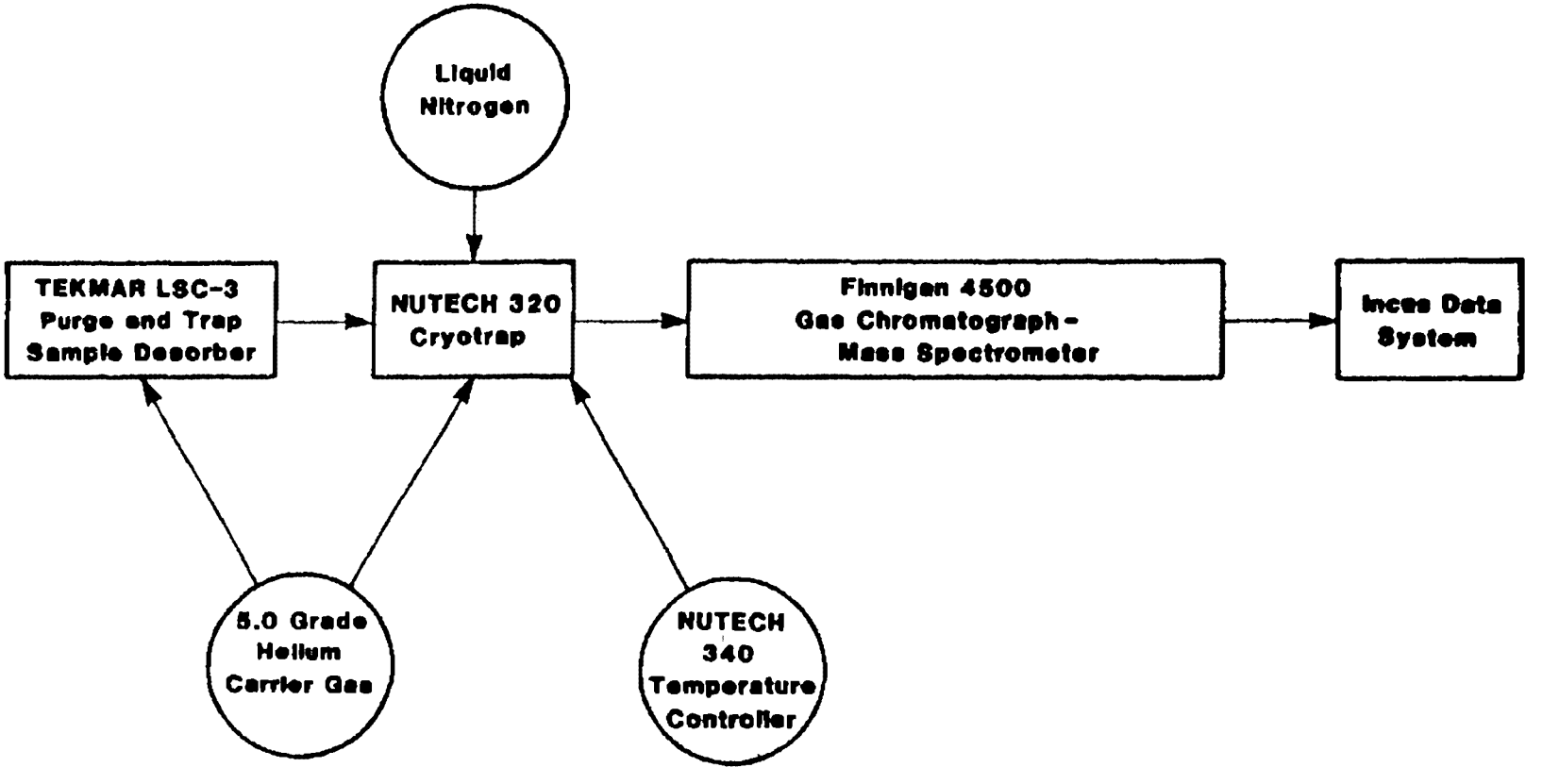

Figure 1. Schematic of GC/MS analytical apparatus.

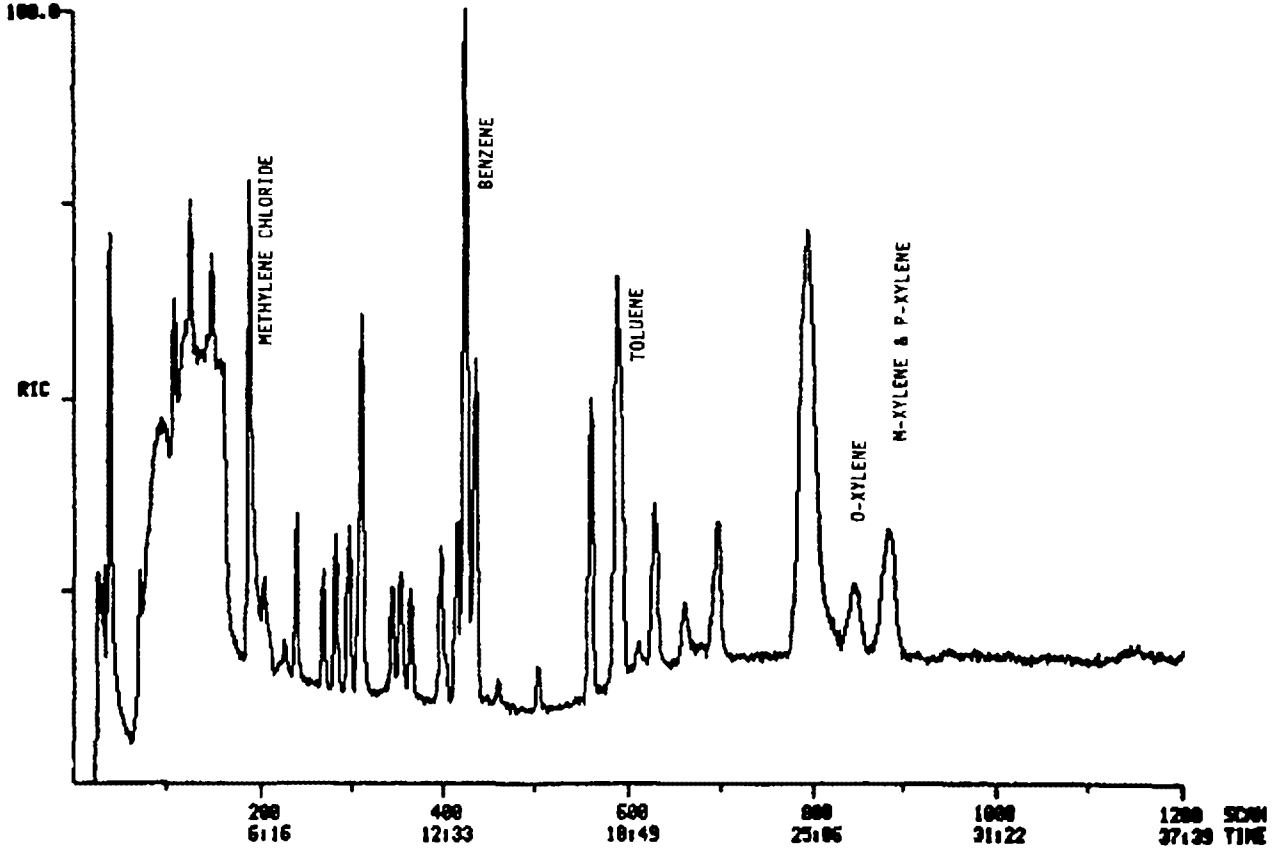

Figure 2. SP-1000 packed column.

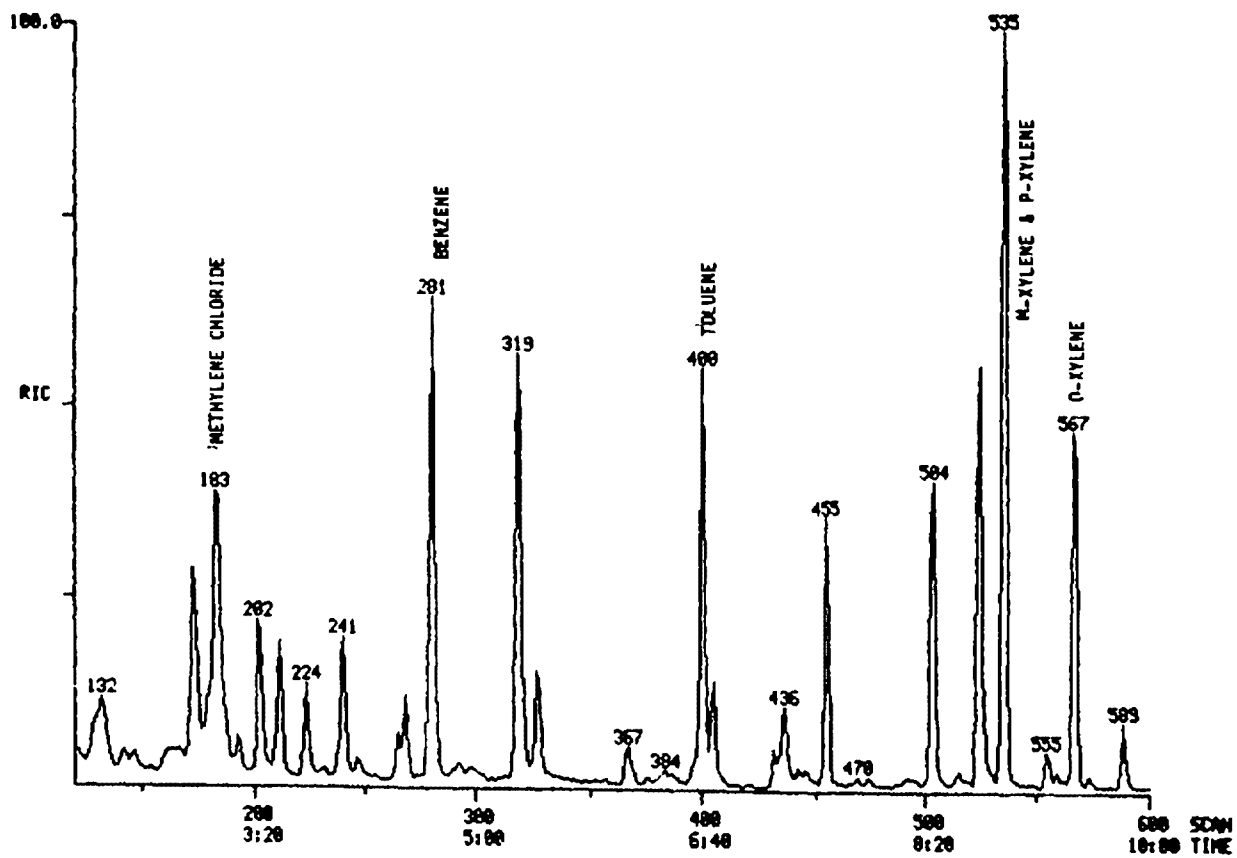

Figure 3. DB-5 capillary column.

EVALUATION OF THE SEMI-VOST METHOD FOR MEASURING EMISSIONS FROM HAZARDOUS WASTE INCINERATORS

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A field evaluation study was completed which assessed the performance of the Semi-Volatile Organic Sampling Train (Semi-VOST) methodology in measuring the concentrations of principal organic hazardous constituents (POHCs) that are emitted from hazardous waste incinerators. The Semi-VOST method is used to measure POHCs with boiling points greater than 100°C. Semi-VOST method performance characteristics were evaluated by previous experimental work performed in the laboratory.[1] Three POHCs examined in the laboratory (toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane) were selected as spiking compounds to evaluate method precision and bias under field conditions. In order to determine compound retention volume of the XAD-2® resin module, distributive volume experiments were performed.

Following the field study, additional laboratory experiments were performed to investigate the analytical methodology used for Semi-VOST and possible interactions of POHCs with the XAD-2® adsorbent resin. Four compounds with poor or variable recoveries in the laboratory evaluation were selected: aniline, pyridine, phenol, and resorcinol. In addition to the discussion of experimental results, several recommendations are presented in order to address elements of the evaluation and Semi-VOST methodology requiring further experimentation.

INTRODUCTION

Resource Conservation and Recovery Act (RCRA) requirements for waste disposal by incineration are that hazardous waste incinerators have a destruction and removal efficiency (DRE) equal to or greater than 99.99% for certain predetermined POHCs. The DREs for particular POHCs are determined by standardized sampling and analysis methods. A listing of potential POHCs appears in Appendix VIII of the Code of Federal Regulations (40 C.F.R., Part 261).

The U.S. Environmental Protection Agency (EPA) has published a compendium of sampling and analytical methods to be used in determining the concentrations of POHCs in the discharge from waste incinerators.[2] Methods are presented for application to various segments of the incineration process including waste feed, aqueous effluents (cooling water or spent scrubber liquor), fly or bottom ashes, and stack gases. Sampling and analytical methodology for the determination of POHCs in stack gases emitted from hazardous waste incinerators have been identified in waste incinerator operation permit applications, and is commonly referred to as Semi-Volatile Organic Sampling Train (Semi-VOST) methodology.

The major focus of the Semi-VOST method evaluation study discussed in this paper is to determine precision and accuracy of the method under actual field operating conditions. Prior to the field test, several laboratory experiments were performed to evaluate the sampling train configuration and the analytical protocols: 1) evaluation of the method formulation; 2) construction of the Semi-VOST sampling hardware; 3) selection of test compounds to challenge the sampling and analytical protocols; and 4) the Semi-VOST laboratory evaluation. Results of the laboratory studies are reported in Reference 3.

METHOD FORMULATION

In the application of the Semi-VOST methodology, gaseous and particulate components are isokinetically withdrawn from an emission source and collected in a multicomponent sampling train (Figure 1). Key elements of the train include a high-efficiency particulate filter and a packed bed of a porous polymeric adsorbent resin (XAD-2®). The filter is used to separate stack gas particles from gaseous substances which are then adsorbed on XAD-2®. As a collection sorbent for semi-volatile compounds XAD-2®, a polystyrene-divinylbenzene copolymer, has the advantage of high surface area (300 m^2/g) combined with an average pore size of 90 A. Following sample collection, the train components are extracted with solvent which is concentrated, and identified/quantified using high resolution gas chromatography coupled with low resolution mass spectrometry.

FIELD EVALUATION STUDY

A field test program was conducted to evaluate the Semi-VOST method performance at an operational hazardous waste incineration facility. The incinerator was designed to destroy hazardous industrial waste (excluding polychlorinated biphenyls) by high temperature combustion. The test program included collecting a matrixed sequence of samples to evaluate method precision, bias, and XAD-2® module breakthrough.

The sampling system was designed to use four simultaneously operating Semi-VOST trains. In order to obtain identical samples of the stack gases at a point of average velocity for each of the trains, a common fixed, heated probe system (quad probe) was used (Figure 2).

Previously obtained laboratory data indicated that compounds which were collected predominantly on the XAD-2® resin modules, exhibited the highest recoveries over a range of test conditions simulating combustion gas conditions. Three of the test compounds with good adsorption and recovery from XAD-2® included toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane. To determine method bias under field conditions, single gas cylinder standards were obtained containing 8 to 10 ppm levels of each of the three compounds in a nitrogen balance. The cylinder gases were passed through a manifold and a series of mass flow controllers to provide a continuous three-component gas stream metered into two of the four simultaneously operating trains. The configuration of the dynamic spiking apparatus is shown in Figure 3. The flow controllers were adjusted to provide an equivalent of 10 times the Minimum Detection Limit (MDL) of each compound as determined by GC/MS through a glass "tee" inserted in front of the condenser coil over a 2-hour sample collection period.

Overall method bias was evaluated by determining the percent recovery of spiked levels of test compounds. Method precision was evaluated by determining the mean percent coefficient of variation (CV) for measured differences between levels of POHCs collected by a series of paired unspiked trains. Retention of semi-volatile organic incinerator emission compounds by the adsorbent resin was evaluated through a series of distributive volume experiments designed to explore the potential for breakthrough of POHCs from the XAD-2® module. During an experiment series, each of the four trains was operated at the same sample flow rate. Two of the four trains were allowed to sample for twice the time of the other two. If breakthrough did not occur, the twofold increase in time at constant sampling rate should have resulted in a similar increase in the amount of sample collected on a compound-by-compound basis, assuming the source was constant in emissions.

For each train, six individual components were recovered and returned to the laboratory for analysis. These were the probe rinse, particulate filter, XAD-2®, coil rinse, condensate and rinse, and impinger contents and rinse. The mixture of eight surrogate compounds listed in Table 1 was selected for sample fraction spiking. Surrogates were added to sample fractions during preparation and analysis to determine extraction efficiency.

RESULTS AND DISCUSSION

Surrogate Recovery

Table 1 lists the mean overall surrogate recoveries from all sample fractions. Mean values range from 75 to 124 percent with CVs ranging from 13.6 to 46.3 percent. The CV measured for ^{13}C-labeled pentachlorophenol (PCP) recoveries was large for all fractions and can be associated with variances typically found in the chromatography of this compound.

Method Bias Determination

Table 2 presents a summary of the analytical results of the dynamic spiking experiments for a measure of method bias. Run numbers are listed as a set of four trains; i.e., runs 1A, 1B, 1C, and 1D are trains A, B, C, and D from run number 1. A and B were trains spiked with the test compounds, and C and D were unspiked trains. For toluene, spiked recoveries varied between 55 and 110 percent. The mean recovery was 101 percent after adjusting the value for the recovery of the d_8-toluene surrogate. Thus, the calculated bias was +1 percent.

Toluene was measured in the probe and coil rinses, as well as the condensate and condensate rinse. The concentrations were found to be in the same range as the corresponding values reported for the train blank sample fractions. In addition, two samples of the same solvent lot used for field sample analysis were analyzed for toluene by GC/MS. The results, when adjusted for the approximate volumes of solvent used for rinsing the coil and condensate reservoirs in the field, were 2 and 3 ng/uL toluene. The toluene concentrations reported in all train blank and sample run fractions, excluding XAD-2® modules, are therefore due to toluene contamination of the solvent used for sample recovery. For this reason, the concentration of toluene in the above fractions was not included in the bias calculation.

For chlorobenzene, the dynamic spike concentration was low relative to the unexpected high levels measured in the stack gas. Therefore, the resulting small concentration differences between the spiked and unspiked samples prevent a realistic estimate of recovery for calculating bias.

The recoveries of 1,1,2,2-tetrachloroethane ranged from 48 to 96 percent. The test compound was detected in one of four condensate rinses analyzed, an indication of compound breakthrough or possibly channeling in the XAD-2® resin module for this particular train. The average of the paired, spiked recoveries for run 1 is 84 percent. The average recovery for 1,1,2,2-tetrachloroethane of 52 percent in run 2 suggests a problem with the dynamic spiking system. During the development and evaluation of the system in the laboratory, several design modifications including the addition of heat tracing were incorporated specifically to reduce the time required for all three compounds to reach an equilibrium. 1,1,2,2-Tetrachloroethane was always the last compound to reach an equilibrium concentration. However the ambient temperatures during field sample collection were extremely cold and may have been responsible for the low recoveries of 1,1,2,2-tetrachloroethane from run 2. Excluding run 2 data, the bias was calculated as -16 percent for 1,1,2,2-tetrachloroethane.

Overall method precision was determined using a pool of seven paired unspiked sample analyses for chlorobenzene. Chlorobenzene was used because it was the only compound always present in the stack gas at sufficient concentration levels to allow method precision determinations. The method precision for chlorobenzene can be separated into three components -- sampling, sample preparation, and GC/MS analysis -- in terms of percent of total variance and percent CV for each component. For the preparations and analyses used, the number of preparations per sample and analyses per preparation is one. The preparation variance was 6.4 percent of the total variance, while the GC/MS analytical

variance was 93.6 percent of the variance. The percent of total variance indicates the amount of scatter in the data; the percent CV indicates the precision of the data. The percent of total variance for sampling, sample preparation, and GC/MS analysis for the field evaluation were 78.5, 1.4, and 20.1 respectively. Most of the variance during the field test was due to sampling. The corresponding percent CVs were 17.6, 2.3, and 8.9, resulting in method precision for chlorobenzene of 19.9 percent, uncorrected for surrogate recovery, and calculated from a data set representing seven degrees of freedom.

Distributive Volume Experiments

Chlorobenzene was detected in all unspiked stack emission samples collected for distributive volume analyses. Sample volumes ranging from one to three cubic meters were used to assess the breakthrough potential for stack gas components. The chlorobenzene levels measured from the XAD-2® fractions doubled with corresponding increases in sample volume, demonstrating good adsorption, retention, and recovery. Analysis of condensate and impinger rinses from the chlorobenzene samples also indicate that breakthrough did not occur.

Data presented in Table 3 are plotted in Figure 4 to test linearity between the chlorobenzene concentration measured and the volume of flue gas sampled. Other POHCs were not consistently found in a sufficient number of unspiked samples to warrant additional distributive volume analysis. A least squares analysis was performed and the variables were found to be correlated (r=0.95) with a "zero" sample volume intercept of 0.1 ug chlorobenzene. The analytical data confirms that no breakthrough occurred because distributive volume theory predicts that the amount of compound retained on the adsorbent is a direct linear function of the sample volume collected when the levels of POHCs are constant. Non-linearity occurs at the compound breakthrough volume.

ADDITIONAL LABORATORY ANALYSIS

Following the field study, additional laboratory experiments were performed to investigate the analytical methodology used for Semi-VOST and possible interactions of POHCs with the XAD-2® adsorbent resin. Four compounds were chosen for experimentation: aniline, pyridine, phenol, and resorcinol. Pyridine, phenol, and resorcinol were chosen because of either poor or variable recoveries measured during previous laboratory studies.[1] Aniline, a basic organic compound, was chosen for its potential to form a salt in an acidic medium. The XAD-2® resin was spiked with an internal standard and transferred to an all-glass Soxhlet extraction thimble. The module was rinsed with methylene chloride, the solution was added to the Soxhlet, and extraction was conducted for 16 hours. The methylene chloride solution was passed through anhydrous sodium sulfate to remove water, concentrated in a Kuderna-Danish (KD) evaporator/concentrator to reduce volume, and a quantitation standard added prior to analysis. o-Xylene was added to the samples as the system internal standard. The XAD-2® sorbent during Semi-VOST sampling becomes wet and acidic due to the presence of water vapor and hydrochloric, sulfuric, and/or nitric acid in the stack. During the laboratory studies, the XAD-2® resin was acidified to pH 2 with aqueous

hydrochloric acid to simulate these sampling conditions. Test compounds were added to pH 2 water and spiked into the resin. Three separate layers from the resin extract were analyzed: methylene chloride, water from a separatory funnel phase separation of methylene chloride, and methanol/water obtained by methanol Soxhlet extraction of the acidic XAD-2® resin. The results are given in Table 4.

The following observations can be made: 1) basic organic compounds (aniline and pyridine) react with an acidic environment to form salts which are soluble in water and insoluble in the methylene chloride extraction medium, thus resulting in poor recoveries; 2) compounds that are water soluble (such as resorcinol) will associate with any water present in the system. The present analytical method involves solvent extraction of wet resin. The solvent is then dried by sodium sulfate for subsequent concentration and GC/MS analysis. Compounds associated with the water present in the solvent are removed by this drying process and not recovered in the analysis. Based on the above, a base extraction of the water phase, and a more polar extraction solvent must be used in the analytical methodology to recover salts and water soluble compounds from the water phase and XAD-2®.

CONCLUSIONS AND RECOMMENDATIONS

Based on results of the method evaluation studies presented in this paper, the following recommendations are made:

- Method bias and precision have been shown to be compound-specific according to properties such as water solubility, chemical reactivity, and adsorption strength (retention volume) on XAD-2. Therefore, a screening method should be developed to determine which Appendix VIII compounds are suitable for sample collection and analysis by the Semi-VOST method.
- Semi-VOST analytical methodology requires modification to include procedural steps that account for salt formation from the basic organic compounds with acids collected by the train during sampling and compounds of high water solubility which are difficult to extract with methylene chloride.
- Additional laboratory dynamic spiking experiments should be performed using a dynamic spiking system redesigned to accommodate single cylinder use. Single gas cylinder use excludes mixing and manifolding the spiked compounds, which will eliminate a large number of flow variables. Deuterated compounds blended in one certified gas cylinder should be used in these experiments. Unlabeled compounds present in the stack emissions can be differentiated from the spiked compounds by GC/MS analysis.
- Dynamic spiking field experiments should be repeated at a hazardous waste incineration site using the redesigned spiking system. The experimental test plan would include determinations of precision, bias, and distributive volume experiments.

SUMMARY

Three test compounds (toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane) were chosen for dynamic spiking experiments to determine bias. The bias values for toluene and 1,1,2,2-tetrachloroethane are +1 and -16 percent, respectively. Bias could not be determined for chlorobenzene since the dynamic spike concentration was low relative to the unexpectedly high levels measured in the stack gas. Method precision for chlorobenzene was calculated from unspiked sample train results, and was separated into three components: sampling, sample preparation, and GC/MS analysis. The results were 17.6, 2.3, and 8.9 percent, respectively. The overall method precision was 19.9 percent for chlorobenzene uncorrected for deuterated spike recovery. Distributive volume experiments were performed using chlorobenzene concentrations of the stack gases to determine sample train breakthrough. No breakthrough was observed at a flow rate of 0.5 cfm for a sample collection period of 4 hours.

Laboratory experiments performed using aniline, pyridine, phenol, and resorcinol showed that basic organic compounds (aniline and pyridine) react with an acidic environment to form salts. The salts of these compounds are insoluble in the extraction solvent and soluble in water that is present in the system. Resorcinol was found to be extremely soluble in water and requires a more polar extraction solvent. Based on the laboratory data, without modification of the Semi-VOST method formulation, compound loss due to water solubility can range from 34 to 75 percent for pyridine and resorcinol.

DISCLAIMER

Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency through EPA Contract No. 68-02-4119 to Radian Corporation, it has not been subjected to Agency review and, therefore, does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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3. J. Homolya, J. McGaughey, D. Wagoner, M. Hartman, J. Margeson, J. Knoll, and M. Midgett, "Validation of the Semi-Volatile Organic Sampling Train Method for Measuring Emissions from Hazardous Waste Incinerators," for presentation at the 78th Annual Meeting of the Air Pollution Control Association, June 16-21, 1985. Paper No. 65.1.

Table I. OVERALL SURROGATE RECOVERIES FROM ALL FRACTIONS

Surrogate compound	Mean recovery, %[a]	CV, %
d_8-1,4-Dioxane	86.6	17.1
d_5-Pyridine	82.3	23.7
d_8-Toluene	75.0	26.4
d_5-Chlorobenzene	85.5	22.2
d_5-Phenol	96.1	13.6
d_5-Nitrobenzene	117	16.9
d_8-Naphthalene	106	15.8
$^{13}C_6$-Pentachlorophenol	124	46.3

[a]Mean of 39 values.

Table II. ANALYSES OF DYNAMIC SPIKING RUNS

Run	Compound concentration, ng/uL								
	Probe rinse	XAD-2®	Coil rinse	Condensate and rinse	Impinger and rinse	Total[af]	Test Compound	Recovery (%)	Adjusted recovery (%)
Toluene									
1A	9.2	10.1	3.6	ND[c]	ND	10.1	18.5	55	64[b]
1B	7.0	17.4	3.2	ND	ND	17.4	18.5	94	110[b]
1C	4.5	2.4	3.7						
1D	5.1	ND	4.3						
2A	2.8	16.0	2.8	1.9[b] (MDL)	ND	16.0	18.5	87	102[b]
2B	ND	20.4	3.2	3.1	ND	20.4	18.5	110	129[b]
2C		ND							
2D		ND							
Train blank	3.1	ND	3.0	4.0	ND				
Chlorobenzene									
1A	ND	23.8	ND	0.7	ND	24.5	3.7	d	d
1B	ND	28.0	ND	ND	ND	28.0	3.7	d	d
1C	ND	26.1	ND						
1D	ND	22.6	ND						
2A	ND	34.7	ND	ND	ND	34.7	3.7	d	d
2B	ND	60.1	ND	ND		60.1	3.7	d	d
2C		20.3							
2D		20.8							
Train blank	ND	ND	ND	ND	ND				

(continued)

Table II. ANALYSES OF DYNAMIC SPIKING RUNS (continued)

Run	Compound concentration, ng/uL						Test Compound	Recovery (%)	Adjusted recovery (%)
	Probe rinse	XAD-2®	Coil rinse	Condensate and rinse	Impinger and rinse	Total[af]			
1,1,2,2-tetrachloroethane									
1A	ND	1.8	ND	ND	ND	1.8	2.5	72	e
1B	ND	2.0	ND	0.4	ND	2.4	2.5	96	e
1C	ND	ND	ND						
1D	ND	ND	ND						
2A	ND	1.4	ND	ND		1.4	2.5	56	e
2B	ND	1.2	ND			1.2	2.5	48	e
2C		ND							
2D		ND							
Train blank	ND	ND	ND	ND	ND				

[a]Including only the XAD-2® trap for toluene.

[b]Toluene dynamic spike recovery adjusted for mean recovery of d_8-toluene surrogate.

[c]ND = compound not detected at its MDL.

[d]Not calculated due to high levels of chlorobenzene in stack emissions.

[e]No adjustment made for surrogate recovery.

[f]Particulate Filters were analyzed and no target compounds were detected.

Table III. ANALYSES OF DISTRIBUTIVE VOLUME RUNS

Run	Sample volume (m^3)	Chlorobenzene ug
3A	1.48	118
3B	2.91	270
3C	1.51	124
3D	2.69	255
4A	0.99	100
4B	1.73	188
4C	1.01	106
4D[a]	1.70	97
5A	0.91	132
5B	1.71	165
5C	0.91	75
5D	1.65	154
Train blank	--	ND

[a]Value eliminated due to mechanical problems during test.

Table IV. XAD-2® RESIN EXPERIMENTS

Compound	% RECOVERY[a]						
	Methylene Chloride	Water	Methanol/ Water	Total[b]	% CV[b]	o-xylene	% CV[b]
Aniline	86.6	0.00	2.89	88.5	4.40	88.2	2.58
Pyridine	54.3	28.0[c]	0.00	82.3	2.01	88.2	1.33
Phenol	84.3	0.00	0.00	84.3	6.91	91.2	1.17
Resorcinol	22.9	69.1[c]	0.00	92.0	6.58	87.9	4.79

[a]The determination of % recovery is based on the quantitation standard ethylbenzene

[b]The total percentage recovery and % CV (coefficient of variation) calculations are based on three individual experiments on each compound.

[c]Based on the normal Semi-VOST methodology, pyridine and resorcinol present in the methylene chloride extract of the wet acidic XAD-2® resin will associate with the residual water and be lost when passed through anhydrous sodium sulfate.

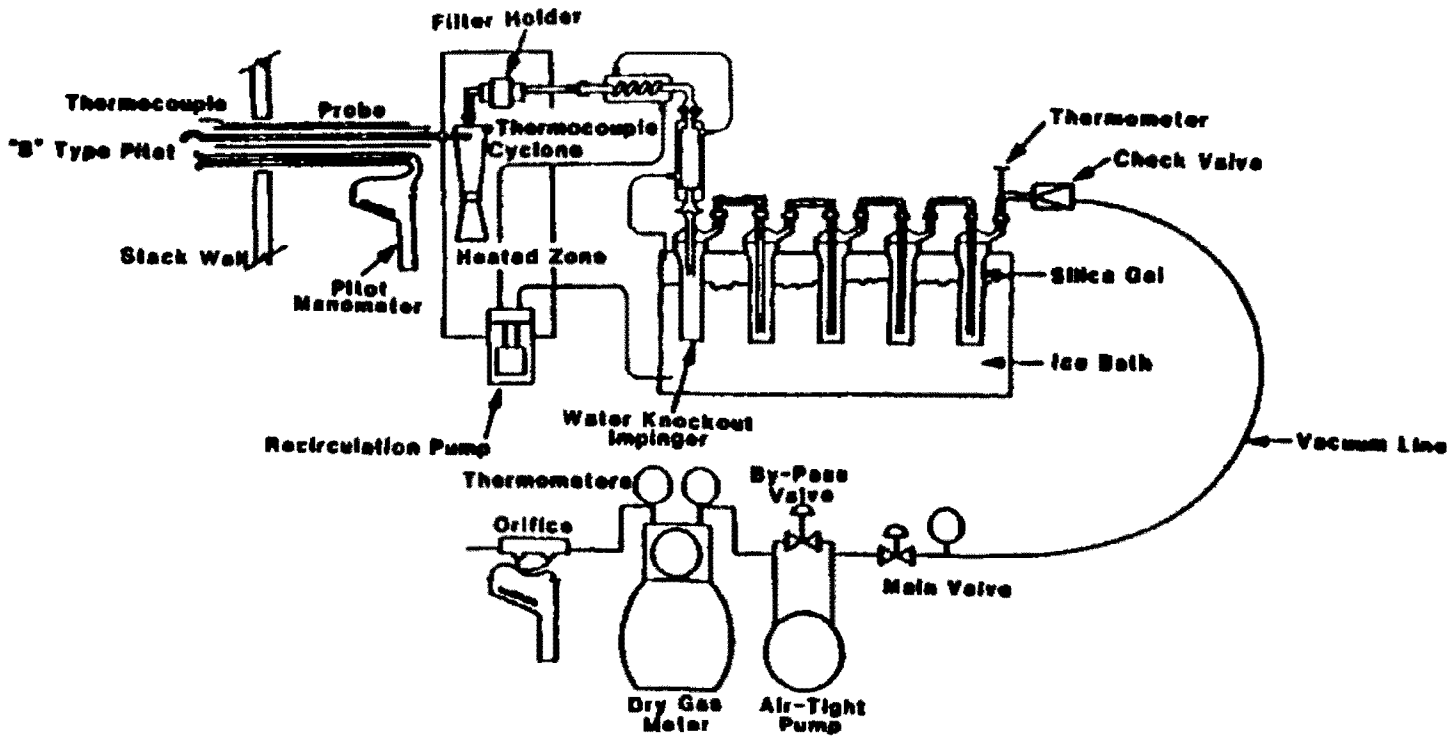

Figure 1. Semi-VOST train diagram.

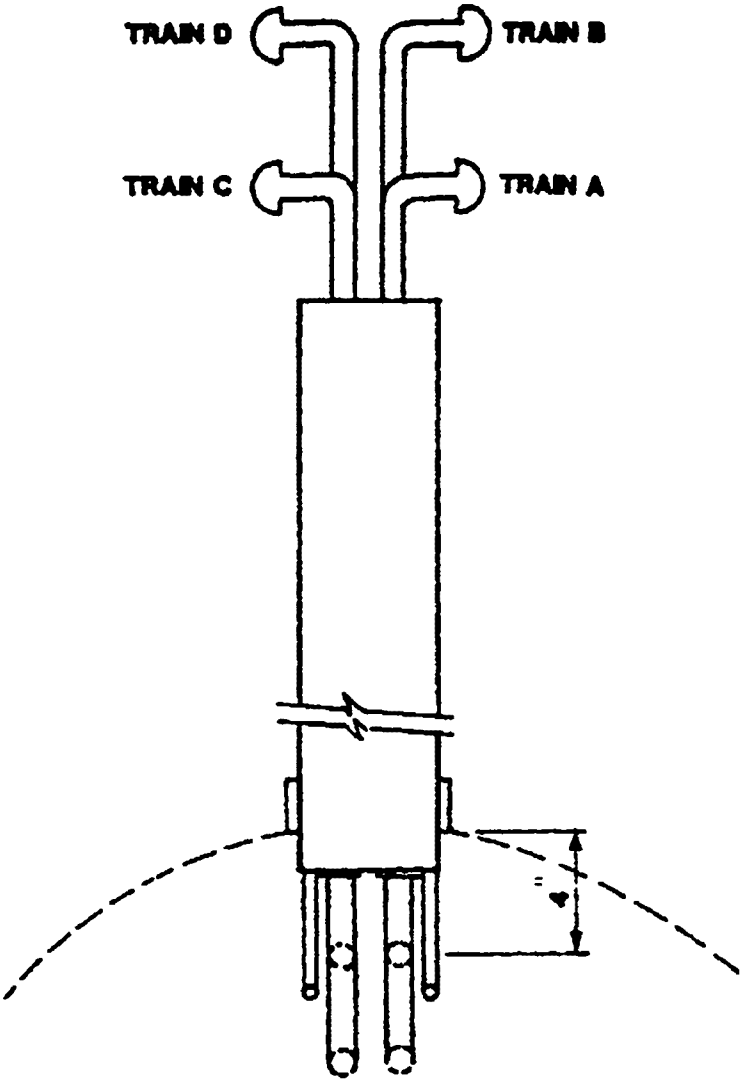

Figure 2. Quad probe.

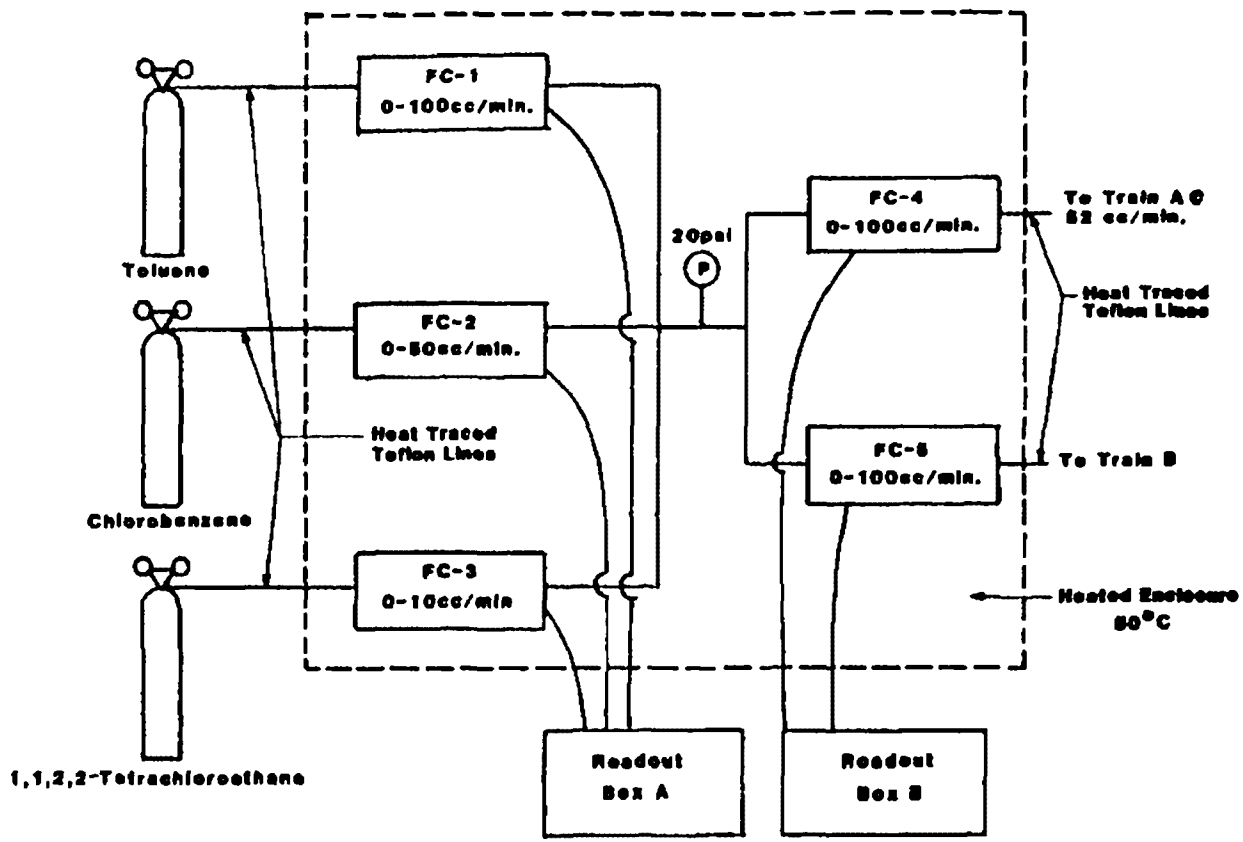

Figure 3. Dynamic spiking apparatus.

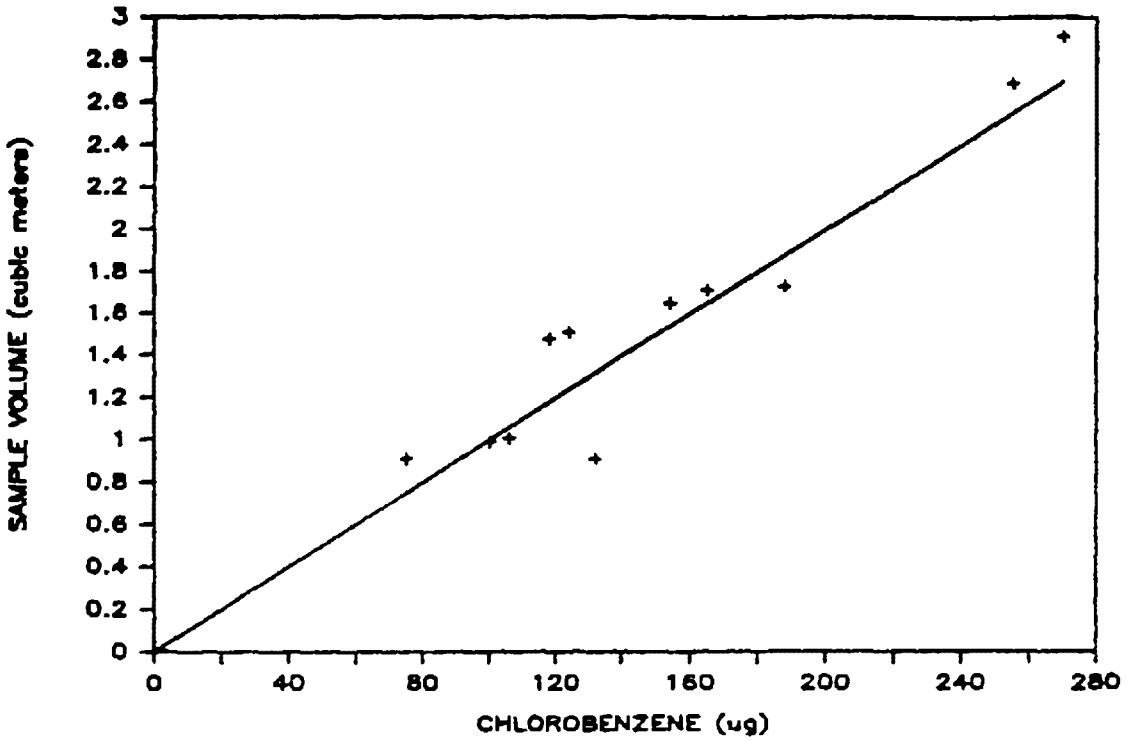

Figure 4. Distributive sample volume collected versus chlorobenzene concentration measured.

DETERMINATION OF ORGANIC AND INORGANIC CHLORINE IN USED AND WASTE OILS

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The U. S. Environmental Protection Agency (EPA) has issued a final rule prohibiting the sale for burning in nonindustrial boilers of used oils contaminated above specified levels with certain metals and total chlorine. When burned as fuel in a small boiler, the contaminants may be emitted to the ambient air at hazardous levels. This regulation establishes a rebuttable presumption that used oil containing more than 1,000 ppm total chlorine has been mixed with halogenated solvents and is a hazardous waste. Rebutting the presumption requires the seller of the oil to prove that this chlorine is not due to halogenated solvents or other hazardous halogenated organics. If the rebuttal is successful, the oil can be sold as fuel up to a level of 4,000 ppm total chlorine.

Methods for determination of total, inorganic, and organic chlorine were investigated and developed to provide the regulated community with appropriate test methods to meet the chlorine testing requirements of this regulation.

Total chlorine was determined by Parr oxygen bomb combustion followed by ion chromatography (IC). An aqueous extraction method, developed for determination of inorganic chlorine, involves the dissolution of an oil sample in toluene (to reduce the effects of surfactants on the extraction) followed by three sequential aqueous extractions and analysis of the combined extracts by IC. Organic chlorine is determined from the difference between total and inorganic chlorine.

These methods were evaluated on both unspiked and spiked virgin and waste oils. Recoveries of total chlorine (when spiked as both organic and inorganic species) of around 90% were achieved at levels between 1,000 and 10,000 μg/g in the presence of water levels ranging from 0 to 50 percent. Recoveries of inorganic chlorine around 90% were achieved at levels between 1,000 and 5,000 μg/g inorganic chlorine.

DETERMINATION OF ORGANIC AND INORGANIC CHLORINE IN USED AND WASTE OILS

1. Introduction

More than 1 billion gallons of used lubricating oil are produced in the United States annually. A significant fraction is sold for burning in small nonindustrial residential, commercial, or institutional boilers, typically after blending with virgin nos. 4 or 6 fuel oils. These used oils frequently arrive at fuel reprocessing or blending facilities contaminated with chlorinated solvents, lead, cadmium, and arsenic.[1] These contaminants may be present as a result of the oil's use or may have been added through mixing with hazardous waste. Reprocessing, with the exception of rerefining, typically fails to remove these contaminants.

When burned as fuel in a small boiler, the contaminants or their combustion byproducts may be emitted to the ambient air in amounts high enough to present potential health hazards to exposed individuals. This concern has lead EPA to propose[2] and later finalize[3] a regulation prohibiting the sale and burning of used oil contaminated at levels in excess of those given in Table I. When a person first claims used oil fuel meets these specification levels, he must obtain an analysis or other information to support the claim.

The final rule establishes a rebuttable presumption that used oil containing >1,000 ppm total chlorine is mixed with halogenated hazardous waste and, therefore, is a hazardous waste. (Because total halogen content cannot easily be determined in the field or laboratory, EPA has agreed to interpret "total halogen" in the final rule as total chlorine.[4]) The presumption may be rebutted by showing that the used oil has not been mixed with hazardous wastes (e.g., by showing it does not contain significant levels of halogenated hazardous constituents). Used oil presumed to be mixed with hazardous waste is subject to regulation as hazardous waste fuel when burned for energy recovery.

In addition, the rule establishes a specification for used oil fuel (i.e., used oil not mixed with hazardous waste) that is essentially exempt from all regulation and may be burned in nonindustrial boilers, provided that allowable levels for designated toxic constituents, flash point, and total chlorine (4,000 ppm) are not exceeded. Used oil exceeding any of the specification levels is termed "off specification used oil" and is subject to regulatory control. This second chlorine threshold is set to ensure that harmful emissions of hydrochloric acid are not emitted from the boiler or allowed to corrode it and reduce its efficiency. The decision process to determine whether the oil can be burned is shown in Figure 1.

The rebuttable presumption has changed from the proposed to the final regulation. In the proposed regulation, the presumption was based on proving that most of the chlorine was inorganic and thus not hazardous. The final regulation requires the seller of the oil fuel to prove that none of the solvents listed under EPA Hazardous Waste Numbers F001 and F002 is present at > 100 ppm or that no other hazardous chlorinated organics are present. These include the degreasing and spent halogenated solvents methylene chloride, tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene, 1,1,2,2-tetrachloroethane, dichlorodifluoromethane, and 1,1,2-trichloro-1,2,2-trifluoroethane.

Between proposal and final rulemaking, EPA decided that levels of inorganic chlorine seldom would cause an oil to exceed the 1,000-ppm level. In addition, EPA based their presumption on the total chlorine level because a practical method for determining the organic chlorine content was unavailable.

Between the time of the proposal and the final rulemaking, the EPA Office of Solid Waste (OSW), and its contractor, Research Triangle Institute (RTI), investigated methods for determining total, inorganic, and organic chlorine in used and waste oils. The results are summarized here and are detailed elsewhere.[5] Another study evaluating methods for determining total chlorine in used and waste oils is in progress. Results will be presented at the EPA/OSW Symposium on Solid Waste Testing and Quality Assurance in July 1986.

2. Development and Validation of Sample Preparation and Analysis Procedures for Total, Inorganic, and Organic Chlorine

2.1 Results of Literature Review

A literature review was conducted to identify the sources and composition of chlorine and other halogens in used and waste oil and to evaluate the previous development and testing of methods for determining chlorine in waste oils. This review indicated that automobile crankcase, industrial hydraulic, and metalworking oils account for nearly two-thirds of the waste oil produced in the United States.[1,6] Major chlorine sources in waste oils are chlorinated solvents deliberately added to the oil, with smaller quantities of other chlorinated organics entering the oil through normal use. Waste oil sampling and aliquoting procedures greatly influence testing program results. Interpretation of results from such testing should consider the representativeness of the sampling, the laboratory aliquoting, and the potential contribution of bottom sediment and water in determining the oil's chlorine content.[7,8]

Methods for determining total chlorine and other halogens have included oxygen bomb combustion/titrations, sodium alcoholate extraction/titration, x-ray fluorescence, neutron activation analysis, microcoulometric titration by an analyzer, oxygen bomb combustion/ion chromatography (IC), and field kits using a chemical colorimetric reaction or a flame photometric response.[9-11].

Methods for determining inorganic chlorine include dissolution of the oil in methyl isobutyl ketone (MIBK), followed by aqueous extraction followed by ion chromatographic or automated chloride analyzer analysis[10] and speciation by a total chlorine analyzer.[5]

Methods for determining organic chlorine as specific organics by gas chromatography/mass spectrometry (GC/MS) generally do not account for all of the chlorine expected from a total determination.[5,9]

2.2 Selection and Development of Test Methods

2.2.1 Total Chlorine Determination. Based on the literature review and our familiarity with these techniques, Parr oxygen bomb combustion followed by IC were selected for determining the total chlorine content of waste oils.[9,12]

The sample (0.5 g) is oxidized by combustion in a bomb containing oxygen under pressure. The liberated halogen compounds are absorbed in a sodium carbonate/sodium bicarbonate solution. Approximately 30-40 min. are required to prepare an oil sample by this method. Samples with very high water content (>50%) may not combust efficiently and may require the addition of a mineral oil to facilitate combustion.

The resulting aqueous sample is injected directly into the ion chromatograph and is carried through the separator column under high pressure by a continuous eluent flow. The separated ions are then passed through a post-separator-column suppressor device that converts the analyte ions into a highly conducting form while converting the eluent ions into a less conducting form. Detection is typically by conductivity. Sample analysis requires approximately 15 min.

The precision and accuracy of IC for determining chloride, fluoride, and bromide in aqueous solution are around 5% RSD and 90% recovery for levels >0.1 mg/l in solution. Detection limits are better than 20 μg/l for chloride and fluoride.

IC is an attractive analytical finish because several halide ions--chloride, bromide, and fluoride--may be determined simultaneously, although bromide in combusted waste oils is best detected with electrochemical detection. If a total halogen determination is desired, these other halogens must also be quantified. In this study, data are reported for both chlorine and fluorine.

2.2.2 Inorganic Chlorine Determination. An aqueous extraction method was developed for determining inorganic chlorine. The method involves the dissolution of an oil sample in toluene (to reduce the effect of surfactants on the extraction) followed by three sequential, aqueous extractions and analysis of the combined extracts by IC. Approximately 2 to 3 hr. are required to obtain the combined extracts. Attempts to develop a method to measure organic chlorine directly were unsuccessful because of losses of the volatile chlorinated constituents during the extractions. Instead, organic chlorine is determined by the difference between total and inorganic chlorine measured on separate aliquots of the same sample.

To ensure that the "oil phase" could be separated from the aqueous phase, the oil sample was dissolved in an organic solvent prior to extraction, as is the case with the qualitative ASTM procedure,[13] which recommends MIBK. In a previous study,[9] MIBK was found to interfere with halide determination by IC. Discussions with Dionex, a manufacturer of IC systems, disclosed that toluene may be used successfully instead of MIBK if the sample sits for a sufficient time to allow the toluene that partitions into the aqueous phase to separate from it and evaporate.

Initially, duplicate 2-ml aliquots of a spiked oil sample were placed in 40-ml glass centrifuge tubes and 20 ml of toluene added to each to dissolve the oil. Then 10 mL of water were added to each tube and the samples vortexed and centrifuged. A white, insoluble material, probably a result of surfactants in the oil, formed at the toluene/aqueous phase interface of both samples. When the toluene and aqueous phases were analyzed for halide content, total recoveries for both chloride and fluoride were 47%, with a greater quantity of each

remaining in the toluene phase. It was concluded that most of the organic chlorine was probably lost in the extraction procedure and that the inorganic chlorine was incompletely extracted or trapped in the white emulsion at the interface of the two phases.

To test the efficiency of this extraction procedure for inorganic halides, a virgin motor oil was spiked with halide solution. A 2-ml aliquot of the spiked oil was extracted three successive times with 10-ml portions of deionized water. Each extraction removed approximately 25% of the available chloride and fluoride. The three extractions removed approximately 60% of the fluoride and chloride.

An alternate extraction procedure was designed that involves a 1:100 dilution of oil with toluene to reduce the level and impact of surfactants associated with the oil. The procedure's extraction efficiency was evaluated by analyzing a variety of spiked virgin and waste oils. One ml of the oil was dissolved in 100 ml of toluene, the sample was thoroughly mixed, and a 20-ml aliquot of this mixture was removed and extracted sequentially three times with deionized water. After each extraction, the aqueous layer was transferred by disposable pipet to a beaker and the toluene allowed to evaporate. Chloride and fluoride in the three separate extracts were determined by IC. The total mass of chloride and fluoride removed per extraction was calculated so that carry-over from extract to extract was not included in the next extraction. This procedure was adopted for determining inorganic chlorine in waste oils.

2.3 Sample Preparation Procedures

2.3.1 Homogenization Procedure. Immediately before removing an aliquot for Parr bomb combustion, each sample was homogenized by vigorously shaking the closed sample container. None of the analyzed samples required the addition of a surfactant to emulsify an insoluble fraction. Because loss of volatile organic components could occur during the homogenization step, the collected samples should have only enough head-space to ensure complete mixing. Replicate and spiked samples were used to evaluate the homogenization procedure.

2.3.2 Preparation of Inorganic Halide-Spiked Oil. Virgin and waste oils, characterized for total halogen content, were spiked with known quantities of an aqueous mixture containing fluoride and chloride such that the amount of water added was approximately 25% of the total volume. The resulting fluoride and chloride levels were between 1,000 and 6,000 μg/g. Each oil and water mixture was shaken in a nearly headspace-free Nalgene® bottle until a homogeneous emulsion formed.

2.3.3 Preparation of Organic Halogen-Spiked Oil. Virgin and waste oils were spiked with water and with either trichlorotrifluoroethane (TFE) or an organic mixture consisting of equal volumes of TFE, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene. The resulting mixtures contained 5 to 50% water and 5,000 to 20,000 μg/g fluorine and chlorine. Each oil mixture was homogenized as described in 2.3.2.

2.3.4 Preparation of Mixed Organic/Inorganic Halogen Spiked Oil. Virgin and waste oils were first spiked with an aqueous inorganic halogen mixture as described in 2.3.2. Then an organic halogen mixture

(as described in 2.3.3) was added to the emulsion that formed, and the sample shaken again. The resulting oil mixtures contained approximately 25% water and 2,000 to 20,000 µg/g fluorine and chlorine.

3. Results and Discussion

3.1 Total Chlorine Determination

Virgin and waste oils, both unspiked and spiked, were analyzed in duplicate or triplicate for chlorine and fluorine content to evaluate the homogenization and Parr bomb combustion procedures. Results are summarized in Table II. The precision of the measurements, expressed as the relative percent difference (RPD) for duplicate analyses or relative standard deviation (RSD) for triplicate analyses, is an indicator of the oil sample's homogeneity. The chlorine and fluorine RSDs and RPDs for all samples analyzed ranged from 1 to 16%, indicating that the homogenization procedure is adequate for samples of this type.

Chlorine and fluorine recoveries obtained for the spiked virgin and waste-oil samples were used to evaluate the homogenization and Parr bomb combustion procedures. Recoveries from the oil samples ranged from 85 to 101% for chlorine and 73 to 90% for fluorine. In general, recoveries of total chlorine (when spiked as both organic and inorganic species) of around 90% were achieved at levels between 1,000 and 10,000 µg/g in the presence of water levels ranging from 0 to 50%.

The method detection limit has not been evaluated, but chlorine and fluorine levels of 50 µg/g in the original oil can be determined. If 0.5 g of an oil containing 50 µg/g chlorine is combusted and the combustate diluted to 100 ml, the IC will measure a solution of around 250 µg/l chloride.

3.2 Inorganic Chlorine Determination

Duplicate aliquots of inorganic halogen-spiked virgin motor oil were extracted according to the procedure described in 2.2.2, yielding chloride and fluoride recoveries of 103 and 70%, respectively. However, the same oil spiked with both inorganic and organic halogen did not mix well, and duplicate analyses of this sample yielded average chloride and fluoride recoveries of 48 and 46%, respectively. The spiked oil sample was allowed to stand overnight, was remixed, and then reanalyzed, starting with the toluene dissolution step. Recoveries for chloride and fluoride were 92 and 96%, respectively.

To test the procedure further, three types of waste oil samples (hydraulic, crankcase, and grinding/cutting) were analyzed in triplicate for extractable chloride and fluoride. With the exception of the chloride value for the grinding and cutting oil, the RSDs were less than 25%. The hydraulic and crankcase oils were then spiked with both inorganic and organic halogen and analyzed in duplicate. Chloride and fluoride recoveries from the spiked hydraulic oil were 42 and 40%, respectively; the chloride and fluoride recoveries from the spiked crankcase oil were 65 and 55%, respectively.

There is a problem in obtaining a representative aliquot from the oil dissolved in toluene. Water in the oil tends to form small beads and settle to the bottom of the flask. No improvement in recoveries

was observed, even when the solution was stirred while an aliquot was removed. To eliminate the aliquoting step, an alternate procedure was developed. A 0.2-g aliquot of a spiked hydraulic waste-oil sample was weighed by difference directly into a 40-ml centrifuge tube, 20 ml of toluene were added, and the tube was vortexed to dissolve the sample. This results in a 1:100 dilution of the oil sample as in the previous method. The sample was extracted sequentially three times with 10-mL portions of deionized water. The aqueous extracts were analyzed individually for chloride and fluoride by IC. Using this procedure, 97% of the extracted fluoride and 98% of the extracted chloride are removed in the first extraction. Similar results were achieved with waste crankcase and virgin motor oils. Therefore, it is recommended that the extracts be combined and the total extract volume measured so that the sample can be analyzed by a single injection into the IC.

To ensure that no organic halogen is extracted into the aqueous phase, four aliquots of a virgin motor oil sample spiked with organic halogen were extracted according to the proposed procedure. The spiking levels were 10,474-μg/g chlorine and 1,088-μg/g fluorine. The aqueous phase from the first extraction of each aliquot was analyzed for total organic halogen on a Xertex-Dohrmann Total Organic Halogen Analyzer. Analyses of the extracts indicate that less than 0.1% of the volatile halogen species partitioned into the aqueous phase.

An attempt also was made to analyze the extracted toluene-oil phase for remaining halogen species. This effort proved unsuccessful because the toluene was found to contain either chlorinated organics or other substances that interfered with the IC determination.

The entire procedure requires approximately 2 to 3 hr. The steps of weighing, adding toluene and water, and mixing require 15 min. Centrifuging and removing the aqueous phase requires 15 to 30 min. Evaporation of toluene requires 1 hr. Combining extracts and measuring the final extract volume requires 10 min.

The precision and accuracy of the extraction/IC method for determinations of inorganic halogens were evaluated by testing spiked virgin and waste oils. The results (Table III) indicate that recoveries greater than 90% and precisions around 10% RSD are achievable at chlorine and fluorine levels between 1,000 and 5,000 μg/g.

The method detection limit has not been evaluated, but inorganic chlorine and fluorine levels of around 50 μg/g in the original oil can be determined. If 0.2 g of oil containing 50-μg/g inorganic chlorine are extracted and the resulting combined extract volume is 30 ml, the extract concentration should be 33 ug/L chloride.

4. Conclusion

An analytical approach has been developed and tested on virgin and waste oils to allow determination of total and inorganic chlorine and other halogens by direct measurement and organic chlorine and other halogens by difference. This approach is shown in Figure 2.

It is not clear whether inorganic chlorine will present a problem either in classifying a used oil as a hazardous waste fuel or as an off-specification fuel. The methods presented here offer a workable

approach to addressing the issue and should be considered. The findings presented here do not necessarily reflect EPA policy.

5. Acknowledgments

The authors acknowledge A. Turner of RTI for carrying out the IC analyses. N. Rothman of ENSECO, R. Tarrer of Auburn University, and M. Branscome of RTI are thanked for providing the waste oil samples. We acknowledge E. Williams for preparing the manuscript.

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TABLE I. USED OIL FUEL SPECIFICATIONS FOR OIL THAT MAY BE BURNED IN NONINDUSTRIAL BOILERS

Constituent/Property	Allowable level for burning without regulation
Arsenic	<5 ppm
Cadmium	<2 ppm
Chromium	<10 ppm
Lead	<100 ppm
Total Chlorine	<1,000 ppm[a]
	<4,000 ppm[b]
Flash Point	>100°F

[a]Level presuming mixing with hazardous waste.
[b]Level above which burning is not permitted if presumption can be rebutted.

TABLE II. ANALYSES OF OIL SAMPLES FOR TOTAL CHLORINE AND FLUORINE (ug/g)

Sample	Chlorine				Fluorine			
	Expected[a]	Measured ± s.d.	% RSD (RPD)	% Recovery	Expected[a]	Measured ± s.d.	% RSD (RPD)	% Recovery
Virgin Oils								
Automobile crankcase								
Spiked w/inorganic halides	5,553	5,523	--	99	1,091	820	--	75
Spiked w/25% water and TFE	8,245	7,093 ± 200	(4)	86	4,357	3,917 ± 93	(3)	90
Spiked w/25% water, inorganic halides, and TFE	13,610	13,787 ± 120	(1)	101	5,408	4,858 ± 22	(1)	90
Spiked w/25% water and OM	10,474	8,922 ± 210	2	85	1,088	899 ± 24	3	83
Spiked w/inorganic halides and OM	15,832	14,678 ± 109	1	93	2,159	1,693 ± 18	1	78
Transmission fluid								
Spiked w/5% water and TFE	16,625	14,554 ± 283	(3)	88	8,846	7,240 ± 253	(5)	82
Waste Oils								
Automobile crankcase								
Unspiked	--	2,372 ± 360	15	--	--	101 ± 10	10	--
Spiked w/inorganic halides and OM	18,101	16,271 ± 517	(4)	90	2,269	1,655 ± 51	(4)	73
Hydraulic oil								
Unspiked	--	4,487 ± 321	7	--	--	51 ± 2	4	--
Spiked w/inorganic halides and OM	20,215	17,403 ± 570	(5)	86	2,219	1,803 ± 46	(4)	81
Grinding and cutting oil								
Unspiked	--	10,802 ± 1,462	14	--	--	98 ± 3	3	--
Automobile crankcase								
Unspiked	--	271 ± 25	(13)	--	--	115 ± 8	(10)	--
Unknown source								
Unspiked A	--	1,372 ± 10	(1)	--	--	44 ± 4	(14)	--
Unspiked B	--	827 ± 28	(4)	--	--	41 ± 2	(6)	--

[a]Expected value is the chlorine or fluorine content based on spike levels.
s.d. = standard deviation.
TFE = trichlorotrifluoroethane.
OM = Organic mixture: 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and TFE.

TABLE III. RESULTS OF SEQUENTIAL EXTRACTIONS OF OIL SAMPLES FOR INORGANIC HALOGENS μg/g

Sample[c]	Expected[a]	Measured ± s.d.[b]	RSD	% Recovery
1. Virgin crankcase oil				
Chlorine	5,449	5,482 ± 47	1	101
Fluorine	1,090	865 ± 3	1	79
2. Waste hydraulic oil				
Chlorine	5,620	5,405 ± 143	4	96
Fluorine	1,115	1,054 ± 26	4	95
3. Waste crankcase oil				
Chlorine	5,627	4,315 ± 90	3	77
Fluorine	1,242	312 ± 27	12	25

[a]Expected value is the inorganic chlorine or fluorine based on spike levels.

[b]Measured value is the inorganic chlorine or fluorine based on analyses of aqueous extracts.

[c]All spiked with inorganic and organic halogen mixture

s.d. = standard deviation

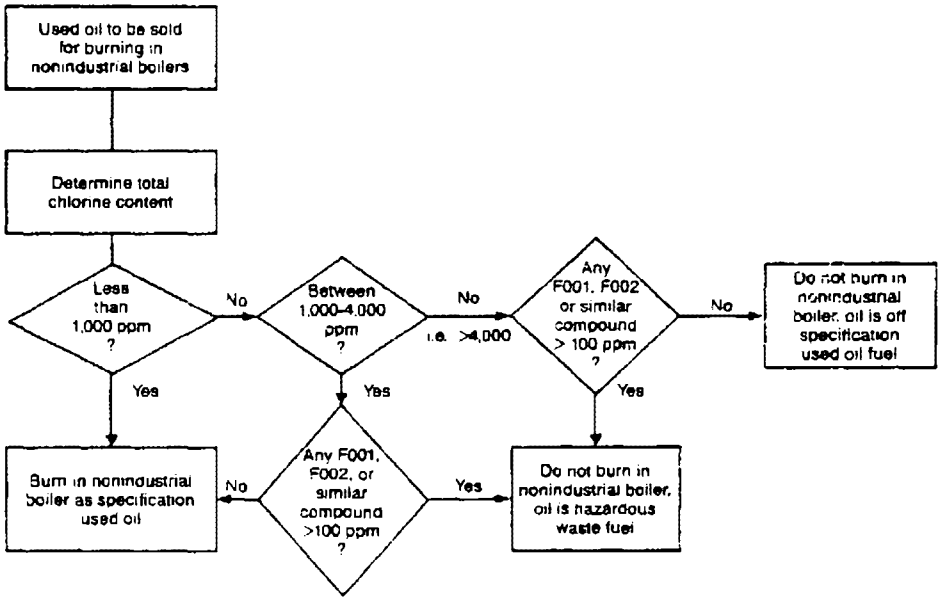

Figure 1. Decision flow chart for regulation of burning of used oil and waste oil fuel in nonindustrial boilers–total chlorine specification.

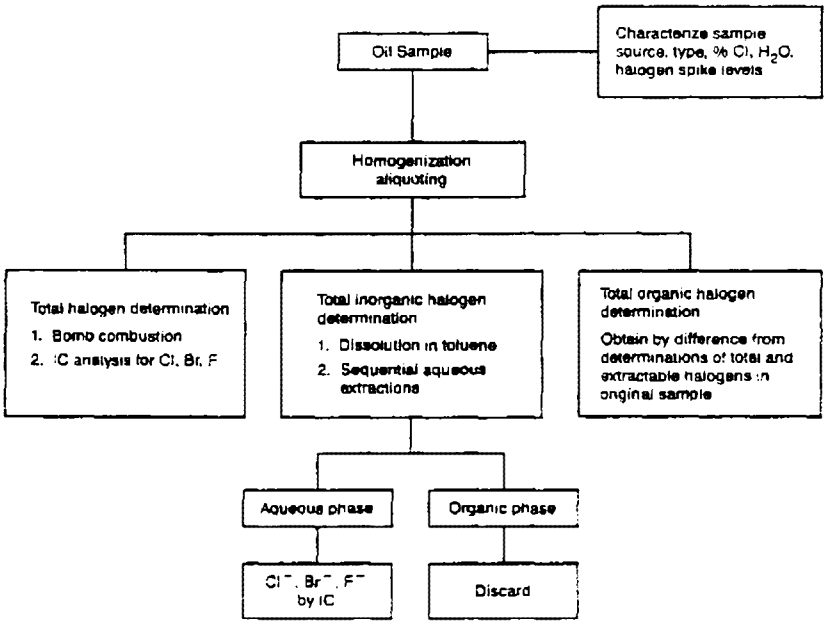

Figure 2. Approach for halogen speciation in waste oils.

EVALUATING THE FIELD PERFORMANCE OF HIGH EFFICIENY AND CATALYTIC WOOD STOVES

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I. Introduction

The superior laboratory performance of catalytic and so-called "high efficiency" wood stoves in reducing air emissions and improving combustion efficiency had little impact in market penetration of these appliances through the winter of 1984-5. Despite an Oregon certification standard and a Colorado statute, fewer than 10% of sales in the Northeast included these high performance stoves. Convinced that both retailers and consumers required credible information about the field performance of these appliances, the Coalition of Northeast Governors (CONEG) and the New York State Energy Research and Development Authority (NYSERDA) planned a field performance study to examine emissions, efficiency and stove safety of high performance stoves versus conventional air tight stoves. The Environmental Protection Agency's (EPA) interest in the durability of catalysts over time prompted their commitment to co-funding the two-year study. EPA's decision to develop a New Source Performance Standard (NSPS) for wood stoves coincided with CONEG and NYSERDA's decision to conduct the study.

In June, 1985, CONEG, serving as project coordinator, issued a $300,000 Request for Proposal (RFP) with the following objectives:

(1) to measure the fuel savings of catalytic stoves, add-on catalysts and high efficiency stoves against conventional air-tight stoves in Vermont and New York State homes under actual operating conditions over a period of two heating sessions;

(2) to measure the creosote build-up in the stovepipe chimneys of both conventional air-tight stoves and the three categories of high performance stoves listed in (1);

(3) to measure the durability of catalytic stoves via laboratory tests of combustion efficiency of the combusters after one season, and after two seasons, and in comparison to earlier laboratory tests of new combusters paid for by participating manufacturers;

(4) to measure the total suspended particulates (TSP) emissions of catalytic high efficiency and conventional air-tight stoves over the duration of two heating seasons--1985-6 and 1986-7;

(5) to measure the POMs emmissions in a selected subsample of the stoves listed above tested for TSP emissions;

(6) to report these findings in comparison to measurements taken of control wood stoves without catalytics and with high efficiency design characteristics; and

(7) to discover possible stove or catalytic design changes or operator characteristics which improve the performance of catalytic stoves.

In August, 1985, CONEG's Technical Review Committee recommended OMNI Environmental Services, Inc. as the strongest bidder of the five qualifying proposals. Since September 1, 1985, OMNI has been under contract to CONEG.

II. Research Tasks and Methodology

To meet the objectives of the study, OMNI selected a total of 66 volunteer households--half from Washington County, Vermont and half from the Warrensburg, New York area. Over 140 households volunteered for the study. The Vermont Agency for Environmental Protection and the New York State Department of Environmental Protection utilized direct mail and media outreach to recruit volunteers for the study. Each applicant mailed in a completed questionnaire providing demographic, structural and wood appliance information. OMNI utilized several criteria--previous wood stove operation experience, safe chimneys, stove and instrumentation installation ease, participant eagerness, geographical proximity and building structure representativeness--to narrow the list. OMNI staff visited each applicant household before making its final selections.

Each of the participants were placed in one of three categories--Group one (32) were catalytic, high efficiency (characterized by extensive baffles, secondary combustion chambers, secondary draft controls, insulated firebox and/or other features to increase efficiency above 60% in accredited laboratory tests) or conventional stoves instrumented for two years to measure accurately fuel usage, stack, indoor and outdoor temperatures, and TSP emissions. Group Two (24) are homeowners who switch over from catalysts

or high efficiency stoves to conventional stoves from the first year to the second or vice-versa. Group Three (6) are homeowners with catalysts which have experienced at least one year of usage before the 85-86 heating season and which will be tested throughout the next two heating seasons as their performance permits. Six homes are available as back-ups in the event of drop-outs or methodological problems associated with the other 60 stoves.

All the participant homes have had their chimneys cleaned at the beginning of the study and will receive cleanings twice during each heating season. The creosote collected from the cleanings will be weighed; a sample will be sent to the Solar Energy Research Institute where a chromatography analysis will determine the chemical composition. Wood piles of every participant are measured and moisture content is determined at the beginning, during the middle and at the end of each heating season. Each participant will also receive a free energy audit of their homes during the study's first year. Each participant agrees to keep a daily log for recording unusual events which may affect fuel usage (e.g. grandmother comes for a visit, chimney fire).

Group One homes have programmable microprocessing/data logging assemblies and in site emissions samplers installed. The former compiles loaded fuel weights and stack, indoor and outdoor temperatures; the latter collects TSP emissions. Of the thirty-two stoves in this category, twelve are catalytic stoves; twelve are catalytic add-on and retrofit units; four are high efficiency stoves; and four are conventional air-tight stoves. (Table 1). Group One homes will provide the most accurate fuel usage data and the only emissions data for all stove types. Group One households will also provide

two years of efficiency data for the catalysts.

Group Two homes are the so-called cross-overs: one year each participant has a high performance stove; another year the household uses its own conventional air-tight stove. The high performance stoves include ten catalytic stoves; ten catalytic add-ons or retrofit units; and four high efficiency stoves. The major research objectives served by Group Two households are the creosote build-up and fuel usage comparisons between high performance and conventional air-tight stoves. Most of the wide-ranging variation in usage explained by structural and operator characteristics are controlled for in this group. Special effort has been made to assure that the conventional and high performance stoves are similarly sized in each household.

Group Three households have catalyst stoves or add-ons with one or more previous years of operating experience. These catalysts are tested for efficiency and emissions in the laboratory at the beginning and end of the 85-86 heating season and the following one, as performance permits. This group is important for its contribution to data on the durability of catalysts. Estimates of the previous wood fuel usage experienced by each catalyst are gauged by operator interviews.

Beginning in July 1985, the Technical Development Corporation--the program manager for CONEG, NYSERDA and EPA--solicited manufacturer interest in participating in the study. By late August, a dozen manufacturers, including at least four catalyst stove, four catalyst retrofit, and four high efficiency non-catalyst firms, had volunteered to donate up to twelve

stoves or catalysts each. By the time OMNI made the final manufacturer selection in October, another five manufacturers had volunteered. Several of the selected models had passed Oregon's certification test, incuding high efficiency, non catalytic stoves. Twelve were chosen in all, representative of models found in New York and Vermont and representative of the stove designs and emissions performances available nationwide. A listing of the participating manufacturers is included in Appendix A.

III. Data LOG'r and Emissions Sampler Description and Operation

Two pieces of specialized equipment are being used for this project. One is a computerized data acquisition system/controller, used for recording temperature, wood weight, coal bed status and flue gas oxygen concentration data. This unit, dubbed the Data LOG'r TM, also controls the sampling intervals of the emission sampling system described below. An electronic scale, mounted beneath a woodbasket, weighs the amount of wood used in each woodstove. This data, with the condition of the coal bed at the time of fuel loading, are recorded in a solid state memory device. Four weeks of continuous data can be recorded at 5-minute intervals without downloading.

The Automated Woodstove Emissions Sampler (AWES) is controlled by the Data LOG'r. At preprogrammed times, the AWES pulls flue gas through a heated filter and an XAD-2 sorbent resin cartridge to obtain a particular sample. The AWES is designed to operate unattended for one week, resulting in an integrated sample for that period. The sampling rate is controlled by a critical orifice, which maintains constant flow. The total sample volume is determined by the time the AWES pump has operated. An oxygen sensor

measures flue O2 concentrations, which are recorded by the Data LOG'r.

IV. Testing Methodology

The total sampler particulate catch and gas volume sampled allow calculation of particulate concentration in the flue (grams/m3). Wood use data, temperatures and flue oxygen concentrations are used to calculate flue gas flow rates. Particulate emissions per heat output (grams/10 6 joule) can be calculated using wood moisture and stove efficiency values. Emission rates and factors (grams/hour and grams/kilogram fuel) can also be calculated.

Samplers are placed in various locations in the stove/chimney system. Most homes are equipped with 2 AWES systems during sampling periods (one week per month, 4 months per heating season). Sampler probes are placed below a catalytic combustor, at the stove flue collar, above an in-flue catalytic add-on or at the chimney exit. This arrangement allows determination of catalytic combustor efficiency, measures disposition of material in the chimney system (as creosote) and actual emissions to the atmosphere. Flue collar measurements allow comparison of stove performance between homes while minimizing flue deposition effects.

POM analysis will be conducted on extracts from the XAD-2 resin. GC/MS analysis for eight POMs will be conducted. These POMs will be reported in the same units used for particulates.

The AWES sampler is currently undergoing comparative testing with a modified EPA Method 5 train to determine comparability. Preliminary results indicate

good correlation.

V. Problems Encountered

The logistics of conducting in-home monitoring and testing in 66 homes in two regions simultaneously under mid-winter conditions are complex. Poor weather and widely distributed study homes slow all activities. Homeowner cooperation has been good, in part due to careful pre-study screening. Several equipment problems delayed the start of data acquisition. Data LOG'r systems were found to have several defective integrated circuits which require software corrections and chip replacement. Additionally, some units were found to generate low intensity radio frequency (RF) signals, which in remote areas with poor signal strength interfered with TV and radio reception during data acquisition periods.

AWES samplers experienced few problems when located inside the home, but rooftop samplers required some modifications to withstand winter conditions. Sample line heaters and lower compartment heaters were added to prevent freezing. In one case a large ham radio antenna created signal interference for the AWES pump relay and O2 sensor. Rooftop installations have been difficult to service due to heavy snow.

Some homeowners have reported difficulties with study stoves. Several catalysts have disintegrated after 3 months of use, requiring replacement. Condensation of water in some flues has resulted in ice buildup in lower chimney sections near the ash clean-out doors. In one case a water/creosote mixture leached through chimney masonry into the living area.

Some complaints of inadequate heat output have also been received. Overall, however, most homeowners appear to be quite pleased with their high efficiency stoves.

VI. Preliminary Test Results

Over three months of wood use, temperature and emission data have been collected in the 32 primary homes. Wood piles measurements and user log books are being compiled for 24 additional homes. Emissions data have been obtained for 6 existing catalytic stoves. Data processing and analysis is beginning as computer software is developed to compile the field data. Some preliminary findings include:

* Wood loading in stove appears to be lighter than previously thought. Values of 30 to 60 kilograms per cubic meter (5 to 9 kilograms per cubic foot) appear to be typical.

* Creosote accumulation is highly variable and appears to be a function of stove operation.

* Catalyst operating temperatures indicate that some combustors may not be operating for a significant fraction of stove operating time.

Data review and analysis will proceed rapidly through the spring and summer. An interim report will be presented to CONEG in mid-summer and will contain data from the first year of data gathering and analysis.

Table I. CONEG Study Stove Types

	Integrated Catalyst	Catalytic Add-on/ Retrofit	High Efficiency Conventional	Existing (Low Efficiency Conventional)
Group I (32 homes + 4 homes as back-ups-- mixed stoves)	12	12	4	4
Group II[a] (24 homes)	10	10	4	24 (one year only)
Group III (6 homes)	6	--	--	--
Totals	28	22	8	4

[a] Stove switched from conventional to high-efficiency device between heating seasons

Appendix 1

Manufacturers Participating in Catalytic Field Study

American Eagle	Catalytic
Brugger Exports	Low Emissions
Catalytic Damper, Inc.	Add-on
C & D Distributors	Add-on
CESCO Industries	Low Emission
Hearthstone	Catalytic
Nu-Tec	Add-on
Pacific Energy	Low Emission
The Earth Store, Inc.	Add-on
Vermont Castings	Add-on
Vermont Iron, Inc.	Catalytic
Woodcutters Manufacturing, Inc.	Catalytic

A SYSTEM TO OBTAIN TIME INTEGRATED WOODSTOVE EMISSION SAMPLES

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A novel system especially designed to obtain time integrated emission samples from woodstoves during normal in-home operation has been developed. The system is comprised of a programmable data logger, a particulate sampler, a wood-use scale, a coal bed status recorder, and temperature sensors. A continuous record of time and woodstove operational parameters is stored in a nonvolatile solid state memory cartridge. Particulate sampling frequency and duration are controlled by the data logger. Relatively infrequent, short-duration samples can be collected over a long time period to provide a representative integrated sample of woodstove emissions which are inherently highly variable. In addition to particulate emissions, woodstove use patterns, reliance on other heat sources, catalyst operation, and typical fuel load densities can be studied with the data base.

Preliminary data collected from homes in Vermont and Oregon during the 1985/1986 heating season are presented here. Mass of particles emitted per mass dry wood burned (emission factors), mass of particles emitted per unit heat output, and mass of particles emitted per hour of stove operation have been calculated for the woodstoves in these homes. Illustrative records of woodstove use and catalyst operation patterns are also presented.

Introduction

Residential wood combustion (RWC) is a significant source of particulate and carbon monoxide emissions.[1] Not only can RWC be considered as a major source of particles and carbon monoxide when compared with other major nationwide pollutant categories such as motor vehicles and industrial point sources (Table I), but locally the impact of RWC can be very high due to its seasonal and regional nature. Exceptionally high atmospheric concentrations of RWC pollutants are often reached during the heating season in communities with poor dispersion caused by valley terrain and wintertime inversions.[2,3] Due to the roof-level, residential source of RWC emissions, human exposure is at a near maximum. Particles originating from RWC contain polycyclic organic material (POM)[4] which has well-demonstrated carcinogenic and mutagenic properties.[5,6]

Unlike more traditional point sources, the combustion emissions from RWC are difficult to quantify. A wide variety of woodstove appliances are commercially available, a wide variety of wood fuel (wood species and moisture content) are utilized, and operating practices, of course, vary widely from home to home. This large number of possible parameters make laboratory testing of woodstoves of limited utility in assessing overall RWC emission levels characteristic of a community. In addition to the variability which is characteristic of RWC, woodstove emissions are pragmatically difficult to sample. Slow stack gas velocities, a high condensible organic content, and a relatively high water vapor content require special modifications of traditional stack sampling techniques to obtain accurate, reproducible results.[7]

Attempts to quantify RWC impacts by emission inventories, ambient sampling, tracers, and modelling have all met with only moderate success. The difficulty in quantifying wood use and emission factors for an area-wide, individualistic source such as RWC makes the results of emission inventory and dispersion modelling approaches, in most cases, illustrative rather than definitive. The ubiquitous chemical and physical characteristics of woodstove emissions limit the accurate application of ambient sampling, tracer, and receptor modelling approaches to specialized situations and, in most cases, results of such approaches can also be considered more illustrative than quantitative.

In an effort to measure woodstove emissions in a "real-world" setting and to provide data that will improve RWC impact assessment, a relatively low-cost programmable data logger (trademark Data LOG'r)/automated woodstoves emission sampler (AWES) system was developed. The system was designed specifically for the in-home, long-term integrated measurement of RWC emissions. Ancillary data, such as indoor, outdoor, flue, and catalyst temperatures, real-time wood usage, coal bed status, and auxillary heater operation are also automatically recorded with the system. The design and operation of the system, as well as preliminary data obtained at several homes during the 1985/1986 heating season, are presented here.

Instrument Design and Experimental Methods

A schematic illustration of the Data LOG'r/AWES configuration is shown in Figure 1. The AWES configuration shown in Figure 1 is primarily for the collection of particulate (including semi-volatile organic compounds) samples for subsequent mass determination and POM analysis. The sampling frequency, sampling duration, and sampling period are controlled by the Data LOG'r which is programmed prior to sampling. The sampling frequency used to generate the preliminary data presented here was once every 30

minutes. The sampling duration was one minute and the sampling period was one week. Consequently, a one week sample (10,080 minutes) represents 336 one minute samples collected at 30 minute intervals. Any combination of sampling frequency, period and duration could have been programmed.

A stainless steel inlet probe was attached to the woodstove or flue. Several points of attachment have been used depending on the stove type (i.e., conventional, integrated catalytic, or retrofit catalytic). The points of attachment generally used were: (1) the stove firebox, (2) the flue collar, (3) the flue above the retrofit device, or (4) the chimney exit. Teflon (trademark) tubing was used to connect the sampling probe to the AWES system. The Teflon tube was sloped such that any condensed water would drain into the heated filter chamber. The filter chamber was operated at 93 ± 25°C. A 100 mm binderless glass fiber filter was used in a glass EPA method 5 filter holder. After the filter, the sample flow was passed through a Teflon cartridge (3 cm I.D. X 9 cm length) containing approximately 30 grams of XAD-2 resin. The temperature of the XAD-2 resin was not controlled. Experimentation revealed that the XAD resin temperature was generally about 6°C above ambient temperature due to the heating effect of the filter chamber and the air pump motor adjacent to the XAD-2 column. After the XAD-2 column, the sample flow passed through approximately 300 grams of 6-16 mesh indicating silica gel to remove water. The sample flow then passed through a Millipore Corporation one liter per minute (nominal) critical orifice. The flow through each critical orifice was calibrated with a wet flow meter prior to installation into the AWES system. The sample flow was then passed through the pump. On the exhaust side of the pump, the oxygen content of the gas stream was measured with a Catalyst Research Corporation model 472062 oxygen sensor cell. The millivolt output (5-15 mv at 20% O_2) was recorded with the Data LOG'r. Flue gas oxygen content is a key parameter in the calculation of total flue gas flow (volume) during the sampling period. After passing through the oxygen cell, the sample stream was exhausted back into the woodstove flue to prevent any indoor air quality impact. A leak check of the sampling system was conducted upon installation at each home.

In addition to controlling the AWES sampler and recording the flue gas oxygen content, the Data LOG'r recorded: (1) time, (2) various temperatures measured with thermocouples and solid state temperature sensors, and (3) was interfaced with a scale and key pad which permitted wood used and coal bed status to be recorded. Table II is a summary of the data which were recorded with the Data LOG'r.

Room temperatures, the internal temperature of the Data LOG'r, the outdoor temperature, and the temperature at a point in or adjacent to any auxillary heater were measured with National Semiconductor LM334 solid state temperature sensors. The sensor in or adjacent to the auxillary heat source was used to determine the total time the auxillary heater was in use. A threshold temperature of 38°C was generally used for this purpose. Type K thermocouples were used to measure flue and catalyst temperatures. Catalyst temperatures in excess of approximately 316°C were used as an indication that the catalyst was ignited.

The Data LOG'r was interfaced with a commercially available electronic scale and a key pad. Wood was weighed each time it was added to the woodstove, and the homeowner entered a description of the coal bed status via the key pad at the time of wood addition. Four coal bed status categories were available for entry. These were: (1) empty or out, (2) even loading of glowing coals, (3) large pieces of burning wood, or (4) large pieces of unburned wood. The scale was calibrated upon installation at each home

with a 4.54 kg weight.

Each Data LOG'r contained an auxillary battery pack for operation during power failures. The length of any power failure was recorded. An audible system failure alarm was also a component of each Data LOG'r.

Data storage was accomplished with a Dallas Semiconductor nonvolatile 32K, solid state memory cartridge. The cartridge was removed from the Data LOG'r on completion of the week-long sampling period. The data from the memory cartridge was down-loaded via a specially designed data cartridge reader to a floppy disk in a compressed hexadecimal data format. Subsequent data manipulation was performed with IBM PC compatible software.

At the time of sampler installation, miscellaneous information such as stove use, stove make, model and age, wood species and age, and other household characteristics were obtained from the homeowner. Wood moisture content was also measured with a Delmhorst Instrument Company wood moisture detector.

The calculated mass of particles collected with the AWES system was the sum of: (1) the mass of particles collected with the heated filter, (2) the mass of material extracted from the XAD-2 resin, and (3) the mass of material removed from the probe, inlet line and interconnecting glassware with methanol and methylene chloride rinses. The XAD-2 resin underwent Soxhlet extraction with methylene chloride for 24 hours. The solution from the Soxhlet extraction, as well as the methanol and methylene chloride rinses, were evaporated at room temperature. The mass of the remaining residue was determined with an analytical balance using pre-weighed beakers. The mass of the filters before and after sample collection was also determined with an analytical balance. Beakers and filters (clean and with sample) were desiccated for 24 hours at 29 to 38% relative humidity. They were then weighed every six hours thereafter until a constant weight was achieved. Blanks were prepared for all aspects of the gravimetric/extraction/rinsing procedures.

Samples selected from POM analysis were spiked with surrogate standards. Three milliliters of a methylene chloride solution containing 6.00 mg/ml 9-phenylanthracene and 6.11 mg/ml 9-methylanthracene was added to the XAD-2 cartridges and allowed to stand for two hours prior to the Soxhlet extraction. Blank XAD-2 cartridges were also spiked and extracted. One half of the Soxhlet extract solutions were used for gravimetric determinations and one half were concentrated with a Kuderna-Danish flask. Analysis was conducted on the concentrate for eight lower molecular weight POM compounds by GC/MS. The eight compounds were: (1) napthalene, (2) acenapthene, (3) acenaphthylene, (4) fluorene, (5) phenanthrene, (6) anthracene, (7) fluoranthene, and (8) pyrene.

Three methods for normalizing and presenting particulate (and POM) data have been incorporated into the data reduction programs. These are: (1) mass of particles per mass of dry wood burned (emission factors), (2) mass of particles per unit of heat output, and (3) mass of particles per unit of time of stove operation. While it is outside the scope of this discussion to present the complete derivation of the equations used to calculate these three parameters, the formulas used are as follows:

Mass of Particulate Emissions/Mass Dry Wood Burned = (1)

$$(MP)(SV)/(FR)(SD)(1-(\%\ O_2/20.9\%)),$$

Mass of Particulate Emissions/Heat Output = (2)

$$(MP)(SV)/(FR)(SD)(HO)(EF)(1 + WDB)(1 - (\% O_2/20.9\%)),$$ and

Mass of Particulate Emissions/Time Stove Operation = (3)

$$(MP)(SV)(MWW)/(FR)(SD)(SP)(HWDB)(1 - (\% O_2/20.9\%)),$$

where,

MP is the mass of particles collected with the AWES system;
SV is the stoichiometric volume of dry gas produced from the complete combustion of wood with a correction for the carbon monoxide content typical of the various woodstove types (e.g., 2% by weight for traditional stove models). The stoichiometric volume can be calculated from the elemental carbon, oxygen, hydrogen, and nitrogen content characteristic of each species of wood;[3]
FR is the AWES flow rate as controlled by the critical orifice (approximately 1 lpm);
SD is the total sampling duration (sampling duration X number of sampling events);
% O_2 is the mean oxygen content of the flue gas during sampling;
HO is the heat output characteristic of each species of wood;[8]
EF is the efficiency factor characteristic of each stove model, burn rate, and wood moisture content. The EF value is the overall efficiency which is the product of the combustion and heat transfer efficiencies. Semi-quantitative estimates of combustion and heat transfer efficiencies can be made from woodstove operation conditions;[9]
WDB is the moisture content of the wood fuel on a dry basis;
MWW is the total amount of fuel burned during the sampling period on a wet basis; and
SP is the sampling period.

While the AWES/Data LOG'r system was located at each home for one week (10,080 minutes), during which 336 one minute sampling events occurred (30 minutes apart), the sampling period (SP) and the total sampling duration (SD) used for calculational purposes were generally less than 10,080 minutes and 336 minutes, respectively. Only data which was collected when the flue temperature was greater than 38°C as recorded by the Data LOG'r were used. The 38°C threshold was used as an indication that the stove was in operation. As with the SP and SD values, the mean oxygen content (% O_2) for the time period when the flue temperature was greater than 38°C only was used for the calculation of particulate emission levels.

Results

Preliminary particulate data for one week of sampling during the 1985/1986 heating season at each of six homes in Vermont and Oregon are presented in Table III. While this preliminary data set is very limited, the particulate emission levels calculated for the woodstoves are reasonable in comparison with the U.S. EPA AP-42 emission factor for woodstoves[10] and the state of Oregon standards.[11] The emission factors for the six homes ranged from 8.2 grams/kg dry wood for a catalytic retrofit stove to 20.4 grams/kg dry wood for a traditional stove. The U.S. EPA AP-42 value is 21 grams/kg dry wood. The calculated mass of particles emitted per hour of stove operation ranged from 11.4 grams/hour to 28.2 grams/hour among the six stoves. The state of Oregon 1986 weather weighted standards are 6 grams/hour for catalytic stoves and 15 grams/hour for non-catalytic stoves. Interestingly, while there was a relatively small difference for the

emission factors (mass particles/mass dry wood) and for the mass of particles per heat output values between the two traditional stoves studied in Oregon, their mass of particles per hour of stove operation values were dramatically different (Table III). Upon review of the Data LOG'r records, it was observed that the mean burn rate was significantly higher for the stove with the higher mass of particles per hour value than for the other stove (1.86 kg wood/hr vs. 1.06 kg wood/hr). This simply implies that more wood burned per unit time was responsible for more particles being emitted per unit time. When the particulate emissions were divided by the mass of wood burned or the total heat output, the values were in effect normalized, albeit many other parameters besides burning have been shown to affect particulate emission levels.

The ability of the Data LOG'r system to track and record woodstove use characteristics is shown in Figures 2 and 3. Mean hourly flue temperatures calculated from measurements made every five minutes and mean hourly flue oxygen concentrations from measurements made every thirty minutes are illustrated for a traditional stove over a twenty-four hour period (Figure 2). Mean hourly catalyst temperatures calculated from measurements made every ten minutes and mean hourly flue oxygen concentrations from measurements made every thirty minutes are also illustrated for a retrofit catalyst stove over a twenty-four hour period (Figure 3). The hourly periods when wood was added to the stoves is shown in both Figures 2 and 3. As can be seen in Figure 2, wood was added to the stove in the morning and in the evening, ostensibly when the occupants arose in the morning and returned home in the evening. Corresponding to the addition of wood, flue temperature rose and flue oxygen concentrations fell. Similarly, the dramatic increase in catalyst temperature and drop in oxygen concentration can be seen for a retrofit catalytic stove when wood was first added in the morning (Figure 3). While it is useful to monitor and record wood stove operating parameters as illustrated in Figures 2 and 3, to evaluate such factors as wood stove use patterns, diurnal changes in atmospheric pollutant levels, burn rates, fuel load densities and catalyst performance, an equally important use of the data is to control sampling equipment on a real-time interactive basis via the programmable Data LOG'r or to assist in subsequent data reduction. For example, emission samples could be collected only when the catalyst was ignited or during the time immediately following wood addition. The particulate emission data presented in Table III was, as discussed, only calculated for the time period when the stove flue temperatures were above 38°C.

It must be emphasized that the data presented here is preliminary and represents a very small fraction of the total information that will be collected during the 1985/1986 and 1986/1987 heating seasons under current programs. Approximately one hundred and ten integrated (week-long) particulate samples will be collected at forty-three homes in Oregon, Vermont, and New York during the 1985/1986 heating season alone. Woodstove operation parameters (Data LOG'r and sensors only) are also being continuously recorded in an additional twenty homes in Oregon during the 1985/1986 heating season. The analysis of particulate samples for POM was in process at the time of this writing. It is anticipated that the extensive data base generated by the AWES/Data LOG'r system will provide significant insight into the engineering and environmental issues that currently surround woodstove use and design.

Conclusions

The AWES/Data LOG'r system which has been especially developed for the in-home collection of long-term integrated woodstove emission samples has

been deployed during the 1985/1986 heating season at some forty-three homes in Oregon and New England. Preliminary particulate samples and woodstove use data from homes located in Vermont and Oregon have revealed the quality and extensiveness of the data base which can be provided by the system. Future applications of the programmable Data LOG'r would include the interactive operation of samplers for the collection of samples for various types of subsequent chemical and biological analyses, as well as the continuous collection of particulate samples with the existing AWES system to further define the emission factors and particulate impacts characteristic of woodstoves.

Acknowledgments

The work presented here was funded in part by the Coalition of Northeastern Governors, Bonneville Power Administration, U.S. Environmental Protection Agency, Wood Heating Alliance, New York State Energy Research and Development Authority, and Missoula City and County Health Department. The authors wish to thank Mr. Stephen J. Morgan of Technical Development Corporation, and Mr. Patrick J. Fox and Mr. Garry C. Insley of the Bonneville Power Administration for their cooperation and assistance.

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TABLE I. NATIONAL EMISSION INVENTORY DATA FOR PARTICLES AND CARBON MONOXIDE[a]

Source Category	Particles (Metric tons X 10^3)	Carbon Monoxide (Metric tons X 10^3)
Residential Wood Combustion	830	5,119
All Point Sources	4,397	7,574
Motor Vehicles	1,112	63,670

a. Data from reference 1

TABLE II. PARAMETERS RECORDED AND/OR CONTROLLED BY THE DATA LOG'R

1. Sampling frequency
2. Sampling duration
3. Sampling period
4. Time
5. Flue O_2 content
6. Room temperature
7. Data LOG'r internal temperature
8. Outdoor temperature
9. Auxillary heat temperature (time heat source is in operation)
10. Flue temperature
11. Catalyst temperature
12. Real-time wood weight
13. Coal bed status at time of wood addition
14. Time and length of power outages

TABLE III. PARTICULATE EMISSION LEVELS FROM REPRESENTATIVE WOOD STOVES

Stove Type/Location	Wood Fuel		Particulate Emissions[b]		
	Species	Moisture[a] (%)	gram particles/ kg dry wood (emission factor)	gram particles/ 10^6 joules (heat output)	gram particles/ hour (stove operation)
Catalytic Retrofit, Vermont	Beech	32	8.2	0.47	11.4
Catalytic Retrofit, Vermont	15% Beech, 85% Maple	30	18.5	1.10	28.2
High Efficiency Conventional, Vermont	Maple	21	11.9	0.76	12.7
Integrated Catalytic, Vermont	50% Beech, 50% Maple	16	10.8	0.66	18.7
Traditional, Oregon	Maple	27	19.0	1.36	27.8
Traditional, Oregon	Alder	20	20.4	1.64	17.8

a. dry basis
b. particulate emissions were calculated for only the time during the week-long sampling periods when the stove was in operation, i.e., when the flue temperature was greater than 38°C

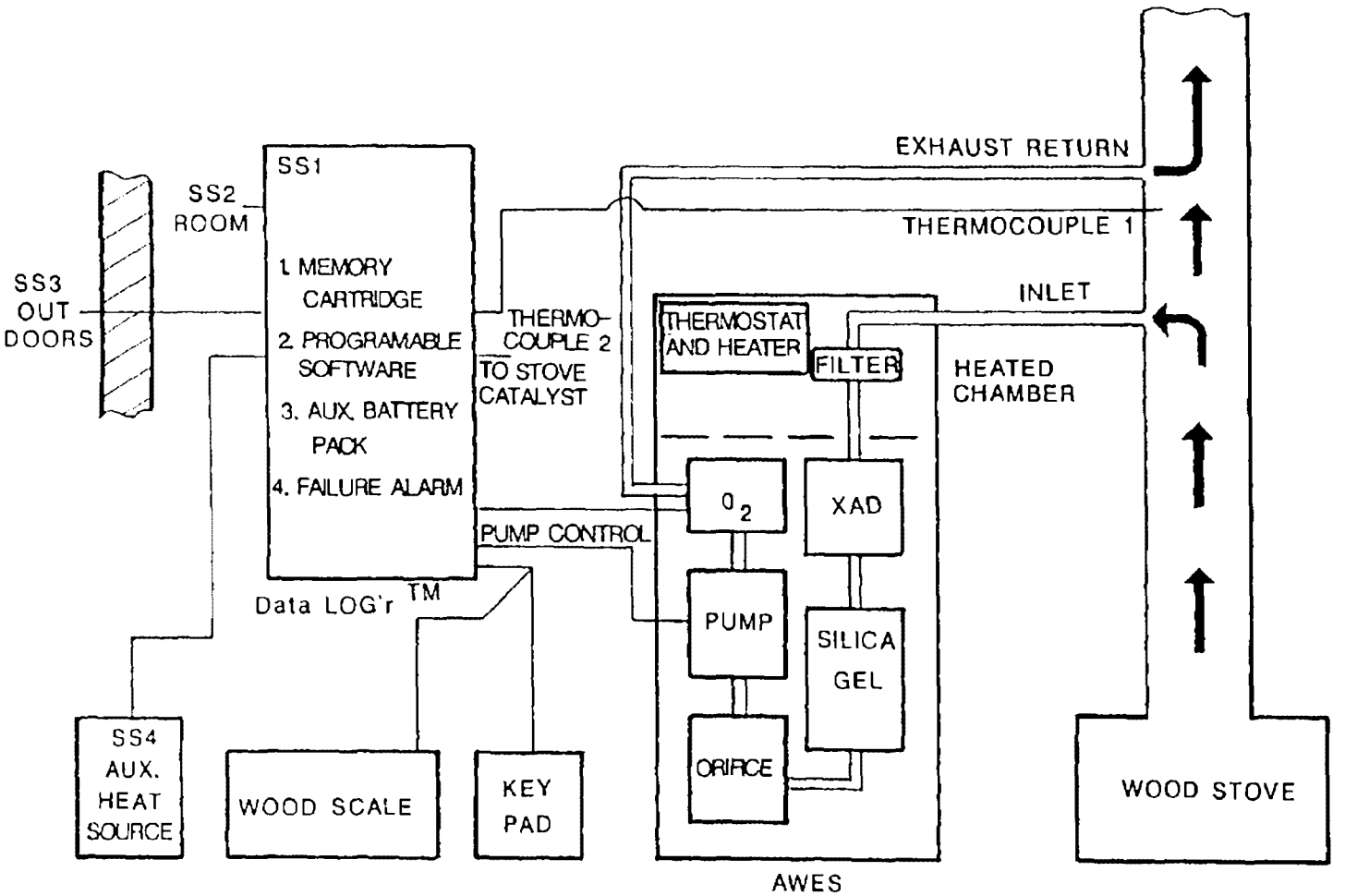

FIGURE I. SCHEMATIC AWES/DATA LOGGER SYSTEM

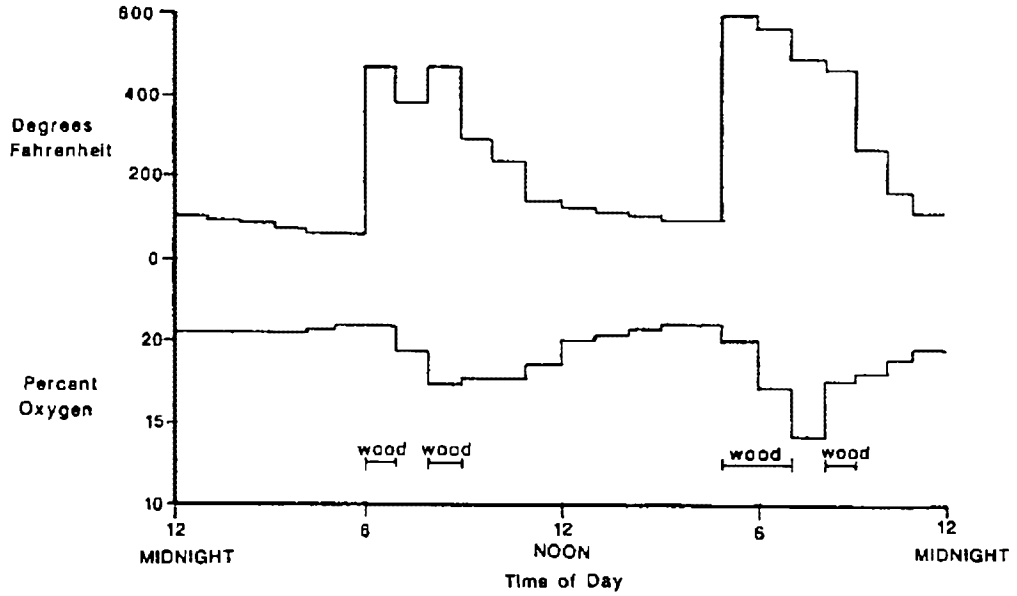

FIGURE 2. MEAN HOURLY FLUE OXYGEN CONTENT AND FLUE TEMPERATURE, TRADITIONAL STOVE

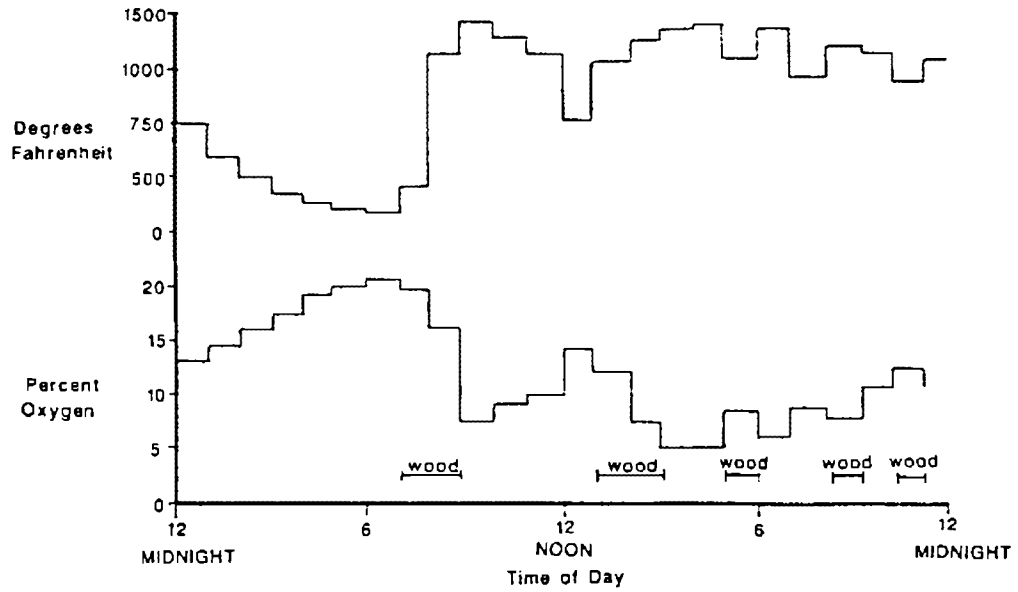

FIGURE 3. MEAN HOURLY FLUE OXYGEN CONTENT AND CATALYST TEMPERATURE, RETROFIT STOVE

RESIDENTIAL WOOD COMBUSTION IMPACTS ON INDOOR CARBON MONOXIDE AND SUSPENDED PARTICULATES

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During the past two decades much effort has been expended in evaluation and abatement of pollutant sources associated with ambient air quality. Only within the past few years has similar attention been given to indoor air quality.

Recent studies conducted by Tennessee Valley Authority during the winters of 1983, 1984, and 1985 have evaluated the impacts of both airtight (catalytic and conventional) and non-airtight wood heaters on indoor air quality in a weatherized home. Carbon monoxide and suspended particulate results for the three studies will be presented in this paper. Depending upon the operating conditions, the wood heaters were found to represent a major source of indoor carbon monoxide and suspended particulates. Several other pollutants (nitrogen oxide and polynuclear aromatic hydrocarbons) were also found to be associated with residential wood combustion.

RESIDENTIAL WOOD COMBUSTION IMPACTS ON INDOOR CARBON MONOXIDE AND SUSPENDED PARTICULATES

Introduction

Indoor air quality associated with use of residential wood heaters has become a matter of importance within the past decade because of increased use of wood heaters for space heating. The use of wood heaters for such purposes has also contributed to ambient air quality problems, especially in some densely populated urban areas. The data base for indoor air quality associated with the use of wood heaters in older homes is very limited, while that for newer, weatherized homes has only recently been investigated by Moschandreas (1-2), Traynor (3-4), Knight (5-6), and others.

The present study was conducted during the winter months of 1983, 1984, and 1985 and was developed to determine the impacts on indoor air quality (IAQ) associated with operating both airtight (conventional and catalytic) and non-airtight wood heaters in a weatherized home. The Tennessee Valley Authority (TVA) and Bonneville Power Administration (BPA) jointly funded the first and third years, while the Consumer Products Safety Commission (CPSC) funded the second year. The test program was conducted by the TVA Energy Use Test Facility staff at Chattanooga, Tennessee.

Experimental Methods

Test System

The test home was a relatively tight (ACH = 0.4), unoccupied residential home with an interior volume of 337 cubic meters. The wood heater to be tested was located in the living room and was placed on electronic weight scales for fuel burn rate determination.

The wood heaters tested during this study included three conventional airtight (AT) units, six catalytic AT units, and three non-airtight (NAT) wood heaters. Each of the wood heaters was tested over a broad range of burn rates associated with damper control in an attempt to determine a relationship between indoor pollutant generation and the wood heater operating mode.

Red oak cordwood (approximately 25-percent moisture, wet basis) was used as a test fuel throughout the three-year test program. In addition, pine cordwood fuel was used during testing in 1985. Limited testing associated with the use of very high and very low moisture fuels (both oak and pine) was also completed during 1985.

Continuous Sampling Methods

Indoor and ambient air samples were monitored using electronic analyzers with CO, NO, NO_2, NO_x, O_3, CO_2, O_2, HC, and SO_2 concentrations recorded and stored on magnetic tape at the end of each

4-minute sampling period. Particulate matter for both indoor and outdoor locations was continuously monitored with an MRI integrating nephelometer with output recorded for each 8-minute interval.

Integrated Sampling Methods

Total suspended particulates (TSP) (< 15 μm) and respirable suspended particulates (RSP) (< 2.5 μm) were collected from two indoor and three outdoor locations using stacked filter unit (SFU) dichotomous particulate samplers provided by the Crocker Nuclear Laboratory at the University of California at Davis. The Crocker Nuclear Laboratory performed gravimetric as well as particle-induced X-ray emission (PIXE) analysis for each integrated sample. Polynuclear aromatic hydrocarbons (PAH) were collected by use of sorbent XAD-2 resin traps. The PAH results were reported in 1985 at the Tenth International Symposium on Polynuclear Aromatic Hydrocarbons (5).

Air Infiltration

Sulfur hexafluoride (SF_6) tracer gas (as described in the ASTM Standard E741-80) was injected into each area of the test home and allowed to decay through natural infiltration. A linear regression using the natural logarithm of the concentrations was used to determine the air exchange rate (ACH) for the test home. This technique enabled variable ACH values which existed during each test period to be evaluated.

Results

General

Detailed TVA test reports (7, 8, and 9) have been prepared for each of the 1983, 1984, and 1985 winter test programs. The final report for the 1985 winter study (9) also contains extensive comparisons with results from the previous two studies. The airtight (AT) and non-airtight (NAT) wood heaters tested during each of the three studies will be referenced in this paper by the year in which they were tested and the heater number assigned to them during that winter test sequence.

A comparison of the indoor carbon monoxide (CO) and total suspended particulate (TSP) results found for airtight (AT) and non-airtight (NAT) wood heaters tested is presented in Table I. The CO and TSP source strengths and indoor-to-outdoor ratios observed during testing of the NAT wood heaters were generally higher than those for the AT wood heaters. CO and TSP source strengths for the NAT units varied from 210 to 530 mg/hr and from 11.9 to 20.6 mg/hr, respectively, while those for the AT units (excluding the 1983 wood heater 4) ranged from 55 to 182 mg/hr and from 4.1 to 7.5 mg/hr, respectively. The results for catalytic wood heater 4 in the 1983 study were not considered to be typical of AT wood heaters, because the unit had severe leakage around the door. This problem has since been corrected by the manufacturer. Wood heater 3 in the 1985 study represented that manufacturer's latest model. The results presented in Table I show that the newer model had the lowest average CO source strength for any wood heater tested.

Test-averaged CO source strength and concentration operating ranges for each of the wood heaters tested are presented in Figure 1. The NAT wood heaters operated with CO source strengths similar to those of the AT units when operated under optimum (fully open or intermediate damper setting) firing conditions. However, when operated under "worst case" conditions (stack damper(s) closed), the NAT units produced much higher CO source strengths. NAT wood heater 4 (Franklin-type, freestanding fireplace) generated a 12-hr averaged CO source strength of 3500 mg/hr during its "worst case" firing mode. All three of the NAT units operated with CO source strengths exceeding the high range of 500 mg/hr established by Moschandreas (1) using similar modeling for indoor CO concentrations generated by gas heating and cooking appliances. It is important to note that the NAT units operated with CO source strengths comparable to AT wood heaters when operated under more favorable firing conditions using less damper control. All of the AT units operated with "worst case" CO source strengths less than the high range of 500 mg/hr established by Moschandreas, and all catalytic AT units (except 1983 wood heater 4) had source strengths below the medium range (300 mg/hr) as established by Moschandreas.

As with source strengths, the NAT wood heaters operated with indoor CO concentrations similar to those of the AT units when operated under optimum firing conditions. However, their "worst case" firing mode produced indoor CO concentrations much higher than for AT units. Table I shows a maximum hourly indoor concentration of 29.6 ppm associated with the "worst case" use of NAT wood heater 4 (a Franklin, freestanding fireplace heater). During the same test a 12-hr indoor CO level of 18.6 ppm was generated, which exceeds the 8-hr National Ambient Air Quality Standard (NAAQS) for CO (9 ppm) by a factor of two. Peak indoor CO concentrations were found generally to be episodic with wood heater fuel reloadings.

Test-averaged TSP source strength and concentration operating ranges for each wood heater are presented in Figure 2. TSP source strengths for the AT wood heaters (except the 1983 wood heater 4) were all less than 15 mg/hr, while that for the Franklin-type NAT wood heater was as high as 65 mg/hr during its "worst case" mode of operation. Only 1983 AT wood heater 4 generated an indoor TSP source strength similar to those of the NAT wood heaters. However, the results shown in Figure 2 indicate that the newer model of this same wood heater (1985 wood heater 3) operated with less overall impact on TSP than any other heater tested in 1985.

The box-type NAT units, during "worst case" operation, generated indoor TSP levels which exceeded the 24-hr secondary NAAQS for TSP (150 $\mu g/m^3$), while the Franklin-type NAT wood heater exceeded the 24-hr primary NAAQS (260 $\mu g/m^3$). The AT wood heaters (with the exception of 1983 wood heater 4) operated with indoor TSP levels less than 100 $\mu g/m^3$.

Moschandreas (2) reported finding a 24-hr indoor TSP concentration of 160 $\mu g/m^3$ in a residence heated by a fireplace, and 24 hr indoor TSP levels of 281 and 230 $\mu g/m^3$ for wood stove space heating. During the 1984 TVA study, NAT wood heater 5 (a Franklin-type, freestanding fireplace) was operated with its front doors open, in a fashion similar to that of a traditional fireplace. The maximum indoor TSP level found during those tests was 132 $\mu g/m^3$ (very similar to that found by Moschandreas). However, the maximum levels of indoor TSP generated by the AT wood heaters during the 1983 (except wood heater 4) and 1985 TVA studies (88 and 93 mg/m^3, respectively) were much lower than those

reported by Moschandreas (281 and 230 $\mu g/m^3$). The findings of Moschandreas for AT wood heaters are more similar to indoor TSP levels found for the 1983 AT wood heater 4 (maximum 24-hr average of 174 $\mu g/m^3$) which had a severe leakage problem around the door sealing area.

Influence of Wood Burn Rate on IAQ

Linear regression analyses of the test data were performed to determine the relationships between wood burn rate and indoor CO source strength, flue gas CO concentration, and indoor TSP source strength for the AT and NAT wood heaters tested using medium moisture (25-percent wet) oak cordwood fuel. The results of these analyses are presented in Table II. Flue gas CO concentration data was not available for the 1983 study, and results from catalytic wood heater 2, tested during the 1985 study, are not included since that unit was tested only at low burn rates.

The indoor CO source strength versus wood burn rate relationships for each of the wood heaters tested during the winters of 1983, 1984, and 1985 are presented in Figure 3. The catalytic AT wood heaters operated with a definite trend of increasing indoor CO source strengths with increasing wood burn rates (with the exception of the 1983 study wood heater 2, which had a poor correlation coefficient of 0.20). This is important in view of the fact that catalytic wood heaters are designed to operate with reduced stack emissions at low burn rates, with less consideration given to operation at high burn rates. However, both the conventional AT and the NAT wood heaters operated with the reverse trend of decreasing indoor CO source strengths with increasing wood burn rates. The AT wood heaters were found to be more closely related to burn rate alone than the NAT wood heaters, since the correlation coefficients were generally higher for the AT units.

A graphical representation of the flue gas CO concentration versus wood burn rate for the 1984 and 1985 studies is presented in Figure 4. The same trends for flue gas CO appear as were found for indoor CO source strengths. These same trends of increasing flue gas CO concentrations with increasing wood burn rate for catalytic AT wood heaters, and decreasing flue gas CO concentrations with increasing wood burn rate for conventional AT wood heaters were also found during the 1982 TVA study (10) of flue gas emissions from AT wood heaters.

The fact that indoor CO source strength and flue gas CO concentrations show the same relationship to wood burn rate for each type of wood heater tested shows that indoor CO source strength is directly influenced by the concentration of CO in the stack gases. However, the magnitude of influence of flue gas CO concentration on indoor CO source strength can be seen to have differed greatly for AT and NAT wood heaters. The NAT wood heaters can be seen to have operated with similarly low flue gas CO concentrations as the AT heaters, but NAT heaters 3 and 4 generated much higher indoor CO source strengths than did the AT heaters.

A greater insight into the relationship between flue gas gas CO concentration and indoor CO source strength can be gained from Figure 5. Flue gas CO concentration versus indoor CO source strength results for box-type and Franklin-type NAT and for AT wood heaters are presented. The NAT

wood heaters were found to operate with much higher indoor CO source strengths while having much lower concentrations of flue gas CO than did the AT wood heaters. The Franklin-type, freestanding fireplace NAT unit operated with the lowest flue gas CO concentrations and yet highest indoor CO source strengths of all the wood heaters tested. The two box-type NAT wood heaters operated with lower indoor CO source strengths, while having higher stack CO concentrations than were found for the Franklin-type NAT unit. The AT wood heaters (both catalytic and conventional) operated with much higher concentrations of stack gas CO, while representing a smaller source of indoor CO than either the Franklin- or box-type NAT units. This paradoxical relationship between stack gas CO concentration and indoor CO source strength is attributed to both continuous and intermittent "back-puffing" of stack gases into the home from the NAT wood heaters.

The indoor TSP source strength versus wood burn rate relationships for the AT and NAT wood heaters tested during the three TVA studies are presented in Figure 6. As with CO, NAT wood heaters were found to generate much higher indoor TSP source strengths than did AT heaters. However, indoor TSP source strengths generated by the AT and NAT wood heaters did not show a consistent dependence on wood burn rate. This implies that some other mechanism was responsible for the liberation of particulate matter into the indoor environment than that responsible for the liberation of indoor gaseous pollutants, such as CO. This is also shown by the low correlation coefficients of the regressed TSP versus burn rate relationships presented in Table II.

Influence of Wood Moisture Content on IAQ

Specific testing was conducted using catalytic wood heater 4 (1985) to determine the effects of the use of variable moisture content red oak and yellow pine cordwood fuels on indoor air quality. The catalytic wood heater CO and TSP source strengths were found to be similar for different wood moisture contents for both low and high burn rate testing. A more detailed discussion of the wood moisture influences on indoor air quality is presented in Reference 10.

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TABLE I. COMPARISON OF CARBON MONOXIDE AND TOTAL SUSPENDED PARTICULATE RESULTS FOR EACH WOOD HEATER

	CO				TSP				
Wood Htr	Indoor[m]	Outdoor[m]	In/Out	SS[n]	Indoor[m]	Outdoor[m]	In/Out	SS[n]	ACH[o]
1985 TVA/BPA AIRTIGHT WOOD HEATERS - All 12-hr tests									
1[a] Av.	0.9	0.5	1.8	126	58.9	49.4	1.2	7.5	0.6
Max Conc.	1.8 (all 1-hr averages)								
2[b] Av.	1.0	0.4	2.5	99	64.5	54.6	1.2	6.4	0.4
Max Conc.	2.4								
3[c] Av.	0.9	0.6	1.5	55	51.5	44.3	1.2	5.4	0.4
Max Conc.	1.4								
4[d] Av.	1.6	0.4	4.0	182	57.0	42.4	1.3	4.1	0.4
Max Conc.	2.8								
5[e] Av.	0.9	0.4	2.3	69	54.5	43.1	1.3	4.3	0.3
Max Conc.	1.3								
1984 CPSC NON-AIRTIGHT WOOD HEATERS - All 12-hr tests									
3[f] Av.	3.0	0.4	7.5	416	118.7	34.3	3.5	11.9	0.4
Max Conc.	9.6								
4[g] Av.	3.6	0.4	9.0	530	166.0	58.0	2.9	20.6	0.5
Max Conc.	29.6								
5[h] Av.	2.0	0.5	4.0	210	140.7	102.9	1.4	12.7	0.4
Max Conc.	5.6								
1983 TVA/BPA AIRTIGHT WOOD HEATERS - All 24-hr tests									
1[i] Av.	1.9	0.8	2.4	162	49.9	36.2	1.4	5.0	0.4
Max Conc.	8.0								
2[j] Av.	1.6	1.3	1.2	70	37.1	31.4	1.2	4.2	0.4
Max Conc.	3.3								
3[k] Av.	1.5	0.9	1.7	95	45.8	26.9	1.7	5.7	0.4
Max Conc.	3.9								
4[l] Av.	3.6	0.6	6.0	375	101.0	25.4	4.0	42.9	0.4
Max Conc.	9.1								

a,b,c,d,j,l - All catalytic, radiant heaters
e,k - Conventional, radiant heaters
f,h - Box-type, radiant heaters
g - Franklin-type, freestanding fireplace heater
i - Conventional, circulator heater
m - Indoor/outdoor concentration CO (ppm), TSP ($\mu g/m^3$)
n - Source strength (mg/hr)
o - Air changes per hour

TABLE II. LINEAR REGRESSION ANALYSIS OF CO AND TSP SOURCE STRENGTHS AND FLUE GAS CO CONCENTRATIONS VERSUS WOOD BURN RATE

Wood Heater Number	CO Source Strength (mg/hr)			Flue Gas CO (%)			TSP Source Strength (mg/hr)		
	Factor	Bias	Corr.	Factor	Bias	Corr.	Factor	Bias	Corr.
1983 Study - Catalytic and Conventional Airtight Wood Heaters									
1 (Conventional)	-65	549	-0.77	-	-	-	-1.3	13.0	-0.75
2 (Catalytic)	-7	97	-0.20	-	-	-	-	-	-
3 (Conventional)	-7	153	-0.64	-	-	-	0.3	2.4	0.64
4 (Catalytic)	17	378	0.33	-	-	-	1.7	7.5	0.31
1984 Study - Non-Airtight Wood Heaters									
3 (Box-type)	-116	1478	-0.56	0.03	0.78	-0.27	-2.0	52.6	-0.20
4 (Franklin-type)	-39	149	-0.14	0.004	0.07	0.17	0.6	54.7	0.05
5 (Box-type)	-29	352	-0.29	-0.01	0.46	-0.06	-0.3	38.9	-0.05
1985 Study - Catalytic and Conventional Airtight Wood Heaters									
1 (Catalytic)	16	51	0.75	0.06	0.47	0.33	-0.01	7.7	-0.51
3 (Catalytic)	5	41	0.67	0.04	0.24	0.42	-0.5	7.1	-0.76
4 (Catalytic)	18	112	0.67	0.28	0.36	0.50	-0.4	5.3	-0.59
5 (Conventional)	-8	102	-0.94	-0.40	2.88	-0.73	1.0	0.8	0.44

CO Source Strength = (Wood Burn Rate * Factor) + Bias
Corr - Correlation Coefficient

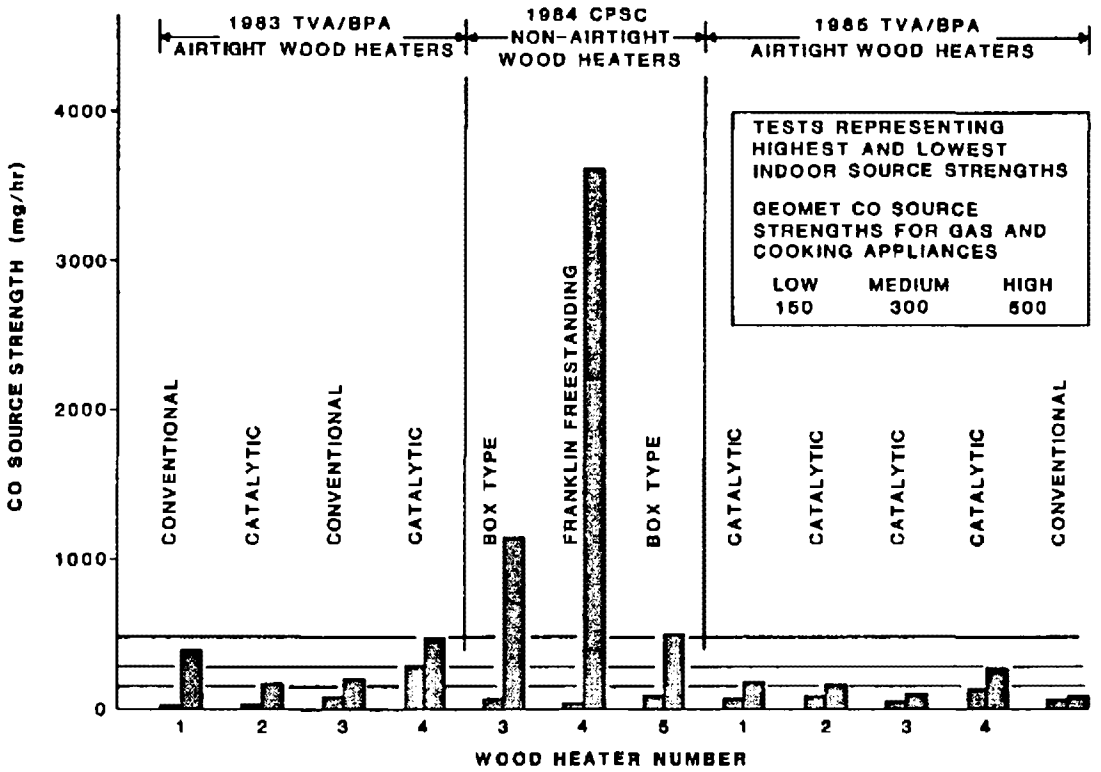

Figure 1. Comparison of Carbon Monoxide (CO) Source Strength Ranges for Airtight and Non-Airtight Wood Heaters

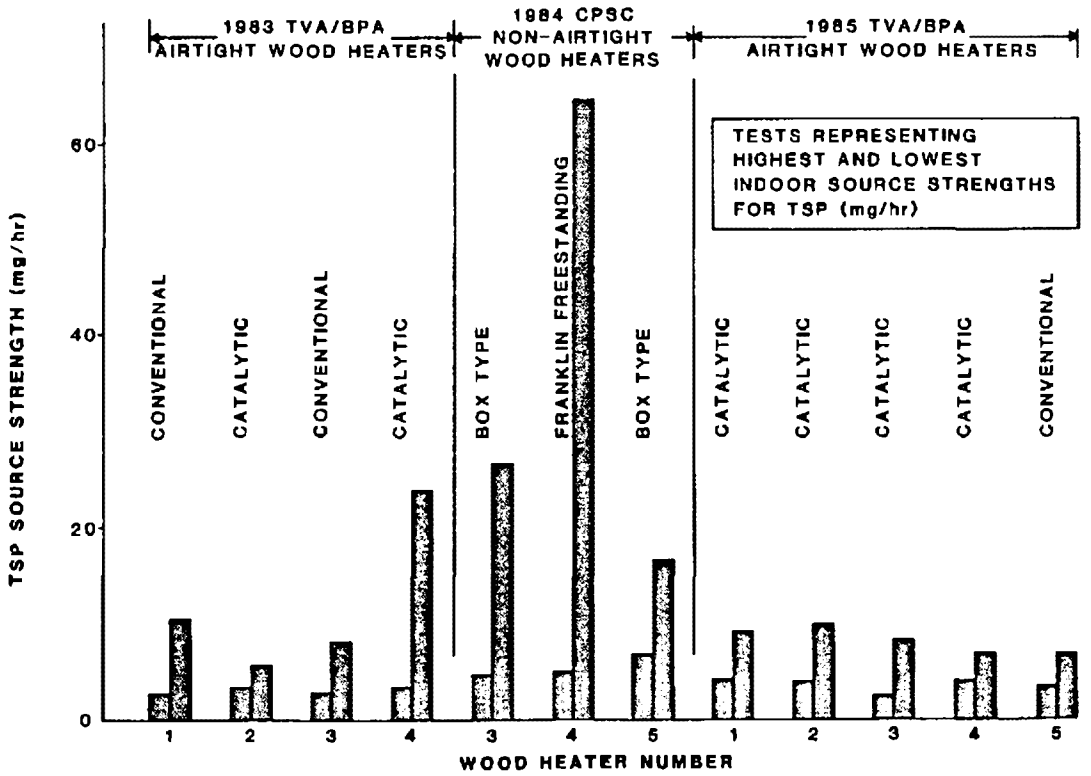

Figure 2. Comparison of Total Suspended Particulate (TSP) Source Strength Ranges (mg/hr) for Airtight and Non-Airtight Wood Heaters

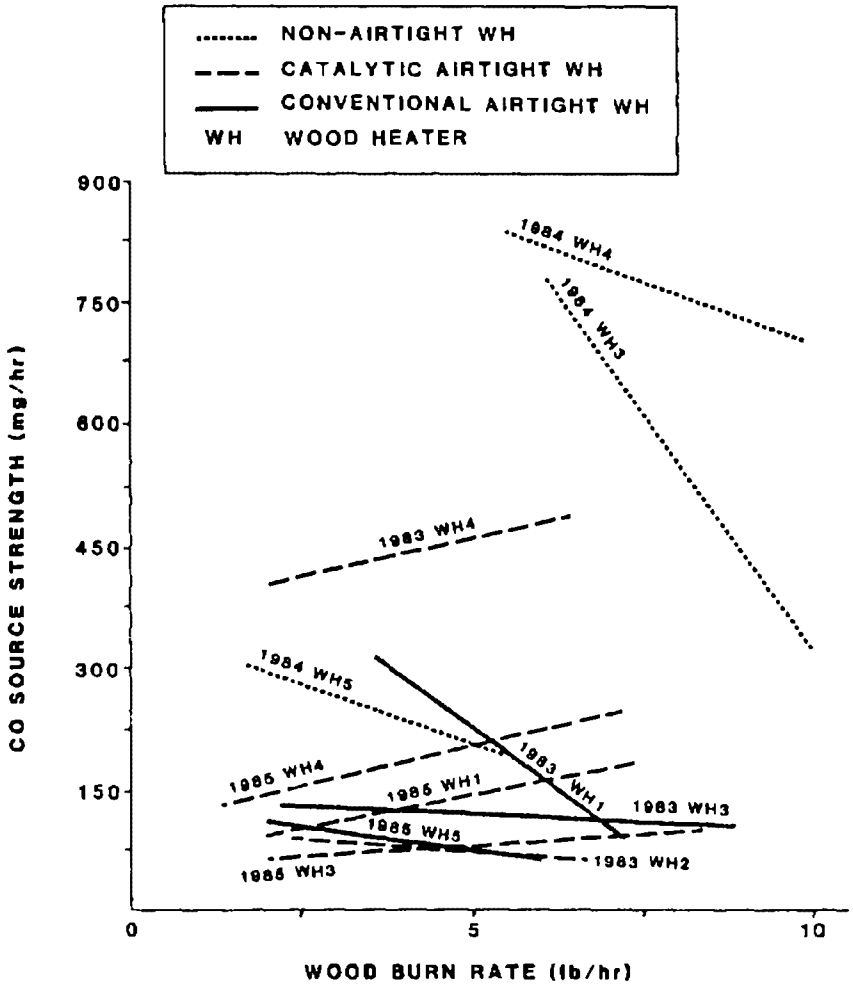

Figure 3. Indoor CO Source Strength (mg/hr) versus Wood Burn Rate (lb/hr) for Airtight and Non-Airtight Wood Heaters

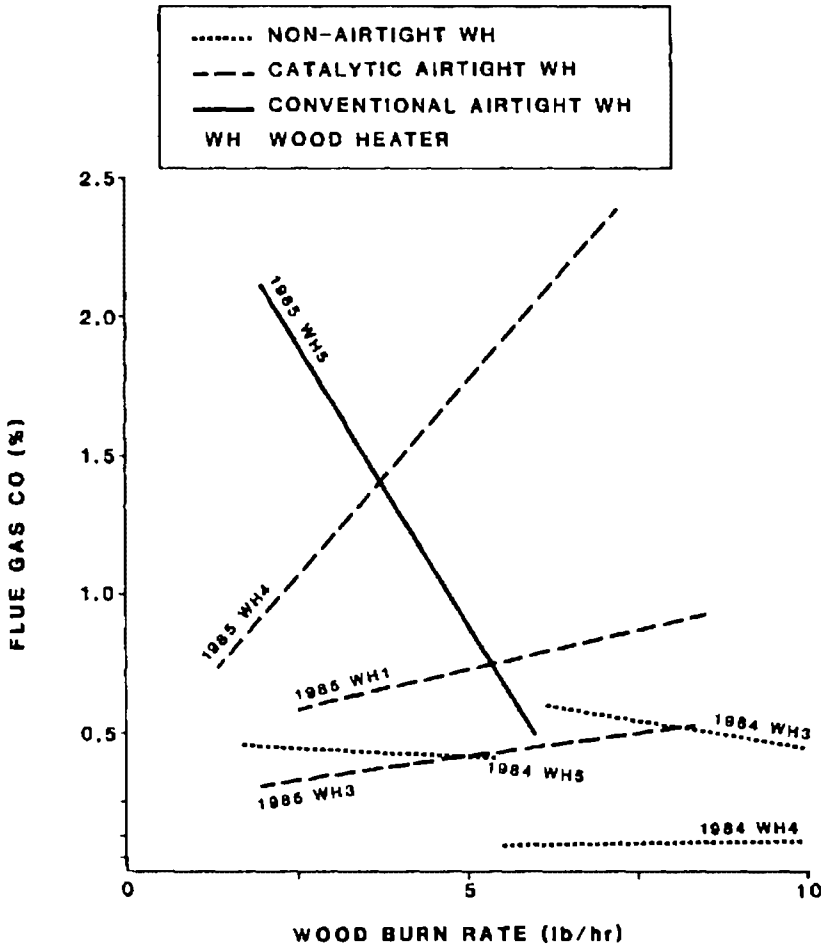

Figure 4. Flue Gas CO Concentration (%) versus Wood Burn Rate (lb/hr) for Airtight and Non-Airtight Wood Heaters

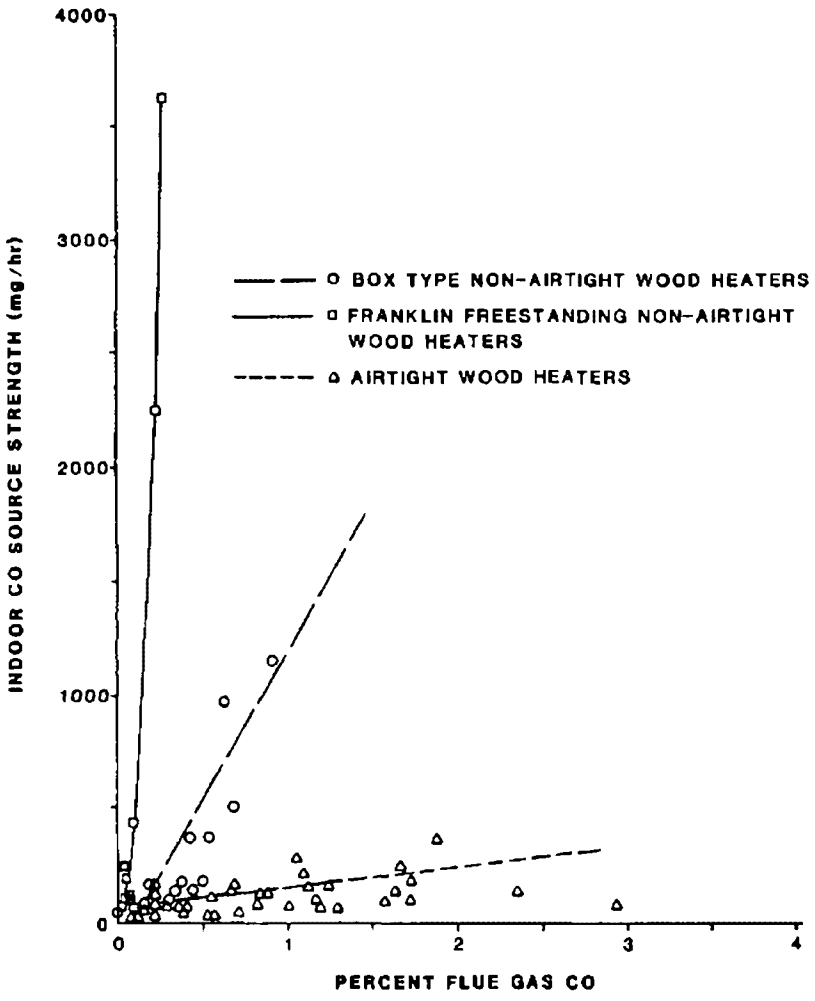

Figure 5. Flue Gas CO (%) versus Indoor CO Source Strength (mg/hr) for Airtight and Non-Airtight Wood Heaters

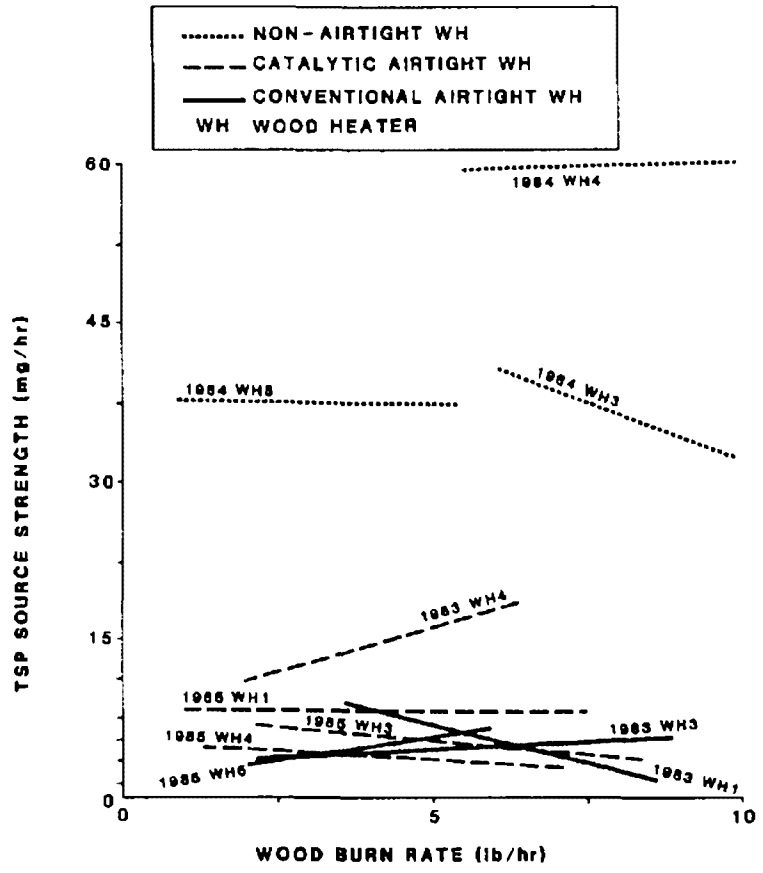

Figure 6. Indoor TSP Source Strength (mg/hr) versus Wood Burn Rate (lb/hr) for Airtight and Non-Airtight Wood Heaters

A REFINEMENT OF THE POTASSIUM TRACER METHOD FOR RESIDENTIAL WOOD SMOKE

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The USEPA currently uses potassium as a tracer for the mass of wood smoke collected on ambient fine particle filters. Total potassium is measured by XRF analysis, and soil potassium is estimated by assuming a value for the K/Fe ratio in soil, multiplying by the Fe present and subtracting from total K analyzed. We suggest a cheaper and more reliable technique wherein water-soluble K is analyzed by ion chromatography. The assumption is that all fine particle smoke potassium (but very little soil potassium) is water-soluble. Preliminary results indicate this may be the case.

A REFINEMENT OF THE POTASSIUM TRACER METHOD FOR RESIDENTIAL WOOD SMOKE

Introduction

The recent vastly increased use of wood as a residential fuel has caused concern over the environmental impact of wood smoke, both as a local pollutant and as a factor in global atmospheric chemistry and energy balances. Forest fires, as well as controlled burning of large areas for agricultural use, also deposit very large amounts of fine particles (< 2.5 μm aerodynamic diameter) in the atmosphere. One of the more obvious effects of large scale wood combustion is visibility degradation (1). In addition, there is concern about carcinogenic materials volatilized from so-called air-tight (oxygen deficient) wood-burning stoves (2).

The need exists for development of sampling and analytical methods related to the characterization of source and ambient wood smoke. In particular, methods related to determining the contribution of wood burning to fine particle mass concentrations in the troposphere are assuming importance in current studies. Such source apportionment methods include emission inventory, source-dispersion models and receptor models (3). Emission inventories require detailed knowledge of what emerges from all sources of pollution in the area studied; source-dispersion models integrate emission estimates with meteorological and mass transport data to predict levels of ambient fine particles; and receptor models use ambient particle loadings and composition along with meteorological data to estimate the number and types of emitters contributing to local air shed fine particle concentrations.

Receptor models are considered of great potential value because they are not dependent on a detailed knowledge of all local sources. As a result, much recent work has concerned the development of realistic approaches to receptor-oriented modeling, using chemical and physical properties of airborne fine particles (4). Stevens (5) has outlined the currently available sampling and analysis methods for use in receptor-modeled source apportion- ment studies of the impact of wood burning on fine particle mass. These methods include use of potassium as a reasonably unique tracer for the mass of wood smoke in the fine particles, although the percentage can vary considerably depending on the type of wood being burned, burn temperature and other factors. For this reason it is desirable to obtain "source signatures" in the area under study.

Because potassium on sample filters can also originate from sources other than wood burning, a correction for this must be made. The predominant non-wood smoke potassium source is wind-blown soil particles. In this instance, iron is used as a quantitative indicator of the amount of crustal material present, and a constant ratio of potassium-to-iron mass in the soil is assumed. The total potassium found by X-ray fluorescence is then reduced by the soil-potassium mass.

The problem with this type of correction is that it either makes an assumption regarding the iron-potassium ratio, or requires analysis of local soil samples (6).

We propose that potassium can indeed be a reliable mass tracer for wood smoke, but present techniques are not taking advantage of a natural correction for non-wood origin potassium; namely, its relative water insolubility.

Wood smoke, being the product of a high-temperature combustion process, will have its potassium associated with simple anions - chloride, sulfate, nitrate, and carbonate. All these are highly water-soluble. Soil potassium will be tied up in complex mineral form - silicates and the like. These sources are not water-soluble to any appreciable degree. Thus, a separation technique involving treatment of the filter sample in aqueous solution should naturally segregate the two forms.

Analysis for wood-smoke potassium is simplified by this separation technique, since ion chromatography can be used for water-extractable potassium.

Experimental Methods

All local sampling was done with a cyclone inlet and pneumatic flow controller. The cyclone inlet, if operated between 22 and 30 liters/min flow rate (at sea level pressure), will separate aerosol particles into fine and coarse fractions. The fine fraction cut point is ~2.5μm aerodynamic diameter; i.e., all particles ≤2.5μm in diameter are collected on the filter, and particles >2.5μm in diameter are deposited in a "cup" and are not analyzed. Cyclone inlets are described by John and Reischl (7). Analysis of fine particles only is justified by the fact that most wood burning emissions are found in the fine fraction, in the form of nonvolatile organics and elemental (soot) carbon (5).

Teflon filters (1-2 μm pore size) were used, since these are suitable for both X-ray fluorescence elemental composition analysis and aqueous extraction. Filters were massed before and after sampling, with a Fisher Gram-Atic microbalance. Before massing, filters were desiccated for twenty-four hours over calcium chloride.

Sampled filters were also obtained from the Inorganic Pollutants Analysis Branch (IPAB) of EPA, Research Triangle Park, N. C. These filters were obtained from an EPA study done in Missoula, Montana in May of 1979. Both coarse and fine particle filters from dichotomous samplers were provided. Filters from other sites will be provided as this study continues.

Filters were sent to IPAB for X-ray fluorescence (XRF) analysis of elemental composition, and were then returned to our lab for ion chromatographic (IC) analysis. As preparation for IC analysis filters were placed in 30-ml nalgene bottles containing solvent solution (normally 0.0025 Molar HCl), and agitated for twenty minutes in an ultrasonic bath. This procedure is described in detail by Stevens, et. al. (8).

Ion chromatographic analysis of aqueous extractable potassium was done on a student-constructed instrument, using a Dionex CS-1 analytical cation column and CSC 2 packed bed suppressor column. A Shimatzu Model C-R3A integrator-recorder was used to quantitate the analytical data.

Concentration standards were injected before and after a run of filter sample solutions. A preliminary analysis was made to indicate the appropriate dilution standards. Potassium concentrations as low as 0.01 ppm were measurable, but the precision and accuracy were limited by large ratios of ammonium to potassium, when the K^+ peak sometimes appeared only as a shoulder on the large NH_4^+ peak. The suppressor column was regenerated with 0.5M NaOH.

Chimney Sampling

The cyclone was clamped on a ring stand base and set on the chimney rim. All sampled chimneys had concrete slabs on top so smoke was directed sideways into the cyclone. Flow rate was maintained at 23 ±2 liters/minute and sampling times were from 5 to 15 minutes. Mass of collected smoke was usually several milligrams.

Soil Sampling

A soil agitator was constructed as shown in Figure 1. A large sintered filter funnel formed the soil container, and air was pumped up through the sintered filter to form a fluidized bed of soil particles. The funnel was attached by a clamp to the pump assembly, so that the funnel was shaken mechanically while the sampling was taking place. The cyclone was held in place 3-5 cm above the soil surface.

All soil samples were screened with a wire sieve having rectangular openings of about 1 mm, before being placed in the agitator.

When available, oiled teflon filters were used for soil sampling and sample masses were typically 1-2 mg.

Ambient Sampling

The cyclone was suspended 1-2 meters above the ground. Sampling times were either twelve or twenty-four hours at 23 ±2 liters/minute. Sample masses were normally a few milligrams.

Results and Discussion

Figure 2 is a plot of EPA XRF potassium, corrected for windblown soil, versus our extracted potassium by IC. These data were obtained from a tray of fine-particle filters provided by EPA-IPAB, from a study in 1979 in Missoula, Montana.

The correction for windblown soil was made by using a K/Fe mass ratio of .53 ± 0.24, obtained as the mean of this ratio for 20 coarse particle filters, also provided by EPA from the same study. The Fe mass on each filter was multiplied by this ratio, and the result was subtracted from total filter K. This is the correction suggested by Lewis & Einfeld (6).

The slope of the best-fit straight line is 1.05 ± 0.09 and the intercept is -255 ng ± 100 ng. Total number of filters analyzed was 20. The independent variable was the IC value, and a ±10% uncertainty was assigned to the XRF data. A similar plot of IC versus XRF data, with uncertainties of ±10-20% on the IC data, yields a slope of 0.92 ± 0.09 and an intercept of 174 ng ± 142 ng.

Conclusion

Our data are limited and should be considered preliminary. We are continuing to process filters from other EPA studies and from the Boone, North Carolina, area. In addition, we are submitting both soil and smoke fine particle filters to EPA for XRF analysis. Results should indicate solubility of soil K and the efficiency of water extraction of all K from smoke fine particles. This data will be presented at the Minneapolis meeting in June.

Acknowledgments

The idea for this project came from R. K. Stevens, Chief of IPAB, ESRL, USEPA, Research Triangle Park, North Carolina. Thanks also to Tom Dzubay and Charles Lewis of IPAB for their advice, and to Tom Dzubay for the XRF work.

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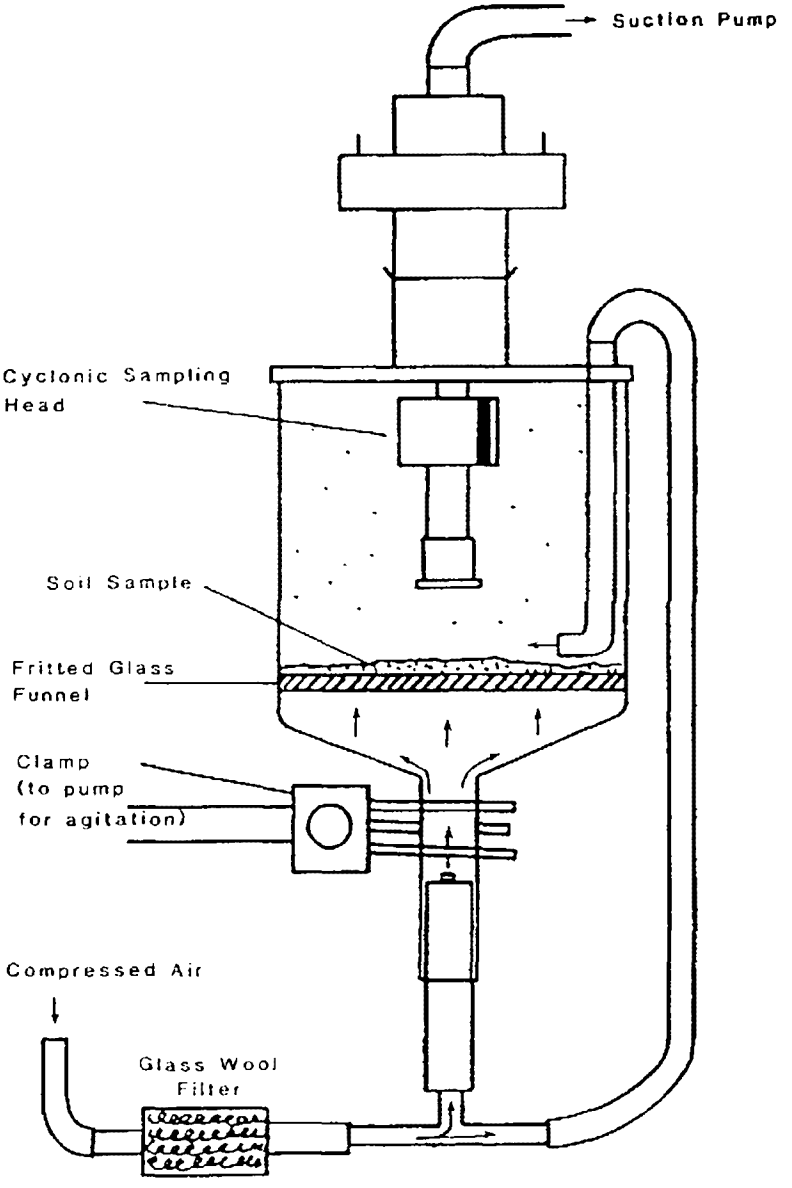

Figure 1. Schematic for soil aerosolizer

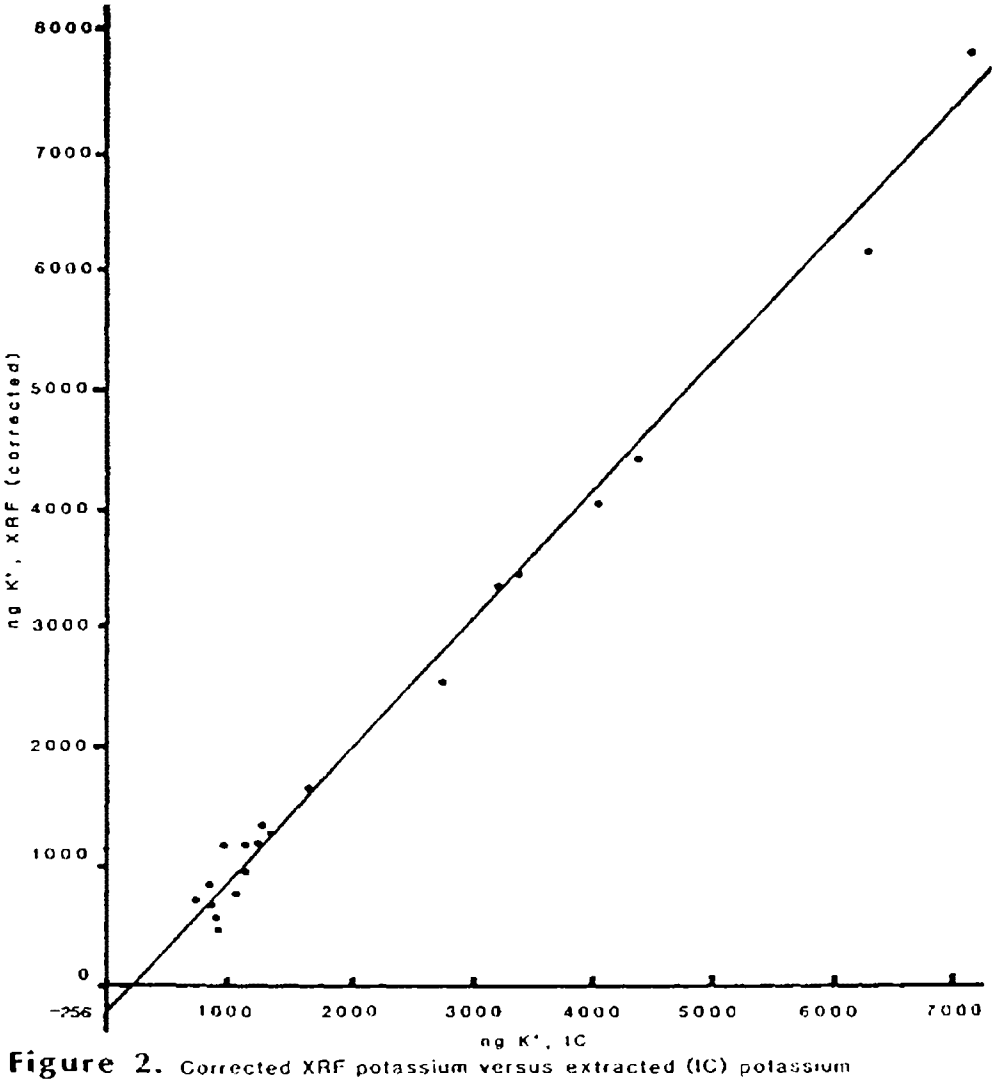

Figure 2. Corrected XRF potassium versus extracted (IC) potassium

TOXIC AIR POLLUTANT EMISSION MEASUREMENT TECHNIQUES FOR NON-STEADY-STATE PROCESSES: A CASE STUDY WITH ETHYLENE OXIDE

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Measurement techniques are well-established for most types of air pollutant emissions from sources operating under steady-state conditions. However, such is not the case with non-steady-state processes, as frequently encountered in many toxic air pollutant emission situations. This paper reviews the measurement technique developed for one such situation, i.e., ethylene oxide emissions from gas sterilizers used in the medical device industry.

Either pure ethylene oxide or an admixture with an inert diluent is typically used in gas sterilizers to treat medical products which cannot withstand heat sterilization. At the end of sterilization, ethylene oxide is exhausted to the atmosphere in a series of intermittent sterilizer evacuations. The operating conditions used during this exhaust cycle result in a highly dynamic condition in the stack. All critical process parameters affecting stack emission measurements vary instantaneously and simultaneously during the entire exhaust cycle. To accurately determine the total weight of ethylene oxide discharged to the atmosphere, it is necessary to monitor all relevant parameters continuously throughout the cycle. Also, all measurements must be made without exposing operators to toxic ethylene oxide.

An accurate measurement of air pollutant emissions from sources operating under non-steady-state conditions requires the use of properly designed orifice meters for gas flow measurements, thermometers with remote sensors for temperature measurements and on-line gas chromatographs for determining exhaust gas composition. This paper discusses a step-by-step measurement technique, including calculational procedures, developed to determine ethylene oxide emissions from sterilizers.

TOXIC AIR POLLUTANT EMISSION MEASUREMENT TECHNIQUES FOR NON-STEADY-STATE PROCESSES: A CASE STUDY WITH ETHYLENE OXIDE

Introduction

Either pure ethylene oxide (EtO) or an admixture with an inert gas is used in sterilization chambers to treat medical products which cannot withstand heat sterilization. Figure 1 presents a typical sterilization cycle using pure EtO. At the end of sterilization, EtO is exhausted to the atmosphere. Typically a sterilizer exhaust cycle includes a series of pressure pulses. Each pressure pulse consists of chamber evacuation to a predetermined vacuum followed by introduction of air into the chamber to bring the chamber up to atmospheric pressure. A water-ring vacuum pump is generally used to evacuate the chamber and each evacuation represents an intermittent EtO discharge to the atmosphere.

A water-ring vacuum pump is a positive displacement pump. The pressure on the inlet side of the pump decreases continuously as the chamber is evacuated. However, the pressure on the discharge side of the pump remains virtually constant (at nearly one atmosphere). The total gas flowrate (SCFM) on the discharge side of the pump, therefore, decreases as the chamber pressure is reduced. Furthermore, the sterilizer gas containing EtO is thoroughly mixed with the seal water in the pump. Due to the relatively high solubility of EtO in water, some of the EtO evacuated from the chamber is absorbed in the seal water. The extent of EtO absorption varies depending upon seal water temperature and total gas flowrate. Thus, all critical process parameters affecting emission measurements - total exhaust gas flowrate, EtO concentration in the exhaust gas and overall gas composition - change continuously throughout a given evacuation. This creates a highly dynamic condition in the exhaust stack.

Measurement Technique

An accurate measurement of total weight of EtO emissions from a sterilizer requires monitoring of the following process parameters continuously over the entire exhaust cycle:

- Gas temperature
- Gas static pressure

- Total volumetric gas flowrate
- Ethylene oxide concentration
- Inert gas concentration (if applicable)

These measurements must be made without exposing operators to toxic ethylene oxide.

Gas temperature and pressure are required to make appropriate corrections to measured volumetric gas flowrates. Gas temperature is measured by a thermometer with a remote sensor located in the stack. Thermocouple wires can conveniently be used for this purpose. A pressure gage, located far from the sampling point, is used for static pressure measurements. Plastic tubing connected to a permanent fitting in the stack can be used for pressure transmission. Temperature and pressure readings should be taken approximately once every minute.

Since the total gas flowrate changes continuously, it is necessary to have the means to monitor flowrate on a continuous basis throughout each evacuation. To accomplish this safely, accurately and inexpensively, it is necessary to install a calibrated orifice meter in the exhaust gas line. Gas pressure drop across the orifice plate should be recorded once every minute. Due to the extremely wide range of stack gas flowrate encountered over the exhaust cycle, it is often necessary to use multiple orifice plates to cover the entire flow range.

EtO concentration is measured using an on-line gas chromatograph (GC). The GC must be standardized prior to and following each test series. Heated gas sampling lines must be used to prevent condensation of water vapor and EtO. Extreme care should be exercised in selecting a proper GC column and a proper detector. For example, Chromosorb 101 or Porapak R can be used for satisfactory EtO separation. Also, a flame ionization detector should be used for low EtO concentrations (less than 5% by volume), while a thermal conductivity detector for high concentrations (5% by volume or higher). Again, measurements should be made as frequently as the GC allows.

In order to calculate the instantaneous volumetric gas flowrate (of the gas stream being sampled) from the orifice pressure drop data and the orifice equations, it is necessary to know the instantaneous gas molecular weight. Therefore, if an inert gas is used in the process, its concentration must also be monitored continuously by an on-line GC.

Data Evaluation

As discussed previously, the exhaust cycle includes multiple chamber evacuations. To determine overall EtO emissions for the entire cycle, the total weight of ethylene oxide exhausted during each evacuation must be determined. This is accomplished as follows:

1. Determine ethylene oxide concentration at each measured point from GC data. This is done by comparing the peak height of each sample with that of a known, certified (NBS traceable) EtO standard.

2. Determine inert gas concentration at each measured point based on GC data as in 1.

3. Plot a graph of EtO concentration vs. elapsed time and a graph of inert gas concentration vs. elapsed time.

4. Determine average molecular weight of the gas at points along the evacuation from the graphs plotted in 3. and assuming that the exhaust gas is saturated with water.

5. Calculate total volumetric gas flowrate (SCFM) at each measured point - based on orifice pressure drop, average gas molecular weight, gas temperature and gas pressure - using orifice equations (refer to Table I).

6. Plot a graph of total volumetric gas flowrate vs. elapsed time.

7. Select a number of points at equal time intervals along the evacuation for further calculations.

8. At each point selected in 7., calculate EtO mass flowrate by combining total volumetric gas flowrate and EtO concentration at that point using the following equation:

$$m = Q\ (y/10^6)\ \ (\rho)$$

where m = mass flowrate of EtO, lb/min
Q = total volumetric gas flowrate, SCFM
y = EtO concentration, ppmv
ρ = density of EtO
= 0.116 lb/cu.ft. at standard conditions (60°F, 1 atm.)

9. Generate a curve of EtO mass flowrate vs. time.

10. Integrate the curve generated in 9. to determine the total weight of EtO exhausted to the atmosphere over the evacuation.

The total weight of EtO Emissions over the entire exhaust cycle is calculated by adding the weights determined for individual evacuations.

Example

Simplified calculational procedures for an example evacuation are presented in this section. Consider an evacuation with a total duration of 10 minutes. Steps 1. through 6. described in the previous section are relatively straight forward and will produce the graphs of total volumetric gas flowrate vs. elapsed time and EtO concentration vs. elapsed time. Table II presents the values of gas flowrate and EtO concentration from these graphs, for ten different points over the evacuation. Each point represents the midpoint of a specific time interval and the valves of gas flowrate and EtO concentration at each point are assumed to be the average valves for the corresponding time interval. Table III presents in-depth calculations.

TABLE I

ORIFICE EQUATIONS TO CALCULATE VOLUMETRIC GAS FLOWRATES

$$Q = C' \sqrt{(h_w)\ (p_f)}$$

where Q = volumetric gas flowrate, SCFM (60°F, 1 atm.)

C' = flow coefficient multiplier

h_w = pressure drop across orifice, in. WC

p_f = flow pressure, psia

The flow coefficient multiplier is given by

$$C' = K_o d^2\ F\ (\sqrt{520/T})\ (\sqrt{29/MW})$$

where K_o = flow coefficient

d = orifice diameter

F = gas compressibility factor ratio

T = gas temperature, °R

MW = gas molecular weight

The values of K_o and d are constant for a given orifice plate and are obtained from the orifice plate manufacturer. The value of F depends upon gas composition. The F value for a gas mixture can be calculated from F values of individual components. For example, at 60°F and 1 atmosphere, F equals 1.0 for air and 1.5 for an inert gas often used in the sterilization process. Then, for a mixture of 50% by volume of air and 50% by volume of this inert gas,

$$F = (0.5)\ (1.0) + (0.5)\ (1.5)$$

$$= 1.25$$

TABLE II

TEST DATA AT SELECTED POINTS

Total Evacuation Time = 10 Minutes

Point No.	Elapsed Time min.	Total Gas* Flowrate, SCFM	EtO** Concen., ppmv
1	0.5	350	165,500
2	1.5	350	163,000
3	2.5	300	160,200
4	3.5	260	160,100
5	4.5	220	157,700
6	5.5	180	157,500
7	6.5	140	156,100
8	7.5	100	155,600
9	8.5	70	155,200
10	9.5	50	155,100

---

* From the graph of total gas flowrate vs. elapsed time

** From the graph of EtO concentration vs. elapsed time

TABLE III

CALCULATIONS TO DETERMINE TOTAL EtO EXHAUST

Time Interval, Δt, min.	Elapsed Time, min.	Flowrate, SCFM	EtO Concen., ppmv	EtO Discharged* During Δt, lb
0-1	0.5	350	165,500	6.72
1-2	1.5	350	163,000	6.62
2-3	2.5	300	160,200	5.58
3-4	3.5	260	160,100	4.83
4-5	4.5	220	157,700	4.03
5-6	5.5	180	157,500	3.29
6-7	6.5	140	156,100	2.54
7-8	7.5	100	155,600	1.81
8-9	8.5	70	155,200	1.26
9-10	9.5	50	155,100	0.90
			Total =	37.58

*EtO discharged during time interval Δt

$$= (Q)\ (y/10^6)\ (0.116\ \text{lb/SCF EtO}) \times \Delta t$$

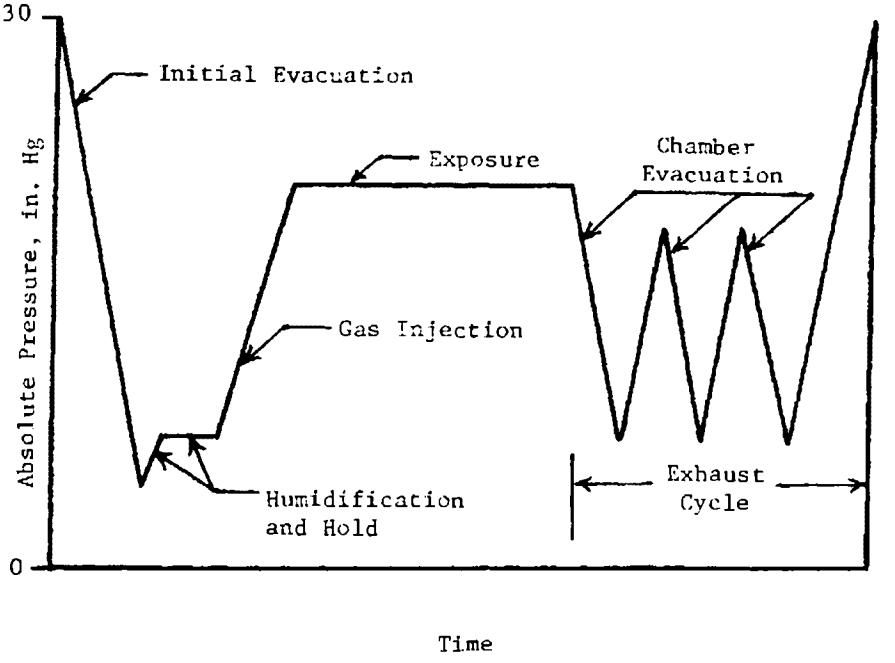
where Q = gas flowrate, SCFM

y = EtO concentration, ppmv

Δt = length of time interval, min.

FIGURE 1

TYPICAL ETHYLENE OXIDE STERILIZATION CYCLE



A UNIVERSAL SAMPLE INTRODUCTION SYSTEM SUITABLE FOR VOC ANALYSIS IN AMBIENT AIR, VOST, WATER, AND SOLID SAMPLES

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Both ambient air and stationary source emission methods use Tenax[R] and/or carbon to determine volatile organic compounds (VOC). Two distinct sample introduction systems are used: cryogenic trapping for ambient air methods and a purge-and-trap apparatus with the volatile organic sampling train (VOST) protocol. The VOST is the principal stationary source method. This paper will discuss the application of a single thermal desorption/purge-and-trap apparatus to the analysis of ambient air, VOST, water, and soil samples. This sample introduction system eliminates the necessity of major equipment alterations and the accompanying instrument downtime incurred when VOC analysis is performed on samples from these various media.

In our work, identical traps containing Tenax or Tenax and charcoal have been used for both ambient air sampling and VOST sampling. Sorbent trap preparation, conditioning, and blank checking procedures are identical. Procedures developed for testing the applicability of both the solid sorbent and the analytical system to the sampling and analysis of individual compounds are described.

The sample introduction system has been used for a wide variety of projects, including the validation study of the VOST protocol and an ambient toxic air monitoring program around a chemical plant. An automated version of this system has been developed that permits unattended sequential analysis of 10 samples.

A UNIVERSAL SAMPLE INTRODUCTION SYSTEM SUITABLE FOR VOC ANALYSIS IN AMBIENT AIR, VOST, WATER, AND SOLID SAMPLES

Introduction

Analytical service laboratories have a need to efficiently maximize the use of expensive, sophisticated instrumentation and highly trained personnel. Toward this end, we have developed a way of using a common sample introduction system for gas chromatography/mass spectrometry (GC/MS) analysis of volatile organic compounds (VOC) in a wide variety of sample matrices. This approach is a versatile compromise in methodology that was developed over a period of several years.

The use of solid sorbents to collect VOC's from ambient air or workplace air is a well established technique. Most of the original applications were for one or a very limited number of components. Since 1976,[1,4] Tenax-GC[R] has been used to collect and analyze multiple compounds from ambient air. The analytical procedure consists of thermal desorption of sampling traps followed by cryogenic trapping of the VOC's and then capillary GC/MS analysis. This technique has been applied to monitoring ambient air in many situations such as in national parks, at hazardous waste sites, and even basements of homes in the Love Canal area. Current interest in toxic VOC monitoring in ambient air and at Superfund sites ensures that a substantial amount of work will continue in this area.

For analysis of ambient air samples, cryogenic trapping after thermal desorption was found to be susceptible to problems during analyses of samples containing high-moisture levels. When desorbed, moisture could freeze as a solid ice plug at the head of the subambient-cooled capillary column, stopping carrier flow. A sufficient volume of water also triggers a vacuum system shutdown in the mass spectrometer. Both of these occurrences result in instrument problems and the loss of irreplaceable samples.

In July 1982, U.S. EPA received a draft report[5] on a volatile organic sampling train (VOST) utilizing Tenax-GC and charcoal solid sorbents. VOST is one of the most common methods used for sampling and analysis to determine destruction and removal efficiency during trial burns at hazardous waste incinerators. The procedure includes thermal desorption of the sample followed by purge-and-trap/thermal desorption introduction to the GC/MS. The problem of very high moisture levels in the stationary source gas was overcome through the use of the water in the purge vessel of the purge and trap concentrator used in EPA Method 624[6] as a means of condensing out excess moisture from the desorbed sample prior to trapping. Because the remaining moisture would still freeze in a subambient capillary column, the analysis was performed on packed columns.

Since that time, the ambient air Tenax Method TO1,[7] the carbon molecular sieve Method TO2,[7] and a method for field validation of ambient air sampling using solid sorbents[8] have been published. The VOST protocol has been validated in laboratory and field studies.[9,10] These methods have much in common, yet enough differences that a laboratory performing analyses for VOC in ambient air, stack gas, water, soil, and sludge samples experiences significant and costly downtime when altering its instrument configuration from one method to another, even though the analysis is for the same type of compounds. The Hazardous Substance List (HSL) contains 35 VOC's that can be determined in water and soil. Method 624 lists 31 VOC's, of which 4 are not on the HSL. The common chlorinated and aromatic solvents on these lists are

also of interest in trial burns at hazardous waste incinerators for RCRA permitting and in ambient air.

The five VOC methods listed in Table I have been validated for use in determining the indicated compounds. Method 5030/8240,[11] as applied in the Contract Laboratory Program of the U.S. EPA, is applicable without additional validation to 35 of the 49 compounds listed. This is more than any of the other methods. VOST has been formally validated for 5 of the compounds. Many of the compounds listed in Table I are also listed in Appendix VIII of 40 CFR Part 61, and are therefore candidate compounds for VOST application during trial burns at hazardous waste incinerators. All five methods may be applicable to additional compounds, but this applicability must be demonstrated. Acceptable laboratory validation procedures for the application of these methods to additional compounds are not contained in the methods.

Over the past 8 years we have performed VOC analyses on thousands of water samples, hundreds of soil samples, approximately 1500 Tenax samples using cryogenic trapping, and another 1000 Tenax samples using a purge and trap apparatus. The majority (90 percent or more) of the Tenax work required the quantitative determination of 10 or fewer VOC's. The compounds varied for each project, but generally only a limited number were detected in any sample at levels greater than 50 ng. In this analytical situation, the additional resolving power of capillary column chromatography is not needed. The packed column technology combined with mass spectrometry is powerful enough for unequivocal results.

The methods used for analysis of Tenax or other solid sorbent samples, whether obtained from ambient air or stationary sources, have many common characteristics. The design and assembly of the sampling traps for ambient[7] and stationary sources[12] are compatible. Both require similar thermal conditioning and blank checking prior to sampling; both are applied to similar compounds; both are subject to similar sampling problems, various moisture levels, and breakthrough; and both require validation procedures to demonstrate applicability to specific circumstances.

Table II shows the similarities in the methods of sample introduction and analysis for the four sample types under discussion. A unified sample introduction system is highly desirable considering the similar methods and equipment and boiling point ranges of their target compounds relative to VOC sampling in ambient air, stationary sources, water, and soil. Such a system would permit the introduction of ambient air and stationary source solid-sorbent samples by thermal desorption, and water and soil samples by purge and trap into a GC/MS without major hardware changes. This would minimize instrument downtime and improve a laboratory's cost-effectiveness to its clients.

The methods used for the last three sample types in Table II have much in common. In the interest of laboratory efficiency and versatility, we have applied the general form of these methods to the analysis of ambient air samples, utilizing the same instrument hardware configuration as the VOST method.[12]

Analytical Equipment and Experimental Procedures

Sorbent Trap Preparation

Tenax-TA (or Tenax-TA and petroleum-based charcoal) is packed into clean glass traps (Figure 1) and thermally desorbed with a purge flow of approximately 40 ml/min purified nitrogen at a temperature of 240°C for 20 hours.

This conditioning is performed using a specially designed manifold/oven with a capacity for 38 individual traps. Extreme care must be used in the application of complex and detailed handling procedures[12] in order to produce traps containing less than 5 ng of any individual VOC.

Blank Check Procedures

Every sorbent trap or trap pair is blank checked prior to use for sampling. The apparatus used to perform blank checking (Figure 2) consists of a thermal desorption unit ("clamshell oven" - Supelco #2-3800) operated at 190°C with nitrogen-purge gas flowing at 40 ml/min to a Tekmar Model LSC-2 sample concentrator, bypassing the water-purge vessel. This system is interfaced to a temperature-programmable gas chromatograph with flame ionization detector. The sample introduction system, the GC column, and temperature program are identical to that employed for GC/MS analysis. External standards prepared from neat liquids in static gas bottles and loaded onto sorbent traps by use of the flash vaporization apparatus shown in Figure 3 are used for quantitation. Conditioned traps have been routinely produced with no greater than 5 ng of any volatile compound present.

GC/MS Analysis

The analytical procedures followed are generally those described in Methods 624 or 5030/8240[6,11] plus additional steps for desorption of Tenax and Tenax/charcoal sorbent traps. A schematic diagram of the sorbent trap desorption and purge and trap apparatus is shown in Figure 2. Internal standards are added to traps with a purge flow in the same direction as the sampling flow direction. Traps are thermally desorbed with a gas flow in the reverse direction from the sampling flow. Sorbent traps are spiked with an internal standard by use of a flash vaporization device (Figure 3) and thermally desorbed for 10 minutes at 180° to 200°C with 40 ml/min organic-free helium gas. For moisture-laden samples, the effluent is passed through 5 ml of organic-free water in the purge vessel; for dry samples, it bypasses the water purger and VOC's are collected on an analytical sorbent trap. After the 10-minute desorption, the analytical sorbent trap is rapidly heated to 180° to 200°C (dependent on target compound volatilities) with the gas flow reversed so that the effluent flow from the analytical trap is directed into the GC/MS. The VOC's are separated by packed-column temperature-programmed gas chromatography and detected by electron-impact low-resolution mass spectrometry. The mass of each VOC is calculated by the internal standard method.

The thermal desorption unit is a modified Supelco high-capacity gas purifier oven ("clamshell oven"). An Omega solid-state digital-temperature controller (Model 300) with thermocouple monitors and controls the desorber oven temperature. This unit can accept trap configurations from 1/16-in.-OD to 5/8-in.-OD and up to 10-in. long.

The purge and trap unit is a Tekmar Model LSC-2, on which all Teflon transfer lines are replaced with 1/16-in.-OD stainless-steel tubing to avoid contamination and/or losses. The transfer lines are wrapped with heat tape to avoid losses. The internal volume of the glass purge vessel is approximately 15 ml, and it contains 5 ml of organic-free water (if appropriate). This vessel is bypassed for dry ambient air samples. For water samples, the thermal desorption unit is bypassed, and the sample is added directly to the purge vessel. For soil samples, a differently designed, larger purge vessel is substituted and the soil and blank water are added to this vessel. Again, the thermal desorption unit is bypassed.

The internal analytical trap consists of a 15-cm section of Tenax, a 3.7-cm section of charcoal, and a 3.7-cm section of silica gel (Tekmar part 14-0124-003). The LSC-2 unit is a commercially available device designed to meet the requirements of Method 624.[6]

The GC/MS consists of a temperature-programmable packed-column gas chromatograph interfaced with an all-glass jet separator to a quadrupole mass spectrometer. All system controls and data acquisition are performed through a minicomputer-based data system. Samples are transferred from the introduction apparatus to the GC via heated 1/16-in. tubing connected to the standard injection port gas supply line. The septum-plugged injection port is used to perform on-column injections by syringe for recovery and tune checks.

The apparatus shown in Figure 3 is used to load standard solutions onto sorbent traps. It consists of a glass evaporation chamber with a septum-plugged side arm for standard injection. The chamber is heated to about 150°C with heat tape and is connected to the sorbent traps with a 1/4-in. stainless-steel union and Supeltex M-1 ferrules. Carrier flow is set at 100 ml/min so that the chamber volume (about 25 ml) is well swept in a 1-minute loading interval.

Autosampler

We collaborated with the Tekmar Company to redesign the Tekmar Model 4200 Automated Dynamic Headspace Concentrator to configure it to function as an automated version of the "clamshell oven" purge and trap sample introduction system. The new instrument, Model 4210 Automatic Desorber, is capable of sequentially desorbing 10 solid sorbent traps or trap pairs with the design shown in Figure 1. Each sample is thermally desorbed with an individually controlled heater and the effluent gas passes through a water-purge vessel (for VOST or moist ambient samples) unique to that sample. There is thus no possibility of carryover of sample components in the water purge vessel from sample to sample. A schematic of this instrument is shown in Figure 4. This unit will accept the same range of trap configurations as the "clamshell oven."

System Modifications for Various Media

The sample introduction system described can easily, with the following few minor modifications, be used for the analysis of VOC's in stationary source (VOST), ambient air, water, and soil samples. The water-purge vessel is removed from the flow stream for analysis of ambient air samples of low-moisture content. When water or soil samples are analyzed, a tubing union replaces the sorbent traps in the purge gas flow line. Soil samples require the use of a purge vessel with a different design (as per Method 5030) than is employed for other analyses.

Results

General Applicability

The sample introduction system described here has been applied in this laboratory to the analysis of ambient air samples collected on a variety of Tenax traps for the entire Hazardous Substance List (HSL) of volatile organic compounds. We have performed a limited recovery test for a methanolic standard of the entire HSL volatiles loaded onto a Tenax and Tenax/charcoal trap pair and thermally desorbed through a water purge vessel compared with an on-column injection of the same standard. Because the response of the three earliest eluting target compounds in the on-column injection was badly

suppressed by coelution with the solvent, their results were discarded. Table III presents recovery values for the remaining 32 targets, 3 surrogates, and 3 internal standards (38 compounds).

The four compounds that fell into the 25 to 50 percent recovery range were all water-soluble ketones which almost certainly would be recovered quantitatively if the water-purge vessel were removed from the flow path from the desorber. That leaves only one compound that fell outside the 70 to 130 percent recovery range. This demonstrates the broad range of applicability of this sample introduction technique.

Method Validation

Because of the wide variety of VOC's, the various procedures must be validated for a specific application. As shown in Table I, each method has been validated and is recommended for different compounds and many additional compounds have been requested for specific applications. The VOST has been validated for trichlorofluoromethane, chloroform, carbon tetrachloride, benzene, and perchloroethylene.[10] Method 624 has been validated for 31 compounds. The U.S. EPA's Contract Laboratory Program has compiled a huge database for the application of Methods 5030/8240 to water, soils, and sludges for the analysis of the 35 HSL VOC's. The range of compounds determined by the VOST can probably be extended closer to the high boiling point limit of Method TO1, considering that the first trap in the VOST is almost identical to the Tenax trap of TO1. If a second Tenax/charcoal trap (as in VOST) is added in series with the present Tenax trap of Method TO1, the range of compounds to which Method TO1 could be applied would probably match the low boiling point limit of the VOST. No appreciable cost increase would occur if these traps were analyzed as a pair. Application of modified methods such as we describe here or use of existing methods to determine compounds for which the method has not been validated demands that a cost-effective approach be developed for laboratory method validation.

A method of validating solid sorbent analysis using the sample introduction system described here was developed during the VOST validation studies. To test the sample introduction system, a standard is prepared containing the compounds of interest. This may be a static bottle gas standard or a methanolic solution. For early eluting compounds, a gas standard is preferred because a large quantity of methanol in the analytical system suppresses the response of compounds with which it coelutes. The standard is injected on-column as a 100 percent recovery calibration point. This standard is then loaded onto a sorbent trap or trap pair using a flash vaporization device.[13] The sorbent trap(s) is then analyzed to determine recovery through the sample introduction apparatus. For water or soil samples, the standard is added directly to the purge vessel. The absolute area response and the internal standard (I.S.) corrected response are both compared. During the VOST validation of five compounds, this laboratory obtained absolute area recoveries of between 78 and 109 percent and I.S.-corrected recoveries between 89 and 110 percent on nine separate weekly system checks. This on-column recovery test demonstrates that the sample introduction system is leak free and capable of delivering the sample to the analytical system without loss and that suitable calibration standards can be prepared on sorbent traps.

For ambient air and VOST samples, the effectiveness of a given sorbent(s) and trap design in collecting and thermally desorbing desired compounds must also be validated. Distributed air volume sampling can be employed for field validation of ambient samples, but is impractical for VOST and may be expensive for ambient air if it invalidates a series of samples from a dis-

tant site, forcing replication of the test. The following procedure is proposed for preliminary laboratory validation of the sampling and analysis approach prior to field application.

After the sample introduction system has been checked for recovery by use of the above procedure, a series of five trap samples are prepared. These may be single-sorbent traps or paired-sorbent traps in series (e.g., VOST). The standard used for the on-column check is loaded on the trap(s) and either 0, 5, 10, 15, or 20 liters (or other volumes suitable to the proposed sampling situation) of air or nitrogen is passed through each trap or trap pair. The entire amount of standard is loaded before any of the measured gas volume passes through the test sample. The measured volume may be dry gas or saturated with moisture depending on whether the application being tested is ambient air or stack gas. The temperature should be constant and known. A flow rate of 0.5 liter/min is convenient for preparing test samples during a concurrent GC/MS run. This constitutes a "worst-case" evaluation since the entire amount of the desired compounds is subjected to the total gas volume rather than as in a real sample where compounds are loaded continuously over the entire sampling volume. The internal standard is added as it would be to a real sample.

The test samples are analyzed and the internal standard corrected recovery for each component is calculated based on the zero gas volume trap being assigned 100 percent recovery. The average recovery for each 5-liter interval is determined (0-5, 5-10, 10-15, and 15-20). The mean of these four values is used to approximate the average recovery for a 20-liter sample.

Table IV shows the results of applying a procedure, similar to the one proposed, to four compounds of interest at an actual industrial site. Compounds C and D gave excellent recovery on all samples. This was anticipated because compound C has been determined on Tenax traps previously and compound D is similar to C and within the recommended ranges of Method TO1 (80° to 200°C). Compounds A and B have boiling points less than 80°C but are within the recommended VOST range of 25° to 125°C. The recoveries show that neither compound A nor B is retained on Tenax for any appreciable sample volume at a flow of 0.5 liter/min; however, the recoveries on the Tenax-Tenax/charcoal trap pairs is significantly improved. Considering that this pair of traps represents only a 60 percent increase in the amount of Tenax used for collection, the majority of the improvement in recovery is attributed to the presence of the charcoal. The recoveries for compounds A and B are presented graphically in Figure 5. Compound A shows slightly poorer recovery on Tenax than B, but significantly better recovery on Tenax-Tenax/charcoal pairs.

Compounds A and B are chemically dissimilar with B being somewhat polar and A having the lower boiling point. The recoveries for compound B on the Tenax-Tenax/charcoal pair for each increasing 5-liter interval were 96, 79, 66, and 56 percent (see Figure 5). For a 20-liter sample, the estimated average recovery is 74 percent. For the application in question, it was decided to keep the sample volume at 15 liters with an estimated average recovery of 80 percent.

During the actual field sampling, distributed air volume samples were collected. Concurrent samples were collected at 1, 1.5, and 2 times the nominal flow rate for sample volumes of 14, 21, and 28 liters. No differences were found in the calculated concentrations for compounds A, B, C, or D. For compounds A and B, this was attributed to the fact that actual field sampling rates were less than 50 ml/min and the laboratory study used 500 ml/min. This indicates that the laboratory validation method is a "worst-

case" approach. This application involved four compounds that, according to listed references, would have required at least two (TO1 and TO2) if not three separate sampling and analysis methods.

Autosampler Validation

We have performed a preliminary evaluation study to compare the Tekmar 4210 autosampler performance with the "clamshell oven" using six compounds which cover a boiling point range from 24°C to 152°C. One water-soluble compound, 2-butanone, was included even though its recovery from the unheated water-purge vessel was not expected to be acceptable. The standards were loaded from gas bottles onto Tenax and Tenax/charcoal tube pairs using a flash vaporization device at three levels (nominally 50 ng, 250 ng, and 1000 ng). Traps were loaded in triplicate at each level for analysis by both "clamshell" and autosampler. Recoveries from trap desorption were determined versus on-column injections of the same standards used to load the traps at all three levels. Results are summarized in Table V. These data indicate that the Tekmar Model 4210 autosampler performs equivalently to the "clamshell oven" for thermal desorption of solid-sorbent trap pairs.

Conclusions

The versatility of the described sample introduction system permits much greater cost-effective use of expensive laboratory instrumentation and personnel by minimizing instrument downtime and the need for an operator to master many different complex methods of analysis.

The described on-column recovery test demonstrates that the sample introduction system is leak free and capable of delivering the sample to the analytical system without loss and that suitable calibration standards can be prepared on sorbent traps.

The use of packed-column GC methods for ambient-air analyses usually does not adversely affect the quality of the data because the columns currently in use have sufficient resolving power to handle all but the most complex samples. In addition, packed columns have a greater sample capacity than capillary columns, which is very important in the thermal desorption of a sorbent trap because the sample cannot be reanalyzed using a smaller aliquot as can solid or water.

A laboratory validation procedure has been developed for the application of solid-sorbent sampling and analysis methods to specific VOC's. We were able to simplify ambient air monitoring for four diverse toxic volatile compounds by employing Tenax-Tenax/charcoal trap pairs. A synergistic effect is apparently created when the two sorbents, Tenax and charcoal, are combined. High-boiling components not amenable to Method TO2 never reach the charcoal and are trapped on the Tenax, while lower boiling components not amenable to Method TO1 are trapped in the charcoal and can be thermally desorbed at the lower desorption temperature required by Tenax.

The autosampler described here was shown to be equivalent in performance to the simple "clamshell" desorber. This type of instrument automation should make laboratory operations much more efficient and lower the cost of VOST and ambient air analyses performed according to the methods described here.

Acknowledgements

Special thanks are extended to Alan D. Zaffiro who performed the majority of the analytical work, to John W. Prohaska who managed the entire VOST validation effort and contributed many helpful suggestions, and to Anthony S. Wisbith for his assistance in evaluating the ambient air data.

The United States Environmental Protection Agency sponsored the VOST validation project, during which a portion of the development work reported in this article was completed.

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TABLE I. VALIDATED VOC'S FOR 5 METHODS (6,7,10,11)

Compound	Boiling point, °C	Methods				
		624	5030 8240[a]	TO1[b]	TO2[c]	VOST[d]
Chloromethane	-24	X	X			
Vinyl chloride	-14	X	X		X	
Bromomethane	4	X	X			
Chloroethane	12	X	X			
Trichlorofluoromethane	24	X				X
1,1-Dichloroethene	32	X	X		X	
Methylene chloride	40	X	X		X	
3-Chloropropene	45				X	
Carbon disulfide	46		X			
trans-1,2-dichloroethene	48	X	X			
Acetone	56		X			
1,1-Dichloroethane	57	X	X			
Chloroform	61	X	X		X	X
Vinyl acetate	72		X			
1,1,1-Trichloroethane	74	X	X		X	
Carbon tetrachloride	77	X	X		X	X
Acrylonitrile	78				X	
Benzene	80	X	X	X	X	X
2-Butanone	80		X			
1,2-Dichloroethane	84	X	X		X	
Trichloroethene	87	X	X	X	X	
Bromodichloromethane	90	X	X			
1-Heptene	94			X		
1,2-Dichloropropane	97	X	X	X		
Heptane	98			X		
2-Chloroethylvinyl ether	108	X	X			
Toluene	111	X	X	X	X	
cis-1,3-Dichloropropene	112	X	X			
trans-1,3-Dichloropropene	112	X	X			
1,1,2-Trichloroethane	114	X	X			
4-Methyl-2-pentanone	119		X			
Dibromochloromethane	120	X	X			
Tetrachloroethene	121	X	X	X		X
1,3-Dichloropropane	125			X		
2-Hexanone	127		X			
Chlorobenzene	132	X	X	X		
1,2-Dibromoethane	132			X		
Ethylbenzene	136	X	X	X		
Xylenes	138		X	X		
Styrene	146		X			
1,1,2,2-Tetrachloroethane	146	X	X			
Bromoform	150	X	X	X		
Cumene	152			X		
Bromobenzene	155			X		
1,3-Dichlorobenzene	172	X				
1,4-Dichlorobenzene	173	X		X		
Benzyl chloride	179			X		
1,2-Dichlorobenzene	180	X				
Nitrobenzene	211			X		

[a] These compounds are reported for water and soils according to the Contract laboratory Protocol as revised September 1984.

[b] The tentative compounds listed for this method are nonpolar ones with boiling points between 80 and 200°C.

[c] The tentative compounds listed for this method are nonpolar ones with boiling points between -15 and 120°C.

[d] The tentative compounds listed for this method are ones with boiling points between 25 and 125°C.

TABLE II. COMPARISON OF METHODS FOR VOC ANALYSIS

Method No.	Matrix	Means of sample introduction	GC column type
TO1	Ambient air	Thermal desorption Cryogenic trapping	Subambient Capillary
TO2	Ambient air	Thermal desorption Cryogenic trapping	Subambient Capillary
VOST	Stack gas	Thermal desorption Purge-trap-desorption	Packed
624	Water	Purge-trap-desorption	Packed
5030/8240	Solids	Purge-trap-desorption	Packed

TABLE III. RECOVERY OF HSL VOLATILE COMPOUNDS

Percent recovery range	Number (%) of compounds
70 to 130	33 (86.8)
25 to 50	4 (10.5)
130 to 150	1 (2.6)

TABLE IV. VALIDATION RESULTS FOR SORBENT MEDIA AND SAMPLE VOLUME

Trap type	Compound	Recovery, % 5.0 L	7.5 L	15 L	20 L
Tenax					
	A	49	17	1	NA
	B	58	39	3	NA
	C	101	98	99	NA
	D	105	118	113	NA
Tenax and Tenax/Charcoal					
	A	90	85	82	74
	B	91	79	60	53
	C	98	99	96	95
	D	98	101	110	100

NA = Not analyzed.

TABLE V. AUTOSAMPLER VALIDATION RESULTS

Compound	Boiling point, °C	Percent recovery Clamshell	Autosampler
Trichlorofluoromethane	24	96.2 ± 7.5	96.9 ± 5.6
Trichloromethane	61	96.1 ± 9.7	98.2 ± 14.9
2-Butanone	80	17.2 ± 7.1	13.6 ± 3.4
Methylbenzene	111	113.6 ± 8.4	116.4 ± 8.0
Tetrachloroethene	121	119.1 ± 10.6	107.3 ± 6.0
(1-Methylethyl)benzene	152	123.0 ± 28.7	111.1 ± 6.4

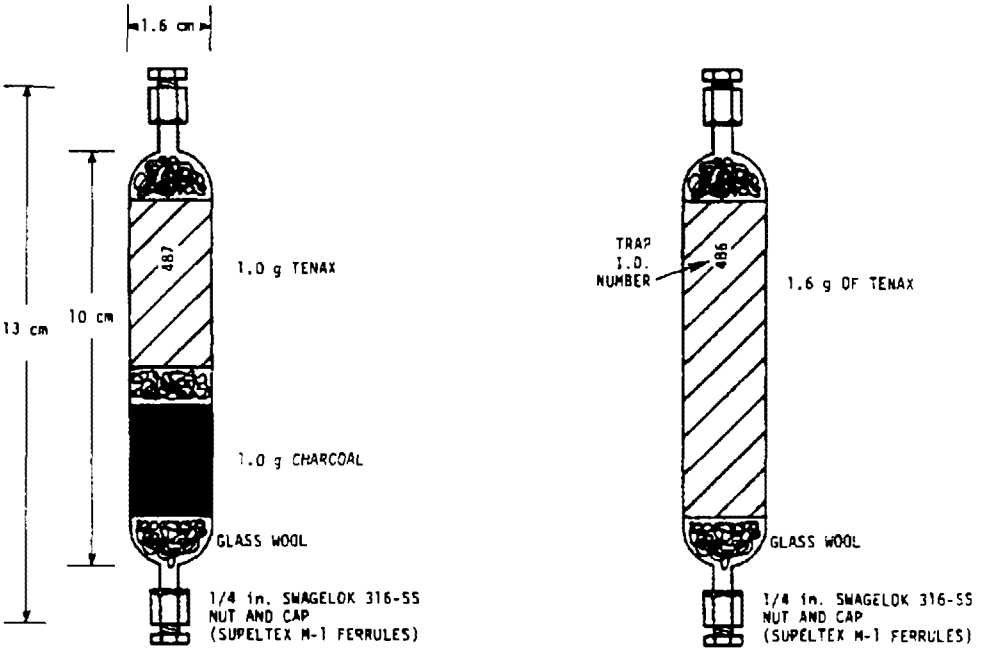

Figure 1. Sorbent trap configurations.

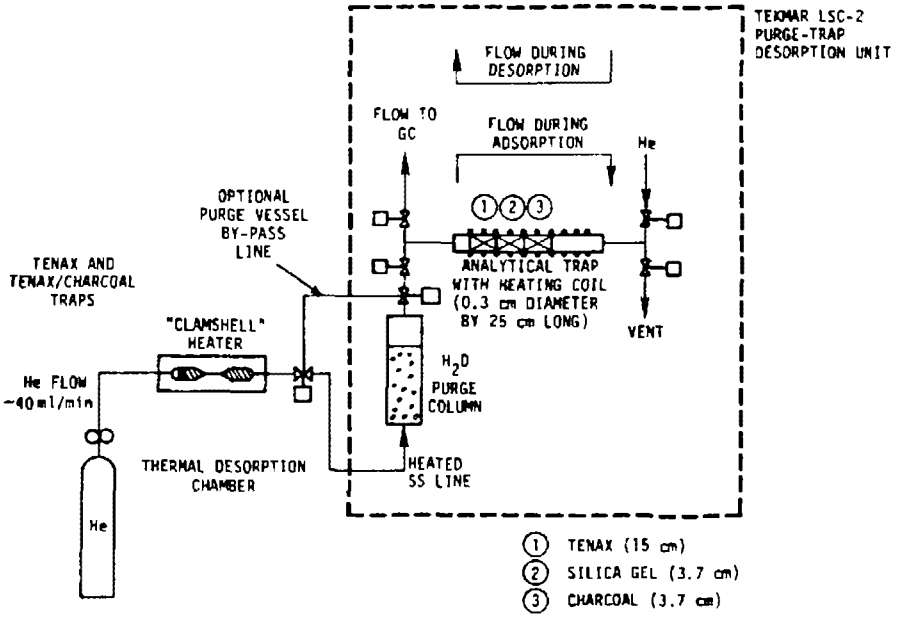

Figure 2. Schematic of sorbent trap desorption and purge and trap apparatus.

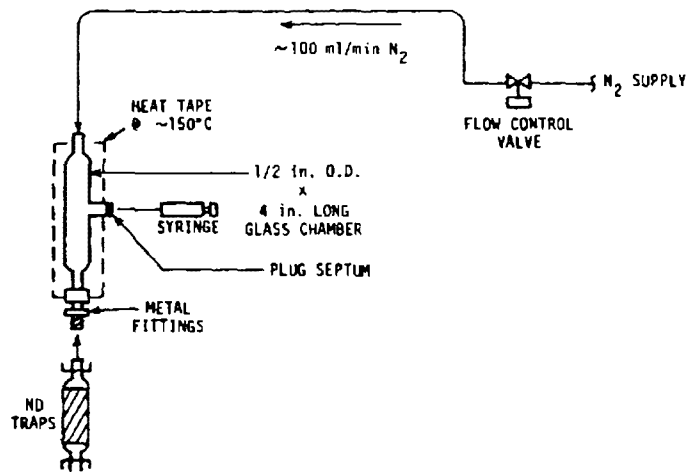

Figure 3. Flash vaporization apparatus for loading standards onto sorbent traps.

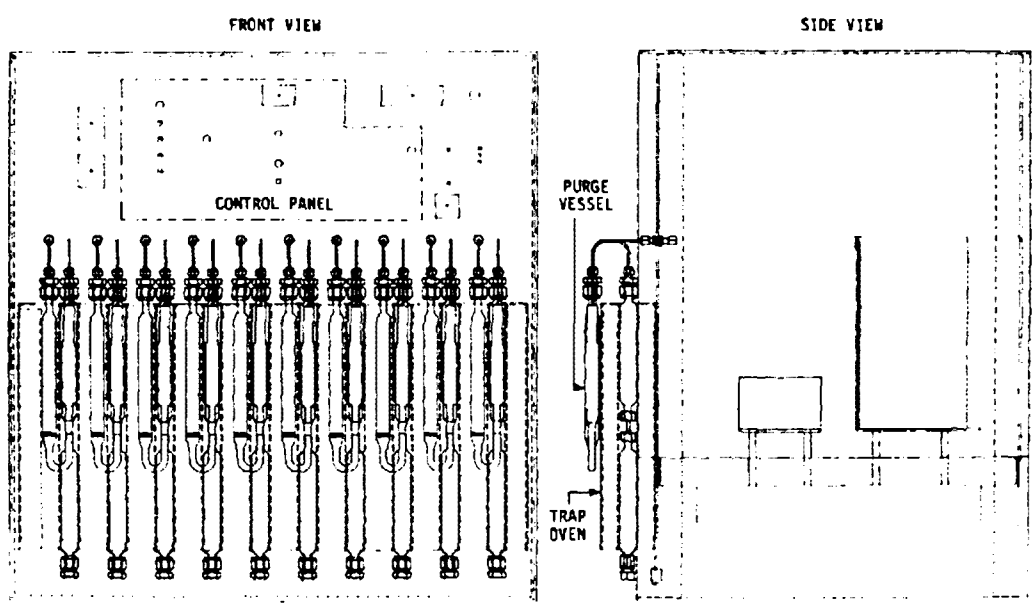

Figure 4. Autosampler for thermal desorption of sorbent traps or trap pairs.

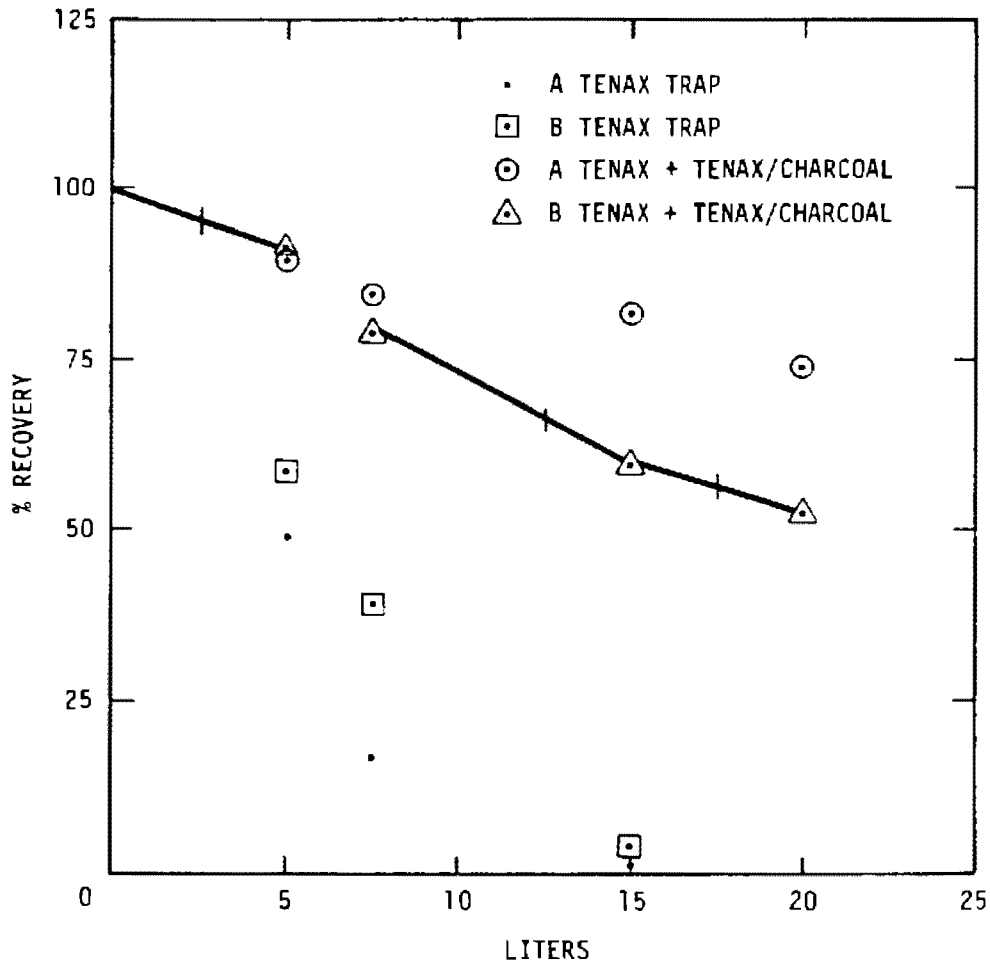

Figure 5. Tenax trap and Tenax + Tenax/charcoal trap pair recoveries for compounds A and B.

EVALUATION OF METHOD 25 NONMETHANE ORGANIC ANALYZER DESIGN

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Under contract to the United States Environment Protection Agency, Research Triangle Institute has been conducting research to improve the precision, accuracy and limit of detection attainable with the EPA Method 25 nonmethane organic (NMO) analyzer. In Method 25, volatile organic carbon (VOC) samples are collected by drawing gas from an emitting source through a dry ice cooled sample trap and into an evacuated collection tank. The hydrocarbon concentration emitted from the source is determined on a per-carbon basis by catalytically converting the trap and tank sample fractions to CO_2 and quantitating the amount of CO_2 produced using the NMO analyzer.

A reduction catalyst evaluation led to the selection of an NMO analyzer reduction catalyst which operates at a moderate temperature and displays no appreciable effect on peak shape.

A gas chromatographic column system which provides better permanent gas separation and hydrocarbon quantitation was also selected for use in the NMO analyzer.

Introduction

Method 25 was developed in the mid 1970's as a means of determining the amount of volatile organic carbon (VOC) emissions from stationary sources. After stack sampling and sample trap recovery, the quantitative measurements of the method are performed on a unit known as the nonmethane organic (NMO) analyzer. This unit is an oxidation/reduction gas chromatograph which separates permanent gases (methane, carbon monoxide, and carbon dioxide) from hydrocarbons so that a total hydrocarbon concentration may be determined. Since the analyzer does not speciate between hydrocarbons, the instrument must respond equivalently to all hydrocarbons to generate valid NMOC data. The equivalency of response is achieved by catalytically oxidizing the hydrocarbons to CO_2 and reducing the CO_2 to methane which is measured by a flame ionization detector (FID). Though the operating principles are simple, there are numerous configurations possible for the NMO analyzer. In the years since the method's inception, each contractor performing Method 25 measurements has attempted to develop this own analyzer configuration with varying degrees of success. The purpose of this evaluation to standardize the configuration of the NMO analyzer and the associated materials necessary for Method 25 analyses.

The main concerns with the present analyzer design as recommended in the Federal Register are 1) overly complex plumbing arrangement; 2) inadequate GC column temperature control; 3) poor separation of nonmethane organics from high concentration carbon dioxide; 4) poor recovery of oxygenated compounds; and 5) unspecified reduction catalyst. The three specific objectives of the investigation were 1) selection of a reduction catalyst and optimization of its operating conditions in relation to analyzer performance; 2) development of a GC column system for the separation of the permanent gases from nonmethane organics; and 3) evaluation of instrument performance with the modifications described above.

Experimental Methods

Reduction Catalyst Evaluation

The NMO analyzer reduction catalyst and its associated operating conditions have a direct effect on the instrument's sensitivity, linearity, and analytical precision. Prior to the reduction catalyst evaluation, three candidates were selected from the catalysts available commercially. Each material was applicable to the hydrogenation of carbon oxides, was readily available and relatively inexpensive. These materials were:

- Low carbon nickel powder, 100 mesh, 99.999% pure, sold by Johnson Matthey Inc.
- 60 to 65% nickel on alumina powder, reduced and stabilized, sold by Alfa Chemical Company.
- 50% nickel on a 1/16-inch extruded support, sold by Harshaw Chemical Company.

Tests of the first two materials allowed comparison of pure nickel with a percent-loading of nickel on an inert support. The powder forms were selected to reduce the unpacked volume of the reactor tube and produce the optimum peak shape. The final material allowed evaluation of the effect of an extruded substrate on peak shape and reduction catalyst efficiency.

Each catalyst was evaluated for both reduction catalyst efficiency and peak shape versus temperature. Three inches of a 1/4-inch OD Inconel® tube were packed with catalyst and installed in a vertical tube furnace. The FID response was calibrated with a one percent methane in air mixture. Reduction catalyst efficiency was evaluated by injecting one cubic centimeter (cc) samples of a one percent carbon dioxide in air mixture through the heated catalyst beds and by measuring the effluent methane concentration by FID. The initial catalyst temperature was 250°C and was increased in 50°C increments up to 400°C. The reduction efficiency of each catalyst was determined by comparing the response factors (area counts/ppmC) produced after CO_2 reduction to methane with the response factor produced by the methane standard. The response factors would be equal in the case of 100 percent catalyst efficiency.

In addition to the reduction efficiency measurements, determinations of peak shape were performed at each temperature. These measurements involved the analysis of a 55.6 parts-per-million (ppm) CO_2 in air standard in addition to the one percent CO_2 standard. The lower concentration standard was used to assess the effect of concentration on the catalyst peak shape produced. A high chart recorder speed was used during peak elution to allow assignment of peak asymmetry factors (see Figure 1). The goal for the peak asymmetry factor was 1.2 or less. This degree of peak asymmetry is considered normal in gas chromatographic analysis.[1] The peak width at one-half height also was used as a quantitative measure of peak broadening.

GC Column Evaluation

Three materials initially were tested as possible chromatographic column materials for use in the NMO analyzer. The analyzer GC column performs the separation of permanent gases (methane, CO, and CO_2) from nonmethane organics. The GC columns used to date have either provided poor separation between the permanent gases and hydrocarbons, or presented difficulty in quantitatively releasing the hydrocarbons upon backflush and heating. The three materials tested were 60/80 mesh Carbopack® B, 60/80 Porasil® B, and 60/80 mesh Unibeads® 1S. The main advantages of the Carbopack® were 1) its nonselective adsorbence which of all organics strongly independently of their structure; 2) was relatively chemically inert; 3) its thermal stability which allowed heat desorption up to high temperatures; and 4) minimal adsorption of water and light gases such as methane.

The Unibeads® 1S and Porasil® B materials were selected because they are able to separate components based on molecular size rather than chemical characteristics, a useful quality in separating permanent gases from nonmethane organics.

Each material was packed into a 2-ft. length of 1/8-in. OD stainless steel tubing and installed in the column oven of a Perkin Elmer 3920-B gas chromatograph. A 10-port stainless steel rotary valve was used to inject one cc aliquots of test gas. An oxidation catalyst consisting of 19 percent chromia on 1/8-in. alumina pellets and operated at 650°C was used to convert the organics to carbon dioxide. The reduction catalyst consisted of a 3-in. long, 1/4-in. OD tube packed with 100 mesh nickel powder which was mounted vertically within a tube furnace. The catalyst was maintained at 400°C using on Omega Model 802M temperature controller equipped with a Type K thermocouple.

A mixture of 20 ppm ethane, 20 ppm propane, 50 ppm carbon monoxide, 50 ppm methane, and two percent carbon dioxide in air was analyzed with the 2-ft. columns of each proposed material. These tests provided data regarding separation of the permanent gases from NMO, total analysis time, accuracy of NMO analysis, and peak shape. Optimal analytical conditions for each column during analysis included column temperature, carrier gas flow rate, and valve switch timing for column backflush.

After selection of a GC column, compound response tests were conducted to ensure that no compounds would interact with the column system and prevent analysis. Samples of carbon dioxide in air, methanol in air, acetone in air, toluene in air, and hexane in air were analyzed at concentrations of 100 ppmC and 10000 ppmC.

Instrument Performance Evaluation

The NMO analyzer, equipped with the selected reduction catalyst and GC column, was tested to determine the linearity, precision, and limit of detection of the new system. Standards consisting of 20 ppm, 200 ppm, and 3000 ppm propane in air, and 50 ppm, 500 ppm, and 10000 ppm carbon dioxide in air were analyzed in triplicate. The relative standard deviation for each set of injections was determined as well as the overall mean response factors. The goals for these parameters were two percent relative standard deviation or less and agreement between the individual response factors and the mean response factor of $\pm$ 2.5 percent.

The detection limit for both carbon dioxide and propane also were measured. Test gases consisting of 20 ppm propane in air and 55.6 ppm CO_2 in air were analyzed in replicate. For each analysis, the peak height,

attenuator setting, concentration, and peak width at one-half height were recorded. Following each analysis, the attenuator was set to a value which prominently displayed the baseline noise on the chart. An injection of zero air then was performed and the height of the largest noise peak within a period of 10 times the sample peak width was recorded and the limit of detection then calculated by Equation 1.

$$C_{LOD} = 1.9718\ h_n\ A_n\ C_s\ /\ h_s\ A_s \qquad (1)$$

where:

h_n = peak height of noise, mm
A_n = attenuation during noise measurement
C_s = sample concentration, ppm
h_s = peak height of sample, mm
A_s = attenuation during sample measurement

This detection limit is equivalent to three times the standard deviation of the noise as recommended by the American Chemical Society Committee on Environmental Analytical Chemistry.[2]

Results and Discussion

Reduction Catalyst Selection

The 50 percent nickel on 1/16-in. extruded support and the 100 mesh nickel powder were tested for reduction efficiency and peak distortion in a temperature range from 250-400°C. The 60-65 percent nickel powder was eliminated from consideration because it presented too high a restriction to carrier gas flow due to its small mesh size. The reduction catalyst efficiency versus temperature data presented in Table I showed the reduction efficiency of each catalyst to increase up to 350°C, after which a slight drop in efficiency was observed. The 100 mesh nickel powder provided better reduction efficiency at all but the lowest temperature. The decrease in reduction efficiency between 350 and 400°C was also less pronounced with the nickel powder.

The peak shape versus temperature data reported in Table II showed each catalyst to produce very broad tailing peaks at low temperature. This result is revealed by the large asymmetry factors and peak width numbers. The peak shape and peak width produced by each catalyst improved as the temperature was increased. The 100 mesh nickel powder ultimately produced the narrowest peaks with the smallest asymmetry factors. At 400°C the peak shape and width observed after CO_2 reduction by the nickel powder was essentially identical to the methane peak shape observed with no reduction catalyst. This result meant that the nickel powder would be essentially "invisible" in the analyzer system with regard to peak distortion effects when used at 400°C.

Development of GC Column System

An initial screening of the proposed column packings served to identify the most promising materials and provided valuable information as to the column dimensions and heating procedures necessary for successful nonmethane organic analysis. In the initial tests, a 2-ft. long, 1/8-in. diameter column of each material was packed and installed in the analyzer system. A test gas mixture consisting of 49.2 ppm of carbon monoxide, 48.9 ppm of methane, 19200 ppm of CO_2, and 19.50 ppm propane was analyzed to determine each material's ability to separate these components. Some secondary tests used a mixture of 50020 ppm CO_2, 24.86 ppm propane, and 10.95 ppm toluene and the mixture used to determine the extent to which relatively heavy compounds were retained. The results obtained are shown in Table III.

The 2-ft. Carbopack® column was unable to separate CO_2 from the other permanent gases or completely separate CO_2 from propane. In subsequent tests using a 6-ft. Carbopack® column, the permanent gases were still unseparated. Injections performed with the gas containing toluene showed the Carbopack® to interact strongly with this compound thereby causing an extremely poor backflush peak. The Porasil® B also was unable to separate the permanent gases and provided only partial separation between CO_2 and propane.

The Unibeads® 1S material proved to be the most promising for use in

the NMO analyzer at the end of the initial screening. A 2-ft. Unibeads® column provided better separation of the permanent gases than had an equivalent length of Carbopack® B. Tests in which hydrocarbon and permanent gases were included showed the hydrocarbons to be separated from CO_2 and to elute as a single peak upon backflushing and heating the column. Due to the superior separation provided by the Unibeads® material, the Carbopack® was eliminated from further consideration.

Though the 2-ft. Unibeads® column provided excellent separation between the permanent gases and hydrocarbons larger than propane, ethane and ethylene were small enough in size that they eluted among the permanent gases. A 6-ft. Unibeads® column operated at 80°C successfully separated the smaller hydrocarbons from the permanent gases but led to unacceptably long CO_2 retention times. This result led to the selection of Carbosieve® G for use as a secondary column material to use in conjunction with the Unibeads® 1S. In the new column system the Unibeads® material was to perform the separation of the permanent gases and larger hydrocarbons while the carbosieve retained the smaller hydrocarbons as the permanent gases eluted. Testing of this column arrangement showed it to be capable of separating the small hydrocarbons from CO_2 while improving the CO_2 retention time. A summary of these tests is presented in Table IV.

It was found that very polar compounds became strongly adsorbed onto Carbosieve®. Methanol samples remained adsorbed onto Carbosieve® even after backflush and heating. This development required a modification of the column system. A 1-ft. section of the Unibeads® 1S was placed in front of the Carbosieve® G to trap methanol and all organics larger than propane. A 2-ft. Carbosieve® section was used to retain the smaller hydrocarbons and separate the permanent gases. A summary of the tests performed with this new column system is shown in Table V.

Single Component Equivalent Response Test Results

The tests of equivalent analyzer response to various hydrocarbons were performed with mixtures of carbon dioxide in air, methanol in air, acetone in air, toluene in air, and hexane in air. The responses of these mixtures at concentrations of approximately 100 ppmC and 10000 ppmC were recorded and compared to the response produced by a methane standard gas. The data generated are presented in Table VI.

In general, the responses produced by the high level gas mixtures agreed better with the methane response factors than did the low level mixtures. Part of the disagreement at low level was due to the fact that the lower concentration organic mixtures were produced by diluting the high level mixtures. Errors of approximately one percent in the dilution process could account for the discrepancies seen at low level considering the fact that the starting concentrations were approximately 10000 ppmC. Even with these dilution errors, the response factor discrepancies observed at low level were no more than a few percent, with the exception of acetone. This compound produced relatively broad peaks at low level, which probably lead to integration errors.

Linearity and Precision Tests

The complete analyzer was tested for linearity and precision by the analysis of propane and carbon dioxide in air. Standards consisting of approximately 20 ppm, 200 ppm, and 3000 ppm propane in air and 50 ppm, 500 ppm, and 10000 ppm carbon dioxide in air were analyzed in triplicate. The relative standard deviation for each set of injections as well as the overall mean response factors then were determined. The goals for these parameters were two percent relative standard deviation or less and agreement between the individual response factors and the overall mean response factor of $\pm$ 2.5 percent. The data obtained are shown in Table VII.

Excellent precision was observed between the individual injections of propane and CO_2 at each concentration as is demonstrated by the low relative standard deviation numbers. Exceptional agreement also was noted between the mean response factors produced at each propane and CO_2 concentration, thereby demonstrating the instrument's linearity over a wide concentration range. The close agreement between the overall propane and CO2 response factors confirms the quantitative processing and catalytic

conversion of organics within the analyzer system.

Determination of the Detection Limit

The final test performed on the analyzer was a determination of the detection limit. The detection limits for both carbon dioxide in air and propane in air were established by the analysis of low level concentrations of each of these gas mixtures, and use of Equation 1. The limits of detection for propane and CO_2 are listed below.

Propane Detection Limit = 0.10 ppm
CO_2 Detection Limit = 0.16 ppm

It should be noted that the detection limit is not the limit at which a compound may be quantitatively analyzed. The limit of quantitation is approximately three times higher in most cases.[3]

Conclusions and Recommendations

Reduction Catalyst

The results of both the CO_2 Reduction Efficiency and the Catalyst Peak Distortion Tests led to the selection of the 100 mesh nickel powder as the recommended Method 25 reduction catalyst. This catalyst provided the most efficient reduction of CO_2 to methane at the temperature required to produce acceptable peak shape. At 400°C the methane peak shape produced following CO_2 reduction was almost identical to the methane standard peak shape observed with no catalyst in the system. This indicated that the reduction reaction had no effect on peak shape when the catalyst was operated at this temperature.

Recommended Chromatographic Column System

A chromatographic column system consisting of a 1-ft. long, 1/8-in. diameter column of 60/80 mesh Unibeads® 1S followed by a 2-ft. long, 1/8-in. diameter column packed with 60/80 mesh Carbosieve® G was selected for the NMO analyzer. In this column system the Unibeads® material is used to trap very small polar compounds such as methanol and all hydrocarbons larger than propane. The Carbosieve® G performs the separation of the permanent gases and retains the smaller hydrocarbons. The column system is heated to 195°C and backflushed to desorb the hydrocarbons for NMO analysis. The advantages of these two materials derive from the fact that each is an uncoated adsorbent material rather than a coated column packing. Being uncoated adsorbents, they are much less likely to irreversibly adsorb hydrocarbons during Method 25 analyses thereby altering the analysis results. A chromatogram of a typical analysis is presented in Figure 2.

Injection onto the column is performed at 85°C. At this temperature there is partial separation of CO and CH_4. Complete separation of these two components may be achieved by performing the injection at a lower temperature. However, the CO_2 elution time will be lengthened slightly in this case. After injection, all compounds through CO_2 should be allowed to elute at 85°C. The column should be backflushed and immediately heated to 195°C after CO_2 elution to desorb the trapped hydrocarbons for NMO analysis. The entire cycle should be approximately six minutes long.

Column Materials Preparation

A cleanup of the column materials is required prior to installation of the column system in the NMO analyzer. Initially the Unibeads® material should be packed in a 1-ft. long section of 1/8-in. OD stainless steel tubing. The Carbosieve® G should be packed into a 2-ft. long section of the same diameter tubing. Each of the column sections should be heated separately with helium flow at 195°C for at least one day, before the column sections are joined. This heating serves to cleanup the materials considerably and greatly reduces the baseline rise seen when the column system is backflushed and heated during NMO analysis. Failure to perform this cleanup step will result in an unusable system.

Nonmethane Organic Analyzer Design

A diagram of the suggested NMO analyzer configuration is presented in

Figure 3. The GC column system is the same as described previously. The oxidation catalyst consists of a 14-in. length of 3/8-in. OD Inconel® tubing which is mounted vertically within a tube furnace. The center 2-inches of the tube are packed with 1/8-in. pellets of 19 percent chromia on alumina catalyst. The remainder of the tube is packed with quartz wool to reduce dead volume and hold the catalyst in place. The oxidation catalyst temperature should be maintained at 650°C. Helium at approximately 30 cc per minute should be used as carrier gas. Oxygen at a flow rate of approximately 2.2 cc per minute should be added to the carrier stream just before the oxidation catalyst.

The reduction catalyst is composed of a 3-in. length of 1/4-in. OD Inconel® tubing, packed with pure 100 mesh nickel powder (Aesar® catalog number 12966). The catalyst tube should be mounted vertically and heated to 400°C within a tube furnace. Hydrogen at a flow rate of approximately 40 cc per minute should be added to the carrier stream immediately before the reduction catalyst. The hydrogen flow rate should be adjusted to provide optimum FID response and prevent flame blowout during valve actuation. The hydrogen in the reduction catalyst effluent is used for the FID flame; therefore the addition of hydrogen at the FID is unnecessary and will only reduce instrument response.

References

1. L. R. Snyder and J. J. Kirkland, Introduction to Modern Chromatography, John Wiley and Sons, Inc., 1979 (pp. 222-225).

2. Joseph E. Knoll, "Estimation of the Limit of Detection in Chromatography," Journal of Chromatographic Science, 23, 422-425 (1985).

3. ACS Committee on Environmental Improvement, Daniel Mac Doughal, Chairman, "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry," Analytical Chemistry 52 2242-2249, 1980.

Table I. Reduction Catalyst Efficiency Versus Temperature.

Catalyst Temp., °C	Sample	Conc. (ppm C)	Nickel Powder Reduction Efficiency	Extruded Catalyst Reduction Efficiency
250	CO_2	10093	73.75	88.13
300	CO_2	10093	100.25	97.73
350	CO_2	10093	103.04	101.33
400	CO_2	10093	101.97	96.80

Table II. Peak Shape Versus Temperature Test Results.

Catalyst Temp., °C	Sample	Conc. (ppmC)	Nickel Powder Asymmetry Factor	Extruded Catalyst Asymmetry Factor	Nickel Powder Peak Width (sec)	Extruded Catalyst Peak Width (sec)
250	CH_4	9850.0	0.643	1.00	1.49	1.55
250	CO_2	10093.0	*	9.21	*	11.80
250	CO_2	55.6	*	*	*	*
300	CO_2	10093.0	7.16	2.71	12.19	2.81
300	CO_2	55.6	6.48	6.43	10.87	3.45
350	CO_2	10093.0	1.53	1.10	1.77	1.83
350	CO_2	55.6	1.51	2.40	1.75	1.84
400	CO_2	10093.0	0.640	0.99	1.61	1.67
400	CO_2	55.6	0.641	1.25	1.62	1.78
400	CH_4	9850.0	0.573	1.00	1.63	1.69

*Peak too distorted for measurement of dimensions

Table III. Column Material Screening Results.

Column Material	Column Length (feet)	Injection Temp., °C	Backflush Temp., °C	Test Gas	Comment
Carbopack® B	2	75	150	CH_4, CO, CO_2, Propane	No separation of permanent gases. Propane not completely separated from CO_2.
Carbopack® B	6	75	150	CH_4, CO_2, CO, Propane	No separation of permanent gases. Propane separated from CO_2.
Carbopack® B	6	75	150	CO_2, Propane, Toluene	Propane and CO_2 are separated. Toluene tails tremendously on backflush and is strongly retained by column.
Porasil® B	2	75	150	CH_4, CO, CO_2, Propane	No separation of permanent gases. Propane partially separated from CO_2.
Unibeads® 1S	2	75	120	CH_4, CO, CO_2, Propane	Partial separation of methane and CO from CO_2. Partial separation of propane from CO_2.
Unibeads® 1S	2	50	120	CH_4, CO, CO_2, Propane	Complete separation of CO/CH_4 peak from CO_2. Complete separation of propane from CO_2 but it elutes too quickly to backflush. Analysis time extended greatly because of lower injection temperature.
Unibeads® 1S	4	75	150	CH_4, CO, CO_2, Propane	Complete separation of CO/CH_4 peak from CO_2. Enough separation between CO_2 and propane for propane to be backflushed. Analysis time faster.
Unibeads® 1S	4	75	150	CO_2, Propane, Toluene	CO_2 peak completely separated. On backflush, propane and toluene are separated partially.
Unibeads® 1S	4	80	150	CO_2, Propane, Toluene	CO_2 peak completely separated. Propane and toluene are still separted somewhat on backflush.
Unibeads® 1S	3	50	150	CO, CO_2	CO_2 completely separated. Propane and toluene elute as a single peak on backflush.
Unibeads® 1S	3	50	150	CO, CH_4, CO_2, Ethane	Ethane separated from CO/CH_4 peak and from CO_2 peak.

Table IV. NMO Analyzer Column Evaluation Test Results.

Column Material and Length	Injection Temp., °C	Backflush Temp., °C	Test Gas	Comment
3 feet Unibeads® 1S	80	NA	CO_2, Ethylene	Complete separation of ethylene and CO_2 but long CO_2 elution time.
3 feet Unibeads® 1S + 6 inches Carbosieve®	110	NA	CO_2, Ethylene	Almost complete separation of ethylene and CO_2. CO_2 retention time reduced.
3 feet Unibeads® 1S + 6 inches Carbosieve®	90	160	CO_2, Propane, Toluene	Propane and toluene elute as a single peak on backflush which tails somewhat.
3 feet Unibeads® 1S + 6 inches Carbosieve®	75	160	CO, CH_4, CO_2, Propane	Separation of CO/CH_4 peak from CO_2. Propane elutes on backflush and tails.

(continued)

Table IV. NMO Analyzer Column Evaluation Test Results (continued).

Column Material and Length	Injection Temp., °C	Backflush Temp., °C	Test Gas	Comment
3 feet Unibeads® 1S + 6 inches Carbosieve®	80	160	CO, CH_4, CO_2, Propane	Separation of CO/CH_4 peak from CO_2. Propane elutes on backflush and tails. Analysis time is faster.
3 feet Unibeads® 1S + 6 inches Carbosieve®	80	180	CO, CH_4, CO_2, Propane	Propane tails less. Analysis time is faster.
3 feet Unibeads® 1S + 6 inches Carbosieve®	80	180	CO_2, Propane, Toluene	Propane and toluene elute as a single peak on backflush.
3 1/2 feet Unibeads® 1S + 6 inches Carbosieve®	80	180	CO, CH_4, CO_2, Propane	Partial separation of CO and CH_4 and better separation of these components from CO_2. Propane is still sharp on backflush.
3 1/2 feet Unibeads® 1S + 6 inches Carbosieve®	80	180	CO, CH_4, CO_2, Ethane, Propane	Partial separation of CO and CH_4. Ethane and propane elute as a single peak on backflush.
3 1/2 feet Unibeads® 1S + 6 inches Carbosieve®	80	NA	CO, CH_4, CO_2, Ethane, Propane	All components were allowed to elute in foreflush mode to confirm ethane separation from CO_2.
3 1/2 feet Unibeads® 1S + 6 inches Carbosieve®	80	NA	CO_2, Ethylene	The ethylene peak was completely resolved from the CO_2 and showed approximately the same retention time as ethane.
3 1/2 feet Unibeads® 1S + 6 inches Carbosieve®	75	180	CO, CH_4, CO_2, Ethane, Propane	Improved separation between CO and CH_4 although they are still partially unresolved. Ethane and propane still elute as a single peak on backflush. Total analysis time is approximately 370 seconds.

Table V. Final Column Analyzer Configuration Test Results.

Column Material and Length	Injection Temp., °C	Backflush Temp., °C	Test Gas	Comment
2 feet Carbosieve® G	95	185	CO, CH_4, CO_2 Ethane, Propane	Almost complete separation of CO & CH_4. Ethane & Propane elute together on backflush.
2 feet Carbosieve® G	95	185	Methanol	No peak elutes.
3-1/2 feet Unibeads® 1S	110	NA	Methanol	Methanol did not elute on foreflush.
3-1/2 feet Unibeads® 1S	110	190	Methanol	Methanol elutes as a broad peak on backflush.
2 feet Carbosieve® G+ 3 feet Unibeads® 1S	95	185	CO, CH_4, CO_2, Ethane, Propane	Almost complete separation of CO & CH_4. CO_2 retention time is very long (app. 4 min.). Ethane & Propane elute together on backflush.
2 feet Carbosieve® G+ 1 foot Unibeads® 1S	85	185	CO, CH_4, CO_2, Ethane, Propane	Almost complete separation of CO & CH_4. CO_2 retention time is much shorter. Ethane & Propane elute together on backflush.
2 feet Carbosieve® G+ 1 foot Unibeads® 1S	85	195	Methanol	Broad methanol peak elutes on backflush.
2 feet Carbosieve® G+ 1 foot Unibeads® 1S	85	195	CO, CH_4, CO_2, Ethane, Propane	Almost complete separation of CO & CH_4. Ethane & Propane elute together on backflush.

Table VI. Equivalent Hydrocarbon Response Test Results.

Compound	Concentration (ppmC)	Response Factor (Area Counts/ppmC)	Percentage of Methane Response Factor
Acetone	8003.8	45.43	100.46
Acetone	99.4	49.61	109.71
Toluene	9973.7	46.95	103.82
Toluene	126.2	47.62	105.30
Hexane	10171.8	44.62	98.67
Hexane	101.3	46.87	103.64
CO_2	10093.0	45.41	100.42
CO_2	55.5	44.95	99.40
Methanol	10010.2	45.04	99.60
Methanol	97.2	45.89	101.48
Methane	9850.0	45.22	100.00

Table VII. NMO Analyzer Linearity and Precision Test Results.

Compound	Concentration (ppm)	Percent Relative Standard Deviation	Mean Response Factor (Area Counts/ppmC)
Propane	19.9	1.42	44.69
Propane	201.0	0.50	44.47
Propane	2419.0	0.31	44.40
CO_2	55.6	0.41	44.95
CO_2	509.0	0.26	45.08
CO_2	10093.0	0.13	45.41

mean propane response factor = 44.52 %RSD = 0.340
mean CO_2 response factor = 45.15 %RSD = 0.525
mean overall response factor = 44.83 %RSD = 0.862

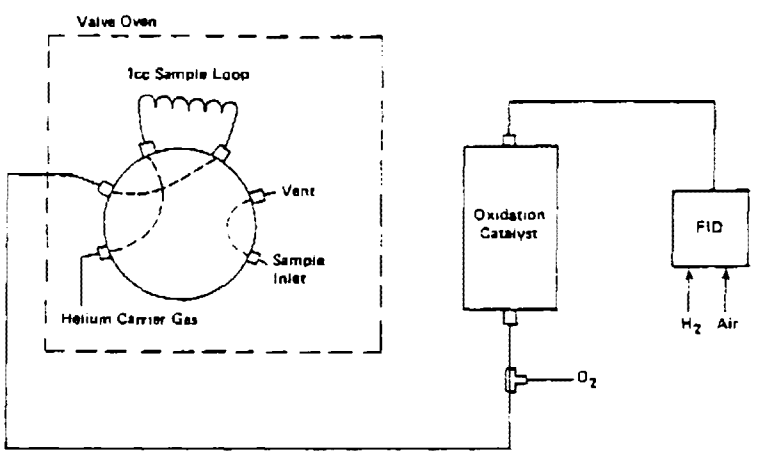

Figure 1. Reduction Catalyst Test Schematic.

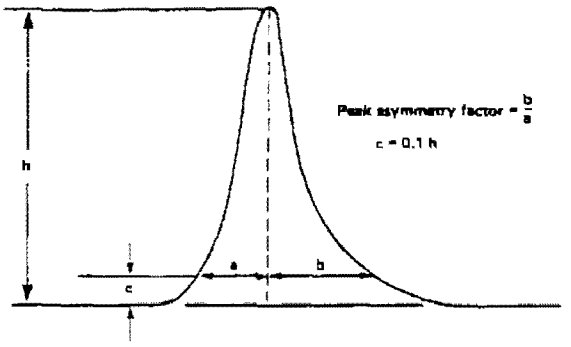

Figure 2. Peak Asymmetry Factor Measurement.

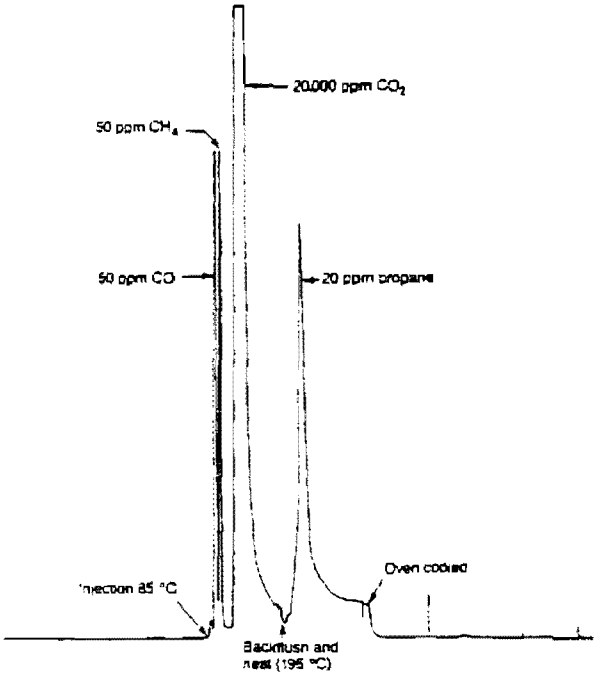

Figure 3. Typical NMO Analyzer Chromatogram.

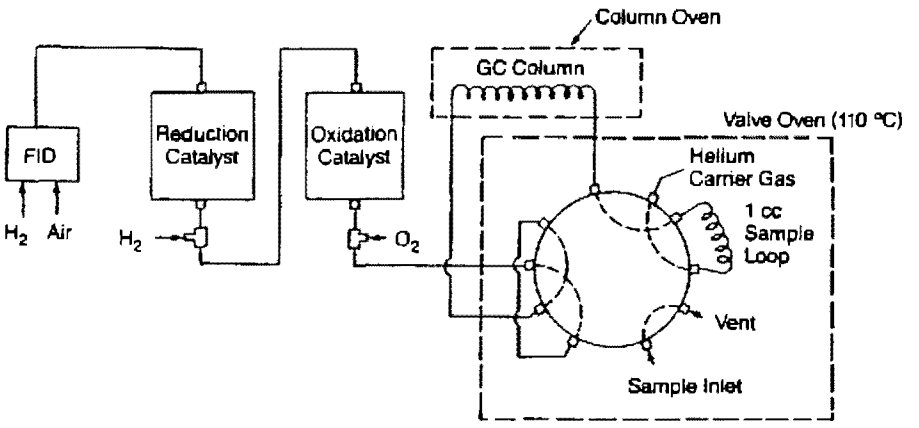

Figure 4. Recommended Nonmethane Analyzer Design.

DEVELOPMENT AND VALIDATION OF SOURCE PM_{10} MEASUREMENT METHODS

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The introduction of particle size into the Ambient Air Particulate Standards suggests the need for size-specific (PM_{10}) particulate measurements at stationary sources as well. Development of PM_{10} sampling methods requires resolution of several potential technical difficulties. First, an aerodynamic sizing device must be selected which can be operated with a 10μm size cut, and which is free of artifacts due to misclassification of particles or anomalous weight changes. The most obvious potential inaccuracy in PM_{10} sampling is due to a "built in" anisokinetic sampling bias caused by the requirement that an inertial particle sampler must run at a fixed flowrate to achieve a predetermined size cut, thus making isokinetic sampling in the manner of Method 5 impossible.

Two promising source PM_{10} measurement techniques have been developed which minimize these potential errors. The first involves a new sampling train design which incorporates emission gas recycle (EGR). In this train, the isokinetically sampled stack gas is augmented by the appropriate amount of filtered recycle gas to maintain the total gas flowrate entering the inertial sizing device at the level required for a 10μm size cut. The second potential method, termed a simulated Method 5 (SIM-5) approach, uses existing sampling hardware with an altered traversing protocol designed to maintain anisokinetic sampling errors for the PM_{10} particle fraction within predetermined limits. Both techniques have been documented as potential sampling methods, including descriptions of equipment, sampling methodology, data reduction and sampling setup computations, QA/QC, and technical references. In addition one first generation prototype and two second generation EGR sampling trains have been constructed and field tested. Four field trials of each PM_{10} method have been conducted, in which the precision of each method (using colocated dual train techniques) and the comparability of each method to the other and to reference isokinetic total particulate samplers (Method 17) were investigated.

DEVELOPMENT AND VALIDATION OF SOURCE PM_{10} MEASUREMENT METHODS

Introduction

A revised ambient air standard that regulates particulate matter smaller than 10 micrometers (PM_{10}) has been proposed and promulgation is expected. Although the proposed PM_{10} standard regulates ambient air concentrations, attainment strategies for the new standard will require information on PM_{10} emissions from stationary sources. Furthermore, PM_{10} emissions regulations under New Source Performance Standards are possible in the future. For these reasons, the EPA Environmental Monitoring Systems Laboratory (Quality Assurance Division) has initiated a research program to develop and validate source PM_{10} measurement methods.

Developing a useful PM_{10} sampling technique involves solving several technical challenges. First, a sampler must be found or developed which can aerodynamically separate particles with aerodynamic diameters less then 10μm. The sampler must be free from artifacts which would misclassify particles (such as particle bounce or sampler cut shifts) or otherwise give inaccurate collected mass determinations (such as wall losses or substrate mass changes). The sampler operating conditions for this particle size cut must be determined in enough detail to allow the operator to calculate, set and maintain the PM_{10} operating conditions in the field. The PM_{10} sizing device also complicates particulate sampling by the introduction of a "built in" anisokinetic sampling bias. In order to maintain a 10μm cut, the gas flowrate through the sizing device must be held at a predetermined value. Without a sampling nozzle of continuously variable cross-sectional area, this fixed flowrate requirement makes isokinetic sampling in the manner of Method 5 impossible. Since anisokinetic sampling bias can be significant for particles near 10μm, this effect cannot be ignored.

Previous work on this problem at Southern Research Institute has led to the development of two potential sampling methods - the Emission Gas Recycle (EGR) sampling train, and the Simulated Method 5 (SIM-5) traversing protocol. The Emission Gas Recycle (EGR) train in principle eliminates the problem of anisokinetic sampling bias by simultaneously allowing isokinetic sampling at the nozzle and fixed flow operation at the inertial sizing device(s)[1,2]. The train design allows the isokinetic flow of gas into the sampling nozzle to be augmented by an adjustable amount of filtered, recycled stack gas upstream of the inertial sizing device. The SIM-5 protocol[3,4] is an alternate candidate PM_{10} method which uses existing sampling equipment (cyclones or cascade impactors without special gas recycle adaptations). The protocol involves synthesizing a duct traverse with fixed flowrate runs, using different sampling nozzles if necessary so that the nozzle velocity at each sample point does not fall outside a specified range relative to the isokinetic velocity at that point. In this manuscript we will describe both potential source PM_{10} methods, including the operating principles, hardware, development, and validation studies for each.

Description of PM_{10} Methods

PM_{10} Sizing Device

The two classes of inertial particle sizing devices commonly used for instack measurements are cascade impactors and small sampling cyclones. Devices of either type can in principle be used for source PM_{10} sampling, both devices have been used in the course of our methods development program. Of the two classes, cascade impactors are more familiar, more widely

accessible, and have a longer history of field use. Impactor stage D_{50} values can be predicted with some confidence over the typical range of stack gas conditions and sampler flowrate. Because of particle bounce and reentrainment, impactors have limited capacity and must generally be operated as multistage devices rather than single-cut classifiers. Multistage cascade impactors provide moderately high resolution particle size distribution data from which PM_{10} concentrations may be inferred by interpolation. These data are obtained at the expense of more complicated preparation, sample recovery and data reduction procedures, thus placing greater demands on the training, experience and insight of the operating team. Likewise, more complicated procedures and greater demands on the sampling crew are required to recognize, prevent, or correct for other non-ideal effects such as gas/substrate interactions. In summary, cascade impactors can be useful for PM_{10} sizing, especially when detailed particle size information is also necessary, at the expense of added time and material costs as well as greater skill and trainng requirements for the sampling team.

Cyclones, on the other hand, are essentially free from problems of bounce, reentrainment, and overloading. They have no substrates and are simple in operation and sample recovery. Cyclones are therefore suitable for single-stage sizing devices. The principal disadvantages of cyclones are not operational, but consist of the more limited understanding of cyclone behavior. Unlike impactors, the D_{50} of a cyclone cannot be adequately predicted from geometric considerations. The variation of the D_{50}'s of typical sampling cyclones with stack gas density, viscosity and flowrate does follow a similar functional form, but laboratory calibrations of each cyclone type must be performed to develop predictive equations for the D_{50} of that cyclone over a range of gas conditions. These equations, moreover, cannot easily be extrapolated to other cyclones or to conditions beyond the range of the calibration data. Therefore, much more extensive calibration data must be obtained for the development and validation of a PM_{10} cyclone than for a PM_{10} impactor sampler.

As mentioned above, both cascade impactors and cyclones were used in this program. A well characterized, commercially available impactor (University of Washington Mark V) and right-angle impactor precollector (SoRI/Flow Sensor design- marketed by Andersen) combination was used for detailed sizing information, especially at sources with low particulate concentrations. Cyclone I of the SoRI/EPA five-stage series cyclone train was used as a PM_{10} cyclone sampler, both as a single stage device or in series with one or more cyclones from the complete train. Previous calibrations of this cyclone have been extended to determine flowrates to produce 10um D_{50} at each of several gas conditions.

Simulated Method 5 (SIM-5) Technique

The Simulated Method 5 (SIM-5) technique was developed using the principle of minimizing PM_{10} measurement errors within the operating constraints of available sampling hardware. Thus commercially available particle sizing devices (cyclones or impactors) and EPA Method 5 gas metering equipment were used without significant hardware modifications.

Several sources of measurement error were considered in the development of the SIM5 protocol. Most of these - such as spatial and temporal variation of emissions, anisokinetic sampling bias, and random measurement errors are common to other emissions sampling methods, especially total particulate sampling. One source of error - misclassification of particles - is unique to size specific particle sampling measurements. While some

degree of misclassification is inevitable due to the imperfect collection characteristics of inertial sizing devices, misclassification generally occurs when the sizing device is not operated at the correct flowrate for a 10μm cut. The magnitude of errors from this effect will depend on the concentration of particles near 10μm aerodynamic diameter, and are therefore not predictable in advance for a general source and particulate control device. Therefore, in order to obtain meaningful PM_{10} concentrations, both PM_{10} methods specify that the flowrate of the inertial sizing device be held constant at the value calculated for a PM_{10} size cut.

Once the decision is made to operate the sampling train at a fixed flowrate, other sources of error which are common to total particulate sampling become more problematic. An isokinetic traverse in the manner of Method 5 is no longer possible. In fact, due to the finite selection of available nozzles, isokinetic sampling is not generally possible at <u>any</u> preselected duct location. In SIM-5 fixed-flowrate (i.e., anisokinetic) sampling is performed within point-by-point restrictions which limit the <u>worst-case</u> anisokinetic error in PM_{10} to a specified limit, in this case ±20%. The development of these restrictions is described in the following paragraphs.

The effect of anisokinetic sampling has been characterized by Belyaev and Levin[5] in terms of an aspiration coefficient, A, defined as measured concentration/actual concentration:

$$A = 1 + (R-1)\frac{B}{B+1} \qquad (1)$$

where R = velocity ratio v/u,
v = duct gas velocity at sampling point (cm/sec),
u = gas velocity entering the sampling nozzle (cm/sec),
B = (2 + 0.617/R)K, K = particle Stokes number with respect to the nozzle, $\tau v/d$,
τ = particle relaxation time $CD^2/18\mu$(sec),
C = Cunningham slip factor,
D = particle aerodynamic diameter (cm),
μ = gas viscosity (poise), and
d = nozzle diameter (cm).

From the form of equation (1) and the observation that B is proportional to D^2, the general behavior of A can be deduced. A approaches 1 (no sampling bias) as R approaches 1 (isokinetic sampling) or as B approaches zero (small particle diameter). For a given anisokinetic velocity ratio, as the particle size increases (B becomes large), the anisokinetic sampling error (A-1) increases in magnitude until in the limit of large diameter the deviation approaches the fractional deviation from isokinetic. (Note that R = 100/I, where I is the familiar percent isokinetic ratio.) In more familiar terms, for typical source sampling conditions (17 liters/min sampling rate, 16 m/sec nozzle velocity) and 10μm particles:

$$A-1 = 0.89\ (R-1)$$

that is, a sample taken at 20% under isokinetic will be biased high by 17.8%.

This same approach can be used to determine anisokinetic sampling limits to remain within a predetermined sampling error. In the current SIM-5 protocol, the limits are chosen to give a maximum sampling error of 20% for 10μm particles. Corresponding limits on R can be obtained by substituting $d=(4QR/v\pi)^{1/2}$ and D=10μm into equation 1 and solving for stream velocity

$$v^{3/2} = \frac{36(A-1)\mu Q^{1/2}(R')^{3/2}}{\pi^{1/2}(R'-A)(2R'+0.617)(10\mu m)^2} \quad (2)$$

The appropriate value of $\mu Q^{1/2}$ depends upon the sampler and the temperature and composition of the gas. If a single stage PM_{10} sampler is used then Q should be the flow rate which provides a 10μm size cut. With a cascade impactor the flow rate is somewhat adjustable, but should be selected to produce at least one size cut above or very near 10μm.

Values for R', where R' is R_{min} and R_{max}, were calculated from Equation 2 for various assumed values of $\mu Q^{1/2}$, which are in the expected range for stationary sources and available sampling equipment. The results are shown graphically in Figure 1 with the upper and lower curves representing R versus v obtained by setting A=1.2 and 0.8 in Equation 2. The function R=v/u, with u a constant, is represented in Figure 1 as the curve designated R(v,u) and running as a nearly vertical line. This function has exactly the same shape and slope no matter where it is centered on the "R=1" line. It is needed in reading the appropriate limits, R_{min} and R_{max}, or the corresponding v_{min} and v_{max}, determined by the value of u. This vertical curve is shifted left or right so that its center (at R=1) matches the nozzle velocity. The limits, R_{min} and R_{max} or v_{min} and v_{max}, are the values where the vertical curve intersects the limit curves appropriate for the $\mu Q^{1/2}$ value. Typically $\mu Q^{1/2}$ is in the range of 750 to 1310 for combustion sources and commercial samplers.

The limits depicted in Figure 1 are broad enough so that the velocities in a point-by-point traverse at most sources will fall within the specified limits. However, in some ducts, velocities at some traverse points will be outside of these limits for one nozzle. In that circumstance, additional nozzles, having limits which include the other velocities, should be used, and the traverse divided into two or more subtraverses with different nozzle diameters.

Another important difference between the SIM-5 protocol and Methods 5 and 17 is the dwell time. In these EPA methods the dwell time is the same for all traverse points. The measured concentration is a velocity weighted average for all points, as it should be for determination of emission rate, because the sampling rate is varied at each point proportional to point velocity. Since flow rate cannot be adjusted from point to point with a PM_{10} sampler, the dwell time at each point must be proportional to the point velocity to obtain a velocity weighted sample.

Emission Gas Recycle Train

Use of the SIM-5 method should allow PM_{10} measurements in which isokinetic error is limited to acceptable levels. The Emission Gas Recycle concept uses modified sampling hardware to eliminate anisokinetic sampling bias. In principle, the EGR train will provide measurements of both PM_{10} and total particulate concentrations with accuracy comparable to Methods 5 or 17.

As indicated above, the EGR train uses two separately-controlled gas flow paths to maintain the required flowrate for the initial sizing device while varying the amount of gas extracted from the stack. These paths converge in the EGR mixing nozzle, shown schematically in Figure 2. Stack gas is extracted at the isokinetic at flowrate Q_s through the sample portion of the EGR mixing nozzle into the inertial sizing component of the sample train. At this point the sample gas is mixed with an adjustable amount, Q_r, of filtered, dry recycle gas to bring the total flowrate in the sizing

device to the amount calculated for PM_{10} operations. The nozzle has several critical requirements. Since the nozzle must be compact enough to allow entry through available sampling parts, the nozzle design must allow the two gas streams to mix in the short distance between the nozzle tip and the cyclone body. The mixing must not cause excessive particle deposition in the nozzle, and the nozzle must not perturb the natural D_{50} of the cyclone. The nozzle design judged to best meet these requirements uses annular mixing as shown in Figure 2. This nozzle allows entry through common four-inch sampling ports. All tests to date indicate that particle deposition in the EGR nozzle are lower than in nozzles of conventional design.

A block diagram of the EGR train is shown in Figure 3. After passing the mixing nozzle, inertial sizing device, and instack sample filter, the sample gas passes through the probe and condenser or impinger train and into the EGR flow control module. As in conventional Method 5 control modules, the gas flowrate entering the control module is controlled by coarse and fine control values (V_1 and V_2, respectively) at the entrance of the sealed pump. At the exit of the pump and absolute filter, the total flow is measured using a laminar flow element (LFE). The gas stream is then split into the recycle and sample flow lines. The sample flow is monitored in the normal manner using a dry gas meter and a calibrated orifice. By mass balance, in leak-free system this flowrate must (on a dry mass flow basis) exactly equal the initial sample flow Q_s extracted from the stack. The recycle gas flowrate is measured using a second laminar flow element. While it is not strictly necessary to measure Q_r, it serves as a useful quality control check on the overall gas metering system. The partitioning between sample and recycle gas is controlled by valves V_3 and V_4 located downstream of the total flow LFE. Valve V_5 was added to the system to extend the range of control to higher recycle percentages by adding back pressure to the sample flow line. The recycle gas line, along with the sample and pitot lines, passes through the heated probe in which the recirculated gas is reheated to the duct temperature. Power to the heater is regulated by a proportional temperature controller using a thermocouple reference sensor located on the surface of the recycle tube.

Operation of the EGR train is similar to standard Method 5 sampling. The total dry gas flow $Q_r+Q_s(1-B_{ws})$ is monitored by using the total flow LFE and controlled using values V_1 and V_2. The sampling flow Q_s (defined as the gas flowrate entering the nozzle) is monitored using the sample orifice and dry gas meter in the normal manner of Method 5 sampling, and controlled using the recycle valves (V_3 and V_4) and the back pressure valve (V_5). Selection of traverse points and sample flowrate are done using standard techniques. In practice, the total flow would first be set to its operating value for the desired size cut, then the sample flowrate adjusted to be isokinetic at the first traverse point. Changes in the recycle flow setting alter the total flow only slightly, so that usually one or two iterations of V_3 and V_4 are needed at a new traverse point. V_5 needs to be adjusted only rarely to insure that the maximum necessary recycle flow can be attained. The only aspect that can be initially confusing to a trained Method 5 operator is that the sample flowrate is adjusted using the recycle valves rather than the customary valves V_1 and V_2.

Field Evaluation of PM_{10} Methods

Both PM_{10} techniques have been developed in an ordered sequence of laboratory and field studies. The basic elements of the SIM-5 technique were developed from a systematic study of sources and magnitudes of expected errors in particulate sampling with existing equipment. The technique was tested against isokinetic samplers and the EGR technique at three sites,

after which the details of the protocol were refined based on field experience. The method was documented in Federal Register format and tested for precision using multiple train techniques at a fourth site. The EGR concept was developed by D.B. Harris of the EPA, who constructed a research sampling train without particle sizing equipment. This design was adapted into a protype field sampling train which incorporated a cyclone PM_{10} sizing device. This train was evaluated in a wind tunnel source simulator and at three field sites. Based on field experience, two upgraded EGR trains were constructed, operating protocols were documented in Federal Register format, operating and data reduction software was developed, and multiple-train test conducted at a fourth site. The results of the field evaluations will be summarized in this section.

The first tests of each technique were conducted at a 56MW coal-fired utility boiler. The sampling location chosen was downstream of an undersized electrostatic precipitator (ESP) which was no longer the primary particulate control device. Particulate concentrations varied considerably with boiler load, ranging from as low as 60 mg/dsm^3 at low load (with 20 mg/dsm^3 PM_{10}) to 2000 mg/dsm^3 at high load (with 400 mg/dsm^3 PM_{10}). In the first test series the EGR train was compared to colocated Method 17 or isokinetic cyclone samplers. In a later SIM-5 test at the same site, a SIM-5 impactor train was compared with colocated Method 17 or isokinetic impactor trains.

The second test was also conducted at a 250MW unit of a coal-fired power plant with ESP particulate control. A duct site with considerable velocity spread was chosen for the measurements. Simultaneous EGR and SIM-5 cyclone runs over a restricted traverse were compared with each other and with single-point isokinetic impactors. Total and PM_{10} particulate concentrations, respectively, averaged about 200 and 105 mg/dsm^3.

The third tests of each technique were conducted at a 220MW coal-fired utility boiler equipped with twin fabric filter particulate control devices. At the baghouse inlet, simultaneous EGR and SIM-5 cyclone traverses were compared with one another, and with SIM-5 impactor and Method 17 runs taken during the same time period. Inlet particulate concentrations of 3600 mg/dsm^3 total and 750 mg/dsm^3 PM_{10} were measured. At the baghouse outlet, simultaneous SIM-5 impactors and Method 17 samplers were run. Low particulate concentrations (15 mg/dsm^3 total, 3 mg/dsm^3 PM_{10}) were observed.

In each of these test series, an individual PM_{10} sampler was operated simultaneously (and colocated when possible) with a reference sampling train (Method 17, an isokinetic PM_{10} sampler, or a sampler using the other PM_{10} method). At the fourth site, dual PM_{10} samplers were colocated with duel Method 17 samplers in order to obtain train precision data in addition to comparison data. The site chosen was downstream of a gravel bed filter particulate control device. In the first test series at this site, dual EGR trains and dual Method 17 samplers were colocated in the sampling plane. In the second test series, dual SIM-5 cyclone trains, dual Method 17 trains, and a single EGR train were operated simultaneously at a single duct location.

Comparison of Reference Measurements

The results of all field evaluations test are summarized in Table I. For the sake of comparison, all differences and confidence intervals are expressed as percentages of the mean value. Notation is also made in Table I where the PM_{10} sampler and the reference sampler were colocated or run simultaneously.

EGR and SIM-5 Precision Tests. At Site 4, colocated pairs of EGR and SIM-5 measurements indicated excellent reproductability between the two trains. In only one instance (SIM-5 PM_{10} concentrations) does the mean difference in the measurements of two nominally identical trains exceed 2.5%. (This bias was found to be due to a systematic difference in cyclone flow rate between the two trains). For both PM_{10} trains, 95% confidence intervals were on the order of ±5 percent. By this measure, the precision of the PM_{10} trains was the same as that of the paired Method 17 trains operated during these tests.

Total Mass Comparisons. Although the primary purpose of the EGR and SIM5 techniques is to measure PM_{10} concentrations, both techniques simultaneously provide a measure of total particulate mass as well. Method 17 reference samples were included since in many PM_{10} applications total mass information is also desirable, and since recovery of total mass is an overall indicator of PM_{10} sampler operation. In principle, the EGR sampler should provide total mass measurements identical to Method 17, since both methods use isokinetic sampling and instack particulate filters. In fact, at both Site 1 and Site 4 the EGR train measured less than Method 17 by a small but significant amount. Mean differences ranging from 5 to 13 percent were observed, in each case larger than the 95% confidence limits. The reason for this small bias is not clear; however, since it does not exceed 15 percent at any site tested to date, we do not consider it an extreme difficulty.

Unlike the EGR measurements, SIM-5 total mass measurements at Test Sites 1, 3, and 4 were not significantly diferent from the paired total mass measurements from Method 17 or other reference isokinetic sampling trains. Since the SIM-5 technique is expected to be less accurate for total mass, these results are encouraging. When total mass data using the two techniques are compared, the results are mixed. At Site 2, the 9 percent EGR - SIM-5 difference is marginally significant at the 95% confidence level. At Site 3 and 4 the EGR and SIM-5 data are essentially the same.

PM_{10} Comparisons. In order to assess the accuracy of EGR and SIM-5 for PM_{10} measurements, single-point, isokinetic particle sizing samplers must be used as a reference. Barring artifacts due to the EGR mixing nozzle, EGR PM_{10} data should have accuracy equivalent to the reference devices. SIM-5 data should by design differ by no more than 20 percent for worst case conditions, and by less than 10 percent for the size distributions at the sites tested in this study. In fact, the PM_{10} values measured by the two techniques at every site differ by over 10 percent but less than 20 percent. At Sites 2 and 4, the EGR PM_{10} value is about 15 percent less than the SIM-5 value. At Site 3, the EGR value is 11 percent greater than the SIM-5 value. All three differences are significant at the 95 percent confidence level. Comparisons with isokinetic impactor trains show differences on the same order of magnitude. These differences, however, are not significant in light of increased confidence limits for the measurements, which were not generally simultaneous.

A significant difference in PM_{10} concentrations may result from at least two causes: A difference in sampling efficiency for sizes less than 10μm, or a difference in the actual D_{50} of the inertial sizing device. For sampling trains which give comparable total mass concentrations, sampling efficiency for the smaller size particles in the PM_{10} fraction should also be comparable. On this reasoning, the PM_{10} difference between the paired EGR and SIM-5 runs at Sites 2-4 may be taken primarily as a measure of any difference in the D_{50} of the two samplers. Any such differene is not consistent in sign at the three test sites, and does not cause average PM_{10}

differences to be greater than 16% at any site tested. In consideration of the favorable precision results of each technique, we conclude that the EGR and SIM-5 techniques may be expected to produce comparable PM_{10} measurements (within ±15 percent) at other similar emissions sources.

As mentioned above, comparisons of PM_{10} between either of the PM_{10} techniques and isokinetic reference trains such as cascade impactors are not generally conclusive due to the effects of source variability on these non-simultaneous measurements. As with the EGR/SIM-5 comparisons, the direction of any difference in sampler cut is not consistant from site to site, so no systematic difference can be demonstrated.

Summary and Conclusions

This paper presents the current status of two candidate PM_{10} methods for stationary emissions sources. Both techniques have been evaluated and modifed where necessary during the course of an extensive laboratory and field testing program. Both have been documented in the format of published EPA methods. During the field trials described in this paper, each technique was found to compare well with the other and with other isokinetic reference sampling trains. While further laboratory and field development of each technique is desirable, the underlying technical principles of both appear to be sound, and both techniques show excellent promise for source PM_{10} sampling.

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Table I. Percentage Differences in Particulate Concentrations Measured During Test Series[a]

	Number of Replications	PM_{10}	Total Concentration
EGR Initial Test: Site 1			
EGR Cyclone - Isokinetic Cyclone[b]	4	-8.3±27%	9.0±29%
EGR - Method 17[b]	8		-11.5±8.3%
SIM-5 Initial Test: Site 1			
SIM-5 - Method 17[b]	3		-16±32%
SIM-5 - Isokinetic Impactors[b]	4	-1.8±22%	-14.0±65%
EGR/SIM-5 Comparison Test: Site 2			
EGR Cyclone - SIM-5 Cyclone[b]	5	-15.5±6.5%	-9.2±8.5%
EGR - Isokinetic Impactors	5-6[c]	-11±31%	1.3±38%
SIM-5 - Isokinetic Impactors	7-6[c]	3.8±25%	14±31%
EGR/SIM-5 Comparison Test: Site 3			
	Inlet		
EGR - SIM-5[b]	6	11±9.8%	1.7±21%
EGR - Impactor	6-5[c]	27±16%	-9.8±16%
SIM-5 - Impactor	6-5[c]	16±16%	-11±14%
	Outlet		
SIM-5 Impactor - Method 17	6-7[c]		-7.4±23%
EGR Precision Test: Site 4			
EGR - Method 17[b]	6		-12.9±4.2%
EGR - EGR_2[b]	6	-2.4±4.9%	-0.9±4.3%
SIM-5 Precision Test: Site 4			
SIM-5 - Method 17[b]	9		0.4±6.3%
EGR - Method 17[b]	7		-4.8±1.7%
EGR - SIM-5[b]	9	-15.8±7.8	
$SIM\text{-}5_1$ - $SIM\text{-}5_2$[b]	9	6.6±3.8	1.2±5.4%

a All differences and confidence intervals expressed as percentages of the mean value. Confidence intervals represent 95% significant level.

b These comparisons were analyzed as pairs since the measurements were simultaneous.

c Where two numbers of replications are given, the first number corresponds to the first listed device and the second to the second device.

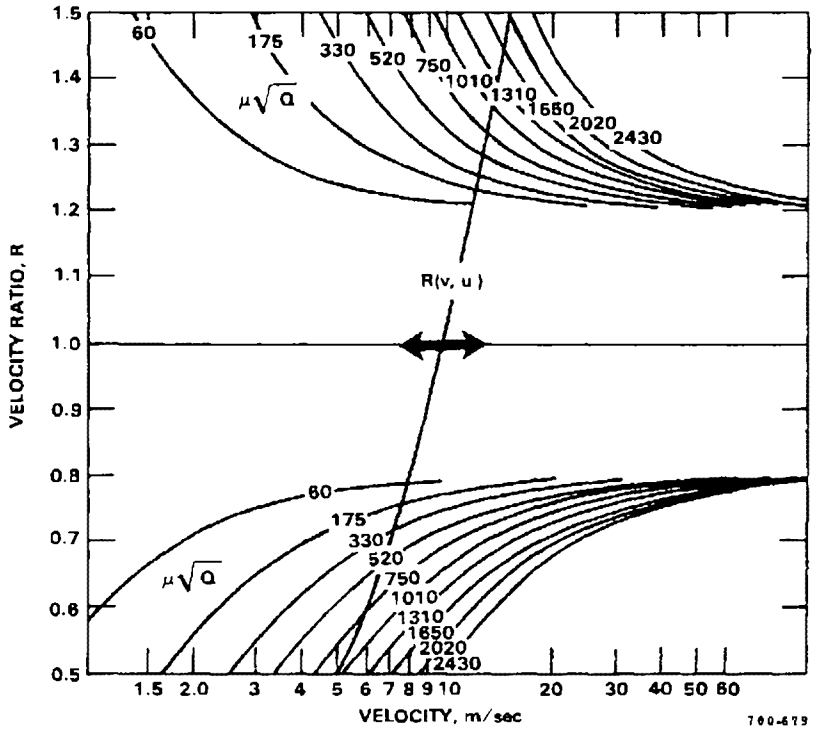

Figure 1. Velocity ratio, R, versus duct velocity to give aspiration coefficient of 1.2 (upper curves) and 0.8 (lower curves) for 10 μm particles.

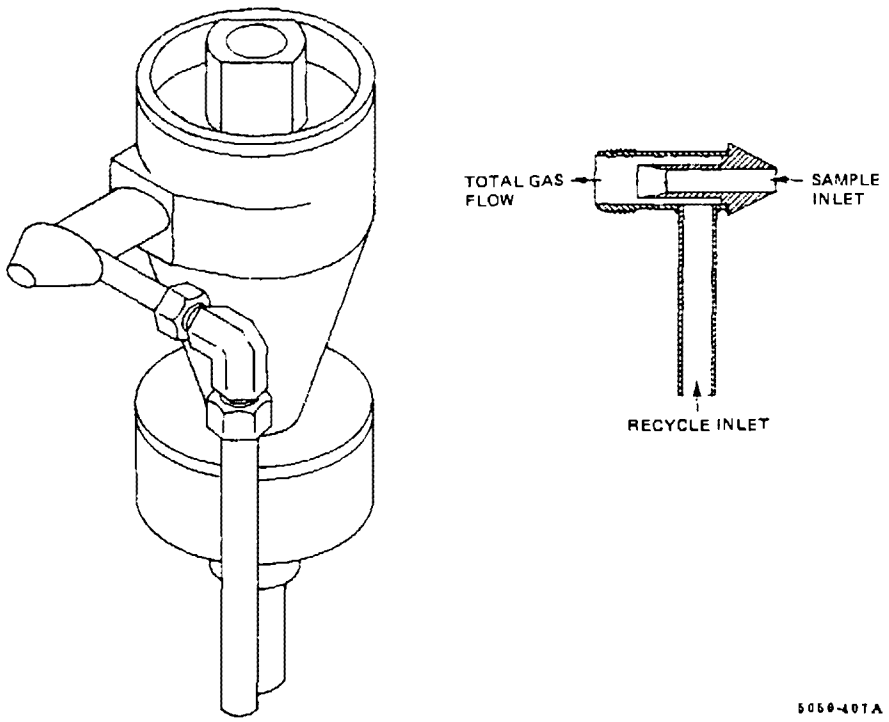

Figure 2. Annular recycle gas mixing nozzles for EGR train using PM_{10} Cyclone I.

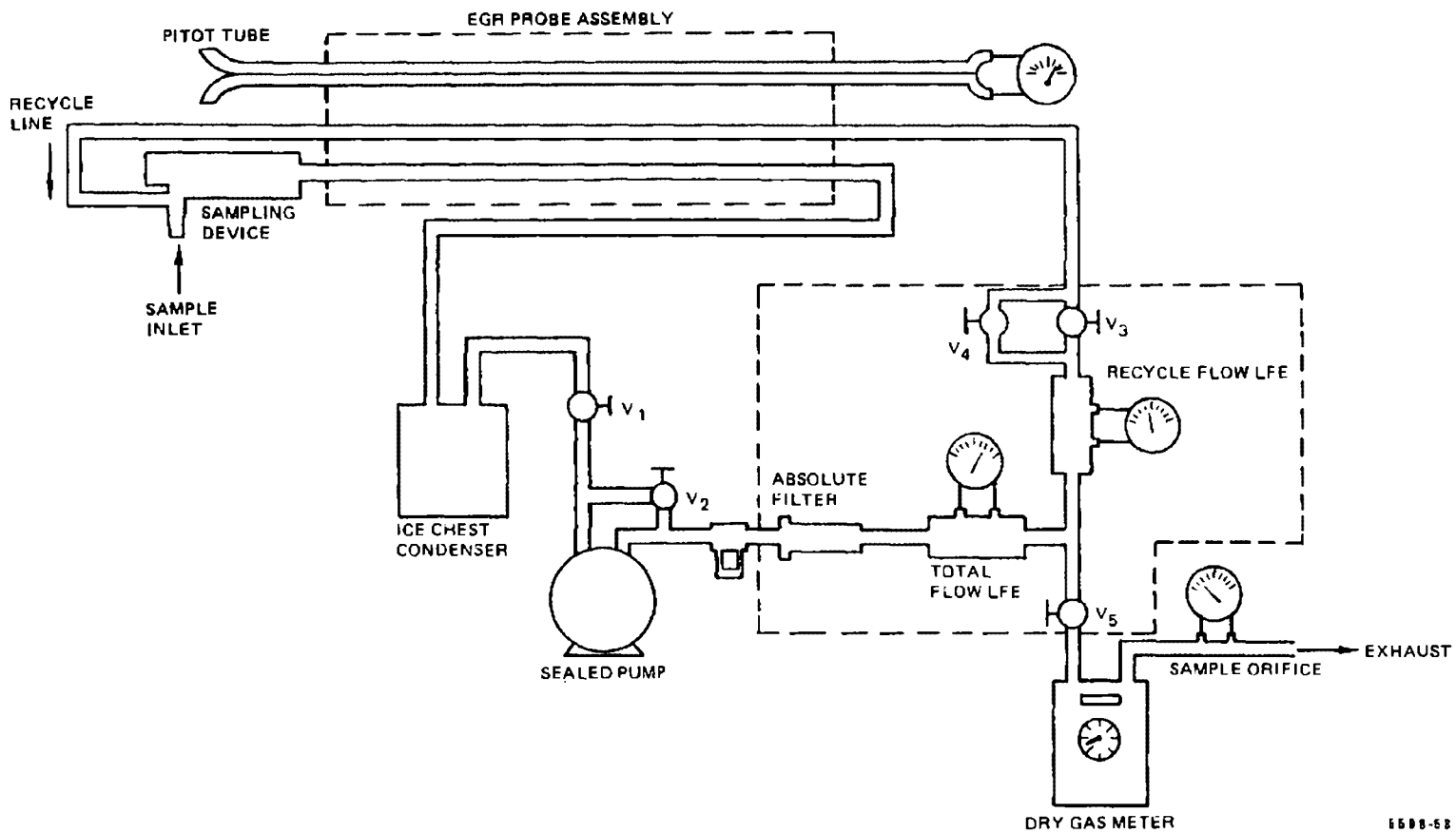

Figure 3. Schematic of emission gas recycle (EGR) train.

STUDIES OF MEASUREMENT METHODS FOR CHLORINE AND CHLORINE DIOXIDE EMISSIONS FROM PULP BLEACH PLANT OPERATIONS

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Methods for determining chlorine and chlorine dioxide emissions from pulp bleaching facilities are employed in control device efficiency studies and in determining compliance with non-criteria pollutant regulations. The dual pH potassium iodide impinger capture method was investigated in laboratory and field studies of (1) the necessity for buffering the capture solutions to avoid generating artificially high chlorine data, and (2) precision of chlorine and chlorine dioxide determinations. A pH-optimized method was developed and tested.

An instrumental method for continually measuring total oxidants or chlorine and chlorine dioxide was developed via modification of a commercial electrochemical chlorine monitor. Comparison testing with the dual pH potassium iodide method demonstrated the utility of the instrumental method for survey purposes.

STUDIES OF MEASUREMENT METHODS FOR CHLORINE AND CHLORINE DIOXIDE EMISSIONS FROM PULP BLEACH PLANT OPERATIONS

Introduction

Non-criteria pollutant regulations are being established by state regulatory agencies for the purpose of regulating ambient concentrations of substances released to the atmosphere by industrial operations. These substances are typically chemicals which are recognized as having adverse health effects at higher concentrations, and are usually limited in workplace atmospheres by regulation (Occupational Safety and Health Act Permissible Exposure Levels - PELs) or by recommendation (American Conference of Governmental Industrial Hygienists Threshold Limit Values - TLVs). The emerging state regulations generally specify a maximum ambient concentration of a regulated substance as a fraction of a workplace limit (e.g., 1/200 of the TLV), and an affected facility is to employ mathematical source emission modelling to calculate the maximum allowable quantity of that substance which may be emitted.

Because of their ability to produce respiratory tract and eye irritation[1], chlorine (Cl_2) and chlorine dioxide (ClO_2) are assigned 8-hour TLVs of 1 and 0.1 ppm, respectively. They are included in many state non-criteria pollutant regulations, and because of their use in the bleaching of pulp, their atmospheric emissions are of concern to the pulp and paper industry.

The various pulp bleaching sequences involve several stages of bleaching and extraction of solubilized organic material. Each stage typically includes reaction with bleaching chemical or caustic extraction solution in a retention tower, washing of the product pulp on a rotary vacuum drum washer prior to subsequent operations, and removal of the filtrate via a seal tank. The vents to the atmosphere from the towers, washer hoods, and seal tanks, may or may not be fan driven, ducted together to common vents, or ducted to gas-liquid scrubbers for emission control. Because chlorine dioxide is always generated on-site, there is a ClO_2 generator vent which may be a source of emissions of Cl_2 and ClO_2, and which may or may not be ducted to a gas-liquid scrubbing device for emission control.

The pulp and paper industry in the United States is in various stages of reducing chlorine and chlorine dioxide atmospheric emissions. In those circumstances where non-criteria pollutant regulations do not impose restrictions on Cl_2 and ClO_2 release, emission control may be undertaken primarily for workplace considerations, if necessary. This control may take the form of reduction in vat residuals of aqueous Cl_2 and ClO_2 (where this is possible), it may involve the use of tall vent stacks, or it may include gas-liquid scrubbing. Scrubbers may utilize sodium hydroxide, cold water, extraction-stage filtrate, weak wash, or aqueous sulfur dioxide solutions.[2,3]

NCASI is conducting a study of bleach plant emissions of Cl_2 and ClO_2, in order to (a) document uncontrolled emission levels, (b) examine the relationship of process operation variables to emission levels, and (c) determine the effectiveness of in place control devices. This activity has required the examination of methods for measuring chlorine and chlorine dioxide emissions, and studies have been conducted on (a) the optimization of a grab sampling, wet chemical method, and (b) a continuous instrumental monitoring method.

Analysis Methods Development

Grab Sampling Method

Background. Gas phase chlorine and chlorine dioxide may be captured in neutral potassium iodide solution in impingers in an extractive sampling system. Because of the dependence of the reactivity of chlorine dioxide with iodide upon solution pH, the post-sampling determination of iodine formed at neutral and acidic pH permits the quantitative measurement of both chlorine and chlorine dioxide:

$$\text{Neutral pH:}\quad Cl_2 + 2I^- \rightarrow I_2 + 2Cl^- \qquad (1)$$

$$ClO_2 + I^- \rightarrow 1/2\ I_2 + ClO_2^- \qquad (2)$$

$$\text{Acid pH:}\quad ClO_2^- + 4H_3O^+ + 4I^- \rightarrow 2I_2 + 6H_2O + Cl^- \qquad (3)$$

Standard practice within the industry has been to use two impingers in series, each containing 2 percent potassium iodide, to sample at a rate of from 1 to 5 L/min, and to collect a sample over a period of from 5 to 30 minutes (using shorter sampling times if the color in the second impinger turns from straw yellow to orange). After sampling, the contents of the impingers are combined and titrated with 0.1 N sodium thiosulfate solution. After the first endpoint, the solution is acidified with sulfuric acid solution, and the titration is continued to the second endpoint. Algebraic manipulation of equations (1) through (3) permits the calculation of gas phase concentrations of Cl_2 and ClO_2 on the basis of the neutral and total acid titration equivalents.

Method Testing and Modification. Although reaction (2) above is for calculation purposes regarded as the full extent of the reaction of ClO_2 with iodide at other than acidic pH values, there is a dependence of the rate of reaction of chlorite with iodide on solution pH, such that at slightly acidic pH values the reaction can proceed to an extent appreciable enough to cause (1) deviation from the 5:1 (total acid:neutral) ratio of equivalents of iodine expected upon titration of a capture solution obtained from ClO_2 only, and (2) an erroneously high calculated concentration of chlorine. Experiments were conducted to demonstrate this second point.

The sampling equipment described in the appendix was employed to sample gaseous emissions from a chlorine dioxide bleaching tower vent. A manifold was constructed from FEP and PFA Teflon® which permitted the collection of six gas samples simultaneously. Twenty mL of 2 percent unbuffered potassium iodide (KI) solution were placed in each first impinger, and a gas sample was drawn at ca. 500 mL/min through each impinger. The pH of the solutions was measured electrometrically. Twelve samples (two sets) were taken, representing a sampling time of from 5 seconds to 4 minutes. The solution pH dropped from an initial value of 6.7 to 6.1, at 30 seconds, then returned to ca. 6.6 at 4 minutes. This was taken as evidence that the pH of unbuffered KI solution could drop during sampling to a level low enough to permit the reaction of chlorite with iodide. This was confirmed in subsequent testing.

A sample was withdrawn from a chlorine dioxide bleaching tower vent into a 30 L Tedlar® gas bag (Pollution Measurement Corporation, Oak Park, IL). To determine that the chlorine and chlorine dioxide were stable with time, analyses of the bag contents by the method of the appendix were carried out. Over a period of one hour, the measured chlorine and chlorine dioxide varied randomly with an average of 66 and 148 ppm, with standard deviations of 12 and 40 ppm, respectively, for five measurements. Another

sample was placed in a Tedlar bag, and using the method of the appendix with 1 minute sampling and potassium iodide solutions buffered with borate and phosphate buffers, the data of Figure 1 were obtained. (The ClO_2 concentration remained constant as a function of pH, averaging 1490 ppm with a standard deviation of 43 ppm, except for pH 4.3 and 5.3 tests, where the ClO_2 concentration decreased.)

To test the hypothesis that the concentration of chlorine formed by conversion of captured chlorite depends upon the initial concentration of ClO_2, experiments were conducted in which a sampling manifold was fabricated from FEP and PFA Teflon which permitted collection of four samples simultaneously, employing trains as described in the appendix. Each impinger pair contained two percent KI solution, buffered essentially as per the appendix formula, but buffered at pH values of 6.4, 7.5, 8.5, and 9.5. Samples were withdrawn from a chlorine dioxide bleaching tower vent over a period of time such that normal variations in bleaching conditions produced variations in chlorine and chlorine dioxide gaseous emission concentrations. The data of Figure 2 were collected, and these data support the hypothesis.

On the basis of the information obtained in these experiments, it was concluded that an iodide solution buffered at pH 7.5 would minimize the formation of "phantom" chlorine due apparently to the reaction of chlorite with iodide at low pH values, but would not cause losses in apparently valid finite chlorine concentrations. Such losses appear at high pH values (e.g., greater than pH 8), and may be due to the reaction of iodine with base to form hypoiodite.

An experiment was performed in which a Tedlar bag containing a gas sample drawn from a chlorine dioxide bleaching tower vent was sampled via the method of the appendix, using a manifold which permitted collection of six simultaneous samples. The experiment was conducted with three sets of impingers containing unbuffered 2 percent KI, and three sets containing pH 7.5 buffered 2 percent KI, and was repeated once to obtain 12 tests. Results are indicated in Figure 3. The average concentrations of chlorine and chlorine dioxide using the unbuffered system were 354 and 1400 ppm, with standard deviations of 63 and 71 ppm, respectively. The average Cl_2 and ClO_2 concentrations employing buffered sampling were 228 and 1440 ppm, with standard deviations of 25 and 22 ppm, respectively.

A separate experiment was performed in which six samples were drawn from a Tedlar bag containing a ClO_2 bleaching tower gas sample. Using the method of the appendix, including buffering at pH 7.5, the average ClO_2 concentration was 1110 ppm with a relative standard deviation of 1.0 percent, and the average Cl_2 concentration was 120 ppm, with a relative standard deviation of 5.8 percent.

Instrumental Analysis Method

Background. Field testing employing the method of the appendix indicated that several bleach plant sources were at some mills highly variable in the concentrations of chlorine and chlorine dioxide emitted. This prompted consideration of the use of continuous monitoring devices for high concentrations (as opposed to workplace level concentrations) of chlorine and chlorine dioxide. Of the several devices available commercially, two were chosen for study. An Anacon (Anacon, Marlborough, MA) electrochemical diffusion based workplace chlorine monitor was fitted by the manufacturer with a Teflon barrier around the sensing electrode, which caused the response to chlorine to be reduced such that high concentrations of chlorine could be measured. (This was designated a 0 to 500 ppm probe by

Anacon.) Laboratory testing of this instrument with gases analyzed by the method of the appendix showed a linear response to chlorine from 0 to 500 ppm, but very low response to chlorine dioxide.

A Delta Model 964 (Delta/Xertex Corporation, Hauppauge, NY) diffusion based electrochemical high concentration chlorine monitor was tested in the laboratory for response to chlorine and chlorine dioxide. The data of Figure 4 indicate that the response to Cl_2 was linear to ca. 400 ppm, and the response to ClO_2 was linear to ca. 250 ppm. Below 250 ppm, the response ratio of Cl_2:ClO_2 was near 1:1.

The Delta Model 964 was tested for time of response to changes in chlorine concentrations. The time response of the system to a pulse of 250 ppm chlorine of a duration of two minutes was satisfactory, as indicated in Figure 5. However, a pulse of 750 ppm chlorine of 14 minute duration produced an unusably long fall time, as indicated in Figure 6.

A modification was made to the Model 964, as diagrammed in Figure 7. Teflon solenoids were configured so that source gas and potassium iodide-scrubbed ambient air could be alternately provided to the Teflon chamber in which the sensor was mounted. A cycle time of 2 minutes on source gas and 4 minutes on air proved satisfactory, as indicated in Figure 8.

In earlier studies of measurement methods for workplace atmosphere chlorine and chlorine dioxide,[4,5] NCASI determined that aqueous solutions of sulfamic acid in midget impingers would trap chlorine, but would quantitatively pass chlorine dioxide, at concentrations in the 0.05 to 2 ppm range. This prompted further modification of the Delta Model 964 system, as indicated in Figure 9. By providing alternate pulses of source gas (Cl_2 + ClO_2), air, source gas passed through sulfamic acid (ClO_2 only), and air, the output indicated in general form in Figure 10 was obtained. Testing with mixtures of gaseous Cl_2 and ClO_2 produced the recovery results indicated in Table I.

Upon testing with mixtures of chlorine and chlorine dioxide, neither of the configurations of the modified Delta Model 964 systems yields data which are accurate enough for non-criteria pollutant analysis reporting purposes. The equipment has proven very useful, however, in continuous monitoring during field studies of factors influencing Cl_2 and ClO_2 emission rates.

Conclusions

The buffered dual pH potassium iodide impinger capture method yields good precision upon analysis of gaseous chlorine and chlorine dioxide mixtures, and buffering at pH 7.5 appears to reduce the chance of obtaining falsely high chlorine concentrations in the presence of high concentrations of chlorine dioxide.

Instrumental methods for continuously measuring gaseous chlorine and chlorine dioxide in bleach plant vents were studied, and modifications made to one commercially available system permitted the observation of short term concentration fluctuations in total Cl_2 and ClO_2. A further modification to provide separate continual quantitation of Cl_2 and ClO_2 proved sufficiently accurate for survey purposes.

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4. "A Laboratory Investigation of Techniques for Instrumentally Measuring Chlorine and Chlorine Dioxide in the Pulp Bleaching Area Workplace," Technical Bulletin No. 412, NCASI, New York (1983).

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Appendix - Method for Measuring Chlorine and Chlorine Dioxide Gaseous Emissions

This method is based upon extractive sampling using midget impingers, sampling at a low sampling rate, ca. 200 mL/min. Greater sampling rates may be used with larger impingers.

The sampling train includes a sample probe and withdrawal line which is an appropriate length, e.g., 3 m of 0.64 cm (0.25 in) od FEP Teflon tubing. This is connected at one end via either Galtek (Chaska, MN) 0.64 cm unions or short pieces of silicone tubing to a tapered stem 30 mL capacity midget impinger with 0.64 cm od inlet and outlet tubulatures (Southern Scientific, Micanopy, FL). Two identical impingers are connected in series behind the first. The third impinger contains silica gel as a dessicant, and its outlet tubulature is connected to the flow control/prime mover equipment.

Two methods may be employed for low flow rate sampling flow control. One method utilizes a dessicant column and a critical orifice downstream of the second impinger, followed by a vacuum pump capable of providing ca. 64 cm (25 in) of mercury vacuum. The orifice is calibrated prior to use, the vacuum at which critical flow is achieved is noted, and in use the high vacuum side of the orifice is always maintained at at least 13 cm (5 in) of mercury vacuum greater than this value. The flow rate at the probe tip is measured before and after sampling with a bubble tube flow meter, as impingers or other restrictive devices upstream of the critical orifice will cause the system flow rate to change from the value obtained during calibration with atmospheric pressure at the orifice inlet.

A second means of controlling flow during low flow rate sampling is to utilize EPA Method 25 evacuated sampling tanks to draw the sample and, via pre- and post-sampling pressure measurements, to measure its volume.

The first two impingers each contain 20 mL of potassium iodide (KI) solution, buffered with potassium dihydrogen phosphate (KH_2PO_4) and sodium hydroxide (NaOH), as follows:

Dissolve 20 g KI in ca. 900 mL deionized water
Add 50 mL of 1 M KH_2PO_4
Add 30 mL of 1 M NaOH
Measure pH of solution electrometrically and add 1 M NaOH to bring pH to between 7.45 and 7.55

When sampling, measure the temperature and pressure in the vent being sampled. Assuming critical orifice flow controls, activate the sample draw equipment and measure the sampling flow rate at the probe tip with a bubble tube flow meter. Insert the probe into the sample port and start a stopwatch. End the sampling (stop the watch) after 30 minutes, or after the color in the second impinger turns from pale yellow to a deeper straw color. After sampling, remove the probe from the vent, and with the probe tip elevated above the impingers, add ca. 5 mL deionized water to the probe so that this drains into the first impinger. Combine the contents of the impingers in a 100 mL beaker, and titrate with sodium thiosulfate solution (0.100 N or less concentrated, depending upon the quantity of iodine being titrated). Record the volume of titrant to the first endpoint (T_N, mL). Add 5 mL of 10 percent sulfuric acid solution, and continue the titration to the second endpoint. Record the total volume of titrant required to go through the first and to the second endpoint (T_A, mL).

To calculate moles of chlorine and moles of chlorine dioxide captured employ the formulas:

$$EqI_2N = (T_N)(10^{-3})(N)$$

$$EqI_2A = (T_A)(10^{-3})(N)$$

$$ClO_2 \text{ moles} = 1/4\ EqI_2A - 1/4\ EI_2N$$

$$Cl_2 \text{ moles} = 1/8\ (5\ EqI_2N - EqI_2A),$$

where EqI_2N and EqI_2A are equivalents of iodine determined in the neutral and (total) acid titrations, respectively, and N is the normality of the sodium thiosulfate solution. Calculate gas phase concentrations of ClO_2 and Cl_2 employing standard EPA calculations. Assume gas phase water saturation in most vents.

TABLE I. GAS PHASE Cl_2 AND ClO_2 MEASUREMENTS
LABORATORY MIXTURE ANALYSIS RESULTS
MODIFIED DELTA 964

True Concentration, ppm		Recovery, Percent	
Cl_2	ClO_2	Cl_2	ClO_2
106	300	78	100
100	298	80	101
107	58	106	132
65	320	86	141

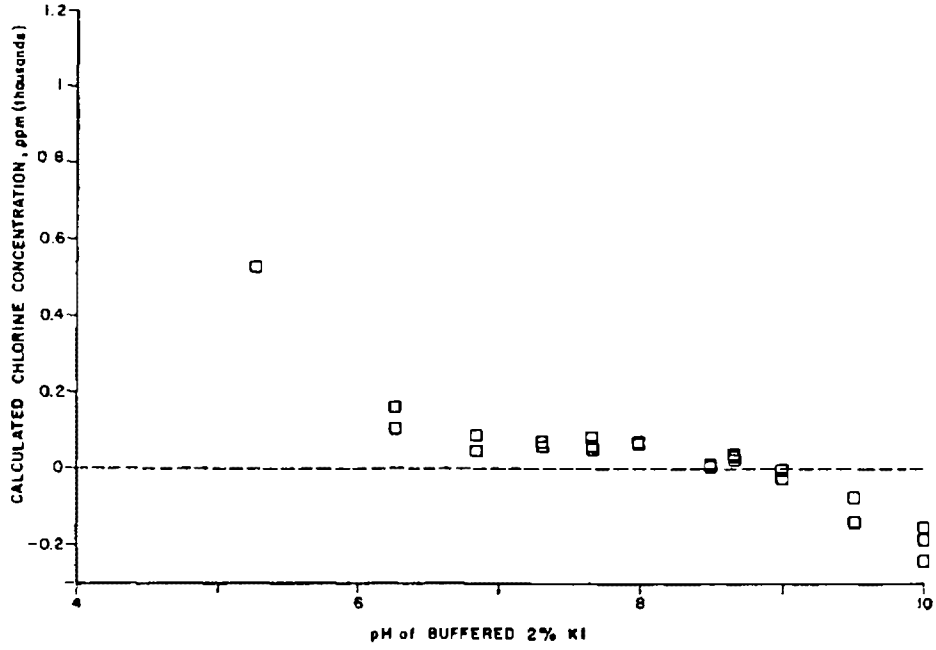

Figure 1 Effect of capture solution pH on observed chlorine concentration.

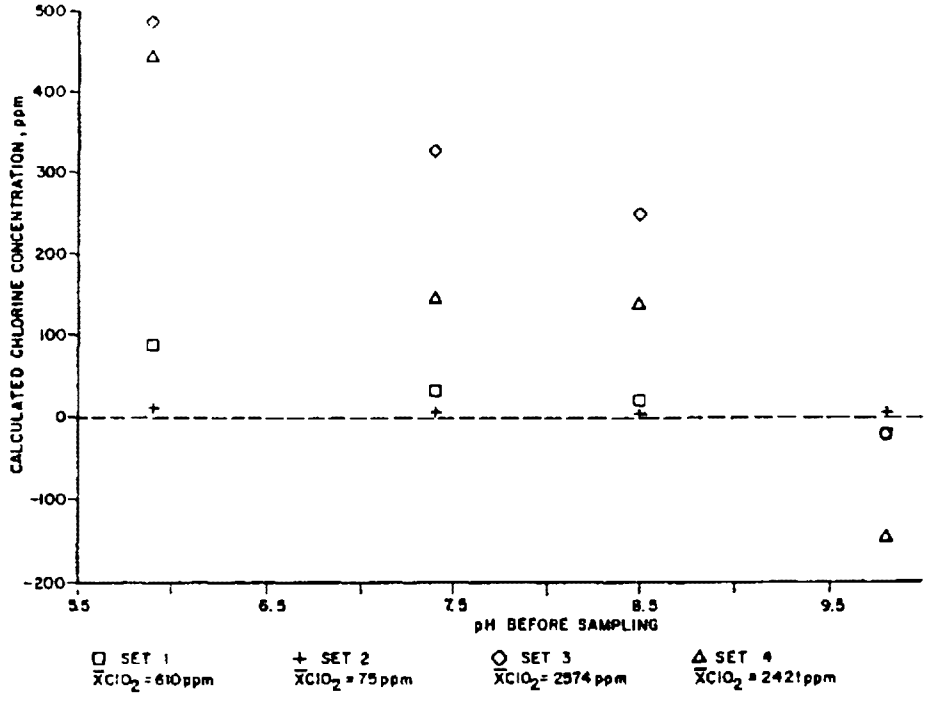

Figure 2 Effect of chlorine dioxide concentration on pH dependence of observed chlorine concentration.

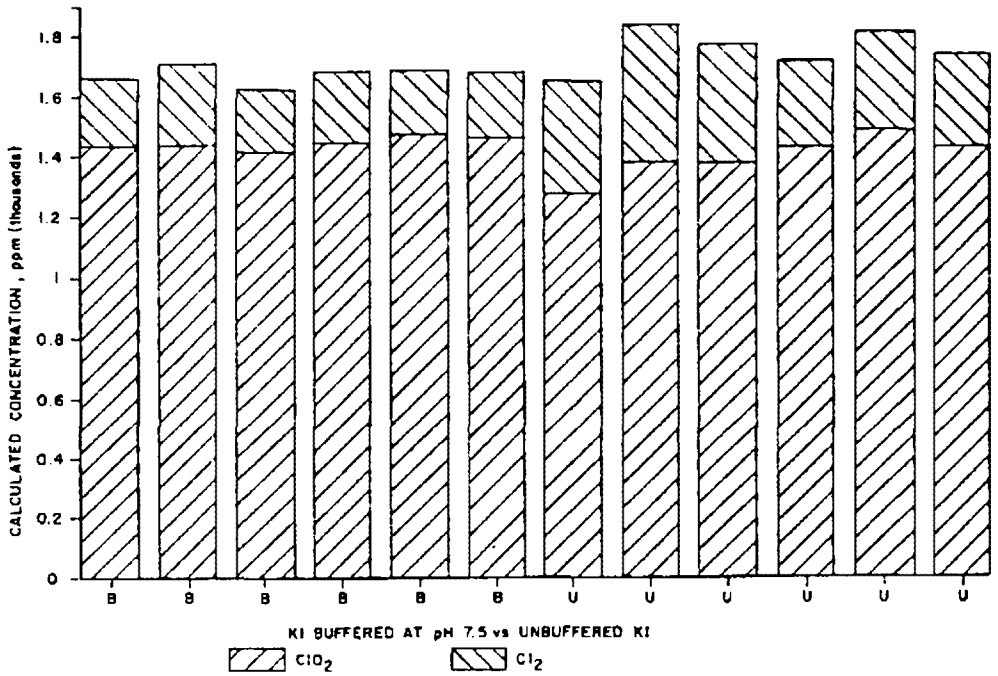

Figure 3 Effect of buffered vs. unbuffered capture solutions on observed chlorine and chlorine dioxide concentrations.

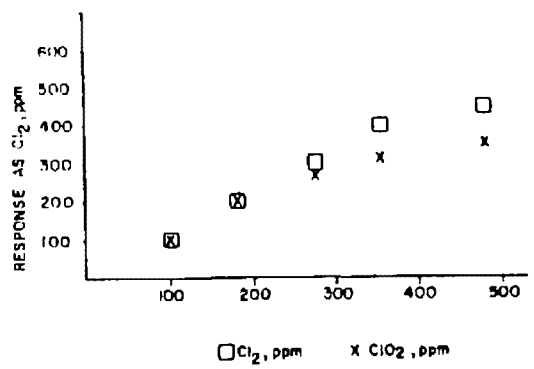

Figure 4 Response of Delta model 964 chlorine monitor to chlorine and chlorine dioxide.

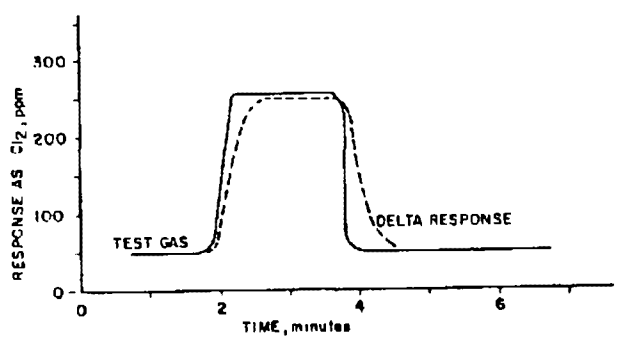

Figure 5 Response of unmodified Delta 964 to a chlorine pulse of short duration.

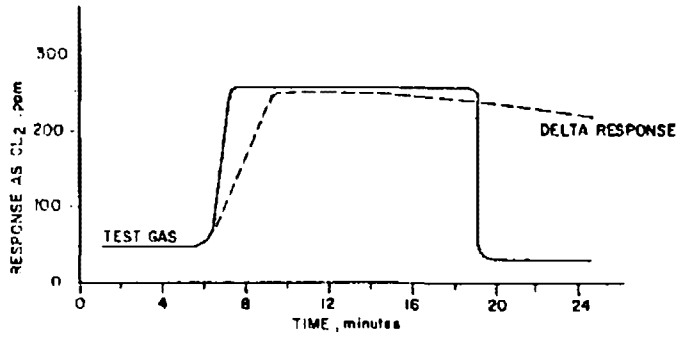

Figure 6 Response of unmodified Delta 964 to a chlorine pulse of long duration.

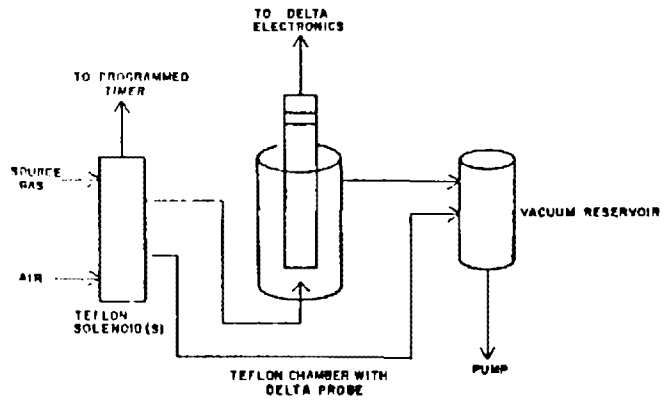

Figure 7 Modified Delta model 964 sample system.

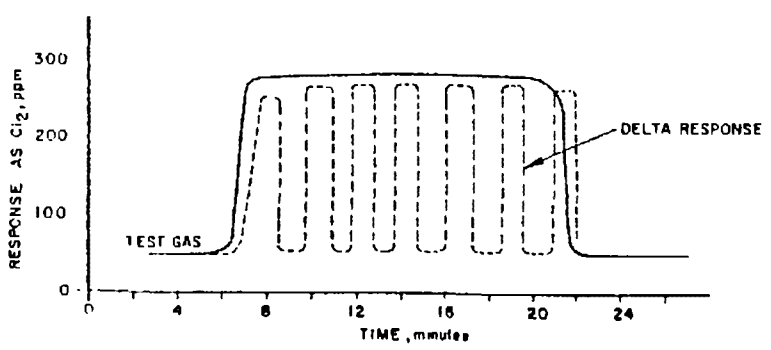

Figure 8 Response of modified Delta model 964 to a chlorine pulse of long duration.

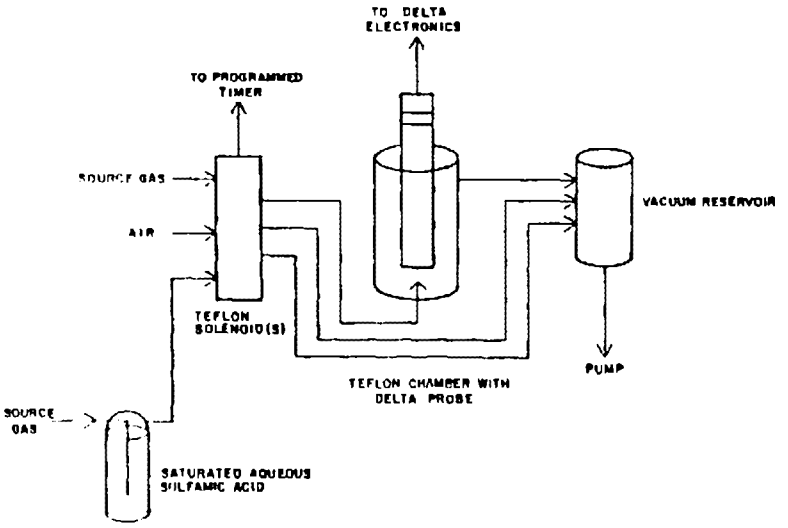

Figure 9 Delta model 964 modified for chlorine and chlorine dioxide speciation.

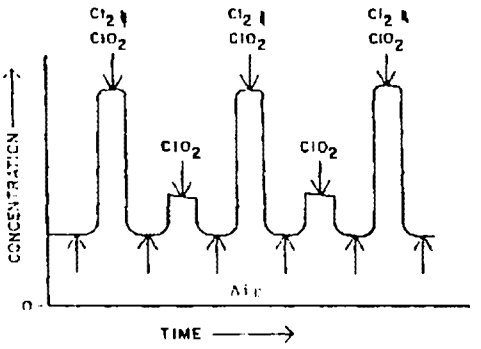

Figure 10 Response of the modified Delta model 964 to a mixture of chlorine and chlorine dioxide.

LABORATORY AND FIELD EVALUATION OF A MODIFIED EPA METHOD 5 TRAIN AND ATOMIC ABSORPTION SPECTROMETRY FOR THE MEASUREMENT OF CADMIUM IN STATIONARY SOURCE STACK GASES

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An initial laboratory and field evaluation study was done to assess the usefulness of a Modified EPA Method 5 sampling train and atomic absorption spectrometry for the measurement of cadmium in stationary source stack emissions. Field evaluations were performed at a municipal solid waste incinerator. This industrial source is currently being evaluated by EPA/QAQPS for cadmium emissions. Also, this methodology is being developed for application, subject to verification, at other sources of cadmium emissions at or above the method detection limit. A formulation of the methodology was tested through the laboratory and field sampling validation phases to evaluate precision and accuracy of the proposed method. Collocated, quadruplicate flue gas samples of 30 and 60 dscf in 1 and 2 hours sampling time were collected to assure an adequate cadmium content, a representative sample including volume of stack gas and duration of sampling time, and production of data to validate the method in terms of between-train precision. The overall accuracy and precision of the analysis procedure were 89.2 percent and 1.7 percent, respectively. The detection limit of the atomic absorption instrument was 0.03 ug/mL. The method detection limit for a 30 to 60 dscf (0.85 to 1.7 dscm) stack gas sample was found to be 0.05 to 0.025 ug Cd respectively per dscf (1.7 to 0.88 ug Cd per dscm). The percent coefficient of variation (precision) of between-train cadmium concentrations averaged 13.5% for the six sampling runs conducted. Separate analysis of the front half (probe and filter) and back half (impingers) of each of the field samples revealed that all of the cadmium was collected in the front half, based upon the results that all the back half samples were below the detection limit. Precision of the cadmium results was not affected by varying the sample size from 30 to 60 dscf. Other source categories should be tested and further laboratory work done to broaden the scope of the method.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) is currently investigating cadmium emissions from stationary sources as a potentially hazardous air pollutant. In the event that EPA makes a determination to regulate cadmium emissions, appropriate methods of sampling and analysis must be available to accurately quantify the emission of cadmium in stack gases from stationary sources.

The Environmental Monitoring Systems Laboratory (EMSL) of EPA located in Research Triangle Park, North Carolina is developing and validating a methodology for sampling and analysis of cadmium emissions. The purpose of this report is to present the results of a field and laboratory study of cadmium emissions measurement methodology. The objectives of the study were as follows:

- Determine the applicability of a Modified EPA Method 5 train and atomic absorption spectrometry for the measurement of stationary source stack gas cadmium.
- Evaluate the precision and accuracy of the proposed laboratory analytical techniques. The techniques consisted of sample preparation followed by analysis for cadmium using atomic absorption spectrometry.
- Assure that the method has a detection limit sufficient to measure expected cadmium in municipal solid waste incinerator flue gas samples of 30 to 60 dry standard cubic feet.
- Combine the results of these determinations to validate the proposed sampling and analytical methodologies.

The method validation was conducted in several stages. The initial effort focused on defining appropriate sampling and analytical procedures. The procedures were then chosen and a laboratory study was conducted to determine overall precision and accuracy of sample preparation and analysis. The next stage of the program involved a field evaluation conducted at a large municipal solid waste incinerator. Other source categories may be tested and further laboratory studies may be conducted to expand the scope of applicability of the methods to include additional stationary sources.

EXPERIMENTAL METHODS

The sampling and analytical methods evaluated in this field and laboratory study were proposed after a thorough literature search. The various methods of sampling, sample preparation and analyses were then compared according to method detection limit, sensitivity, precision, speed, complexity, availability, cost, and overall practicality. After considering these factors and reviewing the literature, it was determined that sample collection using a very slightly modified EPA Method 5 (MM5) sampling train, followed by acid digestion in a Parr bomb and atomic absorption spectrometry would be used for the sampling and analysis of cadmium emissions from stationary sources.

The laboratory validation phase of this work was designed to assess the combined precision and accuracy of the portion of the methodology used for sample preparation and analysis. A National Bureau of Standards (NBS) urban particulate sample was analyzed in this phase. Samples were digested using a mixture of nitric and hydrofluoric acids in a Parr bomb, and analyzed in quadruplicate using three different methods (AAS, ICAP, and NAA).

A weighed amount of each particulate sample was digested along with a glass fiber filter to provide a background matrix consistent with the field samples. Following digestion, each sample was split for analysis by atomic absorption spectroscopy (AAS), neutron activation (NAA) and inductively coupled argon plasma spectroscopy (ICAP). The latter two analytical techniques were used to confirm the results obtained by AAS. Filter blanks were prepared and analyzed to demonstrate the absence of cadmium in the glass fiber filter and acid reagents.

The field test was conducted at a municipal waste incinerator which had previously been tested for cadmium emissions. Cadmium concentrations reported during the previous testing ranged from 23 to 230 ug/dscm. The range of cadmium found in this study was from 32 to 115 ug/dscm. The sampling method employed was a MM5 train which used nitric acid in the first two impingers instead of water. Separate analyses were performed on the front and back halves of the trains to determine the collection efficiency of each half.

In order to assess sampling and sample recovery precision, four "identical" samples were collected simultaneously using a quad-probe. Four simultaneous samples were collected twice each day over a three-day period for a total of 24 samples. Sampling was conducted isokinetically at 0.5 dscfm for all test runs.

Samples were collected for periods of roughly one or two hours to yield total sample volumes ranging from 32 to 65 dry standard cubic feet. The sample volumes were chosen to demonstrate that: 1) cadmium emissions from a municipal incinerator could be measured in samples of this size, and 2) the size of the sample volume would not affect the analytical precision and accuracy of cadmium concentration results.

In order to recover all of the cadmium from the sampling train components the front half probe rinses were combined with the glass fiber filter for digestion and analysis. The impinger solutions and back half rinses were combined and analyzed to determine if cadmium were captured in the back half of the MM5 train.

RESULTS

Prior to any field sampling activities, the precision and accuracy of the proposed analytical procedures were determined. The sample preparation and AAS procedures used to analyze field samples for cadmium had an accuracy of 89.2 percent for analyzing known concentrations of cadmium. The precision of these procedures was 1.7 percent.

The precision and accuracy are based on results as determined by Parr bomb digestion of four aliquots of a National Bureau of Standards Standard Reference Material urban particulate sample and three independent analysis techniques for the aliquots: AAS, ICAP spectroscopy, and NAA. Instrument detection limits for the three techniques were 0.03, 0.03, and 0.12 ug/mL, respectively.

The accuracy (% recovery) and precision (% coefficient of variation) for all three analytical methods are given in Table I. Overall average percent recoveries for each analytical method were as follows: 89.2% for AAS, 99.3% for ICAP, and 94.2% for NAA. The mean percent differences for the duplicates was 1.0% for AAS, 6.2% for ICAP, and 1.7% for NAA. In terms of standard deviation, the values were 0.84, 4.49, 1.09 ug/g for AAS, ICAP, and NAA, respectively. The duplicate means and the standard deviation are measures of precision for three analytical methods and serve as a basis for assessing the relative precision of the analytical methods.

The field testing portion of this study was designed to evaluate the precision of the sampling and sample recovery procedures, the cadmium collection efficiency of the front and back halves of the MM5 train, and the effect of the sample volume on cadmium measurement.

Table II presents the cadmium concentrations and precision assessments for the quad-train field study. The between train pooled standard deviation was 12.39 ug/dscm and represents the overall precision for the field study. In terms of percent coefficient of variation the pooled precision was 13.54% which is a measure of the precision of sampling and analysis.

The within-run or between-train precision shown in Table II is assessed in terms of a standard deviation and percent coefficient of variation. Contributions to these variables result from (1) differences in the sampling trains, (2) variations between trains in the sample preparation and recovery steps, and (3) analytical variability. Between-test pooled variability includes all of the above and: (1) the day-to-day variability of the cadmium concentration in the feed, (2) effects of different plant operating conditions and (3) the potential effect of within-run variability on the cadmium collection.

A second variable which was addressed was the collection efficiency of the sampling train. No cadmium was detected in the back half, indicating that the front half (probe and filter) was very efficient (>99.9% efficiency) in preventing breakthrough of cadmium.

A third variable evaluated in the data set of Table II is the length of the sampling period for each run. Tests 2, 3, and 6 were each conducted for roughly one hour while Runs 1, 4, and 5 were conducted for about 2 hours. An analysis of variance confirmed that there was not a significant difference in the variabilities of the cadmium concentrations of the one-hour compared to the two-hour runs, at the 5% level of significance (95% probability). Thus, sampling times of about one hour will yield concentration data equivalent to that for double the sampling time.

Anomalies in the cadmium concentration data set are described here. The average cadmium concentration level in Test No. 1 was much lower than for Tests 2 through 6. The cadmium concentrations shown for Tests 2 through 6 in Table II reflect a reasonably constant average cadmium concentration in the stack gas. However, there is no reason to suspect that the Test No. 1 samples were collected any differently than other test run samples. Therefore, these data were included in the data analysis. The concentration difference between Run No. 1 and the other runs is probably due to plant operating conditions.

Also, Sample B in test number 6 shows an extremely high value in terms of cadmium per dscm (Table II). Table III shows a comparison of cadmium in terms of gas volume sampled and the amount of cadmium per gram of particulate. The source of high cadmium content of sample B, test number 6 can be only conjecture and cannot be explained adequately or factually. However the Dixon outlier test indicates that this value is an outlier and, therefore, was not included in the statistical analysis.

Table III shows a particulate value for Sample A in test number 4 which is nearly seven times higher than other values of the data set. A large amount of milky material was noted in the two nitric acid impingers, and the filter appeared brownish rather than white. It was observed during this entire field sampling exercise that on all newly tape-wrapped probe liners a thickish fluid exuded from the probe exterior wrapping tape upon heating the nichrome wire. Normally this fluid dripped harmlessly from the probe liner. Upon removal of the probe for Sample A, test number 4, from the stack at the end of the test, inspection of the glass probe liner revealed that it was broken by having been cracked around its entire circumference. However, the glass liner was still held in place by the tape which holds, also, the heating wires in place around the glass liner. It is assumed here that the fluid from this newly tape-wrapped probe liner was pulled into the cracked probe and caused the milky impinger deposit, filter discoloration, and excess particulate weight observed, while at the same time due to its thickish quality sealing the probe sufficiently for an adequate stack gas volumetric sample. Even though the particulate value for this sample was very high, the concentration of cadmium appeared to agree with the other three runs of the test and was therefore included in the statistical analysis.

CONCLUSIONS

Several conclusions and recommendations have been made regarding the proposed use of a slightly Modified EPA Method 5 (MM5) sampling train and atomic absorption spectrometry for the measurement of stack gas cadmium in stationary sources. These include:

1) An MM5 sampling train and atomic absorption spectrometry were found to be applicable for the measurement of cadmium in stationary stack gas samples.

2) Further field evaluations should be conducted to insure the applicability of the MM5 train for stationary sources of different stack gas cadmium concentrations.

3) The overall accuracy and precision of the analytical steps were 89.2 percent and 1.7 percent, respectively. The detection limit of the analytical instrument was 0.03 ug Cd/ml of prepared sample. A very limited cadmium concentration range was investigated. The precision and accuracy should be further investigated with different cadmium concentrations.

4) The method detection limit for a 30 to 60 dscf (0.85 to 1.7 dscm) stack gas sample was 0.05 to 0.025 ug Cd/dscf (1.7 to 0.88 ug Cd/dscm).

5) The percent coefficient of variation of between-train cadmium concentrations ranged from 3.4 to 23.1% for the six sampling runs conducted. The method bias was not affected by total sample volume. Stack gas samples of approximately 30 and 60 dscf were collected, and the cadmium results for the two sample sizes did not differ significantly. Greater than 99.9 percent of the cadmium was collected in the front half of the sampling train for each run. Future developmental testing should include back half analysis to determine whether this analysis is necessary.

6) If a purchased stock solution of cadmium is used for preparation of working standards, the concentration should be verified against an independently prepared cadmium standard.

7) At least one sample from each source should be checked using the method of additions to ascertain that the chemical composition and physical properties of the sample do not cause erroneous analytical results.

Table I. ACCURACY AND PRECISION OF CADMIUM IN NBS STANDARD REFERENCE MATERIAL #1648, URBAN PARTICULATE[a]

Sample ID[b] Number	AAS Accuracy[c] Individual % Recovery	AAS Accuracy[c] Mean	ICAP Accuracy[c] Individual % Recovery	ICAP Accuracy[c] Mean	NAA Accuracy[c] Individual % Recovery	NAA Accuracy[c] Mean
A1	97.4		98.3		105.5	
		97.4		102.5		106.5
A2	97.4		106.6		107.4	
B1	84.0		107.5		92.2	
		84.7		104.5		91.6
B2	85.4		101.5		91.0	
C1	81.3		91.3		69.6	
		82.0		88.2		70.6
C2	82.7		85.0		71.6	
D1	92.0		100.1		107.5	
		92.7		102.2		108.0
D2	93.3		104.2		108.4	
Mean Accuracy	89.2		99.3		94.2	
% Coefficient of Variation, Precision	1.7		7.8		17.1	
Duplicate Differences:						
Mean %:[d]	1.0		6.2		1.7	
Std. Dev. of Random Error[d,e] ug/g	0.84		4.49		1.09	

[a]Based on an NBS cadmium value of 75 ug Cd per gram of particulate.

[b]Sample A was Parr bombed once, Samples B, C, and D were bombed twice.

[c]AAS, Atomic Absorption Spectrophotometry; ICAP, Inductively Coupled Argon Plasma; and NAA Neutron Activation Analysis.

[d]A measure of precision of duplicate determinations on four samples.

[e]Youden, W.J., and E.H. Steiner, "Statistical Manual of the Association of Official Analytical Chemists," AOAC, Arlington, Virginia 22209 (1975), p. 18.

Table II. CADMIUM CONCENTRATIONS AND WITHIN-RUN PRECISION ASSESSMENTS (ug/dscm)

Test No.	Sample Train A	B	C	D	Average x	Standard[a] Deviation	Percent Coefficient of Variation, % CV
1	32.2	32.8	30.4	32.6	32.0	1.10	3.4
2	96.5	85.6	87.2	104.1	93.4	8.63	9.2
3	105.5	115.5	73.5	74.9	92.4	21.36	23.1
4	76.2	88.0	101.2	76.7	84.8	11.67	13.8
5	80.0	111.5	103.3	88.3	95.8	14.24	14.9
6	101.4	328.0[b]	93.8	95.6	96.93	3.97	4.1
					pooled	12.39[d]	13.54[d]

[a]All sample train results reported in micrograms cadmium per dry standard cubic meter, ug/dscm.

$$\frac{\text{probe rinse + filter + impingers (ug)}}{\text{total volume of stack gas sampled } (m^3)}$$

[b]This value was excluded from the data analysis, because when subjected to a Dixon Outlier test[c] for Test No. 6, it did not meet the acceptance criterion of 126.1 ug/dscm, at the 5 percent level of significance (i.e., 95% probability).

[c]The Dixon outlier test may be found in Dixon, Wilford J., and Frank J. Massey, Jr., "Introduction to Statistical Analysis," McGraw-Hill Book Company, New York (1057).

[d]pooled = $\left(\sum_{i=1}^{n} \frac{s_i^2}{n}\right)^{1/2}$

Table III. CADMIUM CONCENTRATIONS, PARTICULATE CONCENTRATION, RATIO OF CADMIUM TO PARTICULATE CONCENTRATION, AND ISOKINETIC RATES FOR EACH RUN[a]

Test No.	A	B	C	D
1				
Cadmium (mg/dscm)	0.0322	0.0328	0.0304	0.0326
Particulate (mg/dscm)	b	b	b	b
Cadmium to Particulate (mg/gram)	b	b	b	b
Isokinetic Value (%)	102.2	104.1	102.6	107.6
2				
Cadmium (mg/dscm)	0.0965	0.0856	0.0872	0.1041
Particulate (mg/dscm)	b	b	b	b
Cadmium to Particulate (mg/gram)	b	b	b	b
Isokinetic Value (%)	100.8	104.2	99.9	100.4
3				
Cadmium (mg/dscm)	0.1055	0.1155	0.0735	0.0749
Particulate (mg/dscm)	38.769	38.782	49.482	36.050
Cadmium to Particulate (mg/gram)	2.72	2.98	1.48	2.08
Isokinetic Value (%)	102.8	100.0	103.5	101.0
4				
Cadmium (mg/dscm)	0.0762	0.0850	0.1012	0.0767
Particulate (mg/dscm)	224.118[c]	34.254	33.767	32.585
Cadmium to Particulate (mg/gram)	c	2.48	3.00	2.35
Isokinetic Value (%)	101.4	101.2	103.1	102.9
5				
Cadmium (mg/dscm)	0.0800	0.1115	0.1033	0.0883
Particulate (mg/dscm)	40.730	44.209	37.192	34.542
Cadmium to Particulate (mg/gram)	1.96	2.52	2.78	2.56
Isokinetic Value (%)	102.6	101.1	102.2	101.5
6				
Cadmium (mg/dscm)	0.1014	0.3280[d]	0.0938	0.0956
Partculate (mg/dscm)	37.872	38.933	35.373	32.424
Cadmium to Particulate (mg/gram)	2.68	8.42[d]	2.65	2.95
Isokinetic Value (%)	101.0	100.0	97.7	101.2

[a]The particulate emission and cadmium-to-particulate ratio values presented in this table are for information only. In any municipal waste incineration process, significant variation might be expected between tests for these values.

[b]Particulate weight was not determined.

[c]Not valid for particulate concentration or cadmium-to-particulate ratio because of broken probe liner which resulted in excessive particulate weight values.

[d]Not valid for cadmium, Dixon outler test.

SAMPLING AND ANALYTICAL METHOD FOR MEASURING METHYLENE CHLORIDE EMITTED FROM STATIONARY SOURCES

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Recent bioassays supported by the National Toxicology Program (NTP) have demonstrated that methylene chloride is a carcinogen in laboratory animals, and other data indicate that it is a mutagen. Human studies have not, however, proved to be conclusive for carcinogenicity. Therefore, EPA initiated an investigation to determine risks to human health through accurate measurement of the emission rates from various stationary sources. This paper describes work performed to select an appropriate sampling and analysis procedure for the investigation and evaluate its accuracy and precision.

A laboratory evaluation of the proposed method was conducted followed by a field test at a methylene chloride manufacturing facility. The analysis technique chosen was gas chromatography with flame ionization detection. In the laboratory evaluation Tedlar and 5-layer aluminized sampling bags were evaluated for methylene chloride stability. Methylene chloride was found to be much more stable in Tedlar than in the 5-layer aluminized bags at part per million levels. The laboratory evaluation also determined the method's precision to be +/-10 %, and the range to be from 1 ppm to 13 %. In the field evaluation analytical accuracy of +/-10 % was determined by analysis of certified standards and comparisons with independent audit cylinders. This is also the best available estimate of overall method accuracy since it was not possible to know the actual methylene chloride concentration in the stack during the sampling period. Sampling precision was determined by sampling four ports simultaneously and comparing the results of each run. Stability of field samples was determined by comparing on-site analyses to the lab analyses after 20 days. Interlaboratory comparisons were done between Radian and EPA/EMSL's laboratories.

SAMPLING AND ANALYTICAL METHOD FOR MEASURING METHYLENE CHLORIDE EMITTED FROM STATIONARY SOURCES

Introduction

Data provided in a recent National Toxicology Program (NTP) bioassay demonstrate[1] that methylene chloride is a carcinogen in two species of laboratory animals, rats and mice, exposed at different dose levels via inhalation. Mutagenicity data indicate that methylene chloride is a mutagen with the potential of inducing gene mutations in exposed human cells. EPA concluded that the available body of information on methylene chloride provides sufficient evidence of carcinogenicity in animals, but the human epidemiological data are considered inconclusive. In the October 17, 1985 Federal Register, EPA initiated regulatory investigation of methylene chloride to determine whether methylene chloride presents an unreasonable risk to human health or the environment and to determine if regulatory controls are needed. These findings created the need for a sampling and analytical method to measure the amount of methylene chloride emitted from stationary sources.

The method uses Tedlar gas sampling bags to collect the samples from the source and gas chromatography with flame ionization detection for the analysis.[2] Sample introduction to the gas chromatograph employs a gas sampling valve or a gas-tight syringe. The chromatographic column used is the EPA-recommended column for volatile organic analysis, Method 624.[3] Certified methylene chloride standards in nitrogen were purchased in cylinders to provide retention time and response vs concentration calibration curves. Methylene chloride standards were also prepared in Tedlar bags.

Concentrations of methylene chloride in stack gases from one part per million to the per cent levels can be analyzed by this method. In the laboratory Tedlar and 5-layer aluminized gas sampling bags were evaluated for stability and water vapor effects at concentrations of 10 ppm to 13 per cent methylene chloride. Field validation of the sampling and analytical method was conducted at a methylene chloride manufacturing facility.

Experimental

The first objective of this work was to search the literature for information on a sampling and analytical method suitable for a variety of emission sources. The method of choice should detect low parts per million through per cent levels of methylene chloride in emissions from manufacturing and user facilities. The method should also be selective for methylene chloride and allow samples to be collected easily with stability sufficient for analysis within two weeks.

The second objective was to evaluate the selected method in the laboratory prior to the field test. The laboratory evaluation began with the preparation of standard curves in the ranges of interest; selection of gas chromatographic conditions; determination of linearity; injection precision; and the minimum detectable limit. Possible interferences from other chlorinated hydrocarbons were also investigated.

The third objective was to study stability in the laboratory at various concentrations and evaluate water effects on the analysis. Also, stability comparisons of Tedlar and 5-layer aluminized bags were completed, as were bag blanking procedures.

The fourth objective was to field test the proposed methodology. A pre-survey of a selected methylene chloride manufacturing facility was conducted and grab samples were taken using Tedlar sampling bags. These samples were analyzed in the laboratory, compared with expected results obtained from engineering calculations, and used to screen for interfering compounds. The pre-survey also established sampling locations, flow rates, and site preparation needs for the field test.

The field test was designed to challenge the proposed sampling and analysis method. The samples were taken using an aluminum manifold with an anemometer inserted to obtain flow data. On-site analyses were done to obtain immediate results. An independent assessment of analytical accuracy was made by analyzing gas cylinders containing unknown concentrations of methylene chloride. These cylinders were provided by an EPA quality assurance contractor.

The field samples were then transported to Radian's and EPA's laboratories for analysis. These results were compared with the on-site results. A sample was also analyzed by gas chromatography/mass spectrometry (GC/MS) to confirm the gas chromatography/flame ionization detector (GC/FID) peak to be methylene chloride and to identify other compounds detected.

Results and Discussion

Laboratory Evaluation

The literature search for sampling and analysis methods for methylene chloride emissions suggested that the simplest and most appropriate sampling technique should use gas sampling bags. The analytical technique chosen was gas chromatography with flame ionization detection. EPA Method 18 uses this sampling and analysis technique for many organic compounds. The suggested analytical column was OV-101, a methyl silicon liquid phase on Chromosorb WHP. This column was tried and found to separate methylene chloride from methyl chloride, chloroform and carbon tetrachloride, but required a 35°C oven temperature. This could present precision and accuracy problems because some gas chromatographs do not maintain constant oven temperatures at 35°C. An alternate column used in EPA Method 624, 1 % SP-1000 on Carbopack B, for volatile organic analysis was tried and showed excellent separation. Temperature programming the oven from 40°C to 200°C at 10°/min reduced the analysis time to 15 min.

Both a gas sampling valve heated to 100°C and a gas-tight syringe were used in the laboratory studies to inject samples into the GC. The precision of injections was comparable with each technique. Standards of methylene chloride in nitrogen were obtained from Scott Specialty Gases. Precision of replicate injections averaged 1.0 %. Stability of a 102 ppm standard over a 3-month period was not significantly different from the 1.0 % precision of injections. The linearity of the standard curve was very good from 5 ppm to 25000 ppm (2.5 %). The per cent levels were injected directly without dilution. The minimum detection limit for this method is estimated to be between 0.5 ppm and 1.0 ppm. This was calculated by extrapolation of the detector response from a 6 ppm audit cylinder, to an expected response that would be at least 2 times the noise level. Standards of methylene chloride with chloroform and carbon tetrachloride

were analyzed for possible interferences and none were found.

The proposed sampling technique was evaluated by studying the stability of methylene chloride standards in Tedlar bags. For comparison purposes and as a possible alternative, 5-layer aluminized gas sampling bags were obtained from Alltech/Applied Science, and also evaluated. The five layers are : 1) inner layer of polyester, 2) polyamide, 3) aluminum foil barrier, 4) polyvinylidene chloride, 5) outer layer of polyethylene terephthalate. The Tedlar bags were obtained from EPA. All bags were initially purged three times with dry nitrogen, then filled with nitrogen and analyzed using the GC procedure. No detectable peaks were found. A measured amount of methylene chloride liquid was vaporized and injected into a stream of nitrogen flowing into each bag at a known rate. The concentrations prepared were approximately 7.5 %, 10.0 %, and 13.0 %. Dilutions of these per cent concentrations were made before analysis. The ppm level bags were prepared by transferring the 102 ppm gas cylinder standard into Tedlar and 5-layer aluminized bags. Each bag was well mixed and analyzed throughout a 9 day period. The results showed a per cent decrease ranging from -1.8 % to -6.1 % for all bags studied. However, at the ppm level there was a significant change in the 5-layer aluminized bags. Within a 2 day period there was a 30 % decrease from 102 ppm to 72 ppm. Figure 1 illustrates that the Tedlar bags decreased only 5.5 %. The instability of the 5-layer aluminized bags is thought to be due to methylene chloride permeating the inner layer of polyester. The Tedlar and 5-layer aluminized bags were then evacuated and purged three times with nitrogen after containing concentrations of 10000 ppm. The bags were then immediately analyzed. The Tedlar bags produced no detectable peaks, whereas the aluminized bags retained approximately 10 ppm after six successive purgings. After considering these results, it was decided not to continue evaluating the aluminized bags. A 10.5 ppm standard was analyzed in the Tedlar bags for a period of 18 days. The results showed a decrease of less than 1.0 %, which is not significantly different from the analytical precision. Water effects within the bags were studied by bubbling the cylinder standard of 102 ppm through water to produce a humidified standard. A Tedlar bag was filled with the humidified standard and analyzed. The results of the humidified bag was compared to the results of the humidified standard analyzed without contacting the Tedlar. There was not any significant difference between the two analyses, proving that humidity does not affect the results.

FIELD EVALUATION

As discussed above, a field test was conducted to challenge the method under real conditions. A manufacturing facility was selected that was expected to have emissions of methylene chloride. An aluminum manifold (6 ft. x 4 in.) was placed in-line with a by-pass on a vent stream, prior to a scrubber unit. The stream was allowed to equilibrate before the Tedlar bags were connected to the four sample ports. Four samples were taken simultaneously to provide sampling precision data. EPA Method 18 uses an evacuated container sampling technique, in which the pump does not contact the sample. The sample bag is placed in a sealed rigid container and the sampling line attached using quick-connect unions. The container is evacuated at a controlled flowrate, thus filling the bag. Due to an approximately 3 psig sample pressure, the evacuated container technique for the bag sampling could not be performed, and the sample pump was not needed. Instead, sample flow into the bags was controlled by placing a flow meter and needle valve between each bag and the sampling port. All flows were adjusted to 0.5 L/min. and monitored every 5 min during the 30 min sampling period to obtain 15 liter of sample. The maximum capacity for

each bag was 30 liter. Anemometer readings were also taken in order to calculate the emission rate of the stream.

All of the samples were then analyzed on-site. Six tests were conducted over a 3-day period on two different vent streams. Four tests were done on one stream and two on the other. A blank and 3 points were used to construct a calibration curve at the beginning and end of each day. All samples were analyzed in duplicate and their averages used to calculate precision between them. For each test the standard deviation and per cent coefficient of variation (% CV) were calculated. All six tests resulted in a pooled % CV of 5.0, with a range of 2.3 to 8.3 %. The analytical accuracy was determined by analyzing two unknown audit cylinders for methylene chloride. The results in Table I show a per cent accuracy of -4 %.[4]

Nine of the 24 samples were transported to Radian's laboratory and randomly distributed and analyzed by Radian and EPA/EMSL. The concentration of methylene chloride found in the field samples ranged from 7500 ppm (0.75 %) to 25000 ppm (2.5 %). The results in Table II show that Radian's re-analysis varied by an average of -2.8 % from the on-site results. EPA used the same column and conditions as did Radian for one set of analyses, and a second column for comparison. The first column's per cent difference from Radian's on-site results was 0.5 %, and the second column's results were -2.2 %. GC/MS results confirmed methylene chloride in the field samples and identified the only other compounds to be chloroform and carbon tetrachloride.

Conclusions and Recommendations

The laboratory and field evaluations have demonstrated that this proposed method has an accuracy and precision of +/-10 per cent over the range of 1 ppm to 13 %. These evaluations show that methylene chloride emissions can be sampled using Tedlar bags, and the analysis can be done up to 20 days later without sample degradation. This work also shows that 5-layer aluminized bags are not acceptable for methylene chloride sampling. It is recommended that an additional field test be done to further challenge this method at the low parts per million levels, and evaluate overall method precision and accuracy.

Acknowledgments

Radian Corporation, Analytical Chemistry Dept., Research Triangle Park, North Carolina, conducted work on this project under Contract No. 68-02-4119 for the Quality Assurance Division, Environmental Monitoring Systems Laboratory of the U.S. Environmental Protection Agency. Joette Steger, Radian Corp., also contributed to the laboratory studies of this work. The authors also would like to thank Denny E. Wagoner, Radian Corp., for his helpful suggestions.

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Table I. Percent Accuracy

Radian, ppm	Actual, ppm	% Accuracy
10.0	10.4	-4.0
5.8	6.0	-3.5

Table II. Interlaboratory Comparisons

Test & Sample Number	Percent Differences from On-Site Results		
	Radian[1]	EPA[1]	EPA[2]
1A	-0.6	4.6	0.6
1B	1.7	—	0.7
1D	-2.7	-6.3	-0.3
2C	—	-7.4	-2.6
4A	-2.8	1.7	-3.1
5A	-5.8	—	—
5B	—	0.9	-5.6
5C	-6.9	5.4	-3.1
5D	—	4.4	-4.0

[1] Column : 6 ft. X 1/8 in. 1% SP-1000 on Carbopack B 60/80
[2] Column : 9 ft. X 1/8 in. 5% OV-101 on Chromosorb WAP 80/100

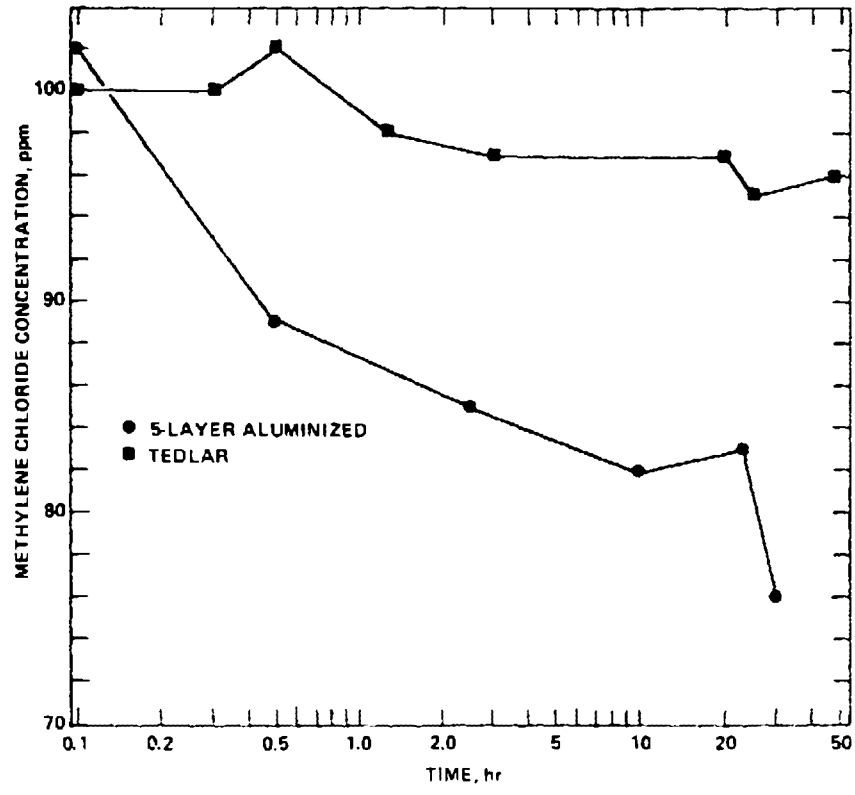

Figure 1. Integrity of Sample Bags for Methylene Chloride.

A SENSITIVE DIRECT MEASUREMENT NO_2 INSTRUMENT

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The LUMINOX LMA-3 is a highly sensitive, lightweight, portable instrument capable of continuously measuring nitrogen dioxide in air. It operates by detecting the chemiluminescence produced when NO_2 encounters a surface wetted with a specially formulated solution containing luminol. Unlike other chemiluminescent instruments it measures NO_2 directly and does not require prior conversion of NO_2 to NO. It does not respond to H_2O_2, NO, HNO_3, NH_3, CO, CO_2, SO_2 or organic nitro compounds at concentrations normally found in air. The only interferences encountered to date are from PAN and O_3 with the response to O_3 being less than 0.2% of its response to NO_2. The response time is less than 1 sec and its sensitivity is 5 parts per tillion (pptv). The chemiluminescent response is found to have a negative temperature dependence of about 2% per degree which is being compensated electronically in the instrument.

The instrument is rugged and simple to operate. It can operate continuously on line power or at least 3 hrs on an internal, rechargeable battery. The LMA-3 has been used successfully in field conditions to measure NO_2 in both polluted and relatively clean air. The measurements have compared satisfactorily with measurements made with the unequivocal Tunable Diode Laser Absorption Spectroscopic method.

INTRODUCTION

The measurement of nitrogen dioxide, NO_2 in air is of paramount importance for a number of reasons. It is a major pollutant affecting both indoor and outdoor air quality. Its presence in the atmosphere, whether from natural or human sources, initiates atmospheric chemistry. NO_2 is the only gas in the troposphere which can be photodissociated by sunlight to produce ozone. The atmospheric chemistry resulting from its dissociation leads to the oxidation of the reduced gases in the atmosphere including CO, CH_4 and NMHCs. For example, model calculations (1) have shown that the NO_2 concentration has, by far, the most pronounced effect on the ozone budget and its height profile in the atmosphere.

NO_2 contributes directly to acid deposition by being converted to HNO_3 mainly by reaction with OH radicals and by dry deposition. It also contributes indirectly by affecting the oxidant level in the atmosphere which converts S(IV) to S(VI).

Evaluation of models developed to attack the problems of photochemical oxidation and acid deposition require accurate measurements of this important species. Monitoring NO_2 at the large number of sites needed for evaluation of these models requires instrumentation which is inexpensive, sensitive, reliable and easy to operate. This paper describes an instrument which meets these requirements and also has sufficiently fast time response to be of interest for dry deposition studies. In addition, its small size and portability makes it highly suitable for indoor and outdoor air quality monitoring.

Principle of Method

The instrument operates by detecting the chemiluminescence produced when NO_2 encounters a surface wetted with a specially formulated, alkaline, luminol solution. Unlike other chemiluminescent instruments, it measures NO_2 directly and does not require prior conversion to NO. Although many oxidizers can produce luminescence with luminol most do so in the liquid phase and require the presence of catalysts such as metal ions. In contrast, chemiluminescence with NO_2 appears to be a surface reaction not requiring the presence of metal ions. Confining the reaction to a surface and using a solution made with deionized water avoids interferences from most other gases.

The method was first described by Maeda et al (2). The sampled air passed over a pool of the luminol solution which was viewed with a photomultiplier. The difficulty with this system is that the surface area is not well defined and any splashing of the solution up the sides of the reservoir results in changing sensitivity.

Stedman and coworkers (3) overcame this difficulty by flowing the solution down a filter paper wetted with the solution, thus providing a defined surface to be viewed by the photomultiplier.

We have made further modifications to produce a commercial instrument, called Luminox LMA-3 and have investigated the parameters of the instrument performance with a view of optimizing its sensitivity and freedom from interferences. These parameters include the composition of the solution,

its flow rate over the surface and the flow rate of the sampled air. We have also examined its temperature dependence.

Description of the Instrument

An operational block diagram of the instrument is shown in Figure 1. The sampled air is drawn through the instrument by a micro pump at a constant flow rate of about 1.5 standard liters per min (SLM). The response of the instrument increases only slowly with flow rate above a rate of about 1 SLM. The air passes along the 2 cm length of a cloth wick wetted with the luminol solution. The solution is continuously replenished at the top of the wick and removed at the bottom by a small, two-stage, peristaltic pump.

The flow rate of the solution down the wick is about 0.05 ml sec^{-1}. A sealed bottle containing 250 ml of the solution located in the instrument provides for 80 hrs of measurement. The used liquid is pumped into another 250 ml bottle, also located in the instrument. If longer operation is desired without replenishing the solution, provision is made for attaching larger reservoirs external to the instrument.

Turning on the power to the instrument activates both the air and the liquid pumps. The instrument operates on either 115 or 220 V AC power or for a minimum of 3 hr from an internal 12 V 1.5 amp-hr gel cell. The battery charges whenever the unit is plugged into the line current.

A photomultiplier views the wick and its signal provides a measure of the NO_2 mixing ratio. The signal is displayed on a LCD readout and the analogue signal is also presented to BNC connectors at the front and the back of the instrument for connection to either a chart recorder or to a data acquisition system. Switches permit the LCD display to read the battery voltage and the photomultiplier voltage. A potentiometer permits zeroing the signal when no NO_2 is presented to the instrument. This condition can be achieved either by scrubbing the NO_2 from the air stream, by using "zero" air or simply by turning off the air pump. The instrument can be calibrated by adding a known concentration of NO_2 to the air stream (e.g. from a permeation device). Based on this calibration the LCD readout can be made to correspond to NO_2 mixing ratios by adjusting the voltage to the photomultiplier by another potentiometer.

The instrument is compact and lightweight, having dimensions of 38 x 20 x 22 cm and a weight of 7 kgm. It has been designed to be very rugged and to prevent any leakage of the solution.

Composition of the Solution

The solution contains luminol (3-aminophthalhydrazide) NaOH, Na_2SO_3 and alcohol, dissolved in carefully deionized water. The presence of Na_2SO_3 in the solution increases its response to NO_2 while decreasing its response to O_3. The addition of one of a number of alcohols was found to enhance the response to NO_2 although we have recently discovered that it can also affect the linearity of the response over an extended range of concentrations (see below).

We have studied the effect of the concentration of each of these components, on the response of the instrument to NO_2 and to potential

interfering gases. In general, the response towards NO_2 was found to increase with concentration of each component, reach a broad maximum and then decrease. A selection was made for a formulation which appears to optimize the sensitivity towards NO_2 while minimizing its response to other gases, particularly O_3.

Interferences from Other Gases

Possible interferences were investigated when a number of gases was added to laboratory air containing a few ppb of NO_2. No signal changes above noise level were observed for additions of CO and CO_2 at concentrations up to 1000 ppm, and for SO_2, NH_3, N_2O_2 and RNO_3 at concentrations below about 100 ppb. Addition of 80 ppb of NO reduced the signal from NO_2 by about 5%.

The only positive interferences encountered were with O_3 and PAN. For the luminol solution selected the response of the instrument to O_3 was 750 times less than to the same concentration of NO_2. For measurements of low levels of NO_2 in ambient air where the O_3 concentration is more than 750 larger it may be necessary to preferentially scrub the O_3 or to make the appropriate correction to the reading.

The response of the instrument of PAN is still somewhat uncertain. Stedman and his coworkers find similar responses to PAN which may be dependent on the nature and concentration of the alcohol content of the solution. The agreement with the NO_2 measurements made with the instrument and with the unequivocal tunable diode laser absorption spectroscopic (TDLAS) method (4) under polluted conditions where the PAN concentrations were expected to be high support the lower response to PAN. However, we intend to do more definite work on this question.

Sensitivity and Response Time

The noise level of the signal, largely due to photomultiplier noise corresponds to less than 5 pptv. This does not mean, however, that the detection limit of the instrument is 5 pptv since we have not demonstrated that there are no interferences from other gases which can contribute to signal corresponding to this amount of NO_2. The zero signal was found to remain within this degree of variance for periods of at least one hour.

The response time of the instrument is demonstrated in Figure 2 when 22 ppbv of NO_2 is suddenly added or removed from the ambient air. The response time is less than 1 sec for a 20% change in mixing ratio and less than 10 sec for a 99% change in NO_2 mixing ratio.

Linearity of the Instrument Response

Earlier work indicated that the signal was proportional to the NO_2 mixing ratio over the concentration range 6 to 100 ppbv. However, simultaneous NO_2 measurements made with the instrument and with the TDLAS system during a field mission in the summer of 1985 suggested that this linearity may not extend to concentrations below 6 ppbv. Figure 3 shows the effect. Subsequent laboratory measurements at low concentrations confirmed this behavior (Figure 4).

These observations led us to reinvestigate the effect of the composition of the luminol solution. This work revealed that changing the choice and the concentration of the alcohol removed most of this non-linearity. Figure 5 shows that the solution currently being used produces a nearly linear response at low NO_2 concentrations.

Temperature Dependence

The dependence of the NO_2 response of the instrument to temperature was studied over the range 5 to 45°C. The instrument was place in an environmental chamber and allowed to equilibrate with the chamber temperature for several hrs. At each temperature the response of the instrument was measured at a number of NO_2 mixing ratios. Figure 6 shows the results obtained from one such experiment.

The instrument shows a linear decrease with temperature in its response to NO_2 amounting to about 2% per deg. An electronic circuit is now being designed to compensate for this temperature dependence. Each commercial instrument will be compensated individually to allow for any small variations from one instrument to another.

MEASUREMENT RESULTS

The instrument has been used to measure NO_2 in urban and rural air and in smog chamber experiments. On a number of occasions intercomparisons were made of simultaneous measurements made with the instrument and the unequivocal TDLAS system. Two examples of such comparison, one made in Metropolitan Toronto, Ontario and the other in rural Ontario are shown in Figures 7 and 8. They show that the Luminox instrument is capable of following the diurnal variations of NO_2 with good integrity. The agreement is general within 10%. There is some suggestion in Figure 8 of the non-linear response of the Luminox instrument at low concentrations, resulting from the use of the earlier formulation of the solution. The agreement between the two methods at higher concentrations suggest little interference from PAN which may, of course, be due either to the lower response of the instrument to PAN or to PAN being present in mixing ratios ten times less than NO_2.

Figure 9 shows one hour average intercomparisons between the two methods made at Claremont, California for a one week period in September 1985. Again the Luminox instrument appears to track the NO_2 variations faithfully. It is, however, interesting to note that just before midnight on September 12th and 13th, very high readings were obtained by both methods, but with the Luminox values being about 35% higher than those from the TDLAS system. Since this discrepancy does not appear for other periods of high NO_2 mixing ratios it is possible that the Luminox instrument might have responded to some other species, which may have been abnormally high during these two nights.

CONCLUSIONS

Chemiluminescence with luminol provides a direct method for measuring NO_2 in ambient air with no necessity to convert the gas to NO as in other chemiluminescent methods. The commercial Luminox LMA-3, based on this method, is light-weight, rugged and portable and is very simple to operate.

It has a sensitivity of better than 5 pptv and a response time less than 1 sec. A formulation for the solution has been found which minimizes interferences from other gases, optimizes the sensitivity and provides near-linear response to NO_2 over a considerable range.

No interferences were found from H_2O_2, NO, HNO_3, NH_3, CO, CO_2, SO_2 or organic nitro compounds at concentrations normally found in air. Interferences with O_3 have been reduced to less than 0.2% of the equivalent concentration of NO_2 by suitable composition of the solution. The interference from PAN is still under investigation.

The instrument response was found to have a negative temperature dependence of about 2% per deg and a circuit is being designed to compensate for this effect electronically.

The instrument appears to be well suited for indoor and outdoor monitoring of NO_2 in ambient air. Its size, weight and price makes it attractive for network monitoring of this species.

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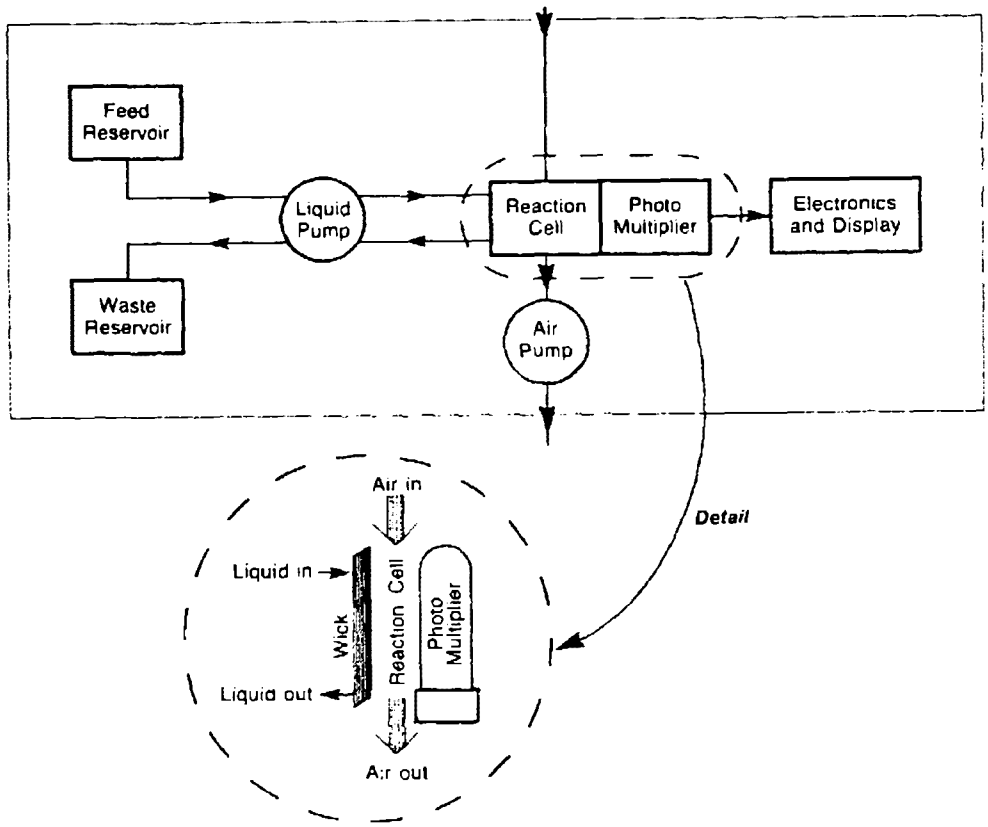

Figure 1 Block diagram of the instrument.

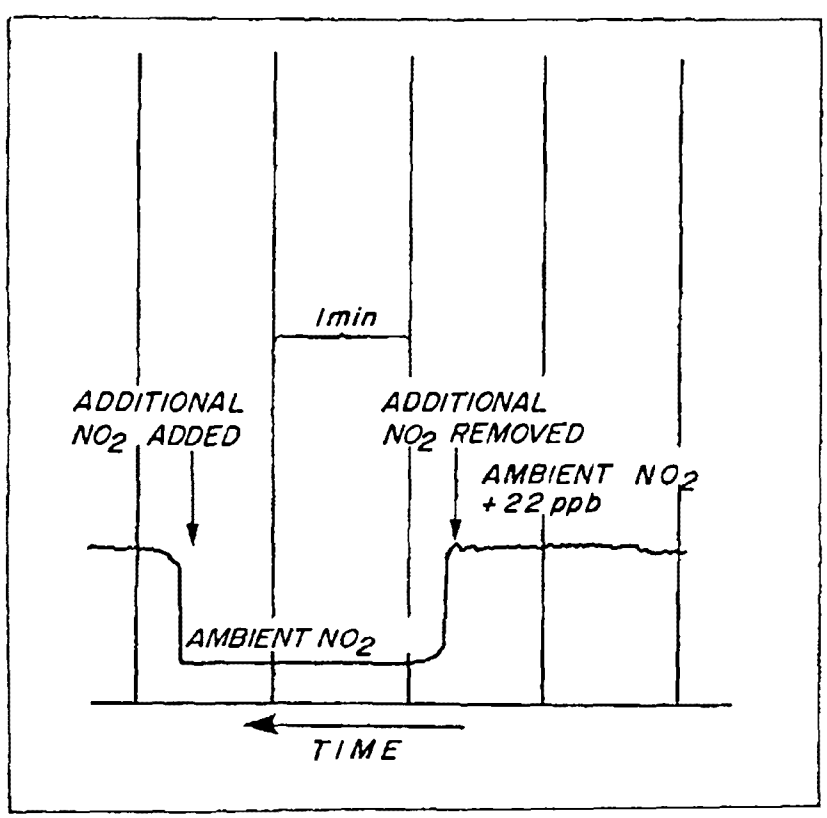

Figure 2 Response of the instrument as a function of time.

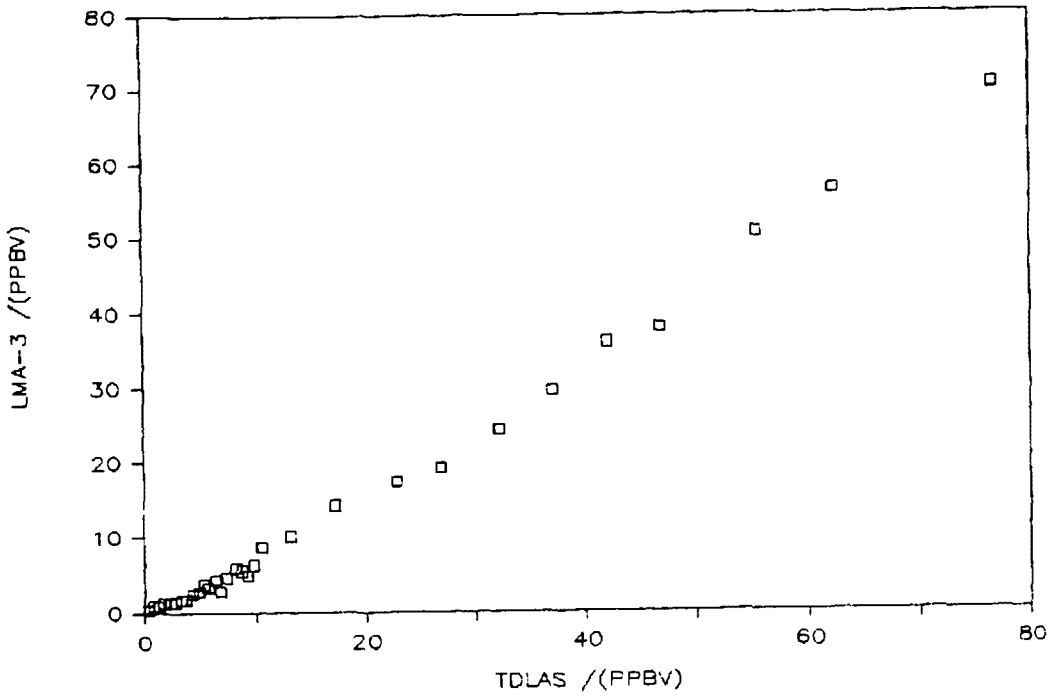

Figure 3 Correlation between NO_2 measurements made with the Luminox instrument and the TDLAS system. Each point represents means of all data acquired simultaneously during the period June 21-29, 1985 at Cold Creek, Ontario. The averages were taken: over 0.5 ppb intervals from 1 to 10 ppb; 5 ppb intervals between 10 and 50 ppb and 10 ppb intervals above 50 ppb.

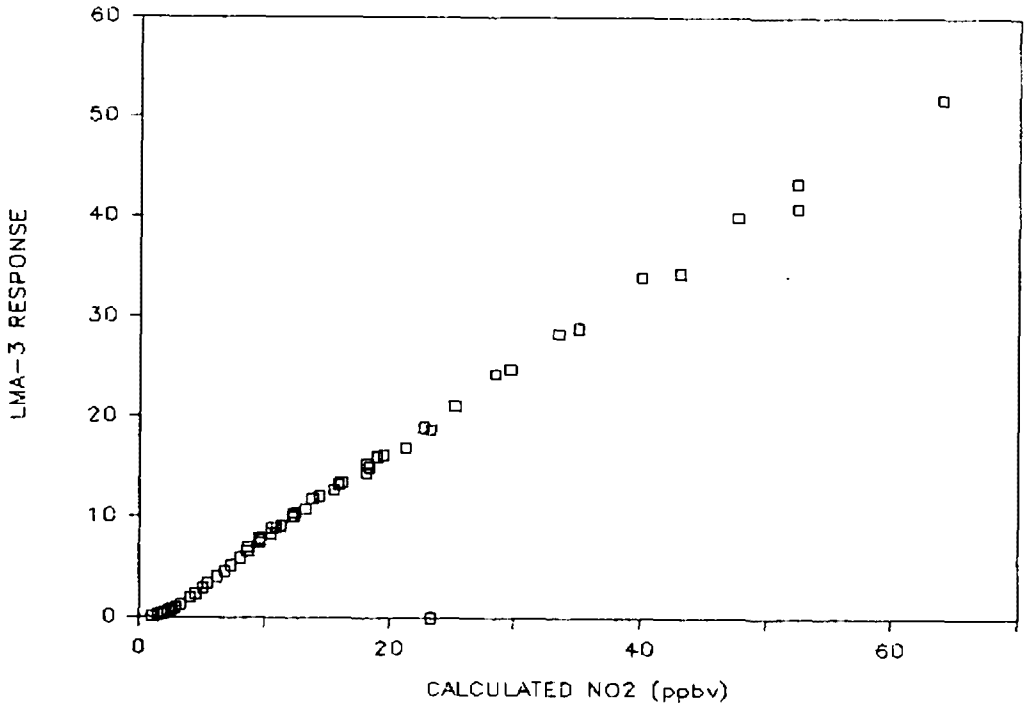

Figure 4 Laboratory test of response of the instrument as a function of NO_2 mixing ratio based on a permeation tube and a dynamic double dilution system. Measurements made with original solution formulation.

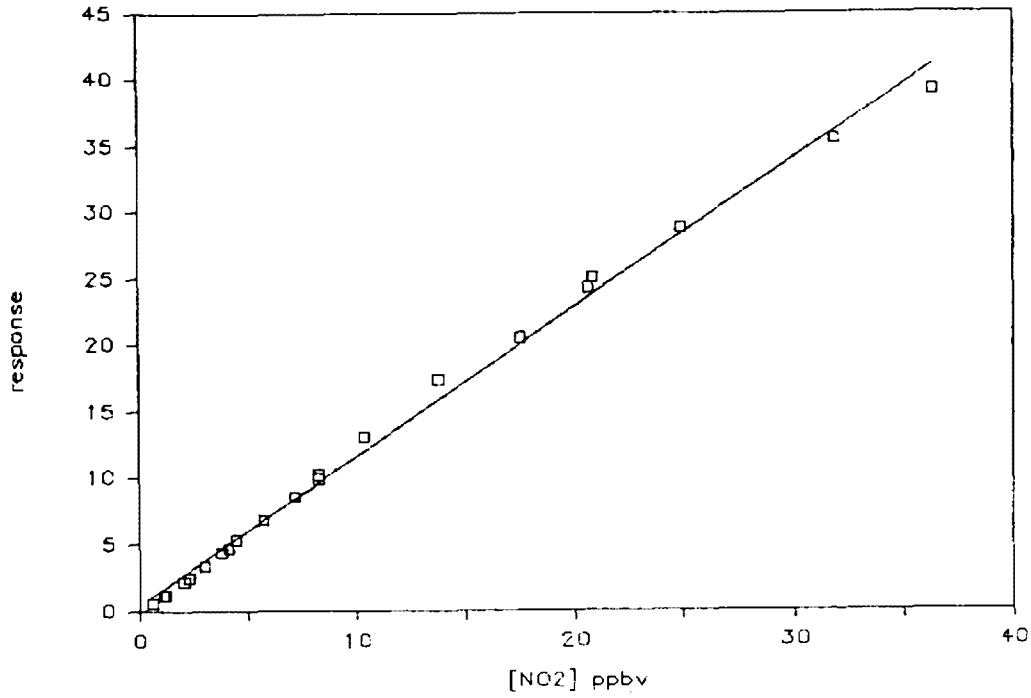

Figure 5 Similar to Figure 4 but using new solution formulation.

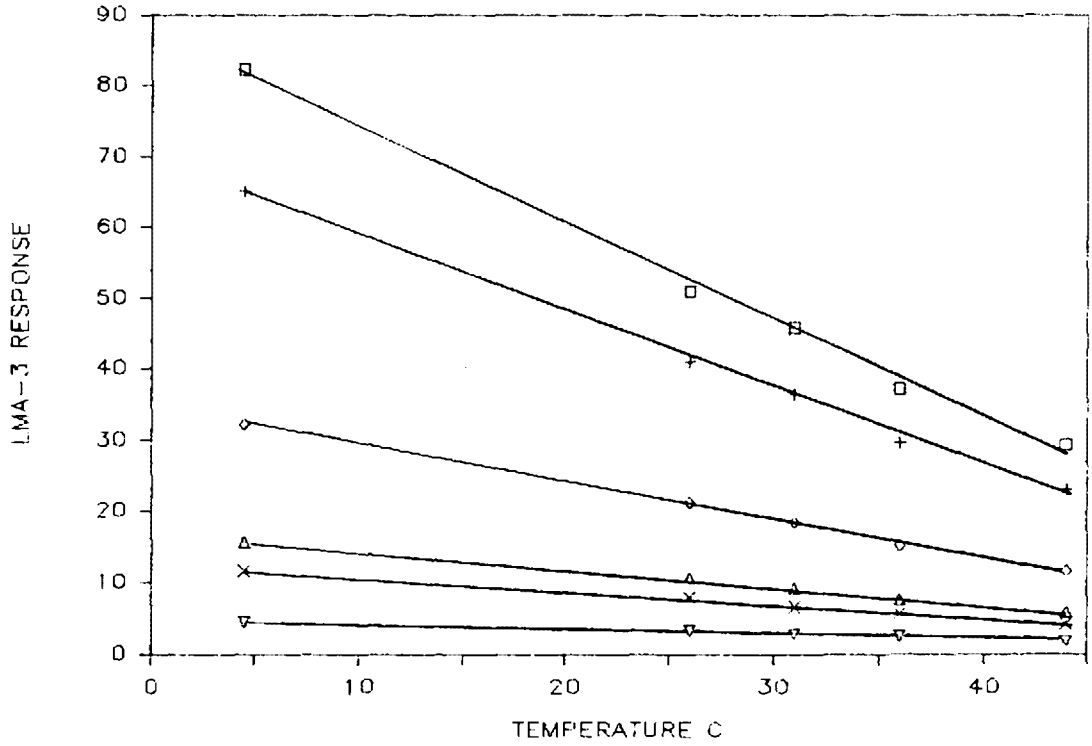

Figure 6 Response of the instrument as a function of temperature for a number of different NO_2 mixing ratios.
(□) 52.8 ppb (+) 41.0 ppb (◇) 20.1 ppb
(△) 10.1 ppb (x) 8.0 ppb (▽) 3.9 ppb

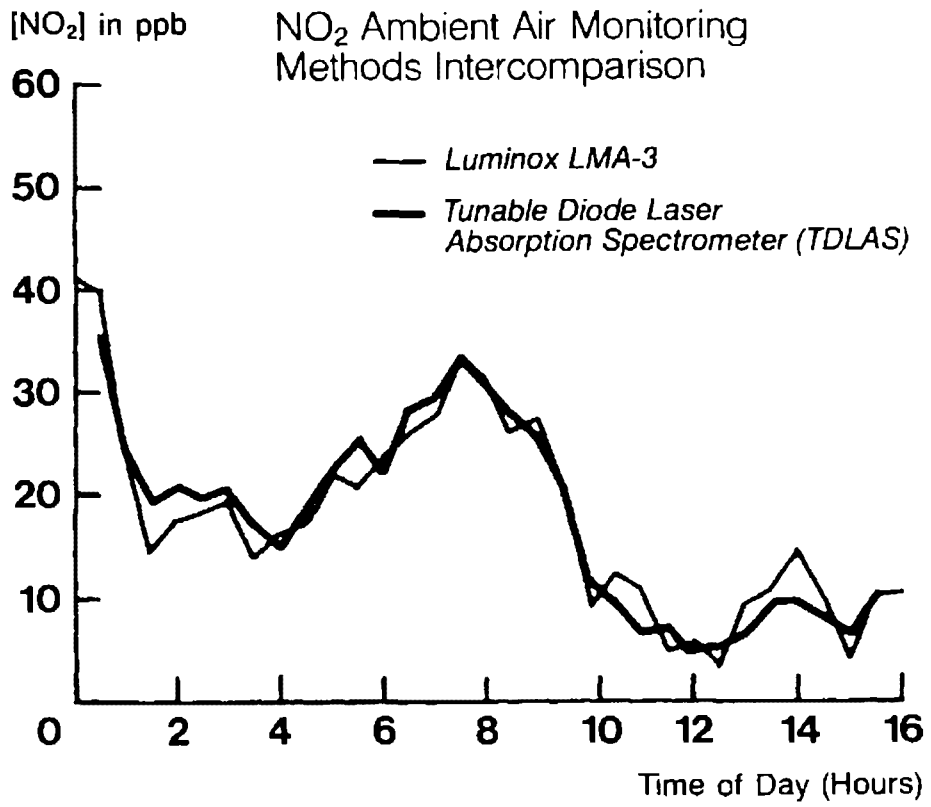

Figure 7 Comparison between 30 min average measurements made by the Luminox instrument (light line) and the TDLAS system (dark line) made in Metropolitan Toronto, June 1984.

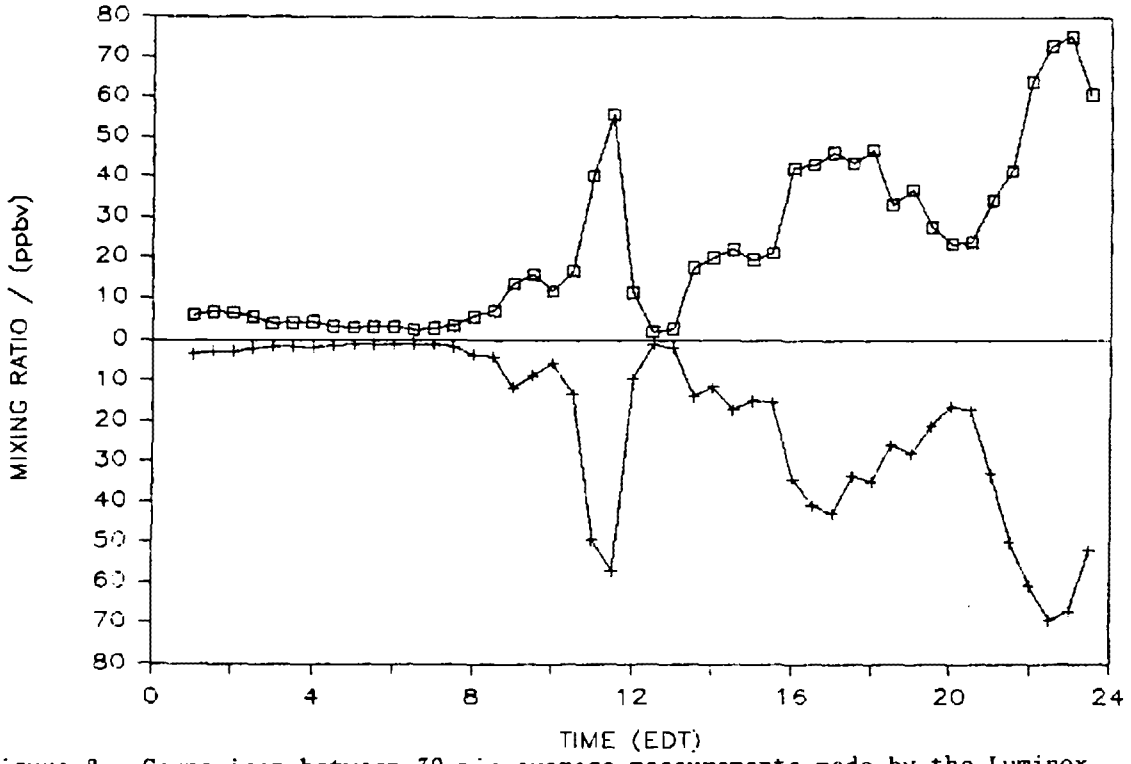

Figure 8 Comparison between 30 min average measurements made by the Luminox instrument (+) and the TDLAS system (□) at Cold Creek Ontario, June 21, 1985.

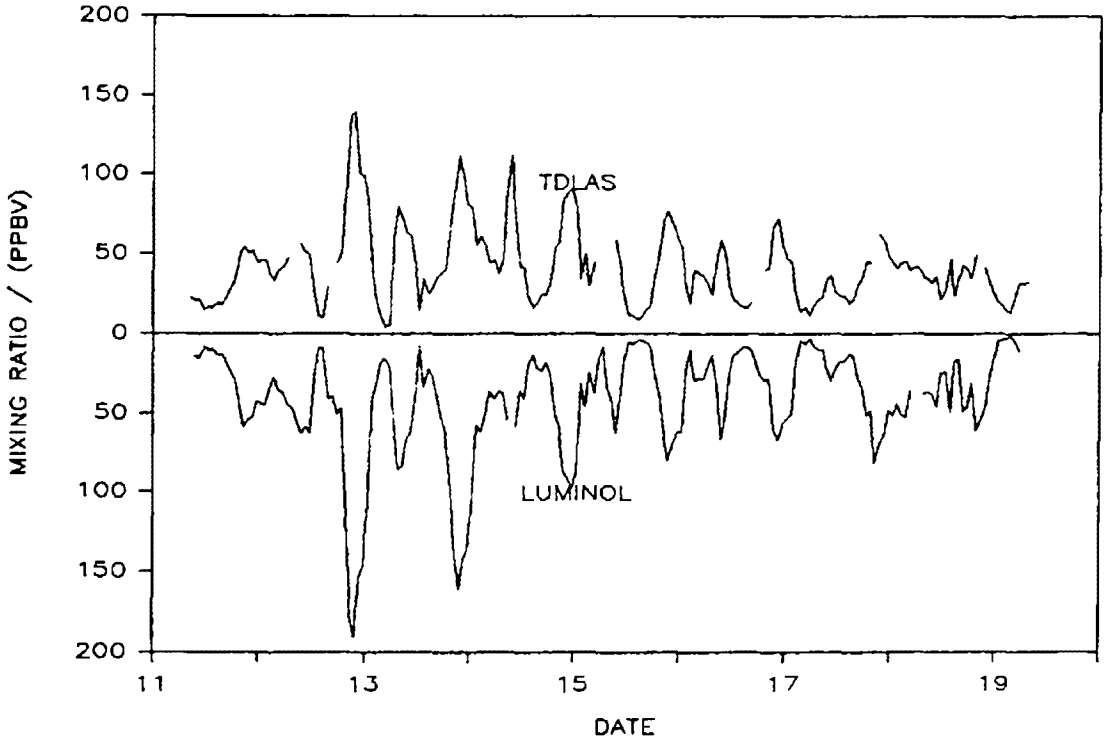

Figure 9 Comparison between 1 hr averages made simultaneously by the Luminox instrument and the TDLAS system at Claremont, CA during September 1985.

DIRECT AMBIENT NITROGEN DIOXIDE MEASUREMENT BY VISIBLE LIGHT ABSORPTION

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A prototype photometric nitrogen dioxide (NO_2) analyzer, constructed by modifying a commercial photometric ozone analyzer, is being evaluated for atmospheric NO_2 measurement. The analyzer operates on the principle of visible light absorption by the NO_2. The zero drift for 5 days and noise for one hour are less than 3 parts per billion (ppb). Interferences from ammonia, nitric oxide (NO), ozone (O_3), peroxyacetyl nitrate (PAN), and sulfur dioxide are negligible. The responses of the photometric analyzer and a commercial chemiluminescent oxides of nitrogen analyzer were compared by devising a smog chamber experiment duplicating the NO_2 reaction in the atmosphere. During the experiment, the response of the photometric analyzer exhibited a rapid decrease of the NO_2 concentration after the NO_2 formation peaked, while the response of the chemiluminescent analyzer exhibited a more gradual decrease probably caused by the positive interference of nitrates such as PAN. The photometric analyzer is also being field tested at the South Coast Air Quality Management District's air monitoring station in Pomona. During August, 1985, the daily NO_2 averages of the photometric analyzer varied from 33 ppb to 78 ppb, while the averages of a parallel chemiluminescent analyzer varied from 32 ppb to 97 ppb. Generally, the daily average of the photometric analyzer is equal to or lower than that of the chemiluminescent analyzer. The maximum difference of 25 ppb occurred on August 24, when the photometric analyzer read 65 ppb while the chemiluminescent analyzer read 90 ppb.

INTRODUCTION

Air quality standards have been established for NO_2 by the Environmental Protection Agency (EPA) because health problems can occur from breathing low concentrations of NO_2 in ambient air. The present national air quality standard for NO_2 is 100 $\mu g/m^3$ (53.2 ppb) averaged over one year. The present California NO_2 standard is 470 $\mu g/m^3$ (250 ppb) averaged over one hour. NO_2 also plays an important role in visibility, photochemical smog production, and acid deposition chemistry.

Chemiluminescence is the most common technique of measuring ambient levels of NO_2. However, this technique measures NO_2 indirectly in terms of NO. The NO_2 is reduced by a converter to NO which reacts with excess O_3 to give gas phase chemiluminescence. In the conversion of NO_2-to-NO, other nitrogenous compounds such as PAN also produce NO causing a positive response in the chemiluminescent NO_2 analyzer. This has been documented by Winer (1).

To overcome the interference problem and to determine atmospheric NO_2 concentrations directly and continuously, a prototype photometric NO_2 analyzer was developed using a differential spectral absorption technique. This absorption occurs during the conversion of radiant energy into other forms, such as dissociation, fluorescence, and radiationless transitions, while the radiant energy is passing through or being reflected from the material. Hall and Blacet[2] have plotted the NO_2 absorption spectrum in the range of 240-500 nanometers (nm).

DESCRIPTION

The prototype photometric NO_2 analyzer is a modified Dasibi Model 1008-AH photometric ozone analyzer with a microcomputer. To modify the O_3 analyzer to measure NO_2, the lamp source, optical filter, mirrors, detector, and absorption cell pathlength had to be changed, because the NO_2 analyzer operates at a different portion of the spectrum than the O_3 analyzer: their absorption coefficients differ. The detector area of the modified analyzer had to be made lightproof to prevent the detector from being exposed to stray visible light that would interfere with the NO_2 measurement.

Figure 1 shows a diagram of the pneumatic, optical, and electronic subsystems. The sample, regulated by a valved flowmeter and drawn in by a vaccum pump, flows into the absorption cell where the NO_2 is measured before the sample is vented.

Light passing through the absorption cell is attenuated in proportion to the concentration of the NO_2 moleucles in the sample according to Beer's law. The light is detected, and the resultant signal is digitally processed for presentation by the readout system.

The absorption cell of the NO_2 analyzer consists of a pair of Kynar-coated aluminum tubes (1 cm diameter), a 400 nm long wave pass filter (Schott GG-400), a quartz window, and two front-surfaced mirrors mounted in the triangular block. Initially, the 71 cm pathlength cell was used for the linearity and interference tests. Presently, a 1.12 meter cell which increases the sensitivity is being used for the field testing in Pomona. The light source is a 406 nm lamp (BHK Model 80-1025-01/406) with a 35 nm bandwidth. This is a low pressure mercury lamp whose interior glass envelope is phosphor-coated. This phosphor absorbs and converts the short wave ultraviolet light (254 nm) produced by the excited mercury vapor to

visible light which peaks at 406 nm. The 400 nm filter is used to reject the ultraviolet light below 400 nm which may produce NO_2 dissociation. The detector is a head-on vacuum type phototube (Hamamatsu R645) which measures the amount of light passing through the absorption cell.

The ambient air sample entering the inlet passes through a 0.5 micron porosity Teflon inlet filter which remove large particulates. The sample flow is either 2 liters per minute with the 71 cm cell or 3 liters per minute with the 1.12 m cell. A three-way solenoid valve directs sample to the NO_2 scrubber (Dasibi ozone scrubber) which removes NO_2 from the sample. After the cell is flushed for 4 seconds, the detector measures in terms of current the amount of visible light passing through the cell. The current is converted by the digital electrometer to a pulse rate (frequency) directly proportional to the light intensity. The pulse from the electrometer is totalized by the six-digit counter for 1.5 seconds. The data from the counter is entered in the microcomputer as the reference measurement.

After the reference measurement, the solenoid valve directs an unscrubbed air sample containing the NO_2 through the absorption cell for the sample measurement.

The microcomputer is programmed to use Beer's absorption law, corrected for temperature and pressure, to calculate the NO_2 concentration. The absorption coefficient value which is required for the calculation is entered on the 3-digit thumbwheel switch. Since the microcomputer software is programmed for a 71 cm pathlength, the absorption coefficient of NO_2 is entered on the thumbwheel switch. When the 1.12 m pathlength is used, the thumbwheel switch has to be readjusted to account for the longer pathlength. The actual value is empirically derived by gas phase titration (GPT). GPT produces a known concentration of NO_2 by mixing O_3 and excess NO. The values derived for the 71 cm and 1.12 m pathlengths are 138 and 240, respectively.

The microcomputer calculates the NO_2 concentration, sending the results to the digital display. The analyzer's digital-to-analog converter reads the three least significant digits of the six digits calculation and produces an analog output signal for the continuous recorder.

The air sample pump is placed outside of the analyzer to minimize any noise created by the electromagnetic interference (EMI).

LINEARITY AND INTERFERENCE TESTS

The response of the photometric NO_2 analyzer with a 71 cm absorption cell was compared against the response of the chemiluminescent NO_2 analyzer in a linearity test. The chemiluminescent analyzer used in this test was a Monitor Labs Model 8440 Oxides of Nitrogen Analyzer (ML).

The ML was calibrated according to the EPA procedure (40 CFR 50.1, Appendix F, July 1, 1977) using GPT. After the ML calibration, the photometric NO_2 analyzer was spanned with a high concentration of NO_2 using GPT and checked against the calibrated ML. A multipoint calibration using GPT was performed. Figure 2 shows the linearity of the photometric analyzer: the zero offset of the photometric analyzer is probably caused by the EMI from the solenoid valve and vacuum pump.

The interference tests for ammonia, NO, and sulfur dioxide were performed in the 1100 cu. ft. reaction chamber of the California Air Resources Board. This chamber is made of square glass panes (2 ft. x 2 ft.) which have aluminum supports. Ultraviolet lamps mounted within the chamber are used to simulate the solar radiation. The chamber is flushed with the treated ambient air from an air purification system, which removes non-methane hydrocarbons, O_3, and NO_2, but not NO and methane. With treated air inside chamber and the ultraviolet lights off, a measured volume of gaseous ammonia, NO, and sulfur dioxide was injected into the chamber using nitrogen as carrier. Knowing the chamber and the injected gas volumes, the concentration was calculated in ppb.

For the O_3 interference test, a Monitor Lab Audit Calibrator with an internal O_3 generator was used to produce various concentrations of O_3. The photometric NO_2 analyzer and a Dasibi Model 1003-AH O_3 Analyzer were connected to the calibrator. The O_3 analyzer was used to verify the O_3 concentration.

For the PAN interference tests, a synthetic mixture of PAN was produced in a 20 liter Tedlar bag. The contents of the bag were verified by gas chromatography, before the bag was connected to the photometric analyzer to check for PAN interference.

The interference test results (Table I) indicate that at the test concentrations the photometric analyzer does not respond to ammonia, NO, O_3, sulfur dioxide, or PAN. The maximum concentrations used in tests of ammonia, NO, O_3, and sulfur dioxide were 1000 ppb, and the maximum concentration of PAN was 250 ppb.

After these tests, a photochemical smog experiment was performed using the reaction chamber to compare the NO_2 responses of the photometric and chemiluminescent analyzers. In addition to the two NO_2 analyzers, other analyzers used in this experiment to monitor the photochemical activity were a Dasibi Model 1003-AH O_3 Analyzer and a Byron Model 401 Hydrocarbon Analyzer. At the start of the photochemical experiment with treated air in the chamber, propylene and NO were injected in the chamber using nitrogen as the carrier. The propylene was measured as non-methane hydrocarbon (NMHC) in parts per million carbon (ppmC). The initial values of NMHC and NO were 5 ppmC and 0.5 parts per million (ppm), respectively. Figure 3 exhibits the concentrations of the pollutants with time after the lamps were activated. The responses of the photometric NO_2 analyzer and ML coincided until the NO_2 formation peaked. After the peak was reached, the response of the photometric analyzer exhibited a rapid decrease in the NO_2 concentration while the response of the chemiluminescent analyzer exhibited a more gradual decrease probably caused by the positive interferences of nitrates such as PAN.

AMBIENT NITROGEN DIOXIDE MEASUREMENT AT POMONA AIR MONITORING STATION

After these tests, the photometric NO_2 analyzer with the 1.12 m path-length was installed at the South Coast Air Quality Management District's (SCAQMD) air monitoring station at Pomona to obtain ambient data. The air monitoring station has a chemiluminescent NO-NO_2 analyzer, Thermo Electron Model 14B/E Oxides of Nitrogen Analyzer (TECO). The SCAQMD calibrated the photometric NO_2 analyzer and the TECO using GPT.

Table II lists the calibrations performed on 5 consecutive days during the week of July 22, 1985. The SCAQMD calibrator at the Pomona station was used to test for zero drift and response of the photometric analyzer. The zero drift fluctuated ± 2 ppb.

To determine the photometric NO_2 analyzer background noise, the analyzer was configured to sample NO_2-free (zero) air. Twenty-five measurements were taken at 2 minute intervals. Noise was determined as the standard deviation about the mean of the zero air measurements. The calculated noise was less than 3 ppb.

Tables III and IV summarize the NO_2 measurements of the chemiluminescent and photometric analyzers, respectively, for August 1985. The concentrations are in parts per hundred million (pphm) averaged over one hour, rounded-off to the nearest pphm (one pphm = 10 ppb). The daily NO_2 average is averaged over a 24 hour period, from midnight to midnight of the following day. Figure 4 shows the differences between the chemiluminescent and the photometric measurements. During the first half of August, the photochemical activity was low, and the daily averages of the two were within $\pm$0.7 pphm. During the latter half of August, the photochemical activity was high, and the photometric NO_2 daily averages had the lower readings. The maximum difference of 25 ppb occurred on the 25th, when the photometric analyzer read 65 ppb while the chemiluminescent analyzer read 90 ppb.

CONCLUSION

A prototype photometric NO_2 analyzer has been constructed and is being tested. The NO_2 analyzer is a modified photometric O_3 analyzer with a different optical system. The response of the NO_2 analyzer is linear, and the noise and zero drift are less than 3 ppb. Interferences from ammonia, NO, O_3, sulfur dioxide, and PAN are negligible. The photometric NO_2 analyzer is performing satisfactorily in the monitoring of NO_2 at Pomona.

More tests are needed to assess its freedom from interferences and long-term stability.

ACKNOWLEDGMENT

The authors wish to acknowledge the technical assistance of Dasibi Corp., the assistance of Battelle with the PAN interference tests, and the cooperation of SCAQMD in using the instruments at the Pomona air monitoring station.

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DISCLAIMER

This report has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the ARB, nor does mention of trade names or commercial products consitute endorsement or recommendation for use.

TABLE I. Response of the Photometric Nitrogen Dioxide Analyzer to Various Gases

Compound	Range of Concentration, ppb	No. of Experiments	Response, ppb
Ammonia	1000	2	<3
Nitric Oxide	100-1000	10	<3
Ozone	100-1000	10	<3
PAN	50-250	5	<3
Sulfur Dioxide	100-1000	5	<3

TABLE II. Daily Calibrations

Day in July, 1985	Zero Level, ppb	NO_2 Response ppb
22	10 ± 2	376 ± 2
23	10 ± 2	374 ± 2
24	10 ± 2	373 ± 2
25	10 ± 2	373 ± 2
26	8 ± 1	370 ± 2

TABLE III. HOURLY AND DAILY SUMMARY REPORT

Pollutant Observed: Nitrogen Dioxide

Method of Analysis: Chemiluminescence

Sampling Interval : 1 Hour

Reporting Units : part per hundred million

Month: August

Year:1985

DAY	CLOCK TIME (Standard Time) 00	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	DAILY AVERAGE
01	5	5	5	5	5	5	6	9	9	7	6	5	4	4	4	4	4	4	5	6	6	5	5	5	5.33
02	5	5	6	5	5	5	6	9	10	9	8	6	6	5	6	5	5	6	7	7	7	7	6	5	6.29
03	5	6	6	6	6	6	7	10	9	10	9	6	5	4	4	5	5	5	7	6	7	7	8	7	6.50
04	7	7	7	6	6	6	8	8	8	8	7	6	5	4	4	4	4	4	5	7	7	7	7	6	6.17
05	6	5	4	4	4	5	7	9	11	12	10	N/A	6	6	5	7	8	6	8	10	9	9	8	8	N/A
06	8	8	8	8	8	8	11	14	16	11	13	8	6	6	6	6	7	8	9	8	7	6	5	6	8.38
07	5	4	4	4	4	6	9	12	11	7	7	6	6	5	5	5	4	4	4	5	5	4	4	4	5.58
08	4	4	4	3	4	5	5	6	8	8	7	6	5	5	4	5	4	4	5	5	5	5	4	4	4.96
09	4	4	4	5	5	5	5	6	7	8	7	6	5	5	5	5	4	5	5	5	5	5	5	4	5.17
10	4	4	4	4	4	4	4	4	5	4	4	4	4	3	3	3	5	5	4	4	4	4	4	4	4.00
11	3	4	4	4	3	2	2	2	3	3	3	2	2	2	3	3	3	3	4	4	4	4	5	5	3.21
12	4	3	3	3	3	4	4	4	4	4	4	5	5	4	4	4	4	5	5	5	5	4	4	4	4.08
13	4	4	4	3	4	4	4	5	4	5	6	5	5	6	6	5	5	5	6	5	5	5	4	5	4.75
14	4	4	4	4	4	4	6	6	6	6	6	5	5	5	6	5	5	6	6	7	7	6	5	4	5.25
15	6	6	5	5	5	5	8	11	9	9	9	6	6	6	5	5	5	5	6	6	6	6	6	6	6.33
16	6	6	5	5	5	5	5	5	5	5	5	5	4	4	4	4	4	4	5	6	5	5	5	5	4.88
17	5	4	5	5	4	4	4	4	4	4	4	5	4	4	4	4	4	4	4	5	5	4	4	4	4.25
18	4	4	4	4	4	4	3	3	4	3	4	4	4	4	4	4	5	4	5	5	6	6	5	5	4.25
19	5	5	5	5	5	6	7	8	7	6	7	5	6	5	5	5	5	5	7	7	7	7	6	6	5.92
20	6	6	6	6	6	6	8	10	12	10	7	4	5	4	4	4	5	6	6	6	6	6	5	5	6.21
21	5	5	5	5	5	5	5	7	9	9	7	6	6	6	6	6	7	8	9	10	11	12	8	9	7.13
22	10	9	9	8	7	8	10	13	13	11	5	6	9	10	7	6	7	7	8	9	8	8	10	10	8.67
23	10	9	9	8	8	8	10	13	16	11	7	9	10	11	9	7	6	6	10	11	11	11	11	11	9.67
24	11	11	11	10	8	9	11	15	16	12	6	9	8	6	6	5	4	4	5	7	10	10	11	11	9.00
25	10	9	7	7	7	7	8	7	9	7	4	4	4	4	4	4	3	5	10	10	9	11	11	11	7.17
26	10	9	8	9	7	6	7	6	7	6	5	3	3	3	3	3	3	3	3	4	5	5	5	5	5.33
27	5	4	4	5	5	5	6	9	8	6	5	4	4	4	4	3	4	6	8	9	8	9	9	9	5.96
28	9	8	8	7	8	9	10	13	12	12	8	7	6	6	7	5	5	6	9	10	9	10	9	9	8.42
29	10	10	8	8	8	8	11	16	16	11	7	7	6	6	6	5	5	5	5	8	10	10	10	10	8.58
30	9	9	9	9	8	8	10	17	16	11	8	7	6	6	7	6	5	6	8	10	10	12	12	12	9.21
31	12	11	9	7	8	8	9	10	11	7	4	5	4	3	3	3	3	3	4	6	6	6	7	7	6.50

TABLE IV. HOURLY AND DAILY SUMMARY REPORT

Pollutant Observed: Nitrogen Dioxide

Method of Analysis: Light Absorption

Sampling Interval : 1 Hour

Reporting Units : part per hundred million

Month: August

Year: 1985

DAY	CLOCK TIME (Standard Time) 00	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	DAILY AVERAGE
01	5	5	5	5	5	5	6	9	9	7	6	5	4	4	4	4	4	4	5	6	6	6	5	5	5.38
02	5	5	6	5	5	5	6	9	10	9	8	6	6	5	6	5	5	6	7	7	7	7	6	5	6.29
03	5	6	6	6	6	6	6	9	9	9	8	6	4	3	3	3	3	4	6	6	7	7	8	7	5.96
04	7	7	6	6	5	5	7	8	7	7	6	5	3	3	3	3	3	4	5	7	7	7	8	7	5.67
05	6	5	4	4	4	5	6	8	10	11	9	N/A	6	5	5	6	7	6	8	10	9	9	8	8	N/A
06	7	7	7	8	8	7	10	13	15	10	12	7	5	5	5	5	6	7	8	8	7	6	5	6	7.67
07	5	5	5	5	4	5	6	8	12	10	7	6	5	5	5	5	4	4	4	5	5	5	4	4	5.54
08	4	4	4	3	4	5	5	6	7	8	7	6	5	5	4	5	4	4	5	5	5	5	4	4	4.92
09	4	4	4	5	5	5	5	6	7	8	8	6	5	5	5	5	4	5	5	6	5	6	5	5	5.33
10	5	5	4	5	5	5	5	5	5	5	5	4	4	3	3	3	3	3	4	4	5	5	5	4	4.33
11	4	4	4	4	3	3	2	2	3	3	3	2	2	2	3	3	3	3	4	4	4	4	5	5	3.29
12	4	3	3	3	3	4	4	4	4	4	4	5	4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
13	N/A	N/A	N/A	N/A	N/A	N/A	N/A	5	4	5	6	4	4	5	5	4	5	5	6	5	5	5	4	4	N/A
14	4	4	4	4	4	4	6	6	6	6	6	5	4	4	5	5	5	6	6	7	7	6	5	4	5.13
15	5	5	5	4	4	4	7	10	9	9	9	6	6	5	4	4	4	5	5	N/A	N/A	N/A	N/A	N/A	N/A
16	N/A	N/A	N/A	N/A	N/A	N/A	N/A	4	4	5	5	5	4	4	3	4	4	4	5	6	5	5	4	4	N/A
17	4	4	4	4	4	4	4	4	4	4	4	5	3	4	4	3	3	3	4	4	5	4	4	4	3.92
18	3	3	4	3	3	3	3	3	4	3	3	3	3	3	3	3	4	4	5	5	6	6	4	4	3.67
19	4	4	4	4	4	5	6	8	7	6	6	5	6	4	4	4	4	5	6	7	7	6	6	6	5.33
20	6	6	5	5	5	5	7	9	11	9	7	4	4	3	3	3	4	5	6	5	5	4	4	4	5.38
21	4	4	4	4	4	4	4	6	8	9	6	6	5	5	5	5	5	6	8	9	9	10	7	8	6.04
22	8	7	7	6	5	5	7	11	11	9	5	5	7	8	5	5	7	6	7	8	8	7	8	7	7.04
23	7	7	7	6	6	6	8	11	13	10	6	8	7	8	7	6	5	6	9	9	9	8	9	8	7.75
24	7	8	7	7	6	6	8	11	12	9	4	6	6	3	2	2	3	3	5	6	9	9	8	8	6.46
25	7	6	5	5	5	5	6	6	6	5	3	3	3	3	3	3	3	4	9	8	7	9	9	9	5.50
26	8	7	6	7	5	4	5	5	6	4	4	2	3	3	3	3	3	3	3	5	5	5	4	4	4.46
27	4	3	3	4	4	4	5	7	7	5	4	3	3	3	3	3	4	6	7	8	8	8	7	7	5.00
28	7	7	6	6	6	7	8	10	9	10	6	6	4	4	4	4	4	6	8	9	8	8	7	7	6.71
29	7	7	7	6	7	6	8	13	13	8	5	6	4	4	4	4	4	5	5	7	8	9	7	7	6.71
30	7	7	6	7	7	6	7	14	12	9	5	5	4	3	5	4	5	5	7	8	8	10	9	9	7.04
31	6	8	6	5	6	6	7	8	8	6	3	4	3	2	2	2	3	3	4	6	5	5	5	5	5.00

FIGURE 1: BLOCK DIAGRAM

ELECTRONIC, OPITCAL, AND PNEUMATIC SUBSYSTEMS

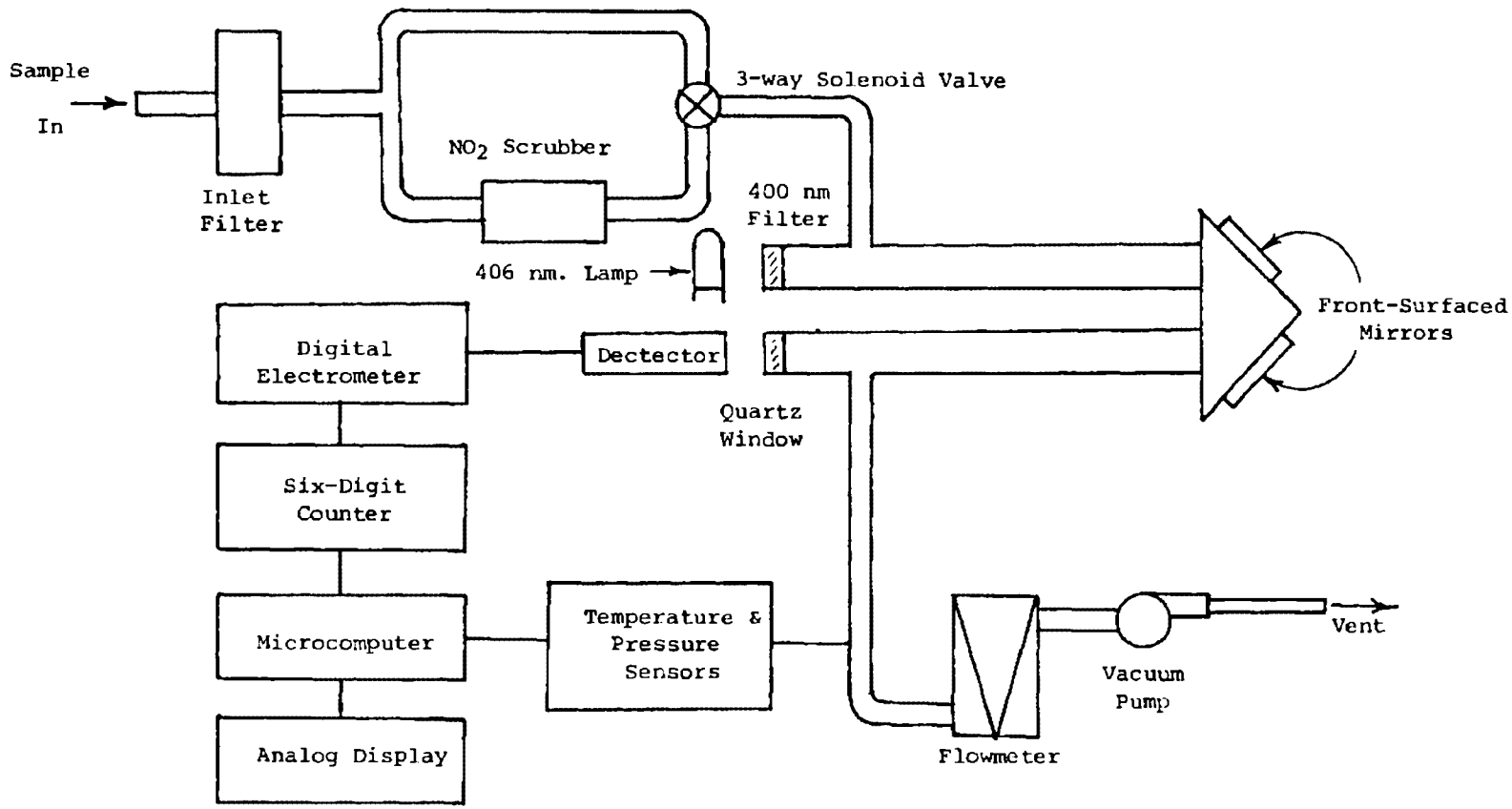


FIGURE 2
LINEARITY TEST

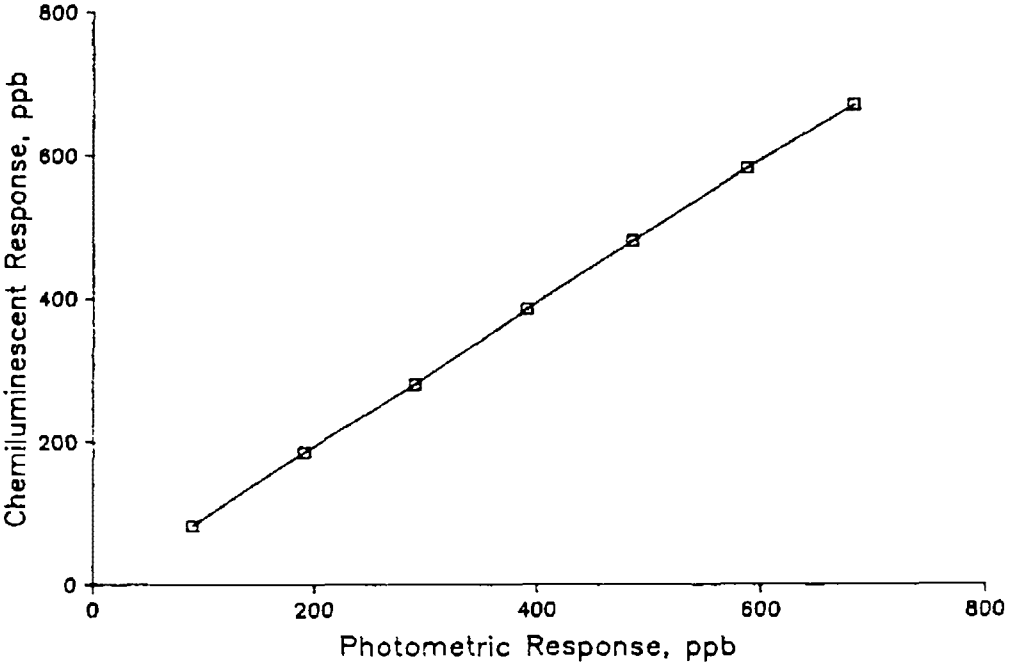


FIGURE 3
PHOTOCHEMICAL SMOG CHAMBER STUDY

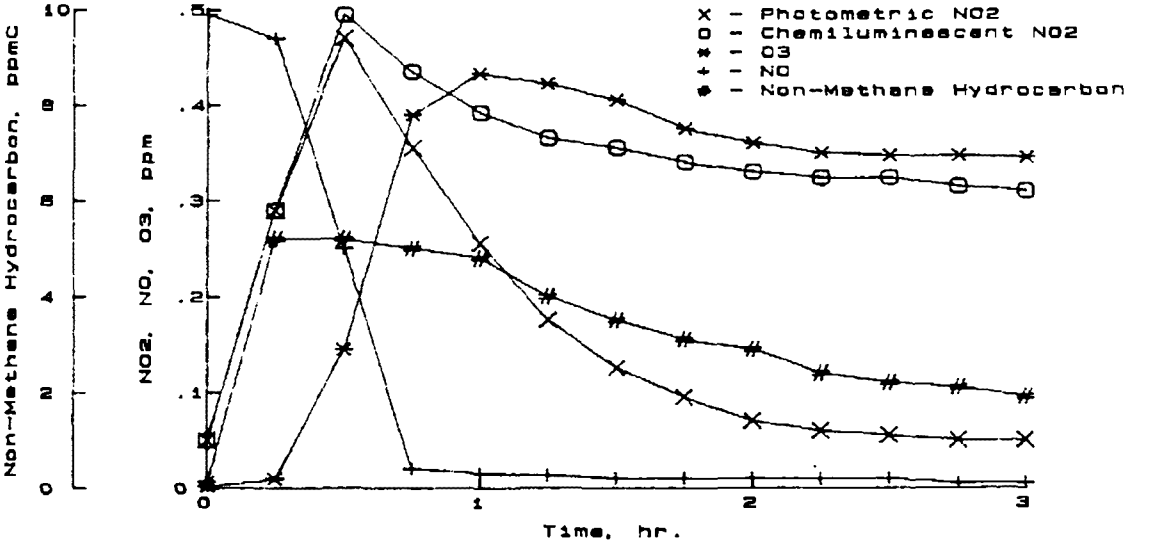
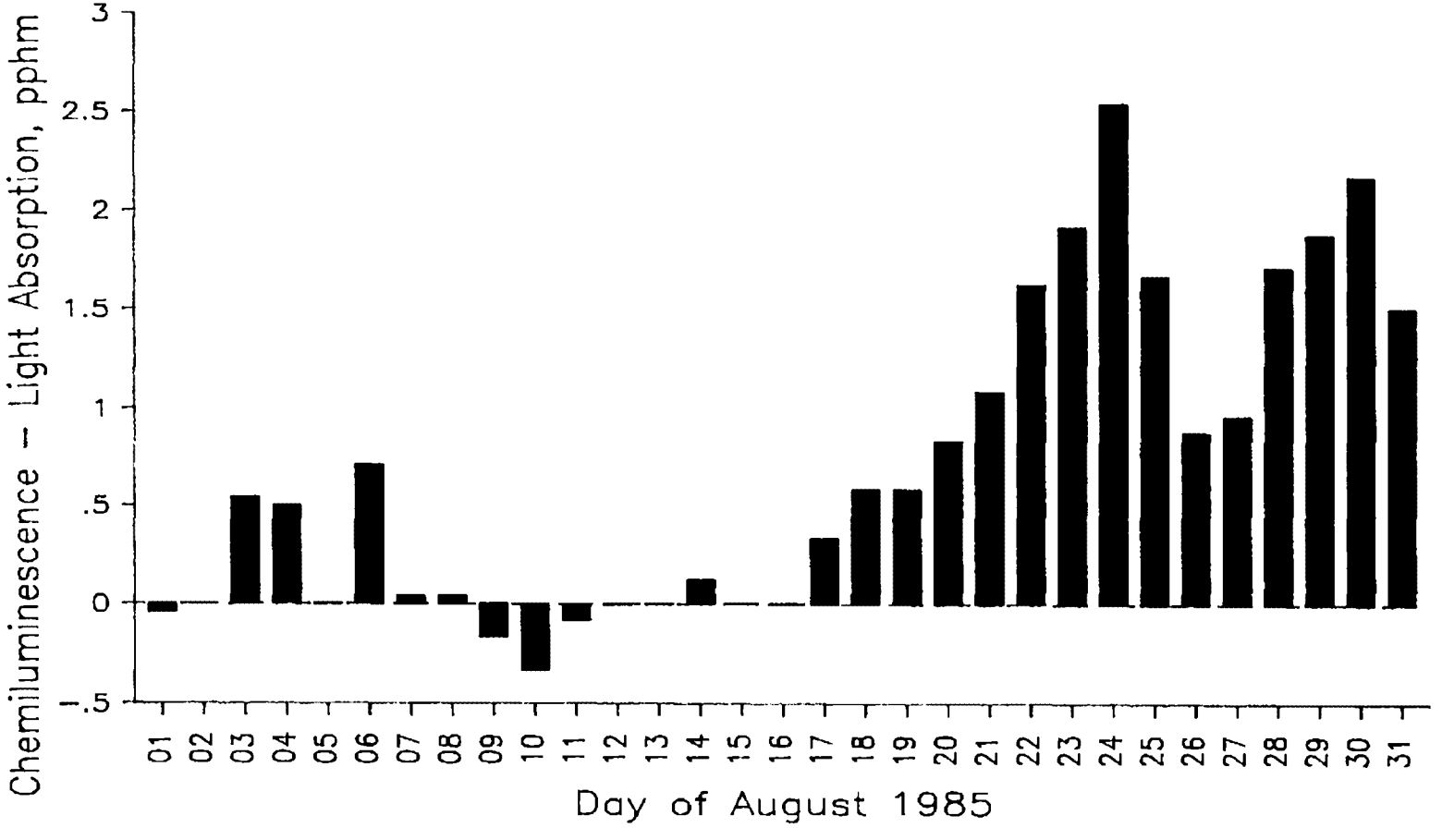


FIGURE 4

DIFFERENCES BETWEEN THE TWO MEASUREMENTS



A COMPARISON OF METHODOLOGIES FOR THE EXTRACTION OF SULFATE ION FROM SIZE-DIFFERENTIATED PARTICLES COLLECTED ON FILTER MEDIA

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ABSTRACT

Four methodologies were studied to develop a simple and reproducible sulfate extraction procedure representative of ambient conditions. Airborne particles were collected with a high-volume sampler and a cascade impactor system. The dry media and size-differentiated particles were subjected to four successive processes to extract sulfate ions: undisturbed dissolution, agitation, heating and boiling. At least 95% sulfate dissolution was achieved in less than 24 hours by simply placing the filter media in deionized water.

A COMPARISON OF METHODOLOGIES FOR THE EXTRACTION OF SULFATE ION FROM SIZE-DIFFERENTIATED PARTICLES COLLECTED ON FILTER MEDIA

INTRODUCTION

Measurement of the chemical composition of atmospheric particles is a critical element in efforts to assess the environmental effects of dry deposition, which has been implicated as a possible cause of damage to both terrestrial and aquatic ecosystems, to construction materials, and to human health. Since sulfate can be a major component of dry deposition, and since it is closely associated with acid deposition, an accurate method for the determination of particulate sulfate is needed.

At the present time, there does not appear to be a consensus on a method for routine measurement of particulate sulfate. Harrison and Pio (1) studied a technique where particulate sulfate was leached from filter samples, using distilled water, first at 70°C for 30 minutes and then overnight at ambient temperature in a mechanical shaker. Dolske and Gatz (2) reported the determination of particulate sulfate by immersion and manual agitation of 47 mm diameter filters in 5 ml of deionized water for three minutes. Jenke (3) compared the performance of three different particle extraction processes. These included an ultrasonic technique, a boiling water method, and a sequential warm solution leach. He also gave considerable attention to the influence of filter-media type on extraction performance.

The purpose of the research presented in this paper is to compare the effectiveness of four extraction processes for the removal of sulfate from particles collected on dry filter media. These are: 1) dissolution in undisturbed, deionized water, at room temperature (i.e., approximately 20°C) for 24 hours; 2) dissolution in agitated, deionized water, at room temperature for 24 hours; 3) dissolution at 70°C in deionized water for one hour; and 4) dissolution at 100°C in deionized water for one hour. Particle samples were collected using a hi-volume sampler and a hi-volume cascade impactor. Dissolution of the particle derived sulfate ion using the four methods was done in succession for each filter starting with undisturbed, deionized water at room temperature.

The four methods chosen represent varying degrees of extraction severity. The simplest and most natural process is the dissolution of sulfate in undisturbed, deionized water at room temperature, for 24 hours. Heating to 100°C for one hour represents a more severe case that is expected to produce the maximum water-soluble particle-derived sulfate ion concentration.

EXPERIMENTAL PROCEDURE

Two high-volume samplers, located within 10 ft (3 m) of each other at the University of Kansas, Lawrence, KS, were used to collect the particle samples. One of the samplers is equipped with an Andersen size-selective inlet (Model GMWA 7000) having a nominal particle-cut diameter of 15 microns. An Andersen rectangular-slotted cascade impactor is located under the size-selective inlet. This combination of particle-size differentiating apparati separates the particles into six distinct fractions. These are particles with aerodynamic diameters of 15 to 7.2 μm, 7.2 to 3.0 μm, 3.0 to 1.5 μm, 1.5 to 0.95 μm, 0.95 to 0.49 μm, and less than 0.49 μm.

The second high volume sampler (General Metal Works, Model GMWL 2000) is of the standard type used to measure total suspended particles in ambient air. Both samplers were operated simultaneously for 24-hour periods between the dates of September, 1984 and July, 1985. Flow rates for the samplers were fixed at 40 cfm using Kurtz flow controllers (Model 310). Filters were placed in the samplers immediately before a test and removed within 2 hours after termination of a sampling run. Standard U.S. EPA laboratory protocol for filter weighing and standard U.S. EPA sampling protocol were used during the course of the study.

The filters used in all sampling runs were Whatman 2000 EPM glass-fiber filters. Collection filters were prepared for laboratory analysis by trimming away large unexposed borders and identification markings with a surgical scalpel. The remaining part of each filter was then cut into approximately one-inch squares and placed in a labeled one-liter beaker. Using a calibrated 500-ml volumetric flask, 500 mls of deionized water were added to each beaker, which was then covered with parafilm. The deionized water was supplied by a Milli-Q Reagent-Grade Water System (Millipore Corp., Bedford, Mass.) and had a specific conductance of 18 megohm-cm.

The filters were allowed to sit (undisturbed) in the deionized water for 24 hours, at which time an 8-ml sample was withdrawn from each beaker with a pipette that was triple rinsed with deionized water before each sample was withdrawn. The 8-ml samples were stored in scrupulously cleaned glass test tubes with teflon-coated screw-cap lids. The test tubes and all other items that could make contact with the samples or the filter solution were carefully cleaned and triple rinsed with deionized water to prevent contamination.

In the next extraction phase, the beakers were placed on a gyroshaker apparatus to agitate the solution in a vigorous fashion for 24 hours. The shaker is connected to a timing device that automatically controls the process for a 24-hour period. After 24 hours, filter pieces and fibers were allowed to settle, producing a clear supernatant from which 8-ml samples were withdrawn.

The final two extraction procedures involved the heating of the filter solutions to 70°C and 100°C. The parafilm was removed from the beakers and a clean watch glass was placed over each one. The beakers were then placed in a temperature-controlled bath for one hour at 70°C. They were then allowed to cool for approximately 30 minutes before being covered with parafilm. After the filter solution cooled to room temperature (i.e., 20°C), 8-ml samples were taken with the pipette. For the final extraction procedure, the above steps were repeated at a temperature of 100°C.

In addition to the actual sample filters, blank filters were processed to determine the contribution of the filter fibers and fiber bonding agents to the total particle-derived sulfate ion concentration. For each field test, a blank high-volume filter (8 x 10 inches) and a blank cascade impactor filter (4 x 5 inches) were subjected to the same extraction procedure. Sulfate ion concentrations from these blank filters were very uniform, as described below. Therefore, the blank values were averaged over the entire study period, and this average value was subtracted from the total sulfate ion concentrations of the respective particle samples.

All of the 8-ml samples were subsequently analyzed for total sulfate ion concentration using ion chromotography (Dionex, Corp., Model QIC). The

analytical procedure followed recommended U.S. EPA protocol using an internal standard (fluoride). The precision of the instrument is ± 5% with an accuracy of ± 2%.

RESULTS AND DISCUSSION

Tables 1 and 2 summarize the total sulfate mass data (filter-blank contributions are subtracted in all cases) for each test and each of the four different extraction techniques. Table 1 presents the cascade-impactor data as the total sulfate mass collected on all five stages plus the back-up filter. Table 2 shows the sulfate mass associated with the total suspended particle catch for each test.

Statistical analyses of this data are presented in Tables 3 and 4. Table 3 shows the ANOVA performed on the cascade impactor data. The null hypothesis being tested is that there are significant differences between the sulfate mass values for the four different extraction techniques. Results of the ANOVA indicate that the null hypothesis is incorrect. In reality, it can be stated with 95% confidence that there are no significant statistical differences in the values produced by the four techniques. This statistical analysis also indicates that the variation in total sulfate mass (which depends on the total atmospheric loading associated with a particular sampling date) is so great as to make insignificant the relatively small variation attributable to the extraction techniques.

Table 4 shows the same type of ANOVA for the total suspended particle data. The same null hypothesis is tested, with similar results. Once again, there are no statistical differences (at the 95% confidence level) between the mass sulfate values determined using the four different extraction techniques.

Although the statistical analysis indicates no significant differences-between the extraction techniques, at the 95% confidence level, another approach is taken to further study possible differences among the techniques. In this approach, the frequency of maximum and minimum sulfate mass occurrence for each extraction procedure is examined. The results of this analysis are presented in Tables 5 and 6. Table 5 shows the frequency of maximum and minimum sulfate mass occurrence for the cascade impactor data. It is obvious that the maximum sulfate mass value usually occurs after heating for 1 hour at 100°C. The minimum value is achieved (in the majority of cases) after a 24-hour detention in undisturbed, deionized water at room temperature (20°C). Further analysis of the data corresponding to f_{max}, the sulfate concentration corresponding to the most frequent occurrence of the maximum value among extraction techniques, and f_{min}, the sulfate concentration corresponding to most frequent occurrence of the smallest value among extraction techniques, indicates a maximum difference between the two frequency data bases of 4.6%. This shows (for the particles collected in this study) that simple extraction of the particles with deionized water at room temperature dissolves at least 95% of the total water-soluble sulfate mass present in the sample.

Table 6 shows the results for the total suspended particle data. The maximum difference between sulfate mass values corresponding to f_{max} and f_{min} is 2.6%. This adds further credence to the statement that at least 95%

TABLE 1

CASCADE IMPACTOR MASS SULFATE VALUES

FOR EACH TEST

Test Designation	24-Hr Det. (mg)	24-Hr Agit. (mg)	1 Hr, 70°C (mg)	1 Hr, 100°C (mg)
G	12.78	12.87	12.27	12.59
H	25.84	25.57	26.89	26.87
I	10.52	10.44	10.34	11.17
J	8.27	9.54	9.20	8.77
K	9.42	9.72	9.87	10.02
L	6.92	6.99	7.16	7.23
M	14.10	14.21	14.36	15.06
N	18.97	19.19	19.28	20.17
Avg. Value	13.35	13.57	13.67	13.99

TABLE 2

TOTAL SUSPENDED PARTICLE MASS SULFATE VALUES

FOR EACH TEST

Test Designation	24-Hr Det. (mg)	24-Hr Agit. (mg)	1 Hr, 70°C (mg)	1 Hr, 100°C (mg)
G	8.66	9.23	8.98	9.28
H	17.16	17.06	15.26	15.36
I	6.66	7.92	8.09	6.67
J	7.69	8.17	8.12	8.35
K	8.31	8.77	8.74	9.02
L	4.24	4.73	4.77	4.81
M	12.82	13.00	13.18	13.33
N	16.40	17.10	17.17	17.46
Avg. Value	10.24	10.75	10.54	10.54

TABLE 3

ANOVA FOR CASCADE IMPACTOR

Source of Variation	df	SS	Ms	F_s (M_{sg}/M_{sw})
Among Groups	3	1.66	0.553	0.014*
Within Groups	28	1140.14	40.719	
Total	31	1141.80		

TABLE 4

ANOVA FOR TOTAL SUSPENDED PARTICLES

Source of Variation	df	SS	Ms	F_s (M_{sg}/M_{sw})
Among Groups	3	1.0	0.333	0.017*
Within Groups	28	555.8	19.85	
Total	31	556.8		

TABLE 5

FREQUENCY OF MAXIMUM AND MINIMUM OCCURRENCE

FOR CASCADE IMPACTOR

Type of Analysis	f_{max}	f_{min}
24-Hr Detention	0	5
24-Hr Agitation	2	1
1 Hr at 70°C	1	2
1 Hr at 100°C	5	0

Percent Difference Between f_{max} and f_{min} = 4.6%

TABLE 6

FREQUENCY OF MAXIMUM AND MINIMUM OCCURRENCE

FOR TOTAL SUSPENDED PARTICLES

Type of Analysis	f_{max}	f_{min}
24-Hr Detention	1	7
24-Hr Agitation	0	0
1 Hr at 70°C	1	1
1 Hr at 100°C	6	0

Percent Difference Between f_{max} and f_{min} = 2.8%

of the total water-soluble sulfate ion is obtained by simple dissolution in deionized water.

Data on background levels of sulfate ion in the blank filters is of interest to the sampling community. During the course of the study, twenty blank filters were analyzed by all four extraction techniques. The maximum sulfate mass contributed by any one of these samples is 0.1 mg. The average value for all the data is 0.08 mg. A maximum variation between two samples of 0.03 mg existed. This indicates a uniform blank level of sulfate mass using the Whatman 2000 EPM glass-fiber filter.

It should also be noted that heating the filter suspensions virtually destroys the adhesive properties of the filter fibers and causes them to disaggregate. When this is done, large quantities of soluble organic matter (presumably originating from dissolution of the filter binder) are released into solution, as reflected by large increases in total organic carbon (determined using a Dohrmann Model DC-80 total organic carbon analyzer).

The results of this study indicate that consistent and accurate determination of water-soluble particulate sulfate can be achieved by simply placing the filter media in deionized water for 24 hours at room temperature. On-going research to examine the impacts of particle-derived sulfate on a natural ecotone near Lawrence, KS, has successfully employed this technique (simple dissolution) for over a year. However, since the chemical composition of particles varies from region to region within the U.S., differences among the four extraction techniques may be significant in other regions.

CONCLUSIONS

The following conclusions are drawn from the results of this study:

1. At least 95% of the water-soluble sulfate in particles collected on dry filter media was solubilized simply by placing the filters in deionized water for 24 hours at room temperature.

2. Whatman EPM 2000 glass-fiber filters displayed background levels of sulfate less than or equal to 0.1 mg, with a maximum variation of ± 0.03 mg.

3. Although the ANOVA indicates no significant differences at the 95% confidence level among the four techniques examined, the maximum water-soluble sulfate mass generally occurred after heating to 100°C for 1 hour and the minimum water-soluble sulfate mass generally occurred after dissolution in deionized water for 24 hours at room temperature.

4. Heating of the filter suspensions caused disaggregation of thefilter fibers and increased the total organic carbon content of the solution considerably.

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FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) AMMONIUM SULFATE ANALYSIS ON TEFLON AIR FILTERS

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This paper reports on the improvement and automation of a method of analyzing ammonium sulfate particles collected on Teflon* membrane filters. The filters were analyzed by transmission measurements using Fourier transform infrared spectroscopy after collection with dichotomous air samplers. The spectra of the blank filters are subtracted from the spectra of the loaded filters and an integration of the 1000-1135 cm^{-1} absorbance band for sulfate leads to a lower limit of detection of 0.2 $\mu g/cm^2$ on 37 mm 2 micron Teflon filters. This corresponds to an ambient concentration of 0.1 $\mu g/m^3$ for a 24 hr, 21.6 m^3 air sample. Ammonium sulfate particulate standards were prepared by sampling the output of a laboratory particle generator. Concentrations were then determined by x-ray fluorescence analysis. An automatic sample changer was constructed which accepts the filter carousel from a Sierra/ Anderson model 245* automated dichotomous sampler. The sample changer is controlled by the FTIR computer. The analysis is nondestructive, automated, and requires no sample preparation.

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) AMMONIUM SULFATE ANALYSIS ON TEFLON AIR FILTERS

Introduction

Sulfur in atmospheric aerosols is generally present in the form of ammonium sulfate. Ammonium sulfate is important in visibility studies, SO_2-to-sulfate conversion processes, and health effects. It also comprises the major portion of the fine particle fraction (< 2.5 μm) of atmospheric aerosols.

Sulfur aerosols are collected with dichotomous air samplers[1] which collect particles in two size fractions, < 2.5 μm and 2.5-15 μm particles to reflect the bimodal distribution of inhalable particulates in the atmosphere. There have been two approaches to automating dichotomous samplers for unattended sampling over time periods of days, weeks, or months. One approach is the linear slide tray sampler developed at Lawrence Berkeley Laboratory (LBL). Another approach is a rotating sample carousel. This second approach is incorporated in the Sierra/ Anderson Series 245 automatic dichotomous sampler.

One means of analyzing the filters is elemental analysis with x-ray fluorescence (XRF)[2]. This is a nondestructive technique that measures the mass of the elemental sulfur on the filter. The chemical form of the sulfur is not determined in this measurement although it is widely assumed that it is predominantly ammonium sulfate.

Another means of analysis for ammonium sulfate is ion chromatography[3]. This is a destructive technique that requires a wet chemical extraction of the filters. It can detect as little as 0.5 μg of ammonium and sulfate ions per sample with 10-12% error for ammonium and 5% error for sulfate. The extraction procedure could alter the species found on the filter.

With the shortcomings of the previous two methods in mind, an alternate analysis technique was sought that would be 1) non-destructive, 2) sensitive, 3) could identify species collected on the filter, 4) was amenable to automation, and 5) required no sample preparation. W. A. McClenny, et al have shown that Fourier transform infrared spectroscopy (FTIR) is a feasible approach[4]. The goal of this present research was to determine if the sensitivity and accuracy of the technique could be improved for ammonium sulfate analysis. In addition, the FTIR instrument was to be configured for automated sample analysis.

Experimental Methods

The FTIR was a Nicolet model 5DXB* which is capable of 2 wavenumber resolution. It is equipped with a 36 megabyte hard disk, a 1 megabyte floppy disk, and 640 kilobytes of extra memory to provide adequate programming and file storage space. It is also equipped with a flipper mirror option to direct the infrared beam out of the main optical bench and into an automatic sample changer compartment containing the loaded Sierra sampler filter carousel. The sample compartment was not enclosed at the time of this study so no purging of laboratory air was possible for these experiments. An airtight enclosure is under construction.

Additional sample focusing mirrors were mounted in the carousel compartment to direct the infrared beam through the Teflon filters and into the deuterated triglycerine sulfate (DTGS) detector. The Teflon filters are placed in circular filter holders which are in turn placed in the circular carousel. The carousel holds 20 pairs of filters. The infrared beam covers an approximately 15 mm diameter area on the Teflon filter to average any nonuniformity in particle deposition. The filters are located as close to the detector as possible to increase the collection of light that is scattered by the filter. The carousel is mounted horizontally over the DTGS detector. There is also sufficient space to install a mercury cadmium telluride (MCT) detector if desired. A stepper motor rotates the carousel to position the filters for analysis. Another stepper motor moves the carousel horizontally to select either the inner or outer concentric circle of filters.

The Nicolet 1280* computer controls data collection, data storage, and the positioning of the correct filter in the infrared beam. It communicates to a microcomputer (BASICON model 2N, Portland, OR*) through an RS232 interface. This microcomputer controls and monitors the carousel stepper motors and microswitches and can be programmed in TINY BASIC or machine language for control applications.

Laboratory ammonium sulfate was generated for calibration purposes and to provide samples to study in the absence of soot and other compounds. Air is passed through 1.4 kg of indicating Drierite* and a series of particulate filters. This clean air is then used to aspirate a solution of ammonium sulfate in water. The liquid particles are passed up through a heater tube, a drying column, a Kr 85 particle deionizer, a final heating tube, and then into the dichotomous air sampler inlet. The laboratory-generated particles produce an absorption spectrum that is identical to that seen in actual ambient samples. Scanning electron micrographs show that the laboratory-generated ammonium sulfate particles are on the order of 2 microns in size while ambient ammonium sulfate particles are in the 0.1-1 micron range. There is also a humidifying option which was not used in these experiments. The apparatus was designed by Roland Otto and built with the help of William Searles at LBL.

Two micron pore size Teflon filters (Gelman TEFLO PTFE* with polymethylpentene support ring) were placed in the Sierra Sampler filter holders and into the carousel. Reference spectra of each blank filter were automatically taken with the number of scans varying from 10 to 1000. Each set of spectra for each filter were then stored on disk for future use in background subtraction. The blank filters were then removed from the Sierra filter holders and put into the 2 by 2 in. filter slide holders suitable for use in the linear slide tray of the LBL automated dichotomous air sampler. A Sierra automated dichotomous air sampler was not available for use. The Teflon filters were then loaded with laboratory-generated ammonium sulfate with depositions ranging from 2-50 $\mu g/cm^2$. The filters were analyzed for total sulfur using x-ray fluorescence. They were then removed from the filter slides and returned to the Sierra filter holders for analysis.

During actual air sampling, the Sierra automated dichotomous sampler samples air with a total flow rate of 1 cmh with a flow rate of 0.9 cmh for the fine particle fraction and 0.1 cmh for the coarse particles. Typical sampling periods are 6, 12, or 24 hr which represents 5.4, 10.8, and 21.6 m^3 of sampled air on the fine particle filters.

Results

Figure 1 shows an FTIR spectrum obtained from a 2 micron Teflon filter loaded with approximately 58.7 $\mu g/cm^2$ of laboratory-generated ammonium sulfate. Figure 2 shows the spectra of a 1-micron (solid line) and a 2-micron (dashed line) blank Teflon filter. The vibrational bands of importance for sulfate are from 596-640 cm^{-1} with a peak at 620 cm^{-1} and from 1000-1200 cm^{-1} with a peak at 1116 cm^{-1}. The ammonium band of interest is from 1300-1550 cm^{-1} with peak at 1420 cm^{-1}. Another ammonium band from 2400-3520 cm^{-1} was not used because it lies in an area of significantly higher baseline noise levels. The ammonium band at 1420 cm^{-1} does not overlap any other band but it does lie in a region of maximum water absorption which would indicate that the instrument should be purged of water vapor to achieve maximum noise reduction for this band. Both sulfate bands overlap Teflon bands in the regions 1150-1250 cm^{-1} and 600-675 cm^{-1}. The Teflon band at 1116 cm^{-1}, below the two strongly absorbing Teflon bands, can clearly be seen because of the relatively high loading of this sample. The smaller sulfate band at 620 cm^{-1} can also be seen by careful comparison to Figure 2.

Figure 3 is a graph of the mass loading in $\mu g/cm^2$ as determined by x-ray fluorescence versus the integrated areas of the ammonium and sulfate bands after background subtraction using the blank filter spectra taken earlier. A linear least squares line was fit to each set of data and a clear linear relationship can be seen. The error in the slope and intercept for each line was calculated and a lower limit of detection (LLD=3σ) was determined using a propagation of errors approach[5]. Table I shows the calculated lower limits of detection for ammonium and sulfate on 37 mm, 2 micron Teflon filters for each absorption band. The last column shows the equivalent ammonium sulfate particulate concentration in air for a 24 hr sampling period (21.6 m^3 sampled air). The data in Figure 3 represents 100 spectral scans with the FTIR spectrometer.

Discussion

Figure 4 shows the spectra of an actual air sample taken in Portage, Wisconsin (note the expanded scale). The ammonium sulfate peaks are exactly the same as those found in the laboratory generated samples. This filter spectra represents one of the higher particulate concentrations measured in this city with the majority of the measurements being much lower than the concentration on this filter. Similar filter samples from Steubenville, Ohio have much higher particulate concentrations the highest having absorbances greater than 2.0. On all air filter samples soot will be found in the fine particle fraction and will be evident as a continuous increase in the baseline of the spectra. No nitrate was found on any of the filters from Portage or Steubenville. Ammonium nitrate particles generated on our particle generator show a prominent nitrate peak at 1340 cm^{-1} overlapping the ammonium peak at 1420 cm^{-1} and a weaker nitrate peak at 828 cm^{-1}.

This technique will not work for glass fiber filters, paper filters, or Nylasorb* filters because these materials cause too much scattering and absorption. Two micron Teflon filters (Gelman TEFLO PTFE with polymethylpentene support ring) are preferred to 1 micron filters because of their lower absorption. The highest absorption peak for the 2 micron filters represents approximately 10-15% transmission while those for the 1 micron filters are totally absorbing. Teflon filters also have a remarkably simple absorption spectrum (see Figure 2). The 2 micron filters have the same collection efficiency as the 1 micron filters.

Integration of the 1116 cm^{-1} sulfate band the provides the best measure of ammonium sulfate. Analysis of the sulfate bands requires subtraction of the blank Teflon filter spectra from the spectra of the same filter after particulate collection in the air sampler. Background subtraction is not an entirely straightforward technique. Subtraction of absorbance bands is extremely sensitive to slight distortions in the spectral data. The subtraction of two spectral files with small differences in absorbance band shapes can result in derivative-like noise far in excess of what would be expected simply by propagation of errors in the subtraction process. This effect can negate any signal-to-noise improvement obtained by increasing the number of scans on the data. Figure 5 illustrates this effect clearly by showing the result of an uneven subtraction of the two Teflon peaks at 1135-1250 cm^{-1}. This subtraction was performed on two spectra of the same blank filter after 1000 scans for each spectra. Spectral distortion may be related to light scattering effects on the detector that result from moving the filter into and out of the infrared beam between spectral scans. The subtraction artifacts can be worse if the spectra from two different filters are subtracted from each other because there can be significant absorption variability between filters. As a result of these "subtraction problems", the sulfate peak at 1116 cm^{-1} was integrated in the region from 1000-1135 cm^{-1} which is in a region removed from the subtraction artifacts due to the large Teflon absorption peaks.

The baseline noise will improve with the square root of the number of scans that are averaged. The number of scans used has to be weighed against the 1.5 sec needed per scan. The analysis for 100 scans requires about 3.5 min per filter while that for 1000 scans requires almost 27 min. The scan speed can be increased by decreasing the resolution of the scan but this would lead to greater subtraction problems. An MCT detector is both quieter per scan and has a greater scan speed at the same resolution but it has less dynamic range than a DTGS detector. This could lead to subtraction problems as well. An MCT detector has not yet been thoroughly tested for this application.

Conclusions

Fourier transform infrarec transmission spectroscopy can provide an accurate and sensitive means of quantifying ammonium sulfate deposition on 2 micron Teflon filters. A necessary requirement, however, is that reference spectra be obtained and stored before sampling to be used in background subtraction. Further increases in sensitivity may be possible with the use of a mercury cadmium telluride detector. If analysis time is not a consideration, then increasing the number of scans should decrease the lower limit of detection. The instrumentation is automated and no sample preparation is required. Specific species can be observed by the presence and identification of absorbance peaks in the spectrum. The analysis is nondestructive.

Further work will consist of analyzing actual air samples and comparing these results with analysis by x-ray fluorescence and ion chromatography. Work will proceed toward quantifying the mass loading of soot as well.

Acknowledgments

We would like to thank Robert Giauque for performing the x-ray fluorescence measurements, William Searles for the mechanical construction of the sample changer, and Roland Otto for use of the particle generator.

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Department of Energy to the exclusion of others that may be suitable.

Although the research described in this article has been funded wholly or in part by the U.S. Environmental Protection Agency through an Interagency Agreement No. IAG-DW89931232-01-0 with the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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Table I

Lower Limits of Detection

	Filter concentration $\mu g/cm^2$	Ammonium Sulfate 24 hours, 21.6 m^3 sample $\mu g/m^3$
Sulfate 596 - 640 cm^{-1}	1.70	0.86
Sulfate 1000 - 1135 cm^{-1}	0.20	0.10
Ammonium 1300 - 1550 cm^{-1}	0.15	0.20

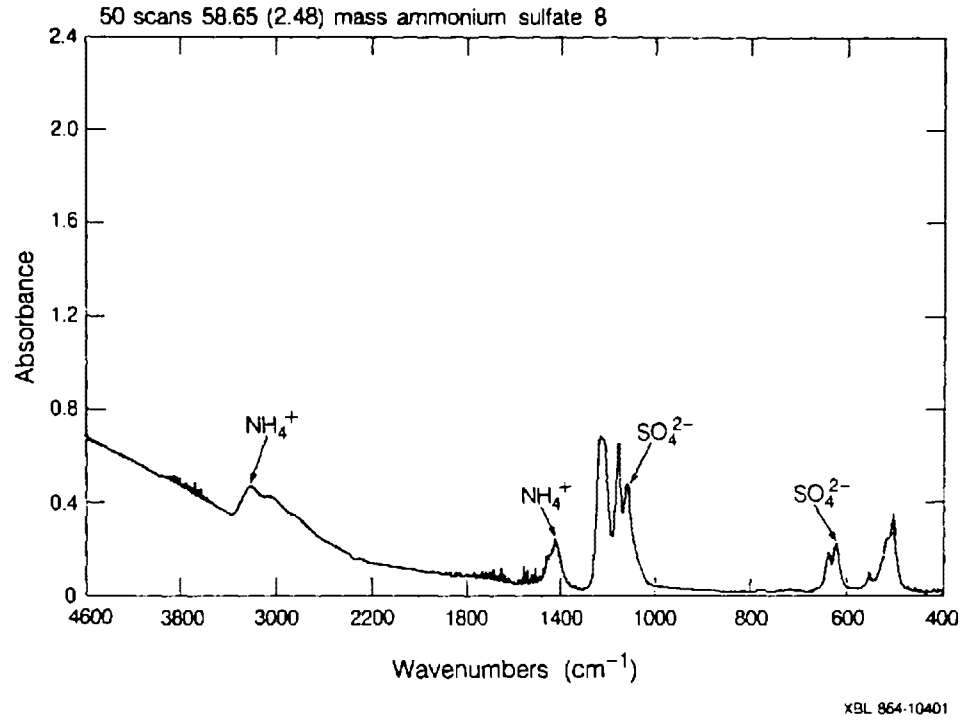


Figure 1. 70 μg/cm^2 ammonium sulfate on a 2-micron Teflon filter.

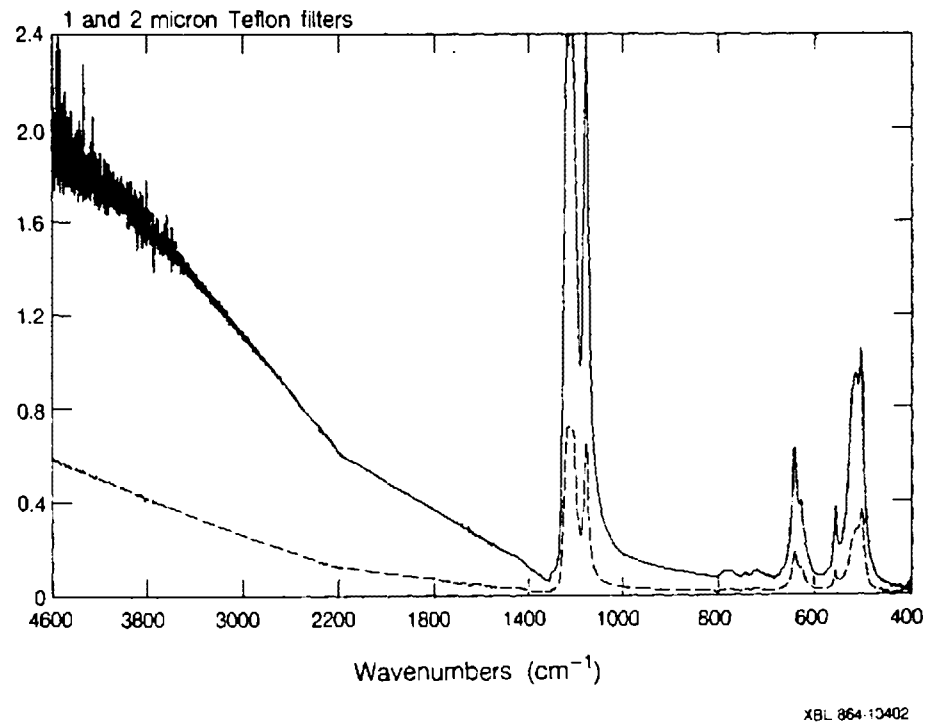


Figure 2. One-micron (solid line) and 2-micron (dashed line) blank Teflon filters.

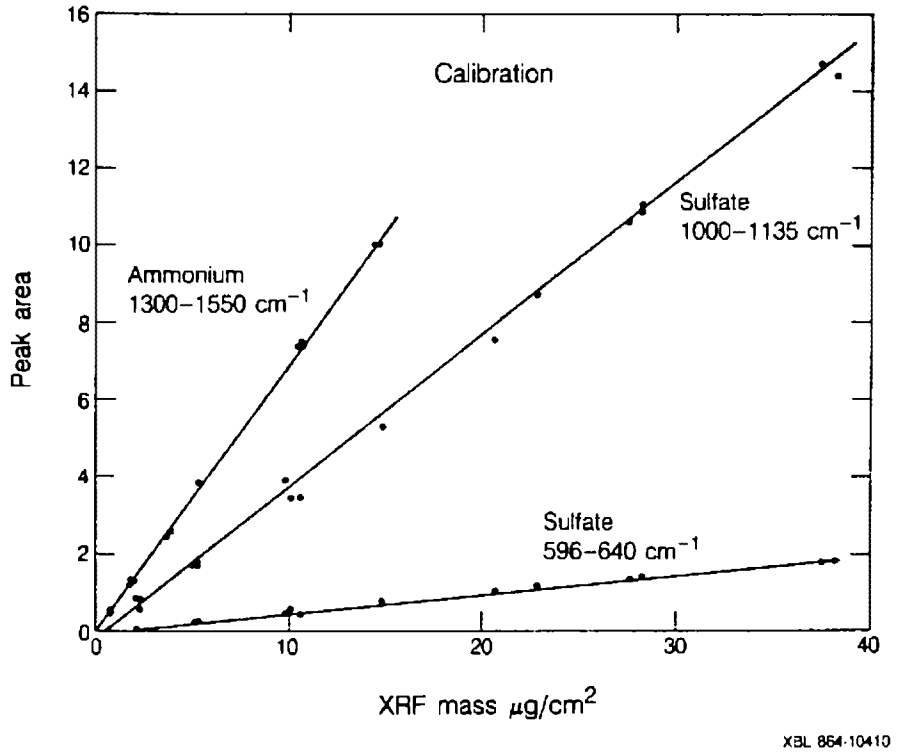


Figure 3. Calibration of ammonium and sulfate.

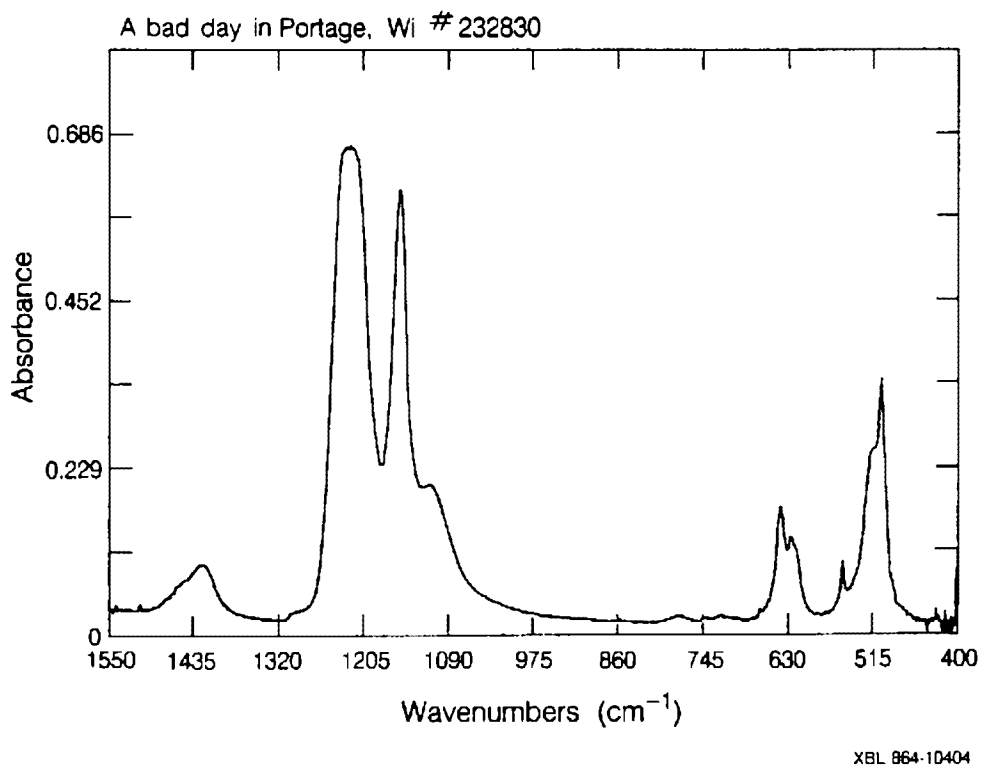


Figure 4. High ammonium sulfate loading for Portage, Wisconsin.

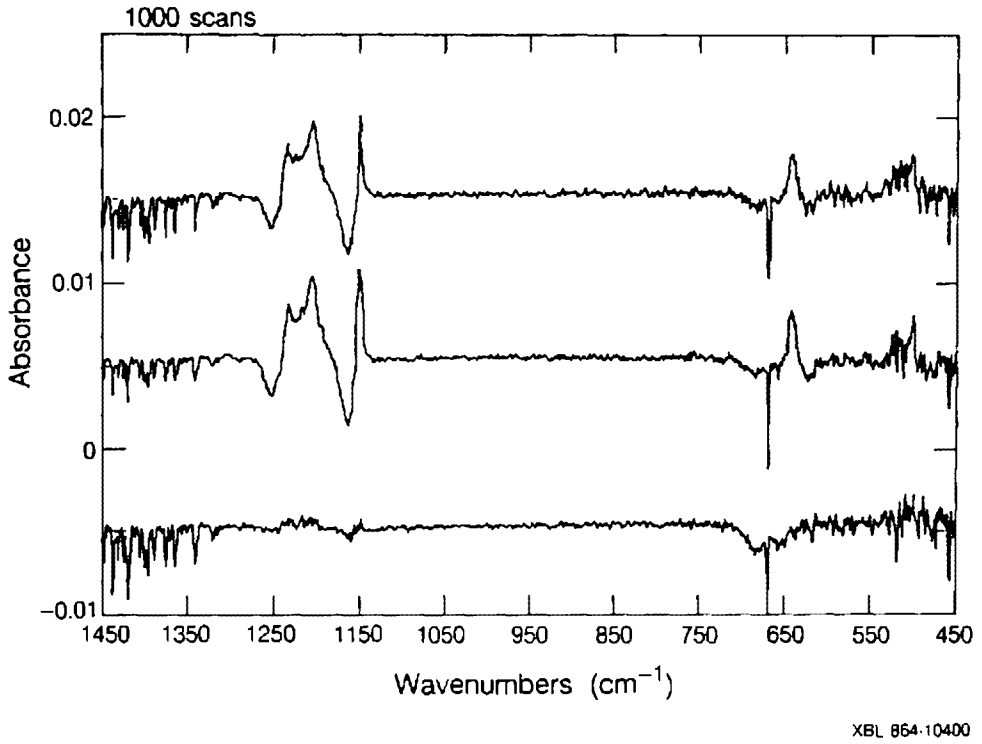
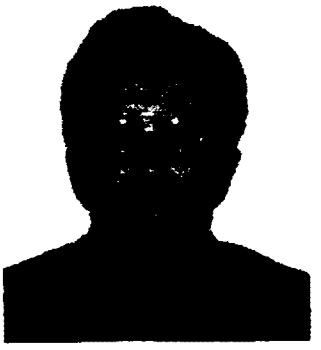


Figure 5. Subtraction artifacts due to blank Teflon filters.

SUBLIMATION SOURCES FOR NITROUS ACID AND N-COMPOUNDS IN AIR



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A new technique has been investigated for the production of parts-per-billion range concentrations of some NO_x type compounds in air. The method is based upon sublimation of oxalic acid in an air stream onto an appropriate target compound with which it reacts to produce a gaseous product. With sodium nitrite and 30-60% relative humidity gas nitrous acid is the predominant product in up to 90% mole percent purity. In very dry air nitric oxide predominates, via redox reaction. Nitric acid in air is produced at low humidities by reaction of oxalic acid with potassium nitrate. Similarly, hydrogen cyanide is produced from sodium syanide and thiocyanic acid from potassium thiocyanate.. The amounts of the gaseous compounds produced dynamically are small but useful for preparing low concentrations in air, usually in the 10 to 500 ng/L range. The identity of nitrous acid was confirmed by chemical and spectroscopic studies and used in the development of a sequential, selective hollow tube system for reactive NO_x compounds. No method was found for producing nitrogen dioxide in air by sublimation. Diffusion and permeation sources of nitrogen dioxide were subsequently studied. Substantial problems were found in the production of pure nitrogen dioxide in air. Large fractions of nitrogen dioxide are converted to nitric acid and nitrous acid, especially in glass systems. Plastic systems are recommended.

SUBLIMATION SOURCES FOR NITROUS ACID AND N-COMPOUNDS IN AIR

Introduction

Testing and development of methods for trace concentration of the reactive nitrogen oxide type compounds, i.e. HNO_3, HNO_2, NO_2 and NO, requires reasonably pure source of these compounds in air at low concentrations. Since all of these are quite reactive with each other in some circumstances and with traces of reducing compound impurities, their preparation in high purity in air is difficult. Permeation devices are available for NO_2 and NO. Nitric acid can be diffused out of a sulfuric acid - nitric acid mixture.

Nitrous acid has been prepared by solution reactions of acids with nitrite ion (1). Nitrous acid has also been prepared from a mixture of NO with NO_2 in the presence of water (2). Nevertheless, these are far from pure sources, always being mixed with large amounts of NO and NO_2.

The use of oxalic sublimation onto sodium nitrite was eventually tried and found useful for preparing good purity HNO_2 in air. Other extensions of this technique were eventually tried.

Experimental

The oxalic acid sublimation apparatus developed and finally used in most work is shown in Figure 1. Filtered compressed air was humidified to the desired level and passed at 0.8 to 1.2 L/min through the 8 mm o.d. tube packed with approximately a 2 cm long section of oxalic acid dihydrate and a 2 cm long section of crystalline sodium nitrite. Humidities were maintained in the 30-60% R.H. range. Sodium nitrite is hygroscopic and so cannot be exposed to very high humidities.

A similar arrangement was used for preparation of nitric acid, nitric oxide hydrogen cyanide, thiocyanic acid. Nitric acid preparation used potassium nitrate as the target compound at low humidity. Hydrogen cyanide was produced when sodium cyanide was the target compound. Thiocyanic acid was produced when potassium thiocyanate was the target compound. Nitric oxide was produced when dry tank air was passed through the sublimation device with sodium nitrite as the target compound. Use of anhydrous oxalic acid is also recommended here.

Sequential, selective hollow tubes were used to preconcentrate effluent gases from the sublimation sources. These were then analyzed by thermal desorption of collected analytes using a NO_x chemiluminescence analyzer (3) (4). The selective hollow tube system provided for NO_x speciation into HNO_3, HNO_2, NO_2 and NO with detection limits near 1 ng per sample.

Results and Discussion

The nitrous acid in air sublimation type source was used under several conditions of humidity and produced the composition shown in Table I. Most notable is the shift in composition from HNO_2 to NO when dry air is used as the carrier gas.

If used to produce nitric oxide at a high purity, a sodium carbonate clean-up tube can be used to remove the small amount of nitrous acid present. When used in a permeation oven, it was found that increasing the temperature above the usual 25°C controlling level increased the percentage of nitric oxide and nitrogen dioxide is produced. A permeation oven fitted with a sublimation source was used for several weeks with over 90% mole fraction of nitrous acid being produced at a rate of 45-55 ng/min.

The identity of nitrous acid in air was confirmed by optical absorption spectroscopic analysis of the nitrous acid from a warmed sublimation source. Table II compares experimental and referenced absorption peaks. Chemical tests were also conducted and found to be positive for HNO_2.

Nitric acid was produced at rates of 50-53% ng/min depending upon temperature but at low humidities (18% R.H.). In general, low concentrations of nitric acid are produced but with almost no impurities.

Nitrogen dioxide was studied as a source from a plastic and glass system. If glass is used and carrier gas system of moderate himidity, large percentages of HNO_3, HNO_2 and NO can be co-present with NO_2. Plastic systems and lower humidity greatly improves the purity of the nitrogen dioxide produced.

Hydrogen cyanide and thiocyanic acid were produced at evolution rates of 25 to 50 ng/min when sodium cyanide and potassium thiocyanate respectively were used as target compounds. Humidity was maintained at 18% R.H. The HCN and HSCN in air samples were analyzed using the same chemiluminescence analyzer system as for the NO_x compounds but oxygen or air were used as the carrier gas and silver was used as the preconcentration surface of the hollow tubes.

Conclusions

A sublimination source is likely the best available technique for producing a low concentration of comparatively pure nitrous acid in air for testing specific analysis methods. Extensions of the technique have been demonstrated for HNO_3, NO, HCN, and HSCN in air. It is apparent that this same approach can also be used for HF, CO_2, SO_2 and H_2S in air.

Sublimation sources are easy and convenient to prepare and use, but very specific analysis schemes must be used for the NO_x type compounds to verify air mixture purity. Although the sources are reasonably constant in output of analyte gas after equilibration, weighing losses cannot be expected to be useful for calibration. Calibration of the source output is likely best done by use of an appropriate specific analysis method.

Acknowledgement

This work was supported in part by the Air Resources Board, State of California.

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Table I. Analysis of HNO_2 Sublimation Sources (Percentage Composition)[a]

Room Temperature Source (23-25°C)

HNO_3	HNO_2	NO_2	NO	R.H.(%)	Comments
0	79.5	18.4	18.4	31%	137 ng/min HNO_2 just prepared (N=1)
0	83	0	17	24%	27 ng/min HNO_2 after 6 weeks
0	91.4	0	8.6	24%	34 ng/min HNO_2 after 7 weeks
1.4	89.2	2.9	6.5	24%	37 ng/min HNO_2 after 9 weeks
0	52	5	43	0	88 ng/min HNO_2 just changed to dry air
0	24.1	3.6	72.2	0	81 ng/min HNO_2 dry air 2 days later
0	89.4	3.4	9.2	24%	111 ng/min HNO_2 larger dia. source (N=3)

[a]Air carrier gas at 0.8 - 1.2 L/min.
Humidity measured at sample outlet.
Mole percent.

Table II. Absorption Spectrum Data for HNO_2

Observed	Reference[a]	ε, cm^{-1} ppm^{-1}[b]	(N=1)
371.6 nm	371.6 nm	2.27×10^{-6}	1
364.3	368.3	3.13×10^{-6}	1
364.8	364.7	$2.63 \pm 0.03 \times 10^{-6}$	2
357.6	357.7	$3.23 \pm 0.56 \times 10^{-6}$	3
354.3	354.3	$4.43 \pm 0.42 \times 10^{-6}$	3
351.0	350.9	$1.43 \pm 0.26 \times 10^{-6}$	3
341.8	341.8	$3.15 \pm 0.72 \times 10^{-6}$	3
338.8	338.8	-	
330.9	330.8	-	
328.1	327.8	-	

[a] Ref. (5) [b] Experimental values

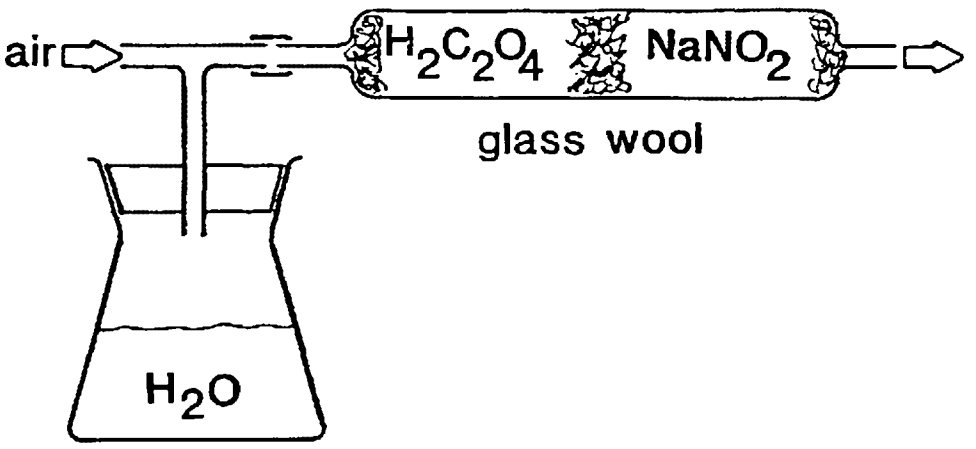

Figure 1 Apparatus Arrangement for Sublimation Sources

UTILIZATION OF A CLASS I, NON-SPECIFIC ADSORBENT, CARBOTRAP, FOR THE PREDICTION OF SAMPLING

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Analysts monitoring airborne contaminants not included in federal methodologies must decide which adsorbent will provide the best adsorption/ desorption efficiencies for the adsorbate. However, because an adsorbate might possess one or more functional groups and can exist in many molecular shapes and sizes, choosing the adsorbent can be difficult. Use of a Class I, nonspecific adsorbent can eliminate concern over which functional group(s) an adsorbate possesses. Carbotrap, a graphitized carbon black, is a Class I, nonspecific adsorbate with the appropriate adsorbing capacity. It allows the analyst to predict the required sampling volume from the molecular geometry of the adsorbate.

Sampling volume predictions depend on two considerations, the surface interactions between the adsorbate and Class I adsorbent, and the physicochemical characteristics of the adsorbate molecules. Knowledge of surface interactions has been used at Supelco to predict sampling volumes. Carbotrap has been packed in traps designed to mimic typical adsorption tubes, and evaluated by using adsorbates with a wide range of functional groups and molecular volumes. Adsorbate/ adsorbent relationships have been characterized in the low coverage region (Henry's Law region), and in higher concentrations, by using sampling (breakthrough) volumes (V_g^t), adsorption coefficients (K_a), and equilibrium sorption capacities (Q_g). Information extracted from these data enables one to predict V_g^t.

Predictions of solvent desorption of an adsorbate from the Carbotrap surface are based on knowledge of the miscibility of the desorbing solvent and the adsorbate, and on Carbotrap surface saturation. Predictions of thermal desorption are related to the quantity of thermal energy required to dissociate the London forces between adsorbate and adsorbent.

Carbotrap effectively adsorbs a wide range of airborne contaminants, allowing analysts to sample at predetermined volumes based on known molecular characteristic values. This eliminates the need to decide which adsorbent is best suited to a particular class of compounds.

UTILIZATION OF A CLASS I NON-SPECIFIC ADSORBENT, CARBOTRAP, FOR THE PREDICTION OF SAMPLING VOLUMES FOR ADSORBATES ACCORDING TO MOLECULAR SIZE AND SHAPE

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Analysts monitoring airborne contaminants in various sampling modes must decide which adsorbent will provide the best adsorption/desorption efficiencies for the adsorbates. Because an adsorbate may possess one or more functional groups and exist in many molecular sizes and shapes, choosing the adsorbent becomes difficult. Utilization of a Class I, non-specific adsorbent (1) can eliminate concern over which functional group(s) an adsorbate possesses. Carbotrap, a graphitized carbon black, is classified as a Class I, non-specific adsorbent (Table I) and has the physical properties necessary to adsorb a wide range of organic compounds (Table II). Furthermore, the hydrophobic surface properties of this adsorbent enable it to adsorb organic compounds in humid sampling modes.

The adsorptive properties of Carbotrap were characterized by following procedures outlined in EPA document #600/7-78-004 (2). The evaluation was focused on the adsorbate/adsorbent interactions occurring in the low coverage (i.e., Henry's Law) region by using the established specific retention volumes (V_g^t), adsorption coefficients (Ka), and equilibrium sorption capacities (Qg) (Table III). Retention volumes for each adsorbate were determined at elevated temperature, then extrapolated via linear regression analyses to obtain retention volume data for ambient (20°C) temperature. From this data, the adsorption coefficient and equilibrium sorption capacity were then determined.

To establish the adsorbate/Carbotrap relationship of several key compounds possessing different functional groups the specific retention volume, adsorption coefficient and equilibrium sorption capacity for eight compounds was obtained and compared to values for the adsorbents Tenax GC and XAD-2 (Table IV).

The data obtained indicate that Carbotrap possesses a greater affinity for the compounds of interest, with the exception of the n-Pentanoic acid/Tenax relationship. The greater interaction in the latter relationship is due to the induced dipole interactions between the acid functional group of n-pentanoic acid and the phenylene oxide functional groups of the Tenax surface.

To expand the information on adsorbate interaction for organic compounds and Carbotrap, 38 adsorbates were evaluated. Table V illustrates, in order of increasing specific retention volumes, the data obtained as well as the correlation coefficients, for each of these adsorbates.

Information extracted from this characterization evaluation, as well as the non-specific characteristics of Carbotrap, allows an analyst to construct a predictive model for sampling volumes based on

the physical characteristics of the adsorbates. The physical properties of polarizability and molecular connectivity were found to provide an excellent measure of both the electronic and structural properties of an adsorbate molecule. Table VI illustrates the equations used to obtain these values. Table VII shows how polarizability and connectivity values are determined.

Linear regression data, focusing on the predictive model, for Carbotrap and eight classes or organic compounds are listed in Table VIII. Secondly, the linear regression data focusing on the eight specific adsorbates, previously mentioned, for the adsorbents Carbotrap, Tenax, and XAD-2, are illustrated in Table IX. The data indicates that tighter correlation is obtained when utilizing a Class I adsorbent, such as Carbotrap.

The utilization of the predictive model is illustrated using two adsorbates: ethylbenzene, and 2-chloroethanol. Table X compares the predicted retention volume versus the experimentally obtained retention volume. Both predictions were made with > 98% confidence.

The predictions of solvent desorption of the adsorbate from the Carbotrap surface are based on knowledge of miscibility of the desorbing solvent and the adsorbate and on the surface saturation of Carbotrap. Table XI illustrates the desorption efficiency data for eight key adsorbates, using carbon disulfide and acetonitrile as the desorbing solvent, and the desorption efficiency data for C4-C8 aliphatic amines utilizing ethanol as the desorbing solvent. Predictions of thermal desorption are a function of the thermal energy requirements necessary to greatly decrease the London (dispersion) forces, assumed by the adsorbate and adsorbent. Table XI also lists thermal desorption efficiency values for the eight key adsorbates mentioned previously.

Carbotrap, a Class I non-specific adsorbent, effectively adsorbs and subsequently desorbs a wide range of organic contaminants, allowing analysts to sample at predetermined sampling volumes based upon known adsorbate molecular characteristic data. This predictive mode eliminates the need to choose specific adsorbents for specific adsorbate monitoring.

REFERENCES

1. Kiselev, A.V., and Yashin, Y.I., "Gas Adsorption Chromatography," Plenum Press, NY, 1969, 11-16.

2. U.S. EPA, "Characterization of Sorbent Resins for Use in Airborne Environmental Sampling" EPA document # 600/7-78-054, 1978.

TABLE I

Classification of Molecules and Adsorbents
by Capacity for Nonspecific and Specific Interaction (1)

Molecules	Adsorbents		
	Type I without ions or active groups	Type II with localized positive charges	Type III with localized negative charges
Group A: with spherically symmetrical shells or σ-bonds	Nonspecific interactions governed mainly by dispersion forces		
Group B: electron density locally concentrated on bonds or links, π-bonds			
Group C: with positive charge localized on peripheral links	Nonspecific interactions	Nonspecific + specific interactions	
Group D: with functional groups having locally concentrated electron density and positive charge on adjacent links			

(1) Kiselev, A.V., and Yashin, Y.I., "Gas Adsorption Chromatography," Plenum Press, NY, 1969, 11-16.

TABLE II

Physical Properties of Adsorbents

	Carbotrap	Tenax G.C.	XAD-2
Surface area (m^2/g)	100.0	23.5	364.0
Particle size (u) mesh size	20/40	35/60	20/40
Density (g/ml)	0.38	0.14	0.38
Pore volume	--	0.053	0.854
Bed weight (g)	0.4637	0.1650	0.3966
Total surface area	46.37m^2	3.878	144.4

TABLE III A

Specific Retention Volume (V_g^t)(20) Equation (2)

$$V_g^t = \frac{\text{ml of gas}}{\text{grams of adsorbent}} = \frac{\text{Calculated volume of gas passing through the system}}{\text{weight (grams) of adsorbent}}$$

$$= j\,F_c\,\frac{(t_r - t_a)}{W_a}$$

= breakthrough volume

TABLE III B

Adsorption Coefficient (Ka) Equation (2)

$$K_a = \frac{V_g^t}{A^\circ_s\,R}\,T_k$$

Where: A°_s = Surface area of sorbent (m^2/g)
T_k = Temperature in °k
V_g^t = S.R. Volume (ml/g)
R = 6.3×10^4ml-mm/mole-°k

TABLE III C

Equilibrium Sorption Capacity (Qg) Equation (2)

$$\frac{C_g = k_a\,A_s\,C_g\,(760\text{mm } H_g)\,(\text{MW sorbate})}{10^\circ}$$

Where: C_g = Gas phase concentration of sorbate in ppm (vol./vol/ = vl/L)
MW = Molecular weight of adsorbate

(2) U.S. EPA, "Characterization of Sorbent Resins for Use in Airborne Environmental Sampling" EPA document # 600/7-78-054, 1978.

TABLE IV

Specific Retention Volumes (V_g^t)(20)
for Carbotrap, Tenax and XAD -2

Adsorbate	V_g^t (20°C) (ml/g)		
	Carbotrap	Tenax	XAD-2
n-Decane	4.79×10^9	1.56×10^7	3.36×10^7
Benzylamine	2.23×10^7	3.57×10^6	1.63×10^7
Chlorobenzene	1.58×10^6	1.51×10^5	4.84×10^5
p-Xylene	4.24×10^7	3.88×10^5	7.95×10^6
p-Cresol	2.06×10^7	1.50×10^7	4.96×10^6
n-Pentanoic Acid	4.31×10^5	9.78×10^5	1.01×10^5
Cyclohexanone	2.04×10^6	1.06×10^6	6.27×10^5
2-Methyl-2-Propanol	6.52×10^3	6.86×10^2	5.42×10^3

TABLE V

Specific Retention Volumes for 38 Adsorbates

COMPOUND	V_{tg} (20) (ml/g)	CORR. COFF. LIN. REG. PLOT
Ethane	1.73×10^{1}	1.00000
n-Propane	5.49×10^{1}	0.99412
n-Butane	4.06×10^{2}	0.99875
Ethanol	4.93×10^{2}	0.99219
Acetic Acid	7.16×10^{2}	0.99690
Propionic Acid	1.66×10^{3}	0.98410
1,2-Dichloroethane	1.94×10^{3}	0.99848
2-Butanone	3.76×10^{3}	0.99611
n-Pentane	5.89×10^{3}	0.99940
2-Methyl-2-Propanol	6.52×10^{3}	0.98650
Benzene	1.17×10^{4}	0.99802
1,1,2-Trichloroethylene	1.27×10^{4}	0.99939
n-Butanol	1.92×10^{4}	0.99643
1,1,2-Trichloroethane	2.47×10^{4}	0.99986
n-Hexane	7.99×10^{4}	0.99871
n-Pentanoic Acid	4.31×10^{5}	0.97190
Phenol	6.16×10^{5}	0.99941
Toluene	6.50×10^{5}	0.99972
Chlorobenzene	1.58×10^{6}	0.99990
Cyclohexanone	3.04×10^{6}	0.99581
n-Butylamine	2.08×10^{6}	0.99935
4-Heptanone	2.44×10^{6}	0.99991
Dichlorobenzene	1.34×10^{7}	0.99925
n-Octane	1.61×10^{7}	0.99989
Ethylbenzene	2.03×10^{7}	0.99989
p-Cresol	2.06×10^{7}	0.99948
Benzylamine	2.23×10^{7}	0.99990
p-Xylene	4.27×10^{7}	0.99963
Acetophenone	6.40×10^{7}	0.99971
Isopropybenzene	1.70×10^{8}	0.99999
n-Propylbenzene	1.72×10^{9}	0.99993
n-Decane	4.79×10^{9}	0.99971
n-Butylbenzene	5.83×10^{9}	0.99937
Biphenyl	3.74×10^{12}	0.99999
n-Hexylbenzene	7.00×10^{12}	0.99989
n-Dodecane	1.63×10^{14}	0.99903
n-Octylbenzene	1.31×10^{15}	0.99985
n-Tetradecane	8.32×10^{16}	0.96309

TABLE VI

Descriptor Calculations

Polarizability

$$a = 0.396R$$

$$R = \frac{n_r^2 - 1}{n_r^2 + 2} \quad \frac{MW}{d}$$

Where: R = Molar refraction
n_r = Refractive index
MW = Molecular weight (grams/mole)
d = Density (grams/cc)

Molecular Connectivity

(1) Assign valence values to each atom (discount the hydrogen atoms).

(2) Designate each bond in the molecule.

(3) Multiply the valence numbers of each atom involved in each bond.

(4) Take the reciprocal square root of the value obtained in Step 3.

(5) Add the individual values obtained in Step 4 to obtain the molecular connectivity value.

TABLE VII

Example of Predictive Model

n-Pentane

Polarizability (α)

n_r = 1.3575
d = 0.6262
MW = 72.0

Therefore:

$$R = \frac{(1.3575)^2 - 1.00 \quad 72.0}{(1.3575)^2 + 2.00 \quad 0.6262}$$

$$a = 0.3964R$$

and $a = 10.0$

Molecular Connectivity (a) (χ)

C --C --C --C --C Where: a, b, c, d are the bonds

$$a = \frac{1}{(1.2)1/2} = 0.707$$

$$b = \frac{1}{(2.2)1/2} = 0.500$$

$$c = \frac{1}{(2.2)1/2} = 0.500$$

$$c = \frac{1}{(1.2)1/2} = 0.707$$

Total = 2.414 = x value for n-pentane

TABLE VIII

Carbotrap Linear Regression Data

Adsorbate Class	Correlation Coefficient
Aliphatic hydrocarbons	0.99604
Aromatic hydrocarbons	0.98414
Alcohols	0.99750
Chlorinated hydrocarbons	0.99162
Ketones	0.99210
Organic acids	0.99130
Organic amines	1.00000 (2 adsorbates)
Total	0.98362

TABLE IX

Comparative Linear Regression Data

Adsorbent Resin	Physical Descriptor	Correlation Coefficient
Carbotrap	α x χ	0.95016
Tenax G.C.	α x χ	0.67481
XAD-2	α x χ	0.84596

TABLE X

Illustration of the Predictive Model

Ethylbenzene

1. (a x x) value = 55.59

$$\text{Log } (V_g^t) = \underbrace{(0.0878)}_{\text{slope}} \underbrace{(a \times x)}_{(x)} + \underbrace{2.3211}_{\text{y-intercept}}$$

$$\text{Log } (V_g^t) = (0.0878)\ (55.59) + 2.3211$$
$$= 7.2019$$

$$V_g^t = 1.59 \times 10^7$$

from experimental: $V_g^t = 2.02 \times 10^7$

2-Chloroethanol

1. (a x x) = 11.6

2. The predictive model equation is:

$$\text{Log } (V_g^t) = (0.0878)\ (a \times x) + 2.3211$$
$$= (0.0878)\ (11.6) + 2.3211$$
$$= 3.34$$

$$V_g^t = 1.09 \times 10^3$$

from experimental: $V_g^t = 0.87 \times 10^3$

TABLE XI

Desorption Efficiency Data

Adsorbate	% Desorption Efficiency		
	Solvent		Thermal
	Acetonitrile	Carbon Disulfide	
n-Decane	100		111
Chlorobenzene	93		113
n-Pentanoic Acid	110	103	111
Benzylamine	108		109
Toluene	102		111
2-Butanone	108	109	105
1-Butanol	106	102	116
2-Ethoxyethylacetate	104	102	109

DEVELOPMENT OF DATA QUALITY INDICATORS FOR TOXIC AIR POLLUTION MEASUREMENTS

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Traditional approaches to assessing the quality of data produced from air pollution measurements have utilized data quality indicators, which are generally quantifiable. These data quality indicators include precision, accuracy or bias, completeness, representativeness, and comparability. The determination of such data quality indicators is achievable through the use of standard reference methods and certified reference materials. The emergence of toxic air pollutants as a potentially significant environmental issue suggests that traditional approaches to determining the quality of such measurements may not be effective or appropriate since standard measurement methods and materials may not always be available. Agency researchers are confronted with new measurement problems unlike those encountered with conventional ambient or point source air pollution measurements. This has led to the development of new measurement methods for individual chemical species heretofore not addressed separately in sampling or analysis. These species include inorganic as well as organic chemicals. Since the characterization of toxic air pollutants cannot wait for individual methods development work to be completed, conventional measurement technology must be adapted. In like manner, traditional data quality indicators must be adapted to describe the unique attributes associated with the sampling and analysis of toxic chemical species.

DEVELOPMENT OF DATA QUALITY INDICATORS FOR TOXIC AIR POLLUTION MEASUREMENTS

Traditional approaches to assessing the quality of data produced from air pollution measurements have utilized data quality indicators, which are generally quantifiable. These data quality indicators include precision, accuracy or bias, completeness, representativeness, and comparability. The determination of such data quality indicators is achievable through the use of standard reference methods and certified reference materials. The emergence of toxic air pollutants as a potentially significant environmental issue suggests that traditional approaches to determining the quality of such measurements may not be effective or appropriate since standard measurement methods and materials may not always be available. In addition, the broad nature of the toxic air pollution problem makes the application of existing methods uncertain in the absence of documented method performance for toxic substances, which may be gas or particulate matter and may be present due to a routine or accidental release.

U. S. Environmental Protection Agency policy requires that each data collection activity conducted by or in behalf of the Agency shall have the quality of the data documented.[1] The documentation is to be based on data quality indicators. In the emerging environmental problem area of air toxics, Agency researchers are confronted with new measurement problems unlike those encountered with conventional ambient or point source air pollution measurements. These problems have led to the initiation of research to develop new measurement methods for individual chemical species heretofore not addressed separately in sampling or analysis. These species include inorganic as well as organic chemicals. Since the characterization of toxic air pollutants cannot wait for individual methods development work to be completed, conventional measurement technology must be adapted. In like manner, traditional data quality indicators must be adapted to describe the unique attributes associated with the sampling and analysis of toxic chemical species.

This paper will discuss general approaches for developing or adapting data quality indicators for toxic air pollutants measurements, including gaseous organic chemicals and airborne particles, and the quality assurance limitations or uncertainties associated with such measurements. The focus will be on current methods being employed in the EPA engineering R&D program directed at toxic air pollutant control and will provide guidance on test program design, Quality Assurance Project Plan preparation, and the selection of appropriate data quality indicators. It will not be possible, however, to cover such a broad scope in great detail. Instead, we shall attempt to lay out a road map for those involved in air toxics measurements to follow and to raise the level of awareness for the difficulties in applying quality assurance and quality control to such measurements. Definitive conclusions, which may be applied to every measurement activity, will be few in number because the air toxics problem does not yield simple solutions. There will be several recommendations for improving our understanding of the problem and our confidence in the quality of our measurements.

Nature of the Air Toxics Problem

Toxic air pollutants have been defined generally as virtually any substance released into air media that may pose an exposure risk to human population. By such a definition, toxic air pollutants also include air quality criteria pollutants, which are currently being regulated. The sources of toxic air pollutants are widely varied and include traditional air pollution sources, such as chemical plants and metallurgical processes, as well as

non traditional sources now being identified in indoor air environments, such as passive tobacco smoke and radon from soil gas. The exposure pathways for the human population are equally diverse, including industrial process accidents such as that which occurred in Bhopal, India, and the routine release of chemicals into the atmosphere as part of the normal operation of countless human activities.

The diversity and uniqueness of the sources of toxic air pollutants make the quantitative assessment of the nature and magnitude of existing and future air toxics problems difficult. A more systematic examination of the problem yields the categorization of air toxics into routine releases, accidental releases, and indoor air quality. These categories are defined formally in Table I.

The nature of each category and the public perception of each varies. For example, each category may differ in the type (e.g., acute, chronic) of exposure most commonly encountered. Accidental releases contribute to acute exposures of the human population generally and indoor air quality to chronic exposures. Nevertheless, there are several cross-cutting factors that may affect all three areas. These include a lack of adequate data to completely assess the problem and uncertainty about the adequacy of current methodology for sampling and analysis.

The routine operation of many industrial and energy processes may contribute to human risk due to the normal discharge of toxic materials to the air. Such routine releases may produce both acute and chronic effects, depending on the quantity of material released and its toxicity. The situation is further complicated in that some materials may not have significant toxicity when emitted, but may react chemically with other substances in the ambient air to produce toxic materials. Moreover, the number of potentially toxic chemicals is extremely large. Over 65,000 industrial chemicals have been listed as having been in commercial production since 1945, many of which may be found to be toxic in relatively small concentrations.

The impact of air toxics emission from routine releases is not understood clearly. In some situations, localized exposure to relatively low concentrations of toxic substances may have been regarded as innocuous from the perspective of acute health effects, but buildup of the substance in the food chain or in tissue and organs may lead to chronic effects. Occupational health data are just now emerging indicating that many current ailments and deaths may have been attributable to exposures to chemicals, which 25 to 30 years ago were presumed to be safe. Furthermore, an insidious aspect of this problem is the potential transport of these substances to other areas. While the highest exposures have been found to occur near large industrial point sources, emissions have been shown to disperse rapidly downwind to affect areas not in the immediate vicinity of the problem. Direct emission of toxic substances alone is only part of the problem. Atmospheric transformation of toxic precursors may pose significant risk to the public as well.

While routine releases of air toxics may originate from almost any human activity, the growth of ambient air toxics stems principally from the growth of this country's industrial economy. Control and mitigation strategies, employed since the early 1970s for criteria pollutants, have also reduced somewhat the air toxics problem for traditional large sources, but smaller, more widely dispersed industrial, commercial, and private source emissions may contribute as much as 75% of the total air toxics cancer incidence. In fact, there are indications that the greatest contributor to

air toxic cancer risk may be combustion products from mobile sources (e.g., automobiles, light duty trucks) and small stationary sources (e.g., home heating).[2] Other, less generally recognized sources of air toxics include wastewater treatment systems (e.g., gas stripping, aerators, flocculators) and solid waste disposal systems (e.g., incinerators).

The accidental release of toxic chemicals into the air is a problem from the perspective of both prevention and emergency preparedness. The ability to successfully deal with this problem depends on an understanding of the true extent of the problem, its causes, the risks it poses to human health and the environment, and an understanding of all current measures to address it. The memory of the accidental release of methyl isocyanate (MIC) in Bhopal, India, and the subsequent deaths of more than 2000 people, is still fresh. Shortly after Bhopal, a similar, but more limited, release occurred in Institute, West Virginia, which produced no fatalities, but led to the evacuation of a number of people living in the immediate vicinity of the plant. Both incidents served to illustrate the inadequacy of some current prevention techniques and emergency preparedness measures.

As is the case with routine releases, few data are available on the effects in the ambient air, both in terms of individual chemical species and mixtures of chemicals in which complex interactions may occur to produce other toxic species. However, data are available on the health effects of some chemicals. In particular, chemicals, which must be registered or have their use approved under legislated authorities issued to government agencies (e.g., FDCA, FIFRA), generally have some health effects data available. Just how relevant such data may be to the ambient environment is not certain.

The emergence of indoor air quality as an environmental concern represents a departure from traditional concerns, yet even the limited data now available suggest that indoor air pollution may pose a greater human health risk than toxics in the ambient air. Many of the same toxic substances found in the ambient air may also be found inside buildings, and sometimes at the same or higher concentrations. Federal, State, and local health authorities are being called upon with increasing frequency to investigate perceived indoor air quality problems, and public awareness of indoor air problems, particularly in regard to radon from soil gas, is very high.

The indoor air environment presents a unique microcosm of the ambient environment that appears to be considerably more complex than the outdoor environment. The exposure to toxic materials may be acute in some cases, like radon and its progeny (or products of radioactive decay), but it is generally regarded as being more chronic. The critical aspect of the debate on whether ambient toxics or indoor toxics pose the greater health risk may be consideration of the fact that most people spend more time inside a home or building than they do outside in the ambient air. One study for the Electric Power Research Institute suggests that people may spend as much as 80-90% of their time indoors.[3]

The causes of indoor air quality problems are many-fold, but a clear cause is the trend to better insulated, "tighter" buildings and homes to improve energy efficiency.[4] It has been found that reduced ventilation is a very effective means of reducing energy costs. In the case of homes, ventilation is the means by which indoor air pollutant concentrations are generally reduced. Most ventilation occurs naturally through open windows. When windows are closed in the heating and cooling seasons, homes are ventilated only by infiltration, or unintentional leakage of air through cracks around windows and doors and leaks in the building frame, driven by a wind-created partial vacuum around the house and indoor/outdoor temperature

differences. This enables toxic pollutants in the ambient air to enter the home and remain for long periods due to infrequent air exchanges. This will add to the pollutant concentrations contributed by indoor sources. The same applies to office buildings and other non industrial buildings where energy conservation efforts have largely reduced air exchange rates significantly.

Thus, the scope of the air toxics problem covers all potentially hazardous materials that may impact human health through airborne transmission. The measurement of air toxics involves virtually all types of currently used air sampling methods. In most situations, the quality assurance/quality control (QA/QC) techniques will be unchanged, but the measurement activity in terms of classic data quality indicators may be difficult to document. To place the problem in the perspective of data quality, it is necessary to discuss the traditional data quality indicators and then place them into the context of air toxics measurements.

Traditional Approaches to Data Quality Indicators

Traditional indications of data quality include precision, accuracy (or bias), representativeness, completeness, and comparability, which are often abbreviated PARCC. Consequently data quality objectives have been expressed in terms of PARCC, which are defined in Table II. It is EPA policy that all measurement related activities will have their data quality objectives documented in a Quality Assurance Project Plan. That is, a written plan must be developed that will set forth the objectives or criteria by which the quality of the technical results will be judged. In this way, the QA Project Plan may be utilized to develop a test program with the necessary quality checks to ensure that the data generated are defensible and are adequate for the original intended use of the data.

The intended use of the data is the key criterion from which all data quality criteria or objectives are derived. For most routine measurements, the state-of-the art methodology is such that data quality indicators (e.g., PARCC) may be readily determined. For air toxics measurements, the applicability of PARCC as data quality indicators is not so clear. The susceptibility of these measurements to external perturbations may make the specification and determination of PARCC values difficult.

For example, some air toxics exist in the form of particulate matter. It has been shown that precision and accuracy are often difficult to determine for particle size measurements.[5] Precision presumes that sampling or analysis conditions be relatively well-defined. Accuracy requires that a known "true" value be available in the form of a standard reference material (SRM) or, more importantly, a Certified Reference Material (CRM). An SRM is a sample of the species of interest in which a known amount is present. A CRM is similar, but it has been carefully assayed and documented by a qualified organization, such as the American Society of Testing Materials or the National Bureau of Standards.

Traditional data quality indicators are frequently associated with Reference Methods, such as EPA Method 5, for total particulate matter determination. Such methods have been tested thoroughly in numerous validation and verification activities, and are well documented in terms of the expected performance of the method (e.g., precision, comparability). The same applies to reference methods developed for chemical analysis in which expected performance data may also be well documented. Even where reference methods are not available, the use of Standard Operating Procedures (SOPs) will frequently yield documentable data quality performance.

In these discussions, some of the data quality indicators (i.e., precision, accuracy, comparability) have been discussed from the perspective of how each pertains to a "standard," either a standard method or reference material. The two remaining indicators, representativeness and completeness, pertain more to the adequacy of the test design. The key to success here lies in adequate study and planning of the test procedure; for example, the technical objectives, the intended use of the data, consideration of outside influences that could adversely impact the data. A good understanding of the nature of the source and the technical objectives of the measurements will enable realistic objectives for representativeness and completeness to be defined.

As noted above, data quality indicators are utilized to establish the data quality (i.e., QC) objectives for the test activity. These objectives establish the quality expectations of the measurement results necessary to satisfy the intended use of the data. That is, how "good" the data have to be in order to have adequate confidence that the technical objectives have been met. These QC objectives, therefore, become the measure of success for the quality of the measurements. When the testing has been done, the quality control results may be compared to the QC objectives to determine how successful the QC techniques were. In this way, the data quality achieved may be evaluated in the context of the original QC objectives. Since measurements are not always performed flawlessly and since unplanned problems may occur, the data quality indicators are helpful in assessing the value of the product data.

Traditional data quality indicators (i.e., PARCC) are used routinely in criteria pollutant programs. With the exception of particle size measurements, measurements for criteria pollutant programs are well-defined and usually supported by the availability of reference methods and certified reference materials. In the case of air toxics, the problem becomes much broader and the applicability of traditional QA/QC techniques must be re-examined.

Applicability of Data Quality Indicators to Air Toxics Problems

Since air toxics can include virtually any potentially hazardous material, either gas or particle, the measurements problems, and, consequently, the QA problem, becomes magnified. Considerable work has already been done to address the air toxics measurement problem, primarily by adapting existing techniques. Since a large fraction of air toxics substances are organic chemicals, efforts to reliably collect, extract, and analyze these substances have increased.[6] Also, some air toxics, particularly metals, exist as particulate matter in the ambient air. The QA problems associated with particle size measurements have been documented.[5] Since the sampling methodology is independent of the chemistry of the particle, the QA concerns apply to all particulate air toxics. The most significant concerns are the lack of a reference method for particle size measurements and the inability to reliably redisperse standard aerosols to check the accuracy of the existing measurements.

In general, it may be said that the lack of standard reference methods and materials constitutes the biggest problem for air toxics QA. There are, however, things that can be done to reduce the impact of the problems. First of all, routine releases and accidental releases are the ones most like traditional criteria pollutant measurements from the standpoints of the types of sources, the phase (gas or particle) of the sample, etc. Clearly, added safety measures need to be employed in some situations, but the sampling and analysis methodology are largely unchanged. That is, samples are collected,

good sample custody procedures are followed, the samples are analyzed, and the results are determined. The impact of the data quality may be increased depending on the known certainty in the method performance and the availability of a known value to check that performance. The use of SOPs will greatly reduce the uncertainty in the results. This recognizes that while SRMs are not as definitive or defensible as CRMs, they are, when properly prepared, excellent tools to document the quality of the method.

In the case of indoor air quality, the applicability of existing measurement techniques is less clear because this is a relatively new environmental concern and measurement technology is still emerging. The sources of indoor air toxics, as noted earlier, are varied in nature and are clearly non traditional from the standpoint of the Agency's historical perspective, especially in the cases of radon from soil gas and passive smoke from tobacco combustion. Measurements methodology research is increasing for both organic and inorganic chemical species.[7] The focus, however, has been on vapor-phase organics.

At present, no reference methods are specifically approved for indoor air toxics measurements. While CRMs exist for a number of organic carcinogens and pesticides, no CRMs are currently available that reflect the mixture of compounds that may be found typically in the indoor air environment. Thus, the uncertainty associated with the quality of indoor air may be greater than that for routine or accidental releases.

In order to quantitatively assess the applicability of the traditional data quality indicators to air toxics measurements, it is necessary to examine each PARCC component individually. At the same time, the limitations and needs can be highlighted.

Precision

While there are a number of methods with potential applicability to air toxics, most are untried or unproven for the wide range of chemical species found in the air toxics arena. Furthermore, many methods are unproven at the low concentrations typically found in the indoor air environment and, in some cases, in the ambient outside air due to routine releases. Caution must be used in applying these methods until such time as additional research can document their performance. If the Agency pursues a strong regulatory air toxics program, then additional reference methods may be required to ensure compliance. In the short term, more effort is needed to document and improve the precision of existing and emerging methods.

Accuracy

Accuracy determination depends on the availability of a "true" value. While CRMs (and SRMs) exist for many compounds, the breadth of the potential air toxics inventory (more than 60,000 chemicals) underscores the need for additional reference materials. The use of standard reference materials should be mandatory, but the appropriate organizations can be encouraged to expand the available inventory of CRMs. Again, this is very important for enforcement considerations, should they become necessary.

Also, the difficulty associated with determining the accuracy of particle size measurements cannot be understated. In such cases, a quantitative measure of accuracy will not be possible, but the careful, comprehensive documentation of the test activity, including the QC techniques employed, will help to give a semiquantitative or qualitative assessment of the data quality achieved.

Representativeness

Representativeness may be particularly difficult to determine for air toxics. The possibility of interferences from chemical transformations in the air toxic "soup" is high. This may be countered somewhat by increasing the available knowledge about the source, but such may not be practical during early source characterization efforts. Moreover, it may be risky to view representativeness as having a broad application beyond that of a specific source. That is, the complexity of the air toxics problem may allow samples to be representative of a unique source and not of a larger population of sources. Representativeness must be defined in terms of the intended use of the data.

Comparability

As just described above, the uniqueness of air toxics sources may make meaningful comparability determinations difficult. Again, it is necessary to have a good understanding of the nature of the source and the intended use of the data in order to define comparability requirements.

Completeness

Completeness is the PARCC component least affected by air toxics application. The principle is unchanged: collect enough valid data to ensure confidence in the quality of the results. This must be done in the planning stage, and it must include an awareness of the method and its limitations, and the intended use of the data.

Summary

Traditional data quality indicators may be used in many instances to describe air toxics measurements, but there will be situations in which a more qualitative discussion will be needed. In every situation regarding air toxics measurements, the intended use of the data should be the driving force for the data quality indicators. In the long term, additional reference materials and reference methods will be needed to adequately document the data quality for air toxics measurements. In the short term, the adaptation of existing methodology to air toxics problems and the emergence of new methodology must be examined meticulously from a data quality perspective to ensure that adequate quality documentation is achievable. The applicability of traditional data quality indicators in this short term may be difficult to accomplish. It may be necessary to provide expanded narrative documentation in order to convey to the user of the data an adequate confidence in the data themselves.

These principles apply equally to the full scope of air toxics emissions: routine releases, accidental releases, and indoor air quality. Methods differ and sources differ, but the measure of the data quality adequacy remains unchanged. As our knowledge and understanding of the air toxics problem grow, our ability to document and defend air toxics measurements will grow as well.

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TABLE I. Air Toxics Categories and Definitions

Routine Releases	Emissions to the ambient air that occur as part of the normal operation of human activities, such as the operation of an industrial process in which an exhaust gas is discharged to the atmosphere.
Accidental Releases	Emissions to the ambient air, which occur as an unplanned discharge, such as the rupture of a storage tank or a process upset.
Indoor Air Quality	Ambient air inside a building or home as opposed to the outside air.

Table II. Definition of Traditional Data Quality Indicators

Precision	A measure of the mutual agreement among individual measurements of the same property, usually under prescribed similar conditions.
Accuracy	The degree of agreement of a measurement (or an average of measurements) of a parameter with an accepted reference or true value.
Representativeness	The degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.
Completeness	A measure of the amount of valid data obtained from a measurement system in terms of the amount that was expected to be obtained.
Comparability	A measure of the confidence with which one data set can be compared to another.

INDEX

A

Adsorption
71, 275, 882
Aerosol
95, 287
Afterburners
230
Agencies
627
Air Exchange Rate
86
Air Flow
239
Air Toxics
351, 385, 513, 893
Aircraft Measurements
375
Alkalinity
615
Ambient Monitoring
176,205,326,330,335,364,431,442,
476,522,554,594,627,764,834,845
Ammonium Sulfate
865
Analytical Methods
36, 467, 522, 534, 639, 748
Aqueous Extraction
615, 701, 856
Artifact
71, 615
Asbestos
12
Atomic Absorption
817
Automation
275, 764, 865

B

Back Trajectories
304
Benzo(a)pyrene
554
Bias
627
Bioassay
1
Blind Samples
627
Boron
304
Building Materials
86

C

Cadmium
817
Canister-Based Sampling
402, 431
Carbon Monoxide
736
Case Study
755
Catalyst
780
Certification Standards
724
Charcoal
71, 674, 764
Chemical Mass Balance
500
Chlorinated Compounds
156
Chlorine
701, 804
Collocated Sampling
522
Comparative Data
419
Computer Applications
275, 467, 488
Conversion
304
Cost
639
Cryogenics
385, 431, 442

D

Data Logger
724
Data Bases
128
Denuder
156, 522
Deposition
304, 856
Detection
651, 780
Detector Tube
95
Diesel Exhaust
250
Dioxin
239, 554
Direct Measurement
834, 845
Dry Purge
674

E

Electron Microscopy
534
Emergency Response
330

Emerging Technology
1
Emission Factors
128
Estimation
513
Ethylene Oxide
755
Evaluation
156, 217, 817
Exposure Study
458, 513
Extractive Sampling
574

F

Fabric Filtration
205
Field Evaluation
146, 402, 713
Field Study
522
Flue Gas
574
Flux Chamber
662
Fog
168
Furans
554

G

Gas Chromatography
71, 287, 314, 326, 330, 335, 385
467, 476, 674, 780, 826
Gasoline
385, 458
Germany
230
Glass Beads
71

H

Halogens
701
Hazardous Air Pollutants
230
Hazardous Chemicals
651
Hazardous Emissions
662
Hazardous Waste
574, 639, 662
Hazardous Waste Fuel
701
Health Effects
351, 513, 826
Hexachlorobenzene
156
Hi-Vol Filters
615
HPLC Analysis
259, 269
Hydrocarbons
335, 375, 419, 500, 780
Hydroxyl Radical
500

I

In situ Sampling
724
Incineration
230, 542, 574
Indoor Air Quality
1, 36, 45, 86, 104, 116, 128, 736
893
Industrial Emissions
351
Industrial Waste
230
Information Systems
128
Information Theory
476
Instrumentation
239, 275, 542, 834
Integrated Air Samples
431
Intercomparison
45, 522
Ion Chromatography
701

L

Light Absorption
845
Linearity
780

M

Manufacturing
351
Mass Spectrometry
467, 476, 594, 674, 817
Maximum Allowable Concentration
95
Measurement Methods
1, 16, 275, 755, 792
Memory Effect
71
Metals
554
Method Development
792
Methylene Chloride
826
Microorganisms
36

Mist
574
Mixtures
467
Mobile Laboratory
594
Models
304, 882
Molecular Characteristics
882
Multi-City Study
419
Multivariate Data
488
N Network Design
176
New Jersey
351
Nitro-PAH
259, 269
Nitrogen Compounds
522, 875
Nitrogen Dioxide
61, 834, 845
Non-Steady State Processes
755
Noncriteria Pollutants
335, 804
Nonindustrial Boiler
701
Nonmethane Organic Compounds
375, 419, 431, 442, 458
O Odors
351, 594
Office Environment
36
Oregon
713
Organics
86, 134, 168, 287, 431, 476, 554, 639
Orifice Meter
239
Oxalic Acid
875
P Particle Distribution
168
Particulates
250, 259, 269, 287, 522, 542, 724
736, 856
Passive Sampling
61, 275
Passive Smoking
16, 25
Pattern Recognition
476
PCBs
205, 554
PCDDs
217
PCDFs
217
Performance Testing
12, 627, 724
Pesticides
168
Petroleum Refineries
500
Phase Distribution
146
Philadelphia
335
Photochemistry
287
Phthalates
554
PM-10
792
Polycyclic Aromatic Hydrocarbons
146, 250, 304
Polyurethane
205
Potassium
748
Precision
442, 627, 780
Products of Incomplete Combustion
674
Programmable Sampler
724
Pulp Bleaching
804
Purge and Trap
674, 764
Q Quality Assurance
364, 522, 893
Quality Control
176
Quinones
259
R Raman Scattering
651
Real-Time Measurement
542, 594
Receptor Modeling
304, 500

Reduction
780
Reference Methods
780, 817, 893
Residences
104, 116, 128
Residential Heating
713, 736, 748
S Sample Degradation
431
Sample Storage
431
Samplers
61, 156, 176, 217, 275
Sampling
134, 146, 217, 385, 402, 431, 574
Sampling and Analysis
128, 304, 364, 375, 458, 826
Sampling Protocol
36
Sampling Techniques
45
Selenium
304
Semivolatiles
134, 156, 176, 217, 724
Silica Gel
95
Smog
442
Soil
764
Solvents
500, 594, 882
Soot
314
Sorbent
71, 176, 335, 662, 764
Source Characterization
128
Source Measurement
792
Source-Receptor Relationship
513
Spectroscopy
651, 865
Stack Sampling
574, 817
State Implementation Plans
442
Stationary Sources
128, 764, 817, 826
Statistical Analysis
287
Study Design
116
Sublimation Sources
875
Submarine
95
Sulfate
304
Sulfate Ion
856
Sulfur Compounds
522
Supercritical Fluid
250
Survey Analysis
25
Syringe Sampling
275
T Temperature Effects
662
Tennessee
104, 116
Thermal Desorption
71, 287, 314, 335, 351, 764, 882
Three-Dimensional Graphics
488
Threshold Limit Value
95, 594
Toxic Organic Compounds
45
Trace Elements
304
Tracers
304, 748
Transport
304
Trapping System
71
V Validation
764, 792
Variable Wavelength UV Detector
250
Vehicular Emissions
287, 500
Vinyl Chloride
326, 330
Visualization
488
Volatile Organic Compounds
45, 86, 104, 314, 402, 594, 764, 780

Volatilization
134
W Waste Oil
701
Water
764, 856
Wood Stoves
713, 724, 736, 748

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/9-86/013	2.	3. RECIPIENT'S ACCESSION NO. PB87 182713/AS
4. TITLE AND SUBTITLE Proceedings of the 1986 EPA/APCA Symposium on Measurement of Toxic Air Pollutants		5. REPORT DATE April 1986
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) U.S. EPA's Environmental Monitoring Systems Laboratory and Air Pollution Control Association		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency Office of Research and Development Environmental Monitoring Systems Laboratory Research Triangle Park, North Carolina 27711		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS same as (9)		13. TYPE OF REPORT AND PERIOD COVERED
		14. SPONSORING AGENCY CODE EPA/600/08

15. SUPPLEMENTARY NOTES
Published by the Air Pollution Control Association, APCA VIP-7

16. ABSTRACT
A joint conference cosponsored by the Air Pollution Control Association and the Environmental Monitoring Systems Laboratory of the U.S. Environmental Protection Agency, was held in Raleigh, North Carolina, April 27-30, 1986. The technical program consisted of 95 presentations, held in ten separate technical sessions. on recent advances in the measurement and monitoring of toxic and other contaminants found in ambient and source atmospheres.

Presentations included: 1) Measurement of Indoor Toxic Air Contaminants; 2) Measurement of Semi-Volatile and Volatile Organic Pollutants in Ambient Air; 3) Chemometrics and Environmental Data Analysis; 4) Acidic Deposition -- Nitrogen Species Methods Comparison Study; 5) Measurement of Hazardous Waste Emissions; 6) Measurement of Wood Stove Emissions; 7) Source Monitoring; and 8) General Papers Related to Quality Assurance and Particulate Measurements.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Release To Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE