

Proceedings of the 1987 EPA/APCA Symposium on

**MEASUREMENT OF
TOXIC
AND RELATED
AIR POLLUTANTS**

**Proceedings of the 1987
EPA/APCA Symposium on
MEASUREMENT OF TOXIC AND
RELATED AIR POLLUTANTS**

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**PROCEEDINGS OF THE 1987 EPA/APCA SYMPOSIUM ON
MEASUREMENT OF TOXIC AND RELATED AIR POLLUTANTS**

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PREFACE

A joint conference for the second straight year, cosponsored by APCA's TP-6, TP-7, and ITF-2 technical committees and the Environmental Monitoring Systems Laboratory of the U.S. Environmental Protection Agency was held in Research Triangle Park, North Carolina, May 3-6, 1987. The technical program consisted of 124 presentations, held in 13 separate sessions, on recent advances in the measurement and monitoring of toxic and related pollutants found in ambient and source atmospheres. Covering a wide range of measurement topics and supported by 33 exhibitors of instrumentation and consulting services, the symposium was enthusiastically received by more than 650 attendees from the United States and other countries. This volume contains the papers presented. The keynote address to the symposium is also included.

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.

This conference, the seventh in a series arranged each year by the EPA/RTP, but the second as a jointly sponsored conference 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 related pollutants found in ambient and source atmospheres. The growing number of responses to this symposium represents an encouraging step in the enhancement of our current measurement and monitoring capabilities.

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

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THE ROLE OF TOTAL EXPOSURE MEASUREMENT IN RISK MANAGEMENT

KEYNOTE ADDRESS

Vaun A. Newill
Assistant Administrator
Office of Research and Development

I am pleased to open the 1987 Symposium on Measurement of Toxics and Related Air Pollutants sponsored by the Environmental Protection Agency and the Air Pollution Control Association. I looked over the subjects you will be discussing over the next few days, and was impressed by the breadth of coverage and the diversity of topics on measurement systems and approaches, including techniques for ambient air, indoor air, acidic deposition, and source monitoring.

I believe that measurement serves a critical role in environmental protection. If we view the dynamics of the regulatory process as a system, then measurement of environmental conditions is one important "feedback mechanism" by which we can judge the effectiveness of these programs in reducing the concentrations of pollutants that may come into contact with man and the environment. Viewed in this way, the data from measurement systems help tell us how much progress we are making in our efforts to control environmental pollution, and thus provide guidance for us in modifying our approaches to make them more effective. In addition, as we face some new chemicals of concern, measurements of pollutant concentrations help us to identify the sources that need to be controlled.

Let me repeat a metaphor that I have heard from monitoring specialists: one with which I feel particularly comfortable. The process is much like a patient visiting a physician when he suspects he is ill. The physician collects data essential in helping him diagnose the problem and recommending a course of treatment. In environmental regulation, we make similar measurements to characterize problems. Base upon this characterization, we develop a control approach. Finally, we use environmental measurements to monitor our progress in correcting these problems. Clearly, environmental measurements are part of the entire regulatory process.

Existing environmental programs articulate as their goal the protection of public health and welfare. Public health clearly refers to human populations, while public welfare has been interpreted as referring to the nonhuman component of the environment, for example, biota and materials. If we consider the human component of environmental protection, then we need to consider both the concentrations and the manner by which pollutants actually reach people. Questions that are fundamental to estimating the risk of pollutants to the general public are: "How many people are exposed to the pollutant?" "What are the sources of these exposures?" "What are the effects of these exposures?" Often we have ample information about sources but do not really know the degree to which people were

exposed to the contaminants released by these sources. Even if the effects of a pollutant at a given concentration were known, we could not determine the risk to public health, because we could not determine how many people were exposed or to what concentrations. In essence, our lack of adequate exposure data prevents us from completing the risk equation.

For the criteria air pollutants, extensive monitoring programs are maintained to measure pollutant concentrations outdoors. These data have been useful for guiding existing regulatory programs, but it is understood that the data collected by these networks reflect only outdoor ambient conditions that may be quite different from the actual concentrations to which people are exposed. In the 1970's, for example, a number of small-scale personal exposure studies showed that pedestrians walking on downtown streets, bicyclists, and others were exposed to concentrations very different from the levels reported by official monitoring stations. Even poorer correspondence was observed for toxic chemicals between outdoor measurements and personal exposures. These findings helped raised the question: "What do fixed monitoring station data mean in terms of the actual exposures of people?"

In the 1980's, we have begun to make important progress toward finding the missing exposure data needed to complete the risk equation and answer these questions. If personal monitors can be used to measure the exposures of pedestrians walking along downtown streets, then why couldn't the same monitors be deployed to estimate the exposures of the entire population of a city? To measure the exposures of everyone in a city of 3 million persons would be expensive, so a simpler approach had to be found. This search for a better method gave birth to the idea of combining probability sampling with environmental monitoring. If one could measure the exposures of a representative probability sample of the population, say 500 persons, then we then should be able to make inferences about the exposures of the entire population. That was our initial reasoning.

A second requirement was a personal monitor that would be carried easily by every participant. Moreover, we wanted a "smart" monitor -- one that could distinguish between microenvironments such as commuting, home, and work. A year or two of hard work by ORD scientists designing a combined monitor and manually operated data logger and averaging device led to the successful construction of the desired instrument.

These concepts led to the carbon monoxide personal exposure monitoring field studies conducted in the winter of 1982-83. In these studies, a screening telephone survey first was conducted of 5,000 members of a representative random sample of the population of each city. Then, from this first stage sample, a second stage probability sample was selected. Ultimately, EPA collected 712 24-hour CO exposure profiles in Washington, DC, and 900 24-hour CO exposure profiles in Denver, Colorado. Because the 2-lb. personal monitor measured concentrations on a continuous basis and because each person carried a diary, it was possible to relate each person's exposures to their activities and the locations they visited. Since the ultimate goal of the CO standard is to keep most people's blood levels under 2% COHb (carboxyhemoglobin), every participant supplied a breath sample to provide a direct indication of CO body burden. Extensive statistical analyses and publications have resulted from these studies, with numerous findings of importance to the Agency and the field of risk assessment.

The Denver-Washington, DC, carbon monoxide exposure field studies are illustrative of what is called the "direct approach" in the newly emerging

field of total human exposure assessment. These two field studies on CO also demonstrated the Total Exposure Assessment Methodology, or TEAM approach. In a TEAM study, one measures directly a set of target pollutants that come into contact with the individual, regardless of whether they arrive by air, water, food, or skin. For CO, the only route of exposure is by air, so air alone is monitored. For some toxic pollutants, such as chloroform, the exposure routes include air, water, and beverages.

There are four basic ingredients of a TEAM study: (1) a representative probability sample of the population of concern, (2) direct measurement of the pollutant concentrations reaching these people through all relevant media including air, food, water, and skin, (3) direct measurement of body burden, and (4) direct recording of each person's daily activities through diaries.

All components seek to determine, with known accuracy, the frequency distribution of exposures of an urban population. At the present time, the TEAM studies have collected data on the exposures of the population to important toxic pollutants in four states, representing 700,000 persons in seven cities. Additional studies now underway in Baltimore covering volatile organic compounds and in Jacksonville covering pesticides will extend this knowledge data base further. A major TEAM study of particles and toxic metals has been mandated by Congress, and will be underway in FY 1987.

Direct measurement of personal exposure presents serious technical challenges to the measurement community. Personal exposure monitors must be small and unobtrusive, light-weight, quiet, rugged and insensitive to vibration, able to operate reliably in untrained hands for long periods without external power, capable of generating observations of known accuracy, and, ideally, capable of providing continuous data. The technical and scientific difficulties in meeting such demanding criteria will be a serious challenge to environmental measurement specialists. Despite the many formidable technical obstacles to developing personal monitors, a number of successful monitors already have been developed and field tested. Even though some problems remain, notable successes have been achieved in measuring carbon monoxide, volatile organic compounds, and pesticides by personal monitoring. These successes notwithstanding, additional methods development research is needed to develop continuous monitors for nitrogen dioxide, passive carbon monoxide monitors, inhaled (respirable) particles, active and passive monitors for formaldehyde, volatile organic compounds, pesticides, and polycyclic aromatic hydrocarbons and related compounds.

Although the direct measurement approach is invaluable for determining, with known accuracy, the exposures of populations and the sources of these exposures, an alternative approach -- the indirect approach -- can be used to estimate exposures without large-scale field studies. To apply the indirect approach, one needs data on the microenvironments people ordinarily visit and the times people spend there. A microenvironment is a location of statistically homogeneous pollutant concentration, such as CO concentrations in a parking garage. By combining microenvironmental concentrations with human activity patterns, it is possible to calculate exposures. A human activity pattern-exposure model has been developed for CO and has been used successfully to predict the exposure distribution of the population of Denver. Despite success with this one model, no validated exposure-activity pattern models yet exist for any of the other pollutants. Additional research is needed to develop, test, and validate exposure models for toxic chemicals. This could yield the data needed for making reliable risk estimates.

Both the direct approach and the indirect approach have the same goal: to predict the frequency distribution of exposures of the target population. With such a frequency distribution, it is possible to state the proportion of the population above any concentration range. Using these data, for example, a regulatory program can be designed with the goal of maintaining some finite percentage of the population below some target concentration. The data also have important policy implications, because they show that reducing exposures by strategies previously not considered often can be more effective in reducing risk than are conventional regulatory strategies. These studies are showing the greater importance of indoor air and human activities in the exposure equation. For example, recent exposure studies indicate that reducing human exposures to tetrachloroethylene can be achieved more effectively by reducing the contact people have with freshly dry cleaned clothes than by controlling industrial point sources. Similarly, human exposures to benzene may be reduced by reducing the contact that people have with cigarette smoke and gasoline vapors.

These and many more discoveries are emerging from the new data that we have been able to collect as a results of our total human exposure research methodology. For the first time, human exposure to being examined as one integrated whole, considering the relative contributions by air pollutants, water pollutants, food, and dermal contact. As the measurement methods have progressed, we have been able to quantify exposure -- all the sources responsible for exposure -- with a precision previously never thought possible. That quantification process gets extremely close to the individual person whose health we are charged with protecting. Let me illustrate this precision with an example. The new TEAM study of particles currently being planned seeks to measure the frequency distribution of the population to inhaled particles. Thus, it should be possible to determine the fraction of a city's population subjected to an exposure exceeding 100 g/m^3 concentration of inhalable particulate as a 24-hour average during a season. These values can be compared with existing monitoring station readings and with existing standards. Activity pattern-exposure models, when they are developed, can be used to extrapolate these findings to other seasons and other cities. Ultimately, using these models we may be able to estimate the fraction of the U.S. population whose 24-hour average exposure exceed 100 g/m^3 for any 8 a.m. to 8 a.m. period during the year. Such quantitative goals give us a clearer target of the regulatory programs required to protect public health.

All of the total exposure field studies conducted thus far have been alike in one respect: they would not have been possible unless the necessary monitoring systems and techniques were available. Thus, development of suitable monitoring methods must receive priority, since developments in this area provide the basic tools needed for all field surveys.

In closing, I hope I have been able to stress the importance of measurement in the environmental protection process. I have used the example of total human exposure measurement, since the technical demands placed on measurement science are perhaps more demanding here than in other areas. Although such measurements are extremely difficult technically, they provide environmental health programs with critical missing data required for assessment of environmental health risk. Indeed, filling the exposure knowledge gap is likely to have the greatest benefit of any of the components of the overall risk equation in reducing our overall uncertainty about overall risk and the sources of human risk to environmental pollution. If we are to implement a risk-based environmental management approach, then we must establish a stronger link between sources of pollutants and the exposures and effects caused by these pollutants. Environmental and exposure measurements will play a critical role in helping us to established this link.

SEPARATION SAMPLING FOR AEROSOL
AND GASEOUS SEMI-VOLATILE ORGANICS -
AN OVERVIEW and EXAMPLE

Donald F. Adams, Consultant
SW 600 Crestview #2
Pullman, WA 99163

INTRODUCTION. Semi-volatile organic compounds (SVOCs) may be present in the atmosphere as vapors and adsorbed on suspended particulate matter. Junge (1) suggested that most organic compounds in clean air with vapor pressures below 10^{-4} torr exist in the vapor phase and compounds with vapor pressures above 10^{-8} torr exist in the particle phase. The SVOCs generally fall in the vapor pressure range of 10^{-4} to 10^{-8} torr.

The vapor/particle (V/P) partitioning is associated with the vapor pressures of the SVOCs, the size and surface area of the suspended particulate matter, and the chemical composition of the suspended particulate matter, i.e. organic or inorganic, and the ambient temperature. The apparent V/P is defined by the adsorbent-retained to filter-retained ratio (A/F).

How closely A/F represents V/P is not known. Many investigators believe that A/F overestimates V/P due to the loss of SVOCs from the filter-collected particles to the sampled air stream. It is also possible that some of the collected particles may adsorb some vapor from the air samples.

SAMPLING. Even the most sensitive analytical techniques and instrumentation suitable for the low levels of SVO concentrations generally encountered in ambient air samples require preconcentration from the bulk air matrix prior to detection and quantification. Thus it is essential to consider problems associated with available preconcentration techniques before any sampling program is undertaken.

Sampling includes the collection of representative samples from a bulk matrix as well as the sample preparation, handling, and storage prior to the actual analytical measurement. Sampling errors are often large compared with the errors of the measurement process. A valuable rule, suggested by Youden, is: "once the measurement step uncertainty is reduced to a third or less of the sampling uncertainty, further reduction in the measurement uncertainty is of little value" (2).

The significance of this is illustrated by the diminishing return error model in which reducing errors in the most precise error source yields a diminishing improvement in the overall error, Table I.

Table I
Diminishing Return Error Model

E_s/E_m	E_o
1	$1.40 \times E_s$
1.5	$1.20 \times E_s$
2	$1.12 \times E_s$
3	$1.05 \times E_s$
4	$1.02 \times E_s$
7	$1.01 \times E_s$

where: E_o = total error in the final result, E_m = errors contributed by the measurement step, and E_s = errors contributed by the sampling steps.

The question of sample integrity is still of major concern in the determination of atmospheric constituents. The accuracy of the reported data may be limited by the sample, despite significant analytical advances.

The organic components of an air sample may be concentrated by: (a) scrubbing in a gas impinger, (b) cryosampling, and (c) adsorption on a solid or liquid-coated solid.

High-volume filtration has been widely used since about 1971. However, filter-derived samples will not provide a true representation of particle/SVO loadings due to adsorption on collected particles and filter-catch volatilization problems. Thus, high volume sampler systems usually consist of a filter for collecting aerosols, followed by an adsorbent bed or polyurethane (PUF) plug to collect vapors as described below.

In 1967, the use of porous polymer beads such as Porapak Q or S was suggested for the room temperature concentration of volatile halocarbons (3). This eliminated the need for cryotrapping for many hydrocarbons and provided for on-column gas chromatographic (GC) injection. Frankel and Black substituted Tenax GC for Porapak Q in 1976 because of its stability at 375°C, ease of decontamination as compared with Porapak Q, and its rejection of water vapor from the sampled air (4).

PUF plugs were recommended in 1974 for the collection of SVOs (5). Unfortunately, the polyester form of PUF is not inert and dissolves in dilute base. Thus, certain classes of compounds may react with the PUF, be altered, or irretrievably bound (6). PUF plug cleanup prior to sampling is tedious, especially when electron capture detector/gas chromatographic analysis is used. PUF plugs may be used over a wide range of sample flow rates, permitting selection from a range of sampling times and flow rates to obtain samples of the minimum size required for satisfactory analysis.

Important factors in the selection of adsorbents for sampling include: (a) collection selectivity, (b) collection efficiency, (c) recovery efficiency, (d) sample storage stability, (e) analyte breakthrough volumes, (f) temperature stability, (g) chemically inert toward analytes (artifact formation), (h) initial cleanup procedure required, and (i) the influence of pretreatments and air matrix components on the adsorption, desorption, and decomposition properties of the adsorbent.

Several criteria for the evaluation of solid sorbents for the collection of gaseous organic pollutants include the field-spiking of duplicate

sorbent tubes, sample blanks, and spiked tubes given identical sampling and analytical treatment to show contamination and recovery factors (7).

Filter samplers suffer from a variable loss of SVOs from the collected particulate matter. Sample losses vary with the ambient temperature and the sampling time following an elevated fumigation episode during an eight- or 24-hour sampling period because of the continuous and variable loss of the collected SVOs to the sample air stream during the remainder of the sampling period. The temperature effect is very important, since the vapor pressures of SVOs nearly double with each 5°C increase. Whether sample losses or gains predominate depends on how and when these variables change during a sampling period as well as how the vapor concentrations vary during each sampling period. Even with a backup vapor collector, the derived analytical data will not realistically reflect the airborne distributions, although tandem sample collection may efficiently retain both particle and vapor phases.

Unfortunately, practical sampling methods have not yet been devised which eliminate the carry through of vapor initially adsorbed on the filter-collected particles to the backup vapor collector or which eliminate artifact formation during the sampling and sample storage steps.

SEPARATION SAMPLING FOR AEROSOL AND GASEOUS SVOs. Prior to about 1970, separation sampling devices were infrequently used. Aerosols are collected by several methods including filtration, centrifugation, electrostatic precipitation, and impaction. All these techniques suffer from the the above-noted errors.

A recent separation technique uses a adsorbent-coated annular tube or tubes followed by a filter and backup adsorbent cartridge or PUF plug (8).

A FIELD STUDY -- SEPARATION OF AEROSOL AND VAPOR 2,4-D HOMOLOGUES. The following discussion describes a practical situation in which separation sampling is an essential aspect to understanding and reducing the serious economic impact associated with aerosol/vapor 2,4-D herbicide transport from the area of application to nearby and distant, off-target, sensitive crops. To date, this nearly 30-year old problem in south central Washington has not yet been definitively solved despite the numerous field and modeling studies conducted by at least four research groups between 1963 and the present time. It is widely recognized that significant, damaging quantities of aerially-applied herbicide formulations can drift away from the target areas. Lesser quantities of off-target drift results from ground applications. Studies as early as 1972 showed that spray drift losses of 2,4-D from the target area may range from 40 to 75% (9).

Although the direct determination of the vapor/particle (V/P) ratios is not yet possible, some estimates of V/P ratios of 2,4-D homologues have been reported using a low volume rotating disk impactor (RDI) followed by a midjet impinger (10), or an XAD-2 cartridge (11).

A wide variety of 2,4-D homologues have been used to control weeds in wheat. In the early 1960's, high volatile (HV) isopropyl and butyl 2,4-D esters were commonly used in eastern Washington and Oregon wheat growing areas. As 2,4-D injury to off-target crops was documented, HV ester use was banned in Washington state. Low volatile (LV) isooctyl, propylene glycol, and butyl ether 2,4-D esters and non-volatile (NV) acids, salts, and amines of 2,4-D were substituted. However, in south central Washington, 2,4-D injury to the highly sensitive grape crop continues to be documented as recently as 1986 despite the use of LV and NV 2,4-D formulations and changes in commercial application techniques.

HV 2,4-D esters are characterized by fewer than six carbon atoms on the side chain (isopropyl and butyl esters). LV 2,4-D compounds have six more carbon atoms on the side chain (isooctyl esters and higher molecular weight esters). The LV 2,4-D esters are within the 10^{-4} to 10^{-8} torr vapor pressure range representative of the SVOs.

Today, there is still a need to determine the physical and chemical forms of the 2,4-D compounds arriving at off-target, sensitive crops, to provide formulation selection and application measures and constraints to eliminate 2,4-D damage to sensitive crops, and to permit continued use of 2,4-D formulations to control weeds in the surrounding wheat fields.

The 1962 and 1963 field studies of the total airborne 2,4-D-type herbicide compounds in the south central Washington grape vineyards raised many questions concerning the mode(s) of herbicide drift or transport from the surrounding wheat fields to the grape vineyards:

- Is the alleged 2,4-D injury to grapes primarily related to "over-the-fence" drift of aerosol spray droplets from nearby wheat fields?
- Are the 2,4-D aerosol droplets volatilizing immediately after release from the spray nozzles and then being transported to adjacent or distant, off-target receptor sites in the vapor form?
- Is the herbicide subsequently volatilized from the treated crops and field surfaces and then dispersed into the atmosphere as the ambient temperature increases from its minimum during the early morning application hours to the afternoon maximum temperature?
- Is some of the 2,4-D arriving via long distance transport of vapor from distant application sites more than ten miles from the receptor vineyards?
- Is some combination of both modes of transport from target to receptor sites involved?
- Are herbicides sorbed on soil particles and transported from the application site to distant receptor sites via wind-blown dust?
- Is the observed crop damage related to illegal application of HV esters?
- Is the observed crop damage related to legal applications of LV or NV 2,4-D forms?
- Is the observed crop damage related to various combinations of all three volatility classes?

To provide information concerning these questions in 1964, Bamesberger and Adams (10) designed an air sampling device for the differential collection of aerosol and vapor fractions of airborne herbicides. This sampling system consisted of a rotating disk impactor (RDI) for collecting the aerosol fraction down to one to three microns diameter, followed by a midjet impinger to collect the gaseous fraction and the small aerosols which pass through the RDI. The design parameters of nozzle diameter, distance between the nozzle and the impactor plate, and the sampling rate were calculated using conventional impaction theory (12). The RDI was based on a rotary electrostatic precipitator in which sulfuric acid aerosol impinged on a rotating, stainless steel disk washed with a stream of water (13).

Our design sampling rate was 1 L/min and the impactor jet was 0.55 mm diam. placed 2 mm from the rotating impactor disk. The aerosol fraction was retained in n-decane. The RDI was sealed with a press-fit glass cup which also was the reservoir for the n-decane. The sampled air first impinged on the impactor disk rotating at 1 rpm into the small liquid reservoir for the collection liquid. The impacted particles were retained in the collection fluid. A Teflon squeegee removed any adhering particles and

dried the impaction disk surface. This reduced the wetted surface of the disk and minimized vapor collection in the RDI. The air sample then passed into a midget impinger containing n-decane or n-decane/5% aqueous NaHCO_3 .

In 1974, the press-fit glass cup was redesigned with a threaded-seal to reduce n-decane loss during handling and transport from field sampling sites to the analytical laboratory. The midget impinger was replaced with an XAD-2 filter cartridge to simplify field use (11).

The RDI has variable errors similar to those of filter sampling. Gases in the sampled air impinge on the dry surface of the rotating disk and briefly contact the surface of the sample collection fluid, permitting some vapor phase collection in the aerosol collection stage of the RDI. The wetted area of the rotating disk was minimized by placing a Teflon squeegee 1 cm above the collection fluid to remove the collection liquid film from the disk during the remaining 200° rotation of the disk. The squeegee also provides partial separation between the sampled air stream and the main body of the collection fluid, to reduce solvent evaporation and minimize absorption of gases from the air sample.

Limited laboratory studies of the RDI showed that about 25% of the highly volatile isopropyl ester of 2,4-D in a laboratory-generated atmosphere was collected in the RDI (10). About 17% of the slightly lower volatile butyl 2,4-D ester (but still defined as an HV ester) collected in the RDI, Table II (10). The relatively high collection efficiency shown for the isopropyl ester was not considered a serious design deficiency for its intended field use, because isopropyl ester had been banned from use by the Washington State Department of Agriculture, and a ban on butyl ester was under consideration. The LV isooctyl 2,4-D ester would be the most volatile of the legal 2,4-D esters to be applied to the wheat fields. Subsequent field use, however, showed significant concentrations of isopropyl and butyl 2,4-D esters through 1980, more than six years after HV esters were banned in Washington.

Table II
Collection Efficiency for 2,4-D Type Herbicides

Compound	Concn., Range, $\mu\text{g}/\text{m}^3$	Collection Efficiency, %	
		Midget Impinger	RDI
Gaseous	0-100		
Isopropyl 2,4-D		97.0	26.3
Butyl 2,4-D		97.0	17.1
Aerosol	0-200		
Isopropyl 2,4-D		89.0	62.1
Butyl, 2,4-D		85.8	71.2

For comparison, losses have been₃ reported from filters of about 50% for anthracene and phenanthrene (10^{-3} to 10^{-4} torr) to 10 to 35% from fluoranthrene through benzo(a)anthracene (10^{-4} to 10^{-9} torr) (15) which are in the vapor range for SVOs (1).

The following discussion is limited to the 1974 field data because the data represent the most extensive two-stage sampling data available and the greatest incidence of grape injury reported between 1964 and 1976 occurred in 1974.

The cumulative average concentrations for the three volatility classes for these three months show that n-butyl ester was the dominant 2,4-D

compound in the 1974 samples. The RDI collected 52% of the average HV 2,4-D esters found. This compares with the laboratory collection of 26% and 17% for isopropyl and butyl esters, respectively. During late May and early June, 1974, the average butyl ester concentration was 0.60 $\mu\text{g}/\text{m}^3$ and the isopropyl ester was 0.23 $\mu\text{g}/\text{m}^3$ - a ratio of 1:3.5. Using this ratio and the laboratory-determined collection efficiencies for these two esters, an average 24% HV collection would be expected - just under half the observed field collection.

The RDI samples contained only 25% of the total butyl ether and 60% of the PGBE ether 2,4-Ds recorded, with an average of 56% of the total LV esters found (10), less than one would expect if the aerosols were greater than 3 micron diameter.

This wide range of collection efficiencies of the RDI in the field is probably related to several factors including (a) variations in ambient temperatures at the time of spray application and sample collection, (b) distance between the sites of application and collection, and (c) some of the other questions listed above such as the RDI collection of wind blown soil particles, etc.

Unfortunately, sampling with the RDI was discontinued following the 1974 field study, because of sponsors' financial constraints. Field samplings between 1975 and 1980 were conducted with single-stage XAD-2 resin samplers. Although this change in sampling technique reduced the analytical costs by 50%, it precluded the accumulation of adequate herbicide P/V ratio transport data to provide sufficient information to assist in understanding the transport questions noted above.

A 1982 study relied extensively on (a) transport modeling within a 10 mile radius, (b) an unlikely time/concentration dose injury threshold relationship assumption for the more sensitive wine grape varieties, (c) an underestimated source strength, and (d) zinc sulfide tracer releases (16).

From 1982 through 1987, the major concern has been focused on aerial applications within 10 miles of the grape vineyards. Many more acres can be sprayed aerially in a day than via ground applications, thus increasing the daily source concentration and emission rate. This raises questions about the assumed source strength for the model. Despite the conclusion from the fluorescent tracer studies that "close-in applications" (within 10 miles of vineyards) were primarily responsible for the grape injury, the question remains whether inorganic zinc sulfide particles appropriately mimic the many complex actions of semi-volatile organic compounds during field application and for a period of several days thereafter.

Many questions are still unanswered concerning the fate and drift distances for the LV and NV 2,4-D formulations presently used, which still cause damage to the grape vineyards. No field sampling studies have been conducted since 1980 to determine which 2,4-D compounds are present in the damaged vineyards, and no studies since 1974 have provided information which might reveal whether the herbicides associated with the damage are primarily in the aerosol or vapor form, or in some ratio of the two forms.

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FURTHER GAP SAMPLER EVALUATIONS OF
SEMI-VOLATILE CHLORINATED ORGANIC COMPOUNDS
IN AMBIENT AIR

N.D. Johnson and S.C. Barton
Ontario Research Foundation
Sheridan Park Research Community
Mississauga, Ontario L4K 1B3

D.A. Lane and W.H. Schroeder
Atmospheric Environment Service
4805 Dufferin Street
Downsview, Ontario M3H 5T4



Abstract

Uncertainties exist in defining deposition mechanisms of airborne semi-volatile chemical species to land and water due, in part, to existing limitations in sampling methods. A gas and particle (GAP) sampler has been developed based upon an annular diffusion denuder technique to separate co-existing phases of high molecular weight organochlorine compounds occurring in the atmosphere. A series of field evaluations has been conducted in the vicinity of Lake Ontario to further evaluate the performance of the sampler and experimentally determine the phase distribution of target compounds such as hexachlorobenzene (HCB) and hexachlorocyclohexanes (α - and γ -HCH). During these field studies attention was given to quality assurance aspects such as triplicate measurements, routine field blanks and dual capillary column gas chromatography analysis. Data suggest that an efficient phase separation of such compounds was achieved by the sampler design and, on the basis of denuder-difference measurements both during the summer and fall months, the largest fraction of these target compounds existed in the vapour phase. Methods to optimize the utility of the sampler are discussed in addition to field results.

Introduction

Atmospheric transport and deposition is considered to be an important pathway by which many toxic chlorinated compounds such as PCBs and pesticides enter the Great Lakes and other water bodies

that are remote from known sources (1). However, input mechanisms for such semi-volatile species that may co-exist in the atmosphere as vapour and as adsorbed components of particulate matter are not well defined. Most investigators have concluded that compounds with vapour pressures in the range of 10^{-4} to 10^{-5} mm Hg (at room temperature) occur predominantly in the vapour state. On the other hand, because of the numerous factors that can affect vapour/particle equilibria (eg. temperature, particle loadings) and the complex nature of airborne particulate matter, it is recognized that currently-available sampling techniques may not adequately distinguish between phases due to probable disruption of the equilibria during filtration. For example, conventional sampling techniques, such as high-volume filtration/adsorption methods, have been used to operationally derive gas/particle relationships (2-4). It is uncertain whether amounts retained by these collection media are representative of the actual gas- and particle-phase distribution since vapour constituents could either adsorb or desorb from filtered particles during sampling under certain conditions. A knowledge of the degree of partitioning between phases in ambient air is necessary for adequate assessments of either potential human health effects or environmental behaviour, impact and ultimate fate of such airborne constituents.

A prototype GAP sampler, based on a denuder difference system, has been developed to simultaneously collect the gas and particle fractions of several persistent organochlorine compounds in ambient air. The initial development and laboratory evaluation of this sampler has been reported previously (5,6). The major objective of this study was to determine the gas- and particle-phase concentrations of selected persistent chlorinated organic compounds in ambient air in southern Ontario and at a remote location in central Ontario. The semi-volatile compounds, HCB α - and γ -HCH, selected for field measurements are often found in rainwater and other environmental samples despite their limited use in North America (7,8).

Methodology

A schematic of the prototype GAP sampler is shown in Figure 1. This sampler comprises a multi-annular diffusion denuder assembly, coated with a binary crushed Tenax/silicone gum coating (to trap the vapour-phase components of the target compounds), that is integrated with a dichotomous sampler (to collect fine and coarse particulate matter). Packed Tenax adsorbers (2 in series) are positioned behind each filter to collect any material that may escape the filters (eg. desorbed vapour during filtration). This unit is operated in parallel with a conventional filter/adsorber sampler (i.e. reference unit to obtain the total airborne constituent concentration). The net difference in amounts collected by filters and adsorbers of both units provides the constituent vapour fraction and the combined filter/adsorber analyses of the dichotomous unit indicates the particulate-associated fraction. Earlier laboratory studies have demonstrated practically removal efficiency and retention of HCB and lindane by the denuder upon exposure to vapours generated at concentrations that might be expected in ambient air.

In this study, field measurements (involving replicated sampling over 24 to 48 hour periods) were conducted at several locations in southern Ontario and at a remote (background) site in the Turkey Lakes watershed north of Sault Ste. Marie (see Figure 2). The first set of measurements were taken during July 1986 in the western portion of Lake Ontario. Air sampling and meteorological equipment was operated simultaneously on the shoreline near Niagara-on-the-Lake and on board the CSS Bayfield (a CCIW Great Lakes research vessel) while it was anchored approximately 5 km off-shore. Similar on-shore/off-shore measurements were conducted in the eastern part of Lake Ontario near Sand Banks Provincial Park and an integrated sample was collected on the ship while it traversed between the western and eastern sites. Triplicate sample sets were taken in the early autumn at the remote Turkey Lakes area site. Other field measurements in southern Ontario were made at a suburban site in Sheridan Park, Mississauga (during autumn, 1986 and winter, 1987) and in Stoney Creek (near Hamilton) at a site approximately 800 meters from an agricultural chemical producer (during the early part of the winter).

Analytical methods to determine the target compounds involved extraction of filters and adsorbers, extract cleanup and analysis by dual capillary column gas chromatography with electron capture detection. In all instances, the lowest of the two column results was assigned with the assumption that any differences in the values between columns represented analytical interferences. In many cases, results between columns were similar while substantial differences were evident on some occasions. The average difference between columns for each compound was found to be : 27% HCB, 15% α -HCH and 57% γ -HCH.

Results and Discussion

Field studies took place over a seven month time period and mean temperatures during sampling intervals ranged from -3.7 to 22.9°C with hourly extremes from -11 to 34°C. Except on two occasions, under very hot summer conditions, temperature extremes were at or below temperature conditions selected in laboratory tests in which high vapour collection efficiency for HCB and lindane by the denuder was demonstrated. The general background nature of the sampling sites is evident from the low suspended particulate concentrations (ie. <10 μ m in size) shown in Table 1. The lowest loadings were encountered at the remote site as might be anticipated. The small difference in the overall mean particulate concentrations between the conventional and GAP samplers (ie. ~5%) confirms the earlier findings that no substantial particle losses occurred on average in the denuders.

Total airborne concentrations of HCB, α - and γ -HCH were generally in the sub-nanogram per cubic metre (of air) range based on conventional sampler measurements performed at all of the sites (see Table 2). Although the mean HCB concentration at Turkey Lakes was somewhat lower than the average amount measured at other

locations in southern Ontario, results were generally similar between sites. These findings are consistent with values reported from other studies. Lindane concentrations were about an order of magnitude lower than either α -HCH or HCB concentrations and were frequently at or near the detection limit of the analytical method used. The higher abundance of α -HCH relative to lindane may reflect environmental (perhaps photochemical) transformation of lindane to the more stable α -isomer. On the basis of measurements conducted in southern Ontario (including preliminary results of measurements in earlier studies) at various temperatures, the total airborne concentrations of all three target compounds were found to decrease with decreasing temperatures. The effect of temperature on airborne concentrations is more apparent from data shown in Table 3 where average concentrations were grouped into $\sim 5^\circ\text{C}$ increments. For example, a 2-3 fold reduction was evident for each compound over a temperature decrease of $\sim 20^\circ\text{C}$. It is presumed that the concentration decrease reflected less volatilization of these compounds from deposits on surfaces at cold temperature conditions rather than decreased usage or production during winter.

Individual measurements of the target compounds and the derived particulate-associated fractions at each sampling site are shown in Table 4. In most instances, the values represent an average of two or three measurement results and appear in approximate chronological order of the study. Generally favourable agreement was found between duplicate conventional sampler results of the total concentrations. It can be seen that little difference occurred between days at each site and results were often similar between sites when sampled at the same time of year. These data suggest a general, low-level, ubiquitous occurrence of these constituents in this study area. Because only one set of samples was taken at each site during preliminary onshore/offshore measurements, it is considered premature to deduce any potential trends between the land and water sites. Lindane concentrations were found to be highest near one suspected industrial source that is known to formulate organochlorine pesticides. It should be noted that sample Sets 1 and 2 at this site were taken during early winter 1985 and Sets 3 and 4 during early winter 1986. At other sites, lindane concentrations were low with greater variability since amounts were near the measurement sensitivity. In practically all cases, these compounds were collected efficiently (i.e. by the first of two Tenax adsorbers positioned in series) in the conventional filter/adsorber sampler and only traces occurred on few occasions in filtered particulate matter. Except for lindane, amounts in field blank cartridges usually represented less than 10% of the total amounts detected. However, spurious results occurred in the occasional blank cartridge that were sometimes suppressed with the dual column analytical approach. On the other hand, blank values were of greater significance in deriving the particulate-associated fractions since amounts detected in adsorbers positioned after the denuder often were low (i.e. approaching blank levels).

The average particulate fractions, derived by denuder difference, also are shown in Table 4 for each site. On several occasions, replicate (eg. duplicate or triplicate) measurements of this fraction with the GAP sampler were similar especially when considering that this fraction is derived by difference from analyses of several components of the system. From the results of these air measurements, it appears that the substances being investigated occurred predominantly in the vapour phase during warm weather as has been found by other investigators. However, under winter conditions (at the Sheridan Park site), a greater fraction of these high molecular weight, semi-volatile constituents appeared to be associated with the airborne particulate matter. That is, greater amounts were detected in cartridges located after the denuder, which presumably resulted from volatilization from filtered particles during sampling. Under the cold weather conditions, the particulate-associated fractions were found to be more variable between days and between replicated measurements. In some instances, only single column GC results were available or other sources of contamination in sampling components were possible and such results (noted with *) were considered to be upper limits. Nevertheless, these data suggest that the denuder efficiently removed the vapour fraction during sampling which was found in earlier laboratory studies.

Conclusions

Specific findings of this field evaluation using an alternative sampling method for semi-volatile organochlorine constituents are;

- particle losses in the denuder were usually small (~4% on average) and the denuder was demonstrated by both lab and field studies to efficiently remove vapours of the target compounds (HCB, α - and γ -HCH). These data suggest an effective gas/particle separation by the design,
- measured target compound concentrations (sub ng/m³) at the sites in southern Ontario were similar to other reported values and were found to decrease at low temperature conditions. Except near a suspected source, lindane was normally an order of magnitude lower than the more stable α -HCH form,
- at moderate temperatures, the mean particulate-associated fractions in the study area, derived by denuder-difference with the GAP sampler, were: ~4% HCB, ~7% α -HCH and <10% γ -HCH. Greater but more variable particulate fractions were evident under cold temperature conditions at a suburban site. These field data infer that such constituents occurred predominantly in the vapour phase at mild temperatures but that particulate deposition may be of somewhat greater significance to the Great Lakes during colder seasons than generally perceived.

Refinements to the sampling system (eg. use of Florisil cartridges, simplification by only selective use of the dichotomous sampler and thermal desorption of the denuder) are presently being tested in order to improve the accuracy of measurements. Similarly, tests to expand the application of the GAP sampler (eg. PCBs) are underway.

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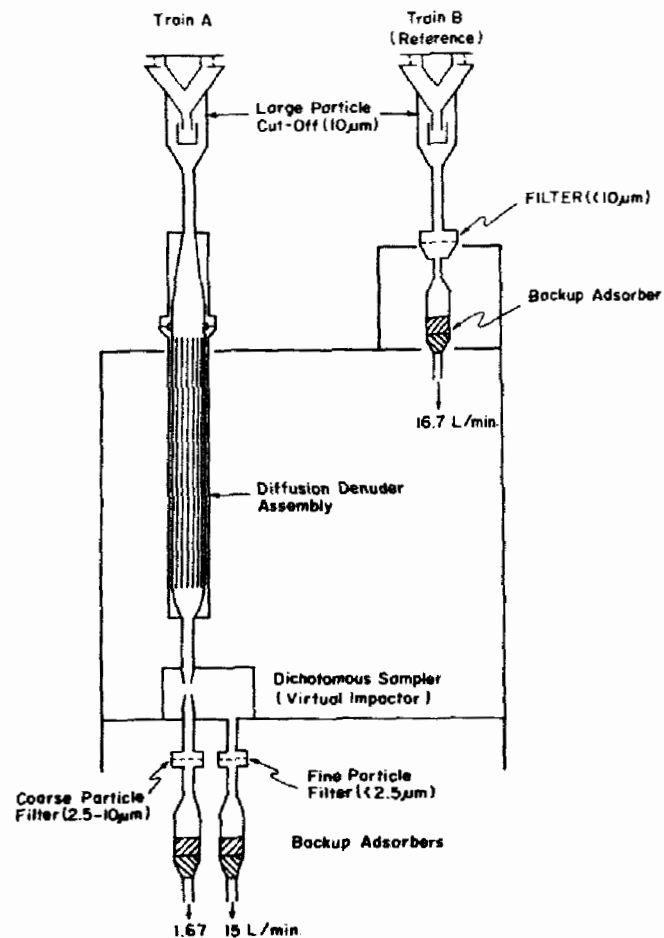


FIGURE 1. SCHEMATIC DIAGRAM OF GAS/PARTICLE FRACTIONATING SAMPLER.

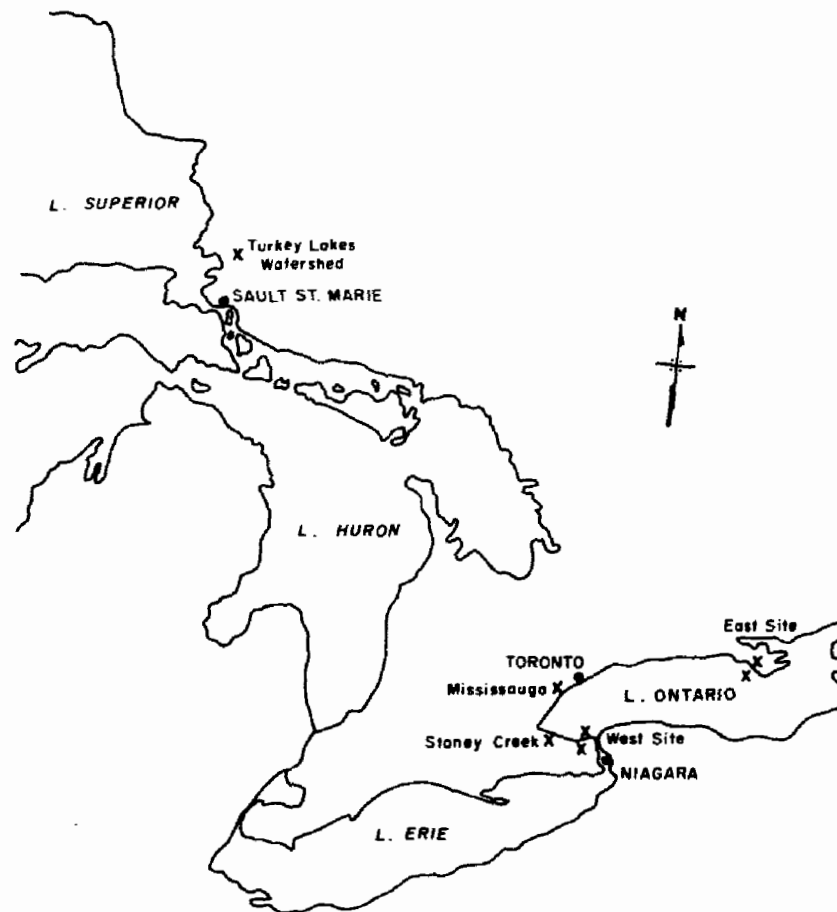


FIGURE 2. SAMPLING LOCATIONS

TABLE 1

Summary of Particulate Concentration (<10 μ m) and Denuder Losses

Location	Part. Conc. (μ g/m ³)	Range (μ g/m ³)	%Fine
Onshore/Offshore	24	16-31	76
Turkey Lakes	6	5-9	50
Sheridan Park	22	8-36	70
Stoney Creek	33	15-53	64
Mean (Conv. Sampler)	21	5-53	
Mean (GAP Sampler)	20	4-46	60

TABLE 2

Summarized Total Airborne Concentrations of Target Compounds
(ng/m³)

Location	Parameter	HCB	α -HCH	γ -HCH
Near Lake Ontario	Mean Range n	0.22 0.07-0.72 25	0.32 0.02-0.66 26	0.04 <0.02-0.07 19
Turkey Lakes Area	Mean Range n	0.13 0.08-0.16 5	0.33 0.16-0.50 5	0.06 0.02-0.10 5
Other Remote Locales	Range	0.03-0.20	---	0.001-0.20

TABLE 3

Total Airborne Concentrations as a Function of Ambient Temperature

Mean Temp. Range (°C)	No. of Samples	Mean Concentration (ng/m ³)		
		HCB	α -HCH	γ -HCH
20-23	5	0.39	0.49	0.04
15-19	6	0.23	0.42	0.05
10-14	6	0.19	0.30	0.03
5-9	4	0.17	0.34	0.03
0-4	5	0.14	0.16	<0.02
-4 to -1	3	0.15	0.15	<0.02

TABLE 4
Summary of
Target Compound Measurements (ng/m³) and Particulate-Associated
Fractions(%) by Denuder Difference

Location	Test Series	Ave. Total Conc.			Ave. Part.Fraction (%)		
		HCB	α -HCH	γ -HCH	HCB	α HCH	γ -HCH
Lake Ontario Onshore/ Offshore	Land-West	0.3	0.7	<0.03	---	---	---
	Ship-West	0.2	0.4	0.06	6	14	46*
	Land-East	0.3	0.3	<0.03	0	---	---
	Ship-East	0.3	0.5	0.07	2	8	~2
	Ship-Moving	0.2	0.5	0.06	0	5	~2
Turkey Lakes	Set 1	0.2	0.4	~0.04	0	10	~0
	Set 2	0.1	0.3	~0.04	5	5	~0
	Set 3	0.1	0.3	0.1*	5	0	~0
Sheridan Pk. (Mod. Temp.)	Set 1	0.2	0.4	0.1	17*	18*	~23*
	Set 2	0.2	0.3	~0.04	4	6	~20
	Set 3	0.1	0.3	0.06	14	8	~67
Sheridan Pk. (Low Temp.)	Set 1	~0.07	<0.03	<0.04	~100*	---	---
	Set 2	0.08	0.1	<0.02	~15	21	---
	Set 3	0.1	0.1	<0.02	~51	35	---
Stoney Creek (near source)	Set 1	0.2	0.1	0.4	60*	---	13
	Set 2	0.1	0.2	0.5	57*	0	10
	Set 3	0.1	0.1	0.1	~73*	28*	10
	Set 4	0.2	0.2	0.1	32	1	0

* Contamination suspected

FIELD COMPARISON STUDY OF POLYURETHANE FOAM AND XAD-2 RESIN
FOR AIR SAMPLING OF POLYNUCLEAR AROMATIC HYDROCARBONS

Jane C. Chuang⁺, Steve W. Hannant⁺, and Nancy K. Wilson[#]

⁺ Battelle Columbus Division, Columbus, Ohio 43201

[#] Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

A study of the sampling efficiency for PAH in vapor using two adsorbents, XAD-2 resin and polyurethane foam (PUF) was performed under summer and winter ambient conditions. Two aspects were investigated: (1) collection efficiency for ambient PAH vapor and (2) retention efficiency for native and perdeuterated PAH spiked onto the adsorbents before sampling. Some spiked PAH which were volatile or reactive were recovered more efficiently with XAD-2 than with PUF. Lower sampling temperature improved the recovery for volatile PAH using PUF, but the recoveries of reactive PAH, such as cyclopenta[c,d]pyrene, were not improved at lower temperature for either adsorbent. An investigation of the stability of PAH collected on quartz fiber prefilters and XAD-2 or PUF backup traps as a function of the storage time was also carried out. Storage at room temperature in the dark for 30 days did not have an adverse effect on the collected ambient PAH or on the spiked perdeuterated PAH with XAD-2 resin. However, a decreasing concentration trend with storage time for naphthalene, anthracene and D₁₂-benzo[a]pyrene collected or spiked on PUF was found. Most of the particle-bound PAH collected on quartz fiber filters were not affected significantly during storage, except that cyclopenta[c,d]pyrene decreased to approximately half the original level after 30 days of storage. Investigation of the degradation product of cyclopenta[c,d]pyrene, pyrene dicarboxylic acid anhydride, showed that the levels of this compound collected on filters increased to about 1.5 times the original value after storage for 30 days. The distributions of PAH between filters and XAD-2 resin found in the stability study corresponded to the volatilities of individual PAH, and most 2- to 4-ring PAH were found to break through the filters. This demonstrated that the use of both prefilters and backup adsorbents is necessary in air sampling for PAH analysis.

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAH) have been studied extensively and have received increased attention in investigations of air pollution recently because some PAH are carcinogens, mutagens or both¹⁻⁵. To understand the human exposure to PAH, reliable sampling and analytical methodology must be established for monitoring PAH in air. Several studies⁶⁻⁹ have shown that filters alone can not retain all the 2- to 4-ring PAH. The XAD-2 resin and polyurethane foam (PUF) have been used to collect PAH vapors¹⁰⁻¹⁴ by various research groups. The overall comparative effectiveness of these two adsorbents and the degree to which quantification of PAH is affected by sampling, handling and storage have not been fully investigated. This uncertainty precludes an accurate assessment of the relative overall merit of each adsorbent.

The objective of this study was to compare the sampling efficiency for PAH vapors of these two adsorbents, PUF and XAD-2 resin, and to compare the storage stability of PAH vapors collected on PUF and XAD-2 resin. The storage stability of quartz fiber filters and investigation of the degradation product of cyclopenta [c,d]pyrene due to storage were also performed.

EXPERIMENTAL METHODS

Sampling

Modified General Metals PS-1 samplers with General Metals bypass motors were employed in the ambient air sampling. The samplers which are described elsewhere¹⁵, were placed on the ground in an open space outside Battelle's laboratory in Columbus, Ohio. This location can be classified as a medium-size, midwestern city with relatively clean air for an urban environment. The sampling was performed on weekends or holidays to reduce the contribution of local vehicle exhaust emissions to the samples. Air was sampled for 24 hrs at a flow rate of 6.7 cfm. Quartz fiber filters were located upstream of the PUF or XAD-2 in all sampling experiments.

In the sampling efficiency comparison study, two sets of three samplers were located in parallel about two feet apart. The three samplers of each set were separated from each other by about one foot. The PUF cartridges were used in one set of three samplers and XAD-2 cartridges were used in the other set. Prior to sampling, two each of the three PUF and XAD-2 were spiked with the following PAH (2 µg of each): D₈-naphthalene, D₁₀-phenanthrene, D₁₀-pyrene, D₁₂-chrysene, D₁₂-benzo[a]pyrene, phenanthrene, anthracene, fluoranthene, pyrene, cyclopenta[c,d]pyrene, benz[a]anthracene, benzo[e]pyrene and benzo[a]pyrene. These experiments were performed twice under the same conditions except that during the first experiment, the ambient temperature ranged from 66-86°F and during the second experiment, it ranged from 17 to 27°F.

In the storage stability study, eight samplers in two sets of four were used. Sampler location was similar to the comparison study described above. In the first experiment, PUFs were used as backup traps, and XAD-2 traps were used in the second and third experiment. All PUF and XAD-2 from the first and the second sampling were spiked with only the perdeuterated PAH, noted in the comparison study, before sampling. After sampling, these PUF and XAD-2 samples were stored in the dark at room temperature for 0, 10, 20, and 30-day intervals before extraction and analysis as replicate pairs. The filters from the XAD-2 sampling were similarly stored and extracted after the same time intervals. The filters from the PUF sampling were not analyzed. The purpose of the third sampling was to provide samples for bioassay analysis and to characterize the polar PAH and possible PAH degradation products. Only the degradation product of cyclopenta[c,d]pyrene, pyrene-1,10-dicarboxylic acid anhydride, is reported in this paper since the study is still in progress.

Analysis

The PUF and XAD-2 cartridges were cleaned before air sampling. The cleanup procedures are described elsewhere^{12,16}. Quartz fiber filters were heated at 400°C for 16 hrs before use. Samples were Soxhlet-extracted for 16 hrs with 10 percent ether/hexane (PUF) or methylene chloride (filter and XAD-2). The extracts were concentrated and analyzed by electron impact (EI) gas chromatography/mass spectrometry (GC/MS) for PAH. Identification of PAH was based on the GC retention times of the individual monitored molecular ion signals compared to that of the internal standard, 9-phenylanthracene. Quantifications of these compounds were based on comparisons of the respective integrated ion current responses for the monitored molecular ions to that of the internal standard using calibration response curves.

The dichloromethane solution of cyclopenta[c,d]pyrene was spiked evenly onto a quartz fiber filter and was exposed to U.V. light for 4 days to obtain a mixture of cyclopenta[c,d]pyrene and pyrene dicarboxylic acid anhydride. The exposed standard solution was analyzed by both EI and negative chemical ionization (NCI), GC/MS. The internal standard, D₉-1-nitropyrene, was used in the NCI method and 9-phenylanthracene was used in the EI method. Identification of this compound in the sample was based on the correct GC retention time and the NCI mass spectrum. Since the accurate concentration of the exposed standard could not be determined, the response factor of this compound to the internal standard was assumed to be 1.

RESULTS

Sampling Efficiency Comparison Study

Analysis of the background (non-spiked) XAD-2 and PUF samples show that PAH recoveries from PUF and XAD-2 are very similar for all compounds except for naphthalene, the most volatile PAH of the series. Levels of ambient naphthalene collected on XAD-2 are about 24 and 12 times higher than those on PUF in the summer

and the winter experiments, respectively. The summer phenanthrene levels are slightly higher for XAD-2 resin than for PUF, but identical levels are observed for both adsorbents in the winter experiment. This finding reveals that XAD-2 resin has better collection efficiency for the more volatile naphthalene than does PUF and that the collection efficiency for naphthalene on PUF improves at lower ambient sampling temperature.

Generally good recoveries are obtained for most spiked PAH from both adsorbents after exposure to ambient air at a flow rate of 6.7 cfm for 24 hrs. The recoveries of D₈-naphthalene from XAD-2 resin were significantly higher than those from PUF, in agreement with the result for native naphthalene noted above. These data suggest that XAD-2 resin is significantly more effective in retaining two-ring PAH. Similarly, lower recoveries of the spiked D₁₀-phenanthrene and spiked native anthracene were obtained from PUF than from XAD-2 resin in the summer experiment. As expected, these PUF recoveries improved significantly in the winter experiment, becoming comparable to those from XAD-2 resin.

The native phenanthrene recovery data cannot be accurately addressed in the summer experiment because the ambient background levels were about 19 times higher than the spiked levels. Thus, due to the expected variations in sampling and analytical procedures, negative recoveries were sometimes observed for spiked phenanthrene. Low recoveries of cyclopenta[c,d]pyrene were obtained with PUF in both the summer and the winter experiments, 40 and 23 percent respectively. The loss of spiked cyclopenta[c,d]pyrene almost certainly results not from volatilization but from decomposition, which is supported by the storage stability results (See below).

Sampling Module Storage Stability Study

For XAD-2 resin, no loss of perdeuterated PAH was detected over the 30-day storage interval. In addition, storage instability over the 30-day period was not indicated for any of the native PAH collected on XAD-2 resin. Only trace amounts of cyclopenta[c,d]pyrene were found in XAD-2 resin, and the variability in the data at these low levels prevent showing the decreasing concentration trend.

For PUF, the D₈-naphthalene storage stability results are not meaningful since only 1.2 percent of the spiked D₈-naphthalene was retained on the PUF at the end of 24-hr sampling. The decreasing concentration trend for D₁₂-Benzo[a]pyrene were observed with PUF. However, this may not cause a serious problem in air sampling, since benzo[a]pyrene is mainly retained in the filter. It appears to be a loss on storage of both native naphthalene and anthracene collected on PUF. Since naphthalene clearly breaks through PUF during 24-hr sampling, we expect that it may be partially lost by volatilization during 30-day storage. The greater loss from PUF of anthracene relative to its isomer phenanthrene is more consistent with the lower chemical stability of anthracene relative to phenanthrene than with a loss through volatilization.

Storage losses over 30-day period were not observed for any of the particle-bound PAH on quartz fiber filters except for cyclopenta[c,d]pyrene. The data for cyclopenta[c,d]pyrene are given in Figure 1. As shown in Figure 1, levels of cyclopenta[c,d]pyrene decrease to about half of the original levels after storage for 30 days in both experiments. Other research groups¹⁷⁻¹⁹ have identified a direct-acting mutagen, pyrene dicarboxylic acid anhydride, as a possible degradation product of cyclopenta[c,d]pyrene in airborne particulate material and other environmental samples. We have investigated the degradation product of cyclopenta[c,d]pyrene in the third stability experiment.

The EI and NCI mass spectra of pyrene dicarboxylic acid anhydride are given in Figure 2. As shown in Figure 2, the characteristic neutral losses of CO₂ and CO are found in the EI spectrum. As expected, only the molecular ion is detected in the NCI condition. For the detection of this compound, the NCI method is much more sensitive than the EI method. Since this compound is highly electro-negative, it is susceptible to the attachment of a thermal electron from the NCI reagent gas plasma, which enhances the detection sensitivity. We can detect pyrene dicarboxylic acid anhydride in the filters only with the more sensitive NCI method but not with the EI method. Analysis of the NCI data showed an increasing concentration trend for this compound on filter samples after 30-day storage. The level of this compound from the 30-day sample was more than 1.5 times of those of the 0-day sample. This finding suggests that particle-bound cyclopenta[c,d]pyrene partially decomposes to pyrene dicarboxylic acid anhydride after a 30-day storage period.

Distributions of PAH between the filter and XAD-2 resin from the stability study in general agree with the volatilities of the individual PAH. This finding indicates breakthrough of 2- to 4-ring PAH from the prefilters. Other research groups⁽⁶⁻⁹⁾ have also reported that most of the volatile PAH were not retained on filters under high-volume sampling conditions. In our study, medium-volume samplers were used and the flow rate (6.7 cfm) was lower than a typical high-volume sampling flow rate. Thus, this observation clearly demonstrates that the use of filters only to collect PAH from air is not sufficient, and correct quantitative results, even for species as large as chrysene, cannot be obtained without the use of back-up adsorbents.

CONCLUSIONS

For air sampling of gas phase PAH, XAD-2 resin seems to have two performance advantages compared to PUF: (1) 2- and 3-ring PAH clearly break through standard PUF cartridges in a typical sampling volume of about 300 cubic meters, and (2) PAH species that are prone to degradation during sampling or during sample storage prior to extraction exhibit greater losses from PUF than from XAD-2 resin. Certainly, the future use of quartz fiber filter/PUF samplers should involve a minimum of sample handling and storage to reduce the losses of volatile and reactive PAH. Little is known about the degradation products of PAH due to sampling and sample handling. The critical issue of whether a significant

part of the mutagenic activity in these types of air samples is from sampling artifacts or is actually present in the sampled air is still not clear, and further investigations need to be carried out in this area.

ACKNOWLEDGEMENTS

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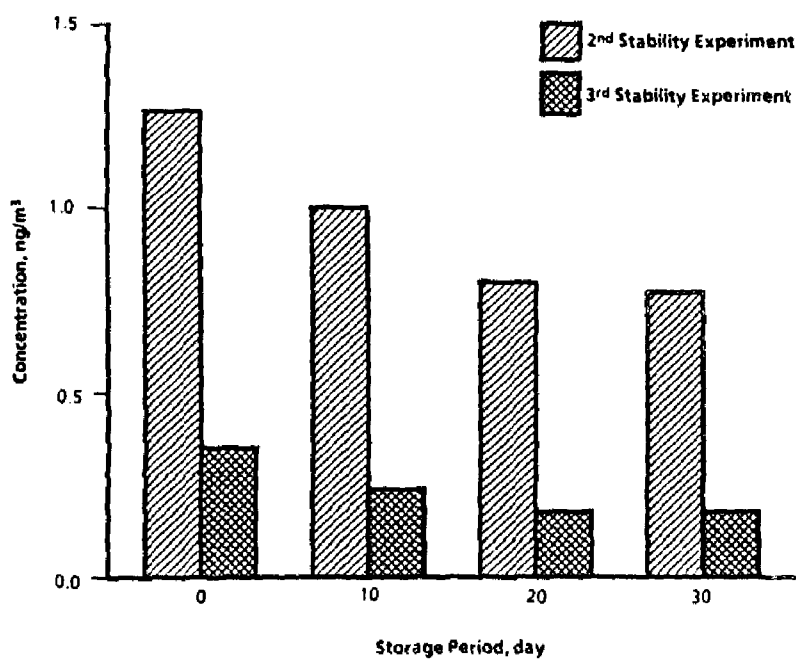


Figure 1. Levels of cyclopenta[c,d]pyrene in quartz fiber filters as a function of storage time

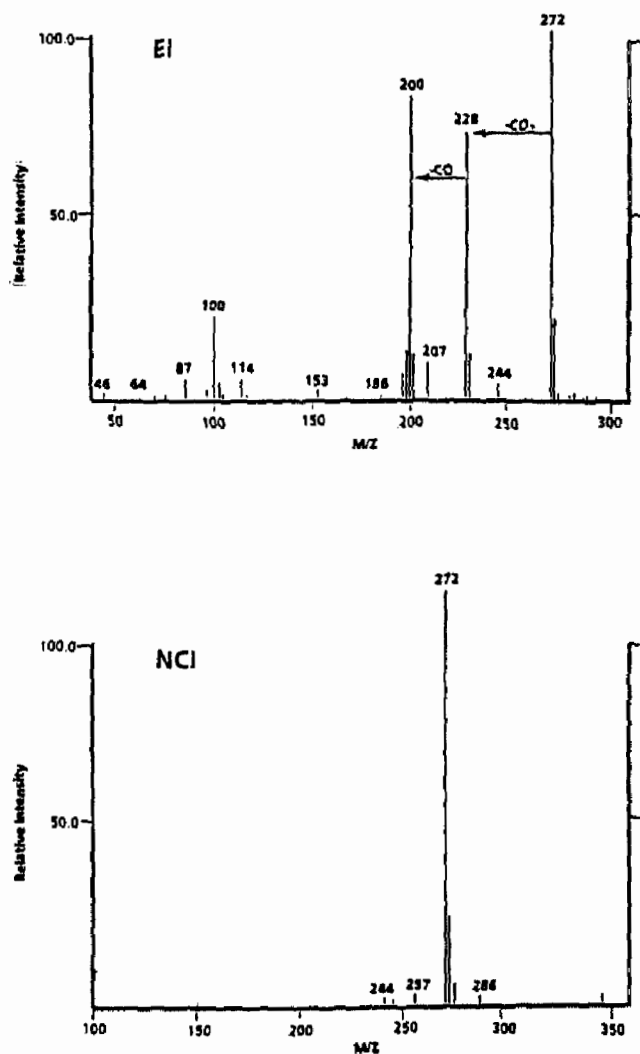


Figure 2. Upper: Electron impact mass spectrum of pyrene dicarboxylic acid anhydride
 Lower: Negative chemical ionization mass spectrum of pyrene dicarboxylic acid anhydride

NON-OCCUPATIONAL EXPOSURE TO HOUSEHOLD PESTICIDES

Andrew E. Bond and Robert G. Lewis
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

Abstract

The U. S. Environmental Protection Agency is conducting a study to develop and validate monitoring methods needed for the determination of human exposure to common household pesticides. The primary objective is to obtain an estimation of the cumulative frequency of non-occupational exposures to home and garden pesticides through the air, dermal, drinking water, and dietary routes. In a nine-home pilot study designed to test methodology, 22 of 28 of the most commonly used household pesticides were detected. Five of these were measured in the air in the majority of the households at concentrations ranging up to several $\mu\text{g}/\text{m}^3$. Personal air measurements suggested that 80% of the total respiratory exposures resulted from indoor air. Subsequent to the pilot study, a large-scale, multi-season monitoring program involving up to 175 homes in a high-use southern U.S. city and about 85 homes in a low-use northern U.S. city was initiated.

In 1985, the United States Environmental Protection Agency instituted the first attempt to develop methodology for determining pesticides exposures in the general population of the U.S.A. The project, known as the Non-occupational Pesticides Exposure Study (NOPES), is designed around the concepts of the Total Exposure Assessment Methodology (TEAM) studies previously conducted by EPA (4). The NOPES project will test whether the TEAM approach can be adapted to develop estimates of exposures to selected pesticides in personal (respiratory) air, drinking water, and from dermal contact in a stratified random sample of the population of two urbanized areas in the United States. The scientific objectives of NOPES are as follows:

- o Adapt the TEAM methodology to pesticides by testing and refining monitoring instrumentation.
- o Collect preliminary data relating exposures through each of three potential routes of exposure (air, water, skin) to pesticide usage levels.
- o Obtain basic knowledge which may be used in future investigations in four topic areas: (i) human exposure model development, (ii) measurement methods development (iii) microenvironmental field studies, and (iv) dosage research investigations.
- o Investigate causal relationships that explain the variability from person to person of exposure to pesticides.
- o Estimate the relative importance of each pathway of exposure to the total exposure for each pesticide.
- o Determine if a predictive human exposure model can be developed to relate data on exposures to usage rates and other factors.

The study, which is currently in progress, is focused on the measurement of exposure to 28 of the most commonly used household insecticides, fungicides and herbicides. Two cities are involved in the study: Jacksonville, Florida, a warm climate city in which household pesticide use is one of the highest in the U.S.A. and Springfield/Chicopee, Massachusetts, a cold-climate area characterized by low household pesticide usage. A total of 260 single-family households will be monitored over three seasons by the completion of the study in 1988.

During August 1985, a pilot study was conducted over a seven-day period in Jacksonville to evaluate and select sampling, analytical and survey methods (2). Nine homes were chosen and presorted into three groups of three homes each on the basis of the level of indoor use of pesticides. Stratification was based on the following four variables: (a) the frequency of indoor application of pesticides to control insect pests; (b) the frequency of use of pest control products on pets; (c) the frequency of indoor applications of pesticides on plants; and (d) the termiticide treatment program of the housing unit. Usage categories were designated from the above variables as "high" 3 out of 4, "medium" 2 out of 4, and "low" 1 or less. In each of the designated low-, medium- and high-use dwellings, 24-hr indoor and outdoor air samples were taken and one resident carried or kept close by a portable sampler at all times during the same 24-hr period for the assessment of personal respiratory exposure. In addition, tap water samples were collected from each household and dermal (hands only) exposures were monitored when participants were applying pesticides. Pre-extracted, white cotton gloves were used for this purpose.

The results of the pilot study demonstrated the utility of the low-volume air samplers, which pumped air at 3.8 L/min through a 22-mm x 76-mm polyurethane foam sorbent trap (3), for indoor, outdoor and personal exposure monitoring. The overall conduct of the pilot study was relatively trouble-free. The study showed that the numbers and concentrations of pesticides in residential indoor air were generally higher by an order of magnitude or more than those in the envelope of air immediately surrounding the building (the mesosphere). Of the 33 pesticides and related chemicals shown in Table I, a total of 24 were detected in indoor air, 21 in personal air, and 25 in outdoor air. Concentrations ranged from 1.7 ng/m³ to 15.0 µg/m³. Five pesticides (chlorpyrifos, diazinon, chlordane, propoxur and heptachlor) were found in 80 to 100% of the indoor air samples at mean concentrations of 0.16 to 2.4 µg/m³. These concentrations were generally one order of magnitude higher than those of the other pesticides measured. In only one instance, however, were the guidelines established by the National Academy of Sciences (1) exceeded. On one of two days of sampling in one high-use household, chlorpyrifos was found at 15 µg/m³, or about 50% higher than the interim guideline for exposures to this termiticide not exceeding three years. Personal air measurement correlated well with indoor air measurements, with corresponding concentrations usually within ± 50% of each other.

All tap water samples collected during the pilot study were negative for all of the target compounds. Detection limits ranged from 0.05 to 1 µg/L depending on the analyte. Only three dermal exposures were monitored so that there was insufficient data for interpretation.

The overall conclusions from the pilot study were that (a) monitoring methodology was effective for monitoring all of the pesticides of interest,

(b) most (>80%) of the total personal exposure to household pesticides could be attributed to indoor air, and (c) the occurrence and concentrations of pesticides found in indoor air correlated well with the level of usage as determined by the presampling survey.

The first phase of the full NOPES project was conducted during August and September 1986 in Jacksonville. There will be subsequent samplings during March - May 1987 and during January - March 1988. Of 267 households screened, 66 were sampled (five short of the goal of 70). Duplicate (simultaneous) samples were taken at six of these, triplicates at three, and replicates (two different days) at nine. A similar number of households are scheduled for sampling during the next two sessions. Some of these households will be monitored once in each of the three seasons, while the remainder will be sampled once or twice in one season only. Stratification of the participating households provides for 50% high-use, 30% medium-use and 20% low-use. A total of 864 samples (804 air, 18 dermal, 18 drinking water and 24 field blanks) should be taken in Jacksonville. The Springfield/Chicopee study will be smaller, encompassing 85 residences over two seasons.

In addition to direct measurements of air, water and dermal exposure, an attempt will be made to estimate dietary exposures to the same pesticides. For this purpose, dietary recall questionnaires will be administered and pesticide residues published by the U.S. Food and Drug Administration as part of its annual Total Diet Study will be used.

As of this writing, the analytical results from about 95% of the 256 samples collected in 75 Jacksonville homes are available in partially reduced form. The air monitoring results for the five most prevalent pesticides are given in Table II. These results are comparable with those found in the nine-home pilot study (2). The higher mean concentration and relatively fewer positive findings of technical chlordane may be the result of more rigorous quality control procedures instituted for the full study. The stricter QA resulted in higher detection limits and required more positive confirmation of the multicomponent mixture. As in the pilot study, no pesticides have been detected in tap water samples analyzed to date. Results of dermal and respiratory exposure measurements are incomplete as of this writing.

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Table 1: Summary of pesticides found in air during Jacksonville pilot study, August 1985.

Pesticide	Number of Households at Which Detected in Air		
	Indoors	Outdoors	Respiratory
Chlorpyrifos	9	7	8
Diazinon	8	7	6
Chlordane	7	3	6
Propoxur	7	4	6
Heptachlor	7	5	6
trans-Nonachlor	6	3	5
Lindane	6	2	3
Heptachlor Epoxide	6	2	3
Aldrin	6	4	3
o-Phenylphenol	5	4	4
Dieldrin	5	4	5
Captan	5	2	4
Folpet	5	4	4
Oxychlordane	5	2	1
Malathion	4	2	1
Bendiocarb	3	1	4
α -BHC	3	2	3
Ronnel	3	1	3
Chlorothalonil	3	3	1
Pentachlorophenol	2	1	0
Dichlorvos	1	1	1
Dicofol	1	2	0
Methoxychlor	1	1	0
p-p'-DDT	1	0	0
cis-Permethrin	0	1	1
trans-Permethrin	0	1	0
Resmethrin	0	0	0
Carbaryl	0	0	0
2,4-D Esters	0	0	0
Atrazine	0	0	0
Dacthal	0	0	0
Polychlorinated Biphenyls	0	0	0

Table 2: Summary of positive findings for most prevalent pesticides found in air during the Jacksonville full study, August 1986.

		Air Concentration, $\mu\text{g}/\text{m}^3$		
		Indoor	Outdoor	Personal Exposure
Chlorpyrifos	Range	0.013 to 2.2	0.012 to 0.21	0.014 to 2.8
	Mean ^a	0.39	0.043	0.34
	Positive ^b	69	23	66
Diazinon	Range	0.059 to 13.7	0.066 to 0.29	0.056 to 4.7
	Mean	1.0	0.15	0.63
	Positive	42	4	41
Propoxur	Range	0.019 to 7.9	0.026 to 0.29	0.022 to 3.9
	Mean	0.46	0.092	0.29
	Positive	53	8	51
Technical Chlordane	Range	0.19 to 3.0	0.21 to 0.63	0.17 to 1.3
	Mean	0.78	0.37	0.61
	Positive	29	7	25
Heptachlor	Range	0.016 to 1.6	0.021 to 0.63	0.018 to 1.6
	Mean	0.39	0.20	0.38
	Positive	29	10	25

^a Arithmetic value of all positive measurements.

^b Number of dwellings of 75 monitored for which at least one sample contained detectable levels of the indicated pesticide.

COMPARISON OF ESTIMATED AND ACTUAL PCB VAPOR EXPOSURE DURING A SOIL EXCAVATION PROJECT

James Neely, CIH and Colin Moy
Ecology and Environment, Inc.
160 Spear Street
San Francisco, CA 94105



A risk assessment was conducted for a chemical processing plant which had used the PCBs Aroclor 1248 and 1254 in its heat exchange fluids. Concentrations of vaporized PCBs were measured at levels one to two orders of magnitude greater than had been calculated in the risk assessment. Further, the PCBs detected consisted of the lighter Aroclor 1232 or a related compound. Because dust was shown to be adequately controlled, the discrepancy between projected and actual vapor-phase PCBs could only be explained by the unforeseen formation of lighter, more volatile PCB species from partial evaporation of Aroclor 1248 and 1254, or failure to detect Aroclor 1232 on the original soil samples. Partial photolysis of the heavier PCBs could also contribute to the formation of the lower chlorinated PCBs detected in air.

In conducting risk assessments for the removal of soil contaminated with the most common PCB products 1248 and 1254, the study results show that it is prudent to use on-site air monitoring or other confirmation techniques to ensure the health and safety of workers and the public during excavation. The need to further investigate health implications of photolysis products, particularly dibenzofurans, is also identified.

Background

The hazardous waste facility discussed in this report was a chemical processing plant which utilized heat-exchange fluids containing PCB 1248 and 1254. Following demolition of the plant, it was determined that the original PCB products or residuals had apparently leaked into surface soils throughout the 3-acre site. Soil was sampled based on a grid pattern that divided the site into roughly equivalent sections. Sampling was continuous, from surface to 6-foot depths, and analysis continued until the vertical extent of contamination was resolved. Additional surface samples were collected and analyzed to delineate the areal extent of contamination. A total of 321 samples were analyzed.

Soil Analyses

Soil samples were analyzed at a laboratory certified by the State of California for hazardous-waste analyses. The contents of each sampling sleeve was homogenized and a portion of the the soil sample was extracted with pure hexane and shaken. Sodium sulfate was also added to absorb moisture and promote mixing. The extract was then analyzed directly without a Florisil clean-up step. EPA Method No. 8080 was followed, as were all required quality-control protocols. Up to 11 of the Aroclor peaks were used to quantitate the sample. Aroclor type was identified by matching peak patterns and retention times to internal standards. The results of this sampling program revealed that site soils contained variable concentrations of PCBs. The average PCB level in the most heavily contaminated soils located within 12 inches of the surface was 326 ppm, with a range of <1 ppm to 4,400 ppm. The chromatograph from soil samples most closely approximated PCB 1254 (see Figure 1).

Exposure Guidelines

For worker exposure to PCBs, the California OSHA 8-hour Time Weighted Average (TWA) Permissible Exposure Level (PEL) as well as the American Conference of Governmental Industrial Hygienists' TWA Threshold Limit Value (TLV) are the same: 1.0 mg/m³ for PCBs containing 42% chlorine by weight (PCB 1242), and 0.5 mg/m³ for PCBs containing 54% chlorine (PCB 1254). The National Institutes for Occupational Safety and Health, citing the potential for carcinogenic effects from PCBs, has established a recommended exposure guideline of 1 ug/m³ (0.001 mg/m³) as a 10-hour TWA for any PCB exposure.

A risk assessment was performed to evaluate potential health hazards arising from direct and indirect human exposure to the site. Because there are no standards for allowable levels of PCBs in outdoor air, the risk assessment proposed a safe exposure guideline of 0.101 ug/m³, for off-site community exposures, based on a calculated allowable daily intake of 2.5 ug/day. This guideline was extrapolated from a mortality study (1) and was designed to maintain a lifetime risk of cancer at less than 10⁻⁵.

Exposure Estimation

PCBs in soils may reside in the vapor, liquid, or adsorbed phase. Direct evaporation from surface soils, diffusion of vapors from underlying strata, and wind-born dust may result in airborne exposures. Many physical and chemical properties of the soil and the contaminant, as well as external environmental factors, affect the rate of evaporation. Examples of physical properties of soils include tortuosity, porosity, and exposed surface area. Chemical properties include moisture content, organic carbon content, vapor pressure, and solubility. Important environmental factors include insolation, temperature, and wind speed (2).

In determining vapor emissions, rate-limiting parameters such as organic carbon adsorption and effective pore space are ignored when developing worst-case exposure assessments. The authors of the risk assessment applied Henry's Law in estimating vapor exposure levels in the immediate site vicinity.

According to Henry's Law:

$$C_v = H_c C_l$$

$$H_c = 1.73 \times 10^{-7} \quad (3)$$

$$C_l = 326 \times 10^{-6} \text{ g PCBs/g soil-water} \times (\text{MW water/MW PCBs})$$

$$C_v = 2.3 \times 10^{-12} \text{ mole fractions}$$

Using the above values and Henry's Law, one calculates that the near-surface contamination will contribute 0.022 ug PCBs/M³ of air.

Air Sampling

An air-sampling station was positioned at each of the four perimeters of the site. Depending upon wind direction and locations of site activities, these stations were moved along each perimeter. The air-sampling pumps (VWR Model 54906) were operated whenever any type of work took place at the site. Samples were drawn at a fixed rate (3.5-4.0 liters per minute) through a 37-mm glass-fiber filter, followed by 400/200 mg Florisil tubes (custom-ordered through SKC Inc.). The air-sampling pumps were calibrated daily using a bubble meter. Rotameters were attached to the pumps; the position of the float was marked during each calibration. Flow rates were then periodically checked and adjusted.

Sample-collection procedures were based on established NIOSH protocols for PCB air sampling (Method 5503) with modification of the tube and filter size to increase the flow rates and thereby reduce detection limits. This method has been validated (4).

Personal air-sample pumps were used to evaluate exposure of equipment operators to PCBs. Two types of pumps were used: a medium-flow (MSA) portable pump using the same glass-fiber filter and Florisil tube as the perimeter sampling pumps; and a low-volume pump (SKC or Sippin) using the filter and tube sizes specified in NIOSH Method 5503. The breathing-zone samplers were worn by workers throughout their daily shifts.

A total of 72 area samples and 11 employee breathing-zone samples were collected. The front section of the Florisil sampling sorbent and the filter were extracted together and analyzed by a Varian 6500 gas chromatograph with an electron-capture detector and a mixed-phase column at an isothermal temperature of 200°C. The procedure is described in NIOSH Method 5503. Aroclor standards and hexane blanks were analyzed periodically during sample tests as required by the method's quality-control protocols. Similar quantitation and identification methods were repeated from the soil testing.

Dust Monitoring

Dust was monitored with a GCA Miniram direct-reading aerosol monitor (detection limit of 0.001 mg/m³) at upwind and downwind positions throughout the site. If the wind was negligible, readings were taken at each of the four perimeters. Readings were taken approximately every 30 to 60 minutes throughout the shift. Downwind readings were compared to upwind readings to see how much dust on-site activities generated.

Wind speed and direction were also measured, with a wind vane and anemometer placed on a six-meter pole at the perimeter of the site.

Results

Analytical results of the PCB air samples showed significantly higher levels of PCB vapors than had been estimated in the risk assessment. Downwind concentrations averaged .563 ug/m³, with a median concentration of .768 ug/m³. Employee exposure levels (large tube and filter samples) averaged 1.845 ug/m³ with a median of 2.180 ug/m³. In addition, results were being reported as PCB 1232, based on the chromatographic comparison to standards, rather than the expected PCBs 1248 and 1254 (see Figure 2). Throughout the project, dust readings on the aerosol monitor were insignificant. The emissions were therefore believed to be associated with PCB vapor. This assumption was confirmed by analyzing filter and tube sections separately. Three of the four samples analyzed contained PCBs in the front section only.

Discussion

Risk analysis and estimation are valuable methods of assessing health hazards at hazardous-waste sites. Legislative mandates for performing these evaluations have been incorporated into the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and its amendments (SARA). However, this study demonstrates the limitations associated with estimating risk based on available soil analysis data; such risk projections may not describe accurately the dynamic field conditions affecting overall airborne exposure levels. On-site air sampling is therefore a critical adjunct to the risk assessment process for PCB remediation.

Three possible reasons for detecting only PCB 1232 in ambient air at a site which was believed to contain only PCB 1248 and 1254 are 1) masking of the PCB 1232 in the soil sample chromatographs; 2) partial vaporization of the heavier PCB mixtures; and 3) photodecomposition of the heavier congeners during soil excavation.

Masking may occur when the concentration of the undetected species is much lower than the quantitated species. The analytical procedure for PCBs utilizes a "best fit" method of determining the congener or congeners in the sample. The peaks from each of the individual congeners in the sample may be discernable if their concentrations are within an order of magnitude; however, the less concentrated congeners may not be identified if sample dilution sufficiently lowers their chromatographic response. Soils containing high levels of PCB 1248 and 1254 and low levels of PCB 1232 could produce vapor emissions identifiable only as PCB 1232, since its vapor pressure is 10 to 100 times greater than PCB 1248 and 1254 (5).

Partial evaporation of the PCB 1248 and 1254 mixtures could also result in vapors characterized only as PCB 1232. The more volatile Cl_1 to Cl_4 biphenyls which constitute 96% of PCB 1232 are also present in PCB 1248 and PCB 1254 at approximate concentrations of 60% and 20%, respectively (5).

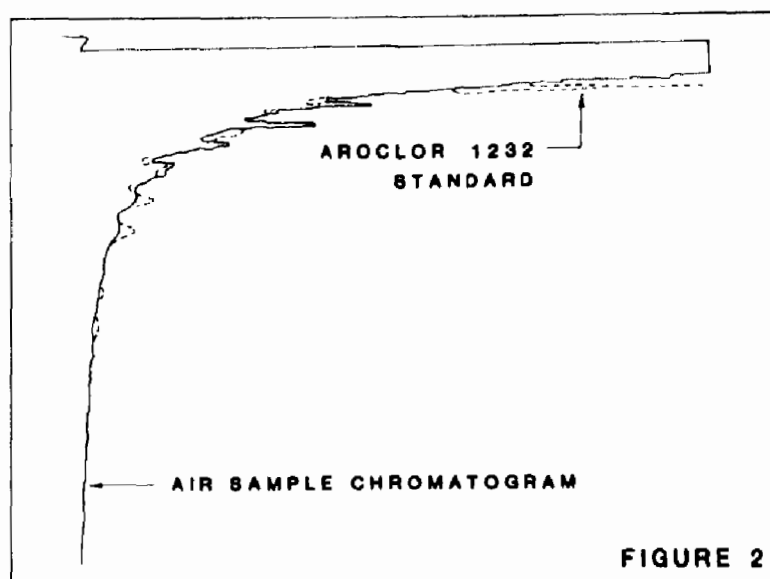
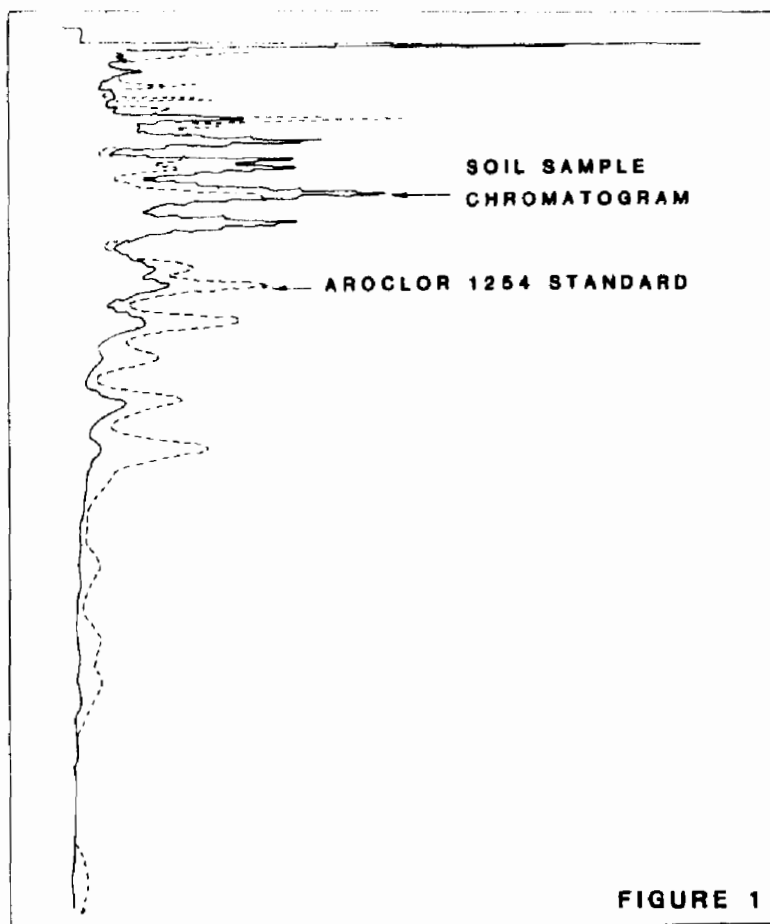
The need to identify adequately all of the PCB congeners present in soils at a given site is illustrated in studies performed by Farmer, et al (6). In their evaluation of evaporation rates of dieldrin from soil, these researchers determined that extremely low soil concentrations (25 ppm) of this semivolatile pollutant produced a maximum saturation vapor density at the soil/air interface equivalent to that of the pure compound.

GC/MS spectrometry (EPA Method 680) can provide better delineation of the various PCB congeners than gas chromatography alone; however, the higher detection limits associated with the GC/MS method prevent use of this technique for analyzing environmental samples containing trace quantities of PCBs. A concentration step, involving a Florisil trap or similar adsorption media, could remedy the detection-limit constraints.

While partial evaporation of and/or failure to detect the presence of PCB 1232 in the soil samples are the most likely causes for the disparity between the soil and air sample results, the potential contribution of photolysis should be examined. Photolysis has also been shown to produce partial dechlorination of PCBs, in addition to producing quaterphenyls, biphenyls and, in the case of hexachlorobiphenyl, chlorinated dibenzofurans (5). These studies dealt with photolysis in water columns; measured breakdown rates were less than 5% per year. Photolysis rates in exposed, aerated soils could be much higher. The health implications of exposure to photolysis break-down products warrants careful examination of these mechanisms.

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GC/MI/FTIR-Improved Capability or New Dimension in Analyses?

J. W. Brasch
BATTELLE
Columbus Division
505 King Avenue
Columbus, Ohio 43201-2593

A commercially available interface between a conventional gas chromatograph and a conventional Fourier transform infrared spectrometer system provides a means to trap GC effluents in a frozen argon matrix and to obtain their IR spectra by reflection/absorption techniques. Chromatographic resolution is maintained by physical separation of the components in the matrix. The combination of low temperature (10°K), matrix isolation (MI), and the ability to signal average for substantial periods of time provides spectra of exceptional quality even with subnanogram amounts of material. This capability reaches sensitivity levels commonly used in many GC/MS analyses and permits IR data to be correlated with GC/MS data under similar, if not identical, GC conditions.

In addition to improved sensitivity, the MI spectral features are much sharper than those in ambient condensed phase spectra. This implies a higher level of information content in the MI spectra. This is indeed the case, and new possibilities for structural elucidation is one result.

These points are illustrated with data from complex environmental samples.

In the course of a research project to evaluate Cryolect performance in environmental analyses, several samples previously analyzed by GC/MS techniques have been studied. One such sample provided a particularly stringent test of Cryolect performance, and the results clearly illustrate the potential of GC/MI-FTIR techniques for complex, "real world" samples. Such potential had been suggested by an earlier study in which MI-FTIR spectra were shown to unambiguously differentiate all 22 isomers of tetrachlorodibenzodioxins (1).

A Mattson Cryolect interfaced to a Varian 3400 GC was used for the analysis. The following GC conditions were used: 30 m, .32 mm id, .25 micron coating, DB-5 column; 1% argon in helium carrier gas, 10 psi head pressure; injector 290, detectors 300; Initial column temp 160; hold 3 min; 30/min to 290; hold 30 min.; 2 μ l injected (splitless).

The effluent from the GC passed through a triple splitter, with 80% of the flow going through a heated transfer line (300°C) to the cold disk (110K) of the Cryolect unit. The remaining 20% of the flow was split equally to an FID detector and an ECD detector.

Infrared spectra were obtained with a Mattson Sirius 100 spectrometer system. Initial spectra were obtained with 100 scans coadded, and a second group of spectra were obtained by coadding 1000 scans. All spectra were at 4 cm^{-1} resolution.

The portion of the GC-run between 13 and 23 minutes is shown in Figure 1. The upper trace is the FID chromatogram and the lower trace is the ECD chromatogram. Seven peaks are numbered in Figure 1. Data obtained for these peaks are as follows.

The spectrum of Peak 1 is shown in Figure 2 above the MI reference spectrum of fluoranthene and is easily identified as such.

From retention times and the previous GC/MS analyses, tetrachloro-dibenzofurans (TCDFs) and tetrachlorodibenzodioxins (TCDDs) were expected in the 20-23 minute region.

The infrared spectrum of Peak 2 is shown in Figure 3, above the MI reference spectrum of 1,3,7,9-TCDD. Again the identification is very obvious, along with evidence for another component (band at 1170 cm^{-1}).

The infrared spectrum of Peak 3 is shown in Figure 4, above the MI reference spectrum of 1,3,6,9-TCDD. The distinct pattern in the 1450-1500 cm^{-1} region makes the identification very certain. Again another component(s) is present (bands at 1105 and 1380 cm^{-1}).

The infrared spectrum of Peak 4 is shown in Figure 5, above MI reference spectra of 1,3,7,8-TCDD and 1,2,4,8-TCDD. The peak is estimated to be a 60/40 mixture of the two isomers.

Figure 6 is the infrared spectrum of the leading edge of Peak 5. With the exception of the 1405 cm^{-1} band, none of the band patterns can be matched to any TCDD isomers. This part of Peak 5 is almost certainly one or more TCDF isomers for which we have reference spectra of only 10 of the 38 isomers. The 1405 cm^{-1} band is due to ^{13}C 2,3,7,8-TCDF.

The spectrum of the trailing edge of Peak 5 is shown in Figure 7 above MI reference spectra of ^{13}C and ^{12}C 2,3,7,8-TCDF. The ^{13}C material was added to the sample as an internal standard during workup for the MS analysis. While most of the bands in the Peak 5 spectrum are accounted for by the two TCDF spectra, bands at ~ 1420 , 1210 , and $950\text{--}900\text{ cm}^{-1}$ indicate the presence of other materials. The spectrum resulting from subtracting the ^{13}C and ^{12}C TCDF spectra from the Peak 5 spectrum is shown in Figure 8. These residual absorptions cannot be matched by any single or combination of other TCDDs or the ten TCDF reference spectra. It, too, is almost certainly one or more of the 28 TCDF isomers for which reference spectra are not yet available.

The infrared spectrum of Peak 6 is shown in Figure 9, above the MI reference spectrum of 1,2,6,8-TCDD, and is unambiguously identified as such.

The infrared spectrum of Peak 7 is shown in Figure 10, above MI reference spectra for ^{13}C and ^{12}C 2,3,7,8-TCDD. The ^{13}C material also was added as an internal standard during the sample workup. The spectra show that a large percentage of this GC peak is the ^{13}C 2,3,7,8-TCDD internal standard, and that there is very little of the native ^{12}C 2,3,7,8-TCDD isomer present. However, the spectra also show another major component(s) with a strong band $\sim 1460\text{ cm}^{-1}$. The result of subtracting the ^{13}C 2,3,7,8-TCDD spectrum from the Peak 7 spectrum is shown in Figure 11, above MI reference spectra for 1,2,3,8-TCDD and 3,4,6,7-TCDF. The correspondence with 1,2,3,8-TCDD bands is obvious. The correspondence with 3,4,6,7-TCDF is far less obvious; however, other work in this laboratory has proved that 3,4,6,7-TCDF coelutes with 2,3,7,8-TCDD under these chromatographic conditions, and the identification can be made with confidence.

In summary, the Cryolect data obtained on this complex environmental sample provided the following information:

- 1) A typical PAH material was unambiguously identified.
- 2) Six TCDD isomers were identified and/or discriminated.
- 3) ^{13}C internal standards can be used for infrared analyses as they are for MS analyses, further suggesting that MI-FT-IR data can be used for quantitative measurements.
- 4) One, unresolved GC peak was shown to have ^{13}C and ^{12}C 2,3,7,8-TCDD, 1,2,3,8-TCDD, and 3,4,6,7-TCDF present. GC/MS data would be unable to discriminate the 1,2,3,8- and 2,3,7,8-TCDD isomers.

- 5) A second unresolved GC peak was shown to have identifiable 2,3,7,8-TCDF (^{12}C and ^{13}C) as well as unidentified component(s) whose spectra indicate one or more additional TCDF isomers. Again MS data could not discriminate these isomers. Infrared spectra of all 38 TCDF isomers would permit the discrimination.

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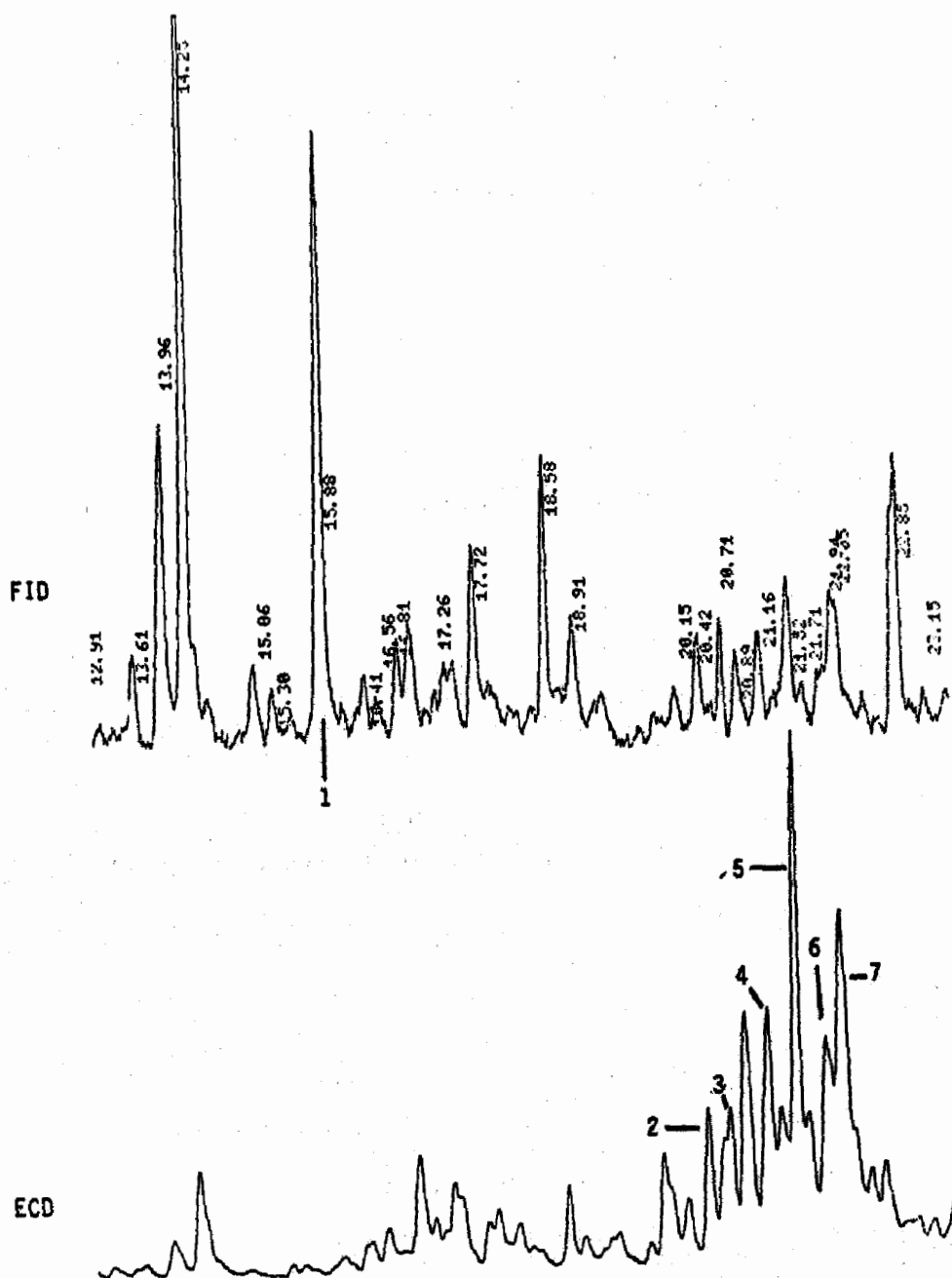


FIGURE 1. PARTIAL CHROMATOGRAMS OF ENVIRONMENTAL SAMPLE

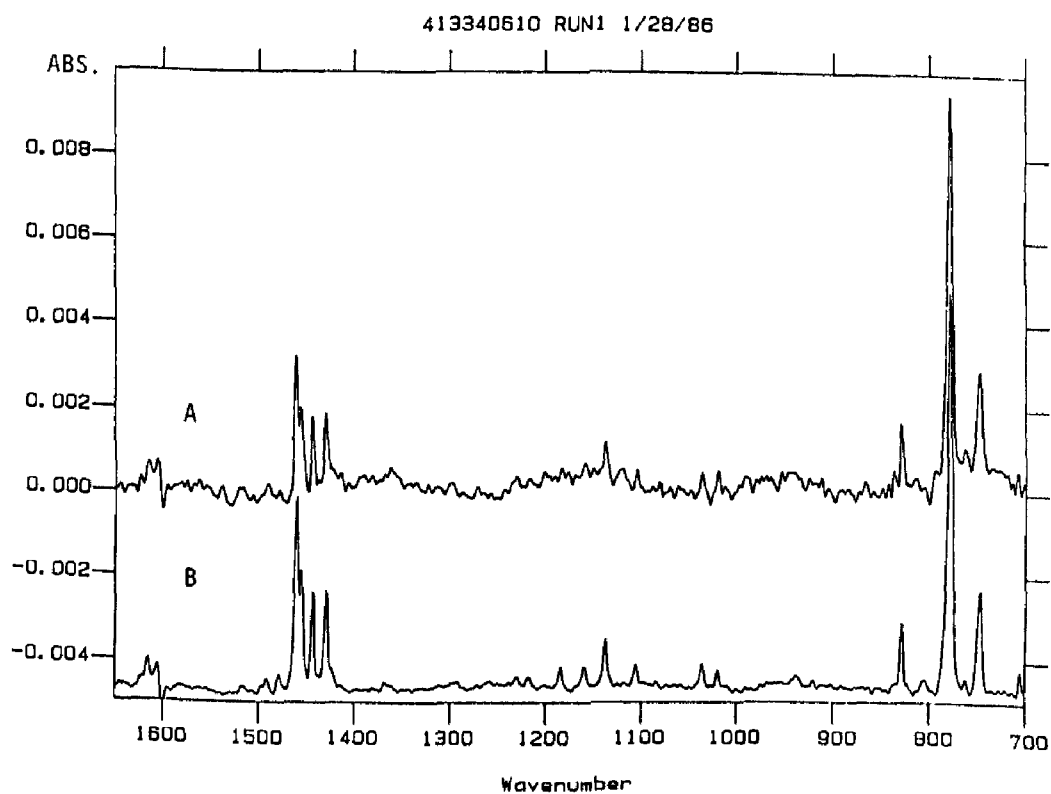


FIGURE 2. A) SPECTRUM OF PEAK #1
B) MI REFERENCE SPECTRUM OF FLUORANTHENE

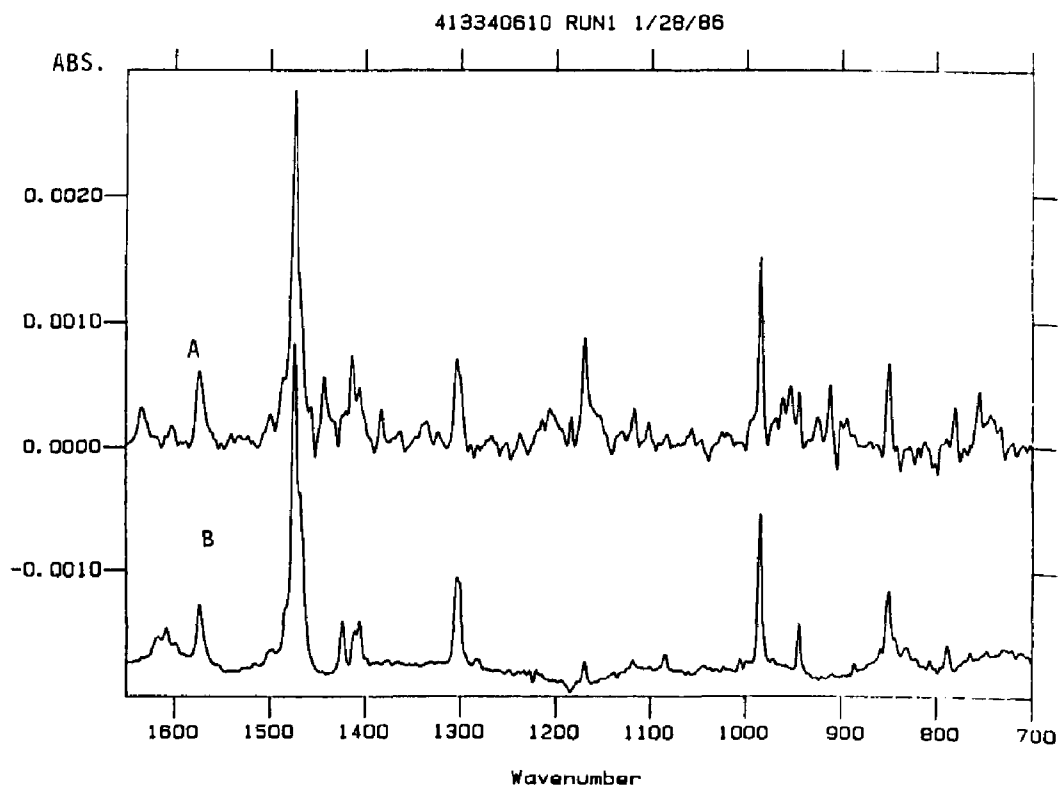


FIGURE 3. A) SPECTRUM OF PEAK #2
B) MI REFERENCE SPECTRUM OF 1,3,7,9-TCDD

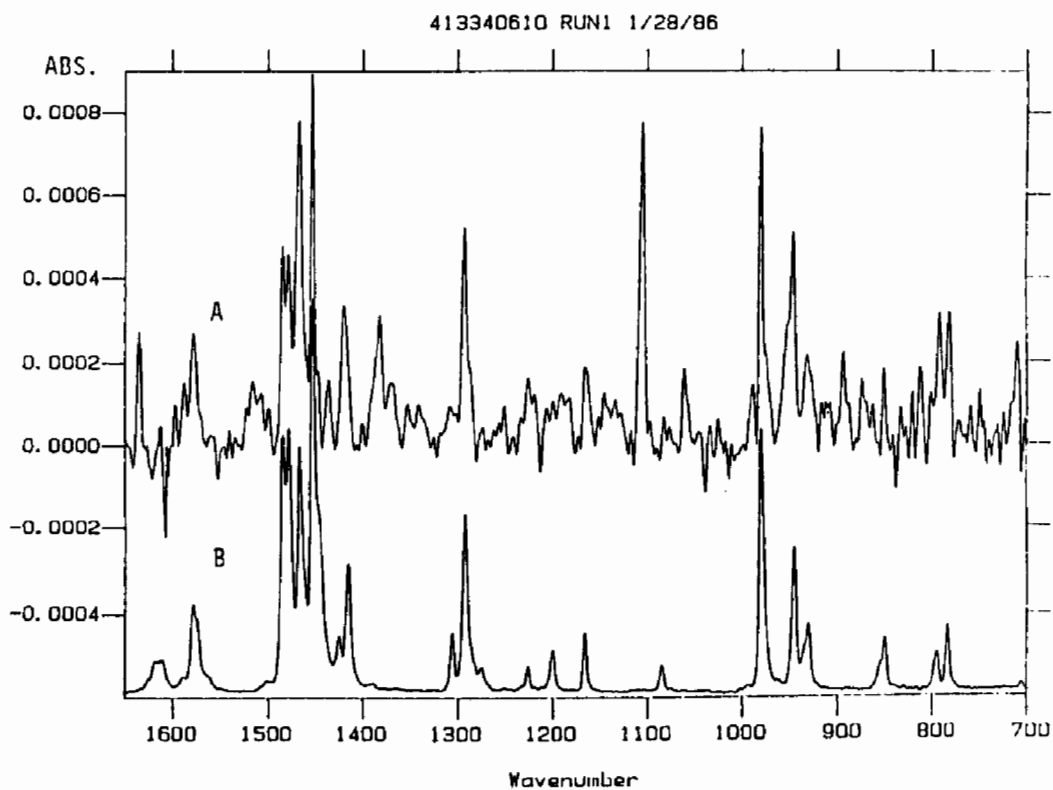


FIGURE 4. A) SPECTRUM OF PEAK #3
B) MI REFERENCE SPECTRUM OF 1,3,6,9-TCDD

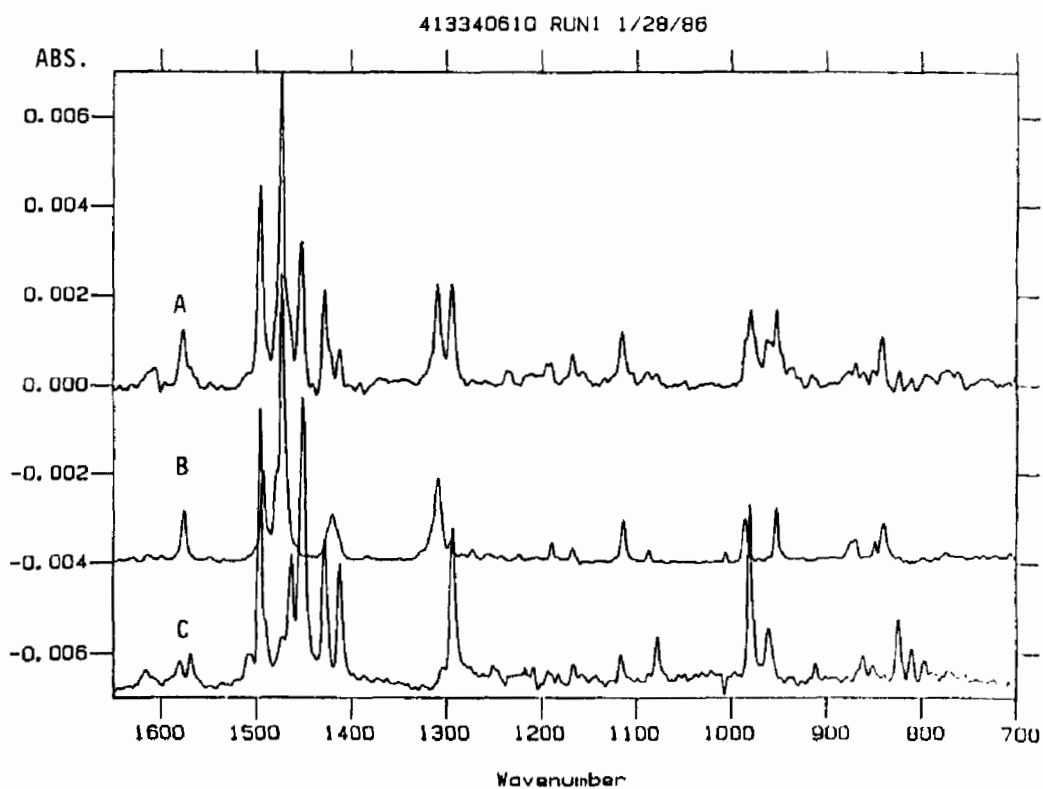


FIGURE 5. A) SPECTRUM OF PEAK #4
B) MI REFERENCE SPECTRUM OF 1,3,7,8-TCDD
C) MI REFERENCE SPECTRUM OF 1,2,4,8-TCDD

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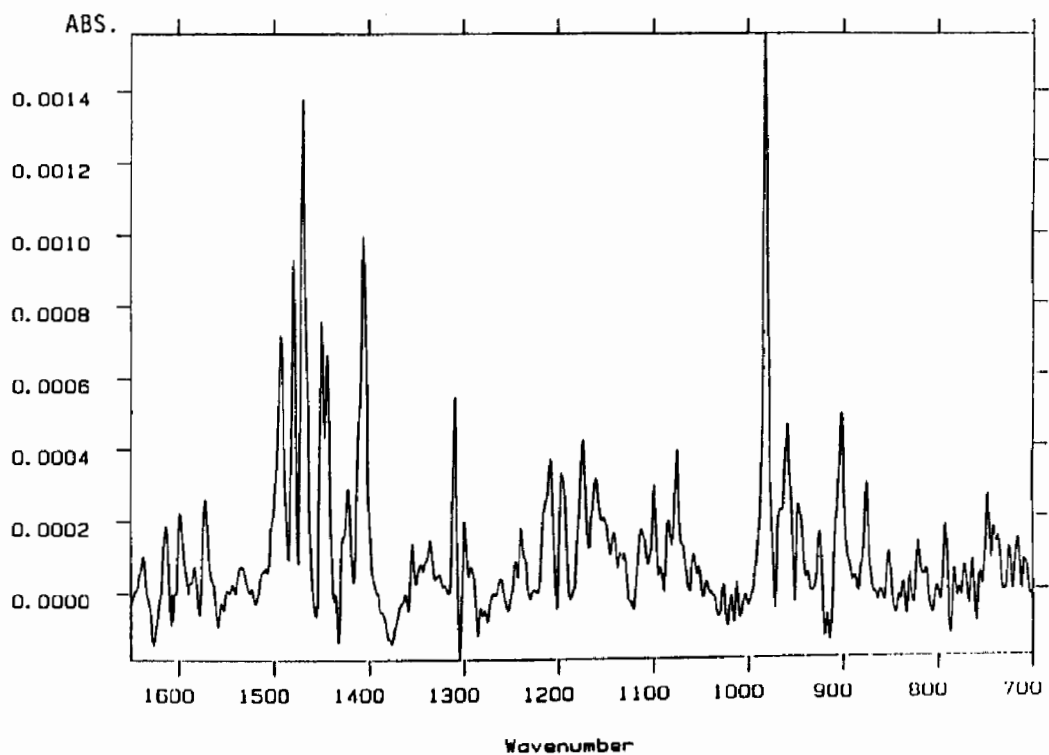


FIGURE 6. SPECTRUM OF LEADING EDGE OF PEAK #5

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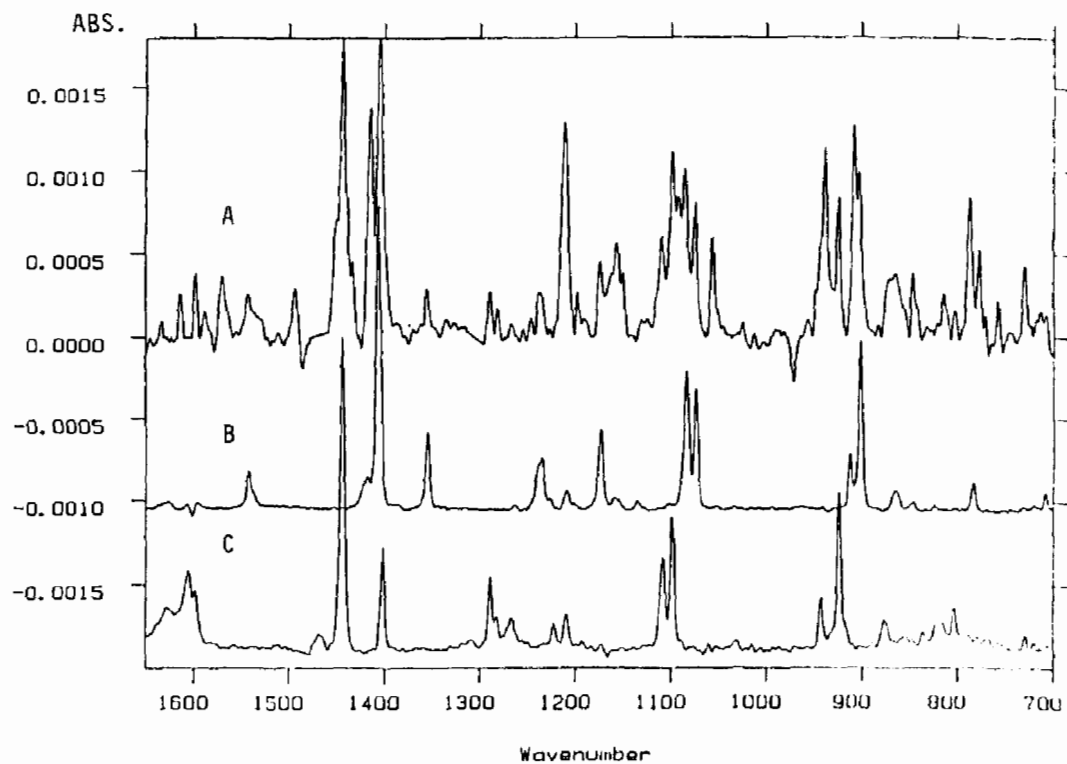


FIGURE 7. A) SPECTRUM OF TRAILING EDGE OF PEAK #5
B) MI REFERENCE SPECTRUM OF ^{13}C 2,3,7,8-TCDF
C) MI REFERENCE SPECTRUM OF ^{12}C 2,3,7,8-TCDF

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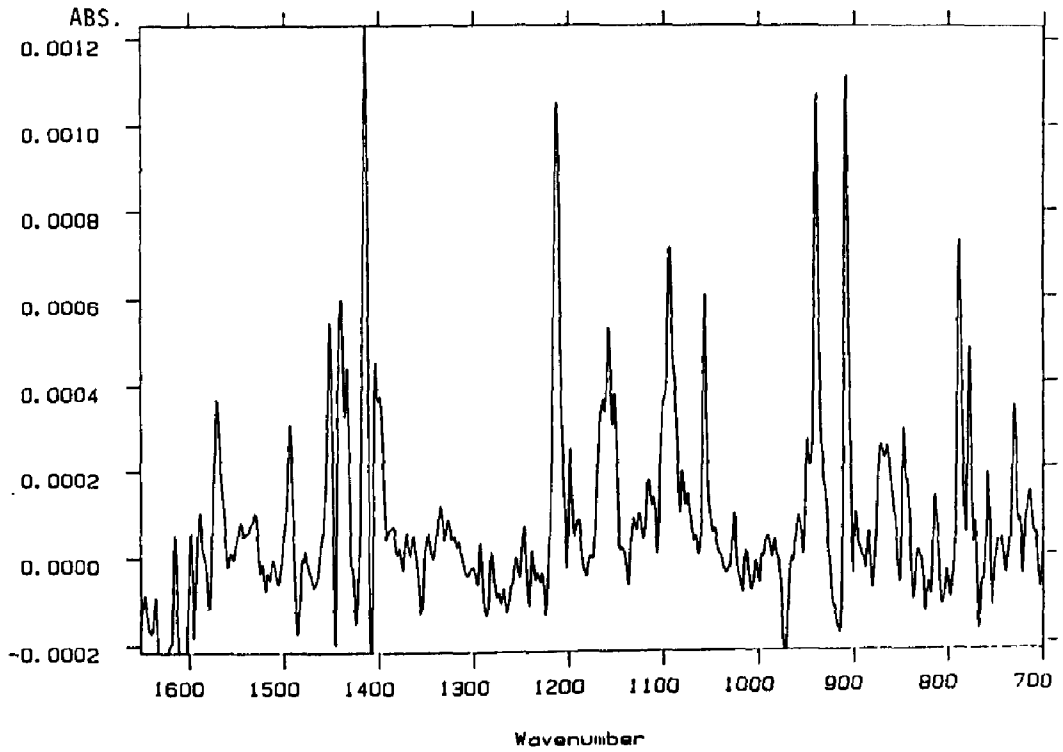


FIGURE 8. RESULT OF DOUBLE SUBTRACT OF ^{13}C and ^{12}C 2,3,7,8-TCDF FROM SPECTRUM OF TRAILING EDGE OF PEAK #5

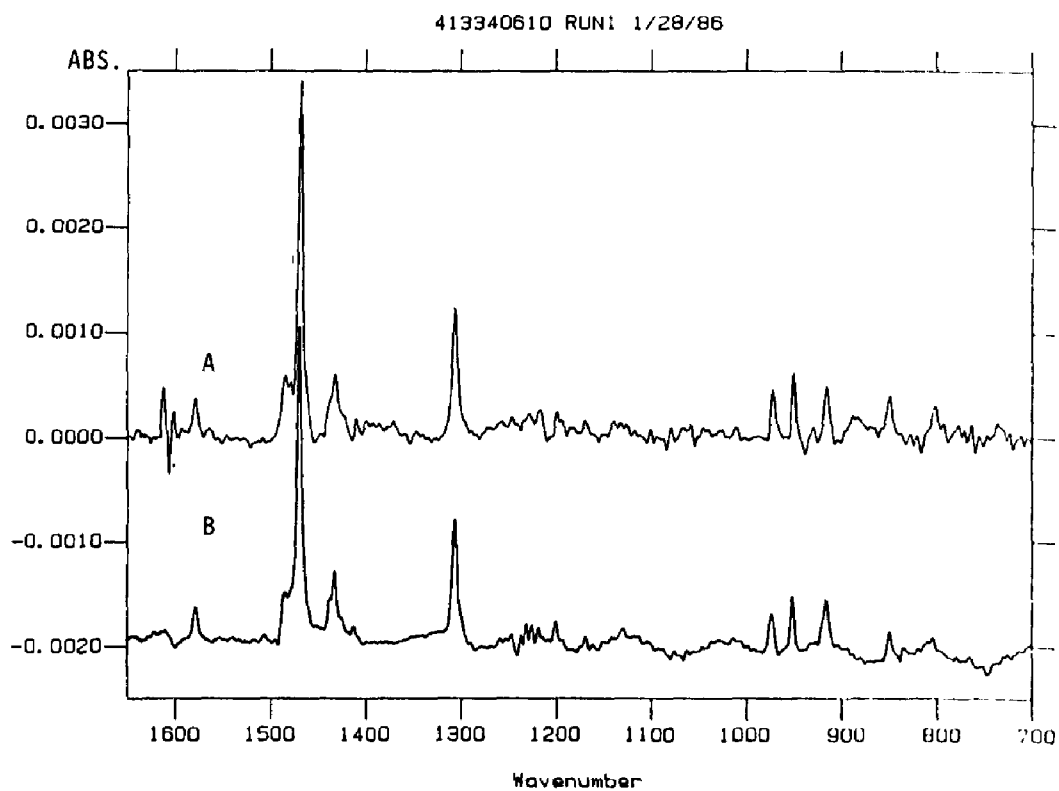


FIGURE 9. A) SPECTRUM OF PEAK #6
B) MI REFERENCE SPECTRUM OF 1,2,6,8-TCDD

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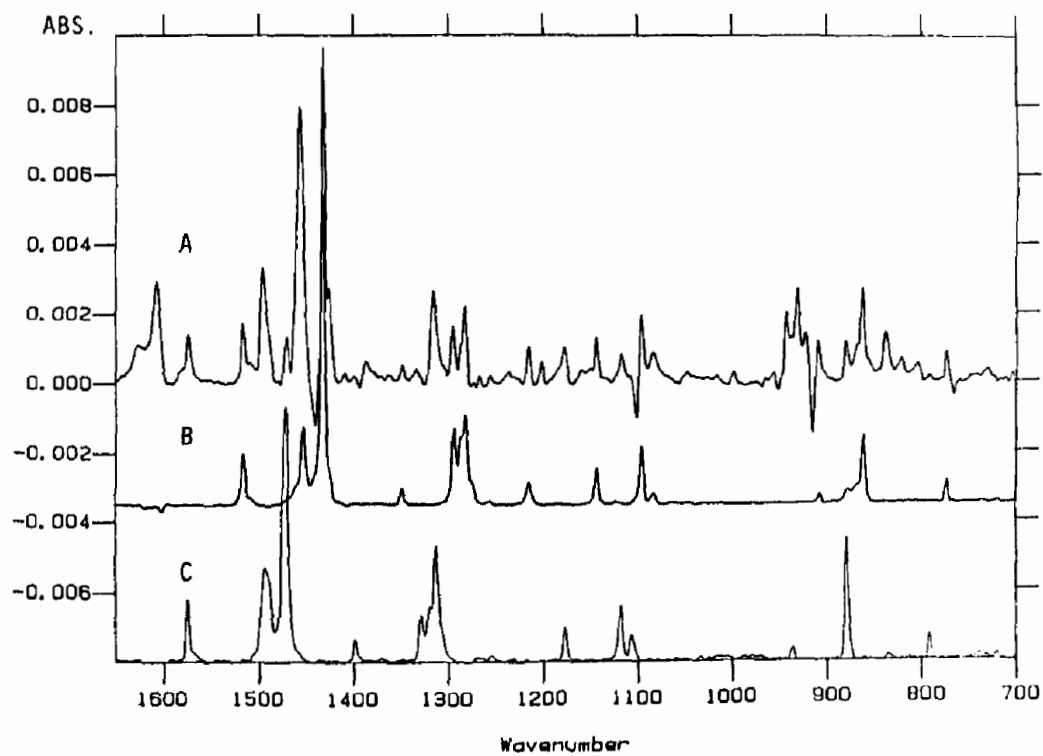


FIGURE 10. A) SPECTRUM OF PEAK #7
B) MI REFERENCE SPECTRUM OF ^{13}C 2,3,7,8-TCDD
C) MI REFERENCE SPECTRUM OF ^{12}C 2,3,7,8-TCDD

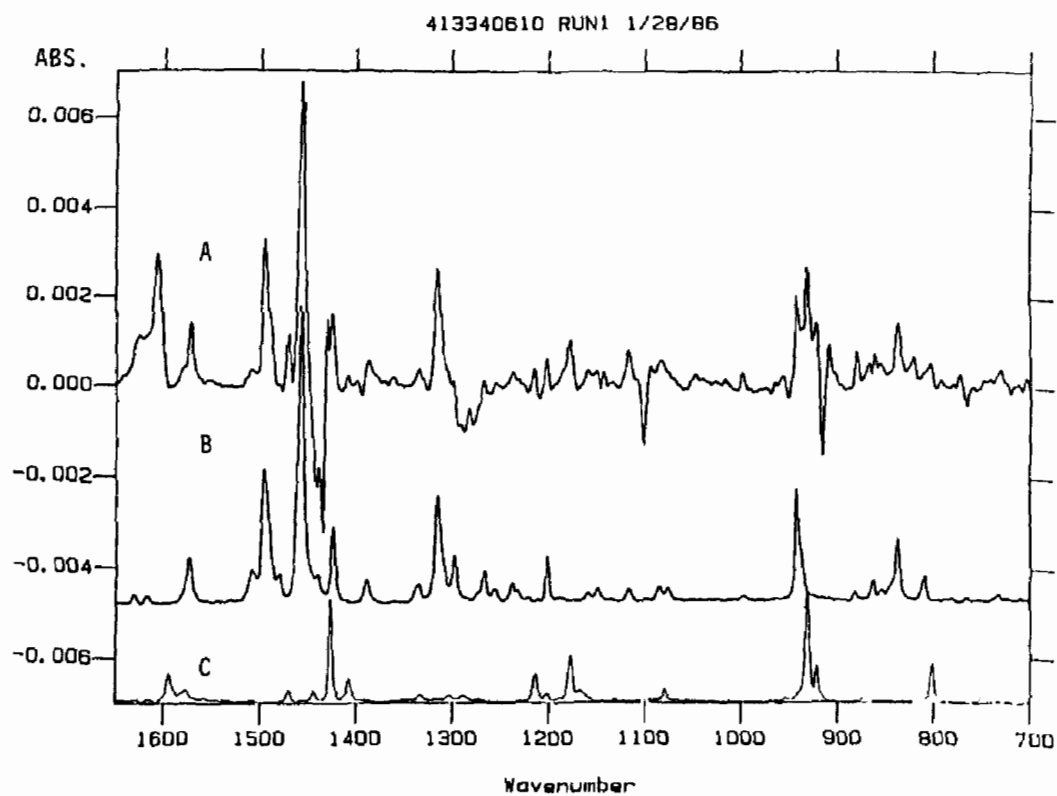


FIGURE 11. A) RESULT OF SPECTRAL SUBTRACT OF ^{13}C 2,3,7,8-TCDD
FROM SPECTRUM OF PEAK #7
B) MI REFERENCE SPECTRUM OF 1,2,3,8-TCDD
C) MI REFERENCE SPECTRUM OF 3,4,6,7-TCDF

GAS CHROMATOGRAPHY/MATRIX ISOLATION INFRARED SPECTROMETRY
FOR THE ANALYSIS OF ORGANIC COMPOUNDS IN AIR

Jeffrey W. Childers
Northrop Services, Inc. - Environmental Sciences
P. O. Box 12313
Research Triangle Park, North Carolina 27709

Nancy K. Wilson and Ruth K. Barbour
U. S. EPA, Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

Abstract

The combination of gas chromatography and matrix isolation infrared spectrometry (GC/MI-IR) is currently being evaluated for the characterization of semivolatile organic compounds (SVOCs) in air. The ability of GC/MI-IR to distinguish between isomeric polycyclic aromatic hydrocarbons (PAHs) is demonstrated. The ability of GC/MI-IR to identify specific PAHs found in complex environmental samples is illustrated by the analysis of an extract from NBS standard reference material 1649 (urban dust/organic).

Introduction

Over the past thirty years, matrix isolation has been an important sampling technique for the infrared characterization of unstable, reactive and transient species (1). To a lesser extent, matrix isolation infrared spectrometry (MI-IR) has been used for the qualitative and quantitative analysis of stable compounds (2). Recently, MI-IR has been combined with gas chromatography for the analysis of complex mixtures (3). The combination of gas chromatography and matrix isolation infrared spectrometry (GC/MI-IR) involves the trapping of the GC effluent in a frozen argon matrix as it is deposited on a rotating gold-plated cryogenic disk (3). The cryogenic disk is enclosed in an evacuated chamber and is maintained at approximately 14°K. Therefore the separated GC effluents remain frozen on the disk indefinitely and can be analyzed by infrared spectrometry after the completion of the GC run.

GC/MI-IR offers several advantages over lightpipe-based "on-the-fly" GC/IR systems. The most significant advantage is an increase in sensitivity. This is realized by the ability to signal-average the infrared spectrum of the matrix-isolated compound from the GC effluent and by the higher concentration of that compound in a small cross-sectional area on the cryogenic disk. Matrix isolation infrared spectra also exhibit sharp spectral features, which result from the elimination of band broadening due to molecular rotations and intermolecular interactions. Another advantage of GC/MI-IR is that the separation

and the detection of components in a mixture are independent steps. Therefore, both the chromatography and the spectroscopy can be optimized.

Efforts in our laboratory involve the development and evaluation of methods for the characterization of semivolatile organic compounds (SVOCs) in air. The application of GC/MI-IR to the identification of target polycyclic aromatic hydrocarbons (PAHs) is illustrated by the analysis of an extract of NBS standard reference material 1649 urban dust/organic (SRM 1649).

Experimental Methods

All data were obtained on a Mattson Instruments Cryolect system. The Cryolect is interfaced to a Mattson Instruments Sirius 100 Fourier transform infrared spectrometer and a Hewlett-Packard 5890A gas chromatograph equipped with a flame ionization detector (FID), on-column injector, and a Hewlett-Packard 3392A integrator. GC separations were carried out using a 30 m x 0.25 mm DB-5 fused silica capillary column with a 0.25 μ m film thickness. The GC oven was held at an initial temperature of 40°C for 4 min then temperature programmed at 8°C/min to 300°C and held at 300°C for 30 min. The effluent from the GC column was split approximately 5:1 between the cryogenic disk and the GC/FID. A weighed amount of SRM 1649 was Soxhlet-extracted for approximately 40 h in methylene chloride. The methylene chloride extract was concentrated, the solvent exchanged to hexane, and then fractionated on a silica gel column. A 1 μ L aliquot of this fractionated extract was injected into the Cryolect system. All infrared spectra were collected at a nominal 4 cm⁻¹ resolution and signal-averaged for 128 scans.

Results and Discussion

The capabilities of GC/MI-IR for the characterization of SVOCs in air are illustrated by the analysis of the SRM 1649 extract, for which a portion of the GC/FID trace is shown in Figure 1. Previously, a reference MI-IR spectral library was compiled of target PAHs. The capability of MI-IR to distinguish between isomeric PAHs is illustrated by the comparison of the MI-IR spectra of benzo[a]pyrene and benzo[e]pyrene, shown in Figure 2. Other PAH isomeric pairs, such as benzo[b]fluoranthene/benzo[k]fluoranthene and chrysene/triphenylene can also be easily distinguished by their MI-IR spectra. This is extremely important considering the wide range of toxicities and the difficulty in separating and/or differentiating PAH isomers by other analytical techniques (e. g., gas chromatography/mass spectrometry).

Several specific PAHs in the SRM 1649 extract were identified by GC/MI-IR. The MI-IR spectrum of the component which elutes at 25.64 min, a retention time close to that expected for either phenanthrene or anthracene, is shown in Figure 3a. A search of that spectrum versus the reference MI-IR spectral library of several PAHs clearly identifies the component as phenanthrene and not anthracene (compare Figure 3a with Figures 3b and 3c). Similarly, the compounds eluting at 29.50 min and 30.20 min were identified as fluoranthene and pyrene, respectively.

The MI-IR spectrum of the component eluting at 37.54 min indicates the presence of a compound with a carbonyl functional group. Upon closer examination of its spectrum shown in Figure 4a, spectral features that are characteristic of benzo[b]fluoranthene are also apparent (Figure 4b). By subtracting a MI-IR spectrum collected at the tailing edge of the GC peak at 37.54 min from a MI-IR spectrum collected at the leading edge of the same peak, the presence of benzo[b]fluoranthene is confirmed (compare Figures 5a and 5b). By using either spectral subtraction or library searches, or the combination of both, the following PAHs were also identified in the SRM 1649 extract: chrysene and triphenylene (34.28 min), benzo[e]pyrene (38.39 min) and benzo[g,h,i]perylene (44.25 min).

Conclusions

The combination of gas chromatography and matrix isolation infrared spectrometry has been shown to be a viable technique for the identification of specific PAH in a complex environmental sample. The ability of GC/MI-IR to distinguish between isomeric PAHs gives it a tremendous advantage over other analytical techniques. GC/MI-IR has the capability to identify target compounds even if they are not completely chromatographically separated from other components in the mixture. GC/MI-IR also has the sensitivity required for the detection of the trace amounts of pollutants typically found in environmental samples. The combination of molecular specificity and high sensitivity indicates a great potential for the utilization of GC/MI-IR for the analysis of complex environmental samples.

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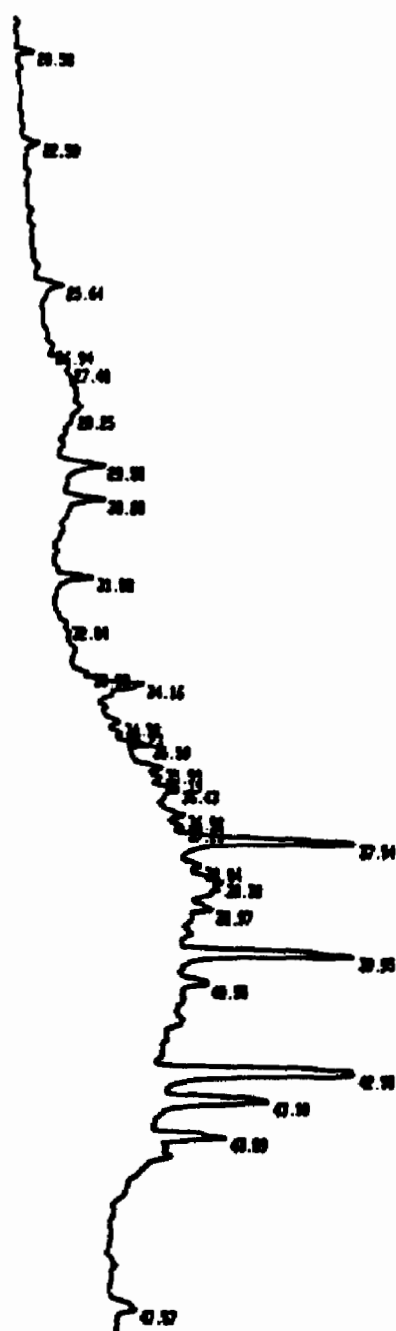


Figure 1. GC/FID trace of SRM 1649 extract.

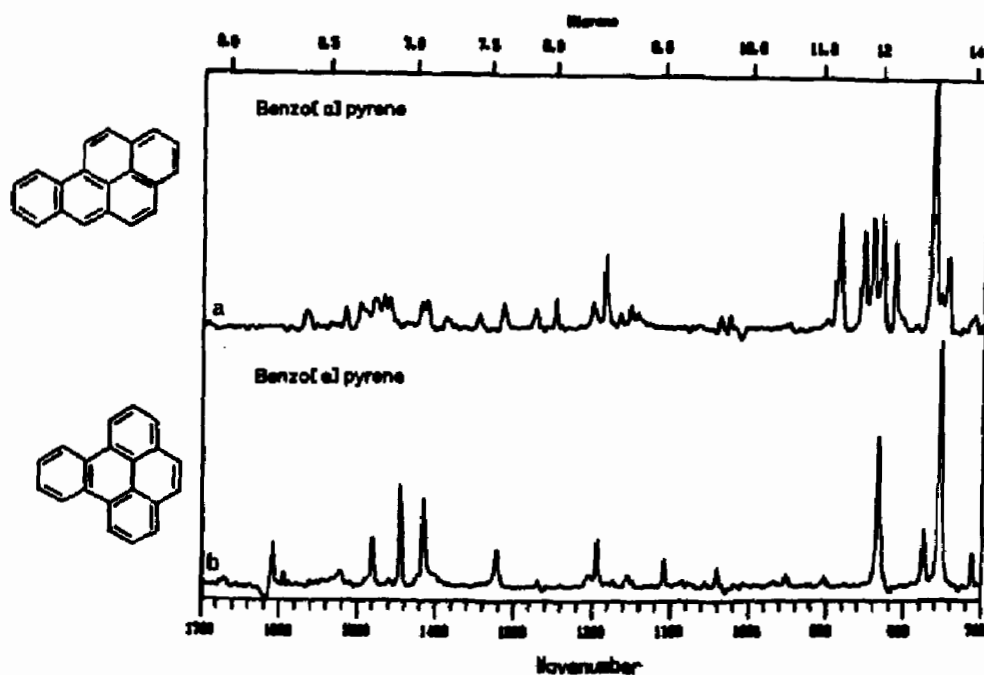


Figure 2. MI-IR spectra of benzo[a]pyrene (a) and benzo[e]pyrene (b).

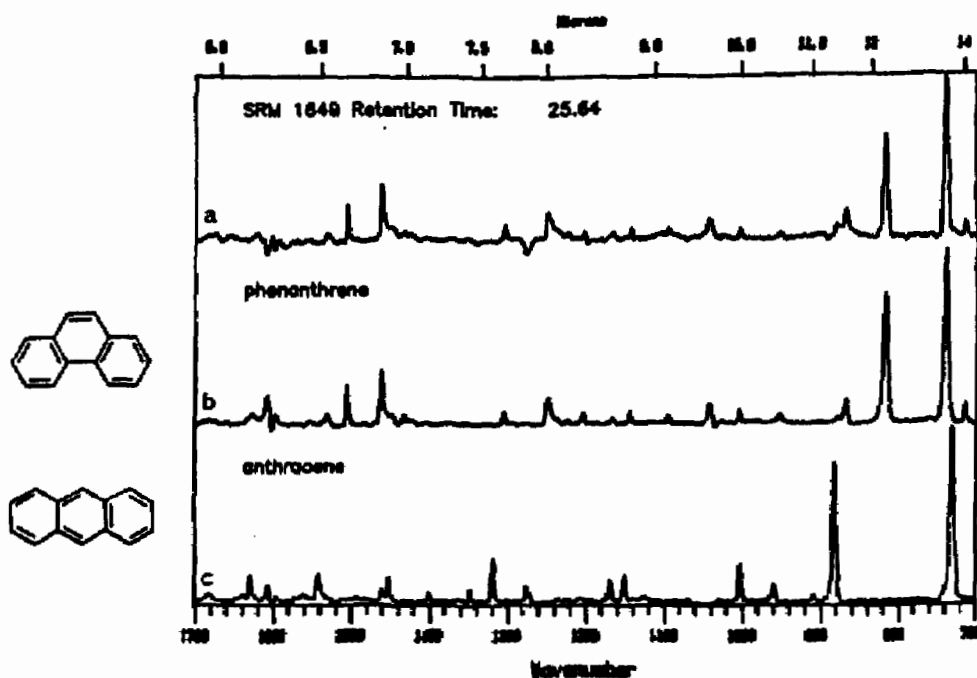


Figure 3. MI-IR spectrum of component eluting at 25.64 min in SRM 1649 extract (a) compared to MI-IR reference spectra of phenanthrene (b) and anthracene (c).

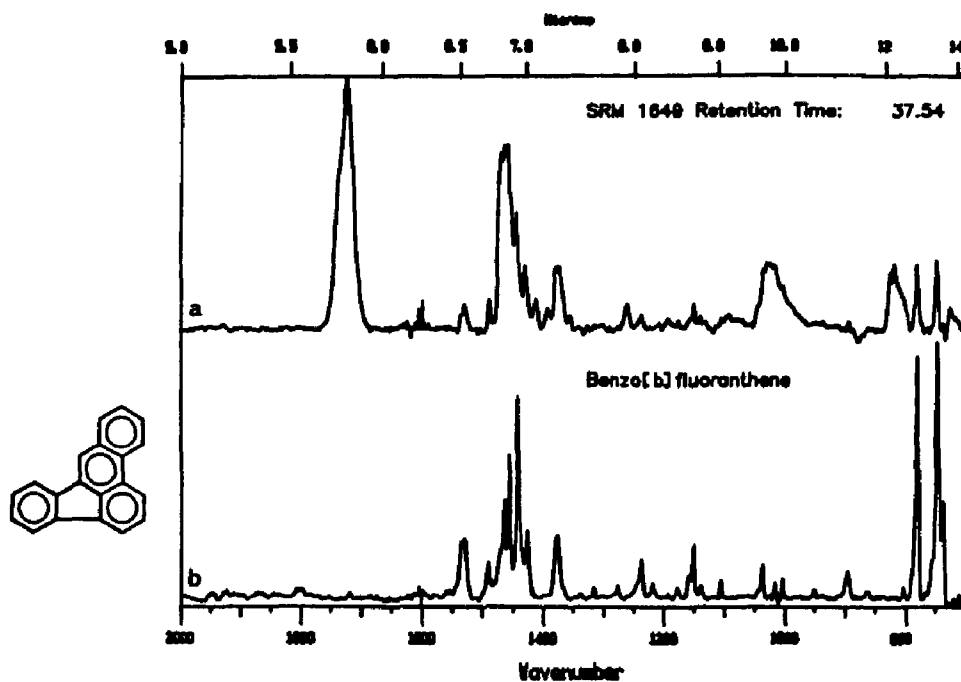


Figure 4. MI-IR spectrum of component eluting at 37.54 min in SRM 1649 extract (a) compared to MI-IR reference spectrum of benzo[b]fluoranthene (b).

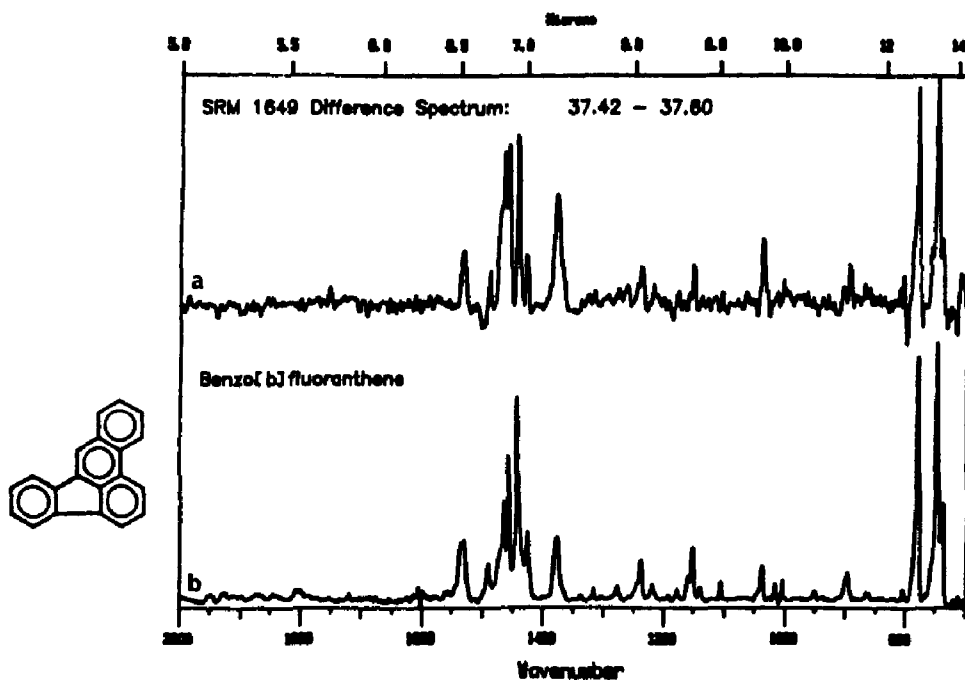


Figure 5. Difference spectrum obtained by subtracting MI-IR spectrum at 37.60 min from MI-IR spectrum at 37.42 min in SRM 1649 extract (a) compared to MI-IR reference spectrum of benzo[b]fluoranthene (b).

SUPERCRITICAL FLUID EXTRACTION AND RECOVERY
OF PAH FROM AIR-BORNE PARTICULATES



Steven B. Hawthorne and David J. Miller
University of North Dakota
Energy Research Center
Campus Box 8213
Grand Forks, North Dakota 58202

Supercritical fluid extraction of PAH from particulates has several potential advantages over traditional methods such as Soxhlet extraction and sonication with liquid solvents. The solvent strengths of supercritical fluids can equal or surpass those of liquids, and can easily be controlled by choice of the supercritical fluid, the extraction pressure, or the addition of solvent modifiers. Many supercritical fluids are gases at room temperature which simplifies analyte concentration steps. We have developed methodology for the supercritical fluid extraction of PAH from particulate samples that yields good recovery, requires only small (1-50 mg) samples, and is simple and rapid to perform. Supercritical ethane, CO₂, and N₂O (with and without 5% methanol modifier) have been evaluated for their ability to extract PAH from urban dust and fly ash. The most effective supercritical fluid (N₂O with 5% methanol modifier by volume) yielded quantitative recovery of PAH from urban dust (SRM 1649) in as little as 30 minutes. In general, 60 minute extractions of PAH from fly ash with supercritical N₂O/5% methanol gave better recoveries than four hours of sonication or eight hours of Soxhlet extraction using either benzene or methylene chloride. A method for the direct coupling of the supercritical fluid extraction step with GC/MS and GC/FID has also been developed that allows for maximum sensitivity by transferring all of the extracted analytes directly into the gas chromatographic column for cryogenic trapping prior to gas chromatographic analysis. Analysis of PAHs from urban dust (SRM 1649) using coupled supercritical fluid extraction with GC/MS gave good agreement with certified values.

Introduction

The rapid and accurate identification and quantitation of organic species associated with air-borne particulates is often limited by the extraction and recovery methods required prior to chromatographic analysis. Traditional extraction techniques generally require large volumes of ultra-pure liquid solvents and several hours of sonication or extraction in a Soxhlet apparatus. After extraction, concentration steps are generally required, which increases the time required for analysis and may lead to analyte loss or degradation. Supercritical fluid extractions have recently been reported to be a powerful alternative method for the extraction and recovery of organic analytes such as polycyclic aromatic hydrocarbons (PAHs) from solid samples^{1,2}. Supercritical fluids can have solvent strengths that equal or surpass those of liquid solvents, and the solvent strength can easily be varied by changing the extraction pressure (and therefore, the fluid density) or by the addition of a polarity modifier such as methanol. Since many supercritical fluids are gases at room temperature, analyte concentration steps are simplified and the direct coupling of the supercritical fluid extraction step with capillary gas chromatography is feasible.

This report describes the development and use of supercritical fluid extractions (SFE) for the extraction and recovery of organic analytes from air-borne particulates. The abilities of several supercritical fluids to extract PAHs from urban dust and fly ash are compared with each other as well as with liquid solvent extractions using sonication and Soxhlet extraction. A method is also presented for the direct coupling of the supercritical fluid extraction step with capillary gas chromatography (SFE-GC). SFE and coupled SFE-GC were used for the extraction of PAHs from National Bureau of Standards SRM 1649 (urban dust) and quantitative values obtained using GC/MS analysis are compared with the certified concentrations.

Experimental Methods

Supercritical fluid extractions were performed using an SFT Model 250-TMP supercritical fluid pump (Lee Scientific, Inc.). Five percent by volume methanol modified CO₂ and N₂O were prepared by pipetting methanol into the empty pump, then filling the pump with liquid CO₂ (or N₂O). (Caution, since N₂O is an oxidant, extractions of large quantities of easily oxidized materials may represent an explosion hazard and should be avoided. As an added precaution for this study, a pressure relief valve set to vent at 400 atm was installed at the top of the pump so that both the pump and extraction cells could be rapidly vented.) Extraction cells were constructed from stainless steel fittings (Parker brand) and consisted of a 1/16 in. female NPT X 1/16 in. tubing union, a 0.5 μ m stainless steel frit, and a 1/16 in. male NPT X 1/16 in. tubing union. Supercritical pressures were maintained inside the extraction cells by using 15 to 30 μ m i.d. X 150 μ m o.d. fused silica capillary tubing for outlet restrictors. Temperature was maintained during extraction by inserting the cell into a thermostatted tube heater. The species extracted during SFE were collected by inserting the outlet restrictor into a vial containing 2 mL methylene chloride and 0.5 μ g of 4,4'-dichlorobiphenyl as an internal standard. PAH quantitations were performed using a Hewlett-Packard Model 5985B GC/MS in the selected ion monitoring (SIM) mode.

The direct coupling of the supercritical fluid extraction step with the gas chromatographic column was achieved by inserting the SFE outlet restrictor capillary directly into the gas chromatographic column through the on-column injection port. Extracted species were cryogenically trapped in the gas chromatographic column which was held at 5°C. After the extraction was completed, the restrictor capillary was withdrawn from the injector and gas chromatographic analysis was performed in a normal manner.

Results

A comparison of the abilities of supercritical ethane, CO₂, N₂O, CO₂/5% methanol, and N₂O/5% methanol to extract PAHs from urban dust and fly ash is given in Table I. Triplicate extractions were performed at 300 atm with each fluid of urban dust and fly ash at 45°C (for the pure fluids) or 65°C (for the methanol modified solvents). The recovery of PAHs from the urban dust (20 mg samples) was based on the values certified by NBS. PAH recovery from fly ash (50 mg samples) was based on deuterated spikes (2 µg/g each of d₁₀-phenanthrene, d₁₀-pyrene, and d₁₂-perylene). Extraction conditions were purposely chosen (i.e., 30 min extractions using a 20 µm i.d. outlet restrictor) to yield less than quantitative recovery in order that comparisons between the different supercritical fluids could be made. The results of the comparative extractions (Table I) show that the methanol modified solvents yielded better recovery of the PAHs from both the urban dust and fly ash. The replicate extractions showed good reproducibility. Lower molecular weight species were more easily extracted than higher molecular weight species in every case, as would be expected based on the higher solubility of the lower molecular weight species.

A comparison between the extraction efficiencies obtained for PAHs from fly ash using the best supercritical fluid tested, N₂O/5% methanol, and those obtained using sonication and Soxhlet extraction is shown in Figure 1. Supercritical fluid extractions were performed at 350 atm for an hour using a 30 µm i.d. outlet restrictor. Soxhlet extractions were performed for 8 hours using 1-gram samples and 50 mL solvent. Sonication extractions were performed using 0.5-gram samples for 4 hours with 10 mL solvent (4,4'-dichlorobiphenyl was used as an internal standard in each case). Figure 1 shows that, in most cases, the supercritical fluid extraction gave better PAH recovery in 1 hour than either 4 hours of sonication or 8 hours of Soxhlet extraction. Sonication did not yield better recovery of any of the PAHs, while Soxhlet extractions yielded better recovery only of the d₁₂-perylene.

The use of coupled SFE-GC/MS is demonstrated in Figure 2 by the analysis of organics from cigarette ash. A 2-mg sample was extracted for 10 min with 300 atm N₂O and the extracted organics were cryogenically trapped in the chromatographic column (60 m X 250 µm i.d. DB-5) as described above. As shown by Figure 2, reasonable chromatographic peak shapes were obtained using the coupled SFE-GC technique. The total extraction and analysis time was 40 min.

Coupled SFE-GC/MS was also used to demonstrate the potential for class-selective extractions using supercritical fluids. A 1-mg sample of urban dust (SRM 1649) was extracted with 75 atm N₂O for 5 min (extraction 1) with the extracted species being collected directly in the gas chromatographic column as described above. After the SFE-GC/MS analysis of this first extract was completed, a second extraction of

the same sample was performed using 300 atm N₂O for 15 min. As shown in Table II, most of the alkanes were extracted during the 75 atm extraction, while most of the PAHs were not extracted until the 300 atm extraction. These initial results demonstrate that the coupled SFE-GC technique can be used to perform class-selective extractions without the need for any intermediate sample collection and class-fractionation steps between the extraction and the introduction into the chromatographic column.

The ability of SFE and SFE-GC/MS analysis to yield quantitative recovery of PAHs from NBS 1649 (urban dust) is shown in Table III. The SFE extraction was performed for 30 min with 300 atm of N₂O/5% methanol (30 μ m restrictor). Extracted PAHs were collected in methylene chloride and analyzed as described above. Coupled SFE-GC/MS analysis was performed using 20 min extractions with 350 atm of N₂O with the extracted species being collected directly in a 30 m X 320 μ m i.d. DB-5 gas chromatographic column. As shown in Table III, both the SFE and the coupled SFE-GC/MS techniques gave good agreement with the certified values demonstrating the ability of both techniques to yield quantitative data.

Conclusions

Supercritical fluid extractions can be used to obtain high extraction efficiencies of PAHs from air-borne particulates in an order-of-magnitude faster time than traditional liquid solvent extraction methods. Coupling the supercritical fluid extraction step directly with on-column trapping of extracted analytes (SFE-GC) can yield quantitative results with a total extraction and analysis time of less than 1 hour. Coupled SFE-GC has an additional advantage in that extracted analytes are quantitatively transferred into the gas chromatographic column thus yielding maximum sensitivity with minimal sample size.

Acknowledgements

The financial support of the U.S. EPA, Office of Exploratory Research, is gratefully acknowledged.

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Table I
Comparison of Different Supercritical Fluids for the
Recovery of PAH from Urban and Fly Ash

	Percent Recovery from Urban Dust				
	ethane	CO ₂	N ₂ O	CO ₂ /MeOH	N ₂ O/MeOH
fluoranthene	53	79	101	103	100
benz[a]anthracene	48	86	104	102	101
benzo[a]pyrene	17	33	40	62	86
benzo[ghi]perylene	14	17	22	29	39
indeno[1,2,3-cd]-pyrene	15	20	26	34	43

	Percent Recovery from Fly Ash				
	ethane	CO ₂	N ₂ O	CO ₂ /MeOH	N ₂ O/MeOH
d ₁₀ -phenanthrene	33	27	42	58	66
d ₁₁ -pyrene	8	8	12	23	41
d ₁₂ -perylene	1	1	1	3	4

Table II
Class-Selective Extraction of Alkanes and PAHs
From Urban Dust Using Coupled SFE-GC/MS

	Percent In Fraction	
	Extraction 1 75 atm N ₂ O	Extraction 2 300 atm N ₂ O
n-alkanes		
C ₂₂	95	5
C ₂₃	94	6
C ₂₄	96	4
C ₂₅	92	8
C ₂₆	89	11
PAHs		
phenanthrene	38	62
fluoranthene	36	64
pyrene	34	66
benz[a]anthracene	21	79
benzo[a]pyrene	2	98
indeno[1,2,3-cd]pyrene	ND	>95
benzo[ghi]perylene	ND	>95

Table III
Quantitation of PAHs from NBS SRM 1649 (Urban Dust) Using
Supercritical N₂O/5% Methanol Extraction and Coupled SFE-GC/MS

	Concentration (µg/g)		
	Certified Value ^a	Supercritical N ₂ O/5% MeOH ^b	Coupled SFE-GC/MS ^c
fluoranthene	7.1 ± 0.5	7.4 ± 0.4	7.3 ± 1.0
benz[a]anthracene	2.6 ± 0.3	2.5 ± 0.3	2.6 ± 0.8
benzo[a]pyrene	2.9 ± 0.5	2.9 ± 0.2	2.8 ± 0.5
benzo[ghi]perylene	4.5 ± 1.1	3.2 ± 0.2	3.6 ± 0.9
indeno[1,2,3-cd]-pyrene	3.3 ± 0.5	2.3 ± 0.2	3.0 ± 0.5

^aValue certified by the National Bureau of Standards.

^bBased on triplicate extractions of 20-mg samples.

^cBased on four replicate analyses of 2-mg samples.

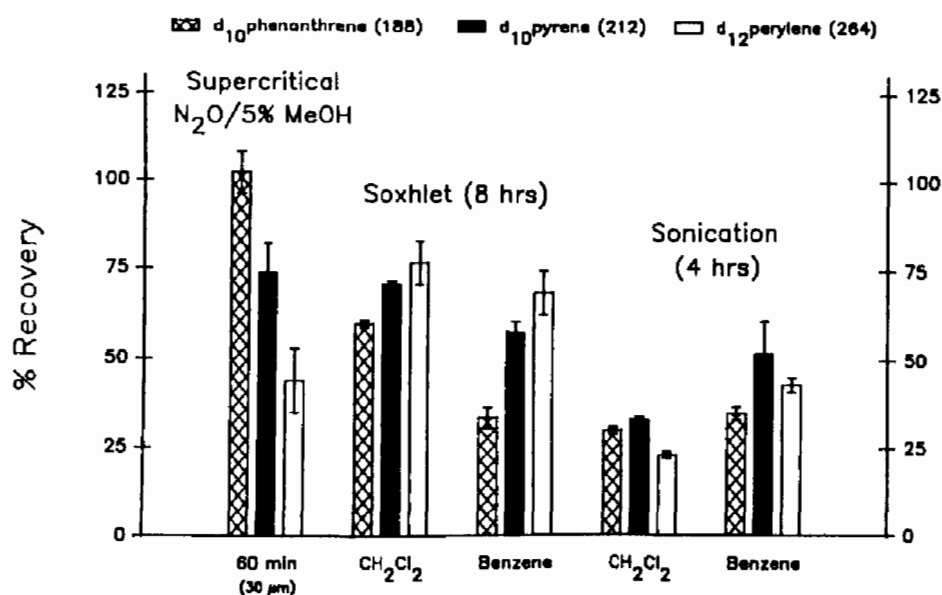


Figure 1. Recovery of PAHs from fly ash using supercritical $N_2O/5\%$ methanol extraction for 1 hour, Soxhlet extraction with methylene chloride and benzene for 8 hours, and sonication with methylene chloride and benzene for 4 hours.

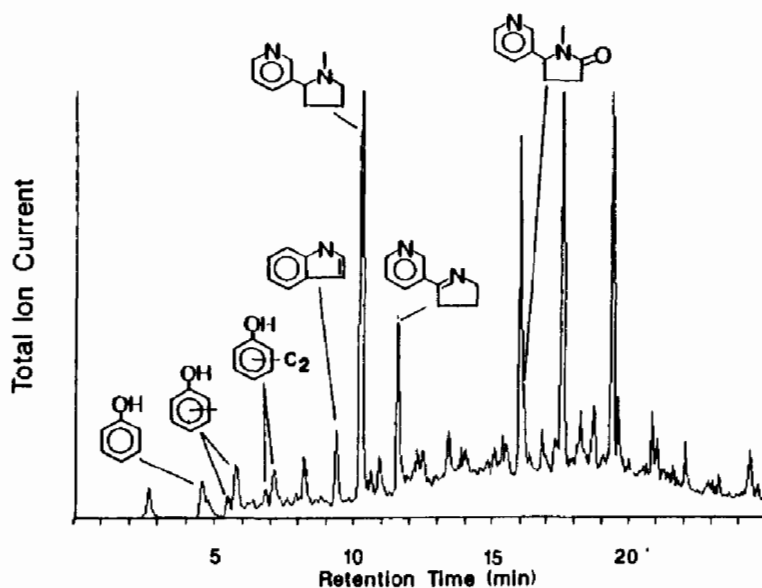


Figure 2. Coupled SFE-GC/MS analysis of a 2-mg sample of cigarette ash. Total extraction and analysis time was 40 min. Tentative identifications were based on their mass spectra.

ANALYSIS OF AIR PARTICULATE
SAMPLES BY SUPERCRITICAL
FLUID CHROMATOGRAPHY



Robert D. Zehr
Northrop Services, Inc. - Environmental Sciences
Research Triangle Park, North Carolina 27709

Nancy K. Wilson
Environmental Monitoring Systems Laboratory
U. S. EPA, Research Triangle Park, NC 27711

Several types of source samples have been analysed by packed column supercritical fluid chromatography for polycyclic aromatic hydrocarbons. The SFC-variable wavelength UV detector combination provides rapid analyses, high specificity, and moderate chromatographic resolution at low separation temperatures. However, low detector sensitivity makes analysis of ambient air samples difficult.

ANALYSIS OF AIR PARTICULATE SAMPLES BY SUPERCRITICAL FLUID CHROMATOGRAPHY

Introduction

The Environmental Monitoring Systems Laboratory of the Environmental Protection Agency continually seeks to apply new techniques to measure air pollutants. This paper will describe some of our continuing work to apply packed column supercritical fluid chromatography to analyze trace organic compounds in air particulate samples.

Experimental Methods

Equipment

The packed column chromatograph is a Hewlett-Packard Model 1082B Liquid Chromatograph equipped with two high pressure solvent pumps, a manual valve injector, a heated column oven, and a programmable variable-wavelength UV detector. Factory-installed options (1) to permit the use of supercritical fluids as mobile phases are as follows: the pumpheads are insulated and cooled by a circulating ethylene glycol-water mixture at -20C. A heat exchanger is placed between the column and detector to eliminate light scattering caused by the turbidity of supercritical fluids. The flow cell in the UV detector has thick windows to permit high pressure operation. System pressure is maintained by a precision back-pressure regulator installed after the UV detector. Finally, system pressure is monitored by two pressure gauges: one measures column head pressure before the valve injector; the other measures system pressure after the UV detector.

A Vydac TP 201 octadecylsilane (ODS) HPLC column was used in this work. Solvents were pesticide quality or equivalent. "SFC Grade" carbon dioxide was purchased from Scott Specialty Gases, Inc. Methanol-carbon dioxide mixtures were prepared by weight in a 1-liter stainless steel sampling cylinder.

When separations required gradient elutions, the chromatograph was programmed to change the mobile phase composition linearly from 1% to 10% methanol/carbon dioxide (w/w). The column oven temperature was set at 65C. The variable-wavelength UV detector was programmed to change monitoring wavelengths at preset times to allow selective detection of each component. Peaks from unknown samples were tentatively identified by comparison of retention times at specific wavelengths with those obtained from standard solutions. Quantitation was performed by manual measurements of peak heights, since high noise levels made the instrument integrator somewhat unreliable.

Attempts were made to install a flame ionization detector (FID) onto the chromatograph. Accordingly, varying

lengths of 5-, 10-, and 20-micrometer ID fused-silica capillary tubing (Scientific Glass Engineering, Austin, TX) were connected to the column outlet to provide flow restriction and to maintain system pressure above the critical pressure; the free ends were inserted into the flame tip of the FID. Flow rates greater than 0.2 mL/min of liquid carbon dioxide either overpressurized the system or snuffed the flame. The instrument was unable to provide stable flow rates less than 0.2 mL/min.

Sample Extraction and Cleanup

Samples of National Bureau of Standards (NBS) SRM 1648 (Urban Particulate Matter) were weighed into pre-extracted cellulose extraction thimbles and extracted with methylene chloride for 16-24 hours in a Soxhlet extractor. The resulting solutions were concentrated and solvent-exchanged into hexane. Aliquots of extracts supplied in methylene chloride were solvent-exchanged into hexane. Extracts were fractionated by column chromatography over silica gel. 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 molecular weights ranging from 178 to 300. Each is frequently found in air particulate samples; several are proven or suspect carcinogens or mutagens.

The PAH fraction from SRM 1648, "Urban Particulate Matter" is shown in Figure 1. This SRM was collected in St. Louis, MO, and is certified for various inorganic constituents. Concentrations for individual PAH compared favorably to the values obtained by Wise and co-workers (2). The large amounts of sample used and the high noise levels shown in the chromatogram indicate that the packed-column SFC-variable wavelength UV detector combination may not be well suited to trace organic analysis in ambient air.

Chromatograms from source samples are shown in Figures 2 through 4. Figure 2 shows PAH in the particulate fraction from the exhaust of a Volkswagen Rabbit diesel engine. The pyrene peak represents nearly 14,000 ug per gram particulate. Higher molecular weight components are present in significant quantities. The coronene concentration is approximately 500 ug per gram particulate. For comparison the chromatogram of a gasoline-powered engine is shown in Figure 3. The pyrene peak represents approximately 1000 ug per gram particulate. Coronene is present to the extent of about 600 ug/gram particulate.

To obtain the chromatograms shown in Figure 4, flue gases from wood stoves were collected using a modified Method 5 sampling train. Particulate matter was sampled on a filter. More volatile constituents passed through the filter and were trapped on an XAD-2 cartridge. The chromatograms clearly show that the filter trapped the higher molecular weight hydrocarbons, as expected, and that the XAD-2 trapped the more volatile PAH.

Conclusions

Several types of air particulate samples have been successfully analyzed for polycyclic aromatic hydrocarbons by packed-column supercritical fluid chromatography. The cleanup scheme provides effective purification and high recoveries of PAH. The packed column SFC in combination with its variable wavelength UV detector yields rapid analyses, with moderate chromatographic resolution at low oven temperatures. However, low detector sensitivity makes analysis of ambient air samples difficult.

Acknowledgments

We thank Drs. Roy Zweidinger and Ray Merrill of EPA for the gifts of source extracts.

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PAH Reference Compounds

Anthracene	Fluoranthene
Pyrene	Chrysene
Benz[a]anthracene	Benzo[a]pyrene
Benzo[e]pyrene	Benzo[b]fluoranthene
Benzo[g,h,i]perylene	Coronene

Table I. PAH used in this work

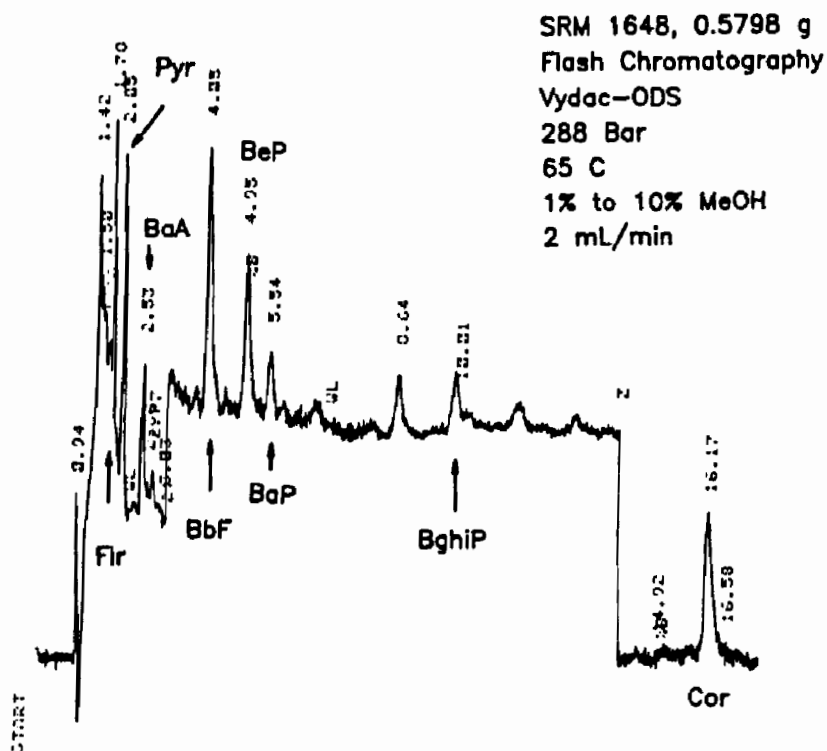
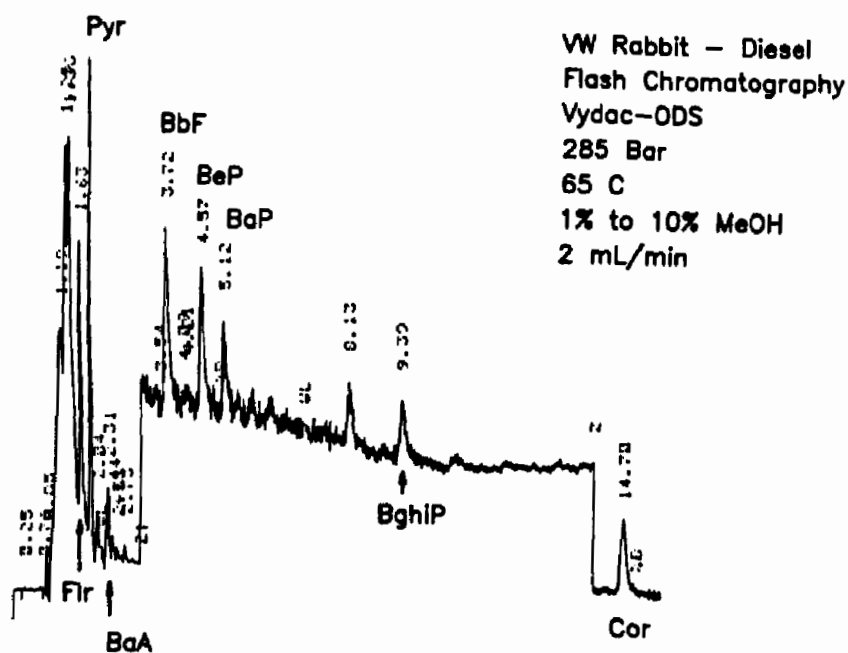


Figure 1. Chromatogram of SRM 1648 extract



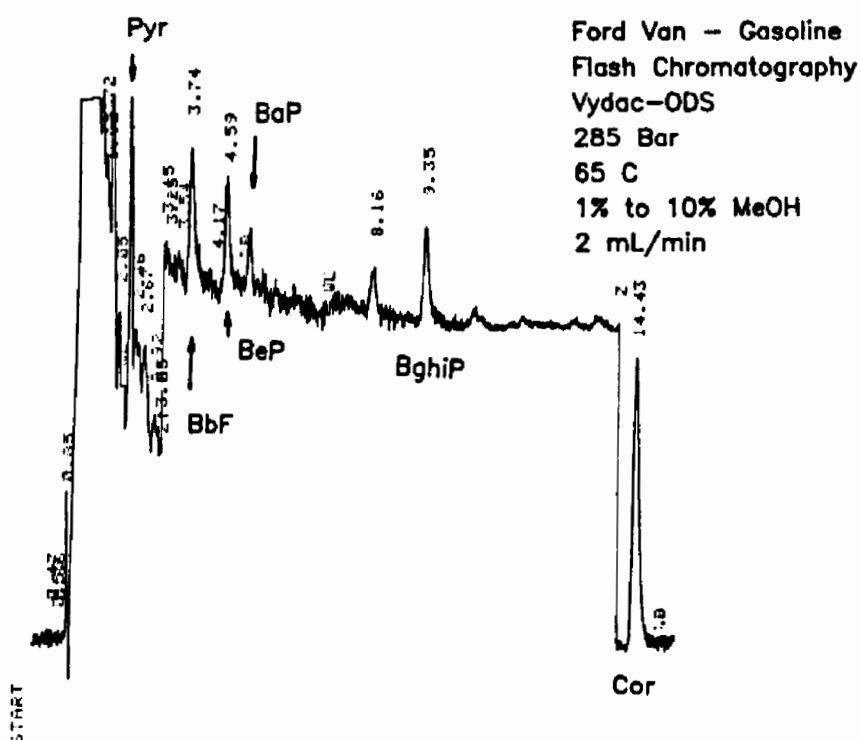


Figure 3. Chromatogram of Ford van gasoline exhaust extract

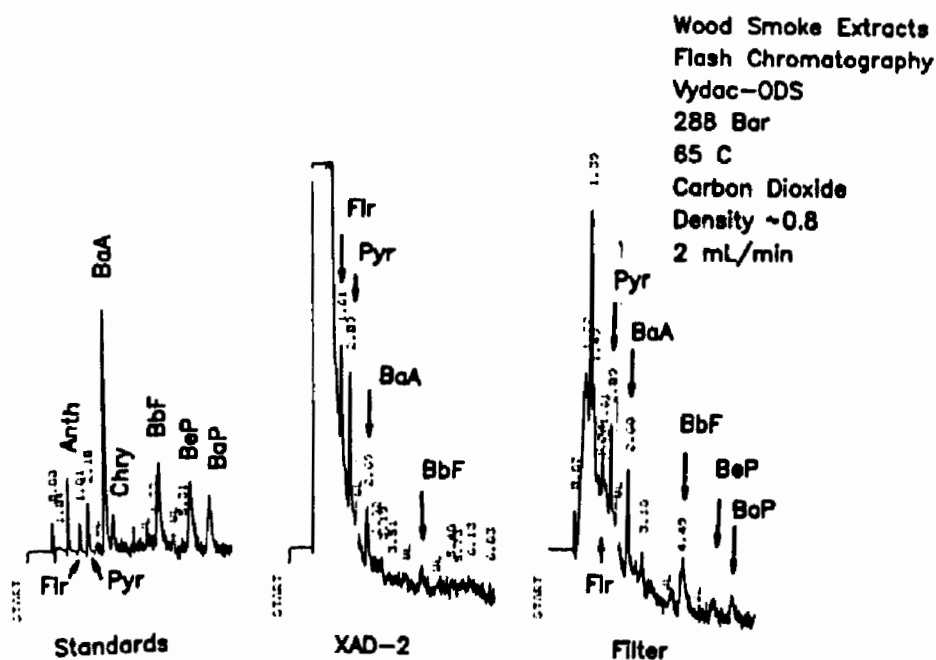


Figure 4. Chromatograms of wood stove emission extracts

Mobile Sources of Polycyclic Aromatic Hydrocarbons
(PAH) and Nitro-PAH: Results of Samples Collected
in a Roadway Tunnel.

Bruce A. Benner, Jr. and Glen E. Gordon
Department of Chemistry and Biochemistry
University of Maryland
College Park, MD 20742

Stephen A. Wise
Organic Analytical Research Division
Center For Analytical Chemistry
National Bureau of Standards
Gaithersburg, MD 20899

A recent review article [1] emphasized the need for further characterizations of the carbonaceous fraction of mobile source emissions, particularly with the impending removal of lead alkyl octane boosters and bromine-containing lead scavengers from regular leaded gasolines. The lead and bromine emitted from the combustion of these fuels have been used as tracers of mobile source emissions for a number of years. Single vehicle emission studies have shed light on the relationship between engine operating parameters and the chemical characteristics of the emissions but they are not suitable for use in source apportionment studies which require emission data from a large number of different vehicles. Air particulate samples collected near a busy highway or in a roadway tunnel would be more appropriate for use in estimating the mobile source contribution of organic compounds to a region.

Suspended particle samples collected in a heavily-travelled roadway tunnel (Baltimore Harbor Tunnel, Baltimore, Maryland) were characterized for polycyclic aromatic hydrocarbons (PAH) and some nitro-PAH by gas and liquid chromatographic techniques. These samples included those collected on Teflon filters and on glass fiber filters for investigating any differences in samples collected on an inert (Teflon) and more reactive (glass-fiber) medium. All samples collected on Teflon were backed-up with polyurethane foam plugs (PUF) which trapped any inherent vapor-phase PAH as well as any compounds "blown-off" the particles during collection. Particle loadings in the tunnel were high enough for sufficient sample to be collected in 1 h periods (approx 50 m³ volume collected) so that relationships between the composition of the emissions and the types of vehicles using the tunnel

might be investigated. Two background air samples (Teflon filters + PUFs) were also collected for comparison of samples resulting from a mixture of stationary and mobile sources with those purely from mobile sources.

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**FIELD EVALUATION OF AN ADSORPTION-THERMAL
DESORPTION TECHNIQUE FOR ORGANIC CONTAMINANTS
IN INDOOR AIR**

David T. Williams
Environmental Health Directorate
Health and Welfare Canada
Tunney's Pasture
Ottawa, Ontario
K1A 0L2

Cecilia C. Chan
John W. Martin
Mann Testing Laboratories Ltd.
5550 McAdam Road
Mississauga, Ontario
L4Z 1P1

This study evaluated, under field conditions, the ability of the multi-sorbent sampling tube thermal desorption technique to identify and to provide quantitative data on selected volatile organic contaminants in indoor air and to provide information on typical levels of these pollutants in the air of homes compared to ambient air at the same location. Air samplers containing multi-sorbent tubes attached to air sampling pumps set at different flow rates were used to collect air samples at twelve homes. The sorbent tubes were analysed by thermal desorption coupled with gas chromatography-mass spectrometry. The precision and accuracy of the method under field conditions and the stability of the organic contaminants during storage of the sorbent tubes are evaluated. Typical results are discussed together with some difficulties encountered in the analyses.

INTRODUCTION

The adsorption/thermal desorption technique (ATD) has been widely used, because of its potential sensitivity, for the analysis of trace levels of organic compounds in air. Many studies have used Tenax as the trapping media (1-3). However, we have previously reported on a laboratory evaluation of a multi-layer adsorption tube for the collection and analysis of a wide range of organic compounds in air (4). The present study was designed to evaluate the use of this technique under field conditions for a selected group of target compounds.

EXPERIMENTAL

Materials

Sorbent cartridges were obtained from Envirochem Inc. (Kembsville, Pa.) and were constructed of pyrex glass (20 cm x 6 mm OD and 4 mm ID) and packed with sequential layers of glass beads, Tenax, Ambersorb XE-340 and charcoal adsorbents. Prior to use the tubes were cleaned by thermal desorption in a sorbent tube conditioner while being purged with high purity nitrogen at a flow rate of 50 ml/min.

Apparatus

Analyses were performed using a modified Envirochem concentrator, Model 780B, interfaced to a Hewlett Packard, Model 5890, gas chromatograph-Finnigan, Model 3300, mass spectrometer combination. An Envirochem automatic desorber unit was attached to the concentrator, with a separate module controlling the temperature and timing of the process. Desorption conditions were: transfer lines at 280°C; initial purge time of 2 min; sorbent tube desorbed at 280°C for 12 min with helium flow of 50 ml/min; traps 1 and 2 desorbed at 300°C with flows of 50 and 2 ml/min respectively onto a J&W DB-5 fused silica capillary column (30 m x 0.25 mm, 1 μ m film thickness) maintained at 40°C. The GC conditions were: column carrier gas (helium) flow of 1.5 ml/min; initial temperature at 40°C for 5 minutes; temperature program rate at 8°C/min to 280°C and held for 20 minutes; the MS settings were: electron multiplier at 1800 eV; electron energy at 70 eV; scan rate of 1 sec/scan; mass range of 34 to 300 a.m.u.

Sample Collection

Air samples were collected at twelve homes during November and December 1986. At each home the following samples were collected: two ambient air samples, four indoor air samples of various volumes and one indoor air sample using two sorbent tubes connected in series. The ambient air samples were collected adjacent to the home and away

from any obvious source of pollution. The indoor air samples were collected on the main floor of the home, usually in the living or family room. Indoor and ambient air samples were collected at the same time; a uniform 90 minute sampling time was used and pump flow rates were adjusted to sample the required volume of air. After sample collection the sorbent tubes were placed in individual screw cap glass tubes and then stored in a tightly sealed container until analysed. Analysis was carried out within two days.

Sample Analysis

Following thermal desorption the GC-MS program was begun and full scan mass spectra were collected. Target compounds were identified by retention times and by full mass spectra or by the presence of appropriate fragment ions. Quantitation was achieved by comparison of peak areas from reconstructed chromatograms of the two or three most intense ions from each compound with corresponding peaks from a standard mixture.

QA/QC Procedures

A blank tube was carried to and from each home and handled and analysed as a sample, except that no air was sampled through the tube. Each week three tubes fortified at a low level (approx 70-80 ng) and three tubes fortified at a medium level (approx 700-800 ng) with a standard mixture of target compounds, together with a blank tube, were transported to and from one sampling site and analysed by thermal desorption GC-MS.

To assess the stability of the organic target compounds on the sampling tube a limited storage study was carried out. Triplicate sorbent tubes fortified at low and medium levels (approx 70-80 and 700-800 ng respectively), together with a blank tube, were stored for 0, 1, 3 and 7 days under normal storage conditions and then analysed by ATD/GC-MS.

Preparation of Standards

A stock standard solution was prepared by injecting a known amount (200-400 μ l) of each compound into a 10 ml reactiflask fitted with a Minnert valve. Aliquots of the resulting solution were injected into a helium filled bottle equipped with a septum top to produce gaseous standards. To fortify sorbent tubes aliquots of the gaseous standard were introduced onto the glass bead layer of sorbent tubes held at room temperature in the desorber unit.

RESULTS AND DISCUSSION

Most of the target compounds investigated in this study were detected in indoor air at 1 to 10 $\mu\text{g}/\text{m}^3$ except for the aromatic and straight chain hydrocarbons which tended to be present at 10 to 50 $\mu\text{g}/\text{m}^3$. In a few houses, relatively high levels ($> 100 \mu\text{g}/\text{m}^3$) of chlorinated hydrocarbons were detected (e.g. 1,1,1-trichloroethane). Full data analysis has not yet been completed but air levels for the target compounds are shown in Tables I and II for two houses. House #4 (Table I) shows typical background levels for the target compounds except for naphthalene whose level is higher than in the other homes. These data also show that outdoor air levels are significantly less than indoor air levels. The agreement of the data is extremely good ($<10\%$ RSD) for the four indoor air samples of differing air volumes. The data from the two tubes in series indicate that there is little breakthrough of the target compounds from the front tube. Data from house #5 (Table II) presents some interesting results using this air sampling approach. In this house, two target compounds (n-butanol and acetone) appeared to be present at relatively higher concentrations. Saturation hence occurred with the sorbent tubes of larger sample size, however, the low volume sorbent tube was able to provide quantitative data for these compounds. On the other hand, compounds that were present in low concentrations were not detected in the low volume tube but are consistently found at similar concentrations in the sorbent tubes with larger sample size. Problems can be encountered in this technique if the sample size is too large since the MS detector can be saturated with respect to certain ions. This will prevent accurate quantitation unless alternative ions, specific to the compound of interest, can be utilised. However, the use of less intense ions is likely to lead to poorer precision and to significantly increase the time required for data analysis. In some cases saturation was so complete that no quantitative data could be obtained. Coelution of two compounds with similar ion fragmentation is also possible. In the current study benzaldehyde was found to coelute with a C3-benzene and, consequently, no data could be obtained for benzaldehyde.

Data for the fortified QA/QC sorbent tubes for house #4 are shown in Table III. Recoveries are good ($> 70\%$) and the precision is usually better than 15% RSD. Data from the storage study indicated that there was little loss of the target compounds during seven days storage.

The ATD GC-MS technique, therefore, shows considerable promise for indoor air sampling but a number of samples of different air volumes should be collected to avoid the technical difficulties discussed in this paper.

ACKNOWLEDGEMENTS

The technical assistance of A.M. Taylor and typing by V. Schellenberg are gratefully acknowledged.

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TABLE 1. TARGET COMPOUND AIR LEVELS (ug/m3)- HOUSE #4

COMPOUND	OUTDOORS		INDOORS				SERIES HI FLOW TOP	SERIES HIGH FLOW BOTTOM
	#1	#2	#1	#2	#3	#4		
ACETONE	-	-	51.8	59.3	SAT.	SAT.	36.3	1.1
METHYL ETHYL KETONE	-	-	6.8	7.0	5.6	6.5	5.8	-
DIETHYL ETHER	-	-	1.7	3.5	1.5	1.6	1.4	-
n-BUTANOL	-	-	-	-	-	-	-	-
BENZENE	4.4	3.6	4.8	8.9	5.5	6.3	6.5	1.6
DICHLOROMETHANE	-	-	8.2	8.3	6.7	7.3	9.1	1.2
HEXANE	-	-	5.2	-	5.5	6.6	6.3	0.9
ETHYL ACETATE	-	-	3.5	-	4.2	4.6	3.3	-
TOLUENE	4.5	6.0	29.4	24.2	29.3	30.6	31.4	1.4
1,1-DICHLOROETHYLENE	-	-	-	-	-	-	-	-
STYRENE	-	-	5.6	5.6	5.3	5.5	5.6	-
p & m-XYLENE	1.7	2.2	20.8	20.2	19.4	21.4	21.9	0.7
o-XYLENE	0.7	1.1	13.5	12.4	12.9	13.4	13.2	0.3
ETHYL BENZENE	1.0	1.3	8.4	8.5	7.9	8.1	8.8	-
CHLOROBENZENE	-	-	-	-	-	-	-	-
CHLOROFORM	-	-	1.1	-	1.0	1.0	1.2	1.0
NAPHTHALENE	2.0	2.7	76.2	82.7	66.9	73.0	85.6	3.3
TRICHLOROETHYLENE	-	-	-	-	-	-	-	-
1,1,1-TRICHLOROETHANE	-	-	4.5	4.0	3.0	3.7	4.7	-
p-DICHLOROBENZENE	-	-	3.3	-	2.6	1.9	2.3	0.5
CARBON TETRACHLORIDE	-	-	-	-	-	-	-	-
n-UNDECANE	-	-	59.9	47.5	54.9	59.0	59.0	1.0
TETRACHLOROETHYLENE	-	-	4.7	-	4.3	4.5	4.6	-
	8.5	28.7	25.4	2.9	45.2	39.6	22.7	22.7

SAT. = SATURATION

TABLE II

COMPOUND	OUTDOORS		INDOORS				SERIES HI FLOW TOP	SERIES HI FLOW BOTTOM
	#1	#2	#1	#2	#3	#4		
ACETONE	-	4.3	SAT.	233.4	SAT.	SAT.	SAT.	0.9
METHYL ETHYL KETONE	-	-	22.7	33.7	16.6	15.5	17.8	-
DIETHYL ETHER	-	-	-	6.5	-	-	-	-
n-BUTANOL	-	-	29.2	37.4	SAT.	SAT.	42.0	TR
BENZENE	14.1	5.5	9.7	17.4	9.6	11.9	11.6	1.0
DICHLOROMETHANE	1.6	1.2	3.5	4.2	2.9	3.4	4.6	0.2
HEXANE	2.5	1.1	15.4	15.1	15.9	16.0	17.7	TR
ETHYL ACETATE	-	-	3.0	-	3.6	3.4	2.7	-
TOLUENE	14.4	14.4	52.7	58.6	51.0	51.2	55.8	0.9
1,1-DICHLOROETHYLENE	-	0.5	1.0	2.0	1.0	0.9	1.1	-
STYRENE	-	0.8	3.1	2.8	3.0	3.0	-	-
p & m XYLENE	14.9	13.5	65.9	63.1	59.9	64.0	69.5	0.7
o-XYLENE	2.4	2.5	18.9	19.6	18.7	18.8	18.3	0.1
ETHYL BENZENE	3.3	2.6	12.0	9.6	10.7	11.1	11.9	0.3
CHLOROBENZENE	-	-	-	-	-	-	-	-
CHLOROFORM	-	0.2	1.0	-	0.7	1.0	0.7	-
NAPHTHALENE	1.5	1.6	5.2	4.5	6.2	6.6	5.4	0.2
TRICHLOROETHYLENE	3.3	1.8	0.8	-	0.6	0.6	0.6	-
1,1,1-TRICHLOROETHANE	-	-	6.3	5.6	4.0	5.5	5.8	-
p-DICHLOROBENZENE	-	-	1.9	-	2.3	2.3	1.8	0.5
CARBON TETRACHLORIDE	-	-	2.2	-	1.8	1.9	2.3	-
n-UNDECANE	-	0.8	26.1	21.9	28.6	28.3	26.5	-
TETRACHLOROETHYLENE	-	1.1	7.2	5.6	6.4	6.4	6.8	-
VOLUME SAMPLED (L):	8.1	37.9	26.2	2.3	47.2	41.7	23.1	23.1

SAT. = SATURATION

TR = TRACE AMOUNT DETECTED

TABLE III RECOVERIES (ng) OF FORTIFIED TARGET COMPOUNDS

COMPOUND	LOW LEVEL SPIKES			MEDIUM LEVEL SPIKES			FORTIFICATION (ng)	
	1	2	3	1	2	3	LOW LEVEL	MED LEVEL
ACETONE	72.1	71.6	77.9	491.0	567.5	584.3	79.1	791.0
METHYL ETHYL KETONE	76.4	69.8	75.4	601.9	736.7	743.6	80.2	802.0
DIETHYL ETHER	60.2	50.8	53.7	428.0	503.1	556.4	69.9	699.0
n-BUTANOL	66.6	62.6	51.3	620.9	721.3	754.6	81.0	810.0
BENZENE	63.8	56.4	63.5	623.3	808.4	864.0	87.3	873.0
DICHLOROMETHANE	78.0	73.6	79.0	460.0	544.6	577.0	66.1	661.0
HEXANE	52.0	46.6	49.1	468.2	567.3	579.4	63.0	630.0
ETHYL ACETATE	89.0	100.8	94.6	665.5	836.8	871.7	90.2	902.0
TOLUENE	71.0	67.4	68.6	672.2	886.8	977.8	86.3	863.0
1,1-DICHLOROETHYLENE	45.8	42.2	44.8	409.0	507.4	509.4	71.6	716.0
STYRENE	101.0	86.1	93.5	724.0	1005.4	1199.0	91.1	911.0
p-m-XYLENE	146.7	129.3	140.6	713.0	1634.0	1824.6	153.0	1530.0
o-XYLENE	88.6	76.1	82.1	688.4	954.0	1089.0	88.4	884.0
ETHYL BENZENE	85.6	73.5	79.2	655.8	881.4	1003.2	84.6	846.0
CHLOROBENZENE	84.6	68.6	68.8	643.4	881.4	979.4	82.5	825.0
CHLOROFORM	82.3	58.2	60.8	526.6	646.6	688.6	73.7	737.0
TRICHLOROETHYLENE	71.6	62.6	66.8	551.2	701.5	773.4	73.5	735.0
1,1,1-TRICHLOROETHANE	56.4	51.1	58.1	487.0	610.0	627.4	64.9	649.0
p-DICHLOROBENZENE	126.5	81.1	83.1	678.3	1052.8	1305.6	81.2	812.0
CARBON TETRACHLORIDE	66.2	65.0	69.8	578.4	742.0	763.6	78.9	789.0
TETRACHLOROETHYLENE	78.2	66.2	70.4	615.3	828.8	934.6	80.8	808.0

PERFORMANCE TESTING OF RESIDENTIAL INDOOR AIR CLEANING DEVICES

Mallory P. Humphreys,

Energy Use Test Facility, Tennessee Valley Authority,
Chattanooga, Tennessee



A study is underway by the Tennessee Valley Authority to evaluate the performance of a cross section of the residential air cleaning devices available on the market. The test procedure being used in the study follows the guidelines of the Association of Home Appliance Manufacturers "Standard Method (AC-1) for Measuring Performance of Portable Household Electric Cord-Connected Room Air Cleaners (1)" and is similar to test procedures employed by Lawrence Berkeley Laboratories in a 1984 study (2) of room air cleaners. The test procedure involves filling a room-sized test chamber with a contaminant, mixing to obtain a uniform concentration, and measuring the contaminant decay rate both with ("induced decay") and without ("natural decay") the air cleaner operating. Mass balance modeling of the various source and removal terms involved is then used to calculate effective cleaning rate and removal efficiency for each pollutant monitored. The pollutants monitored include respirable suspended particulates (RSP [down to 0.03 micron particle diameter]), generated from cigarette smoke injection; and common gaseous pollutants (CO, NO₂, SO₂, and hydrocarbons [HC—expressed as equivalent methane]), generated from cylinder gas injection. Six portable room air cleaners have thus far been tested in the study: (1) console electrostatic precipitator (ESP); (2) table-top ESP; (3) high efficiency particulate air (HEPA) filter console; (4) table-top negative ion generator (NIG); (5) catalytic/HEPA filter console; (6) sorbent/HEPA filter console. Devices 1 through 4 were tested for removal of RSP only, while devices 5 and 6 were tested for removal of both RSP and gaseous pollutants. The devices were tested at both maximum and minimum flow rates. A minimum of four replicate tests were performed for each test condition.

PERFORMANCE TESTING OF RESIDENTIAL INDOOR AIR CLEANING DEVICES

Introduction

Reduction of residential home ventilation rates through increased weatherization or new construction practices, can result in containment of indoor pollutants within homes. One strategy for controlling residential indoor contaminants that is gaining recognition is air cleaning. In the past few years a variety of residential air cleaning devices have become available on the market. This study was initiated by the Tennessee Valley Authority to evaluate the performance of a cross section of the air cleaners available to the residential consumer.

Theory

The contaminant decay rate in the test chamber is described by the following differential equation:

$$\frac{dC_i}{dt} = \frac{\dot{S}}{V} + \frac{PQ_f C_o}{V} - \frac{Q_f C_i}{V} - KC_i - \frac{\eta Q_d C_i}{V}$$

where

C_i	= pollutant concentration inside chamber
t	= time
\dot{S}	= indoor pollutant generation rate
V	= volume of chamber
P	= penetration or transmission factor
Q_f	= infiltrating and/or ventilating air supply
C_o	= pollutant concentration outside chamber
K	= pollutant reactivity or deposition rate
Q_d	= volumetric air flow rate for the device
η	= system removal efficiency

This mass balance includes two sources of indoor pollutants: the source inside the test cell (\dot{S}) and the outside source term ($PQ_f C_o$); and three removal rates: removal by exfiltrating air ($Q_f C_i$), removal by all other forms [e.g., deposition, reaction] (KC_i), and removal by the air cleaner ($\eta Q_d C_i$). For a chamber decay experiment, where there is no internal source and where the outdoor aerosol source is negligible, the mass balance equation simplifies to:

$$\frac{dC_i}{dt} = - \frac{Q_f C_i}{V} - KC_i - \frac{\eta Q_d C_i}{V}$$

If it is assumed that the exfiltration and reactive removal terms are the same for the "natural" and "induced" decay periods of testing, then the difference between the observed decay rates represents the air cleaner removal term ($\eta Q_d C_i / V$). The system removal efficiency (SRE) of the device is represented by " η ", while the effective cleaning rate (ECR) [or clean air delivery rate (CADR)] is represented by " ηQ_d ".

Results

A summary of the composite average RSP and gaseous pollutant mitigation results (representing averages of a minimum of four replicate tests) is presented in Table I and in Figures 1 through 4. AHAM mathematically simulated clean air delivery rate (CADR [synonymous with RSP effective cleaning rate]) indices required for 75-percent particulate removal in 30 minutes from rooms varying in size from 60 to 300 sq ft, are presented in Table II and are included in Figure 1.

RSP effective cleaning rates observed during testing ranged from 30 cfm (for the table-top NIG) to 125 cfm (for the console ESP). Relative to the AHAM simulated CADR indices presented in Figure 1, the table-top models tested would provide adequate RSP removal only for small rooms (less than 80 sq ft), whereas, the console models would provide adequate RSP removal for rooms ranging from 160 to 300 sq ft in size. RSP removal efficiencies (Figure 2) ranged from 33-percent (for the table-top ESP) to 82-percent (for a HEPA filter console). Highest RSP removal efficiencies were observed for the three HEPA filter console models and the console

ESP under minimum flow rate operation. RSP removal efficiencies for both electrostatic precipitators were increased during the minimum flow rate operation, because of the longer residence time of particles within the devices.

Gaseous pollutant mitigation results for the catalytic and sorbent/ HEPA filter consoles are presented graphically in Figures 3 and 4. The AHAM Test Standard (1) does not specify determination of gaseous pollutant mitigation performance; however, the principles of mass conservation outlined in the "Theory" section of this paper apply to gaseous pollutants as well as particulate matter. Catalytic device 5 contained a 50:50 mixture of activated carbon and specially developed room temperature catalyst (composed of a solution of copper and palladium salts on a porous alumina substrate). The manufacturer claims NO₂ and SO₂ removal through chemisorption, CO removal through catalytic oxidation, and HC removal through adsorption. Device 6 contained a specially developed sorbent material (no specific information is available concerning the nature of the material). Both devices were effective for removal of NO₂ and SO₂, but were much less effective for removal of CO and HC. Gaseous pollutant removal efficiencies for devices 5 and 6, respectively, averaged: 37 and 11 percent for NO₂, 54 and 32 percent for SO₂, 4.1 and 0.4 percent for CO, and 1.6 and 2.2 percent for HC. Device 5 was more effective in removal of gaseous pollutants than was device 6 because of the combined effect of the catalyst and sorbent (activated carbon) materials. The removal efficiencies for both devices were higher during minimum flow rate operation because of the longer residence time of the airstream within the devices.

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TABLE 1. SUMMARY OF RSP AND GASEOUS POLLUTANT MITIGATION RESULTS

DEVICE NUMBER	DEVICE TYPE	FLOW RATE (cfm)	POWER CONSUMP. (watts)	RSP		TEMP (F)	RH (%)	NO2		SO2		CO		HC	
				ECR (cfm)	SRE (%)			ECR (cfm)	SRE (%)	ECR (cfm)	SRE (%)	ECR (cfm)	SRE (%)	ECR (cfm)	SRE (%)
4	Sorbent/	88	109	68.5	77.8	73	53	7.9	9.0	24.3	27.7	0.3	0.6	1.1	1.2
	HEPA Filter Console	34	54	27.8	81.8	73	56	4.5	13.2	12.1	35.4	0.1	0.0	1.1	3.2
5	Catalytic/	116	162	87.9	75.8	77	53	40.1	34.6	58.0	50.0	3.0	2.6	1.7	1.5
	HEPA Filter Console	43	101	33.8	78.4	78	62	17.0	39.5	24.7	57.4	2.4	5.6	0.7	1.6
4	Table-Top	--	40	30.4	--										
	NIG	--	29	30.1	--										
3	HEPA Filter Console	170	294	116.2	68.4										
		133	216	96.9	72.9										
2	Table-Top ESP	107	77	38.4	33.6										
		58	56	33.4	57.4										
1	Console ESP	203	266	125.2	61.7										
		129	111	100.7	78.1										

DEVICES 1 THROUGH 4

NOT DESIGNED

FOR

REMOVAL

OF

GASEOUS

POLLUTANTS

* NIG not equipped with internal collection media.

TABLE 11. AHAM MATHEMATICALLY SIMULATED CADR INDICES REQUIRED TO PROVIDE AN ESTIMATED 75% REMOVAL OF TOBACCO SMOKE, DUST, OR POLLEN IN 30 MINUTES FOR VARIOUS ROOM SIZES

AIR EXCHANGE RATE OF ROOM (1/hr)	CLEAN AIR DELIVERY RATE INDEX (cfm)							
	*							
	60 sq ft Room	80 sq ft Room	120 sq ft Room	160 sq ft Room	200 sq ft Room	250 sq ft Room	300 sq ft Room	
2.5	12	15	25	30	40	45	60	
1.0	25	35	50	76	80	100	125	
0.6	30	35	60	70	90	125	150	

* Assuming 8 ft ceiling

To determine the CADR required to accomplish the equivalent removal in 60 minutes, divide CADR Index by 3.

To determine the CADR required to accomplish the equivalent removal in 15 minutes, multiply CADR Index by 3.

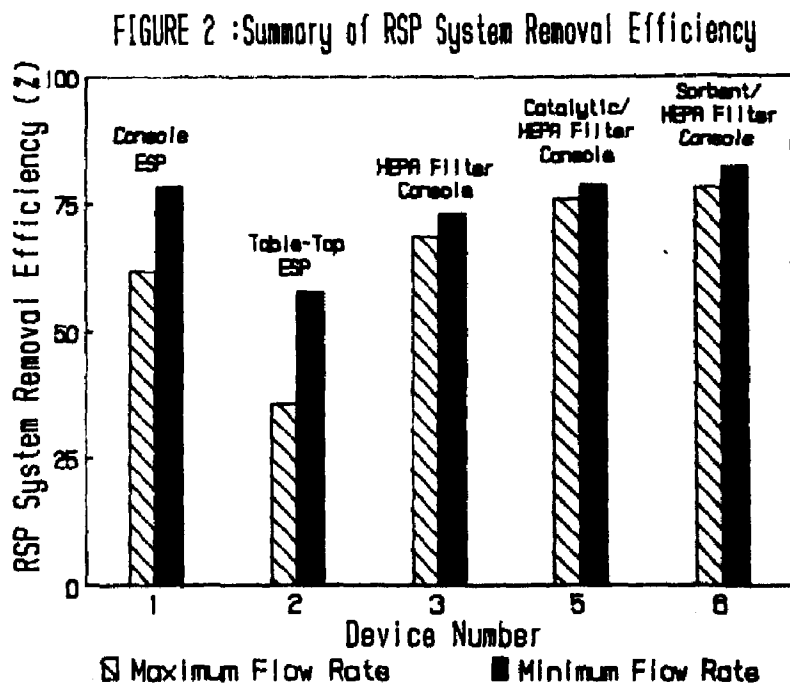
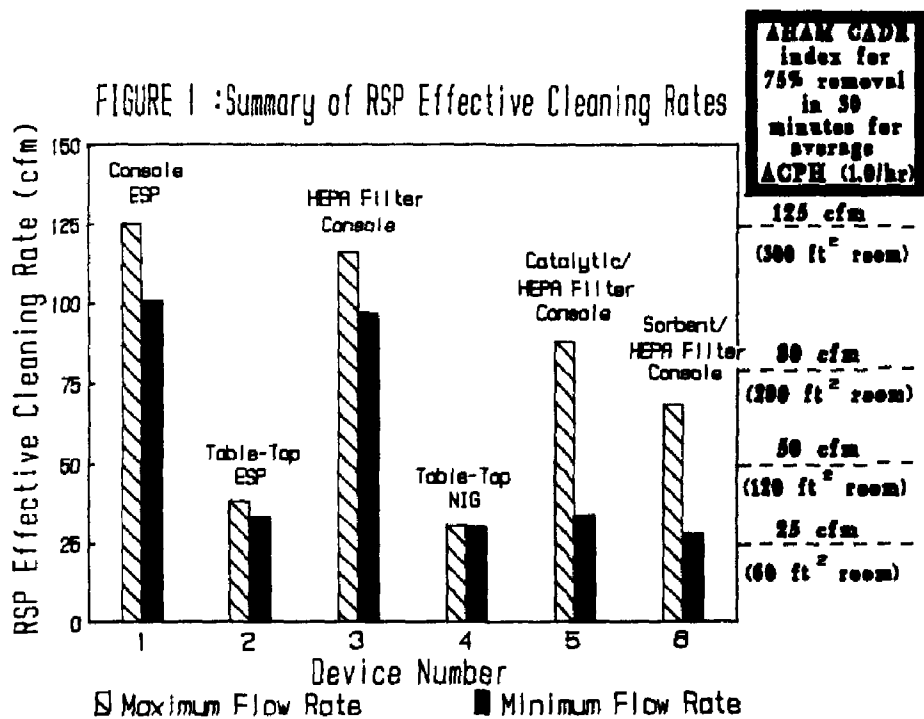


FIGURE 3 :Summary of Gaseous Pollutant
Effective Cleaning Rates

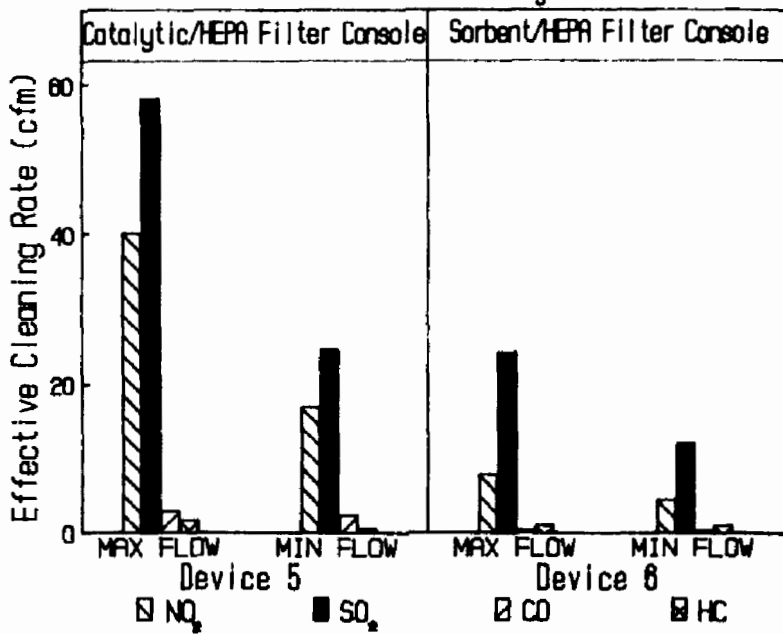
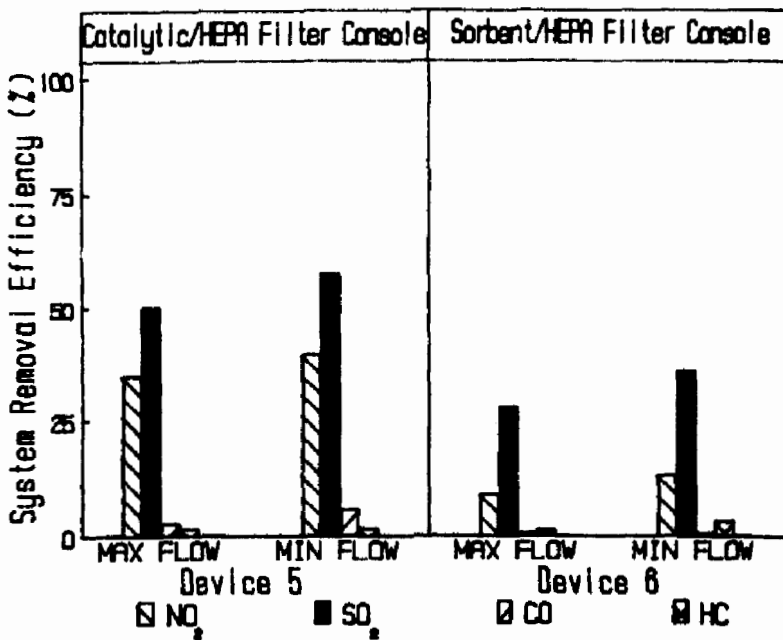


FIGURE 4 :Summary of Gaseous Pollutant
Removal Efficiencies



**EVALUATION OF ORGANIC EMISSIONS TO THE INDOOR
ENVIRONMENT VIA SMALL CHAMBER TESTING**



Bruce A. Tichenor
Indoor Air Branch
U. S. EPA, Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

John E. Bunch and Mark A. Mason
Acurex Corporation
Research Triangle Park, NC 27709

The contamination of the indoor environment has recently emerged as a major area of concern to health and environmental professionals. Indoor air pollutants of interest include organic and inorganic vapors and particles. As part of EPA's research in indoor air quality (IAQ), the Air and Energy Engineering Research Laboratory is conducting research to determine the emissions of organic vapors from building materials and consumer products commonly used in homes, offices, and public access buildings. Samples of the material/product are placed in small environmental test chambers, and measurements are conducted via gas chromatography to determine emissions rates for various organic species. The temperature, humidity, and flow rate of the air through the test chambers are carefully controlled. Data are presented on the organic emissions from a typical consumer product: liquid floor wax.

EVALUATION OF ORGANIC EMISSIONS TO THE INDOOR ENVIRONMENT VIA SMALL CHAMBER TESTING

Introduction

The contamination of the indoor environment has recently emerged as a major area of concern to health and environmental professionals. Indoor air pollutants of interest include organic and inorganic vapors and particles. A number of indoor air pollutants have been extensively studied (e.g., formaldehyde from particleboard, radon from soil, and numerous contaminants from tobacco smoke). Except for formaldehyde, however, only limited information is available on organic emissions from the wide variety of building materials and consumer products found in homes and offices. As part of EPA's research in indoor air quality (IAQ), the Air and Energy Engineering Research Laboratory is conducting research to determine the emissions of organic vapors from building materials and consumer products commonly used in homes, offices, and public access buildings.

Samples of the material/product are placed in small environmental test chambers, and measurements are conducted via gas chromatography to determine emissions rates for various organic species. The temperature, humidity, and flow rate of the air through the test chambers are carefully controlled. To date, tests have been conducted on the following products/materials: caulking compound, floor adhesive, particleboard, moth repellent, liquid floor wax, and wood stain. Other papers^{1,2,3,4} have presented data on several of these materials; the present paper focuses on the liquid floor wax tests.

Experimental Facility

EPA's Indoor Air Source Characterization Laboratory consists of the following components: a clean air conditioning and delivery system, an incubator containing two 166 liter environmental test chambers, sampling manifolds, and sample collection adsorbers using Tenax and charcoal. A permeation system for quality control is included. The environmental variables are monitored and controlled by a microcomputer. Organic analyses are conducted by thermal desorption, concentration using purge and trap, and gas chromatography (GC) using flame ionization detectors (FID). A separate microcomputer provides GC data analysis. All data are input to spreadsheets for further analysis.

Experimental Procedures

Headspace Analysis

Prior to evaluation in the environmental test chambers, materials are evaluated by headspace analysis. A sample of material is placed in a 1 liter Teflon-lined container which is purged with nitrogen at 50 ml/min for 30 minutes. The exit flow is collected on Tenax and analyzed after thermal desorption. Gas chromatography/mass spectroscopy (GC/MS) analysis provides identification of the compounds contained in the material's emissions. Approximately 10 of the compounds are selected for measurement in subsequent chamber tests.

Chamber Testing

The experimental design was developed to provide insight into the effect of air exchange rate, loading, and temperature on the emission characteristics of the liquid acrylic floor wax (AFW). Table I (Test Matrix) provides the experimental conditions for the nine tests that were conducted. All tests were at 50% relative humidity, except test AFW8.1 which was at 20%. The floor wax was spread on aluminum plates using a sponge applicator. The weight of wax applied was determined by weighing the sponge before and after application. The plates were coated in the chamber, and the test start (time = 0) was established when the door to the chamber was closed. The first sample was collected at the 15 minute mark.

Experimental Results

Organic Compounds Measured

The following compounds were identified by headspace analysis and were measured during the chamber testing: C-9 substituted cycloalkane, trimethyl cyclohexane, methyl octane, C-9 substituted alkane, methylethyl cyclohexane (2 isomers), nonane, dimethyl octane, ethyl toluene, trimethyl benzene, decane, and undecane. Total organics (as decane) were also measured.

Chamber Concentrations

Figure 1 shows the concentration of total organics, nonane, and ethyl toluene vs. time for test AFW2.1. The symbols represent measured values; the lines represent the "best fit" of a model⁵ developed to analyze the data. This plot is typical of all the tests, where the initial concentration decreases several orders of magnitude (from $>100,000$ $\mu\text{g}/\text{m}^3$ to near the analytical detection limit) over the test duration. Figure 2 shows how the composition of the emissions changes over time. Five compounds are plotted vs. time as a percent of total organics. Note that undecane increases as a percent of the total, indicating that its volatility is generally less than that of the other compounds. Methyl octane and nonane show decreases, providing evidence of higher volatility. The percentages for decane and ethyl toluene remain relatively constant.

Emission Rates

Figure 3 shows the emission factors for total organics and four individual compounds for test AFW2.1. Note that the emission rates decrease several orders of magnitude over the test duration. Also, the rate of change of the emission factors varies between individual compounds. This reflects the differences in volatility discussed above.

Effects of Test Variables

The effect of air exchange rate (N) and loading (L) on emission rates of total organics is shown in Figure 4. At the beginning of the test, the higher the N/L value, the higher the emission rate (ER) (f.e., for $N/L = 16.1$, $ER = 10,750$ $\mu\text{g}/\text{cm}^2\text{-hr}$; $N/L = 8.2$, $ER = 3620$; and $N/L = 4.0$, $ER = 2470$). This occurs, in part, because the high air exchange rates cause reduced chamber concentrations due to dilution which in turn increases the vapor pressure driving force. After about 1.5 hours, the emission rates are highest for the low N/L values due to the more rapid depletion of the source at high air exchange rates.

The effect of temperature on emissions was not determined. Only two tests (AFW8.1 and AFW9) were conducted at high temperature. Visual examination of the concentrations for these two tests compared to tests AFW2.1 and AFW7 indicates somewhat higher values for the higher temperature. Further data analysis is required, however, before the effect of temperature can be described.

Quality Control

An internal standard (hexane) is used to evaluate the precision of the organic measurements. For the nine tests, the average percent recovery of the internal standard was 102.2 ± 16.9 for 109 samples. The recovery values for each test were used to calculate the concentrations of the measured compounds.

Conclusions

Emissions from a liquid floor wax cause initial chamber concentrations of total organics $>100,000 \text{ ug/m}^3$ which decrease to near the analytical limit over the test duration. Differences in the volatilities of individual compounds cause the composition of the emissions to vary over time. Emission factors vary from >1000 to $<1 \text{ ug/cm}^2\text{-hr}$ over the first 10 hours. High air exchange rates cause high emission factors during the first few minutes of the test; by the end of the test the emission factors are highest for the low air exchange rates. The effect of temperature on emissions awaits further analysis.

References

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TABLE I. TEST MATRIX - LIQUID FLOOR WAX

Test No.	Temperature (°C)	Air Exchange Rate (hr ⁻¹)	Sample Area (cm ²)	N/L(a)	Duration (hr)
AFW1	20.9	1.94	200	16.1	70.3
AFW2.1	22.0	0.47	200	3.9	47.2
AFW3	20.0(b)	0.50(b)	100	8.3	145.3(c)
AFW4.1	22.5	0.99	200	8.3	46.9
AFW5	20.0(b)	0.25(b)	200	2.1	52.4
AFW6	21.8	1.96	400	8.1	47.7
AFW7	20.7	0.50	200	4.2	47.7
AFW8.1	35.3	0.50	200	4.2	48.4
AFW9	36.6	0.50	200	4.2	46.4

(a) $N/L = \text{Air Exchange Rate (N)} / \text{Loading (L)}$; $L = (\text{Area of Sample}) / (\text{Volume of Chamber})$; Volume of chamber = 0.166 m³

(b) Estimated values based on setpoints. Computer malfunction caused loss of measured values.

(c) Test extended over weekend.

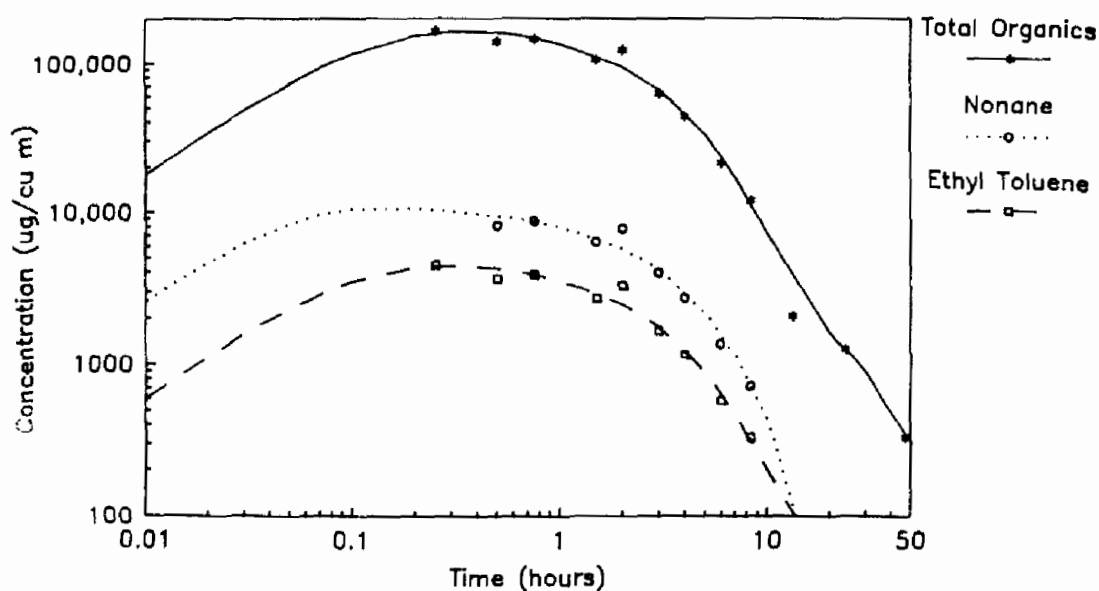


Figure 1. Chamber Concentration vs. Time
Floor Wax – Test AFW2.1

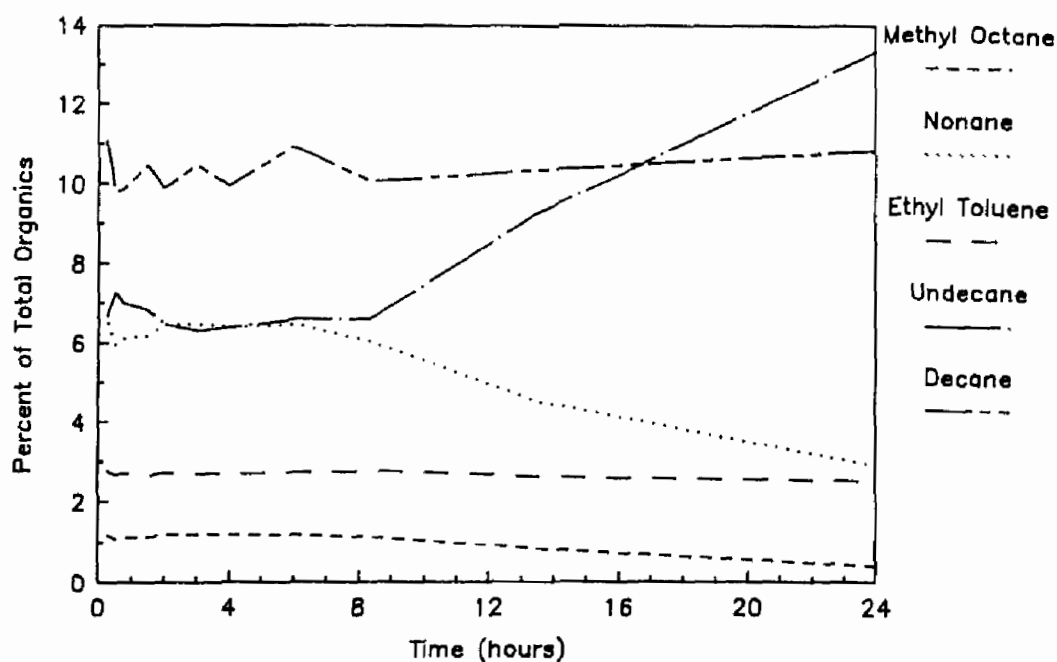


Figure 2. Emission Composition vs. Time
Floor Wax – Test AFW2.1

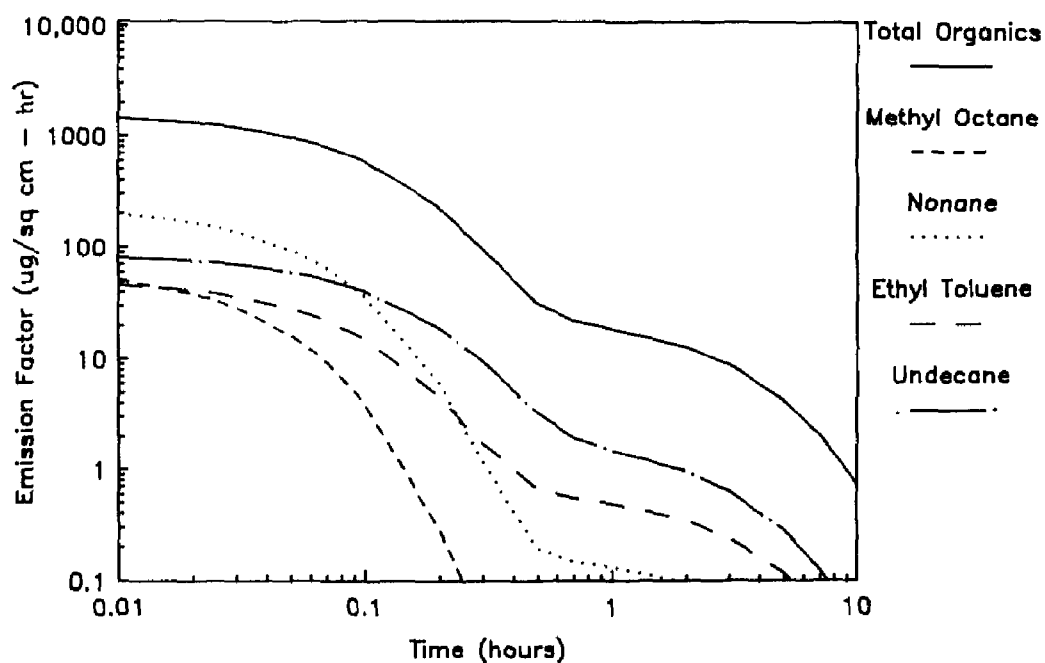


Figure 3. Emission Factors vs. Time
Floor Wax - Test AFW2.1

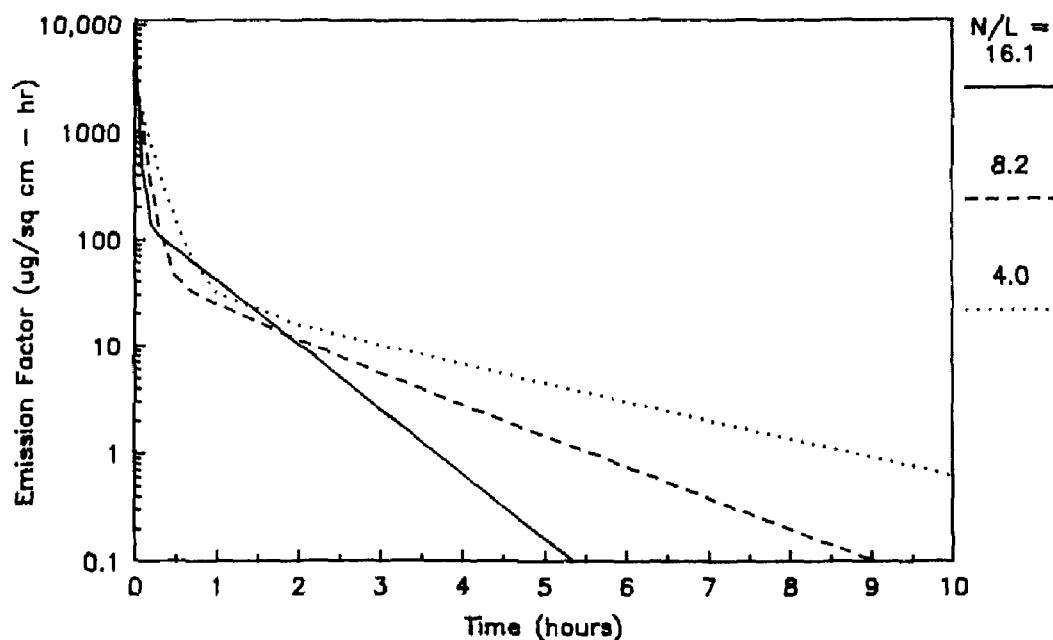


Figure 4. Effect of N/L on Emission Factors
Floor Wax - Total Organics

CHAMBER STUDIES CHARACTERIZING ORGANIC EMISSIONS FROM KEROSENE SPACE HEATERS

James B. White
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC

Brian P. Leaderer and Patricia M. Boone
John B. Pierce Foundation Laboratory
Dept. of Epidemiology and Public Health
Yale University School of Medicine
New Haven, CT

S. Katharine Hammond
Dept. of Family and Community Medicine
University of Massachusetts Medical School
Worcester, MA

Judy L. Mumford
Health Effects Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC

Abstract

This paper reports the results from Phase I of a three phase study to characterize and model particulate and organic emissions from unvented kerosene space heaters. Phases I and II involved test chamber evaluations of the source, while Phase III will use a test house to validate the chamber model. Phase I emissions from 12 heaters, covering a range of design types and Btu ratings, were screened during start-up and three steady-state operating conditions (normal, low, and high flame settings) to select candidate heater types for an intensive Phase II evaluation. Aerosol mass, size distribution, extractable mass, mutagenicity, and conventional gas (CO, NO_x, etc.) measurements were made for all the heaters tested. Volatile and semivolatile organics were measured on a subset of the heaters.

Introduction

Previous chamber and field studies investigating the nature of air contaminants from unvented kerosene space heaters and resulting human exposures, (Ref. 1-3), have focused on the emissions of CO, CO₂, NO_x, and SO₂. Little has been published on the chemical, biological, and physical nature of the volatile and semivolatile organics and particles emitted by unvented kerosene space heaters. Phases I and II of this cooperative agreement concentrated on the characterization of kerosene space heater emissions in an environmental test chamber. Phase III will validate the model derived from the chamber in a test house.

Phase I screened 12 commercial heaters currently in-use to identify 4-6 heaters and use conditions for inclusion in a Phase II evaluation. The evaluation criteria were set in Phase I to select at least one heater of

each type that produced the most particulate mass and/or mutagenic activity. In addition, Phase I determined emission factors of the classical air contaminants (CO, CO₂, NO_x, etc.) for a number of kerosene heaters under a range of fuel consumption rates.

Phase II of the project will provide a detailed characterization of particle and organic emissions (extractable particle masses, semivolatiles, volatiles, bioassays of all extracts, trace elements, acid aerosols, elemental/organic carbon, etc.). The results of Phases I and II will be used to design and conduct the EPA test house studies in North Carolina which will verify the model developed in the chamber studies. This paper will describe Phase I and present the results that are available to date.

Methods

The experiments were conducted in a fully controlled and well mixed 34 m³ environmental chamber (Ref. 2). The temperature in the chamber during all of the heater runs was kept below 30°C. Cooling was accomplished by passing the recirculated air in the chamber over a cooling coil. The temperature of the coolant was maintained at approximately 22°C, well above the dew point of the air in the chamber, to prevent condensation of air contaminants. The fresh air exchange rate, measured for each experiment, was typically about 1.2 air changes per hour (ach). Complete mixing was maintained with a recirculation rate of 20 ach.

Twelve different kerosene heaters were tested: five radiant (R), three convective (C), three combination radiant/convective (C/R), and one double radiant (R/R). Two heaters were tested twice. The manufacturer-rated heater outputs ranged from 8,200 to 17,500 Btu/hr (8,650-18,460 kJ/hr). Most of the heaters were new. Two fuels were tested: one K-1 kerosene (sulfur content of 0.06% and ash content of 0.002%) was used for the initial heater tests and one duplicate run; and the second K-1 kerosene (sulfur content 0.02% and ash content 0.016%) was used for the other duplicate run.

Each kerosene heater was placed in the chamber on a Potter scale at least a 1/2 hour before the experiment was started, and the ventilation and recirculation rate of the chambers was set. During the initial 1/2 hour before the heater was lit, background levels were obtained of all continuously measured parameters and particle size distributions.

Each kerosene heater was fired up after the first 1/2 hour and run continuously for approximately the next 5 hours. At the end of 5-1/2 hours the heater was shut off, and the decay of air contaminants was measured. During these 5 hours, each heater was operated in three modes: normal, low, and high flame settings. The first operating mode (normal flame setting) lasted from heater start-up to 2-1/2 hours into the experiment. Once steady-state conditions were reached in the chamber, the heater flame setting was adjusted to low, and a new steady-state was reached after 1-1/2 hours. After steady-state was reached at the low setting, the heater flame setting was readjusted to high, with a new steady-state level achieved after an additional 1-1/2 hours. The heater was then shut off, and the decay of contaminants was traced for 1 hour without any adjustment of the chamber test conditions. Air contaminant gas and particle deposition rates (removal by the chamber surfaces) were determined by comparing the decay rates of the gases and particles to that of CO₂.

The heater flame settings were determined by visual inspection utilizing the picture guides contained in the operator's manuals which accompany the heaters. Actual fuel consumption rates were recorded with the Potter scale throughout heater operation. Steady-state chamber conditions were defined as CO₂ levels change at a rate of 0.01% per 5 minute period. Since CO₂ is non-reactive all other gases and particles, whether reactive or non-reactive, will have reached steady-state by the time CO₂ has.

Continuously monitored gases (NO_x, SO₂, CO, CO₂, and non-methane HC), temperature, dew point, and condensation nuclei (CNC) were measured and recorded during the full 6-1/2 hours of each experiment. Particle size measurements (Electrical Aerosol Analyzer--EAA--and Optical Particle Counter--OPC) were recorded for 10 minute periods before the heater was turned on, for 30 minutes during heater start-up and shutdown, and for 10 minutes during steady-state conditions.

Integrated total mass samples for trace elemental analysis (XRF) were collected on up to seven personal pumps spread through the chamber. Total mass samples for organic chemical analysis and mutagenicity testing were collected for each experiment using a medium volume sampler (i.e., PM-10 sampler without the sizing head) and pre-extracted filters. The filters were refrigerated and shipped to the University of Massachusetts for weighing and extraction. The filters were extracted with dichloromethane and solventexchanged to dimethyl sulfoxide. The extracts were then sent to EPA's Health Effects Research Laboratory, RTP, NC, to bioassay for mutagenicity using a modified Kado micro-suspension assay (Ref. 4). This modification uses Salmonella typhimurium TA98 both with and without S9 activation.

In addition, three heater runs doubled as trial runs to develop the protocol for Phase II. A XAD sample for semivolatile analysis and mutagenicity testing (attached behind the PM-10 sampler) was collected for these heaters as was a VOC grab sample using SUMMA canisters. Only the preliminary results on the total mass, size distribution of the particles, and particulate mutagenicity will be presented and discussed in this paper.

Results and Discussions

Table 1 summarizes the particle mass and volume data for each heater run. The particle volume data indicate that the highest mass emissions for radiant heaters generally occur between heater start-up and steady-state at normal flame setting (buildup). The convective heaters tested did not generally demonstrate a pronounced peak during heater start-up. Steady-state conditions associated with normal-flame-setting radiant heaters emitted more particles (higher particle volume concentrations) than during low or high flame settings. Convective heaters typically produced the highest particle volume concentrations during the high flame setting. The lowest particle volume concentration for all heater types was generally associated with a low flame setting. Particle size distribution measurements indicate that the particles produced by all the kerosene heaters are less than 2.0 μm with the peak volume occurring in the 0.15 μm size range.

Total mass concentrations as measured by the personal pumps exhibited considerable variability, with a low level of 73 $\mu\text{g}/\text{m}^3$ and a high of 721 $\mu\text{g}/\text{m}^3$. No clear pattern is evident for the total mass concentrations in relation to the type of heater or Btu rating of the heater. One heater (R/R) produced particle mass levels substantially higher than the others and with large variability between runs. Since only one heater of this design was tested, it is not known whether the high levels are particular

to this heater or to the general category of heaters with this design. There was little variability in the particle mass levels associated with the old and new heater comparison runs (C/R), apparently indicating little or no effect by the age of the heater. Particle mass levels for the same heater with different fuels (repeat radiant heater run) were higher for the higher ash content fuel.

The emission rates were estimated from the total mass concentrations as measured by the personal pumps over the full operation period of each heater, the effective removal rate of particles (ventilation plus loss to surfaces), and the total fuel consumed during each experiment. The estimated emission rates follow the total mass concentrations. The particle mass emission rates do not demonstrate any trends associated with heater type or manufacturer's Btu rating. Excluding the R/R heater, the emission rates vary by a factor of four. Using this range of emission rates for a 1,500 ft² (139 m²) house with a 7 ft (2.1 m) ceiling and an effective particle removal rate of 1 ach, the estimated range of steady-state particle mass levels (particles < 2.5 μ m) would be from 12 to 50 μ g/m³. Levels would be considerably higher if the emission rate for the R/R heater were used.

Table 2 summarizes the particulate mass collected by the medium volume sampler and the mutagenic data derived from the filter extracts. Because replicates were not available, only general observations can be made. As a whole, the radiant heaters appear to produce a less mutagenic extract than the other heaters; the combination (i.e., R/R, C/R) heaters appear to produce more mutagenic activity than the radiant or convective heaters.

Based on these results four heaters were selected for Phase II analysis. (See Table 2.)

Conclusion

Preliminary results of this research project indicated that unvented kerosene space heaters are a significant source of respirable suspended particles indoors. There is considerable variability in the emissions that is not associated with heater type or manufacturer's Btu rating. In addition certain heater types appear to produce mutagenic particles. The complete chemical analysis of the particles (the identity and quantity of volatile and semivolatile organics emitted by the kerosene heaters) will be available soon.

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The objective of this cooperative agreement between the U.S. EPA and the J. B. Pierce Foundation is to identify and develop emission rates for important organic air contaminants emitted by unvented combustion sources. A large scale environmental test chamber at the Pierce Foundation was used in this work to assess the nature and emission rates of air contaminants from 12 unvented kerosene space heaters, including radiant and convective heaters. Emphasis was placed on measuring the organic emissions from these sources as well as determining the mutagenic potential of the emissions. Classical air contaminants were also measured. The sources were screened over a range of conditions (i.e., source types, source ages, and fuel type and consumption) typically encountered in the real world to identify the range of individual (or categories of) emissions. The screening runs were then used to target a subset of heaters for an intensive evaluation of emissions. The data from these studies are presented and will be incorporated into indoor air models for evaluation in EPA's test house.

TABLE 1: Particle Emissions from Kerosene Heaters Tested

KEROS. HEATER TYPE ^a	RATED OUTPUT Btu/hr ^b (kJ/hr)	TOTAL MASS ^c ($\mu\text{g}/\text{m}^3$)		PARTICLE VOLUME ^d ($\mu\text{m}^3/\text{cm}^3$)				ESTIMATED EMISSION RATE ^e ($\mu\text{g}/\text{g}$)
		Personal pumps		Buildup	Normal	Low	High	
R	9,300 (9,810)	130	+/- 13	222	47	33	38	62
R	9,300 (9,810)	104	+/- 9	168	50	67	58	44
R	10,500 (11,076)	201	+/- 16	745	102	71	100	80
R ^f	12,500 (13,186)	73	+/- 14	162	109	56	102	25
R ^f	12,500 (13,186)	166	+/- 23	81	72	70	40	44
R	12,500 (13,186)	151	+/- 12	240	136	70	122	56
R/R9	12,600 (13,291)	533	+/- 23	512	342	211	299	175
R/R9	12,600 (13,291)	721	+/- 31	812	812	643	1097	260
C	8,200 (8,650)	79	+/- 7	45	45	18	52	20
C	12,700 (13,397)	148	+/- 28	137	137	147	214	47
C	17,100 (18,038)	188	+/- 19	--	45	48	46	59
C/R ^h	9,400 (9,916)	91	+/- 7	223	74	28	89	54
C/R ^h	9,400 (9,916)	98	+/- 15	239	50	26	53	53
C/R	17,500 (18,460)	132	+/- 50	100	100	66	138	27

a R (radiant), R/R (double radiant), C (convective) and C/R (combination).

b Btu output as advertised by manufacturer.

c Total mass was collected by from 4 to 7 personal pumps spread throughout the chamber and a PM-10 sampler without the head.

d Volume is calculated from the EAA particle size data (0.01 - 1.0 μm). The buildup particle volume is the largest volume calculated (2 minute size distribution measurement) during the period of heater start-up to normal steady-state. The normal, low, and high volumes are the average of fifteen 2-minute size distribution measurements taken during steady-state air contaminant concentrations associated with normal, low, and high fuel burning conditions.

e Calculated from personal pump mass, fuel consumption, and effective removal.

f Same heater with different fuels (one 0.06% S, 0.002% ash; and two 0.02% S, 0.016% ash).

g Same heater, duplicate runs.

h Same heater model (first one is new and other is old).

EPA'S INDOOR AIR QUALITY TEST HOUSE
1. BASELINE STUDIES

Merrill D. Jackson
U.S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

Russell K. Clayton, E. Eugene Stephenson, William T.
Guyton, and John E. Bunch
Acurex Corporation
P.O. Box 13109
Research Triangle Park, NC 27709

EPA has acquired a test house in the Research Triangle Park, NC, area for indoor air quality research. The test house will be used to measure the outgassing of chemicals from common household and building materials, to determine the effects of residential activities which release organic emissions, and to evaluate indoor air quality control technologies. The results of testing in EPA's laboratory size environmental test chambers will be compared to those obtained under normal household conditions.

The test house is a typical three-bedroom, two-bath, one-story frame house with natural gas heat.

This paper will describe the baseline studies which provide the required characterization of the test house. These studies include blower door and SF₆ tests for air leakage and exchange rates; pollutant stratification, migration, and surface reactivity evaluations; and analysis of the baseline inorganic gases and total organic hydrocarbon levels in the house before any test materials are allowed into the house.

INTRODUCTION

The Environmental Protection Agency has an indoor air quality program in which common household and building materials are tested in small and large chambers for either outgassing or emitting volatile organic compounds. Examples are the outgassing of caulk and the emissions from unvented kerosene heaters. The chambers range from 50-liter laboratory units to room size chambers. Once the emission concentration values have been determined in the chamber experiments and models have been developed for full scale applications, the model must be evaluated in a house under normal usage.

The Air and Energy Engineering Research Laboratory of EPA leased a house for the purpose of evaluating these models and indoor air quality control technologies, as well as providing interlaboratory support such as bioassay sample collection for EPA's Health Effects Research Laboratory and the evaluation of samplers and methods for indoor air quality studies for EPA's Environmental Monitoring Systems Laboratory.

The house meets the requirements for our program including:

1. Wood Construction
2. One-Story
3. No Basement
4. Single Family
5. Gas Forced Air Heat
6. Three Bedroom, Two Bath
7. Five to Seven Years Old
8. 1200-1500 Square Feet (100-150 Square Meters)

A multi-storied house was not desired at this time due to modeling constraints, and wooden construction was required as the most common type in the nation. The age requirement was based on the need to select a house which had already outgassed the volatile and semi-volatile compounds from the original materials of construction, and which was built with the energy savings features brought on by the oil energy crisis.

We have the authority to make any changes to the house needed for the program such as replacing the subflooring, carpeting, or cabinets; adding paneling; or painting or staining the interior or exterior. An attached garage, running the full width of the house, has been outfitted as an instrumentation room which is attached, yet isolated from the test areas.

DESCRIPTION

Sampling and analytical instrumentation for the following is available or installed at the test house:

1. Organic Compounds
 - a. Volatiles
 - b. Semi-volatiles
 - c. Total Hydrocarbons

2. Inorganic Compounds
 - a. Sulfur Oxides
 - b. Carbon Monoxide
 - c. Carbon Dioxide
 - d. Nitrogen Oxides
 - e. Nitrogen Oxide
 - f. Ozone
3. Particulate
 - a. Filters
4. Air Exchange Rates
 - a. Blower Door
 - b. Sulfur Hexafluoride
5. Meteorological
 - a. Temperature
 - b. Wind Direction
 - c. Wind Speed
 - d. Relative Humidity
 - e. Barometric Pressure

The volatile organics are sampled with Tenax cartridges at flow rates of 250-1000 ml/min. Semi-volatiles are collected on XAD-2 resin traps using a modified medium flow (4 cfm or 0.0019 m³/sec) sampler. Inorganics and total hydrocarbons are measured by continuous monitors, for which a dilution system is available for calibration. This allows a standard curve of any reasonable range to be run on each instrument and does not require the storage of numerous cylinders of low concentration gases which have a short shelf life. Clean air is used as the diluent. Particulate samples are collected using quartz (mass) and Teflon-coated glass fiber (bioassay) filters using 4-cfm samplers. The blower door method uses a commercially available unit with standard operating procedures (1), while the SF₆ method requires that grab samples be taken hourly after the release of a specified volume (10-20 ml) of SF₆ tracer gas. The Tedlar bag samples are analyzed by gas chromatography with flame ionization detection to determine the rate of loss in the gas concentration. A meteorological tower in the backyard has a readout in the garage.

An IBM-AT computer controls all the sampling times and records the readings from all the continuous monitors and the weather data. The control system can handle up to 10 locations within the house. These locations can be moved easily. At present eight are inside the house and two are outside for ambient measurements during experimental runs.

The first products to be tested in the house are unvented kerosene heaters. In preparation for these tests, certain characterization tests were made, including blower door, SF₆, and continuous monitor runs both inside and outside the house. In the two rooms where the emissions from the kerosene heaters will be monitored (the den where the heater will be located and the bedroom farthest from the den), stratification, migration, and reactivity tests were also performed. The rooms were sampled at elevations of 6, 36, 64, and 94 in. (0.15, 0.91, 1.63 and 2.39 m) above the floor. These heights represent a person lying on the floor, sitting in a chair, standing in the room, and the ceiling level, respectively.

The blower door test was run normally with all the doors and windows closed and then with one window in the den open 2 in. (0.05 m). The manufacturers of unvented kerosene heaters recommend that one window be opened slightly during the heater operation.

RESULTS

The results of the blower door tests are in Table 1.

TABLE 1. BASELINE BLOWER DOOR STUDIES

CONDITION	ACH 50 Pa	ACH Norm	EqLA		EFLA	
			in. ²	m ²	in. ²	m ²
NORMAL	15.28	0.90	256	0.165	133	0.086
WINDOW OPEN	17.36	1.02	319	0.206	176	0.114

ACH = Air Changes per Hour
EqLA = Equivalent Leakage Area
EFLA = Effective Leakage Area

The blower door tests showed that the normal ambient air exchange rate [approximated by dividing the 50 Pa ACH by 17 (1)] for the test house is in the generally accepted range for energy efficient houses of its age. The equivalent leakage area is defined as the area of a round sharp-edged orifice that, at a pressure of 10 Pa, would leak the same as all the house's leaks at 10 Pa. Effective leakage rate is defined as the area of a specially shaped bell-mouthed nozzle that, at a pressure of 4 Pa, would leak the same as all the house's leaks at 4 Pa.

The results of the stratification test are given in Table 2

There is no apparent difference between the outside and the inside air nor is there any stratification in the two rooms of the house.

The results of the migration and reactivity tests will be included in a later publication along with the kerosene heater test data.

Organic background tests will be run during the unvented kerosene heater study as well as further tests on sink effects of the walls, carpet, and other materials in the house at the time of the tests.

Materials planned for study in the future include moth cakes (paradichlorobenzene), floor wax, wood and wall finishes, and paneling.

TABLE 2. STRATIFICATION AND BASELINE CONTINUOUS MONITORING RESULTS

LOCATION (in.)	CO ppm	CO2 ppm	NOX ppm	NO ppm	THC ppm
OUTSIDE	1.14	398	0.08	0.07	0.09
DEN (6)	1.21	422	0.06	0.06	0.10
DEN (36)	1.24	436	0.06	0.06	0.10
DEN (64)	1.23	438	0.06	0.06	0.10
DEN (94)	1.24	439	0.06	0.06	0.10
AVERAGE	1.23	434	0.06	0.06	0.10
BEDROOM (6)	1.22	455	0.06	0.06	0.09
BEDROOM (36)	1.20	442	0.06	0.06	0.09
BEDROOM (64)	1.11	393	0.06	0.06	0.09
BEDROOM (94)	1.11	393	0.06	0.06	0.09
AVERAGE	1.16	421	0.06	0.06	0.09

SOX = <0.01 ppm for all locations

REFERENCE

1. Operation Manual, Minneapolis Blower Door, 920 West 53th Street, Minneapolis, MN 55419.

SEMI-VOLATILE ORGANIC COMPOUNDS IN RESIDENCES

David J. Anderson and Ronald A. Hites
School of Public and Environmental Affairs
and Department of Chemistry
Indiana University
Bloomington, Indiana 47405

This research focuses on the identification and quantification of semi-volatile organic compounds (vapor pressures $1 - 10^{-7}$ mm Hg) in the indoor air of single-family dwellings. This general category includes chlorinated pesticides, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAH). Samples were taken using polyurethane foam (PUF) as a sorbent with small, low-flow pumps. Extracts were analyzed by gas chromatographic mass spectrometry (GC/MS) and gas chromatography with electron capture detection (GC-ECD). Indoor concentrations of these compounds were elevated when compared to typical outdoor concentrations. Derivatives of hexachlorocyclopentadiene, such as alpha- and gamma-chlordane, were detected in the living area of one home at levels up to 60 times the outdoor concentration. The concentration of gamma-chlordane in the basement of this home was three orders of magnitude higher than outdoor levels. Indoor sources for these chemicals are implied.

Introduction

Because the average person spends about 90% of his or her time indoors, it is important to know the identities and concentrations of indoor air pollutants. A chronological summary of major U. S. indoor air research reveals the neglect of organic pollutants in early indoor air research (1). There has been some research on volatile organic compounds, but there are few data on semi-volatile organic compounds (2-4). Our research involves the identification and quantification of chlorinated pesticides, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAH) in the indoor air of single-family homes. Indoor concentrations of these compounds were measured in 12 homes and compared to typical outdoor concentrations. Possible sources of these chemicals are proposed for some of the compounds.

Experimental Section

Homeowners were solicited by a news release which appeared in the local newspaper; questionnaires were used to select a set of homes for sampling. The questionnaires requested general information about the size and age of the home and about possible sources of organic chemicals. The majority of the homes were located in the Bloomington, Indiana area and were sampled during May-October, 1986.

Air samples were taken using polyurethane foam (PUF) traps and constant flow pumps. The PUF was cut into small plugs which were 22 mm in diameter and 8 cm in length. Two Dupont P-4000A constant flow pumps (E. I. du Pont de Nemours & Co.) and two SKC Aircheck VII pumps (SKC Inc.) were used for sampling. The pumps were calibrated with a large volume soap bubble flowmeter. A nominal flow rate of 3 L/min and sample volumes of approximately 2 m³ were used. Both brands of pump contain servo mechanisms to maintain the flow rate at $\pm 5\%$ of the set value during sampling. All flow rates in this work were within this tolerance. The PUF plugs were placed in glass sampling tubes under slight compression to prevent air seepage around the edges. Sampling was carried out in duplicate by means of a glass tee connected to the inlet of the pump. The sampler design was based on the one described by Lewis and MacLeod (2).

The PUF plugs were pre-extracted prior to use with glass-distilled grade solvents. A 24 hour Soxhlet extraction with acetone followed by 24 hours with hexane was used. The pre-extracted plugs were dried under vacuum at approximately 50^o C for 24 hours. The PUF plugs were carried through the entire pre-extraction and drying steps in groups of three; this provided two plugs for replicate samples and one blank in each group.

Samples and blanks were stored at -10^o C prior to Soxhlet extraction with a 1:1 mixture of acetone and hexane. The internal standards for the PCB analyses (4,4'-dibromobiphenyl) and the PAH analyses (d₁₀-fluorene, d₁₀-phenanthrene, and d₁₀-pyrene) were spiked directly onto the PUF plugs prior to this extraction. The internal standard for the chlorinated pesticide analyses (2,2',3,4,4',5,6,6'-octachlorobiphenyl) was spiked into the sample extracts after sample extraction and concentration. The extracts were concentrated by rotary evaporation and gentle blowdown under a stream of clean, dry nitrogen.

All pesticide analyses were carried out on a Hewlett-Packard 5985B gas chromatographic mass spectrometer (GC/MS) using electron capture,

negative ion, mass spectrometry (ECNIMS) and operating at an ion source temperature of 100⁰ C and a pressure of 0.4 torr; 30 m x 0.25 mm DB-5 fused silica capillary columns (J&W Scientific) were used for all separations. Selected ion monitoring (SIM) was used for quantification, and a confirmation ion for each compound was also monitored. The confirmation ions were selected from the same isotopic cluster as the quantification ions.

PCBs were measured on a Hewlett-Packard 5890A gas chromatograph and were detected using a ⁶³Ni electron capture detector (ECD) and a Hewlett-Packard 3392A integrator. A Hewlett-Packard 7673A automatic sampler was used for the introduction of all samples and standards. The PCBs were quantified as Aroclor 1242. The total area of the 16 largest peaks in the Aroclor 1242 mixture was used. All values were blank corrected.

PAH analyses were done on a Hewlett-Packard 5995A GC/MS system operated in the SIM mode using electron impact ionization. The SIM program used the most abundant ion produced for each PAH (in all cases the molecular ion) as the quantification ion. The identification of isomeric PAH was verified by matching chromatographic retention times to a standard.

Results

The concentrations of gamma-chlordane, alpha-chlordane, and trans-nonachlor in the homes are given in Figure 1. All data are averages of two replicate samples and are blank corrected. The outdoor concentrations of these compounds are low. The outdoor samples were taken at two locations in Bloomington. Note that two homes (12 and 63) have indoor concentrations which are elevated with respect to the outdoor samples and that the three compounds co-vary with one another; the correlation coefficient is at least 0.98 for the three compounds. The most likely reason for this co-variation is that they have the same ultimate source. These compounds are all present in technical-grade chlordane, which is a termiticide.

The source of chlordane in home #63 was investigated using multiple, simultaneous samples taken throughout the home. The concentrations in the basement averaged 12 times higher than in the living areas. This home was treated with chlordane in the late 1970's, according to the current resident. It seems likely that chlordane has infiltrated through cracks in the basement walls, if sub-surface injection is assumed to have been used for application. Large cracks in the basement walls were found upon inspection of the home. A similar hypothesis is proposed for home #12 based on interviews with the homeowner; home #12 was treated for termites in 1974.

The concentrations of heptachlor in the homes are shown in Figure 2. Heptachlor is also found in technical-grade chlordane, but it does not co-vary with the compounds discussed above ($r < 0.4$). Also, the concentrations of heptachlor are about a factor of 10 greater than the chlordane. Homes 61 and 62 were treated for termites in 1977 and 1984 respectively. The exact formulation of the termiticides used is uncertain, but there is a possibility that heptachlor was used. A commercial mixture of chlordane and heptachlor, known as Termide, is available (4). Heptachlor has a higher vapor pressure than the chlordanes, thus, it is possible that higher soil outgassing rates have contributed to the generally higher heptachlor concentrations.

Dursban (also known as chlorpyrifos) is an organophosphorous pesticide; it is used as a soil insecticide and for the control of household pests. Owners of the two homes which showed the highest levels of dursban both indicated the use of dursban on the questionnaire. The treatment in home #60 was once every two weeks, by the homeowner, with a product containing dursban. The spraying in home #62 was conducted on a monthly basis by a professional service.

Aroclor 1242 is the only PCB mixture present in the indoor air of the homes tested. The concentrations of Aroclor 1242 are presented in Figure 3. The high indoor concentrations imply indoor sources. However, some of the homes were built after the use of PCBs was banned in the mid-1970's. Homes 34 and 52 were built in 1983 and 1985, respectively, and should not contain indoor sources of PCBs. The presence of electrical equipment has been suggested as a source of PCBs in indoor air (3), and indeed electrical equipment may be a source in some of the homes in our study, such as home #62 which was built in 1973. The building in which our laboratory is located was completed in 1962 and is, no doubt, serviced by electrical equipment which contains PCBs.

The concentration profiles for fluoranthene and pyrene do not reveal any significant trends; attempts to correlate the PAH data with smoking, or other combustion sources, failed. Home #62 was sampled on a weekend when three of the occupants who smoked were home, and the wood-burning fireplace was in use. There appear to be no elevated levels of PAH in this home, based on the results from this one set of samples. Similarly, smoking was evident during the sampling of home #61, but smoking did not produce indoor concentrations which were elevated over the indoor concentrations of PAH in non-smoker's homes. The elevated levels of PAH in our laboratory are due to an input from the make-up air for our chemical fume hoods. There is a coal-fired power plant near the building in which our laboratory is located; the PAH are coming in through the air ducts from the outdoor air.

Conclusions

The elevated indoor concentrations of these compounds are dependent upon many factors, one of which is the presence of an indoor source. Relative volatility of the various compounds may also be important in determining indoor concentrations. Finally, the rate of exchange between the indoor and outdoor air is an important variable which must be measured to understand the role of indoor/outdoor mixing. Indoor concentrations of these compounds were not statistically higher in homes which had the doors and windows closed during sampling when compared to homes which had the doors and windows open during sampling. But, the quantification of ventilation rates may allow the differentiation of changes in indoor concentrations which occur due to mixing from those changes which are related to indoor sources.

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Acknowledgment

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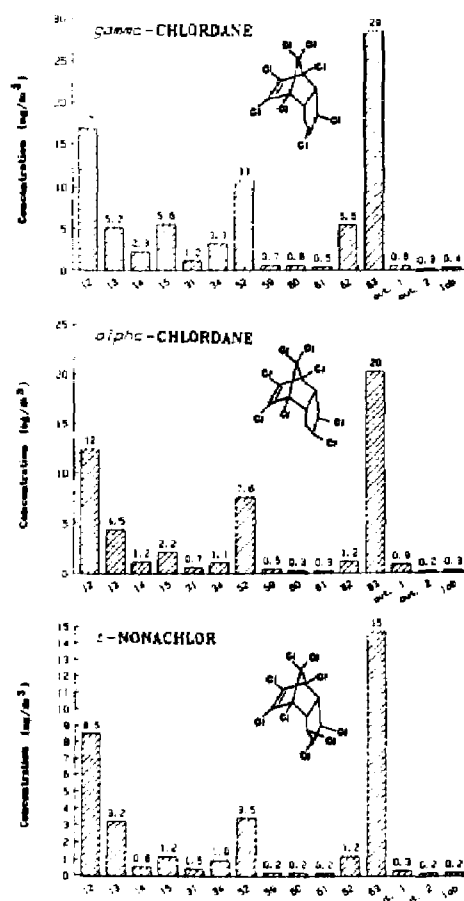


Figure 1. Concentrations of three components of technical-grade chlordane in the indoor air of homes. (Vertical scales are different.) Horizontal axis numbers are home identification numbers. Outdoor samples are designated "out. 1" and "out. 2". Laboratory concentration is labeled "lab".

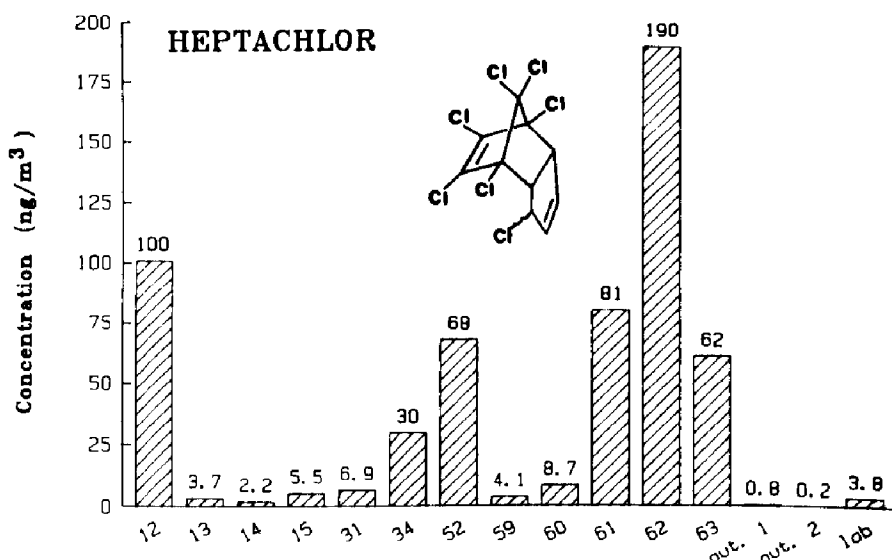


Figure 2. Concentrations of heptachlor in the indoor air of homes. Horizontal axis numbers are the same as in Figure 1.

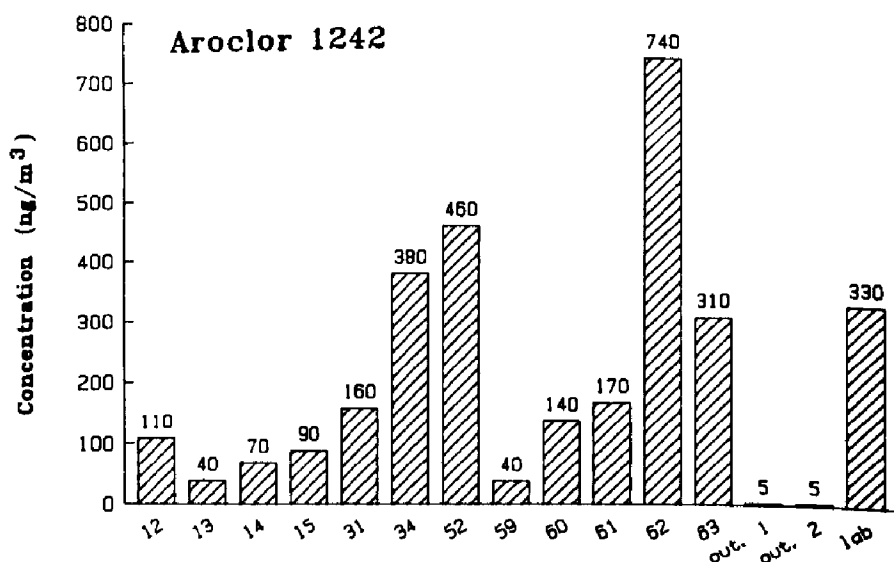


Figure 3. Concentrations of PCRs in the indoor air of homes (reported as Aroclor 1242). Horizontal axis numbers are the same as in Figure 1.

EMISSION RATES OF VOLATILE ORGANIC COMPOUNDS FROM
BUILDING MATERIALS AND SURFACE COATINGS

Lance A. Wallace
U.S. EPA
Washington, DC

Robert Jungers
Environmental Monitoring Systems
Laboratory
U.S. EPA
Research Triangle Park, North Carolina

Linda Sheldon
Research Triangle Institute
Research Triangle Park, North Carolina

The U.S. EPA measured emissions of 32 volatile organic compounds (VOCs) from 31 building materials. All materials were collected from one building for headspace studies; nine materials were investigated in follow-up chamber studies. Twenty-four building materials emitted measurable levels of the target VOCs. About 20 VOCs were elevated in the newly-constructed building by factors of 5-500. Major sources included adhesives, paint, vinyl and rubber molding, foam insulation, linoleum tile, carpet, and particle board.

Introduction

The U.S. EPA measured air concentrations of 32 VOCs in six buildings (two offices, two homes for the elderly, one school, and one hospital) in 1984-86^{1,2,3}. As part of this study, emissions of all target VOCs from 31 building materials were measured.

Procedures

All emission testing was performed on materials used in the construction of a new single-story office building in Fairfax, Virginia. Most of the 22 solid building materials tested were subsamples of the actual materials used in construction and were collected at the sampling site in January 1985. The remaining solid materials, plus the nine solvent-based materials, were purchased from the manufacturer. Manufacturing lots were matched where possible to materials actually used in the building.

Each of the solid materials collected at the building site were temporarily stored (< 2 weeks) in individual plastic bags (Mobile Kordite[®] large capacity 1.5 mil) in nonlaboratory areas at Research Triangle Institute. For permanent storage, the materials were individually wrapped in heavy duty aluminum foil and placed in an outdoor metal storage shed to minimize the potential for contamination from laboratory solvents and chemicals. Samples were stored for a maximum of four months prior to testing. Solvent-based materials were stored in their containers as received.

Preliminary headspace experiments were performed to determine both the identities and approximate levels of volatile organic emissions from each of the 31 building materials. For solid materials, one or two pieces (approximately 2 x 4 cm) were cut from the material. For solvent-based products, the material was first mixed, then applied with a Teflon spatula to one side of a clean glass microscope slide (5.5 x 2.6 cm). The prepared slides were allowed to dry at 23°C for seven days protected from both dust and laboratory solvents.

During testing, the prepared sample material was placed in a wide-mouth glass jar, which was sealed with a custom-built Teflon head. Dry, purified nitrogen was introduced to the jar at 15 mL/min and allowed to vent for 60 to 90 minutes. After this equilibration period, a Tenax GC cartridge was placed into the sampling head. For solid materials, the headspace was purged through the sorbent overnight at 15 mL/min. Solvent-based materials were tested for approximately 30 minutes. Blank samples were collected from empty jars under identical conditions to assess contamination.

Nine materials were selected for detailed emission studies using 12-L chambers under controlled conditions of temperature, humidity, and ventilation. A sample of material was placed in one of the four chambers and the chamber sealed. The ventilation rate was set and the samples allowed to equilibrate overnight at 25°C and 48% relative humidity. Purified air was supplied to each chamber at a rate of 0.1 L/min. From each chamber 0.033 L/min of this air was removed by pumping through an empty sampling tube, while the other 0.067 L/min was vented outside the chamber. A fan blade attached to a magnetic stir bar provided thorough mixing of the chamber atmosphere throughout the experiment. After the equilibration period, Tenax GC cartridges replaced the empty sampling tube to collect organic compounds from the gas stream. Chamber blanks were prepared by leaving one of the chambers empty and collecting a

sample of the air from the empty chamber for 6 hours in order to detect background contamination.

Tenax GC cartridges exposed during the chamber experiments were loaded with approximately 250 ng of bromofluorobenzene as an external standard, then thermally desorbed and injected into a high resolution capillary column. Samples were analyzed by either GC/MS or GC/FID.

Target chemicals were identified during GC/FID analysis by comparing relative retention times for the samples and standards. For each material tested three or four samples were collected with at least one exposed cartridge being analyzed by GC/MS. Comparison of these results to GC/FID results assisted in positively identifying target chemicals. Only those chemicals identified at high levels without chromatographic interferences were quantitated by GC/FID.

Results

In the headspace experiments, 24 of the 32 target chemicals were emitted from one or more of the 31 materials.

In general, aliphatic and aromatic compounds were emitted in larger quantities than halogenated compounds (Table 1). Exceptions included 1,1,1-trichloroethane from cove (molding) adhesive and tetrachloroethylene from latex paint.

In the chamber experiments, the nine materials tested emitted 22 of the target organics (Table 2). Chamber results for the six solid materials agreed well with the headspace results, but were sharply different for the three solvent-based coatings. Temperature, humidity, time of curing, and the amounts used all differed between the experiments -- apparently in sufficient amounts to cause order-of-magnitude differences in calculated emission rates.

The building from which the materials were collected was monitored both indoors and outdoors within two weeks of its completion, before the occupants moved in (Table 3).

The monitoring results often compared well with the results of both the headspace and chamber experiments. For example, the aromatic hydrocarbons with the highest indoor air concentrations (ethylbenzene, *m*-ethyltoluene, and 1,2,4-trimethylbenzene), generally show highest emission rates from all of the building materials, including the carpet, linoleum tile, all of the plastic materials and the solvent materials such as adhesives, paint, and caulk. Particle board is probably a major source of α -pinene. Finally, at the time monitoring was being performed, vinyl core molding and adhesive were being applied throughout the building. It is likely these materials are major contributors to 1,1,1-trichloroethane, ethylbenzene, and the xylenes found in the air samples.

Conclusions

Previous studies by Molhave⁴ and Wallace⁵ have identified and quantified VOC emissions from building materials and finishings. Results are not fully comparable because of differences in aging time and chamber conditions.

However, it is possible to identify major sources of the 5-500-fold increases in indoor air concentrations observed in new buildings. These include adhesives and paints as likely major contributors of many VOCs, and foam insulation, vinyl and rubber molding, particle board, and telephone cable as major contributors of individual VOCs.

In view of the great differences observed between headspace and chamber results for the paints and adhesives, and also of the likely variations in composition of different brands, it does not seem possible at present to quantify emission rates from these materials within an order of magnitude. However, it is clear that elevated concentrations occur in new buildings (and probably in renovated buildings) and may cause symptoms such as those observed in "sick building syndrome."

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Table I. Summary of Emission Results

	Emission Rate ($\mu\text{g}/\text{m}^3 - \text{h}$)			
	Aliphatic and Oxygenated Aliphatic Hydrocarbons	Aromatic Hydrocarbons	Halogenated Hydrocarbons	All Target Compounds
Cove adhesive	287	3800	650 ^a	4737
Latex caulk	252	380	5.2 ^b	637
Latex paint	111	52	86 ^c	249
Carpet adhesive	136	98	- ^d	234
Black rubber molding	24	78	0.88	103
Small diameter telephone cable	33	26	1.4	60
Vinyl cove molding	31	14	0.62	46
Linoleum tile	6.0	35	4.0 ^e	45
Large diameter telephone cable	14	20	4.3 ^f	38
Carpet	27	9.4	-	36
Vinyl edge molding	18	12	0.41	30
Particle board	27	1.1	0.14	28
Polystyrene foam insulation	0.19	20	1.4	22
Tar paper	3.2	3.1	-	6.3
Primer/adhesive	3.6	2.5	-	6.1
Latex paint (Bruning)	-	3.2	-	3.2
Water repellent mineral board	1.1	0.43	-	1.5
Cement block	-	0.39	0.15	0.54
PVC pipe	-	0.53	-	0.53
Duct insulation	0.13	0.15	-	0.28
Treated metal roofing	-	0.19	0.06	0.25
Urethane sealant	-	0.13	-	0.13
Fiberglass insulation	-	0.08	-	0.08
Exterior mineral board	-	0.03	-	0.03
Interior mineral board	-	-	-	-
Ceiling tile	-	-	-	-
Red clay brick	-	-	-	-
Plastic laminate	-	-	-	-
Plastic outlet cover	-	-	-	-
Joint compounds	-	-	-	-
Linoleum tile cement	-	-	-	-

^a1,1,1-Trichloroethane (minimum value)^b1,1,1-Trichloroethane (4.9) and Trichloroethylene (0.3) (minimum values)^cTetrachloroethylene^dNo detectable emissions^eTrichloroethylene (3.6)^fTetrachloroethylene (3.8)

Table 2. Calculated Emission Rates ($\mu\text{g}/\text{m}^2 - \text{h}$) of Target Compounds During Chamber Experiments

	Vinyl Cove Molding	Black Rubber Molding	Poly- styrene Foam Insulation	Linoleum Tile	Carpet	Particle Board	Cove Adhesive	Carpet Adhesive	Latex Paint Glidden
<u>Aromatic Hydrocarbons</u>									
Benzene	-a	-	-	-	-	-	-	-	17
Ethylbenzene	1.8	1.7	15	0.45	-	0.14	547	211	12
m-Xylene	5.9	6.9	1.7	0.92	-	0.20	1185	717	50
Styrene	0.14	0.43	6.2	0.63	-	0.18	--	-	1.9
o-Xylene	1.9	3.9	0.39	0.89	0.83	0.08	202	301	28
Isopropyl benzene	0.38	0.33	1.7	0.41	-	0.15	-	53	8.9
n-Propyl benzene	0.68	0.72	0.86	0.84	-	0.22	-	53	13
m-Ethyltoluene	3.4	4.6	0.44	3.2	-	-	-	281	57
1,3,5-Trimethyl- benzene	1.7	2.7	0.08	1.4	-	0.10	-	212	32
o-Ethyltoluene	0.41	2.0	0.07	1.3	-	0.07	-	97	18
1,2,4-Trimethyl- benzene	2.3	7.1	0.17	4.7	.063	0.20	-	216	33
1,2,3-Trimethyl- benzene	1.4	5.5	0.03	2.5	.027	0.06	-	151	20
<u>Aliphatic Hydrocarbons</u>									
α -Pinene	0.19	1.4	-	-	-	6.8	-	-	-
n-Decane	10	14	-	-	0.23	-	-	-	360
n-Undecane	22	29	-	1.2	7.1	-	-	3245	250
n-Dodecane	34	9.7	-	0.45	6.4	-	-	2295	110

Table 2. Calculated Emission Rates of Target Compounds During Chamber Experiments (continued)

	Vinyl Cove Molding	Black Rubber Molding	Poly- styrene Foam Insulation	Linoleum Tile	Carpet	Particle Board	Cove Adhesive	Carpet Adhesive	Latex Paint Glidden
<hr/>									
<u>Oxygenated Hydrocarbons</u>									
<u>n</u> -Butyl acetate	-	0.42	-	-	-	-	-	-	-
Ethoxyethyl acetate	-	-	-	-	-	-	-	-	-
<hr/>									
<u>Chlorinated Hydrocarbons</u>									
1,1,1-Trichloro- ethane	0.30	0.11	-	-	-	-	-	-	-
Trichloroethylene	0.12	-	-	1.3	-	-	-	-	1.9
Tetrachloro- ethylene	0.11	-	-	-	-	-	-	-	289
Chlorobenzene	1.8	0.31	0.38	-	-	-	-	-	-
<u>p</u> -Dichlorobenzene	-	0.97	0.47	-	-	0.18	-	-	-
<u>o</u> -Dichlorobenzene	-	-	0.20	-	-	-	-	-	-

^aNo detectable emissions

Table 3. Average Concentration and Possible Sources of Volatile Organics in a Newly Constructed Office Building

Compound	Average Concentration (ug/m ³) Over 72-hour Measurement Period		Possible Sources (from Tables 1 and 2)
	Indoors	Outdoors	
<u>Aromatic Hydrocarbons</u>			
Xylenes	62	5	Adhesives, paint, molding, insulation
Ethylbenzene	54	2	Adhesives, insulation, paint
Trimethylbenzenes	130	0.5	Carpet adhesive, paint, molding, linoleum tile
Ethyltoluenes	40	2	Carpet adhesive, paint, molding, linoleum tile
Propylbenzenes	10	0.4	Carpet adhesive, paint
Benzene	3	4	Outdoors
Styrene	3	0.6	Insulation
<u>Aliphatic Hydrocarbons</u>			
n-Decane	520	0.9	Paint, molding
n-Undecane	220	0.4	Carpet adhesive, paint, molding, carpet
n-Dodecane	180	0.1	Carpet adhesive, paint, molding, carpet
α-Pinene	15	0.1	Particle board
<u>Chlorinated Hydrocarbons</u>			
1,1,1-Trichloroethane	17	1	Cove adhesive
1,2-Dichloroethane	0.8	0.2	Linoleum tile
Trichloroethylene	0.5	0.1	Linoleum tile
Chlorobenzene	0.6	0.02	Insulation, molding
p-Dichlorobenzene	0.3	0.07	Molding, insulation
Tetrachloroethylene	0.5	0.4	Outdoors, paint
Carbon tetrachloride	0.4	0.6	Outdoors

INHALATION EXPOSURE FROM VOLATILE ORGANIC CONTAMINANTS IN DRINKING WATER

- (1) Lynn Wilder, Region III, Technical Assistance Team,
- (2) Gerald T. Heston, On-Scene Coordinator
- (3) Michael Zickler, Sr. On-Scene Coordinator
- (4) Richard Habrukowich, TATL, Technical Assistance Team

An increasing number of groundwater/residential well water volatile organic contamination problems has raised questions concerning the amount of human inhalation exposure to these organics. Typically, health risk assessments of contaminated drinking water have only addressed the exposure for the ingestion of volatile organics. However, over the last several years, questions have arisen concerning the amount of exposure occurring through the inhalation route during typical home water use (i.e. showering). Results from a recent study showed that 80% of trichloroethylene volatilized in a model shower system using room temperature water. Thus, exposure to volatile organics during showering could make inhalation an important factor in health risk assessments of contaminated potable water supplies.

EPA Region III's ERS recently conducted a study under the authority of SF 104 (b) to go beyond the previous laboratory study and obtain exposure information from inhabited homes. In this research, trichloroethylene concentrations were measured in the water and air over the duration of a typical showering period in several residences with trichloroethylene-contaminated drinking water supplies. From these findings, human inhalation exposures are estimated and compared with exposures from ingestion.

- (1 & 4) Roy F. Weston, Inc., Region III Technical Assistance Team,
53 Haddonfield Road, Suite 306, Cherry Hill, NJ 08002
- (2 & 3) U. S. EPA, Region III Emergency Response Section, 814 Chestnut
St., Philadelphia, PA 19107

Introduction

Residential wells (groundwater) in a Pennsylvania community have been shown to be contaminated with high levels of trichloroethylene (TCE), and in some cases with low levels of tetrachloroethylene (PCE) and methylene chloride. As part of an EPA Region III, Emergency Response Section (ERS) CERCLA Removal, before in-house carbon filtration units were installed, a study was conducted to determine the amount of TCE that volatilized from the contaminated groundwater during showering.

Typically, health risk assessments from contaminated drinking water have only addressed the exposure for the ingestion of volatile organic contaminants (VOC's). Drinking water standards and health advisory values for contaminated water are based upon ingestion exposure only. An increasing number of groundwater/residential well water volatile organic contamination problems have raised questions concerning the amount of human inhalation exposure from these organics. Specifically, questions have arisen concerning the amount of inhalation exposure incurred during typical residential water usage (i.e., showering).

Physical properties of VOC's such as vapor pressure and limited solubility in water, make these contaminants favor the air phase in an equilibrium situation. Thus, greater concentrations will be found in air. Volatile organics tend to be more of a contamination problem in groundwater than in surface waters for several reasons. Surface waters have a large surface area in contact with air. Equilibrium forces tend to drive VOC's out of the aqueous phase and into the air. Since groundwater has less contact with air, equilibrium forces tend to keep most volatile organic contamination in the water phase. In the case of private wells using groundwater, most of the equilibrium process occurs once the water reaches a tap or showerhead. At these points, not only does the water come in contact with air, but the droplet form in which the water leaves the tap creates a large surface area ratio of air to water. This aeration process drives most of the volatile organics out of the aqueous and into the air phase.

A recent study using a model shower system¹ has shown that even with room temperature water, 80% of TCE volatilized from incoming water. When water temperature was increased, greater than 90% of TCE volatilized. Over the duration of the "shower" the concentration of TCE in air steadily increased, showing no signs of reaching an equilibrium with the water phase. Thus, exposure to VOC's during a typical showering period could be quite large, making inhalation exposure a factor in health risk assessments of contaminated drinking water supplies.

Using the International Commission for Radiological Protection² rates and volumes for reference air intake, an estimated 1 to 1.2 cu meters of air is inhaled per hour for an average adult male or female. Thus, in a 15 to 30 minute shower, 0.25 to 0.3 cu. meters and 0.5 to 0.6 cubic meters of air is inhaled, respectively.

The amount of retained TCE in the body through inhalation has been estimated at 36-75%³. Using a TCE retention factor (RF) of 70, 70% of the TCE inhaled is absorbed by the lungs and the remaining 30% is exhaled.

The Drinking Water Equivalent Level (DWEL) for TCE is 260 ug/L (1.40 mg/m³). Additionally, the 10-6 cancer risk level of TCE is 2.8 ug/L (0.02 mg/m³). The November 13, 1985, Federal Register proposed maximum contamination levels (PMCLs) of 5.0 mg/L (.027 mg/m³).
Experimental Methods

Air Analysis

At each residence the MIRAN 1A* portable ambient air analyzer was set up and calibrated. All bathroom doors and windows were closed and any fans turned off. One end of Teflon tubing was attached to the MIRAN inlet port; the other end was placed approximately 1 foot in front of the showerhead (5.5 feet above the shower floor) above the spray. After a baseline reading was obtained for 5-10 minutes, the water flow rate was calibrated and the water was brought to room temperature. The shower was then turned on and allowed to run for 30 minutes.

Grab air samples were taken for private laboratory analysis after the shower had run for 15 to 30 minutes. The inlet port of a 1 liter Tedlar bag was attached to the MIRAN outlet port and allowed to fill. Samples were placed on ice.

After 30 minutes, the shower water was terminated, the Teflon tube was disconnected and a final baseline reading was taken for 5 to 10 minutes.

Water Analysis

To calculate the well concentration of TCE, a water sample was collected in a 40 ml VOA bottle before the shower began. A duplicate sample was collected for private laboratory analysis. During the shower run, a water sample was collected every 10 minutes in two locations. One set of samples were collected near the MIRAN inlet tube, and the second set was collected near the shower floor.

Samples were analyzed for TCE (headspace analysis) using a portable GC with a PID detector (Photovac)*. Standards and samples were analyzed in duplicate. As a QA measure, initial well water duplicate samples were sent to a private laboratory for analysis (volatile organic analysis by EPA Method 601).

Results

The results of continuous air monitoring in each of the four residences is shown in Table I. Concentrations were calculated for every 10 minutes of the shower run and after 10 minute after the shower was terminated.

Laboratory results of grab samples taken at 15 and 30 minutes after the start of the shower were typically 10-15% higher than these readings. These differences were probably due to differences in analytical methods and techniques. Therefore, results of the continuous air monitoring method (MIRAN) are conservative in nature.

From this data, assuming 0.3 and 0.6 m³ of air inhaled for a 15 to 30 minute period, respectively, the TCE concentrations inhaled are displayed in Table II. The final column in the table displays the amount of TCE absorbed through the lungs, assuming a 0.70 retention factor (RF).

As Table II displays, depending on the TCE concentration in water, an exposure range from 1.3 to 17.2 mg occurred over the duration of a 30 minute shower.

Results of grab water samples taken before and during the shower period are shown in Table III. Split samples analyzed by a private laboratory agreed closely with the initial water concentrations (time). Water samples were taken at two locations: at the "head" near the MIRAN inlet, and at the "feet" at the shower bottom.

From the data in Table III, a rough percent volatilization can be calculated. These percentages were derived using the following calculation:

$$\% \text{Volatilization} = \frac{(\text{initial TCE conc} - \text{TCE conc at sampling point})}{(\text{initial TCE conc in water})}$$

Results of these calculations are displayed in Table IV.

Conclusion

The results of this study indicate that during a shower, significant amounts of TCE volatilize. In every case, inhalation exposures after 10, 20 and 30 minutes exceed the DWEL, PMCL, and the 10⁻⁶ cancer risk. Table V compares the amount of TCE absorbed by the lungs with the corresponding DWEL and 10⁻⁶ cancer risk value for that time period.

The values of TCE absorbed (Table V) are conservative considering that the shower water was room temperature. Had the instrumentation used been able to withstand water vapor, much higher exposure values may have been found.

Water analyses reveal that at room temperature, from 23-53% of TCE has volatilized by the time it reached the MIRAN inlet sampling port location (5.5 ft. above the shower floor). Samples collected near the shower floor indicate that TCE continues to volatilize as contaminated water droplets fall through the air. At a point just before reaching the shower floor, from 64-74% of TCE had volatilized from the shower water. If the water temperature had been increased to normal showering temperatures, a greater amount of TCE may have volatilized.

Table VI compares the amount of exposure to TCE from the route of inhalation versus ingestion. At lower concentrations, inhalation and ingestion exposures appear to be equivalent. At higher concentrations, however, higher exposures occur through ingestion.

When compared to Table VII, Table VI shows that both routes of exposure exceed all standards and risk values. Therefore, the treatment method of the contaminated water supply should address both routes of exposure. If, for example, affected residents were supplied with bottled water, but were still allowed to continue bathing and showering in the contaminated water, the amount of exposure through inhalation would exceed the DWEL, PMCL, and

10⁻⁶ values. Thus, by not completely addressing the problem, the public health may remain unprotected.

Inhalation of volatile organics is a significant route of exposure from contaminated water supplies. Indeed, long-term health risk values are exceeded through inhalation alone, without even taking exposure through ingestion into consideration. Therefore, inhalation exposure values should be considered along with other exposure routes when drinking water standards and health risk numbers are formulated. The possibility of inhalation exposure should also be considered when contaminated water problems are addressed.

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- * Reference to products and manufacturers are for illustration only; such references do not imply product endorsement by the U. S. Environmental Protection Agency.

TABLE I. TCE Concentrations in Shower Air During a 30-Minute Showering Period.

<u>Resident Number</u>	<u>Well Water Conc., ppb.</u>	<u>Time Min.</u>	<u>TCE Conc. ppm</u>	<u>TCE Conc. mg/cu. M.</u>
1	725	0	0	0
		10	---	---
		20	---	---
		30	0.5	2.7
		40	---	---
2	7,975	0	0	0
		10	2.0	11.9
		20	2.9	15.6
		30	3.5	21.0
		40	1.7	9.2
3	720	0	0	0
		10	1.0	5.4
		20	1.1	5.9
		30	1.3	7.0
		40	0.1	0.5
4	21,800	0	0	0
		10	6.1	32.9
		20	7.2	38.8
		30	8.9	48.0
		40	3.8	20.5

Dashed lines indicate no readings.

TABLE II: TCE Inhalation Exposure Calculations During a 30-Minute Shower Period.

<u>Resident Number</u>	<u>TCE Well Conc., ppb.</u>	<u>Time Min.</u>	<u>Amount Inhaled (mg)</u>	<u>Amount Absorbed (mg)</u>	<u>Total (mg)</u>
1	725	0	0.0	0.0	1.3
		30	1.6	1.3	
2	7,975	0	0.0	0.0	6.8
		10	2.4	1.7	
		20	3.1	2.2	
		30	4.2	2.9	
		40	1.8	1.3	
3	720	0	0.0	0.0	2.0
		10	1.1	0.2	
		15	1.2	0.8	
		30	1.4	1.0	
		40	0.1	0.1	
4	21,800	0	0.0	0.0	17.2
		10	6.6	4.6	
		20	7.8	5.4	
		30	9.6	6.7	
		40	0.8	0.5	

TABLE III. TCE Concentrations in Shower Water at "Head" and "Feet" Locations During a 30-Minute Shower Period.

<u>Resident Number</u>	<u>Time Min.</u>	<u>"Head" TCE Conc. (ppb)</u>	<u>"Feet" TCE Conc. (ppb)</u>
1	0	725	---
	10	---	---
	20	588	264
	30	384	140
2	0	7,975	---
	10	5,773	4,328
	20	4,920	2,448
	30	3,840	1,668
3	0	720	---
	10	704	226
	20	440	280
	30	504	206
4	0	21,800	---
	10	9,984	4,600
	20	9,992	5,076
	30	10,924	7,200

Note: TCE concentration in water may fluctuate due to changed groundwater concentrations.

Dashed lines indicate no readings.

TABLE IV. Percent Volatilization of TCE From Water During a 30-Minute Shower Period.

<u>Resident Number</u>	<u>TCE Well Conc. ppb.</u>	<u>Average % Vol. "Head"</u>	<u>Average % Vol. "Feet"</u>
1	725	33.0	72.1
2	7,975	39.3	64.7
3	720	23.7	63.8
4	21,800	52.8	74.2

TABLE V. TCE Amount Absorbed During Showering Compared with Standards and Risk Values.

<u>Resident Number</u>	<u>Time Min.</u>	<u>TCE Absorbed (mg)</u>	<u>DWEL (mg)</u>	<u>10x-6 Risk (mg)</u>	<u>PMCL (mg)</u>
1	0	0	0	0	0
	10	---	---	---	---
	20	---	---	---	---
	30	1.3	0.6	0.012	0.016
2	0	0	0	0	0
	10	1.7	0.2	0.004	0.005
	20	2.2	0.56	0.008	0.011
	30	2.9	0.84	0.012	0.016
3	0	0	0	0	0
	10	0.2	0.2	0.004	0.005
	15	0.8	0.42	0.006	0.008
	30	1.0	0.84	0.012	0.016
4	0	0	0	0	0
	10	4.6	0.2	0.004	0.005
	20	5.4	0.56	0.008	0.011
	30	6.7	0.84	0.012	0.016

Dashed lines indicate no readings.

TABLE VI. Comparison of Ingestion and Inhalation Exposures of TCE at Various Concentrations in Potable Water.

<u>Resident Number</u>	<u>Well Water TCE Contamination (ppb)</u>	<u>Amount TCE Inhaled (mg) *</u>	<u>Amount TCE Ingested (mg) **</u>
1	725	1.3	1.5
2	7,975	2.9	15.9
3	720	1.0	1.4
4	21,800	6.7	43.6

* After a 30-minute shower.

** Assuming a consumption of 2 liters of water.

TABLE VII. Inhalation and Ingestion Values of DWEL, 10-6, PMCL.

	<u>Inhalation* (mg)</u>	<u>Ingestion** (mg)</u>
DWEL	0.84	0.52
10-6	0.012	0.005
PMCL	0.84	0.01

* Assuming a 30-minute inhalation time.

** Assuming a consumption of 2 liters of water.

SAMPLING FOR GAS PHASE NICOTINE IN ENVIRONMENTAL TOBACCO SMOKE WITH A DIFFUSION DENUDER AND A PASSIVE SAMPLER



Delbert J. Eatough, Cynthia L. Benner, José M. Bayona, Fern M. Caka, Hongmao Tang, Laura Lewis, John D. Lamb, Milton L. Lee, Edwin A. Lewis and Lee D. Hansen
Chemistry Department, Brigham Young University, Provo, Utah 84602

Nicotine is unique to, and a major constituent of, environmental tobacco smoke. The nicotine in mainstream smoke is present in the particles, while nicotine in freshly diluted environmental tobacco smoke is present mostly in the gas phase. Several other organic nitrogen bases including pyridine, vinyl pyridine, nicotyrine, myosmine and cotinine are shown to be present in the gas phase of environmental tobacco smoke by the use of a benzenesulfonic acid-coated annular diffusion denuder sampler. Benzenesulfonic acid was also used in a passive sampler to collect basic gas phase compounds from environmental tobacco smoke. The concentrations of nicotine and other nitrogen-containing organic bases were determined by ion chromatography, gas chromatography and gas chromatography-mass spectrometry. The passive sampler was calibrated against the annular denuder sampling system in experiments with samples from a Teflon environmental chamber and with samples collected in indoor environments with low to moderate concentrations of environmental tobacco smoke. The results indicate that nicotine in the environment is present both in particles and in the gas phase, and that gas phase nicotine is removed from indoor environments at a faster rate than other constituents of environmental tobacco smoke, and therefore is not a surrogate for exposure to other components of environmental tobacco smoke.

Introduction

Environmental tobacco smoke (ETS) may be a major contributor to indoor air pollution in environments where smokers are present (1). The identification and quantification of ETS exposure is important because of irritant and suspected health effects associated with involuntary exposure (1,2) and the large population which is exposed. Tracers of ETS used in the past include respirable (or total) suspended particulate matter (RSP), CO, nitrogen oxides, nicotine, N-nitrosoamines, aromatic hydrocarbons, acrolein, and frequency of smoking. Of these various tracers, only nicotine is unique to

ETS (1,2). While nicotine is present at relatively high concentration where smoking occurs, the use of nicotine as a tracer of ETS is complicated by the fact that nicotine is found primarily in the gas phase in indoor environments (3-6). Furthermore, gas phase nicotine may be removed from the environment at a faster rate than aerosol nicotine or the particulate portion of ETS (1,7). Thus, the concentration of gas phase nicotine may underestimate exposure to ETS (1,2). In order to determine the appropriateness of nicotine as a marker for ETS exposure, accurate and sensitive methods are needed for determining both gas and particle phase nicotine indoors.

The gas-particle distribution of a semi-volatile compound will be affected by the collection procedure as a result of volatilization of the semi-volatile compound from particles collected during the sampling process. Thus, any sampling procedure which attempts to first remove particles and then sample the gas phase material after the particle filter will overestimate the concentration of semi-volatile components since gases evolved from the particles on the filter become indistinguishable from gas in equilibrium with the particles. The only way to reliably determine both the gas and particle phase concentrations of a semi-volatile compound is to first sample the gases and then collect both particles and evolved gases with an appropriate filter pack system. The gas phase species may be collected with a diffusion denuder (4) or a passive sampler (9).

This preliminary report describes the use of both a passive sampling device (PSD) and an annular diffusion denuder sampler to determine both gas and particle phase nicotine and other nitrogen-containing organic bases in ETS in an experimental chamber and in indoor environments. There are three objectives of the research reported here. The first objective is to develop techniques for the simultaneous determination of gas and particle phase nicotine and other nitrogen-containing bases in indoor environments; the second is to develop a PSD for the determination of personal exposure to gas phase nicotine; and the third is to test the use of these techniques in typical indoor environments.

Experimental

Sampling Gas Phase Nicotine. Gas phase nicotine and other bases were collected with benzenesulfonic acid (BSA) coated annular diffusion denuders (4). Two or three denuder sections were used to check for complete collection of gas phase compounds by the denuder surface.

Particle Sampling. The concentration of particle phase nicotine was determined by sampling with quartz filters placed after the BSA coated diffusion denuders. Nicotine lost from the particles on the quartz filter was collected on a BSA saturated filter placed after the quartz filter.

Passive Gas Phase Nicotine Sampler. The concentration of gas phase nicotine was determined using the EPA PSD (9) (Scientific Instrumentation Specialists) with a 22 mm glass fiber filter saturated with a 1 M BSA aqueous solution in the central chamber of the PSD.

Environmental Chamber Studies. The 30 m³ Teflon chamber and associated equipment have been described (4). Replicate experiments were conducted in which 1, 2, 3 or 4 cigarettes (1R1 Kentucky Reference, University of Kentucky) were burned in the chamber using a standard smoking cycle. After equilibration of the combustion products in the chamber for a few minutes, samples were simultaneously collected with both the denuder and passive sampling systems over a three hour period. The flow rate (10-20 slpm) through the denuder sampling system was controlled with Tylan mass flow

controllers.

Indoor Environmental Studies. Three denuder and passive sampling systems were used to collect ETS in several indoor environments. Samples were collected just outside an office in which a single smoker was present and also in an office lunchroom with a few smokers present for short periods during the day. Samples were also collected in a home where two of the occupants were smokers. Samples were obtained over 6-8 hour periods.

Analytical Techniques. Filters and BSA passive samplers were extracted with H₂O in an ultrasonic bath. Diffusion denuders were extracted with 5 mL of H₂O. A fraction of the extracted sample was analyzed for nicotine by ion chromatography (4) using a UV-absorption detector. An aliquot of the solution was made basic with NaOH, and the nicotine was extracted into CH₂Cl₂. The nicotine and other nitrogen bases in the resulting CH₂Cl₂ solution was determined by capillary column gas chromatography and gas chromatography-mass spectrometry (GC-MS) (10). Extraction efficiencies were determined both by standard spiking experiments and by repeat extractions.

Results and Discussion

The gas-particle phase distributions of various organic nitrogen bases in ETS determined from analysis of gas and particle samples with the annular diffusion denuder and from analysis of particles collected on a quartz filter (10) in the chamber studies are given in Table I. This gas-particle phase distribution is affected by the concentration of nicotine in the chamber as shown by the data in Table II. The difference in the mole ratio of gas phase nitrogen bases to gas phase nicotine is little affected by changing the concentration of nicotine in the chamber from 4 to 1 $\mu\text{mol}/\text{m}^3$, Table II, because almost all of the nicotine is present in the gas phase in both experiments. However, the ratio of gas phase nitrogen bases to particle phase nicotine is nine times larger when the concentration of nicotine in the chamber is 1 $\mu\text{mol}/\text{m}^3$ compared to 4 $\mu\text{mol}/\text{m}^3$, reflecting the decrease in the percent of nicotine present in the particle phase from 10% to 2% for the two experiments.

The gas phase nicotine may be reliably collected by the PSD as shown by the data in Figure 1 for samples collected in both the chamber and indoor experiments. The collection of nicotine by the passive sampler is expected to follow Ficks First Law of Diffusion,

$$M = [C] D A/L$$

where [C] is the concentration gradient from the PSD surface to the sampled air, D is the gas diffusion coefficient (0.063 cm²/s for nicotine, ref 4), A is the cross sectional area of the diffusion channel, and L is the length of the diffusion channel. For the PSD configuration used in this study, the expected value for M, the mass flow, is 30.3 cm³/min based on previously reported data (9). We expect that the value for M in the sampler as used by us will be slightly lower than this value because the glass fiber filter does not fit snugly into the center cavity of the PSD. The value for the mass flow determined from the data in Figure 2 is 25.4±0.9 cm³/min, in reasonable agreement with the previously reported data. Similar agreement has been found between empirical and theoretical mass flows for a passive sampler using sodium bisulfate as the acidifying agent for the collection surface (6). The data comparing the denuder and PSD for those samples collected in the indoor environments are shown in Figure 2. The line in Figure 2 is drawn with the slope obtained from the data in Figure 1 and a zero intercept. As indicated by the data in Figure 2, the detection limit for nicotine with the PSD as used in this study is about 5 nmol/m³ (0.5 $\mu\text{g}/\text{m}^3$) and the precision is about ±25% for a sample collected over an eight

hour period. The detection limit of the annular denuder for gas phase nicotine is more than an order of magnitude lower than that for the PSD. The reproducibility of replicate denuder samples is about $\pm 15\%$, thus making it possible to obtain accurate data even at low concentrations of environmental gas phase nicotine with sample periods of less than an hour.

Previously reported results using a BSA annular denuder to sample for ETS nicotine in the environmental chamber (4) showed that 92% of the nicotine was present in the gas phase, with total nicotine concentrations of about 2000 nmol/m^3 . The data obtained with the annular denuder in the present study was used to determine the gas-particle distribution of nicotine in both the chamber and environmental studies over a wide concentration range. The results, given in Figure 3, show that the gas-particle phase distribution of nicotine in ETS in the Teflon chamber varies only slightly with nicotine concentration below about $3000 \text{ nmol nicotine/m}^3$. Linear regression analysis of this portion of the chamber data gives $r = 0.91$ with a slope of $-0.00004 \pm 0.00033 \text{ \%/(nmol/m}^3\text{)}$ and an intercept of $97.5 \pm 0.8 \text{ \%}$. However, the fraction of nicotine present in the gas phase in the indoor environments is highly variable. This may be due to the adsorption of nicotine by non-ETS particles or to a more rapid deposition loss of gas, relative to particle, phase nicotine to indoor surfaces. The loss of gas phase nicotine in a chamber with metal walls is much more rapid than the loss of pyridine or vinylpyridine (7). Information on the relative importance of these two mechanisms can be obtained by comparing the mole ratios of gas and particle phase nicotine to other gases from ETS.

Data are available in this study to test the relative importance of the two possible mechanisms which could contribute to the observed change in the gas-particle distribution of nicotine in the chamber as compared to the home. The concentrations of gas and particle phase nicotine determined for a set of triplicate samples collected in the home were 122 ± 43 and $5.0 \pm 1.5 \text{ nmol/m}^3$, respectively. The extracts from the BSA denuders for these samples were analyzed for the various compounds shown in Table I. The mole ratio of the major gas phase bases to gas and particle phase nicotine for this sample set, along with the corresponding values obtained from the studies in the chamber, are shown in Table II. The mole ratios of pyridine and vinylpyridine to gas phase nicotine are 7 and 4 times larger, respectively, in the home than in the chamber. In contrast, the mole ratios of these compounds to particle nicotine are the same, within experimental error, for both the chamber samples at lower nicotine concentrations and the samples collected from the home. The results are consistent with the loss of gas phase nicotine (and myosmine) from the home atmosphere at a rate much faster than that for the loss of particle phase nicotine. In fact, the data suggest that particle phase, but not gas phase, nicotine may be a reasonable tracer for ETS. Additional data are needed to further characterize the deposition loss of various components of ETS.

Nicotine is a semi-volatile compound, and particle phase nicotine cannot be accurately sampled on a filter because of loss of nicotine from particles during sampling. This point is well illustrated by Figure 4 which compares the concentration of particle phase nicotine found using the annular denuder sampling system to that collected on the filter only. Particle phase nicotine lost from the quartz filters during sampling of ETS averaged $59 \pm 28 \text{ \%}$ of the total for the chamber samples and $41 \pm 30 \text{ \%}$ of the total for the samples collected indoors. The range in particle phase nicotine lost during sampling on a quartz filter was 20 to 97 % of the total for the chamber samples and 4 to 94 % of the total for the samples collected indoors. Clearly, data obtained using a filter pack sampling system will not accurately reflect the gas and particle phase concentrations of ETS in

indoor environments.

The passive sampling device and annular diffusion denuder sampler described here can measure exposure to very low concentrations of environmental gas phase (and in the case of the denuder, particle phase) nicotine. Particle phase, but not gas phase nicotine may be a surrogate for ETS. Future studies should focus on the variations in the ratios of these potential tracers as a function of amount of smoking, age of the indoor air mass, ventilation and types of furnishings, and presence of other sources.

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Table I. Gas and Particle Phase Organic Nitrogen Bases Identified in Environmental Tobacco Smoke Equilibrated in a 30 m³ Teflon Chamber.

Chemical Class	Class wt% of Particle	Identified Compounds	<u>μMol Compound/Mol CO</u>		% Compound in Gas Phase
			Gas Phase	Particles	
Particles				3.09 \pm 0.22g/mol CO	
Bases	10.9 \pm 1.2	Nicotine	10600 \pm 1700	920 \pm 80	92.0 \pm 2.6
		Myosmine	380 \pm 30	110 \pm 75	78 \pm 10
		Nicotyrine	16 \pm 6	61 \pm 16	21 \pm 6
		Cotinine	21 \pm 2	84 \pm 44	20 \pm 15
		Pyridine	415 \pm 18	< 5	100
		Vinylpyridine	752 \pm 460	< 5	100
		Bipyridine	79 \pm 7	< 5	100

Table II. Mole Ratio of Gas Phase Organic Nitrogen Bases from Environmental Tobacco Smoke with Respect to Gas Phase and Particle Phase Nicotine in Samples from a 30 m³ Teflon Chamber and from a Home.

Nicotine Phase	Sample	<u>Mole Ratio with Respect to Nicotine in Indicated Phase</u>			
		Pyridine	Vinylpyridine	Bipyridine	Myosmine
Gas Phase	Lab High [] ^a	0.039 \pm 0.002	0.071 \pm 0.043	0.007 \pm 0.001	0.036 \pm 0.003
	Lab Low [] ^b	0.053 \pm 0.008	0.066 \pm 0.012	0.005 \pm 0.006	0.027 \pm 0.003
	Home	0.307 \pm 0.059	0.249 \pm 0.037	0.007 \pm 0.002	0.037 \pm 0.003
Particles	Lab High [] ^a	0.451 \pm 0.040	0.817 \pm 0.50	0.086 \pm 0.010	0.413 \pm 0.048
	Lab Low [] ^b	5.20 \pm 0.8	6.47 \pm 1.2	0.49 \pm 0.55	2.65 \pm 0.29
	Home	7.36 \pm 1.4	5.97 \pm 0.88	0.16 \pm 0.05	0.89 \pm 0.07

^aSamples collected in the environmental chamber. [Nicotine(g)] = 4 μ mol/m³, % total nicotine in gas phase = 92%.

^bSamples collected in the environmental chamber. [Nicotine(g)] = 1 μ mol/m³, % total nicotine in gas phase = 98%.

Figure 1. Mass flow rate to the PSD vs the concentration of nicotine in environmental tobacco smoke in a chamber and in indoor environments.

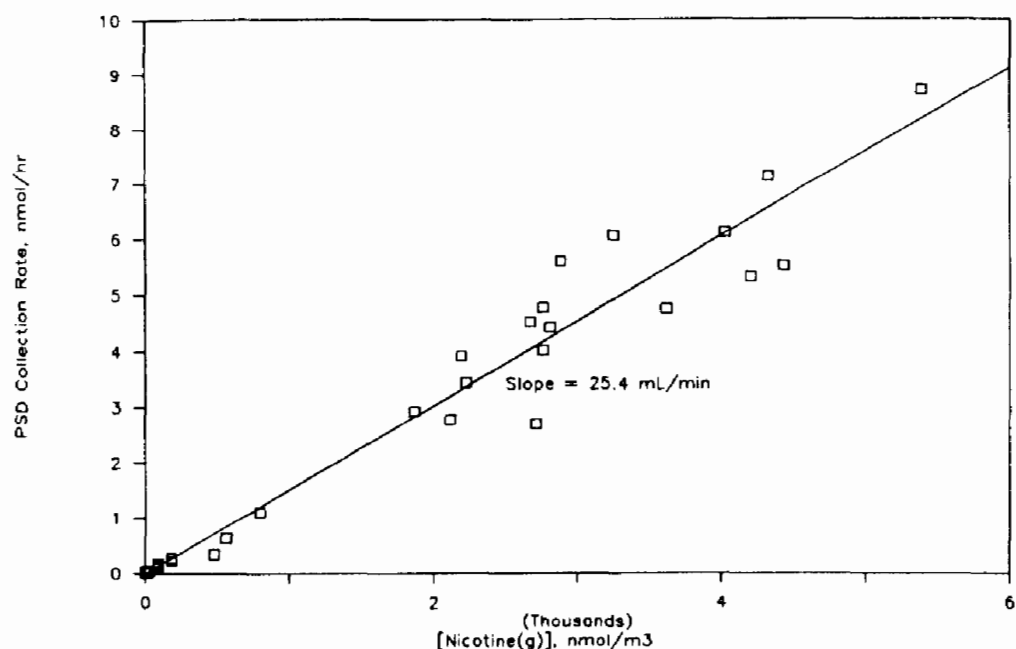


Figure 2. Mass flow rate to the PSD vs the concentration of nicotine for low concentrations of nicotine in environmental tobacco smoke in indoor environments. The solid line is drawn with a zero intercept and the slope for the data in Figure 1.

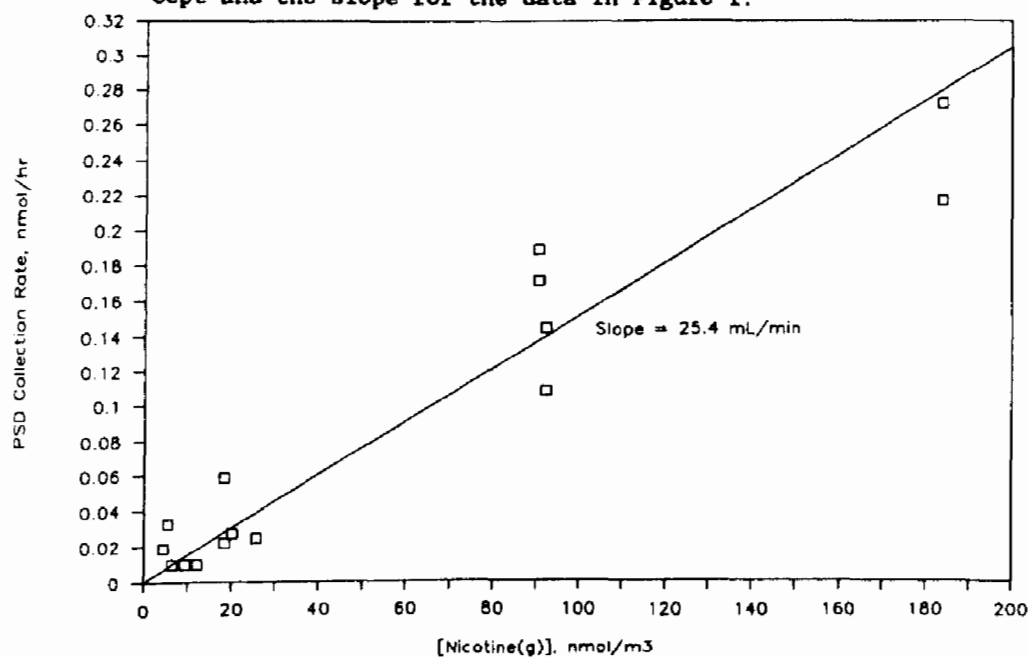
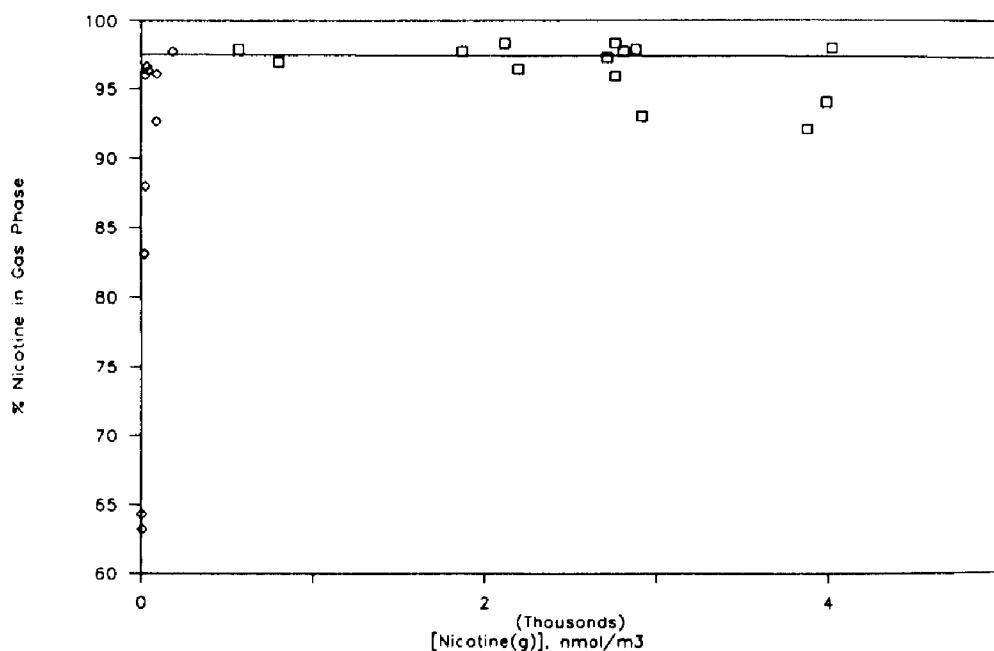


Figure 3. Percent of nicotine present in the gas phase vs nicotine gas phase concentration for samples of environmental tobacco smoke from a Teflon chamber, \square , and from indoor environments, \diamond .



ORGANIC VAPOR PHASE COMPOSITION OF SIDESTREAM AND
ENVIRONMENTAL TOBACCO SMOKE FROM CIGARETTES*

Cecil E. Higgins, Roger A. Jenkins, and Michael R. Guerin
Organic Chemistry Section
Analytical Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6120

Environmental tobacco smoke (ETS) has received considerable attention because of its contribution to indoor air pollution. While some studies have attempted to estimate the exposure of humans to ETS constituents by extrapolating from information gleaned from investigations of sidestream smoke (SS), few studies have reported a direct comparison between the composition of SS and that of ETS. In the study reported here, we describe the relative compositional similarities and differences between the vapor phase of SS and that of ETS. SS was generated under different conditions. Both a new laminar flow chamber, which prevents significant alteration of the near-cigarette environment, and a modified Neurath chamber were used for SS generation. ETS samples were collected from an office environment. Vapor phase samples were collected on multi-media resin sorbent traps and analyzed using thermal desorption gas/liquid chromatography employing flame ionization, nitrogen-specific, and mass selective detection. Influences on the compositional profiles by the manner in which the SS is generated are described, as well as the differences between SS and ETS composition resulting from phase transition.

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Introduction

The impact of environmental tobacco smoke (ETS) on the quality of indoor air has been an issue receiving considerable attention. While a number of studies have been performed on indoor air composition (1,2), data regarding the specific contribution of ETS to the chemical composition of indoor air has been limited (3). There are significant difficulties in determining both such a contribution and potential human exposure to ETS. For example, there are significant contributions to constituent levels from other sources, and exposures to ETS are often episodic and of varying concentration. To this end, investigators have sought to estimate ETS composition and potential exposures to it by extrapolating from the composition of sidestream smoke (SS) and mainstream tobacco smoke (MS), the latter being much more well-understood. There are at least two deficiencies with this approach. First, in the extrapolation to SS composition from that of MS, the observed variability of SS constituent deliveries is much less than those of MS, creating greater uncertainty in the SS composition than would otherwise be warranted (4). Secondly, in many procedures used to generate SS for chemical studies, the generation system may severely alter the environment immediately around the cigarette, resulting in uncertainties about the relevance of the resulting material to that produced under smoldering conditions in a normal ambient environment.

The purpose of this study was to compare, both qualitatively and quantitatively, the organic vapor phase composition of SS generated under maximally relevant conditions with that of the vapor phase of ETS produced from the same cigarette type in a field situation. A collection system was employed which provides for trapping of a wide volatility range of vapor phase constituents. The primary issue addressed was one of comparability: Is the relative composition of the vapor phase of ETS substantially different from that of the SS which produces it?

Experimental

The trapping system consists of a stainless steel tube, 20.5 cm long x 0.46 mm I.D., packed with three sorbent materials. Approximately 1.7 mL of 35-60 mesh Tenax-GC (Alltech/Applied Science) is backed with approximately 0.8 mL of 20-40 mesh Carbotrap (Supelco, Inc.), a graphitized carbon black, which is, in turn, backed by 0.3 mL of Ambersorb XE-340 (20-60 mesh, Rohm & Haas). After conventional resin cleaning procedures prior to construction, the material is packed in the stainless steel tubes, separated by small plugs of silylated glass wool, and desorbed for several hours at 270°C with helium at a flow of 20 mL per minute. Desorption flow is always in the direction of the Ambersorb being the upstream end, while collection flow is in the reverse direction. In this manner, constituents breaking through the Tenax are retained by the Carbotrap, and so forth.

Pumps used to collect samples with the triple sorbent traps were flow-throttled diaphragm pumps (Cole-Farmer Air Kadet). ETS samples were collected at flows of 500 mL per minute, typically for 60 minutes. For collection of the more concentrated SS vapor phase, flows of 20-30 mL per minute for 10 minutes were employed. In order to minimize collection of smoke particulate phase constituents on the trap, Teflon-coated glass fiber filters (Pallflex TX 40 H 120 WW) were placed immediately upstream of the trap.

To generate sidestream tobacco smoke, a laminar flow SS chamber developed at ORNL was employed (5). The system consists of a tapered glass chamber, into which air flows through two stainless steel laminarizing screens. The laminarized air acts to collimate the smoldering plume from the cigarette firecone. Temperature and relative humidity mapping inside the chamber indicated that the environment around the cigarette is not substantially different from that outside the chamber in a room-like environment. For these studies, air flow through the chamber was 30 L/minute, equivalent to 2.8 cm/sec in the vicinity of the cigarette.

All cigarettes used in the study were Kentucky Reference 1R4F, a filtered, low-tar-delivery reference cigarette, quite similar to cigarettes currently popular in the U.S. market. The cigarettes were puffed during SS generation using an ADL/II smoke exposure system (Arthur D. Little, Inc.) modified to smoke at one 35 mL puff per minute. Mainstream smoke (MS) particulate matter was collected immediately downstream of the cigarette butt on a standard Cambridge glass fiber filter pad (6). MS vapor phase was expelled into a Tedlar gas sampling bag, so as not to contaminate the incoming air. For comparison purposes, some SS was generated using an enclosed, water-jacketed chamber (7).

In order to produce an environment of ETS, 1R4F cigarettes were smoked on the same modified ADL/II as that described above. Also, as described above, MS particulate matter was collected on glass fiber filters, while the vapor phase was expelled into gas sampling bags. Cigarettes were smoked in a conventional office with a volume of about 37 m³. The ventilating system was a single pass through type, and air exchange rates (with the door shut) averaged 5.4 ACH. The door to the office was opened periodically to simulate human entry and egress. Temperature and relative humidity were not controlled, although typically averaged 38% at 24°C. Ambient particle concentrations were monitored using both an automated reporting piezoelectric microbalance (Model 5000, TSI, Incorporated, St. Paul, MN) and an ORNL-modified, commercially available forward scattering particle concentration sensor (Model RAS-1, MIE, Inc., Bedford, MA). Gravimetric analysis of particulate filters upstream of the triple sorbent traps yielded particle concentrations generally in good agreement with those determined with the automated piezobalance.

Structural identification of individual constituents was performed using a gas chromatograph/mass spectrometer (GC/MS, Hewlett Packard Model 5985). Quantitative analyses were performed by GC (Perkin Elmer Sigma 2), outfitted with both a nitrogen/phosphorus detector (NPD) and a flame ionization detector (FID). Data visualization and reduction was performed using a Maxima Chromatography Workstation. In both cases, the vapor phase samples were analyzed by thermally desorbing the trapping system at 270°C with a helium gas flow of 10-12 mL/minute in an oven external to the GC. Desorbate was transferred via a 30 cm length (heated) of fused silica capillary to a stainless steel cryoloop (liquid nitrogen) at the head of a 60 m x 0.32 mm ID fused silica capillary column coated with DB5 (1.0 micron film thickness). Temperature programming was initiated when the liquid nitrogen bath was removed from the cryoloop. The oven was held at 0°C for 10 minutes, followed by programming to 230°C at 2.5° per minute, followed by a 30 minute hold. Column effluent was split such that about 40% was directed to the NPD, and the remainder to the FID. Quantitation was performed using external standards.

Results and Discussion

The manner in which sampling and analysis is performed can have a significant impact on the results obtained. For example, nicotine is associated with the particle phase of mainstream tobacco smoke. In contrast, there is an increasing body of evidence (8,9) to indicate that nicotine resides exclusively in the vapor phase of SS and ETS. This is due to the more alkaline conditions which exist in the cigarette firecone during smoldering and the much higher volatility of nicotine in its free base form. However, because nicotine is retained on filters typically used to collect smoke particulate phase (9), one might be led to the erroneous conclusion that nicotine resides in the particulate phase of these matrices as well. For this study, the vapor phase was defined as that material which passed through the filters under the conditions of sampling. While it was presumed that the Teflon coating of the glass fibers provides for a less absorptive and more inert surface, some preliminary evidence was obtained which suggests that even these types of filters retain higher molecular weight nitrogen-containing compounds. Basifying the filter surfaces with sodium hydroxide increased the amount of these constituents passing through the filters and being retained by the vapor phase traps. However, we have not yet developed a consistent treating procedure, so that the work presented here does not compensate for retention of vapor phase constituents on filters.

The material used in the traps to retain the species impacts on the visualized composition of the vapor phase. Tenax-GC is used in many laboratories as a near universal sorbent medium, but it is subject to relatively rapid breakthrough for C_6 and lighter compounds (10). In our present system, the use of a second stage and a third stage sorbent significantly increases the number of constituents visualized and reduces breakthrough. Comparisons of constituent retention by Tenax-only and the triple sorbent traps indicated the retention of substantially more volatile constituents, including acetonitrile, isoprene, 2-butanone, and acrylonitrile by the latter. In addition, breakthrough of most of these species, under the sampling conditions of the experiments, were on the order of a few percent. Reproducibility of the sampling system appears to be very good for most constituents. During simultaneous determinations of ETS atmospheres, relative standard deviations (RSD) for determinations of acrylonitrile, benzene, pyrrole, and limonene ranged from 2-10%. For compounds such as isoprene, 2-butanone, and toluene, RSDs ranged from 15-30%.

The system employed to generate the SS for study potentially has an influence on the relative composition of the smoke. For example, the vapor phase composition of SS generated using an enclosed, water jacketed chamber (7) was compared with that of the SS generated using the ORNL laminar flow system (5). In order to compensate for differences in the amounts of material collected, responses obtained for individual constituents were normalized to those of toluene. For many of the major, more volatile constituents, relative ratios obtained for the jacketed chamber were quite similar to those obtained using the laminar flow system. However, for some of the major, less volatile constituents (ethylbenzene, m+p xylene, limonene, pyrrole, and pyridine), the relative ratios were a factor of 2-4 lower. Within this range of variability, the overall compositional profiles were quite similar.

Deliveries of selected SS vapor phase constituents generated using the laminar flow system are reported in Table 1. The variations in the

measured deliveries ranged from a low of 13% for toluene, to a high of 33% for ethylbenzene. Isoprene and toluene were the most prevalent organic vapor phase constituents eluting prior to limonene (the upper limit of our study). Propionitrile, 2-butanone, benzene, pyridine, pyrrole, m+p xylene, and limonene all were delivered at levels in the range of 200-400 ug/cigarette.

In Figures 1 and 2 are compared high resolution GC profiles of SS with that of ETS, using flame ionization and nitrogen specific detection, respectively. Qualitatively, the composition of ETS vapor phase from acetonitrile through limonene is quite similar to that of ETS. However, a number of differences can be observed. First, in the FID profile, the major constituent eluting one minute after benzene appeared in some chromatograms, but not all, making it difficult to identify using GC/MS. The major compound eluting immediately prior to limonene (tentative structural identification suggests that it may be a diol) appears predominantly in ETS vapor phase samples. Otherwise, the overall profiles are quite similar. For the nitrogen containing compounds (Figure 2), several of the higher boiling constituents, eluting after picoline, appear to be present in the ETS vapor at proportionately higher levels than they are in the SS vapor phase. Experiments performed in our laboratory indicated that this was not an artifact of the sampling conditions for ETS. We speculate that more volatile constituents initially residing in the particulate phase of SS immediately following generation may evaporate with time, to become part of the vapor phase of ETS. We have also observed this phenomenon with relatively high molecular weight hydrocarbons, such as neophytadiene, evaporating from the particulate phase of SS as it undergoes substantial dilution (11).

In Table 2 are listed quantities of several major constituents of ETS vapor phase for which confirmatory GC/MS and retention time matching using authentic standards have been performed. Comparison of the relative (to toluene) composition of ETS vapor phase constituents (in Table 2) with that of SS constituents (in Table 1) indicates differences of only a factor of 2-3. All of this data was obtained at relatively high ETS particulate concentrations (330 ug/m^3). While this particulate level represents a relatively smoky environment, it is well within the range of levels reported for typical ETS particulate concentrations (12). Interestingly, for those constituents for which Maximum Allowable Exposure (MAE) levels have been established by OSHA, the levels observed in this study were often two to three orders of magnitude below those limits. However, the levels determined here are substantially greater than those which might be predicted from the SS emission rates and SS particulate deliveries. For example, the amount of SS particulates generated from the 1R4F using the generator described above is about 26 mg/cigarette (5). This includes any vapor phase constituents (such as nicotine) adsorbed on the filter. Correcting this apparent particulate delivery for vapor phase nicotine retained by the particulate filter and extrapolating the 850 ug/cigarette SS toluene delivery to an ambient ETS particulate level of 330 ug/m^3 would suggest an ambient toluene contribution of 12 ug/m^3 , a factor of 6 less than that observed. Background levels of toluene were determined to be about 10 ug/m^3 , or less than 20% of the difference. It is likely that evaporation of lower boiling constituents of SS particles upon dilution into a larger volume reduces their effective mass concentration. This, in turn, diminishes their efficacy as a predictor of ETS vapor phase levels. Wall losses, settling of the larger particles, or inaccuracies in the determination of the particle concentration by the piezobalance due to evaporation of the particles during collection may

also contribute to inaccuracies in the estimation. This is additional justification for direct measurement of the constituent of interest for the purposes of exposure assessment.

Conclusions

Methodology for the characterization of the vapor phase of sidestream and environmental tobacco smoke has been presented, along with the levels of selected constituents. Examination of the high resolution GC profiles suggests that the relative composition of the major constituents of ETS vapor phase is reasonably similar to that of the SS which produces it, within a range of 2-3. More detailed examination will be required to determine the relevance of this observation for minor constituents, at lower ETS levels, or for a wider range of cigarettes. Even at a relatively high ETS level (as described by particulate concentration), the concentrations of major vapor phase constituents appear to be much lower than the Maximum Allowable Exposure limits established by OSHA. However, levels were determined to be higher than that which might be estimated by extrapolation from SS particulate deliveries.

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Table 1. Deliveries of Selected Sidestream Smoke Vapor Phase Constituents
Kentucky Reference 1R4F Cigarette
ORNL Laminar Flow Sidestream Generator

Constituent	Deliveries*, ug/cigarette (mean \pm one standard deviation)	
	Nitrogen-specific Detector	Flame Ionization Detector
Acetonitrile	1090 \pm 213	b
Isoprene	a	2494 \pm 724
Acrylonitrile	182 \pm 66	176 \pm 36
Propionitrile	177 \pm 57	246 \pm 72
2-Butanone	a	402 \pm 53
Benzene	a	370 \pm 75
Pyridine	283 \pm 79	283 \pm 69
Pyrrole	301 \pm 101	372 \pm 93
Toluene	a	848 \pm 113
4-Picoline	126 \pm 63	b
Ethylbenzene	a	119 \pm 40
m+p xylene	a	311 \pm 59
Limonene	a	332 \pm 94

a. No detectable response on nitrogen - phosphorus detector.

b. Not well quantitated using flame ionization detector.

*, N = 3

Table 2. Concentrations of ETS Vapor Phase Constituents

ETS particle level: 330 ug/m³
ETS nicotine level: 120 ug/m³*

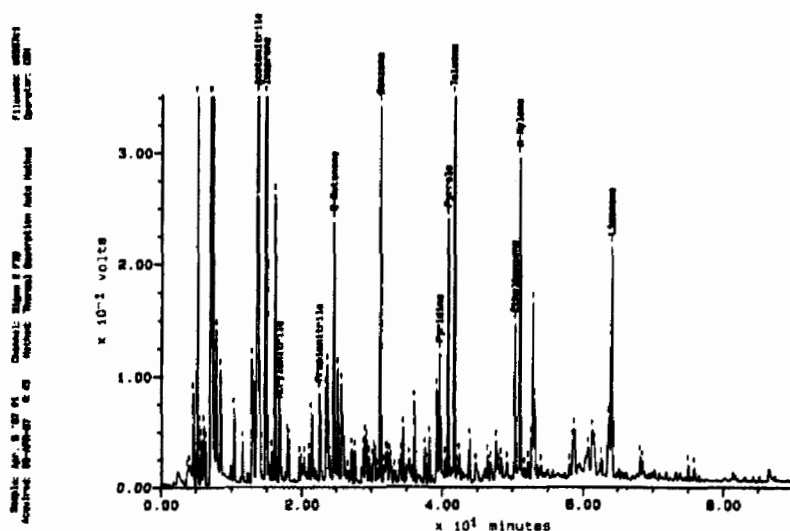
Constituent	Concentration, ug/m ³	
	Nitrogen-specific detector	Flame ionization detector
Acetonitrile	14 ± 3	15 ± 8
Isoprene	a	47 ± 6
Acrylonitrile	2.0 ± 0.6	4.5 ± 0.1
Propionitrile	4.4 ± 0.5	b
2-Butanone	a	48 ± 17
Benzene	a	16 ± 3
Pyridine	11.7 ± 0.6	11 ± 0.6
Pyrrole	9.5 ± 0.7	11 ± 1
Toluene	a	70 ± 22
4-Picoline	8.8 ± 1.1	b
Ethylbenzene	a	8.9 ± 0.9
m+p xylene	a	11 ± 3
Limonene	a	16 ± 2

a. No detectable response on nitrogen - phosphorus detector.

b. Not well quantitated using a flame ionization detector.

*. ETS nicotine levels determined by the method of Hammond, et al. (13) using the filters ahead of the vapor phase traps.

Sidestream Generator (FID)



Environmental Tobacco Smoke (FID)

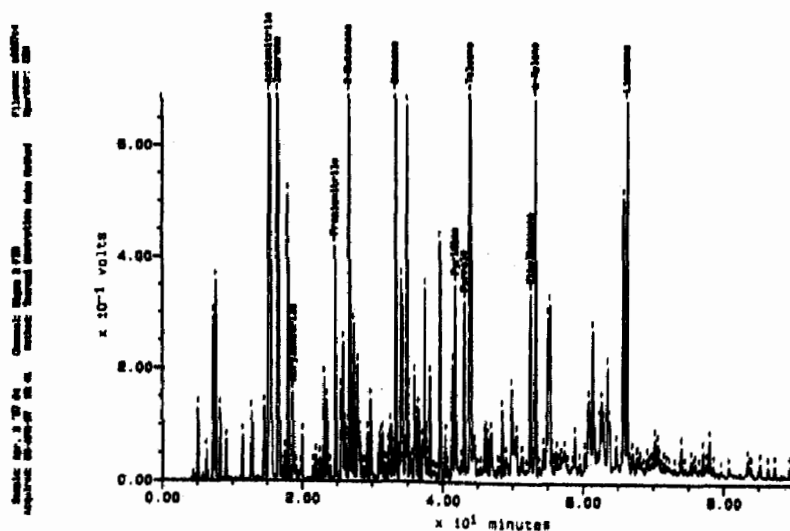
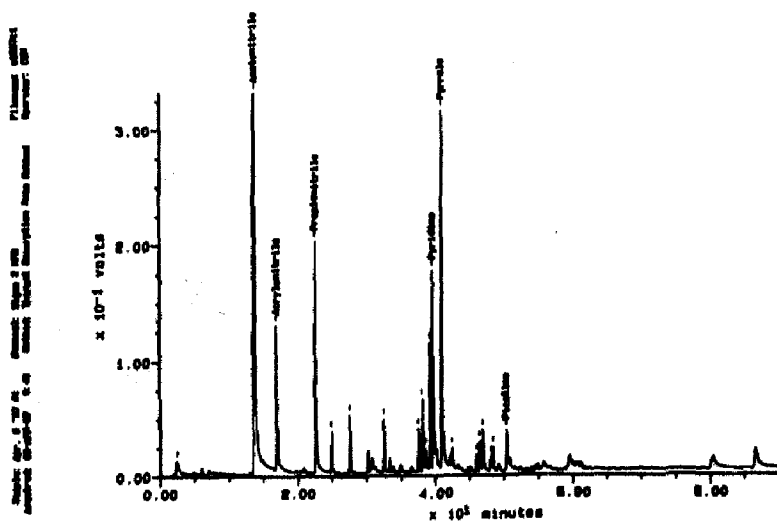


Figure 1 Comparison of chromatographic profiles obtained with flame ionization detector (FID): sidestream vs. environmental tobacco smoke vapor phase.

Sidestream Generator (NPD)



Environmental Tobacco Smoke (NPD)

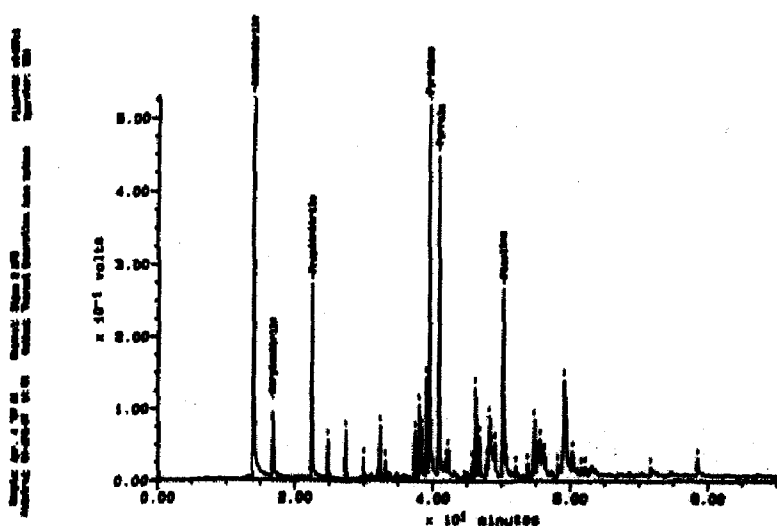


Figure 2 Comparison of chromatographic profiles obtained with nitrogen/phosphorus detector (NPD): sidestream vs. environmental tobacco smoke vapor phase.

STUDIES ON DUST DEPOSITIONS IN CERTAIN
INDOOR AND OUTDOOR ENVIRONMENTS OF SECUNDERABAD

S.H. Raza, B. Nirmala, M.S.R. Murthy
Dept of Botany
Osmania University
Hyderabad, 500 007, India



The paper presents the measurement of dust depositions in certain indoor and outdoor environments of Secunderabad. Railway Station platforms and a big domestic mess were selected for indoor studies. Nacharam, an highly industrially polluted area was selected for outdoor studies.

Size, weight and heavy metal composition from the dust sweeps of indoor environments were analysed. The concentration of air borne dust particles was $3.06 - 5.4 \text{ g/m}^2/\text{m}$ in railway station where as in mess it was $1.86 - 2.9 \text{ g/m}^2/\text{m}$. Dust depositions on the leaf surfaces of trees growing in industrial areas were quantified. Pithecolobium dulce is found to be a very good dust monitor. Polyalthia longifolia is susceptible to dust pollution.

INTRODUCTION

Dust pollution has been found to be a growing problem in major cities of India both in indoor and outdoor environments. Dust fall is undesirable due to its deleterious effects on air quality and human health (1). The need to monitor and control the elevated levels of particulate pollution in indoor environments has been subject of great concern. The provision of many conventional dustfall monitoring stations in outdoors for a detailed study is found to be very expensive. Phyto monitoring of dust can serve as a valuable and inexpensive alternative (2, 3). Hence an attempt has been made to analyse the levels of particulate matter in indoors of Secunderabad and also to investigate the probable use of trees as monitors of dust pollution. For the study the leaf surface depositions of dust of two different sites were considered for comparative evaluation.

MATERIAL AND METHODS

Two different types of indoor environments, viz. railway station platforms and a domestic mess in Secunderabad were selected for the purpose. Dustfall was measured by glass plate method. 10 cm² glass plates coated with thin layer of grease were kept at desired sites nearly 5 metres above the ground level. Weight of the dust deposition (g/m²), size of the dust particles (microns) and heavy metals viz. Fe, Co, Zn, Mn and Cu were analysed (4) from dust sweeps for 3 seasons. The leaf samples of 10 trees were collected in 3 different seasons from Nacharam industrial area (Industrially polluted area) and University Botanical Gardens (Control area) for the assessment of dust deposition in the outdoor environments. The leaf samples of trees growing under isoecological conditions were collected from 10 metre height and were analysed for the dust depositions as described by Bhatnagar et al (5). Chlorophyll of leaf samples was analysed (6).

RESULT AND DISCUSSION

The size and weight of dust particles of the two indoor environments studied is presented in Table-1. It is evident that the dust accumulations were more in both the sites in summer. The dust deposition was also more in the railway station platforms than in domestic mess. It must be due to the burning of coal and large influx of passengers. The weight and size of dust particles was found to be increasing considerably as a function of increase in the duration of exposure. There was nearly 20 times difference in 1 day and 30 day accumulation. It shows that in the absence of continuous control, the dust depositions would create problems on human health. The size of the particles was not in the respirable range i.e., 0.02 - 5 microns. The relationship between concentration of particulates with particulate diameter was found significant ($Y = 0.83 + 0.32x$; $r = 0.71$). The low values in dust accumulation in rainy season suggest that indoor levels respond very rapidly to changes in the ambient levels. 8.3-50 mg/m² indoor deposition

rates are reported by Funso Akeredolu (7) in the domestic houses of Nigeria. The studies conducted by Michael et al (8) in Arizona reported mostly suspended particulates in the ranges of 25.5 - 28.2 ($\mu\text{g}/\text{m}^3$). In the present investigation it is found that particulate matter pertaining to concentration of the dust was considerably high which could be due to the emissions of wood and coal combustion.

The composition of certain heavy metals of dust sweeps is presented in Table-2. The heavy metal analysis shows comparatively higher concentration in indoor environments of railway station. Mostly the heavy metals could be emitted from the combustion of coal and dust carried in by the incoming passengers (9). The sequence of concentration of heavy metals in the dust was $\text{Fe} > \text{Mn} > \text{Zn} > \text{Cu} > \text{Co}$. However the study showed that the concentration of heavy metals did not exceed the normal limits in any of the two sites (9).

The amount of dust deposition on leaves in polluted area is more than the dust on the leaves of less polluted area. The same trend is observed in all 3 seasons. However the deposition of dust was minimum in rainy months (Table-3). There was a great deal of variation in dust trapping efficiency of trees. The range being 67-88 g/m^2 was relatively rich in Pithecolobium dulce, Mangifera indica and Cassia fistula. In Caesalpinia pulcherima and Azadirachta indica 37-60 g/m^2 of dust deposition was observed. In the remaining trees such as Polyalthia longifolia the deposition was found to be poor, the range being 6-37 g/m^2 . Pithecolobium dulce is a fast growing perennial and evergreen plant with a compact hedged canopy. This could be the reason for its higher degree of dust trapping efficiency. Cone shaped canopy and deciduous nature might be cause of low dust trapping efficiency in Polyalthia. However Caesalpinia pulcherima, Cassia fistula etc. were found to be intermediate in nature because of compound leaf character which rather acts as a sieve for the dustfall.

The concentration of chlorophyll got decreased in the leaves to the extent of 50% particularly in certain trees like Polyalthia longifolia, Dalbergia sissoo (Table-3). The reduction of chlorophyll in the leaves could be due to the deposition of dust in layers. The similar such observations were made in Cassia fistula, Dalbergia, Polyalthia longifolia (10, 11). The point of interest is that the decline in chlorophyll concentration in polluted areas would serve as a measure of air quality and the degree of susceptibility of trees to dust pollution.

CONCLUSION

The knowledge on heavy metal composition, size and weight of dust sweeps in indoor environment would serve as a measure of particulate pollution, in minimizing possible damages on human health. Trees resistant to dust pollution can act as sinks of pollution. The morphology and canopy of the trees play a greater role in the dust trapping efficiency. Chlorophyll content of plants in polluted environment is a purposeful parameter in calibrating the pollutant concentration in outdoor environment.

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TABLE - I. Size (microns) and weight(g) of dust collected in two different indoor environments.

		1 day		30 days	
		Size	Weight	Size	Weight
Railway Station	W	9.7	0.23	48.2	5.1
	S	10.7	0.27	49.4	5.4
	R	9.1	0.25	18.6	3.0
Domestic Mess	W	7.7	0.13	23.3	2.5
	S	8.7	0.15	9.8	2.9
	R	7.5	0.21	19.6	1.8

TABLE - II Composition of certain heavy metals of dust sweeps (ppm)

		Fe	Co	Zn	Cu	Mn
Railway Station	W	25.9	0.27	1.17	1.14	13.3
	S	66.0	0.50	1.23	2.11	14.6
	R	18.0	0.20	0.95	0.76	10.3
Domestic Mess	W	15.9	0.05	0.95	0.55	6.6
	S	13.9	0.21	2.04	0.84	15.9
	R	9.9	0.33	0.95	1.29	6.6

W - Winter

S - Summer

R - Rainy

TABLE - III Dust deposition on different trees and chlorophyll content.

Name of the tree	S		LP R		W		S		HP R		W	
	Dust	Chl	Dust	Chl	Dust	Chl	Dust	Chl	Dust	Chl	Dust	Chl
<u>Azadirachta indica</u>	17.4	2.3	7.9	13.9	12.4	9.9	37.5	1.0	24.3	12.8	32.9	6.5
<u>Anona squa mosa</u>	23.2	3.6	6.3	11.4	16.3	8.4	33.4	1.4	15.0	8.4	15.0	7.0
<u>Caesalpinia pulcherima</u>	34.9	2.4	24.3	15.9	43.3	11.6	48.3	1.1	35.4	12.4	37.3	8.0
<u>Cassia fistula</u>	40.8	3.7	24.3	11.7	31.3	9.3	88.0	0.6	46.3	9.3	54.5	6.4
<u>Dalbergia sissoo</u>	12.6	1.9	4.3	12.0	6.4	8.0	41.6	0.4	6.0	8.4	4.4	5.4
<u>Eugenia jambolana</u>	12.4	2.1	6.1	12.5	9.6	10.1	34.8	1.6	9.6	7.6	16.4	10.0
<u>Mangifera indica</u>	30.4	3.1	8.9	13.0	22.6	7.6	67.8	1.64	28.6	8.9	36.4	9.0
<u>Pongamia glabra</u>	13.0	3.9	8.0	11.8	10.4	7.3	25.6	2.4	4.5	6.4	15.0	6.4
<u>Polyalthia longifolia</u>	12.4	3.1	3.4	13.6	5.4	8.4	22.9	1.3	9.3	7.4	12.4	5.3
<u>Pithecolobium dulce</u>	54.3	2.5	24.9	16.1	34.4	12.4	76.3	2.7	34.3	11.3	48.9	9.8

LP - Less polluted area;
 HP - Highly polluted area;
 S - Summer
 R - Rainy
 W - Winter
 Chl - Chlorophyll (mg/g dry wt)
 Dust - $\text{g/m}^2/\text{m}$

LOSS OF NITRIC ACID WITHIN INLET DEVICES
FOR ATMOSPHERIC SAMPLING

B. R. Appel, V. Povard and E. L. Kothny
Air and Industrial Hygiene Laboratory
California Department of Health Services
2151 Berkeley Way, Berkeley, CA 94704

Seven inlet devices, primarily cyclones, were evaluated for nitric acid transmission efficiency at simulated day- and nighttime conditions. The units employed were fabricated from solid PTFE, perfluoroalkoxy-coated aluminum, PTFE-coated glass, and stainless steel. Transmission efficiencies for precleaned units ranged from 18 to > 100%, and were generally lower under simulated nighttime conditions. Residence time and surface composition were the predominant design parameters influencing HNO_3 transmission. Devices with calculated HNO_3 residence times < 0.2 sec exhibited minimal HNO_3 loss. Atmospheric sampling provided more effective conditioning of the coated aluminum cyclone than did laboratory sampling of nitric acid in purified air. Solid PTFE or PTFE-coated glass inlet devices are preferable to the coated aluminum cyclone for atmospheric HNO_3 sampling.

Introduction

Results from the 1985 California Air Resources Board-sponsored Nitrogen Species Methods Comparison Study (NSMCS)¹ suggest that differences in measured HNO_3 between methods could be influenced substantially by the degree of loss of HNO_3 within sampler inlets. The use of one inlet system fabricated from polytetrafluoroethylene (PTFE) appeared to result in substantial HNO_3 loss. Other systems with PTFE inlet devices showed no such loss. In an effort to elucidate the problem, seven inlet devices were evaluated for nitric acid transmission efficiency at their normally employed flow rates. Most were cyclones employed previously by various research groups. The devices evaluated were fabricated from solid PTFE, perfluoroalkoxy (PFA)-coated aluminum, PTFE-coated glass, and stainless steel.

Experimental Methods

The devices evaluated are listed in Table I together with their internal volumes. Internal volumes include those of any additional plumbing ahead of the filter sampler used to collect HNO_3 . Nitric acid was generated with a Unisearch Associates permeation tube maintained at 53°C. The acid was diluted to a total volume of 7 cfm with purified ambient air. The seven units compared were attached to symmetrically arrayed stainless steel ports of a cylindrical sampling manifold. The equivalence of the seven 1.5 in. ID ports was assessed by parallel HNO_3 sampling with open-face filter holders connected to each port containing Nylon filters. Sartorius 0.65 μm pore size Nylon filters were used in all cases. A precision of 7.5% or better was observed at equal flow rates in two trials.

Samplers operating at 16 to 28 lpm sampled from the 1.5 in. ports, and that at 10 lpm, from a 5/8 in. ID port. Each device employed a 47 mm Nuclepore open-face holder and Nylon filter attached at the downstream end. In addition to the seven devices, two open face Nylon filters ("control filters") operated directly attached to sampling manifold ports, with one attached to each size port, sampling at 10 and 20 lpm, respectively. Transmission efficiency was evaluated relative to the HNO_3 sampled with the control filter from the same size port. At 50% RH, HNO_3 concentrations measured with the control filter at 10 lpm were about 10% lower than those at 20 lpm, suggesting greater wall loss in the sampling manifold port. At 80% RH, no significant difference was measured in the HNO_3 concentrations at the two flow rates.

All inlet devices were precleaned with a 1-hour, hot water soak followed by a methanol rinse and drying in particle-free air. Filter holders were water washed and air dried as above.

Three, 6-h trials were performed at 50% RH, 20°C, and three at about 80% RH, 13°C to simulate day- and nighttime conditions, respectively. Second and third trials were done immediately following filter changes, and reflect the effects of conditioning from preceding trials. Following the third trial at each condition, the cyclones were rinsed with two, 5 ml aliquots of 2.7 mM HCO_3^- , 2.1 mM CO_3^{2-} ion chromatography eluent solution (IC eluent) to assess recoverability from the walls. Nylon filters were extracted in IC eluent and, together with washings, analyzed by IC for nitrate. Supplementary experiments are described below.

Results

Transmission efficiency results for the 6-h trials are given in Table II. These ranged from 18% for the first trial with the stainless steel cyclone to 114% for the Teflon-coated glass impactor. At 50% RH, all inlets showed increasing transmission with increased cumulative dosage (Figure

1). The AIHL-design² PFA-coated aluminum cyclone was initially quite inefficient, but increased rapidly in efficiency with dosage, never equalling, however, that for the solid PTFE or Teflon-coated glass devices. Transmission efficiencies at simulated nighttime conditions were consistently lower than at simulated daytime conditions, excepting the stainless steel and PFA-coated cyclones. Most showed higher efficiencies for the initial trial (Figure 2). Greater retention of the acid by increased amounts of water remaining in the devices is probable. At both simulated day and nighttime conditions, the PTFE-coated glass impactor showed the highest transmission efficiency.

Recoveries of nitrate from the filters plus washings of the devices following HNO_3 trials at simulated daytime conditions were about 60% for samplers a and b, (Table I), and 90 to 110% for the remaining samplers. In the simulated nighttime trials, except for sampler d (Table I), recoveries exceeded 90%. The higher recoveries for simulated nighttime trials may reflect diminished loss of HNO_3 by volatilization because of increased water buildup in the cyclones.

Figure 3 shows nitric acid transmission efficiencies for the first 6-h trial at 50% RH against calculated residence times within each device (including additional plumbing described in Table 1). An excellent negative correlation was observed regardless of wall composition or design. Devices with residence times < 0.2 sec showed $> 80\%$ transmission efficiency without previous conditioning.

The AIHL-design PTFE and PFA-coated cyclones are nearly identical except for wall composition. To permit a direct comparison, both units were operated at 20 lpm without additional plumbing (i.e. with filter holders containing Nylon filters attached directly to the exit ports of each cyclone). Two control filters sampled in parallel. Figure 4 shows results for three successive trials at simulated daytime conditions. Dosages for each trial were about half those in the preceding experiment at 50% RH. Even without the additional glassware, the PFA-coated cyclone showed consistently lower transmission of nitric acid. Little or no conditioning effect was evident for this cyclone, whereas a small effect can be seen with the PTFE unit. A decreased conditioning effect is consistent with the lesser dosages employed.

The reproducibility of the behavior of the PFA-coated AIHL design cyclone was assessed by sampling HNO_3 in parallel with two such cyclones. Table III shows the results for this comparison, indicating relatively little difference in transmission efficiency between the two units. The agreement observed indicates that damage or imperfections in the PFA coating is unlikely to be influencing HNO_3 transmission.

The relatively low efficiency for transmission of HNO_3 observed with the PFA-coated cyclone can be contrasted with that following conditioning by atmospheric sampling. Following the NSMCS, this cyclone and its attached glassware were evaluated for transmission of laboratory-generated HNO_3 without precleaning. Experimental techniques used were the same as those described above. The nitric acid concentration, $15.6 \pm 2.0 \mu\text{g}/\text{m}^3$, measured with control filters, was similar to that employed in the present work. However, sampling periods for each of three trials were two rather than six hours, providing mean dosages for each trial of $36 \mu\text{g}$. For three trials, the mean nitric acid measured sampling through the cyclone and glassware was $15.2 \pm 1.5 \mu\text{g}/\text{m}^3$. Thus, the average transmission efficiency was not significantly different from 100%. In addition, comparison of NSMCS atmospheric nitric acid results obtained with the denuder difference method³, in which both units were preceded by PFA-coated AIHL cyclones, showed, on average, daytime nitric acid results which were about 15% higher than those by Fourier transform infra-red spectroscopy^{4,5}.

Accordingly, the atmospheric nitric acid results as well as laboratory trials with the ambient air pre-conditioned PFA-coated cyclone are in marked contrast to the present laboratory findings.

Conclusions

1. Transmission efficiencies for nitric acid through initially clean inlet devices can vary greatly.
2. Residence time and surface composition substantially influence nitric acid transmission efficiency through inlet devices. Residence times < 0.2 sec minimize HNO_3 loss.
3. Atmospheric sampling provides more effective conditioning of inlets for HNO_3 transmission than does sampling of laboratory-generated HNO_3 .
4. Solid PTFE or PTFE-coated glass inlet devices are preferable to PFA-coated aluminum for HNO_3 sampling.

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Table I. Inlet Devices for Nitric Acid Transmission Efficiency

<u>Device Code</u> lpm	<u>Device</u>	<u>Volume, ml</u>	<u>Sampling Rate,</u>
a	AIHL-design PFA-coated aluminum cyclone	475 (with glassware)*	28**
b	Andersen stainless steel	(with ss extension)†	20
c	AIHL-design PTFE cyclone	83	20
d	RTI PTFE cyclone	60	15.6
e	PTFE-coated glass cyclone††	75	16
f	PTFE-coated glass impactor††	35	16
g	U. Calgary PTFE cyclone (EPA design)	62	10

* Volume without glassware is 85 ml.

** The PFA-coated AIHL cyclone was operated at 28 lpm but the nylon filter sampler downstream sampled at 20 lpm.

† Volume without stainless steel extension is 85 ml.

†† University Research Glassware, Carboro, N.C.

Table II. Efficiency of Transmission of Nitric Acid Through Inlet Devices (%)*

Device Code	Trials at 50% RH, 21°C			Trials at 80% RH, 13°C		
	A	B	C	A	B	C
a	28.0	54.3	74.1	52.4	46.9	43.4
b	18.0	26.5	38.4	65.4	31.8	27.1
c	85.1	92.7	105	74.8	66.1	63.3
d	81.3	90.5	103	62.1	65.1	59.7
e	91.3	95.5	105	65.0	68.8	59.5
f	104	102	114	81.2	80.5	75.1
g	74.3	88.4	91.9	65.6	58.4	53.2

HNO₃ Concentrations (μg/m³)

20 lpm:	9.90	11.0	11.2	6.22	5.48	4.17
10 lpm:	9.07	9.66	11.1	(7.98)**	5.45	4.17

* Conditions: 6-h trials
sampling rates per Table I

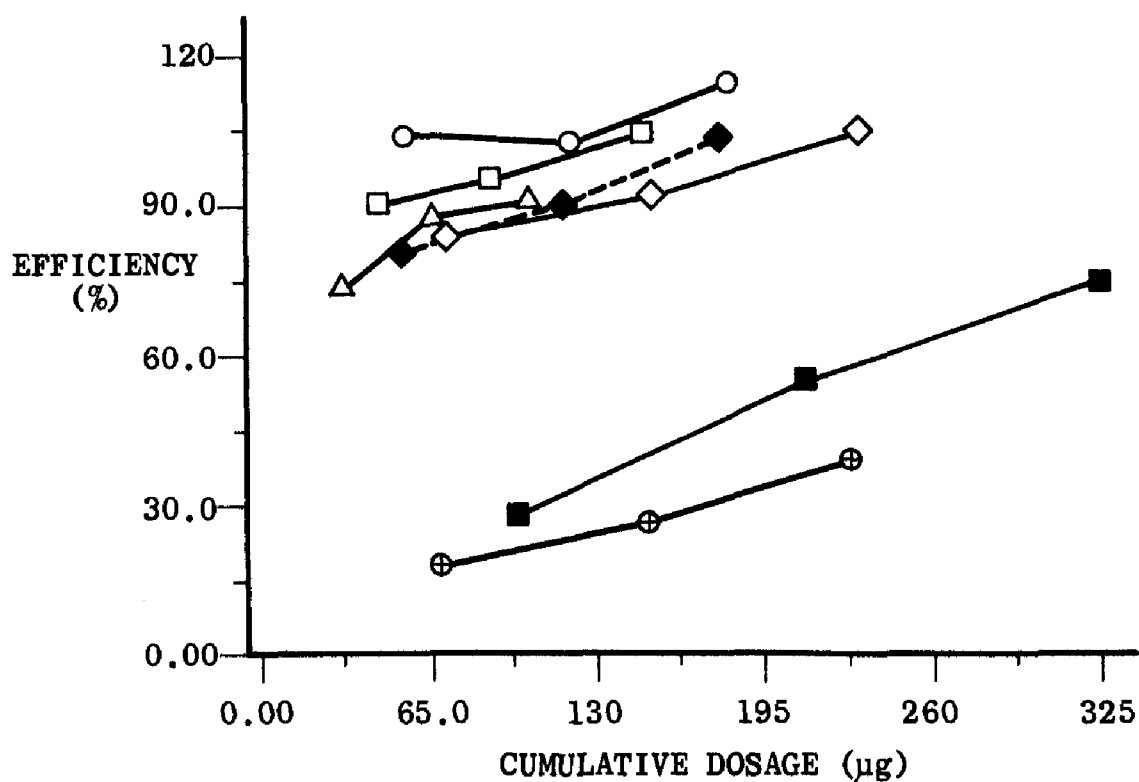
** Suspect result, not used for calculation.

Table III. Comparison of Two PFA-Coated AIHL Design Cyclones for HNO₃ Transmission Efficiency (%)

Device/Trial	A	B	C
1	35.7	40.3	47.9
2	30.9	47.0	46.3
HNO ₃ Conc. (μg/m ³)	7.9 ± 0.6	8.6 ± 0.4	7.0 ± 0.05

a. Conditions: 3 hr sampling
20 lpm
20°C
RH Range 53%-64%

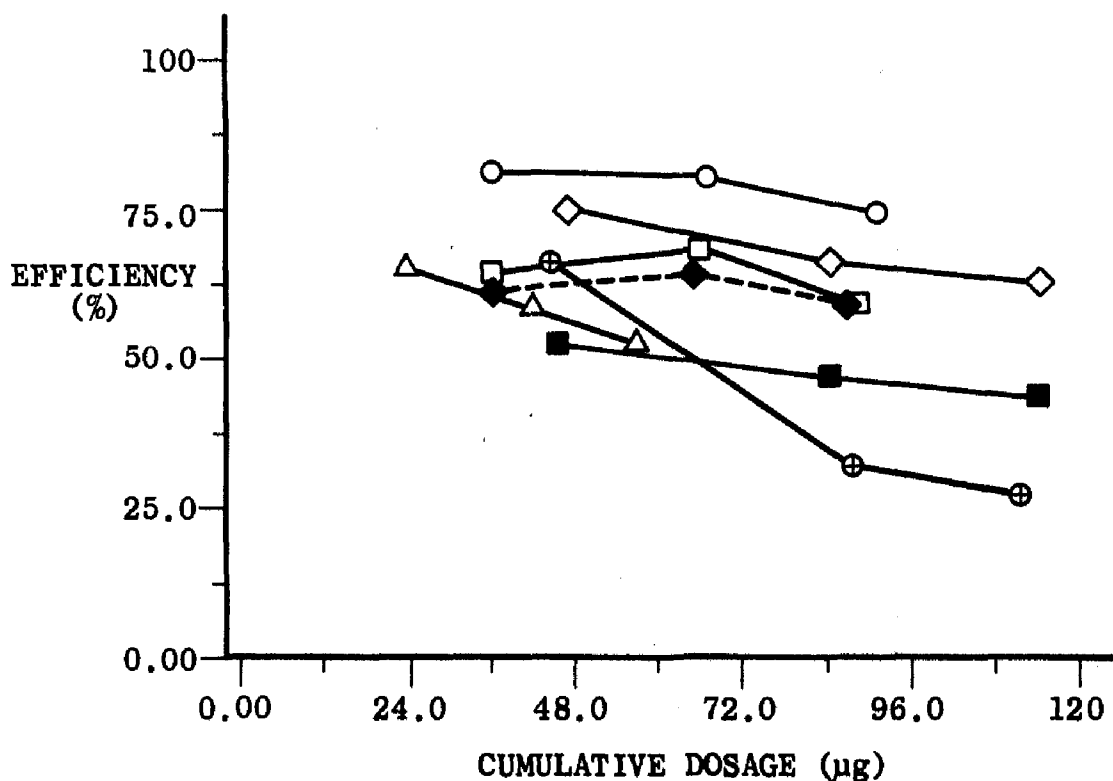
**NITRIC ACID TRANSMISSION EFFICIENCY
50% R.H.**



- PFA-COATED AIHL CYCLONE (ALUMINUM)
- ⊕ STAINLESS STEEL (SIERRA-ANDERSEN)
- ◇ AIHL CYCLONE (PTFE)
- ◆ RES. TRIANGLE INST. PTFE CYCLONE
- EPA PTFE-COATED GLASS CYCLONE
- EPA PTFE-COATED GLASS IMPACTOR
- △ U. CALGARY PTFE CYCLONE

Figure 1

**NITRIC ACID TRANSMISSION EFFICIENCY
80% R.H.**



- PFA-COATED AIHL CYCLONE (ALUMINUM)
- ⊕ STAINLESS STEEL (SIERRA-ANDERSEN)
- ◇ AIHL CYCLONE (PTFE)
- ◆ RES. TRIANGLE INST. PTFE CYCLONE
- EPA PTFE-COATED GLASS CYCLONE
- EPA PTFE-COATED GLASS IMPACTOR
- △ U. CALGARY PTFE CYCLONE

Figure 2

HNO₃ TRANSMISSION vs. RESIDENCE TIME
50% R.H.
FIRST TRIAL

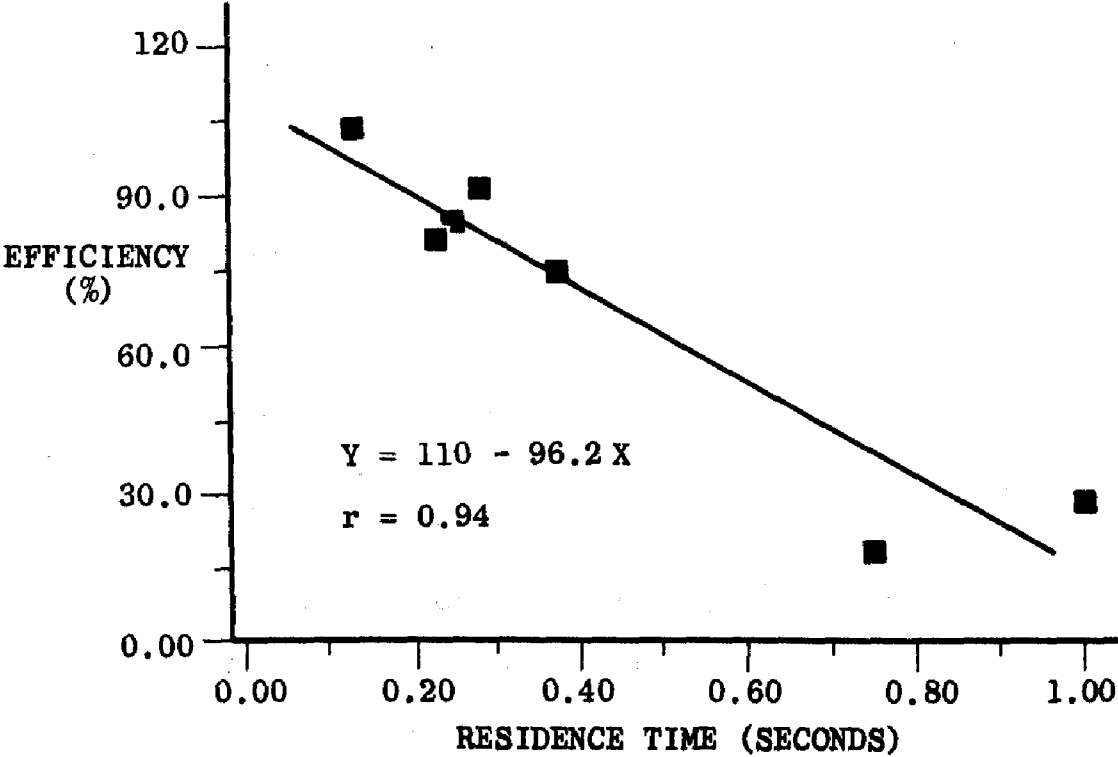


Figure 3

NITRIC ACID TRANSMISSION EFFICIENCY
50% R.H.

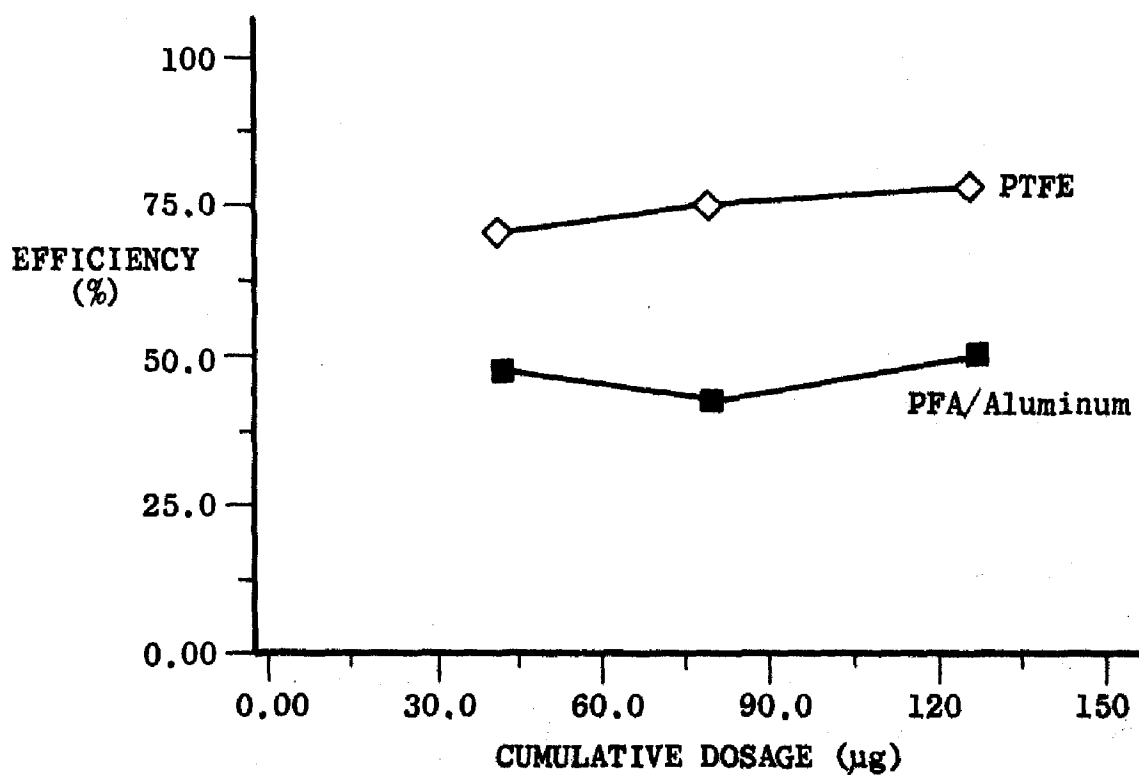


Figure 4

A STUDY OF THE PERFORMANCE OF ANNULAR DENUDERS AND PRESEPARATORS

by

Teri L. Vossler, Robert K. Stevens, and Ralph E. Baumgardner,
USEPA/ASRL, RTP, NC, 27711

INTRODUCTION

For the past five years a number of investigators have been involved in developing reliable sampling and analysis procedures to measure ambient concentrations of HNO_3 , SO_2 , nitrates and sulfates, which contribute to acidic deposition. Filter packs consisting of an inert filter followed by a treated filter appeared to provide reliable data for sulfates and SO_2 . But measurement of HNO_3 and nitrate has proven to be more difficult due to losses of HNO_3 in the sampling system (e.g., inlet) and difficulties in differentiating vapor phase HNO_3 from HNO_3 produced from the dissociation of NH_4NO_3 during sampling. Denuder technology has been shown to circumvent this problem (1-3). In the California Air Resources Board sponsored Nitrogen Species Comparison Study, a variety of techniques, including those using denuder technology, were intercompared. One important finding of this intermethod study was the apparent loss of acidic gases (e.g., HNO_3 and SO_2) in the Teflon inlet assemblies used by some of the participants (4).² This report describes recent results from our efforts to design inlets to quantitatively transport HNO_3 and SO_2 to annular denuder tubes for their collection, while simultaneously removing coarse particles ($> 2.5 \mu\text{m}$) from the air stream. Comparisons of results obtained with various types of inlets when coupled with annular denuders to measure SO_2 , HNO_3 , HNO_2 , nitrates and sulfates will be discussed.

EXPERIMENTAL

Sampling: Samples were collected using two annular denuder systems (ADS) run simultaneously. Various combinations of preseparators were employed for each sampling run to remove coarse particles. Preseparators tested were a Teflon-coated glass cyclone, Teflon-coated glass impactors and quartz impactors with no coating. These preseparators, along with the denuder tubes, were fabricated by University Research Glassware Co., Carrboro, NC. Each preseparator preceded two annular denuder tubes in series, which were for the collection of acidic gases, namely SO_2 , HNO_3 and HNO_2 . The annular denuder sections were separated by a 25 mm open (not annular) cylindrical space in order to allow the flow upon exiting the first tube to be restored to laminar conditions before entering the second tube. Details of the annular denuder tube design and operation have been described previously (2). The purpose of having the second denuder is to correct for deposition of particles and/or relatively unreactive gases which would have been collected with equal efficiency on the first denuder and which appear as the ions of interest (i.e., NO_3^- , NO_2^- , and SO_4^{2-}) in the IC analysis. All denuder tube assemblies were followed by a filter pack assembly. The filter packs consisted of a 47 mm 2 μm pore size Teflon filter for the collection of fine particles, followed by a 47 mm Nylasorb (similar to Nylon) filter for the collection of HNO_3 formed from the dissociation of NH_4NO_3 particles originally on the Teflon filter. Filters were each supported by a stainless steel screen and separated by a Teflon spacer. Teflon filters were weighed before and after sampling using a Mettler ME22 electrobalance in a 50%

Acid M.313

relative humidity controlled environment to obtain total fine particle mass.

The denuder tubes for the collection of acidic gases were coated with a 1% glycerine and 1% Na_2CO_3 solution in a 1:1 mixture of methanol and distilled water. A 10 mL portion of this solution is introduced into the tube, which is capped and rotated to completely coat the annular surface. The excess solution is then decanted and the tubes dried by allowing clean air to flow through them.

For five sampling runs a third annular denuder tube was used to separate out NH_3 from the air stream. Because the diffusion coefficient of NH_3 is three times higher than that of HNO_3 , a shorter (100 mm, vs 200 mm for HNO_3) annular denuder tube could be used to obtain 99% collection efficiency of NH_3 . A solution of 2% citric acid in methanol was used to coat the tube.

Samples using paired annular denuder systems were collected over a period of four months in 1986 and 1987 on the roof of the EPA laboratory in Research Triangle Park, NC, typically for 21.5 hours starting at 3:00 PM and finishing at 12:30 PM the following day. Each ADS assembly was housed in a separate box designed to shield against precipitation. A dichotomous sampler was run concurrently with four of the paired samples in order to evaluate the effectiveness of the ADS inlets to remove coarse particles. The dichotomous sampler fine particle fraction and one of the paired ADS Teflon filters were analyzed via XRF analysis so that comparisons could be made.

Sample Extraction and Analysis: The ADS was assembled and disassembled on a clean laboratory work table. Nylasorb and Teflon filters were each put into a clean, separate 100 mL polycarbonate container. Denuder tubes were extracted with two 5 mL portions of IC solution (0.0045 M NaHCO_3 and 0.0018 M Na_2CO_3). This was accomplished by capping one end of the tube, adding 5 mL of the extraction solution, capping the other end of the tube, rotating the tube to wet all surfaces, and then decanting the extract to a 25 mL polycarbonate vessel. Samples were disassembled and extracted immediately after sampling was completed. Samples and extracts were stored at 5°C until they were analyzed by ion chromatography for NO_3^- , NO_2^- and SO_4^{2-} through a 2000i Dionex IC unit. Filters were extracted ultrasonically in 10 mL IC solution for 20 minutes prior to analysis. On some occasions when the average temperature during sampling was $\leq 10^\circ\text{C}$, the IC chromatogram showed evidence of incomplete oxidation of the SO_2 collected on the first annular denuder in the form of a sulfite peak. However, the concentration associated with this peak was small ($\leq 5\%$) in relation to the total sulfate measured on the first denuder.

For samples which included a third denuder tube for the collection of NH_3 , extraction was done with distilled water following the procedure described above. Sample extracts were analyzed for NH_3 by the method of colorimetry.

RESULTS AND DISCUSSION

Ion concentrations measured in the second denuder were subtracted from ion concentrations measured in the first denuder to correct for unreactive interfering species, as described previously. This correction averaged 10% for NO_3^- , 2% for SO_4^{2-} and 16% for NO_2^- . The net NO_3^- , NO_2^- and SO_4^{2-} concentrations were converted to equivalent concentrations as HNO_3 , HNO_2 and SO_2 , respectively. Particulate SO_4^{2-} was obtained from the Teflon filter extract results. Particulate NO_3^- was obtained from the sum of Teflon and Nylasorb filter extract results. The paired SO_2 results differed by an average of 3.4%. (Percent difference is defined as half the difference of the two ADS results divided by the average of the two results). The duplication was not quite as good for HNO_3 and HNO_2 , whose paired results differed by an average of 6.4% and

8.3%, respectively. One anomalously high percent difference for HNO_2 and for HNO_3 are not included in these results. Generally, the high and low values measured for SO_2 and HNO_3 were not biased toward one denuder assembly or the other, as indicated by the average concentration for each denuder. This was not the case for HNO_2 , as one denuder assembly yielded for most samples an 8% average higher concentration than the other. The cause of this phenomenon has not been determined. A summary of these results is presented in Table I.

The impactors designed for and used in this experiment provided a theoretical D50 cutpoint of $1.7 \mu\text{m}$ (5), while the cyclone was designed to have a D50 cutpoint of $2.5 \mu\text{m}$ (6). The dichotomous sampler has a well characterized D50 cutpoint of $2.5 \mu\text{m}$ (7). The differences in cutpoints of the impactors and cyclone used in this experiment apparently had no effect on the HNO_3 and SO_2 collection efficiency, as evidenced by the lack of bias in the paired denuder results.

The results obtained for samples which included a third denuder for the collection of NH_3 were slightly better than the results given above for HNO_3 and SO_2 for the first 17 samples. Paired HNO_3 concentrations differed by 5.5% (compared with 6.3% for the previous samples), and paired SO_2 concentrations differed by only 1.8% (compared with 3.4% for the previous samples). HNO_3 concentrations agreed only to within 15%. Comparisons could also be made for paired particulate samples with this sub-database, as none of the filters were set aside for XRF analysis. Fine particle sulfate and nitrate paired results agreed quite well, to within 5%. The paired NH_3 results agreed to within 16%, compared with an analytical precision of 4%. It is expected that contamination plays a greater role in NH_3 measurement. A summary of these results is presented in Table II.

The relative concentrations of gas phase HNO_3 and particle phase NO_3^- are governed by shifts in the equilibrium $\text{NH}_4\text{NO}_3(\text{s}) \rightleftharpoons \text{HNO}_3(\text{g}) + \text{NH}_3(\text{g})$. Table III shows the average ratio of HNO_3 (gas) to NO_3^- (fine particles) as a function of average temperature and relative humidity for each sampling period. For samples where the average temperature was low ($< 6^\circ\text{C}$) and the average relative humidity was $> 70\%$, $\text{HNO}_3/\text{NO}_3^-$ was < 1 ; i.e., the NH_4NO_3 dissociation constant was low. The gas-to-particle ratio was > 1 for those low temperature samples with an average relative humidity $< 70\%$. This is consistent with the relationship of Stelson and Seinfeld (8) which shows the NH_4NO_3 dissociation constant to decrease with decreasing temperature and increasing relative humidity. Furthermore, for higher temperature sampling periods (average temperature $> 10^\circ\text{C}$), the average $\text{HNO}_3/\text{NO}_3^-$ was > 2 . The lowest values of this ratio for $> 10^\circ\text{C}$ sampling periods averaged < 1 and occurred when the average relative humidity was $> 90\%$. The gas-to-particle ratio was only 0.4 for a sample with average relative humidity of 98%, which is where the NH_4NO_3 dissociation constant drops off rapidly. Thus, the data presented here qualitatively follows the relationship presented by Stelson and Seinfeld for the dissociation of NH_4NO_3 as a function of temperature and relative humidity. However, the relationship cannot be verified quantitatively because our data correspond to nearly a full day of sampling, which results in loss of detail.

The differences in the D50 cutpoint between the denuder inlets and the dichotomous sampler proved to be a problem when comparing the XRF results of the fine particle filters from the ADS and the dichotomous sampler. Elements whose size distributions extend above or below the D50 cutpoint of either sampler will yield different results for the two samplers. These comparisons are presented in Table IV. Note that although the ADS inlet for the first three samples listed had a lower cutpoint ($1.7 \mu\text{m}$) than the dichotomous sampler ($2.5 \mu\text{m}$), the total fine particle mass measured for those ADS samples was significantly higher than the fine particle mass measured for the corresponding dichotomous samples. (Gravimetric mass is measured to within a percent or

better). One possible explanation for this result is that coarse particles are penetrating the inlet and denuder tubes and adding to the fine particle mass. The impactor stages were not greased for the prevention of particle bounce in order to avoid the possibility of interfering with the collection of acidic gases.

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Table I - Average of Results Obtained with ADS

Species	Average $\mu\text{g}/\text{m}^3$	Range	Average % Difference
HNO_2	1.7	0.7 - 3.7	10.4% (8.3% w/out outlier)
HNO_3	1.6	0.4 - 3.0	8.4% (6.4% w/out outlier)
SO_2	8.9	0.5 - 20	3.4%
NO_3^-	1.2	0.3 - 2.7	-
SO_4^{--}	4.7	0.2 - 10	-

From 17 sampling periods of about 22 hours each between Oct. 27, 1986 and Dec. 7, 1986.

Analytical precision ranges from < 0.5% for all species at > 1 ppm to 8% for sulfate or 2% for nitrate and nitrite at < 0.5 ppm.

Table II - Average of Results Obtained with ADS for Collection of Ammonia

Species	Average $\mu\text{g}/\text{m}^3$	Range	Average % Difference
NH_3	0.32	0.10 - 0.57	16%
HNO_2	1.03	0.64 - 1.55	15%
HNO_3	1.37	0.93 - 1.95	5.5%
SO_2	19.67	12.6 - 32.2	1.8%
NO_3^-	1.05	0.41 - 2.14	3.6%
SO_4^{--}	2.99	2.38 - 4.68	4.6%
Fine Mass	16.2	13.1 - 21.6	2.0%

From 5 sampling periods of about 21.5 hours each between Jan. 21, 1987 and Jan. 25, 1987.

Table III - Atmospheric Conditions and Nitric Acid to Particulate Nitrate Ratios

Start Day (1986)	Avg. Temp. °C	Avg. RH %	Total Precip. mm	HNO ₃ /NO ₃ ⁻
10/27	15.8	--	--	3.76
10/28	11.2	81	--	3.05
10/29	13.2	83	--	1.08
10/30	13.7	78	--	3.10
10/31	14.6	78	--	2.74
11/5	16.8	92	--	1.06
11/6	15.9	83	trace	1.26
11/7	14.3	98	trace	0.40
11/16	8.9	--	--	2.57
11/17	11.0	--	trace	2.97
11/18	11.1	77	trace	1.39
11/19	5.6	67	7.2	1.01
11/20	5.2	88	1.9	0.81
12/4	3.8	57	--	2.00
12/5	-0.45	65	--	1.69
12/6	-0.88	71	trace	0.64
12/7	3.5	71	trace	0.48

Table IV - Elemental Concentrations of Fine Particle Fraction from XRF

DATE	SAMPLER	MASS	CONCENTRATION, ng/m ³					
			PB	AL	K	FE	SI	S
10/29	Denuder	33,600	37	267	174	42	241	1970
10/29	Dichot.	30,600	38	208	200	67	235	3030
11/5	Denuder	47,300	34	216	183	20	128	2850
11/5	Dichot.	43,500	43	178	229	52	230	4310
11/6	Denuder	36,000	24	219	84	29	148	2400
11/6	Dichot.	29,100	27	180	95	47	127	3690
11/18	Denuder	15,400	11	167	50	20	234	1600
11/18	Dichot.	11,100	8	133	50	11	209	1530

Impactor preseparator used with denuder : 10/29, 11/5, 11/6
Cyclone preseparator used with denuder : 11/18

EVALUATION OF METHODS USED TO COLLECT AIR QUALITY DATA
AT REMOTE AND RURAL SITES IN ALBERTA, CANADA.

Eric Peake and Allan H. Legge
Kananaskis Centre for Environmental Research
The University of Calgary
Calgary, Alberta, Canada T2N 1N4

As part of a major study on acidic deposition in the province of Alberta, Canada (the Acid Deposition Research Program), an atmospheric sampling system was designed to collect acidic and basic gases, and fine particles, for subsequent chemical analysis. The Kananaskis Atmospheric Pollutant Sampler (KAPS) consists of a series of annular denuder tubes to collect nitric acid, nitrous acid, sulphur dioxide and ammonia and dual filter packs to collect fine particles. Large particles are removed by a cyclone at the inlet. The system has been in operation at a remote mountain site and at two rural locations in Alberta since August of 1985. Each system is mounted on an air quality monitoring trailer containing the necessary vacuum pump, mass flow controllers and a switching system which allows sequential sampling on four units or repeated sampling on each of the units over a period of several days. A computer controls the sampling program and records flow rates. Sampling units are prepared and analyzed in a central laboratory.

The KAPS system has proven in laboratory studies and in field trials at remote and rural locations to be an effective and reliable means of collecting acidic and basic gases. Using a 12 h sampling period, atmospheric concentrations of less than 0.009 ppb SO_2 or $0.04 \mu\text{g m}^{-3}$ HNO_3 can be collected for analysis by ion chromatography. In the first 19 months of continuous field operation, data recovery was over 85% with most of the loss resulting from condensation in the unheated system. At a remote mountain site, where a 48 h sampling period was used, median concentrations of SO_2 , HNO_3 , HNO_2 , and NH_3 were low, 0.22, 0.12, 0.03, and $0.25 \mu\text{g m}^{-3}$, respectively. The mean SO_2 concentration was $0.56 \mu\text{g m}^{-3}$, considerably higher than the median, whereas the mean HNO_3 , HNO_2 , and NH_3 values did not differ greatly from the median. Concentrations of SO_2 , HNO_3 , and NH_3 at the two rural sites, which may be influenced by area, point source, and agricultural emissions were five to fifteen times greater than at the remote site.

Introduction

In 1985, a multi-year research program known as the Acid Deposition Research Program (ADRP) was initiated in the Province of Alberta, Canada. The ADRP is sponsored by the Provincial Government, the Canadian Petroleum Association, the Energy Resources Conservation Board, and the Utilities Group, and has the objective of determining the current status and future potential for regional scale environmental effects of acidic deposition on ecosystems in Alberta. In order to meet this objective, it was necessary to develop atmospheric monitoring systems capable of measuring low concentrations of a variety of gaseous and particulate pollutants which are known to affect air quality and ecosystems.

Commercial analyzers are available to monitor some of these pollutants, such as SO_2 , NO , NO_2 , NH_3 , CO , CO_2 , and O_3 , but, with the exception of CO , CO_2 , and O_3 , they are not sensitive enough to measure concentrations found in areas not directly under the influence of urban, industrial, or agricultural emissions. Furthermore, commercial monitoring systems are not available to measure nitric acid, which is believed to be a major contributor to acidic deposition in some areas of eastern North America. A number of investigators have utilized filter packs and denuders to collect acidic gases which are then analyzed by conventional wet chemical procedures.^{1,2,3,4,5} An improvement in the denuder methods was the introduction of the annular denuder which allows sampling at relatively high flow rates facilitating the measurement of low concentrations of atmospheric gases.⁶ This prompted an investigation of the annular denuder system for the collection of low concentrations of gases at a remote location and at sites in rural areas influenced by a point source and by area sources. A unique package was designed, consisting of a combination of annular denuder tubes to collect SO_2 , HNO_3 , HNO_2 , and NH_3 , and filter packs to collect fine particles for subsequent analysis by ion chromatography, by x-ray fluorescence spectroscopy, and colorimetrically. This paper briefly describes the design, testing, and characteristics of the Kananaskis Atmospheric Pollutant Sampler (KAPS) and summarizes the preliminary results and experiences of 19 months of continual field use at three sites.

Experimental Methods

Equipment Design

The basic design of the KAPS system is shown in Figure 1. A Teflon cyclone with a particle size cutpoint of about $2.2 \mu\text{m}$ depending upon the sample flow rate, removes large particles at the inlet. The flow is then split into two streams each of which is regulated by a mass flow control unit (Tylan Corporation, Carson, California or Sierra Instruments, Carmel Valley, California). One stream passes into a filter pack which collects particles for XRF analysis, the other stream enters three annular denuder tubes in series. Each tube has an inner diameter of 1.0 cm, an annulus width of 0.16 cm, and a length of 25 cm. The first two tubes are coated with sodium carbonate to collect acid gases and the third tube with citric acid to collect ammonia. Fine particles, which pass through the denuder tubes, are collected on a Teflon filter,

followed by a nylon filter to collect any volatile nitrate derived from the decomposition of particulate ammonium nitrate. The tubes and filter packs are mounted in a rigid tubular plastic case designed to withstand high winds, and then sealed prior to shipment of the unit to the sampling sites. The units are mounted on a metal stand in groups of four on top of the air quality monitoring trailers which contain flow control, timing, and computerized flow monitoring systems as well as instruments for collecting related meteorological and air quality data.

Laboratory Tests

A series of laboratory experiments was carried out to determine the optimum operating parameters for the KAPS system with respect to the amount of material collected for chemical analysis and the efficiency of the annular denuders.

It was first necessary to determine the detection limit for SO_4^{2-} , NO_3^- , and NO_2^- by analyzing coated but unexposed denuder tubes, determining the standard deviation in these analyses, and then calculating the detection limit. On five different days, a total of 24 tubes were coated with sodium carbonate and twelve tubes coated with citric acid. The tubes were extracted twice with distilled water prior to analysis for anions by ion chromatography (Dionex, Sunnyvale, California, Model 2020i) or for NH_4^+ by autoanalyzer (Technicon Instruments Corporation, Tarrytown, New York).

The capacity of the tubes to collect SO_2 , HNO_3 , and NH_3 , and their collection efficiency as a function of flow rate was tested. Sulphur dioxide emitted at the rate of $1.24 \mu\text{g min}^{-1}$, was diluted with purified air at flow rates varying from 2 to 42 litres per minute using a vacuum pump, Tylan mass flow controller, and a precision standards generator (Kin-Tek Laboratories, Inc., Texas City, Texas, Span Pac Model 271). Sulphur dioxide concentrations at the entrance and exit of the annular denuder tubes were monitored using a Tracor 270HA Atmospheric Sulphur Analyzer (Tracor Inc., Austin, Texas). Studies were also carried out with a HNO_3 permeation source (Kin-Tek) and with an NH_3 source (Metronics Associates Inc., Santa Clara, California). The denuder tubes were analyzed for SO_4^{2-} , NO_3^- , and NH_4^+ as previously described.

Interferences in the collection and analysis of SO_2 and HNO_3 caused by the gaseous pollutants, hydrogen sulphide, carbon disulphide, and nitrogen dioxide, found downwind of natural gas processing plants were evaluated. Gas standards were diluted using the Kin-Tek calibration system, a nitrogen oxides analyzer (Monitor Labs, Inc., San Diego, California, Model 8840) was used to measure NO_2 concentrations, and the Tracor 270HA monitored the sulphur species.

Field Trials

The precision of the method was evaluated in two experiments using six systems operated simultaneously at a flow rate of 7 Lpm with a 12-hour sampling period. These tests were conducted at the University of Calgary which is located upwind of the Calgary city centre.

Upon completion of the precision studies, KAPS systems were installed at three air quality monitoring stations. One station is located in a remote mountain site in the Rocky Mountains, 70 km W of Calgary, Alberta; the second is located in an agricultural area about 1 km SE of a natural gas processing plant, 30 km from Calgary; and the third site is 7 km W of that plant. These systems have been in operation since August of 1985. The sampling rate is 10 Lpm with either two 12-hour sampling periods every second day, or a repetitive 12-hour sampling period on each of four days on a given unit.

Results and Discussion

Laboratory Studies

The mean amount of SO_4^{2-} determined by the analysis of 24 unexposed annular denuder tubes was $0.60 \mu\text{g}$ with a standard deviation of $0.40 \mu\text{g}$ per tube. Given a detection limit of 4.65 times the standard deviation*, the detection limit was $1.9 \mu\text{g}$ per tube. Based on a 12-hour sampling period at 7 Lpm, this corresponds to 0.086 ppb SO_2 in the atmosphere. The detection limit for NO_3^- was $0.04 \mu\text{g m}^{-3}$ and for NO_2^- was $0.09 \mu\text{g m}^{-3}$.

The recovery efficiency of the annular denuder in collecting sulphur dioxide ranged from greater than 99% at a flow rate of 2 Lpm to 72% at 42 Lpm. The recovery efficiency at flow rates in the range 14 to 21 Lpm was high at 91 to 97%. Three replicate tubes, at a flow rate of 21 Lpm, showed retentions of 94, 91, and 97% of the introduced sulphur dioxide. Low flow rates give a high collection efficiency but high flow rates have the advantage of more material being deposited on the denuder tubes, giving an effective reduction of the detection limits in terms of $\mu\text{g m}^{-3}$ of air. Thus, flow rates of 7 Lpm and 20 Lpm were chosen for subsequent tests.

In one series of tests, $1600 \mu\text{g}$ of SO_2 was introduced over a 21.5 h period into a denuder tube at the rate of $1.24 \mu\text{g min}^{-1}$, together with purified air at the rate of 7 Lpm. Continuous monitoring of the output from the tube with the Tracor 270HA Atmospheric Sulphur Analyzer showed no breakthrough of SO_2 over this period. This was confirmed by attaching a second tube to the first and analyzing the second tube for SO_4^{2-} . No evidence was found of uptake of hydrogen sulphide or carbon disulphide by the denuder tubes nor was there evidence of uptake or outgassing of SO_2 by the Teflon cyclone and Teflon inlet system. Nitric acid was retained by the sodium carbonate denuder tubes with near 100% efficiency as was ammonia on the citric acid coated tubes. Losses of nitric acid, however, may be occurring in the inlet cyclone.*

Denuder tubes coated with sodium carbonate retain nitrous acid and a portion of any $\text{NO}_2(\text{g})$ in the atmosphere. Thus, the NO_3^- retained by the first tube in the KAPS system represents the maximum HNO_3 concentration and needs correction for NO_2 uptake. The mechanism of NO_2 retention may be conversion to HNO_3 in the system.* If HNO_3 is generated from NO_2 within each denuder tube, the percentage retained by each tube should be nearly equal and can be used to correct

the nitrous acid data. When NO_2 from a cylinder was introduced through a series of three tubes, the NO_2 concentrations, as measured with a NO_x analyzer at the inlet of the first tube and at the outlets of the first, second, and third tubes were 302, 189, 175, and 164 ppb, respectively. The percentage losses of NO_2 were 37, 7, and 6, on the first, second, and third tubes, respectively. These data fit the hypothesis assuming that the source of NO_2 was impure and contained about 110 ppb HNO_2 .

Field Trials

The precision of the method was evaluated using six KAPS units simultaneously sampling the ambient air at the University of Calgary. Atmospheric concentrations of pollutants were low but the results presented in Table 1 show reasonable precision. Using the analysis of the second tube to correct the data from the first tube for NO_2 and particle deposition, concentrations were: SO_2 , $3.13 \mu\text{g m}^{-3}$; HNO_3 , $0.18 \mu\text{g m}^{-3}$; and HNO_2 , $0.71 \mu\text{g m}^{-3}$ in the Calgary atmosphere on the night of June 17, 1985, and 3.10, 0.18, and $1.54 \mu\text{g m}^{-3}$ for SO_2 , HNO_3 , and HNO_2 , respectively, on the night of June 18.

The KAPS system has been in operation at three field sites since August, 1985. Median and mean concentrations of species collected on the three annular denuder tubes contained in each KAPS unit are given in Table 2. The median SO_2 concentration collected on tube 1 at the remote Fortress Mountain site was low, $0.48 \mu\text{g m}^{-3}$ when analyzed as SO_4^{2-} . The mean was much higher, $1.71 \mu\text{g m}^{-3}$. When outlier values, greater than three standard deviations from the mean were removed, the mean was reduced to $1.09 \mu\text{g m}^{-3}$ still well above the median showing that the data are not normally distributed. A median SO_2 concentration of 0.077 ppb was determined by subtracting the tube 2 sulphate concentration from that of tube 1. The corresponding median SO_2 concentration at Crossfield East, the rural site closest to a natural gas processing plant, was 1.06 ppb and at Crossfield West, 7 km in a predominantly upwind direction, was 0.95 ppb. Median nitric acid concentrations were 0.12, 0.15, and $0.14 \mu\text{g m}^{-3}$, median nitrous acid concentrations 0.03, 0.14, and $0.22 \mu\text{g m}^{-3}$, and median NH_3 concentrations 0.25, 1.14, and $1.44 \mu\text{g m}^{-3}$ at the Fortress Mountain, Crossfield West, and Crossfield East sites, respectively, reflecting the isolation of Fortress Mountain.

Data recovery over the first 19 months of operation has been greater than 85 percent. The major problems encountered with the denuder tubes were: wet tubes which resulted in a 5.2% loss of data; broken tubes, 1.2% data loss; and leaks, 2.4% data loss. The problem of wet tubes may be reduced by a cyclone drain and by heating the system above the dew point. Considering the rugged terrain over which the units are transported to the Fortress Mountain site, often under adverse weather conditions, the breakage of denuder tubes was low. This is partly due to the thick outer denuder tube wall, 2.9 mm, and a rigid case surrounding each unit. Other problems included wet or ruptured filters, power failures, computer failure, pump failure, and problems caused by a lightning strike.

Conclusions

The KAPS system, which contains annular denuder tubes and filter packs, has proven, in both laboratory tests and field applications to be an

effective means of collecting both acidic and basic gases as well as fine particles for subsequent chemical analysis. With a detection limit of less than $0.1 \mu\text{g m}^{-3}$ for SO_2 , gaseous nitrate, and gaseous nitrite when using a 12 h sampling period, it has the capability of collecting low concentrations of pollutants found in the atmosphere at remote and rural locations. The reaction of acidic and basic gases with collected particles is minimized and the amount of particulate nitrate, including volatilized ammonium nitrate, can be determined. The units, which are prepared and sealed in a central laboratory, have proven in field operations to be rugged and functional in design.

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Table 1. Mean concentration and standard deviation of six replicate samplings of the Calgary atmosphere, flow rate 7 Lpm ($\mu\text{g m}^{-3}$).

	SO_4^{2-}	NO_3^-	NO_2^-
June 17, 16:05 to June 18, 8:10			
First Tube	4.95 ± 0.35	0.21 ± 0.06	0.79 ± 0.07
Second Tube	0.21 ± 0.06	0.03 ± 0.02	0.08 ± 0.02
June 18, 17:30 to June 19, 08:10			
First Tube	4.90 ± 0.26	0.22 ± 0.06	1.73 ± 0.11
Second Tube	0.25 ± 0.10	0.04 ± 0.01	0.19 ± 0.05

Table 2. Median and mean concentrations of species collected by KAPS annular denuder tubes at three locations ($\mu\text{g m}^{-3}$).

	Tube 1			Tube 2			Tube 3
	SO_4^{2-}	NO_3^-	NO_2^-	SO_4^{2-}	NO_3^-	NO_2^-	NH_4^+
Fortress Mountain, n = 341							
Median	0.48	0.17	0.07	0.15	0.05	0.04	0.25
Mean	1.71	0.24	0.11	0.29	0.07	0.06	0.31
Revised Mean	1.09	0.20	0.10	0.25	0.06	0.05	0.28
Crossfield West, n = 396							
Median	4.49	0.23	0.21	0.41	0.08	0.07	1.14
Mean	6.00	0.41	0.27	0.51	0.10	0.09	1.50
Crossfield East, n = 397							
Median	5.18	0.22	0.32	0.47	0.08	0.10	1.44
Mean	8.08	0.39	0.51	0.75	0.12	0.15	1.89

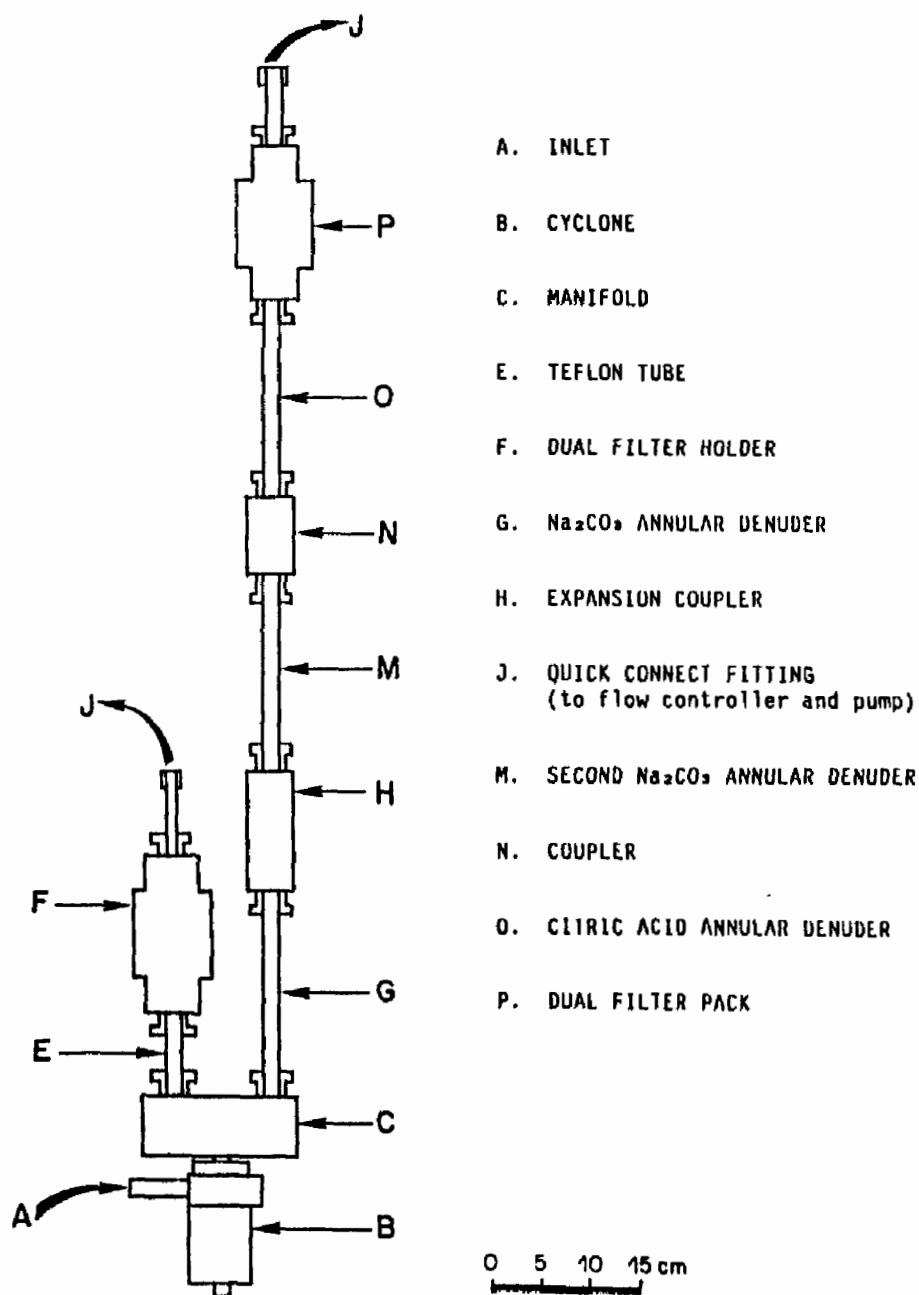


Figure 1. Schematic of Kananaskis Atmospheric Pollutant Sampler (KAPS).

COMPARISON OF THREE AEROSOL SAMPLING TECHNIQUES AND THE DIFFERENCES IN THE NITRATE DETERMINED BY EACH

Stanley A. Johnson and Romesh Kumar
Argonne National Laboratory
Argonne, Illinois



Ambient aerosol samples were collected simultaneously with three different methods, one a size fractionated impactor sampler and two filter samplers. Infrared spectroscopy was used to analyze the collected aerosol using attenuated total internal reflection for the impactor samples and direct transmission through ultra-thin teflon membrane filters for the filter samples. All samples were analyzed as soon as possible after collection; some were reanalyzed after being stored in closed petri dishes for up to 10 days.

A major purpose of the study was to evaluate the neutralization of acidic sulfate aerosols after sample collection by the filtration techniques. No acidic sulfate was found in any of the samples collected during the field study. However, significant differences were observed in the nitrate content of the samples collected by the different samplers. Also, in several samples collected with the ATR impactor the nitrate content decreased upon storage. In some cases the nitrate absorbance bands diminished to zero; in other cases the nitrate initially decreased and then remained stable; in yet another case, a high level of nitrate persisted over several days. The results indicate that two different types of nitrate compounds were present in the samples, one more "volatile" than the other, although the infrared spectra were consistent with both of them being ammonium nitrate.

Introduction

Infrared (IR) spectroscopy has been used for several years for the analysis of ambient aerosols.^{1,2} Typically, the aerosol sample is collected by any one of several possible sampling techniques, transferred to a suitable matrix, and analyzed by transmission,

internal reflection, diffuse reflectance, or acoustic Fourier-transform infrared (FT-IR) spectroscopy. Techniques have been developed recently that permit direct FT-IR analysis of samples collected by impaction on internal reflection elements,³ or samples collected by filtration on thin teflon membrane filters.⁴ These newer approaches have the advantage of minimal sample handling and no special sample preparation, making them amenable to real time analysis.

The direct infrared analytical methods^{3,4} were compared during a field study to evaluate the neutralization of acidic sulfate aerosols after sample collection. Samples were also collected using a set of denuder tubes ahead of the filter, to determine the effect on sample chemistry of removing ammonia and acidic gases from the sampled air stream.

Experimental Methods

The three aerosol sampling methods used were: (1) the "Canadian Filter Pack" (CFP),⁵ (2) the Annular Denuder System (ADS),⁶ and (3) the Attenuated Total Reflection (ATR) impactor.³ Aerosol samples were collected during the summer and fall of 1986 at the Argonne dry deposition monitoring site, ~35 km southwest of Chicago, IL. Because of the greater sensitivity of the ATR technique compared to that of the filter methods, a much finer time resolution is possible with the ATR impactor technique than either of the other two techniques. Thus while samples were collected over 24 h periods for the CFP and the ADS, consecutive 4 or 6 h samples were collected with the ATR impactor. The CFP collects all particles in the sample air stream. The ADS removes large particles with a cyclone preseparator and the reactive gases with three consecutive annular denuder tubes, before the particles are collected on the teflon membrane filter. The ATR impactor collects only 0.5–1.0 μm aerodynamic diameter particles.

The collected samples were analyzed with a Digilab (Cambridge, MA) Model FTS-14 FT-IR using direct transmission through the teflon membrane filters for the CFP and the ADS samples, and total internal reflection for the ATR impactor samples collected on KRS-5 internal reflection elements. Infrared spectra from the filters and the ATR impactor have been quantified for NH_4^+ and SO_4^{2-} , but not yet for the NO_3^- . Therefore in the discussion below, only the infrared absorbance values are used for the NO_3^- analyses. All samples were analyzed as soon as possible after collection, typically a few hours, and stored in closed petri dishes. Some samples were reanalyzed after storage times of up to 10 days.

Results

No acidic sulfate was detected in any of the samples; therefore the potential neutralization of acidic sulfates on filters could not be evaluated. However, some very interesting changes were observed in the NO_3^- content of the samples, and these are discussed below.

Figure 1 shows the FT-IR spectra of concurrent samples collected by the three sampling methods. The spectra in Figure 1a were obtained within a few hours of sample collection; upon reanalysis of the samples five days later, the spectra shown in Figure 1b were obtained. The three spectra in Figure 1a are virtually identical, *i.e.*, NH_4^+ (1400 cm^{-1}), NO_3^- (1340 cm^{-1} and 840 cm^{-1}), and SO_4^{2-} (1100 cm^{-1} and 620 cm^{-1}); all exhibit similar relative absorbance. Further, even though the CFP and the ADS samples include a wide range of particle sizes while the ATR sample covers only submicrometer

particles, the major constituents of all samples were the same, ammonium sulfate and ammonium nitrate. Figure 1b shows that after five days of storage all species were essentially unchanged. Figures 2a and 2b show the spectra obtained immediately after collection and 6 days later for another set of samples. In Figure 2a the CFP and the ADS filter samples show a weak indication of NO_3^- in the 1340 cm^{-1} region, while the ATR sample clearly shows strong NO_3^- with both the 1340 cm^{-1} and 840 cm^{-1} absorption bands. However, Figure 2b shows that the NO_3^- disappeared completely from the ATR spectra after 6 days, while the weak bands persisted in the filter samples.

Nitrate was observed in one or more of the 4 h samples collected with the ATR impactor during 11 of the 15 days of sample collection. In the CFP samples, NO_3^- was detected on only 7 days; and on the ADS filter NO_3^- was found on 8 days. The nitrate "volatility" was observed only in the ATR impactor samples; in every case where NO_3^- was seen on the CFP or the ADS filters, it was persistent upon storage. The rate of disappearance of the NO_3^- during sample storage was quite variable. In some cases all of the NO_3^- disappeared in one day. In other cases, a rapid initial decrease was followed by a residual NO_3^- that was stable with time. This *could* indicate nitrate from different sources, such as aerosol present in an aged air mass along with fresh aerosol injected by local sources. In the one case where a high NO_3^- persisted in the ATR sample over several days of storage (Figure 1), the NO_3^- level was substantial throughout the 24 h sampling period.

For the ATR samples that lost NO_3^- on storage, a corresponding loss of NH_4^+ was also seen. Calculations indicated that indeed the NO_3^- and NH_4^+ losses were equivalent to a loss of ammonium nitrate, and that the remaining NH_4^+ was in the correct proportion with SO_4^{2-} for ammonium sulfate. It was thought that perhaps after ammonium nitrate was lost from the sample, the residual nitrate would correspond to a different compound. However, even in these samples enough NH_4^+ was still left to balance both the SO_4^{2-} and the NO_3^- . Therefore some other factor must account for why some of the ammonium nitrate was volatile and some was more stable during storage.

The ATR impactor samples showed distinct diurnal variations, but no regular pattern was apparent. Figure 3 presents spectra from six sequential 4 h samples taken with the ATR impactor. On this day all major ions changed substantially over the 24 h period. Note especially the fact that NO_3^- goes from virtually nothing to a high level and back to almost zero. Also note that although both the SO_4^{2-} and NO_3^- increased during the day, the maximum concentrations of the two ions did not occur in the same time period.

Conclusions

This limited field study shows that samples collected by three different techniques, one a total filter sample, another a filter sample denuded of ammonia and acidic gases, and an impactor sample of submicrometer particles only, showed very similar infrared absorption spectra. Finer time resolution, ATR impactor-collected samples sometimes showed the presence of "volatile" ammonium nitrate, which was not present in any of the filter-collected samples. In addition to the "volatile" ammonium nitrate, a more stable ammonium nitrate was also often observed in these samples.

The ATR impactor samples showed significant diurnal variation in the concentrations of NH_4^+ , NO_3^- , and SO_4^{2-} from one sample to the next, which variation was lost

in the filter samples. These data point up the desirability of conducting fine time resolution sampling, and of developing real time or near real time sampling and analytical instruments.

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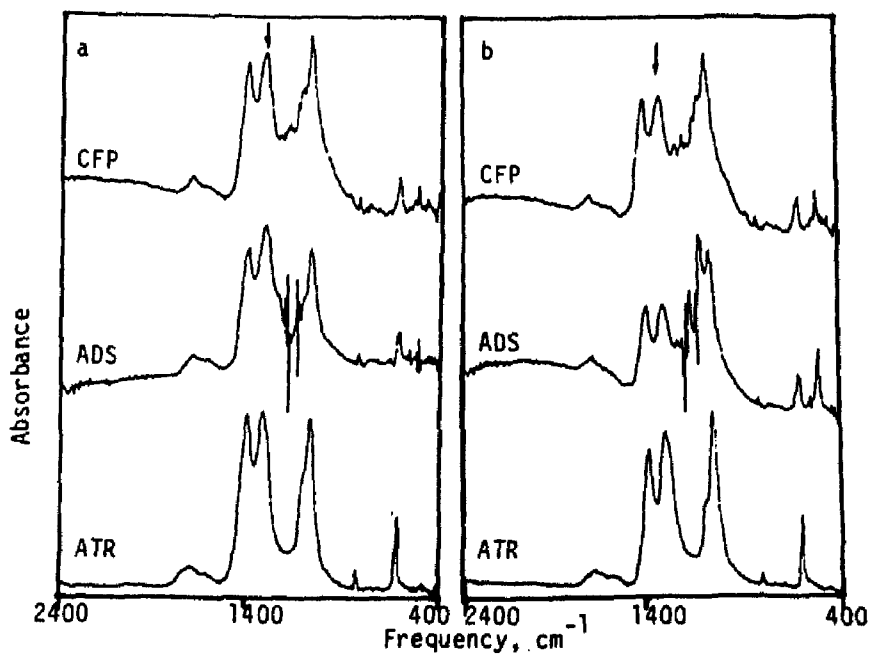


Figure 1. Infrared spectra of samples collected concurrently on Nov. 5-6, 1986.

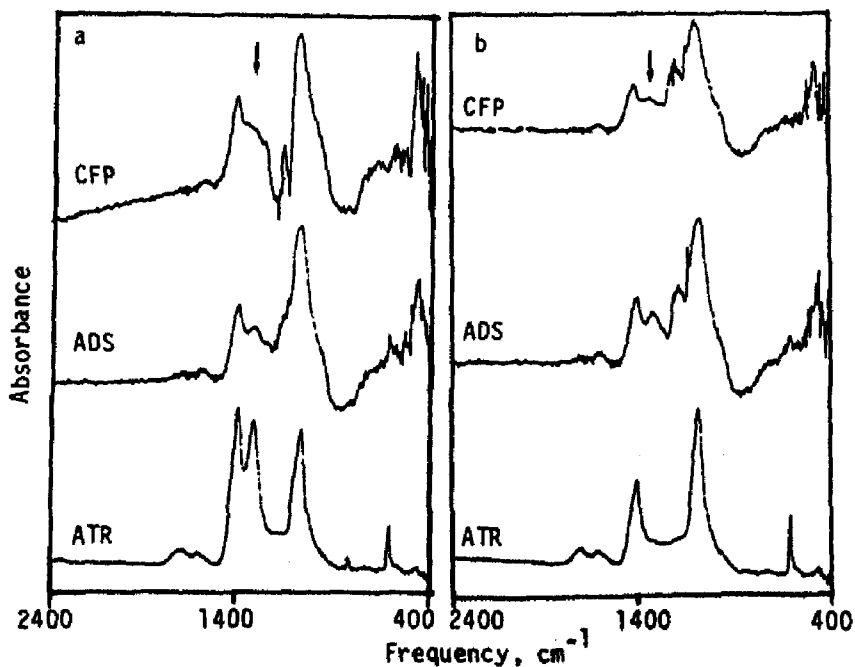


Figure 2. Infrared spectra of samples collected concurrently on Oct. 14-15, 1986.

Comparison of three sampling methods; (a) spectra recorded soon after collection, (b) spectra recorded from the same sample six days later. Arrows indicate the position of the 1340 cm^{-1} nitrate absorption band.

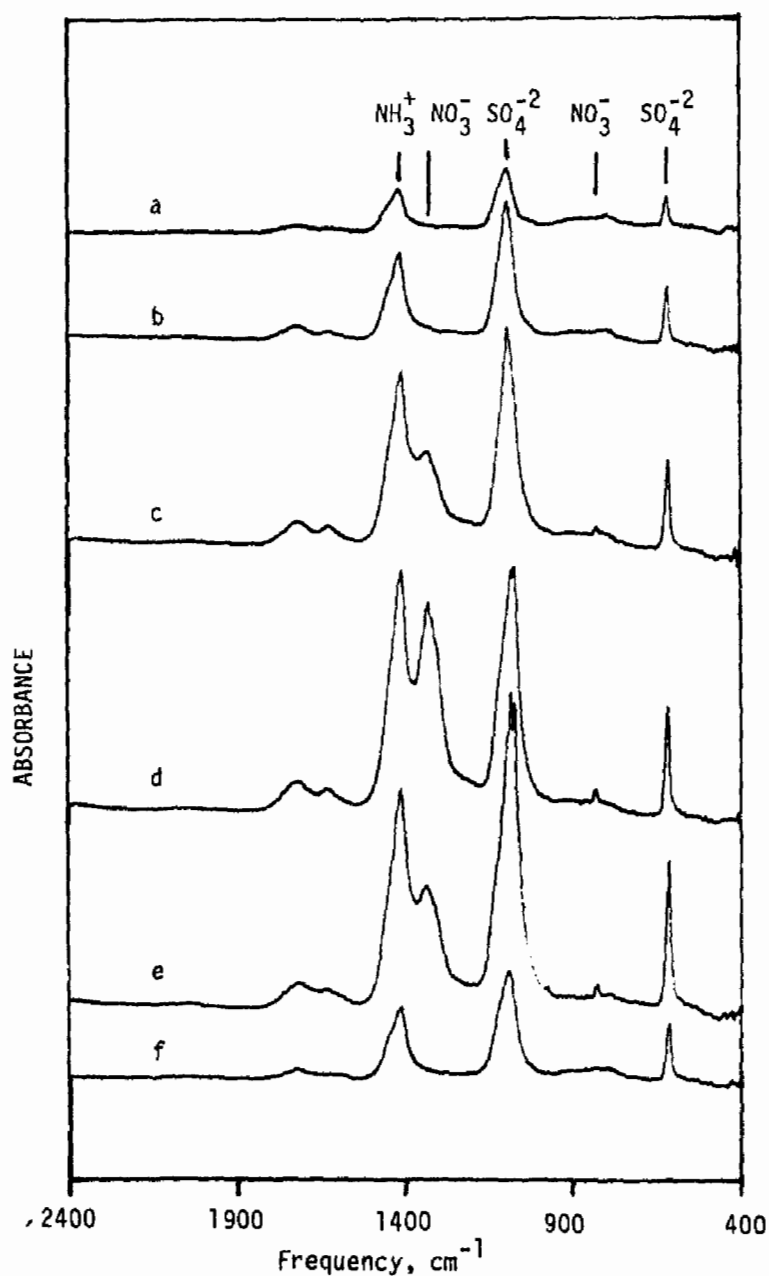


Figure 3. Infrared spectra of six sequential samples collected with the ATR-impactor on October 27-28, 1986. Times of collection were: (a) 1330-1730, (b) 1730-2130, (c) 2130-0130, (d) 0130-0530, (e) 0530-0930, (f) 0930-1330.

**Wet Deposition on Forest Canopy at
Mt. Mitchell, North Carolina**



Vinod K. Saxena and Ronald E. Stogner
Department of Marine, Earth and Atmospheric Sciences
North Carolina State University
Raleigh, North Carolina

One of the most recent examples of the severe environmental impact of global and regional air pollution has been identified to be the forest decline at high elevations in Europe and North America. First identified as "waldsterben" (death of forest) in West Germany and now commonly accepted as forest decline has been noticeable in eastern U. S. beginning 1980. Alarmed by the West German plight, the U. S. Environmental Protection Agency launched a project entitled, "Mountain Cloud Chemistry/Forest Exposure Study" in May, 1985. Under the program, relevant atmospheric chemistry and micrometeorological measurements have already started or are underway at the following locations: three sites at Whiteface Mountain (New York), two sites at Hubbard Brook/Mount Moosilauke Experimental Forest (New Hampshire), three sites in Mt. Mitchell State Park (North Carolina), three sites in Shenandoah Park (Virginia), one site at Whitetop Mountain (Southwestern Virginia), and one site in Maine. During summer, 1986, in the Mt. Mitchell State Park, we erected two meteorological walk-up towers, one (16.5 m tall) at the Gibbs Peak (2,006 m MSL on the mountain ridge) and the other (22 m tall) at the Commissary Ridge (1,760 m MSL on the eastern slope). Although the southeastern U. S. experienced drought during the summer, 1986, the Gibbs' Peak tower was exposed to clouds during more than 70% of days. The direct cloud interception by forest canopy is a major mechanism for acidic deposition at Mt. Mitchell and hydrological and chemical inputs are governed by sedimentation, impaction and evaporation processes which, in term, are controlled by the prevailing windfield and cloud microstructure.

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Results from initial runs of a direct cloud interception model indicate that wet deposition from such sources constitute a significant source of ionic input to the forest canopy. Values obtained compare favorably with those obtained by other authors. Our calculations indicate that such sources contribute on the order of $1.75 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of H^+ ion deposition to Mt. Mitchell area forest. These numbers are even more significant, considering the drought conditions during the summer, 1986. Our results also indicate that short term cloud events (less than $1/3$ of a day) may contribute high amounts of ion deposition due to their high acidity and frequent occurrence.

Introduction

Forest decline at high elevation ecosystems has become increasingly apparent during recent years. Such decline is particularly evident in mountain spruce-fir ecosystems, which often remain immersed in clouds for prolonged periods of time. Mt. Mitchell (2,038 m MSL, $35^\circ 46' \text{N}$, $82^\circ 16' \text{W}$) area forest, for example are exposed to clouds about 258 days per year on the average¹. This prolonged exposure to acidic clouds, may greatly enhance wet deposition of ionic substances at such sites.

One type of wet deposition, which is particular to such mountain sites, is direct interception of impinging cloud droplets. Wet deposition amounts, on these mountain area forest canopies, may be significantly under estimated, if such sources are not taken into consideration². Direct measurements of wet deposition to forest canopies, through techniques such as: stemflow, throughfall and the use of surrogate surfaces, are difficult to accurately obtain as well as relate to the complex forest canopy. A more general and easily applied method is the use of deposition models. A model to calculate wet deposition, due to direct cloud droplet interception has been developed and is currently in use by the Mountain Cloud Chemistry/ Forest Exposure Program (MCCP). The model is described in detail by Lovett³. We have used this model to calculate cloud water deposition rates at Mt. Mitchell.

The model requires wind speed, temperature, relative humidity, solar radiation, liquid water content and droplet modal size. All parameters were obtained during the 1986 summer, as part of the MCCP program. The measurements were made at the Mt. Gibbs site. This paper presents the results from model runs using the 1986 summer data obtained at Mt. Gibbs.

Experimental Methods

Two research sites were established in the Black Mountains of North Carolina. Each site is equipped with an aluminum walk-up tower, which extends about 10 m above the surrounding forest canopy. The first site is located at Mt. Gibbs. The second site is located at Commissary Ridge, about 0.75 km southeast of Mt. Mitchell and some 200 m below the Gibbs summit site at an elevation of 1,760 m MSL. Table 1 list parameters measured during the 1986 summer at Mt. Gibbs.

Table 1

<u>Parameter</u>	<u>Instruments</u>
Temperature, Relative Humidity, Wind Speed, Wind Direction, Solar Radiation, Pressure, Precipitation	Electronic Weather Station (Operated continuously)
Cloud Water Chemistry	Active and Passive Cloud Water Collectors
Precipitation Chemistry Ozone, SO ₂ Gas Concentrations	NADP Collector (weekly) Continuous Gas Monitors
Droplet Size Distribution, Liquid Water Content	Forward Scattering Spectrometer Probe(FSSP)

Model Methodology

Meteorological parameters needed for model runs were obtained from data recorded by the electronic weather station (EWS). One hour averages were used for the model runs. Two important deviations need to be mentioned here. First, the model uses values at the canopy-top (about 8 m, in our case), while our measurements were made at 16.5 m above the ground. Since we had no real-time turbulence data, to estimate vertical profiles, we have chosen to use the 16.5 m values directly here. Secondly, Lovett et. al.² define Net Deposition as Gross Deposition (that is all water captured) minus Evaporation. Our experience has shown that the model's evaporation scheme is extremely sensitive to relative humidity measurements in the 95-100% range. Presently, there are no tested, field worthy instruments which are capable of accurate measurements of relative humidity in this range. We have, therefore, chosen to calculate Gross Deposition, neglecting evaporation. While both of these points will combine to over estimate the actual deposition, there are other factors, which will be discussed later, which will combine to decrease the estimates. The resulting values may not be far from the true deposition.

The microphysical input parameters needed were obtained from five minute averages of one second FSSP data. These five minute averages were used to compute the one hour values that were used in model runs. Liquid water content (LWC) values were obtained from integration of the droplet size distribution data. The LWC values from our FSSP data compare well with LWC values obtained by other methods at other MSCP sites.

Ionic deposition rates were obtained by multiplying H⁺ concentration values from cloud water samples collected hourly using the cloud water collectors listed in Table 1. Data from the 1986 summer show that there is no statistical difference in the chemistry of samples (333 hours were sampled) collected from either the passive or active collectors. We have used samples from the passive collector. Field H⁺ concentrations were used in our computations.

Results and Discussion

Droplet size distribution measurements were successfully obtained during three cloud events of 1986 summer. These events occurred on the following dates: July 5, August 30 - September 1 and September 10 - September 12. The July 5 event was of short duration lasting only about five hours. The two remaining events were long events, lasting more than thirty six hours. We have used the July and August events for our estimates. The July event is typical of most short events at Mt. Mitchell in both physical and chemical composition. The August event is typical of long term events, physically, however it is about an order of magnitude less acidic than most long events.

Figure 1 shows microphysical characteristics of the two events as recorded by the FSSP. The LWC, total droplet concentration and average droplet size are shown for the two events. The July event was a valley fog event, probably enhanced by orographic lifting. The event occurred in the early morning hours and lasted until about noon. The event became extremely patchy shortly after sunrise, with official cloud water samples being discontinued at 0630 EST. A sharp inversion was evident at sunrise, which completely dissipated by noon. Field pH measurements for the event ranged from 3.17 at the outset to 2.99 at the end of the event. This drop in pH was probably due to the dissipation of fog droplets, thereby concentrating their solution contents.

The August event lasted more than forty eight hours and was associated with a weak upper level disturbance. The event yielded light precipitation during the latter stages of the event. The profiles (Fig. 1) for this period indicate a drop in all three parameters, this we believe can be attributed to a shift to a size range larger than the effective cut off diameter for the Probe. Although the probe is capable of measuring droplets up to 47 μm onboard an aircraft, we suspect the actual cut-off diameter is smaller (probably about 25 μm) when used for ground based measurements due to lower sampling velocities. However, no laboratory tests are yet available to support this contention. The probe, probably will under-estimate the actual LWC in mature cloud systems. The above factor, coupled with the lower acidity of the August event will result in lower ionic deposition estimates for our long duration events. This in combination with the fact that the 1986 summer was one of extreme drought for the southeast region will tend to cause the estimates of normal ionic deposition in the Mt. Mitchell area to be underestimated. This will be offset somewhat by the factors (previously mentioned) which tend to over-estimate deposition. We feel, therefore that, the resulting errors in our estimates are small.

Wet deposition was calculated by one hour model runs using the data mentioned above. The data could then be combined with field chemical data to produce hourly ionic deposition rates. Finally, knowing the total number of hours of each type of cloud event that occurred during the summer (May - September) and the average ionic deposition from these two representative events, we were able to estimate annual ionic deposition to the Mt. Mit-

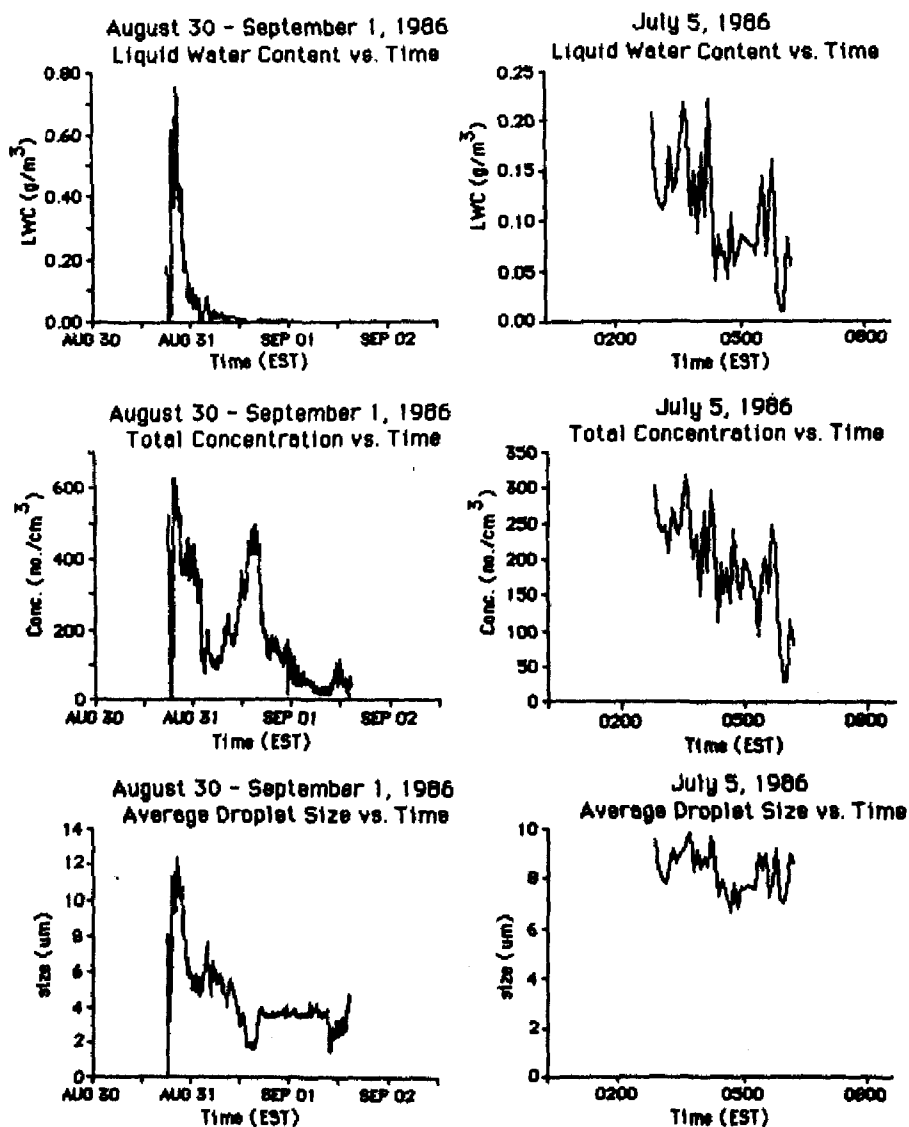


Figure 1 Microphysical parameters measured at Mt. Gibbs, NC. Values shown are five minute averages of one second FSSP data.

shell area ecosystems. Due to the drought conditions, it is likely that these annual estimates are somewhat low.

Model runs for the July event indicate hourly wet deposition rates on the order of 0.13 mm hr^{-1} from direct cloud interception and ionic deposition rates on the order of $10^{-4} \text{ kg ha}^{-1} \text{ hr}^{-1}$ from such sources. Runs for the August event indicate hourly wet deposition rates on the order of 0.27 mm hr^{-1} and ionic deposition on the order $10^{-4} \text{ kg ha}^{-1} \text{ hr}^{-1}$ from direct interception sources. Extrapolating cloud occurrence data taken from the summer to the entire year, yields annual ionic deposition rates of $1.35 \text{ kg ha}^{-1} \text{ yr}^{-1}$ for short term events and $0.40 \text{ kg ha}^{-1} \text{ yr}^{-1}$ for long term events. The total of $1.75 \text{ kg ha}^{-1} \text{ yr}^{-1}$ compares well with that of Lovett et. al. who provided a value of $2.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$. These values are also obtained from actual measurements, while Lovett et. al. assumed a typical LWC and modal droplet size.

Concluding Remarks

Our results indicate that wet deposition from direct interception sources is a significant source of ionic input to mountain forest canopies. Values estimated from measured parameters obtained near Mt. Mitchell, N.C. compare favorably with those obtained by other authors at other locations.

Wet deposition rates from such sources were found to be on the order of a few tenths of mm hr^{-1} , with resulting ionic deposition rates on the order of $10^{-4} \text{ kg ha}^{-1} \text{ hr}^{-1}$ for both short and long duration events. However, due to the more acidic nature and more frequent occurrence of short duration events, these short events may contribute more ionic deposition per year than do their long duration counterparts. Finally, due to extreme drought conditions which existed during the 1986 summer in the southeast region, the estimates presented here may actually be lower than normal for Mt. Mitchell. Further work is in progress to refine our computations.

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DRY DEPOSITION OF OXIDES OF NITROGEN

D. Stocker, D. H. Stedman, B. Evilsizor and M. Burkhardt
Chemistry Department
University of Denver
University Park
Denver, Colorado 80208

Eddy Correlation is the best approximation available as an absolute method for the determination of dry deposition. In order to perform an eddy correlation study of the flux of a pollutant gas, that gas needs to be measured with a time response of less than one second. We have shown that we are capable of making these measurements for ozone and for the oxides of nitrogen NO and NO₂. In order to be sure to be determining all the important flux of the oxides of nitrogen out of the atmosphere, it is important to be able to determine the flux of nitric acid (HNO₃). We therefore propose to build a molybdenum converter which will allow eddy correlation studies of nitric acid.

Determining the concentration of peroxyacetyl nitrate has always been difficult. We have developed a fast portable method which can separate PAN from interferences in ambient air and monitor its concentration.

Key words: Oxides of Nitrogen, NO, NO₂, HNO₃, PAN, O₃, luminol, molybdenum and Eosin-Y.

The dry deposition of many atmospheric species to various types of ground cover has not been characterized (1). The equation:

$$F = \overline{c'w'}$$

forms the basis for the eddy correlation technique. Average fluxes are measured directly by correlating the fluctuations in concentration, c' , with the fluctuations in the vertical wind, w' , without the need for assumptions involving eddy diffusivities or other inferred quantities (2). This method requires state of the art fast response instrumentation (> 1 Hz) (3,4) to be deployed in the field along with computers for data acquisition and reduction. A micro-meteorologically suitable site is required for eddy correlation studies. Ideally the site should be level, with a uniform surface (no upwind obstacles which could introduce a non steady-state turbulent flow). The atmosphere should also be well mixed so that chemical and dynamic steady-state prevails.

Meteorological instruments

The (u,v,w) wind components are measured using a Gill propeller anemometer mounted at a height of 5-7m on a tower upwind of the trailer which houses the instruments. Air samples are drawn from the tower into the trailer using a high volume sample pump (at a flow rate of ca. 180 lpm) through 5/8 inch i.d. Teflon tubing, the chemical sensors draw samples from the main air stream. The time taken for a sample to travel the length of the tube and reach the analyzers is < 2 s. This lag is taken into account in the data analysis. The response frequency of the chemical sensors sampling through the intake tube is approximately 1 Hz.

The response frequency of the Gill anemometer is also about 1 Hz, depending on the wind speed (5). The flux measurements thus sample the frequency spectrum from 1 Hz up to the averaging time of 25 minutes. At typical wind speeds, the loss of flux by neglect of longer scale eddies is probably insignificant. The loss of eddies faster than 1 Hz is predicted to lead to an underestimate of flux not exceeding 15% (5). This correction can be included in the data analysis.

A platinum wire thermometer is mounted on the tower in close proximity to the sample intake. Its response frequency is about 10 Hz.

NO_x

The NO_x (NO, NO₂ and PAN) instrument monitors the intensity of light emitted following the reaction of nitric oxide with ozone (6,7). The higher oxides of nitrogen (principally nitrogen dioxide and peroxyacetyl nitrate) are

reduced to nitric oxide using a heated molybdenum converter at 400°C , see Figure 1. The short length of tubing in front of our converter has such an affinity for HNO_3 that the response to HNO_3 changes is over a minute. Using a radiative heating system, we propose to build a molybdenum converter in which 400°C molybdenum is the first surface which is impacted by the sample air, see Figure 2. This configuration will allow eddy correlation studies of HNO_3 .

Chemiluminescent Ambient Air Monitors

By altering the configuration of the Chemiluminescent Ambient Air Monitor (CAAM), see Figures 3, 4 and 5, the following species can be monitored: 1) NO_2 2) PAN 3) HNO_3 and 4) O_3 . The first three species are measured by the chemiluminescence reaction of NO_2 with basic luminol solution (8). Detection of NO_2 takes place in the analyzer cell where luminol solution and ambient air come into contact. Light produced from the reaction of NO_2 and luminol is detected by an EMI 9924B (or Hamamatsu R268) photomultiplier tube (PMT). The photocurrent is converted by the electrometer to a 0 to 10 volt output signal that is linearly proportional to the NO_2 concentration. The response of the chemiluminescent monitors is about 7 Hz.

Ozone is measured by using the chemiluminescent dye Eosin-Y in ethylene glycol in place of luminol (9).

PAN and HNO_3 instruments require special intake systems and operate at slower response rates. Eddy Correlation studies are not possible at these rates but the gradient method could be used to determine the flux of these species. The concentration of PAN can be found by coupling a CAAM instrument with a gas chromatograph. PAN and NO_2 are separated using a polyethylene glycol 400 on Chromosorb W HP column with NO_x free ambient air as the carrier gas. The peroxyacetyl nitrate can be separated and detected once every 15 seconds. The HNO_3/NO_2 analyzer is a variation of the luminol chemiluminescence detector for NO_2 . A species-determinator intake system consisting of a hot-glass beads converter, a CrO_3 converter, and filters of nylon and teflon is used for HNO_3 measurement. An automatic timing and valve sequencing circuit controls the intake air flow that alternates between readings for NO_y (NO , NO_2 , PAN and HNO_3) and for $\text{NO}_y\text{-HNO}_3$. During operation the teflon filter removes particulate matter from the sample air. HNO_3 in the air sample is then converted to NO_2 in the hot-glass beads trap. Excessive reduction is corrected by use of a CrO_3 converter just prior to the NO_2 detector. A valve periodically switches a nylon filter inline which selectively removes HNO_3 from the air sample. The value for the HNO_3 is obtained as a difference between the two measurements.

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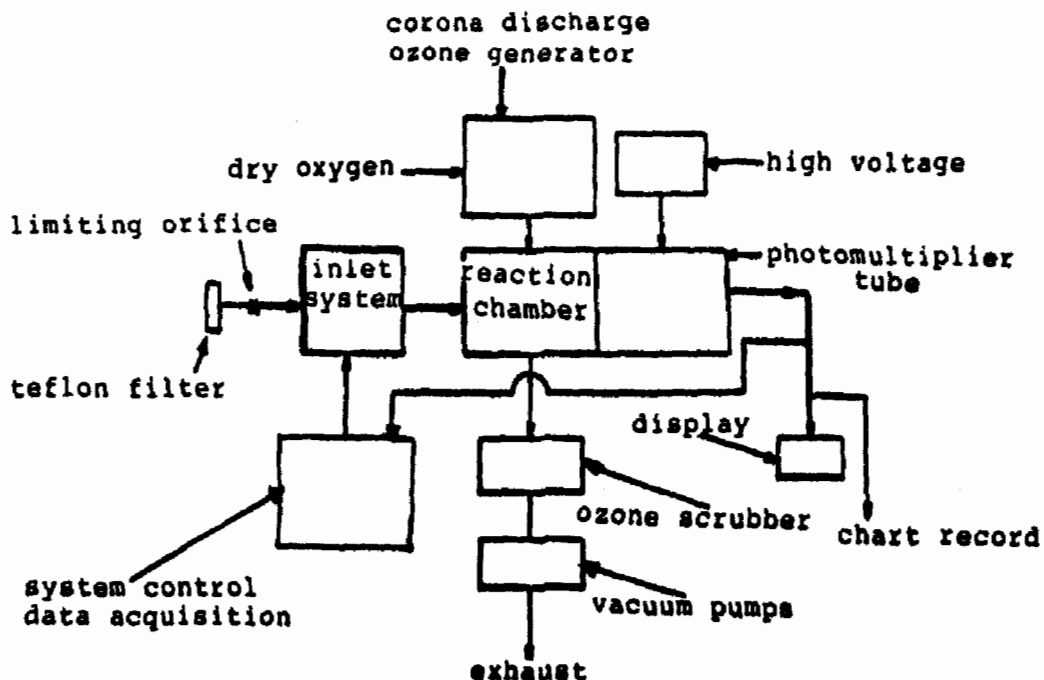


Figure 1 Block diagram of the NO_x detector.

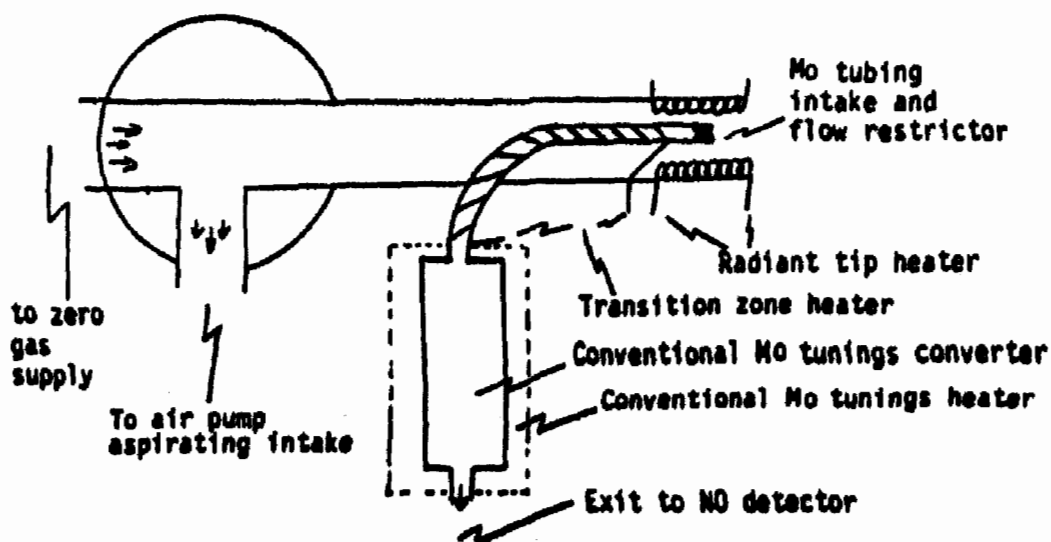


Figure 2 A schematic of the FAST CONVERTER inlet system for HNO₃ studies using the NO_x detector. The rotary valve at the left controls whether the intake is pulling in ambient air or pushing out zero air.

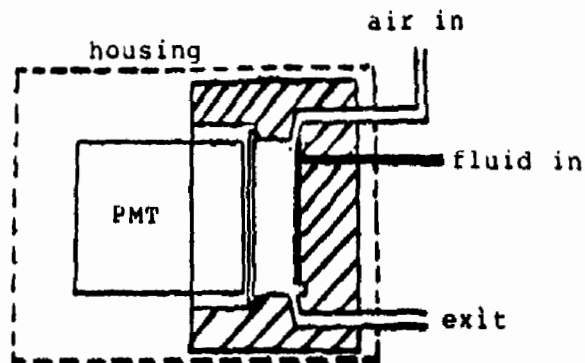


Figure 3 Design of the CAAM detection cell that uses Eosin-Y in ethylene glycol or luminol solution.

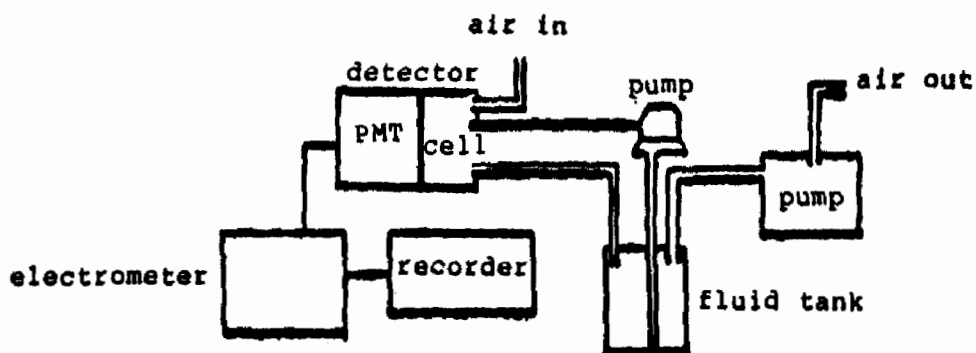


Figure 4 Block diagram for the NO_2 analyzer.

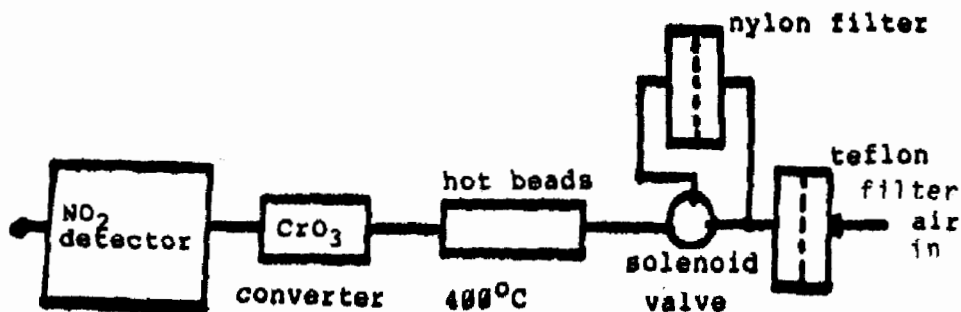


Figure 5 Inlet system for HNO_3 detection.

Establishment of the National Dry Deposition Network

by

Barry E. Martin & Jack C. Suggs

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711
APRIL 1987

Establishment of the National Dry Deposition Network

Introduction

In an effort to coordinate Federal Acid Rain activities, Congress passed the Acid Precipitation Act of 1980. This Act established a Task Force to develop and implement a comprehensive National Acid Precipitation Assessment Program (NAPAP) that would increase our understanding of the causes and effects of acid deposition. The program includes both research and monitoring data bases on which administrative decisions can be made. To fulfill this latter requirement, NAPAP established the National Trends Network (NTN). Since the NTN measures only the wet component of acid deposition, the NAPAP assigned EPA the responsibility to design, deploy, and operate a network to measure the dry components of acid deposition. EPA delegated this responsibility to the Environmental Monitoring Branch (EMB), Monitoring and Assessment Division (MAD), Environmental Monitoring Systems Laboratory (EMSL), Research Triangle Park (RTP), NC. The EMB/MAD/EMSL has designed a network which will consist of up to 100 stations and will be established over the next 5 years. This network is being established to address the following objectives: establish a data base from which an estimate of dry deposition flux and deposition velocities can be made; determine the temporal and spatial distribution of dry deposition in the U.S.; assist in determining the relationship between dry deposition, wet deposition, and environmental effects; and collect data to test and improve regional deposition models.

Since there is no reliable mechanism to monitor dry deposition velocities or dry deposition fluxes, the network will monitor the following parameters from which dry deposition velocities and fluxes can be estimated: particulate sulfate (SO_4^{2-}), particulate nitrate (NO_3^-), nitric acid (HNO_3), sulfur dioxide (SO_2), ozone (O_3), wind speed (WS), wind direction (WD), temperature (T), delta temperature (ΔT), solar radiation (SR), relative humidity (RH), and precipitation (P). Because of the uncertainties surrounding some of the sampling techniques and because of the complexity of the project, a prototype network of six stations was established by EMSL in 1984. These six stations evaluated the performance of monitoring equipment under expected operating conditions. The experience gained in this effort has guided EMSL in the final equipment selection and will be used to refine the station operating procedures. These six stations have become part of the 100 station network. The prototype stations are located at Research Triangle Park, NC; Pennsylvania State University, PA; Oak Ridge, TN; Whiteface Mt., NY; and West Point, NY. A sixth station is also located at West Point, NY as a collocated station. These sites were chosen because of existing monitoring activities for acid deposition at each site and the interest in acid deposition of the principal investigators at the stations. The stations in the prototype network were installed and maintained by a contractor. The operation of the station is by agreement with the principal investigators at the stations.

A contract was awarded in September 1986 to Environmental Science & Engineering, Inc. (ES&E) of Gainesville, Florida to assume operation of the prototype network and to expand the network to 100 stations over the next five years. The parameters to be monitored are the same as in the prototype network. Figure 1 shows the proposed locations of the dry deposition monitoring stations. Due to the need to evaluate the Regional Acid Deposition Model (RADM) by 1989, the first 40 stations will be located in the eastern United States. The remaining 60 stations will be distributed over the contiguous United States.

Discussion

In the prototype network, the particulate sulfate and nitrate, nitric acid, and sulfur dioxide were measured weekly using a stacked filter pack system currently in use in Canada.¹ This stacked filter pack is operated over a 7 day sampling period and consists of two separate samples - one integrated over the daytime hours and the second integrated over the nighttime hours. Both the daytime and nighttime samples consist of a single filter holder containing three filters in series. The first filter, made of Teflon, is for particulate removal and is analyzed for sulfate and nitrate. The second filter is nylon and is analyzed for nitric acid. A Whatman 41 filter impregnated with K_2CO_3 /glycerin analyzed for SO_2 is the third filter. The flowrate of the system is maintained at 1.5 lpm by a mass flow controller. The filter holder material is made of Teflon. The Teflon filter samples are water extracted and analyzed using an ion chromatograph (IC). The nylon filter, which collects gaseous nitric acid, is water extracted and analyzed by IC. The treated Whatman 41 filter is extracted with 0.03% hydrogen peroxide and analyzed for sulfate using a colorimetric procedure. In addition to the Canadian Filter (CF) pack sampler, two other techniques suitable for routine monitoring applications were evaluated during 1986 at selected prototype stations. These techniques include the PM_{10} Size Selective Inlet High Volume Sampler (SSI) & the Transition Flow Reactor Sampler (TFR)². The filters collected in the network are supplied by EMSL/RTP, NC and analyzed by an EPA contractor. The continuous O_3 and meteorological data are collected at the field sites on data cassettes which are returned from the stations weekly. Data are reduced and validated by EPA and the EPA in-house contractor. A validated data set is available from the EMSL/RTP, NC.

One objective of the prototype network was to determine method precision under actual field conditions. Table 1 gives the precision in terms of the (%) coefficient of variation (i.e., standard deviation divided by the mean $\times 100$). The precision for the CF pack and PM_{10} Size Select Inlet High Volume Sample (SSI) methods was estimated by the yearly average of individual weekly estimates of the % coefficient of variation (CV) between collocated instruments located at the West Point sites. Daytime and nighttime estimates of precision were calculated separately for each type of filter used by the filter pack. Alternatively, precision for the TFR method was calculated as the average % coefficient of variation between weekly measurements from the left and right channels of the same instrument. Estimates from different sites were pooled. With the exception of HNO_3 the "within" instrument variation for the TFR was higher (less precise) than the "between" instrument variation for both the CF Pack and SSI methods. However, for comparison purposes, neither of the collocated sites employed a TFR sampler.

Prior to April 1, 1986, the collocated sites (003 and 004) at West Point, New York were equipped with similar CF Pack samplers. No significant bias between the two collocated sites was detected during this period. Beginning in April 1986, The collocated sites at West Point were outfitted with CF Pack samplers with different filter holders. The CF Pack at site 003 used an all Teflon filter holder and the CF Pack at site 004 used a Polycarbonate filter holder manufactured by Nuclepore. For the period beginning April 1986 until January 1987, a slight increase in the %CV was noted for some pollutants.

A statistical test indicated that the increase in %CV was due to the following significant biases:

- 1) HNO_3 (daytime) at site 003 was 9.5% higher than site 004,
- 2) SO_4^{2-} (nighttime) at site 003 was 6.2% higher than site 004,
- and 3) SO_2 (nighttime) at site 003 was 14.9% higher than site 004.

As a result of these biases, CF Pack estimates of precision are given for the period prior to the change in filter holders.

Table 2 summarizes the method comparisons, which are based on weekly percent differences (i.e., Percent Diff = $(\text{Meth 1} - \text{Meth 2}) / [(\text{Meth 1} + \text{Meth 2}) / 2] \times 100$). This ratio is approximately equal to the difference between the logarithms of the method measurements (i.e., $\ln(\text{Meth 1}) - \ln(\text{Meth 2})$) and, if certain assumptions hold, approximates a normal distribution centered around zero with standard deviation proportional to the coefficient of variation³. Statistical outliers were removed and only data above the minimum detectable range for each method were used in the calculations. The large difference (156%) between CF Pack and SSI is thought to be due to the loss in NO_3^- on SSI filters due to daytime temperatures. The CF Pack results were not affected by temperature as much since different samplers were operated for daytime and nighttime sampling and averaged to provide a full 24-h measurement for each week. The concentrations levels ($\mu\text{g}/\text{m}^3$) over which these method comparisons apply are summarized in Table 3.

There were not enough weekly pairs to make valid statistical tests for CF Pack vs TFR or TFR vs SSI using NO_3^- measurements.

Summary

The experience gained in the operation of the prototype network indicates that the Canadian Filter (CF) Pack sampler provides the best available approach to monitoring for concentrations of acidic components which can attribute to dry deposition. The CF Pack sampler was simpler, more reliable, and more precise than the other units tested. As newer and more sophisticated designed samplers are developed, EMSL will consider their use in the NODN. Before a new sampler or technique will be considered for inclusion in the NODN, it must demonstrate reliable operation under actual field conditions.

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Table 1

Precision Expressed as the Average of Weekly Estimates of Coefficients of Variation (%) for Collocated Data. Canadian Filter Pack Estimates are Only for the Period Prior to April 1986.

			NO_3^-	#WKS	SO_4^{2-}	#WKS	HNO_3	#WKS	SO_2	#WKS	% NO_2	#WKS
Method	Filter	Time										
Filter Pack (FP)	Teflon	Day	8	6	5	9	-	-	-	-	-	-
		Night	6	6	8	10	-	-	-	-	-	-
	Nylon	Day	-	-	6	10	9	8	-	-	-	-
		Night	-	-	10	10	11	8	-	-	-	-
	What-man	Time										
		Day	-	-	-	-	-	-	2	7	-	-
		Night	-	-	-	-	-	-	5	10	-	-
SSI	Filter	Time										
	SSI	Weekly	9	21	7	37	-	-	-	-	-	-
TFR	Filter	Time										
	TFR	Weekly	43	10	21	82	18	74	31	67	22	62

Table 2. Method Differences Expressed as a Percent (%) of Their Average

Pollutant	Comparison	N	Site						Weighted Average
			1	2	3	4	5	6	
HNO ₃	FP-TFR	43	-11.9	-12.3				-5.1	-9.5*
NO ₃	FP-SSI	103	154.6**	154.0**	167.5**	163.6**	144.3**		155.9**
	FP-TFR	4	157.3	27.0					92.1
	TFR-SSI	8	-41.1	146.3					5.8
SO ₂	FP-TFR	46	12.1	17.2*				55.7*	29.1**
SO ₄	FP-SSI	131	-6.1	0.6	-2.7	-2.7	-3.8		-2.7
	FP-TFR	56	22.7	33.3*				36.5**	31.8**
	TFR-SSI	28	-29.6**	-17.7*					-24.0**

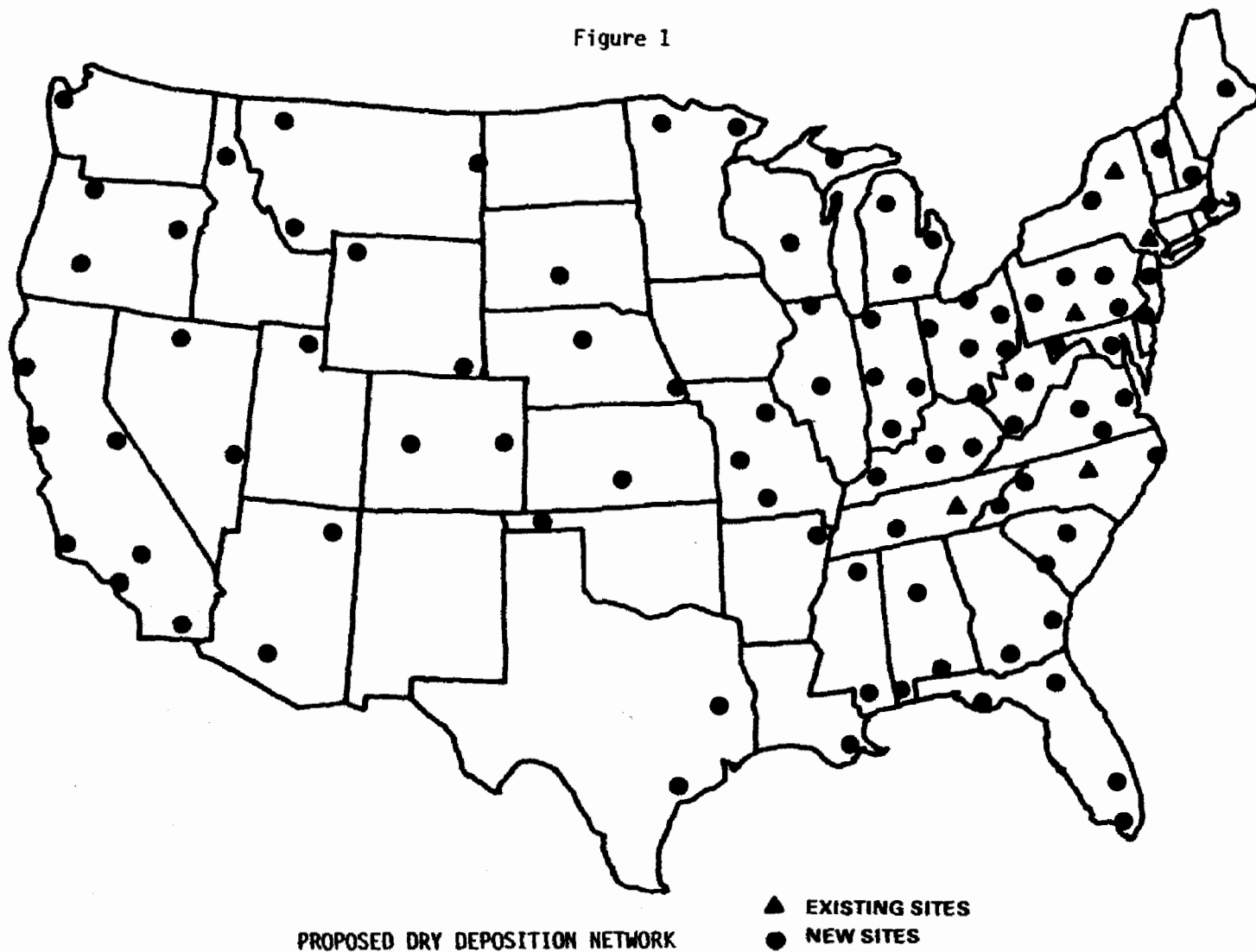
* indicates a statistically significant difference at the $\alpha = .05$ level

** for the $\alpha = .001$ level

Table 3. Range of Pollutant Concentrations ($\mu\text{g}/\text{m}^3$)

Pollutant	Concentrations ($\mu\text{g}/\text{m}^3$)			
	N	Min	Max	Mean
HNO ₃	378	.18	19.84	1.86
NO ₃	462	.10	24.60	.83
SO ₂ ⁻²	328	.27	52.59	8.54
SO ₄	684	.30	20.29	5.82

Figure 1



Measurement of Atmospheric Organic Acids:
Considerations Regarding Sampling Artifacts and Potential Interferences

Kochy Fung
ERT, Inc., Newbury Park, CA.

Introduction

Low molecular weight organic acids, primarily formic and acetic acids, have been measured, although infrequently, in the atmosphere and in precipitation in both rural and urban areas of the United States. These organic acids are emitted directly into the atmosphere from sources such as motor vehicles and can be formed in the atmosphere from the photochemical oxidation of a variety of organic compounds. Organic acids may provide a significant source of precipitation acidity in rural and some urban areas. More recently, health effects researchers have hypothesized that low molecular weight organic acids may be substantial contributors to the total acidity of fog droplets in urban areas such as Los Angeles, with potentially important implications on human health effects from acidic fogs.

In order to understand more completely the photochemical processes that can lead to the formation of low molecular weight organic acids in the gas and aerosol phases during urban photochemical episodes, as well as to assess the levels, the measurement of organic acids in ambient air is essential. However, atmospheric concentrations of organic acids have been measured only on a very limited bases, typically using an alkaline medium (filter or impinger solution) following a particulate prefilter for the collection, and analyzing an extract of the filter or the impinger solution for the acids. For example, Kawamura et al¹ used the filter technique and found an array of C₁ - C₁₀ organic acids in Southern California, with acetic and formic being the most abundant. This type of sampling approach using an alkali medium can suffer from some serious artifacts:

- hydrolysis of peroxyacyl nitrates to the corresponding acids. It is well-known that these compounds are extremely sensitive to alkali. Peroxyacetyl nitrate (PAN), a major air pollutant in smog, is hydrolyzed to acetate² or peroxybenzoyl nitrate (PBzN) to benzoic acid. The hydrolysis of these compounds is complete even in 0.005 N KOH and has served as the basis for the measurement of ambient peroxybenzoyl nitrate³.
- disproportionation (Cannizzaro Reaction). Hydroxides promote the disproportionation (autooxidation) of aldehydes such as formaldehyde and benzaldehyde to the corresponding alcohols and acids. The rate of this reaction is dependent on the strength of the hydroxide. Since formaldehyde levels may reach as high as 48 ppb in some parts of Southern California, this reaction, if proceeds rapidly, can lead to serious errors in the organic acid measurement.
- oxidation of aldehydes by ozone or H₂O₂. Aldehydes, such as formaldehyde and acetaldehyde, are commonly present in the atmosphere especially in the urban environment. If these aldehydes are collected by the sampling medium and are converted to the corresponding acids by O₃ or H₂O₂ in the sampling air stream, an artifact will result. However, these reactions are pH dependent, and become less favorable as the pH of the medium increases.

- alkaline hydrolysis of esters. A recent report on hazardous pollutants in Class II landfills⁴ by the South Coast Air Quality Management District indicates that substantial amounts of C₁ to C₄ alcohols and the esters formed from these alcohols with C₁ to C₄ carboxylic acids, are emitted along with other organics from the five landfills monitored. However, no free organic acids were found, apparently due to the abundance of alcohols to esterify these acids. If organic acid measurements are conducted using alkaline collection medium, hydrolysis (saponification) of these esters which are also collected by the medium to the parent acids (carboxylate) may proceed. The rate depends on the strength of the alkali and the type of esters. Esters of formic acid, for example, saponify rapidly⁵.
- volatilization of salts of organic acids from the prefilter to the collection medium. It is probable under some atmospheric conditions that particulate formate or acetate on the prefilter are converted to the parent organic acids which are volatile via reaction with strong acids (e.g. HNO₃, H₂SO₄ or HCl) in the sampling air stream and be trapped by the collection medium downstream. However, the formation of acetate or formate is not likely to occur unless there is an abundance of NH₃ to completely titrate all of the strong acids that are in the air. It will also take a change of wind flow pattern to bring in sufficient strong acids from outside sources to neutralize the NH₃ before this volatilization process can occur. Thus, this artifact is not expected to proceed appreciably.

Experimental Approach

The preceding discussion indicates that serious sampling artifacts are possible when using the existing technique for organic acids. The basic problem lies in the use of alkali which promotes the variety of undesirable reactions. Sampling may in fact be accomplished without complication using an impinger containing only distilled water if one considers the true Henry's Law constants (25°C) for formic and acetic acid are ~2,800 times larger than PAN. This indicates that water is a good collection medium for the acids, but a very poor one for PAN. An experiment conducted in the authors laboratory showed that no decrease in PAN concentration was noted by the gas chromatograph with electron capture detector when a PAN test atmosphere at 60 ppb was drawn through a distilled water impinger at 1 lpm. In other words, little PAN is collected with this technique. Also the other problem associated with using an alkaline collection medium disappear because this collection medium is neutral. Further, significant improvement in the collection efficiency can be achieved if the trapping is conducted at ice temperature because the solubility of gases (the acids) in water are much greater.

To assess the collection efficiency using this approach, tandem impingers were used to sample at 1 lpm scrubbed air which was drawn through an impinger containing a known concentration of acetic acid in water. An inline particulate filter prevented any droplets of acetic acid from reaching the sampling impingers. The front impinger contained 10 ml of distilled water and it was kept in ice during the one-hour experiment. The back impinger, not iced, contained 0.05 N KOH and was used for assessing breakthrough. By varying the strength of the acetic acid solution, different concentrations of acetic acid in air were achieved. Acetic acid was chosen as the representative organic acid because it is normally present in the atmosphere and because PAN is a major interference in its measurement. Upon completion of sampling, the volume of liquid in each impinger was measured and its content analyzed for acetate using ion chromatography.

Another experiment was performed to determine how the temperature of the impinger solution might vary as a function of flow rate and inlet air temperature. It was thought that if the temperature of the collection medium varied too much, collection efficiency could suffer. A thermocouple was used to measure the solution temperature under varying sampling flow rate (1-5 lpm) while the ambient air temperature was $\sim 23 \pm 2^\circ\text{C}$.

To assess how much interference PAN would have been if the collection was done using an alkaline medium, an ambient air sample was taken outside of the laboratory at Newbury Park, CA. A Teflon filter was used to remove the particles followed by two impingers in series. The upstream impinger with distilled water was iced. The second impinger with 0.05 N KOH was at ambient temperature. After sampling, the impinger solutions were analyzed for acetate using ion chromatography.

Results & Discussions

Table 1 shows the results of the collection of acetic acid using water at $\sim 0^\circ\text{C}$ as the collection medium. It is apparent that excellent collection efficiency was achieved (average 90.5%) even at the highest acetic acid concentration tested (~ 640 ppb). The breakthrough as detected by the second impinger would not occur under ambient sampling conditions, since the concentration of acetic acid is in the order of a few ppb.

The results in Table 2 indicates that fluctuations in temperature of the collection medium during sampling would not be a problem since increasing the flow rate from 1 lpm by a factor of 5 only brought the temperature up by 4°C .

The ambient air sample collected with the tandem impingers showed ~ 6 ppb of acetate in the front aqueous impinger and ~ 13 ppb of acetate in the back alkaline impinger. Thus ~ 19 ppb of acetate would have been collected if a single alkaline impinger was used, and all of it would have been taken as acetic acid. But actually, only 6 ppb was acetic acid, as measured using the present technique. PAN, which would have been a serious interference, was only collected by the second impinger using alkali.

In conclusion, using ice water as an impinger collection medium for organic acid is a viable technique and avoids major interferences which other integrating techniques have suffered. Further development and refinement of this technique will be pursued to address the other potential, though considered minor artifacts delineated earlier.

TABLE 1
COLLECTION OF ACETIC ACID BY TANDOM IMPINGERS

CH ₃ COOH SOURCE, %	MICROGRAM PER SAMPLE	
	FRONT IMPINGER, ²	BACK IMPINGER, ³
0.1	84.5	9.6
	82.8	7.7
0.05	19.2	0.8
	20.2	N.D. ⁴
0.01	4.2	N.D.
	3.9	N.D.

1 1 lpm for 1 hour

2 water, impinger iced

3 0.05 N KOH

4 not detected, $<0.1 \mu\text{g}$

TABLE 2
CHANGES IN IMPINGER SOLUTION TEMPERATURE AS A
FUNCTION OF SAMPLING FLOW RATES

Flow Rate lpm	Water Temp. °C
1	1.0
2	2.0
3	2.0
4	3.0
5	4.0

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TRIFLUORINATED POLAR AROMATICS: CANDIDATE RECOVERY
STANDARDS FOR COMBUSTION STUDIES

Charles H. Lochmüller and Anna G. Edwards
Department of Chemistry
Duke University
Durham, North Carolina 27706



Mutagenicity assays indicate that, even in the absence of mammalian tissue homogenate activation, the moderately polar and highly polar extract fractions of combustion source samples exhibit high mutagenic behavior. Polar compounds, which could be employed as internal and recovery standards are needed to assess the results of field sampling as well as to improve analyte quantitation by GCMS or LCMS. Prior to a field testing of such compounds, a complete evaluation of their analytical characteristics and suitability would be required.

The suitability of several trifluoromethylated compounds has been examined in the work completed thus far and further evaluation studies are in progress to improve internal standard compound selection from among these choices. Fluorinated compounds were proposed because they are not widely found in the environment and because they are uniquely suited to mass spectrometric detection. The proposed compounds were evaluated for recovery from silica gel fractionation and reversed-phase, HPLC. Those moderately polar compounds which showed good recovery from silica gel fractionation, reversed phase column elution, and identifiable MS fragmentation patterns were: 4-amino-3-nitrobenzotrifluoride, 2-amino-5-nitrobenzotrifluoride, and 4-methoxy-3-nitrobenzotrifluoride. For highly polar fractions, 2-amino-5-(trifluoromethyl)pyridine and 2-hydroxy-5-(trifluoromethyl)pyridine might serve as good reference compounds. Data collection for a Principal Components Analysis of the chromatographic behavior of these compounds is presently underway in our laboratory.

Introduction

Results of the Ames Salmonella mutagenesis bioassay on wood smoke^{1,2} and diesel exhaust³ emission extracts indicate that moderately polar and polar compounds account for substantially more direct-acting mutagenic activity than the relatively non-polar polycyclic aromatic hydrocarbons. Kamens *et al.*¹ reported that the direct-acting mutagenicity of wood smoke particulate extracts was contained in the most polar fractions. When the extract was exposed to O₃ and NO₂, in the dark, the mutagenicity increased substantially and compounds containing nitrogen were detected by GCMS. Kleindienst *et al.*² reported that the mutagenicity of both gas and particulate phase components of wood smoke emissions increased with irradiation in the presence of NO₂. Schuetzle *et al.*³ reports that the moderately polar fractions of diesel exhaust particulate extracts exhibited the highest mutagenic behavior; as much as 30% of the direct-acting mutagenicity of unfractionated fractions was attributed to 1-nitropyrene. Thus, the potential health hazard of polar compounds, in general, and possibly of nitrogen-containing polar compounds, in particular, argues for a sound methodology for their assay.

An internal standard compound should improve not only control studies of environmental monitoring but polar compound assaying as well. An internal standard should be chemically similar to the compounds assayed, so that its response reflects any physical or chemical perturbations to the system. Yet it should be sufficiently different from the compounds assayed in order to make its detection simple and unquestionable. By definition, an internal standard compound should not be present in the sample. Fluorinated compounds are proposed here for combustion studies because they do not normally occur in the environment. The unique isotopic abundance of fluorine should be readily detected in high resolution mass spectra. In low resolution mass spectra, compound detection should be possible from the fragmentation pattern.

The candidate compounds were evaluated for their recovery from silica gel fractionation and from reversed phase HPLC. The column recovery studies were performed first. Successive elution by hexane, methylene chloride and methanol was performed for silica gel fractionation.

Principal components analysis⁴ of the candidate compounds based on their compound/mobile phase covariance is presently underway to further establish the suitability of a given compound from among the choices. When applied to a large data matrix, it can determine how many factors account for the non-random variation in the data. Those factors can be used to identify chemically similar compounds. In the present treatment, the HPLC capacity factors of the compounds in aqueous methanol and aqueous acetonitrile mobile phases were measured. By evaluating how the compounds cluster with data already available in our laboratory⁵, a better evaluation of the suitability of an internal standard will be possible.

Experimental

The trifluoromethyl compounds were obtained from several sources. The Eli Lilly Corp. donated 2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzamine (trifluralin). Ishihara Sangyo Kaisha, LTD donated 2-hydroxy-5(trifluoromethyl)pyridine and 2-amino-5(trifluoromethyl)pyridine. The following compounds were obtained from Aldrich Chemical Company, Inc. : 4-amino-3-nitrobenzotrifluoride (4A3NBTF); 4-methoxy-3-nitrobenzotrifluoride (4M3NBTF); 2-amino-5-nitrobenzotrifluoride (2A5NBTF); 2-methoxy-5-nitrobenzotrifluoride (2M5NBTF); and

2-nitro-4(trifluoromethyl)phenol (2N4TFPh). Acetophenone was obtained from Fisher Scientific. All solvents were HPLC grade from Mallinckrodt, Inc. Solvents were filtered through 0.45µm filters and degassed prior to sample preparation and column elution.

The HPLC instrumental set-up for the column recovery studies included a Waters 6000A Solvent Delivery System, a Perkin-Elmer LC-420B Auto Sampler injection system, and a Hewlett Packard 1040A Diode Array Detector (HP 1040A DAD). Compound recovery from a reversed phase C18 column (Perkin-Elmer 5 µm particles, 12.5 cm, 0.46 cm ID) was performed in 80:20 (v/v) methanol:water. Compound recovery was determined from comparing pre-and post-column absorptivity ratios. The absorptivity ratio was defined as the ratio of the slope of the absorbance calibration curve for trifluoromethyl compound versus the slope of the absorbance calibration curve for acetophenone each at their respective ultraviolet wavelength maxima. The ratio of the slopes of absorbances of calibration solutions as measured in 1.0 cm cells in a Cary 2300 Spectrophotometer was defined as the pre-column absorptivity ratio. The ratio of the integrated areas at each compounds wavelength maximum on the HP 1040A DAD was labeled the post column absorptivity ratio. The difference between pre-column and post-column absorptivity ratio in relation to the precolumn ratio defines the recovery of trifluoromethyl compound. The column recovery for solutions which gave an absorbance between 0.1 and 0.25 on the Cary 2300 were measured first. Differences of two percent or less at this concentration range indicated no measureable compound column loss. A hundred-fold dilution of these calibration solutions produced chromatographic peak heights which were approximately seven times greater than the noise envelope of the HP 1040A DAD. The relative standard deviation of integrated peak areas varied from twenty percent to five percent at this concentration level. Recovery measurements by reference to acetophenone were considered unsound and the difference between measured and expected peaks areas (based on dilution of the calibration solution) was computed to assess compound recovery. Differences of five percent or less at this lower concentration level were concluded to indicate no measureable compound loss.

Sample recoveries from silica gel fractionation were determined by a procedure developed by Battelle⁶. The trifluoromethyl compounds were individually dissolved in methylene chloride, and solvent exchanged to hexane by rotary evaporation between the addition of two aliquots of hexane. The sample, now in hexane, was transferred to a silica gel column which had been prepared in a disposable pipet. The hexane fraction was discarded and methylene chloride and methanol fractions collected. These solutions were analyzed by RPLC with gradient solvent programming from 60% to 90% methanol:water.

Data collection for the Principal Components Analysis was collected utilizing the same approach as that used for the column recovery studies. In addition, the column and eluant were thermostatted at 22°C. The aqueous methanol and aqueous acetonitrile solutions were prepared by volume for isocratic elution of the compounds studied.

Mass spectra of the compounds were obtained from two sources. Mass spectra from a Finnegan LCMS using water-methanol showed fragmentation patterns which suggest chemical ionization-like conditions. Mass spectra obtained by direct probe insertion into a Hewlett Packard 5988A GCMS gave fragmentation patterns under electron impact conditions.

Results

Column Recovery

The column recovery results on the candidate compounds are compiled in Table I. Except for 2N4TFPh, better than 98% recovery for all compounds at the high concentration

level was observed. The results for 2N4TFPh are not necessarily indicative of appreciable compound loss on the C18 column. Studies of other polar phenols⁷ suggest that these compounds are appreciably ionized during elution resulting in a concomitant shift in their wavelength absorption maxima. Because ion-pairing conditions were not examined in this study, no additional work was performed on this compound. The difference between observed and expected integrated peak areas for the diluted solutions are given in Table II. Except for trifluralin, column recovery was good at the low levels examined. The mass of the compounds, given in Table II, indicates picogram recovery of these trifluoromethyl compounds.

Silica Gel Fractionation

The results from silica gel fractionation are presented in Table III. Except for 2A5TFP and 2H5TFP, all the compounds appeared in the methylene chloride fraction. The pyridine compounds precipitated from solution when the solvent was changed from methylene chloride to hexane. A different fractionation procedure would be needed for these very polar compounds. The recovery of the compounds which eluted in the methylene chloride fraction was good at both high (10^5 pg) and low (10^4 pg) sample levels.

Mass Spectra

While greater fragmentation was observed with direct probe insertion than in LCMS, loss of fluorine was evident in both low resolution systems. Because direct insertion yields spectra which would be expected under electron impact conditions, those results will be discussed here. Except for 2M5NBTF and trifluralin, the intensity of the (M-F) peak was at least 15% of the base peak for all of the compounds. The parent peak was the base peak for 4A3NBTF, 2A5NBTF, 2M5NBTF, 2A5TFP, and 2H5TFP. For 4M3NBTF, the parent peak was 56.2% of the base peak at m/z 174. Yet this compound had the most intense (M-F) peak with a value of 30.6% of the base peak.

Conclusions

The column recovery, silica gel fractionation and mass spectra results indicate that 4A3NBTF, 2A5NBTF, and 4M3NBTF might be suitable internal standards for recovery studies of moderately polar compounds. Each compound was recovered in high yields from the methylene chloride fraction. Each compound was recovered from the C18 column at the lowest quantifiable levels possible on our instrumental set-up. Although 2M5NBTF was recovered in high yields as well, it was excluded from consideration because its (M-F) peak was very low. While silica gel recovery results for 2A5TFP and 2H5TFP were inconclusive, their recovery from the C18 column and their (M-F) fragmentation peaks suggest that additional studies on these compounds might be used to determine their suitability as internal/recovery standards for highly polar fractions. Principal Components Analysis based on compound/solvent covariance should aid in deciding if which compound shows better chromatographic behavior suitability for a given sample type. An analysis of the variation in capacity factors with solvent composition for proposed compounds in combination with existing data for nonpolar and polar compounds, such as those available in our laboratory, may have general value in reference compound selection processes.

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Table I. Reversed-phase, HPLC Column Recoveries

Compounds	Percent Recovery
4-amino-3-nitrobenzotrifluoride	99.94
2-amino-5-nitrobenzotrifluoride	99.29
4-methoxy-3-nitrobenzotrifluoride	98.80
2-methoxy-5-nitrobenzotrifluoride	100.21
trifluralin	98.83
2-amino-5(trifluoromethyl)pyridine	98.80
2-hydroxy-5(trifluoromethyl)pyridine	99.97
2-nitro-4(trifluoromethyl)phenol	43.66

Table II. Column Recovery At Lowest Levels Examined

Compound	Rel. % Diff.	Weight Range (pg)
4-amino-3-nitrobenzotrifluoride	5.4	449 - 1124
2-amino-5-nitrobenzotrifluoride	9.2	1560 - 3903
4-methoxy-3-nitrobenzotrifluoride	1.2	903 - 2258
2-methoxy-5-nitrobenzotrifluoride	0.65	915 - 2288
trifluralin	-27.0	1560 - 3903
2-amino-5(trifluoromethyl)pyridine	-0.98	1872 - 4680
2-hydroxy-5(trifluoromethyl)pyridine	-0.45	1682 - 4206

Table III. Recovery From Silica Gel Fractionation

Compound	Percent Recovery High Level*	Percent Recovery Low Level**
4-amino-3-nitrobenzotrifluoride	-5.2 (+/- 3.1)	-5.2 (+/- 5.1)
2-amino-5-nitrobenzotrifluoride	-5.9 (+/- 1.3)	-8.8 (+/- 4.6)
4-methoxy-3-nitrobenzotrifluoride	-8.2 (+/- 0.3)	-5.0 (+/- 2.9)
2-amino-5(trifluoromethyl)pyridine	0.0	0.0
2-hydroxy-5(trifluoromethyl)pyridine	0.0	0.0

*10⁵ pg

** 10⁴ pg

MOBILE TANDEM MASS SPECTROMETRY FOR THE CHARACTER-
IZATION OF TOXIC AIR POLLUTANT (TAP) SOURCES

B.I. Shushan, SCIEX®, 55 Glen Cameron Rd., Thornhill,
Ontario L3T 1P2
G. DeBrou, Ontario Ministry of the Environment, Air Resources
Branch, 880 Bay Street, Toronto, Ontario M5S 1Z8
S.H. Mo & W. Webster, New York State Dept. of
Environmental Conservation, 50 Wolf Rd., Albany, NY 12233

The recent marriage of tandem mass spectrometry (MS/MS) to mobile Trace Atmospheric Gas Analyzer (TAGA®) technology has resulted in an analytical system capable of real-time direct air analysis for TAP's, VOC's and odor compounds at concentrations as low as a few parts-per-trillion. This direct analytical approach obviates problems associated with conventional trapping methods. Since their introduction in 1983, the design of mobile TAGA® MS/MS laboratories has undergone significant development. The latest design comprises a customized 30 foot transit motor coach configured with a TAGA® 6000EM MS/MS system and ancillary equipment. This paper discusses the incorporation of a sorbent cartridge purge unit into the TAGA® system to assist in rapidly distinguishing between isomeric compounds (eg., ethylbenzene and xylene) using GC/MS/MS. Such isomer pairs are indistinguishable by direct MS/MS techniques. Another recent design addition is a meteorological station comprising wind speed and direction monitors. The met. data are acquired and stored by the MS/MS data system and displayed continuously to the TAGA® operator. The met. station is positioned on top of a 30 foot motorized telescoping tower housed within the mobile laboratory. Combining real-time TAP analysis with met. data, it was possible to rapidly and accurately characterize plume profiles and emission frequencies. The mobility of the TAGA® detector permitted the pin-pointing of point source and fugitive emission. Examples are provided for industrial emissions of methyl-ethyl ketone and dimethyl sulfide. A simple method of on-site calibration was used based upon head space syringe injection. Under interactive computer control, calibration constants were determined in ca. 5 minutes per compound within the ambient air matrix. Other recent software developments are presented including the ability to simultaneously monitor up to 128 different compounds with real-time output in concentration units.

Introduction

The critical need to provide rapid analytical data in the field in response to the release (accidental or otherwise) of chemicals into the environment has prompted the development of portable, transportable and mobile analytical instruments.¹ Since air is the most mobile of the environmental media, it has the most critical needs for timely analysis. The 'on-site' approach to air analysis has many advantages particularly if the detector is sensitive, specific, and capable of real-time response. Mobile mass spectrometers incorporating ion sources capable of direct air sampling (such as atmospheric pressure chemical ionization APCI) have been in operation since 1978 and have demonstrated efficacy in a number of on-site applications including emergency response,² plume tracking,³ chemical waste dump site monitoring, and odor source characterization⁴ to name but several. Mobile tandem mass spectrometer (MS/MS) systems have been in operation since 1983 and have demonstrated a much greater specificity than single MS systems.^{5,6,7} The present work discusses applications of the TAGA® 6000EM mobile MS/MS laboratory for on-site analysis of toxic-air pollutants (TAP), volatile organic compounds (VOC) and odor causing compounds.

Instrumentation

A schematic of the TAGA® 6000EM ion optics is shown in Figure 1. A more complete description of the TAGA® instrument can be found elsewhere;⁸ briefly, however, airborne compounds are ionized directly in the high pressure ionization source. Ion source pressures can range from atmospheric (as in APCI) to as low as 0.1 to 1 Torr (for glow-discharge CI). Under APCI the ion source samples streams of air at rates up to 9 l.sec⁻¹. These high sampling rates eliminate wall- and memory-effects permitting instantaneous response to airborne contaminants. Ionization occurs in this high flow of gas converting compounds into pseudo-molecular ions (ions indicative of molecular weight). The ions are focussed through an orifice into the high vacuum analyzer portion for MS or MS/MS analysis. The glow-discharge CI ion source samples air at rates of ca. 35 ml. min⁻¹ through a heated direct air sampling inlet (DASI) which in turn samples from a high volume flow of air (up to 9 l sec⁻¹). Once again this high flow assures instantaneous response and minimal memory effects. The APCI source is very sensitive to polar compounds whereas the CI source, using charge transfer from N₂⁺, O₂⁺ and NO⁺, is sensitive toward the chlorinated hydrocarbons and aromatics.

Results and Discussion

Figure 2 shows a typical identification of a VOC from a complex chemical mixture using MS/MS. The complexity of this mixture (ambient air containing auto exhaust) is represented by the number of peaks in the CI/MS spectrum shown in Figure 2, (top) - each peak represents a pseudomolecular ion of a neutral introduced to the ion source. The complexity is typical of an urban air sample. Using MS/MS a single ionized component can be isolated and identified in the following manner; selected with Q1 (the first quadrupole), fragmented by collisions with Argon gas in Q2, and the fragment ions analyzed by Q3. The result is a CAD (collisionally activated decomposition) fragment ion spectrum of the constituent at m/z 106⁺ (Figure 2, middle). Subjecting this CAD spectrum to a library search results in an identification of the 106⁺ ions as those of o-xylene (Figure 2, bottom). Such an identification takes a matter of seconds to

accomplish so qualitative analysis of airborne mixtures can be rapid. In this case the CAD fragmentation pattern is typical of C2 substituted benzenes, therefore setting Q1 and Q3 to the appropriate mass settings (say 106 and 91 respectively) and continuously monitoring, the MS/MS detector becomes a real-time specific chemical monitor for C2-benzenes. Up to 128 different parent/fragment ion pairs can be monitored at once in this manner. Real-time quantitation is possible using response factors stored in the computer. Response factors are derived through one of two calibration procedures: (i) a simple headspace injection technique which requires that the vapor pressure of the compound is known and (ii) the use of precalibrated pressurized bottled gas mixtures containing standards which are diluted appropriately. The former technique uses user-interactive software to derive a five-point calibration curve in about 5 minutes.

The quantitative and qualitative accuracy of the TAGA® 6000 mobile MS/MS has been tested under the auspices of the US EPA (Environmental Monitoring Systems Lab) vis-a-vis non-real-time techniques (eg., cryotrap GC) and results of these tests indicated excellent agreement amongst the technologies.⁹ One of the disadvantages of real-time MS/MS analysis cited by EMSL on this study was that some isomeric VOC cannot readily be distinguished. For example, although o-xylene scored highest in the library search for the 106⁺ ion in Figure 2, 106⁺ could also be due to ethylbenzene, p- or m-xylene or a combination of these C8 aromatics i.e., their CAD spectra are very similar. This limitation has been overcome by the incorporation of a sorbent tube purge unit (Envirochem, Unacon thermal desorber model 810A) which is coupled to the TAGA® MS/MS system's GC (varian 3400) by a heated nickel transfer line. The GC is interfaced to the TAGA® by a probe which inserts into the CI ion source. In the present work a 25m BP-5 (SG&E) capillary column (0.25 mmID coupled directly to the CI source) was used to chromatographically separate isomeric C8 aromatics collected by sorbent tube trapping. The GC/MS TIC trace of automobile exhaust in ambient air is shown in Figure 3. The individual constituents were identified by their molecular ion mass and MS/MS fragment ion spectra. The sorbent material used was a combination of Tenax® and Ambersorb®. The thermal desorber-GC/MS/MS combination will obviate many of the isomer differentiation problems associated with real-time MS/MS detection. In typical field use after mobile MS/MS monitoring identifies the location of a plume, sorbent samples can be obtained, capped and stored in the on-board refrigerator for later analysis by GC/MS/MS. This scenario could also be performed using SUMMA® cylinders and cryo-trap GC/MS/MS.

In order to test the quantitative capabilities of this Thermal Desorber-GC/MS/MS combination, sorbent tubes containing 0,2,10,50 and 250 ng of chlorobenzene were sequentially desorbed into the GC/MS/MS while a prominent and specific (MS/MS) fragmentation reaction for chlorobenzene was monitored (i.e., $M^+ \rightarrow [M-Cl]^+$ or $112^+ \rightarrow 77^+$). The chlorobenzene was one of 10 standard components introduced into the tube via a multiple component diffusion source. Because of the specificity of MS/MS, the response to chlorobenzene was free of interference from the other 9 constituents and this peak response was integrated (see inset Figure 4). Figure 4 shows the integrated response vs. amount injected which resulted in a linear calibration curve ($R=0.9997$) and a response factor of 3440 counts per ng. Because we are sampling using MS/MS and pulse counting, the inherent instrument "noise" is essentially zero (the inset of Figure 4, due to the 2 ng chlorobenzene desorption, shows a noise level before the GC peak evolution of 80 integrated counts. The signal, on the other hand, is

approx. 8000 integrated counts). If one assumes a sampling volume of 3 l of air per sorbent tube (1/2 hour sampling time), we are obtaining a S/N of 100 for a concentration level of 0.13 ppb (v/v) of chlorobenzene and an inherent detection limit of 4 ppt (S/N=3). The real-time detection limit for chlorobenzene using the same ion source is ca. 2ppb in ambient air. Incorporating trapping, thermal desorption-GC/MS/MS, detection limits are, in this case, augmented by several orders of magnitude over real-time response.

Another relatively recent addition to mobile TAGA® systems is the incorporation of meteorological data directly into real-time monitoring data acquisition permitting the observation of meteorological and concentration data simultaneously. Specifically, wind speed and direction are very useful in determining source location and characteristics. An example of such an analysis is shown in Figure 5 for the detection of methyl ethyl ketone (MEK) emanating from an industrial source. While the meteorological data are being collected the mobile TAGA® laboratory remained stationary.

The met data are collected using a Lambrecht model no. 1453 meteorological data collection head mounted on a 30 foot motorized telescoping tower. A significant TAGA® response to MEK from this source was observed only when the wind was over 5 knots and out of the East or East-Northeast. Depending upon meteorological conditions and topography, plumes can be very well defined and quite narrow. As long as wind is variable (which it often is), only with the use of a real-time detector system will an accurate determination of potential peak-exposure be possible to obtain. In this case, for example, the mean level was 10 ppb while peak-levels inside the plume exceeded 100 ppb. These peak levels would not have registered using non-real-time technology (i.e., time weighted average).

Another case where meteorological data are also valuable is when the source is intermittent. Figure 6 shows the TAGA® real-time response to dimethyl sulfide (DMS) which is being monitored in the vicinity of a paper mill. The significant feature to note about this figure is that the level of DMS varies considerably whereas the wind speed and direction are relatively constant.

The large surge in DMS between 6 and 10 minutes is obviously not due to a meteorological change and must be a property of the source. As it turned out, this episode of DMS release was due to the purging of the pulp-digesters at this paper mill causing levels of DMS to rise up to approximately ten times higher than the TWA and, certainly high enough to cause odor problems in the surrounding neighbourhoods albeit for brief periods. Conventional trapping methods would not have been able to fully characterize this phenomena the time-weighted-average-TWA-concentration doesn't reveal temporal distribution. While odor problems may not impact on the health of the community odors are an important public concern.

Generally speaking, odorous or irritating substances are polar, or reactive, or both, and these properties render these compounds difficult to trap and store especially for subsequent GC analysis. It has been our experience that direct detection by TAGA® systems using APCI or CI is often the only way to detect these types of compounds at the low levels which these chemicals can cause sensory problems. Combining the ability to detect these 'difficult-to-analyze' compounds with the mobility of the TAGA® offers an effective and rapid way of pin-pointing the source and

eventually of abatement. An example of such a mobile monitoring application is presented in Figure 7.

A mobile analytical survey was undertaken in response to odor complaints in the vicinity of a rubber-products manufacturer. The TAGA® detector identified aniline and benzothiazole as possible contributors to these odor complaints by stationary sampling in the neighbourhood. A mobile survey was undertaken whereby these and other compounds were monitored while the mobile TAGA® laboratory criss-crossed streets downwind of the plant. The mobile portion of the survey took some 17 minutes, a short enough duration to ensure no great changes in meteorological conditions. The response to these analytes is shown in Figure 7, top. The distance away from the suspected source is indicated above each peak response which signifies a traverse of the plume. From these data it is apparent that both aniline and benzothiazole originate from the same source (their plumes track together). The plume concentrations decrease with increasing distance from the source however, the plume width remains fairly narrow and well defined even at 800 m. Such dispersion data are important when planning the location of stationary monitoring stations to continuously monitor the levels of TAP's emanating from such sites. Plotting up points of concentration versus sampling location renders a 2-D plot such as that in Figure 7, bottom. The plume contour is sufficiently well defined to pinpoint the source of contamination to the very building from where it originated.

Conclusion

This paper has demonstrated applications of the TAGA® 6000EM for on-site ambient air analysis for TAP, VOC and odor compounds in the ppt-ppb range. On-site and mobile analysis offers the flexibility and opportunity to change sampling protocols in response to changing meteorological conditions. Only the combination of real-time meteorological data with real-time concentration data provides key information for full characterization of the source, such as temporal variations. Mobile analysis provides plume tracking capabilities and spatial distribution of pollutants making possible rapid location of actual points of emission. Finally, the addition of ancillary trapping-thermal desorption-GC/MS/MS methods overcomes problems of isomer differentiation and augments real-time detection limits by many orders of magnitude.

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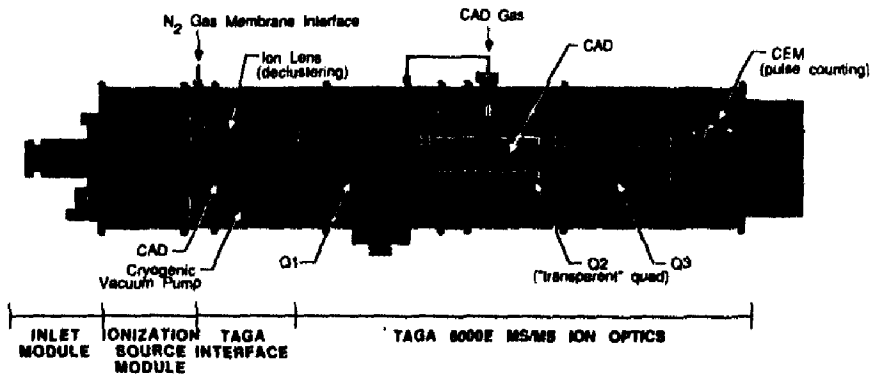
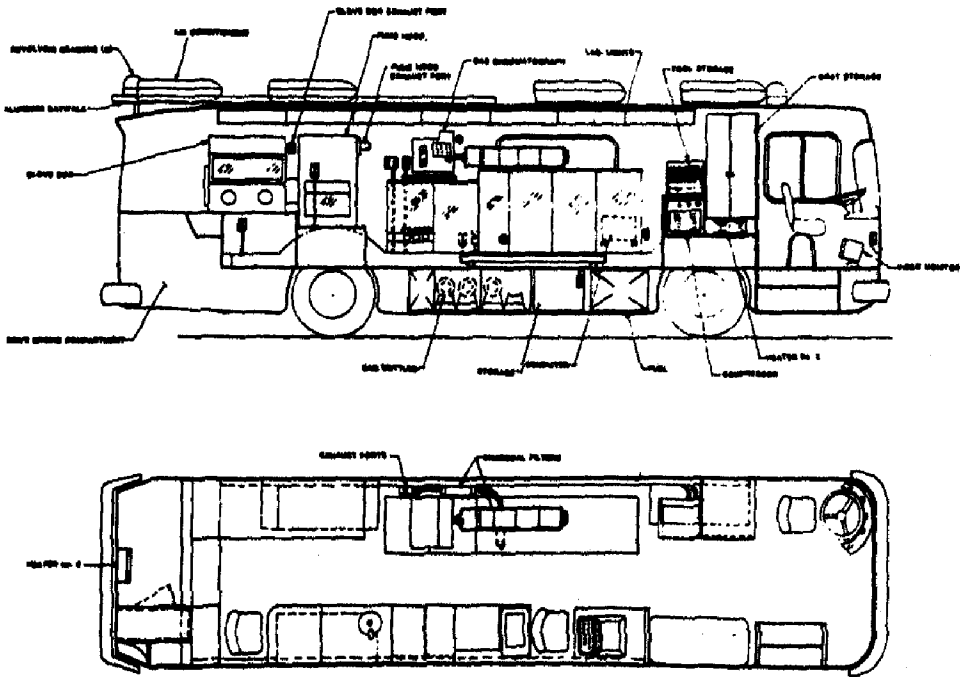


Figure 1: Schematic of the TAGA® 6000EM mobile tandem mass spectrometer



Schematic of TAGA 6000EM mobile analytical laboratory

Note: Due to lack of space, all figures could not be included. A reprint of this paper will be mailed to you by contacting: Dr.Bori Shushan, c/o SCIEX, 55 Glen Cameron Rd., Thornhill, Ontario, CANADA, L3T 1P2, (416)881-4646

PORTABLE PHOTOIONIZATION SYSTEMS WITH
COMMUNICATIONS AND DATA RETRIEVAL CAPABILITY
FOR EMERGENCY RESPONSE TO TOXIC CHEMICAL
LEAKS AND SPILLS

M. COLLINS
PHOTOVAC INTERNATIONAL INC.
741, PARK AVENUE
HUNTINGTON, NY 11743

R.D. YOUNG
PHOTOVAC INC., Unit 2
134 DONCASTER AVENUE
THORNHILL, ONTARIO L3T1L3 CANADA

In the current environmental, political and legal climate, there is a pressing need to improve emergency response at toxic chemical handling and manufacturing sites. Associated with this is the vital requirement for sensitive automated field-portable instruments which can readily be deployed to site locations in emergency situations where there has been a leak or spill of toxic chemicals and where this has to be continuously monitored.

One useful instrument which can be stationed at a perimeter boundary of a plant, landfill or underground storage tank site, is the total ionizables monitor which utilizes the photoionization detector. This instrument is microprocessor-controlled, self-calibrating, draws its own samples and can sequence by multiplexing through four channels. The unit can be calibrated to read directly in ppm with programmable "Warning" and "Danger" levels. On-board RS232 interface with auto-dial telephone modem allows remote data transfer and built-in data logging capability enables programming of sampling interval and duration.

The total ionisables monitor can be used to establish the presence of chemical plumes and further identification and measurement of individual compounds can be monitored with the microprocessor controlled 10570 portable photoionization gas chromatograph. This unit also has auto-dial modem with RS232 interface to transfer chromatographic analysis data. The analytical capability of the 10570 has been significantly enhanced by the use of wide bore capillary columns which have been encapsulated in an epoxy resin for field resilience.

Automated Total Ionizables Present (AUTOTIP) Air Analyzer

Instrument Features

The basis of the AUTOTIP is a sensitive photoionization detector (PID) capable of detecting airborne chemical contaminants from 0.1 - 2000 PPM. A built-in pump draws air sample through the PID and the extent of ionization of gases and vapors is measured in terms of a calibrated parts per million (ppm) output displayed in digital mode.

The AUTOTIP is contained in a waterproof enclosure approximately 9 in. high, 12 in. wide and 5 in. deep and the weight of the instrument is approximately 15 lb. Figure 1 gives a pictorial view of the unit. Figure 2 shows the layout of the program keyboard and indicators. Access to the keyboard is via a outer door with a window which permits viewing of the display and indicators. The keyboard and indicators are mounted to the inner door which can in turn be opened to enable the user to insert or withdraw various option cards. Four L.E.D.s are also located on the inner door. Green indicates "Normal" running, amber and red indicate two alarm levels "Warning" and "Danger" respectively. The fourth L.E.D. signals a "Fault" with the system. AUTOTIP is based on the 6809 microprocessor with up to 32K of program memory and up to 16K of data memory. A sample probe line is connected to the unit and the line can extent up to 1000 ft.

Operation

"Program" and "Option" keys will enter the program mode for chosen functions and these keys also enable numeric entry. The "Exit" key will abandon any program changes made and return the user to the monitoring mode. "Clear" will delete the latest entry and "Enter" will take the user to the next step.

The top line of the display is used to prompt the next entry and the bottom line is used to enter the date and time. Switching the AUTOTIP "On", will prompt the user to enter the calibration interval (in minutes) followed by the concentration of the calibrant. The unit will then self-calibrate at the programmed interval. Various pertinent parameters indicating the two alarm levels, date and time can be programmed. Using the "Test" key, and a series of test codes enables electronic diagnostics on the system.

The "Option" keys permit data logging over a sample interval and timed duration. In the multiplexing mode, the frequency of each sample input and duration can be entered. For remote surveillance, the baud rate is entered. With modem operation, the phone number to call is entered.

The 10570 Portable Photoionization G.C.

The features of this instrument are shown in Figure 3. The design of its PID has been reported previously (1,2) and incorporates an ultraviolet light source excited by electrodeless RF coupling. The PID operates with air as carrier gas and achieves unprecedented sensitivity to a large number of gases and solvent vapor (benzene can be detected to concentrations as low as 0.1 part per billion (ppb) in a 1ml sample of air).

Analytical Technique

The 10S70 employs the precolumn/backflush technique in order to perform continuous, unattended monitoring. A Teflon probe line, (which can extend up to 40 ft), is connected to the instrument. Air sample is drawn into the sample loop within the 10S70 via a small internal pump and a precisely determined portion of the sample loop is automatically injected into two columns in series on a timed basis.

The versatility of this precolumn/backflush configuration has been enhanced by the incorporation of wide bore capillary columns into the 10S70. For reasons of fragility, these columns have found limited use in field portable G.C.s but, an encapsulation method has recently been developed which protects the columns against vibrational or frictional damage. A typical chromatogram of a vapour mixture is provided in Figure 4. This result was achieved using a 10m x 0.53mm i.d. CPSil 5CB, (5u film) capillary column configured as a precolumn/backflush system.

Communications Function

The 10S70 is equipped with an RS232 interface and can be connected to a remote terminal or specially programmed computer. In addition, the 10S70 has a telephone modem so that remote communications can be performed over a phone line. By programming the 10S70 with the appropriate telephone number, the instrument can "call in" to an off-site location and a password system prevents access to the instrument by unauthorized personnel.

A new software package has been developed which allows chromatograms to be automatically stored on disc and the data to be subsequently retrieved. A reference chromatogram can be scale expanded and smoothed to subtract ghost peaks and other artifacts. Figure 5 shows a reference and last sample chromatogram superimposed for comparison and verification of chemical identity.

Conclusion

With the capability to communicate and be remotely controlled, the AUTOTIP and 10S70 G.C. enable considerable time saving in terms of the hours the environmental scientist has to operate at the site. With the phone line connections, the terminal can be set up off-site at another facility from which the situation can still be monitored safely.

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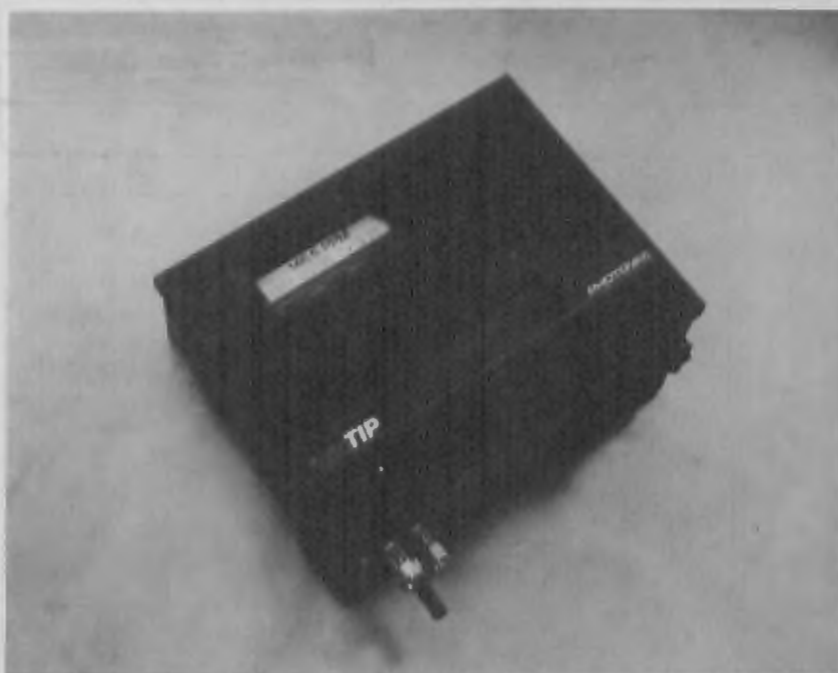


Figure 1 Automatic total ionizables present (AUTOTIP)
air analyzer.

Figure 2 Autotip keyboard and indicators.

<div style="border: 1px solid black; padding: 5px; margin-bottom: 5px;"> 0.123 PPM </div> <div style="display: flex; justify-content: space-between; padding: 5px 0;"> APR. 15/87 11:27 </div>			
FAULT	NORMAL	WARNING	DANGER
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

P R O G R A M	DATE	TIME	TEST	
	1	2	3	ENTER
	CALIBRATE	WARNING	DANGER	
	4	5	6	CLEAR

O P T I O N S	DATA LOG	MULTIPLEX	REMOTE	
	7	8	9	EXIT
	ANALOG			
	-	0	-	ALARM REPLY



Figure 3 10S70 Portable photoionization G.C.

FIGURE 4

SEPARATION OF VARIOUS SOLVENTS USING
AUTOMATIC INJECTION OF A VAPOR MIXTURE

Column: 10 m x 0.53 mm CP Sil 5CB
(cut in a 1:8 precolumn:
analytical column arrangement)

Flow rate: 20 mL/min.

Chart speed: 1 cm/min.

Total Analysis Time: Approx. 20 minutes

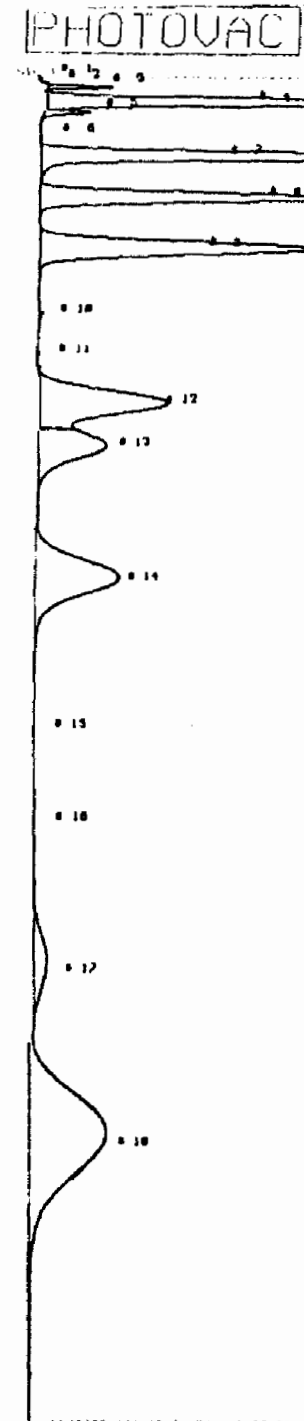
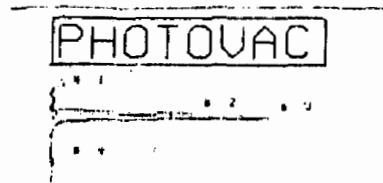


CHART # 1200.4
JAN 20 82 9:3
SAMPLE RUN
ANALYSIS # 3 AUTO INJECT
TEMPERATURE 22 FLOW 20ML MIN
GAIN 5 CP-SIL5
OFFSET 0.0 MV
SCANNING SPEED 1 CM/MIN
SLOPE GENS. 5 MV/SEC
WINDOW 10 Percent
MINIMUM AREA 100 mVSEC
PLOTTER DELAY 10.0 Sec
ANALYSIS TIME 1200.4 Sec
CYCLE TIME 0 Min

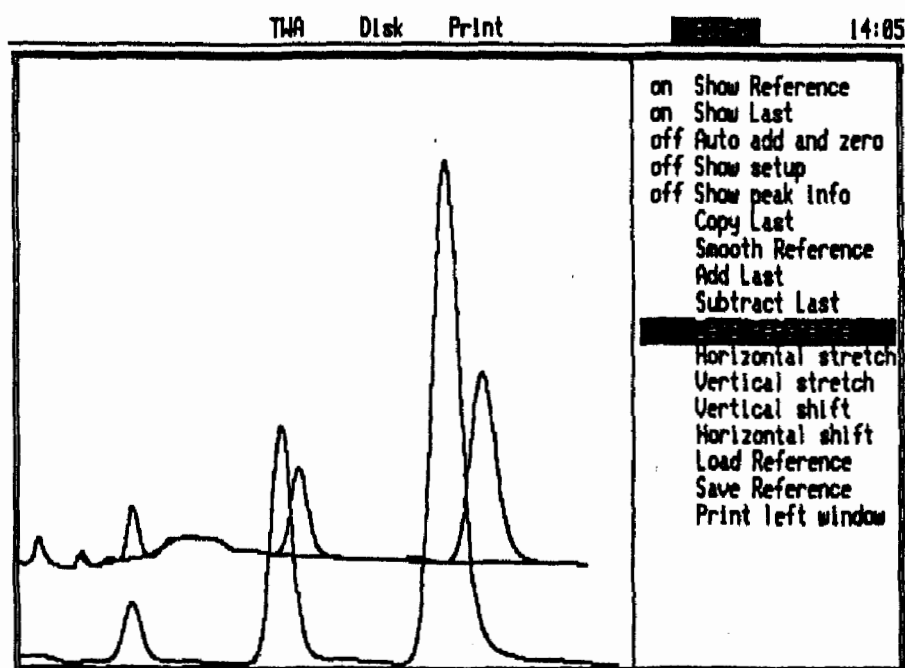


ISOPROPYL ALCOHOL
PROPYLENE OXIDE

JAN 20 82 9:3
SOURCE FIELD: 28
SOURCE POWER: 40
SAMPLE LEVEL 0.0 10.0
CAL LEVEL 0.0 0.0
EVENT 3 LEVEL 10.0 100.0
EVENT 4 LEVEL 10.0 11.0
EVENT 5 LEVEL 11.0 220.0

COMPONENT NAME	PEAK	RT	AREA/PPM
ISOPROPYL	1	1.7	500.0 PPM
ALCOHOL	2	21.4	52.0 PPM
ISOPROPYL	3	21.6	49.7 PPM
ETHANOL	4	24.4	19.1 PPM
BENZENE	5	34.7	6.4 PPM
ETHANOL/ETHANOL	6	37.5	5.4 PPM
ETHANOL	12	37.5	5.4 PPM
ETHANOL/ETHANOL	13	38.5	14.2 PPM
ETHANOL	14	42.4	5.2 PPM
ETHANOL	15	44.1	4.0 PPM
ETHANOL	16	44.1	12.0 PPM

FIGURE 5 CHROMATOGRAPHIC DATA RETRIEVED FROM DISC



Printer is now printing
Press enter to shift lowest point of Reference down to bottom of window.

EVALUATION OF PHOTOVAC 10S50 PORTABLE
PHOTOIONIZATION GAS CHROMATOGRAPH
FOR ANALYSIS OF TOXIC ORGANIC POLLUTANTS
IN AMBIENT AIR

Richard E. Berkley
Methods Development and Analysis Division
U.S. EPA, Environmental Monitoring Services Laboratory
Research Triangle Park, North Carolina

Analysis of toxic organic vapors in air is usually done by preconcentration from air, followed by GC/MS analysis. The preconcentration step is a source of numerous errors which limit the credibility of quantitative results. Also, the method is expensive and slow. A method of getting data quickly and inexpensively for screening purposes is needed. Also a method which does not involve preconcentration might provide a valuable supplement to GC/MS data. An instrument which may be capable of meeting these needs is the Photovac 10S50. It is a portable gas chromatograph equipped with a sensitive photoionization detector. It is claimed to be capable of detecting 0.1 part per billion of benzene in air.

During laboratory evaluation, the benzene detection limit of the Photovac 10S50 was estimated to be 95 femtograms, equivalent to a concentration of 0.03 part per billion. The instrument was subjected to preliminary field evaluation in Houston, Texas. Low levels of apparent contamination by calibrant were observed. Several unidentified compounds were present at high levels for which the unit was not calibrated. The apparent maximum possible level of chloroethylene was 0.5 parts per million. Apparent maximum possible levels for multiply-chlorinated ethylenes were less than 25 parts per billion. Apparent maximum possible levels of benzene and toluene were less than 10 parts per billion.

Introduction

Analysis of vapor phase organic compounds in ambient air is usually done by gas chromatography using a mass spectrometer as detector (GC/MS). The principal advantage of GC/MS is its selectivity and range of applicability. Its principal disadvantage is that preconcentration of analytes is necessary because GC/MS cannot tolerate large quantities of oxygen and water and because mass spectrometers cannot detect ambient levels of analytes in samples small enough to be chromatographed. Unfortunately, preconcentration produces many errors. Efficiency of collection and delivery to the GC/MS is low and variable for many compounds, and numerous artifacts are formed (1). Although preconcentration and GC/MS analysis of organic vapors in ambient air is at best a semiquantitative method which is expensive and labor-intensive, its effectiveness in qualitative analysis makes it virtually indispensable. However, a method of analyzing pollutants directly without separating them from air, especially if it were based upon a completely different approach to sampling and detection, might supply data unspooled by gross sampling errors. However, to detect one part per billion by volume of benzene in one milliliter of air would require the capability of detecting three picograms.

Photoionization detectors are sensitive enough to detect many toxic organic pollutants without preconcentration. Though more sensitive than GC/MS they are less selective. For such a sensitive detector, preconcentration would not be required so most sampling errors could be avoided. Without sampling errors, a chromatographic peak which appears within the retention time window of a particular compound must be due to the presence of that compound or another with similar retention time. Positive identification is not established from such an observation, but the "identified" compound cannot actually be present at a higher level than indicated without some negative interference in the sampling or chromatographic processes. Therefore data for most compounds would provide credible estimates of the upper limits of true concentrations.

The Photovac 10S50 is a portable gas chromatograph with a highly sensitive photoionization detector. It is primarily designed for industrial hygiene analysis of airborne organic compounds. It is self-contained, mounted in an aluminum case with internal electric power and carrier gas supplies. The unit measures 46 X 16 X 34 centimeters (18.25 X 6.25 X 13.25 inches) and weighs 11.8 kilograms (26 pounds). It is equipped with a microcomputer which controls sampling and analysis and processes data, and it has a built-in printer-plotter. This unit possesses significant advantages over conventional gas chromatographs:

- a. It is portable.
- b. Its detector is sensitive enough to respond to ambient background levels of benzene, toluene, and the chloroethylenes without preconcentration. It could be used as-is to screen for these compounds in ambient air or near hazardous waste sites. It also could be used to supplement or complement GC/MS analysis.
- c. Typical analyte concentrations are far below levels which could overload the column and lead to tailing or distortion of peaks.
- d. It is tolerant of oxygen and blind to water. Separation of analytes from air is unnecessary.
- e. It can be transported without special preparation.

There are also some disadvantages:

- a. Detection is not specific. "Identification" of a compound is evidence, but not proof, of its presence.
- b. The unit may only be operated at ambient or slightly elevated temperatures. This limits the quality of chromatographic resolution, and only compounds which have high vapor pressures at ambient temperatures can be analyzed.
- c. Calibration standards of known accuracy are difficult and expensive to prepare.

Experimental

An extrapolated detection limit for benzene was determined (2). Aliquots of NBS Standard Reference Material No. 1805 (0.254 parts per million of benzene in nitrogen) were injected into the unit with gas tight syringes at a constant gain of 50, and data for each injection were stored on disk. Output signal was sampled at intervals of 0.2 second. The benzene peak was displayed, and start and end points for the peak were determined by inspection and input to the computer. Peak area was measured by drawing a line between the start and end points and summing the heights of all data above the line. The standard deviation of the 40 baseline points immediately before the beginning of the peak plus the 40 baseline points immediately after the end of the peak was calculated. These data were stored on disk, and another program was used to retrieve them, plot peak area (volt*second) versus amount injected (picograms), and perform a linear regression analysis. The slope was 0.502 volt*second/picogram with an intercept of 6.4 volt*second and a correlation coefficient of 0.999. The aggregate standard deviation of baseline points for all peaks was 0.0238. The detection limit was taken to be twice the aggregate standard deviation of baseline points divided by the slope, or 95 femtograms. It was equivalent to a concentration of 0.03 parts per billion by volume of benzene at 25 C, which was lower than the manufacturer's claim of 0.1 part per billion and much lower than required to detect 1 part per billion of benzene in air. This was an extrapolated detection limit, the smallest sample actually injected being 1.63 picograms. The detection limit of 95 femtograms was lower than the value of 800 femtograms obtained by Clark and coworkers who used a Photovac 10A10 chromatograph with the same detector (3). It was higher than the extrapolated detection limit of 17 femtograms obtained in our laboratory using the same method with a Photovac 10A10 which was operated at maximum gain.

Field operation of the unit was carried out in Houston, Texas during March, 1987. The calibration library was generated upon arrival in the field using as standards commercially prepared mixtures of six compounds in nitrogen. Most sampling was done from inside an automobile by using the sampling pump to draw in air through a length of teflon tubing. Typical data are shown in TABLE 1. It is evident that contamination of the unit by compounds present in the Mixture used for recalibration must have contributed to the levels of some of the compounds observed. The levels actually present could not have exceeded the amounts shown. They must be presumed to define true upper limits to the levels of target compounds which could have been present. Nevertheless, it is apparent that this unit, as-is, should easily be capable of detecting the part per million or lower levels of benzene, benzene derivatives, and halocarbons which raise concern about public health when they are found near hazardous waste sites and other sources.

Results and Discussion

Several problems were encountered during evaluation. The most serious were related to lack of temperature control in the column compartment. Sunlight falling on the instrument rapidly heated the interior. At a gain of 100 this caused a large upward baseline drift. When the unit was moved out of the sun, the baseline drifted downward and disappeared from the chart for about half an hour. Retention times and detector sensitivity also vary with temperature. The internal solenoid valves were another source of heat. They are mounted adjacent to the column enclosure and generate considerable heat when energized. This can cause significant temperature excursions over time periods much shorter than the duration of a run. It was noticed that when the unit was manually recalibrated immediately after a calibration run, the indicated temperature often dropped by a centigrade degree during the short interval while the first quantitation report was being printed. The temperature sensor is not located inside the column enclosure, so it was not apparent how much column temperature actually was affected by the solenoid valves.

Miscalibration (failure to calibrate the right peak) is apt to occur if automatic sampling is attempted at high gain. Extraneous peaks are seen at high gain in all calibration gases, even NBS Standard Reference Materials. The number of them changes with temperature. Because the calibrant peak is identified by peak number, the appearance of variable numbers of extra peaks limits feasibility of unattended operation at high gain. When a peak other than the calibrant receives the peak number designated for the calibrant, that peak becomes recognized as calibrant, and its area is matched with the concentration information for the calibrant being used by the microprocessor. Typically, the peak is much smaller than the real calibrant peak, and necessarily has a different retention time. This puts the unit catastrophically out of calibration until the next time the true calibrant peak is found during a calibration run. The only means of preventing such errors is timely action by the operator. Miscalibration could cause serious errors in time-weighted averages of results obtained during unattended operation at high gain.

It is difficult to provide suitable calibration standards for such a sensitive instrument. Part per million levels of most potential target compounds in nitrogen or air can be purchased, some of them traceable to NBS standards, and these are suitable for compiling calibration libraries. For field recalibration, levels in the low part per billion range are needed in order that the instrument can be operated at high gain. Such standards are not widely available; they are expensive to prepare; contaminants are likely to be present at levels similar to calibrant; and storage stability could be a problem. Such problems are not the fault of the instrument manufacturer or of the producers of calibration standards. They are inherent problems of working at such low levels.

Several minor software problems were observed. The unit was not able to report results below one part per billion. It could be "fooled" into doing so by entering a calibration gas concentration which was one or more orders of magnitude higher than the true one and then making corresponding corrections to resulting data. If practiced regularly, such an expedient must eventually lead to confusion. It would be better if the software were adapted to report part per trillion levels. Integrations performed at high gain may refer to the baseline level at the start of the run, rather than the baseline at the time the peak eluted. If the baseline has drifted, as it is likely to do at high gain, a considerable integration error will result. Also, the way in which the baseline is drawn in for an integration is dependent in a poorly-predictable way on which integration parameters

have been entered. A better integration subroutine or a better explanation of it would be useful. When entering information into the microprocessor, mistaken key punches are irreversible. The operator has no option but to continue with whatever procedure was inadvertently started. The consequences can vary from a loss of recalibration data to an annoying wait for the printer to finish printing unwanted information.

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Disclaimer

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

TABLE 1. SAMPLING AMBIENT AIR IN DEER PARK AT A TAMS SITE. (a)

3-26-87 J. P. Bonnette Junior High School in Deer Park. Partly cloudy.
Wind NE light. Approximately 20 C. Texas Air Control Board
Monitoring Site.

Time of day	15:00	15:13		
Chloroethylene	*	130		
Retention time (seconds)	11.0	11.4		
1,1-Dichloroethylene	*	2		
Retention time (seconds)	43.8	44.5		
Benzene	*	D		
Retention time (seconds)	131.6	131.9		
Trichloroethylene	*	8		
Retention time (seconds)	204.8	207.8		
Gain	100	100		
Unit temperature (C)	32	31		
Time of day	15:24	15:37	15:49	16:02
Chloroethylene	*	121	93	89
Retention time	10.9	11.5	11.5	11.5
1,1-Dichloroethylene	*	D	ND	ND
Retention time	44.5	44.9		
Benzene	*	D	D	D
Retention time	132.2	132.2	131.9	132.2
Trichloroethylene	*	8	5	4
Retention time	208.8	209.3	209.8	209.3
Gain	100	100	100	100
Unit temperature (C)	32	31	31	32

* Calibration run.

D Detected below 0.5 part per billion.

ND Not detected.

(a) Concentrations are in parts per billion.

**HALOCARBON ANALYSIS OF NMOC AIR SAMPLES
BY GC/MEGABORE/ELECTRON CAPTURE DETECTOR**



A.L. Sykes,
Radian Corporation
Analytical Chemistry Department
Research Triangle Park, North Carolina

Harold G. Richter
Office of Air Quality Planning and Standards
Office of Air and Radiation
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina

The U.S. EPA has for a number of years sponsored a Nonmethane Organic Compound (NMOC) air monitoring program. For the past three years Radian Corporation has conducted the most intensive nation wide sampling and analysis program under contract to EPA. The primary gas chromatography (GC) analysis procedure for NMOC measurement has been a cryogenic preconcentration direct flame ionization (PDFID) method, trapping approximately 300 mL of air on a glass bead trap, followed by ballistic heating to 90°C and detection by flame ionization. During the previous year's effort an additional GC analytical procedure was incorporated into the program. A 6-port gas sampling valve was used to inject 1 mL of sample onto a J&W DB-624 Megabore¹ fused silica column with electron capture detection. The DB-624 column was designed to separate 27 volatile halocarbon priority pollutants without subambient oven temperatures. The detection limits of these halocarbons ranged from 2 to 35 parts per billion in each 1 mL of sample. Calibration standards were prepared in the range of 35 to 50 ppb by dilution of known amounts of each compound in hydrocarbon free air. Over 170 ambient air samples were analyzed during the program in addition to 2 EPA audit samples.

HALOCARBON ANALYSIS OF NMOC AIR SAMPLES BY GC/MEGABORE/ELECTRON CAPTURE DETECTOR

Introduction

Radian Corporation has assisted EPA for the past three years in acquiring an excellent database of NMOC data. The PDFID method, with argon cryotrapping has proven to be a good procedure that can provide NMOC results from many air monitoring sites. There has been much interest in volatile halocarbons and "air toxics" in the urban environments, but the traditional technique of NMOC does not provide halocarbon speciation or quantification. The work discussed here is a more in-depth study of NMOC air samples collected in July, August, and September 1986, and has provided EPA and the States with additional information as to the halocarbon content at various NMOC air monitoring sites across the nation.

Experimental

Description of Analytical Procedure

Ambient air samples were collected in evacuated 6-liter Summa polished stainless steel canisters over a three hour period which resulted in approximately 15 psig of pressure. The canisters were previously cleaned by a series of four evacuations to 5mm Hg, and pressurizing to 40 psig with cleaned, dry air. These samples were analyzed for NMOC by the PDFID method. After argon cryotrapping the ambient air on a glass bead trap, the GC oven was ballistically heated to 90°C, and the response integrated over a 2-min time period. Propane was used as the calibration standard.

The samples were then analyzed by GC/electron capture detection, which was selective for halogenated and other electronegative compounds (ie. oxygen and nitrogen containing). A gas sampling valve was used to inject 1-ml of sample onto a DB-624 megabore fused silica capillary column. The megabore column was 30 meter x 0.53mm i.d., and was developed by J & W Scientific, Inc. for purgeable organics as specified in EPA methods 601, 602, and 624.² These methods are intended for analysis of water samples using a purge and trap concentration technique, which Radian did not use. Method 601 also uses the Hall Detector which is specific for chlorine and bromine compounds, and 602 is for organic purgeables with flame ionization detection. Method 624 is a GC/MS procedure.

Instrument and Conditions

Instrument:	Varian 3400 gas chromatograph
Detector:	Ni ⁶³ Electron Capture @ range 10
Data System:	Spectra-Physics Model 4270
Column:	J & W, DB-624 Megabore, 0.53mm x 30m fused silica
Carrier gas:	Helium @ 5 mL/min
Makeup:	Nitrogen @ 25 mL/min
Injection:	Valco 6-port gas sampling valve with 1.0 mL loop
Valve Temp:	100°C
Inj. Temp:	100°C
Detector Temp:	250°C
Col. Temp:	35°C to 140°C @ 5°C/min

Calibration Procedures

A calibration stock solution (20ppm) in methanol of purgeable organics containing 31 compounds for EPA Method 624 analysis was obtained from ULTRA

Scientific. Only 24 compounds were resolved or detected using the ECD/megabore column. A gaseous working standard was prepared by injecting a known volume of the stock solution into a stream of zero air flowing into a 6-liter stainless steel container. The container was then pressurized to a known volume. The working standard concentrations ranged from 17 ppb to 35 ppb in air. One mL of the working standard was injected using the Valco valve. The concentration in ppb of each compound was divided by the area counts to calculate its response factor. These response factors were multiplied times each compounds' area counts to obtain its concentration. The detection limits of the compounds of interest were 1 ppbV, except vinyl chloride and chloroethane, which were 8 and 35, respectively. Gas chromatography/mass spectrometry was used to verify the elution order of these compounds. The following is a list of the compounds and their retention times:

Compound	RTmin	Compound	RTmin
Chloromethane	3.23	Bromodichloromethane	13.28
Vinyl chloride	3.52	<i>trans</i> -1,3-dichloropropene	14.33
Bromomethane	4.13	<i>cis</i> -1,3-dichloropropene	15.63
Chloroethane	5.08	1,1,2-trichloroethane	16.03
1,1-dichloroethylene	6.09	Tetrachloroethylene	16.47
<i>trans</i> -1,2-dichloroethene	7.54	Dibromochloromethane	16.96
Chloroform	9.54	Chlorobenzene	18.68
1,1,1-trichloroethane	9.93	Bromoform	20.48
Carbon tetrachloride	10.33	1,1,2,2-tetrachloroethane	21.79
1,2-dichloroethane	10.71	1,3-dichlorobenzene	24.22
Trichloroethylene	12.21	1,4-dichlorobenzene	24.54
1,2-dichloropropane	12.61	1,2-dichlorobenzene	25.41

Results and Discussion

Table I summarizes the halocarbon concentration data by compound. The frequency of occurrence gives the number of samples in which the compound was found. Only 15 of the 24 target compounds occurred at or above the method detection limits. The frequency of occurrence of these compounds varied from a minimum of one for 1,1,2,2-tetrachloroethane to a maximum of 142 for *cis*-1,3-dichloropropene. The average occurrence was 47. The mean concentration of the compounds ranged from 1.1 ppbV for carbon tetrachloride to 434 ppbV for chloroethane, averaging 45.2 ppbV overall. Chloroethane had the highest maximum concentration of 8327 ppbV. A closer look at comparisons between frequency of occurrence and mean ppbV concentrations reveals that only vinyl chloride occurred above the average for both. Bromomethane had the second highest occurrences, but only a mean concentration of 8.7 ppbV. Tetrachloroethylene had the fourth highest occurrence at 92, with a low mean concentration of 2.9 ppbV.

Table II summarizes the halocarbon concentration data by site. The mean concentrations ranged from 16.8 ppbV for site #8 to 239.9 ppbV for site #14. The measured maximum ppbV values ranged from 59 at site #3 to 8327 at site #14. The average number of identifications among all sites was 47. The summary statistics in Tables I and II are representative of the samples collected at the sites and apply to those halocarbons identified. The statistics should not be used to represent all halocarbon compounds, or to be representative of average of concentrations across the country.

Two audit samples, designated "A" and "B" in Table III, containing seven halocarbons each were provided by EPA-QAD. These audit samples were used to obtain an estimated accuracy of the sampling and analysis method. The concentrations in the original samples, and the measured results are

given in Table III. The percent bias ranged from -56.4 to -7.7, averaging -27.0. The absolute percent bias averaged 35.3.

Conclusions and Recommendations

From the results of this work we can conclude that ambient halocarbon measurements can be easily conducted on NMOC air samples with adequate detection limits and compound selectivity using a commercially available Megabore fused silica column with electron capture detection. The Megabore column allows good compound separation without subambient oven temperatures. This prevents water vapor in the sample from freezing and plugging the column. Direct injection onto the column was done without the need of preconcentration techniques.

Recommendations are to expand the current analytical system to measure air toxics by combining a versatile sample interface and multi-detector GC/Megabore column analytical system. Radian Corporation is currently developing and will evaluate such a system which will include photoionization/flame ionization/electron capture detectors. The sample introduction interface will allow a choice of unconcentrated, adsorbent trapping, or cryotrapping techniques to be used with gas chromatographs with multiple detectors or with mass spectrometers.

Acknowledgments

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References

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2. Federal Register, 40 CFR Part 136; Vol. 49, No. 209; Friday Oct. 26 1984, EPA Methods 601, 602, 624.

Table 1. 1986 HALOCARBON DATA SUMMARY, BY COMPOUND

Halocarbon	Frequency of Occurrence	Halocarbon Concentration, ppbV		
		Min	Mean	Max
Vinyl chloride	102	7.9	78.8	662.0
Bromomethane	127	1.0	8.7	126.0
Chloroethane	37	8.6	434.1	8327.0
1,1-Dichloroethylene	3	2.7	51.9	92.9
Chloroform	35	1.3	8.2	48.3
1,1,1-Trichloroethane	91	1.0	2.5	5.9
Carbon Tetrachloride	2	1.0	1.1	1.2
Trichloroethylene	17	1.1	7.0	68.7
cis-1,3-Dichloropropene	142	3.2	24.9	66.2
1,1,2-Trichloroethylene	14	8.7	63.1	228.0
Tetrachloroethylene	92	1.0	2.9	66.2
Dibromodichloromethane	2	1.8	8.0	14.2
1,1,2,2-Tetrachloroethane	1	1.2	1.2	1.2
1,3-Dichlorobenzene (m)	23	4.5	24.2	163.0
1,4-Dichlorobenzene (p)	22	2.9	37.1	294.0
Overall		1.0	45.2	8327.0

Table II. 1986 HALOCARBON DATA SUMMARY, BY SITE

Site Code	Number of Identifications	Min	Halocarbon Concentrations, ppbV	
			Mean	Max
1	44	1.0	60.9	611
2	39	1.0	55.0	517
3	24	1.4	17.4	59
4	34	1.2	28.4	211
5	39	1.2	13.7	79
6	40	1.1	26.4	538
7	45	1.0	39.6	1220
8	46	1.0	16.8	82
9	42	1.0	17.4	183
10	50	1.0	30.0	513
11	37	1.1	20.0	126
12	33	1.0	49.7	1188
13	44	1.1	23.5	294
14	40	1.0	239.9	8327
15	35	1.0	75.2	1701
16	39	1.0	22.1	105
17	51	1.0	38.6	343
18	28	1.5	36.3	211
Overall	710	1.0	45.2	8327

Table III. HALOCARBON AUDIT SAMPLE RESULTS

Compound	Audit Sample Concentrations, ppbV		Measured Concentrations, ppbV		Percent Bias		Absolute Percent Bias	
	A	B	A	B	A	B	A	B
Chloroform	27	13	21	13	-22.2	- 7.7	22.2	7.7
1,1,1-Trichloroethane	45	21	33	17	-26.7	-19.0	26.7	19.0
Carbon tetrachloride	34	17	17	9	-50.0	-47.1	50.0	47.1
1,2-Dichloroethane	55	27	24	13	-56.4	-51.8	56.4	51.8
Trichloroethylene	48	24	22	11	-54.2	-54.2	54.2	54.2
1,2-Dichloropropane	44	22	57	15	29.5	-31.8	29.5	31.8
Tetrachloroethylene	42	21	30	18	-28.6	-14.3	28.6	14.3
Average					-21.6	-32.3	38.2	32.3
Overall average						-27.0		35.3

A PROTOTYPE SAMPLER FOR PRECONCENTRATING AND
TRANSFERRING VOLATILE ORGANIC COMPOUNDS FROM
AMBIENT AIR TO PASSIVATED CANISTERS

by

Michael W. Holdren and Deborah L. Smith
Battelle Columbus Division
505 King Avenue
Columbus, OH 43201-2693

and

William A. McClenny
Environmental Monitoring Systems Laboratory
MD-44
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

INTRODUCTION

The Methods Development and Analysis Division of the Environmental Monitoring Systems Laboratory (EMSL) of the U.S. Environmental Protection Agency is responsible for the development and evaluation of state-of-the-art and emerging analytical techniques for the determination of organic compounds in ambient air. Recently a prioritized list of volatile organic compounds has been established by EPA. EMSL is focusing on further development of analytical methodology for the determination of these compounds.

Developmental efforts during previous work (Contract No. 68-02-3487 (WA-37 and WA-22)) resulted in the following: (1) an automated gas chromatograph (GC) system that uses reduced temperature preconcentration to collect volatile organic compounds (VOCs) and (2) documentation of adequate storage of volatile organic compounds in Summa polished canisters. The automated GC system has operated in a sampling and analysis mode at several field sites using reduced temperature preconcentration to enhance system sensitivity. Other sampling scenarios have involved utilizing the Summa polished canisters to collect and temporarily store a sample prior to analysis with the automated GC which was based at the research laboratory.

The current task is a feasibility assessment of non-cryogenic preconcentration techniques. Specifically a prototype sampler was developed to collect and transfer VOCs to temporary storage vessels (Summa polished canisters). The sampler incorporates parallel Tenax traps to sequentially adsorb and desorb organic species in ambient air. Sample enrichment is achieved by utilizing less volume flow in the transfer process than in the collection process. This paper discusses the design, construction and preliminary evaluation of the prototype system.

EXPERIMENTAL

INSTRUMENTATION

Backflushing Sample Preconcentrator

A diagram of the prototype backflushing sample preconcentrator (BFSP) is shown in Figure 1. All component parts have been mounted onto an aluminum carrying case and include the following:

- (1) An 8-port 2-position switching valve and actuator (Hach Company).
- (2) Two Tenax traps (10" by 1/4" S.S. U-tubes) wrapped with heating wire. Each trap contains 0.7 grams of 35/60 mesh Tenax GC.
- (3) Two temperature controllers (Omega Engineering, Inc.).
- (4) Nitrogen (0-10 cc/min) and air (0-500 cc/min) mass flow controllers and console (Tylan, Inc.).
- (5) A dual diaphragm pump (Thomas Industries, Inc.).
- (6) A timer for control of valve actuator and trap heaters (designed and built at Battelle Columbus Division).

The timing cycle for the backflushing sample preconcentrator is shown in Figure 2. At time zero trap No. 1 is in the desorption position with heat being supplied via temperature controller No. 1. Trap No. 2 is at room temperature and is in the collection position. After 7 minutes into the run, temperature controller No. 1 is turned off to prepare trap No. 1 for collection which will be initiated 8 minutes later (i.e., 15 minutes from time zero). After 15 minutes into the run the valve actuator is activated so that trap No. 2 is now in the desorption position with heat being supplied via temperature controller No. 2. Trap No. 1 which has cooled to room temperature is now in the collection position. Approximately 1 minute is required to reach the trap desorption temperature (180°C) while five to six minutes is necessary to cool the trap to room temperature. The valve and heater timing intervals can be varied from several minutes to one hour. During the actual test runs, the BFSP unit was operated as follows:

collection cycle: 15 minutes
 heat desorption cycle: 7 minutes
 desorption temperature: 180°C
 nitrogen flow: nominally 7 ml/min
 air flow: nominally 120 ml/min

Expected concentration enrichment factors were calculated as the ratio of the measured air and nitrogen flow for each experiment.

Whole Air Canister Filling System

The canister filling apparatus consisted of the following. A stainless steel pump (Metal Bellow Corp., Model MB-158) directed flow through a mass flow controller (Tylan MC-260) and into a stainless steel canister. The mass flow controller was maintained at 20 ml/min during sampling.

Canister Cleaning Apparatus

In preparation for use with the BFSP unit or with the whole air filling system, each canister was sequentially filled (15 psig) and evacuated (25" Hg) five times using ultra zero air 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 organics originating in the pump oil

from back-streaming into the can. Following the final evacuation each canister was connected to the appropriate filling apparatus.

Automated Gas Chromatographic System

Sample canisters were analyzed with an automated GC system employing cryogenic trapping techniques. Briefly, the system is equipped with flame ionization and mass selective detectors. A 50 m by 0.32 mm i.d., OV-1 fused silica column (Hewlett Packard) was used to resolve the volatile organic compounds. Optimum analytical results were achieved by temperature programming the gas chromatographic column from -50°C to 150°C at 80°C/min. Zero grade helium (Matheson) served as the carrier gas (3 mL/min). The column exit flow was split so that 1 mL/min entered the mass spectrometer, while the remaining flow passed through the flame ionization detector.

A Perma Pure dryer (Model MD-125-48F) with a tubular hygroscopic ion-exchange membrane was used to remove water vapor selectively from mixed gas streams. The dryer was purchased in a shell and tube configuration. Sample flow through the tube was maintained at 40 mL/min with a mass flow controller (Tylan MC-260). A counter-current flow of dry zero air (200 mL/min) was used to purge the shell.

PROCEDURE

Laboratory test runs involved challenging the BFSP unit with a dilute calibration mixture of 41 organic compounds (2 to 3 ppb each). The BFSP canister sample results were ratioed with the results from the direct analysis of the dilute calibration mixture to obtain a measured enrichment value for each compound. These measured enrichment values were compared with calculated enrichment values (ratio of airflow/nitrogen flow) in order to determine collection/recovery of the 41 compounds with the BFSP unit.

Two ambient air test runs were carried out at an unoccupied home. During each run two canister samples were collected; one with the BFSP unit and the other with the whole air collection apparatus. Again, measured enrichment values were compared with calculated enrichments in order to determine collection/recovery efficiencies.

RESULTS AND DISCUSSION

Table 1 shows the experimental results from the two ambient air tests. Twenty compounds, identified by retention time and quantified with a flame ionization detector during the tests, are listed in the table. Concentrations obtained from the analysis of whole air canister samples are shown, along with corresponding concentrations from the analysis of can samples collected with the BFSP unit. Enrichment factors for each compound are determined by ratioing the two concentrations. In viewing these ratios it is evident that for n-butane and i-pentane (compounds No. 1 and 2), compound breakthrough is occurring, as indicated by the lower ratios.

For the remaining compounds a mean ratio of 17.3 (+ 13.8%) was calculated from the test No. 1 data while a mean ratio of 15.4 (+ 9.9%) was determined from test No. 2 data. Expected enrichment ratios were based upon the actual flow ratio of air to nitrogen during each run. Ratios of 17.4 and 15.7 were determined respectively for test 1 and 2. In comparing

these flow ratios with concentration ratios determined experimentally, excellent agreement is observed (17.3 vs 17.4 and 15.4 vs 15.7).

Experimentally determined breakthrough volume for n-pentane is 4.5 liters per gram of Tenax (1). In the above experiments 1.8 liters of air (per 0.7 grams of Tenax) was sampled with each cycle of the BFSP unit. If one assumes a safe sampling volume to be approximately 50 percent of the breakthrough volume (i.e., 2.3 l/g), then the above sampled volume (2.6 l/g) indicates that n-pentane breakthrough is probably not occurring. However compounds such as n-butane and i-pentane (i.e., with lower breakthrough volumes) will not be efficiently recovered under the experimental conditions used with the BFSP unit.

Figure 3 shows the results from one of the laboratory test runs which involved challenging the BFSP unit with a dilute mixture of 41 organic compounds (2 to 3 ppb each). Concentration enrichment is plotted as a function of compound number. For most of the compounds a consistent enrichment value is obtained. However, for the more volatile compounds lower enrichment values are observed (compounds 1 through 11). Again, we believe that these compounds are not efficiently retained on the Tenax adsorbent under the experimental conditions used with the BFSP unit (i.e., breakthrough volumes are being exceeded). A mean measured enrichment of 33.4 is obtained if one excludes compounds 1 through 11. This value compares well with the calculated enrichment of 35.0. In further examining the data, one observes that peaks 40 and 41 (1,2,4-trichlorobenzene and hexachlorobutadiene) show somewhat lower than expected enrichment ratios. Closer inspection of the BFSP unit during the desorption temperature cycle showed that a maximum bed temperature of only 135°C was obtained at a temperature set-point of 180°C. Subsequent experiments utilizing a higher temperature set-point, resulted in better recovery of these two compounds.

CONCLUSIONS AND RECOMMENDATIONS

A prototype sampler has been shown to collect and transfer VOCs from ambient air to temporary storage canisters. The system employs parallel Tenax traps to adsorb and desorb organic compounds from an air environment. Sample enrichment has been achieved by utilizing less volume flow in the transfer process (desorption step) than in the collection process (adsorption step). Preliminary tests of the sampler have indicated that the system successfully functions as designed. Calculated sample enrichments (15 to 35-fold) based on volume flow ratios were in excellent agreement with experimentally determined concentration ratios.

The results of this study have demonstrated the feasibility of a non-cryogenic preconcentration technique that can be used in the field in conjunction with stainless steel canisters to provide VOC enriched samples. These enriched samples can then be transported to the laboratory for subsequent analysis. The primary advantages of this approach over conventional field sampling with Tenax cartridges are the following:

- (1) The somewhat high and variable amounts of individual compounds (1 to 50 ng per cartridge) normally found in field "blanks" are not observed with the BFSP unit. We suspect that Tenax storage and handling conditions are prime contributors to the blank problems. Since the BFSP unit is used on a near real-time basis, the above problems are not of concern.

- (2) The enriched canister sample from the BFSP unit can be conveniently and repetitively analyzed by one or more instruments.

In the present study a preliminary evaluation of the backflushing sample preconcentrator has been completed. Additional studies need to be carried out using higher enrichment ratios and testing other adsorption/desorption regimes. Other adsorbents need to also be examined for their ability to retain the more volatile organics. Compound selective adsorbents, such as the silver/silver oxide sorbent for NO₂ (WA-10), and dinitrophenyl-hydrazine sorbent for aldehydes, could be employed with the BFSP unit. With slight modifications to the BFSP near real-time monitoring of select compounds could also be achieved.

ACKNOWLEDGEMENT

The research described in this article was funded by the U.S. Environmental Protection Agency. However it does not necessarily reflect the views of the agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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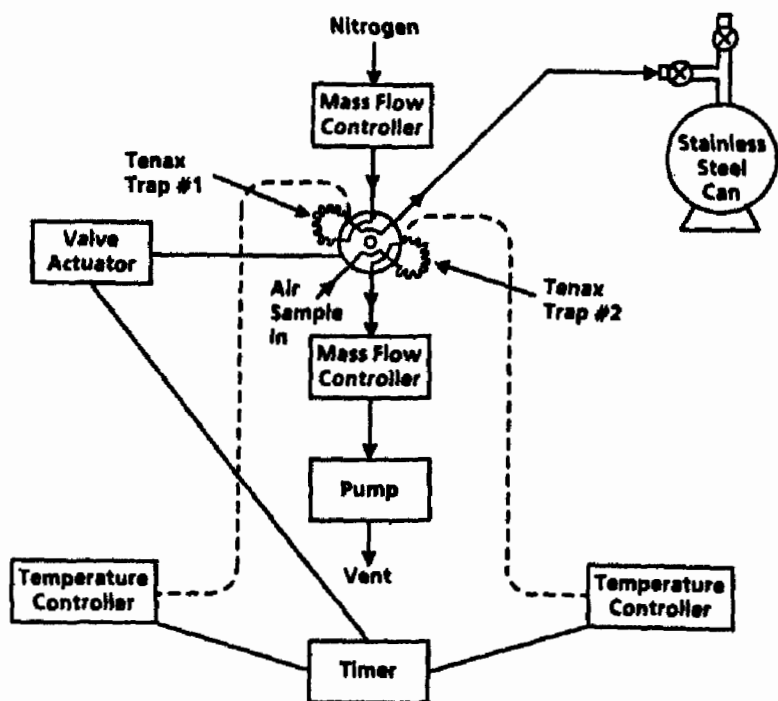


Figure 1. Diagram of prototype backflushing sampler.

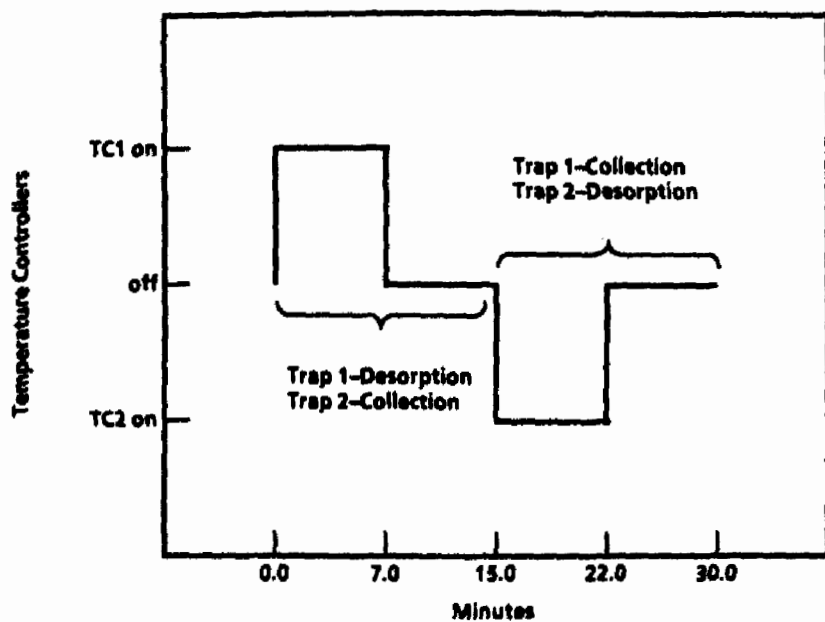
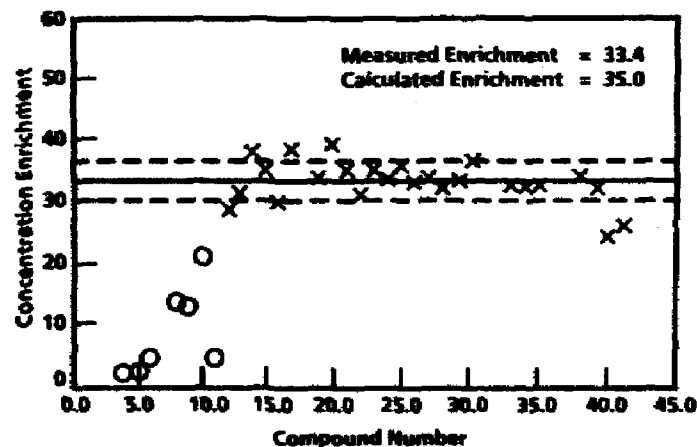


Figure 2. Diagram of timing cycle for the backflushing sampler.



1. dichlorodifluoromethane
2. methyl chloride
3. 1,2-dichloro-1,1,2,2-tetrafluoroethane
4. vinyl chloride
5. methyl bromide
6. ethyl chloride
7. trichlorofluoromethane
8. 1,1-dichloroethene
9. dichloromethane
10. 3-chloropropene
11. 1,1,2-trichloro-1,2,2-trifluoroethane
12. 1,1-dichloroethane
13. cis-1,2-dichloroethene
14. trichloromethane
15. 1,2-dichloroethane
16. 1,1,1-trichloroethane
17. benzene
18. carbon tetrachloride
19. 1,2-dichloropropane
20. trichloroethene
21. cis-1,3-dichloropropene
22. trans-1,3-dichloropropene
23. 1,1,2-trichloroethane
24. toluene
25. 1,2-dibromoethane
26. tetrachloroethane
27. chlorobenzene
28. ethyl benzene
29. m-xylene
30. styrene
31. 1,1,2,2-tetrachloroethane
32. o-xylene
33. 4-ethyl toluene
34. 1,3,5-trimethyl benzene
35. 1,2,4-trimethyl benzene
36. benzyl chloride
37. m-dichlorobenzene
38. p-dichlorobenzene
39. o-dichlorobenzene
40. 1,2,4-trichlorobenzene
41. hexachlorobutadiene

Figure 3. Measured enrichment ratio plotted against compound number (41 organic compounds).

TABLE 1. COMPARISON OF CONCENTRATIONS (ppb) OBTAINED FROM THE ANALYSIS OF CANISTER SAMPLES DIRECTLY VERSUS THE ANALYSIS OF CANISTER SAMPLES COLLECTED WITH THE BACKFLUSHING SAMPLE PRECONCENTRATOR

Compound	Retention Time Minutes	Test #1			Test #2		
		Direct	BFSP	Ratio	Direct	BFSP	Ratio
1. n-Butane	5.38	12.6	56.4	4.5	4.6	17.2	3.7
2. i-Pentane	7.86	12.3	143	11.6	3.6	38.0	10.5
3. n-Pentane	8.73	9.3	151	16.2	2.6	38.6	14.8
4. 2-Methylpentane	10.87	7.3	123	16.8	1.7	25.2	14.8
5. 3-Methylpentane	11.27	7.3	86.9	11.9	*	21.4	*
6. n-Hexane	11.81	7.3	125	17.1	1.6	25.6	16.0
7. Methylcyclopentane	12.45	5.3	89.6	16.9	1.2	18.5	15.4
8. Benzene	13.10	7.3	103	13.6	3.8	50.9	13.4
9. 2-Methylhexane	13.72	5.0	93.5	18.7	1.2	20.9	17.4
10. 3-Methylhexane	13.94	3.6	70.9	19.7	1.0	18.1	18.1
11. n-Heptane	14.61	4.0	72.8	18.2	1.1	19.9	18.1
12. Ethylcyclopentane	15.03	3.4	58.1	17.1	0.9	13.9	15.4
13. Toluene	15.94	15.8	270	17.1	8.6	128	14.9
14. Tetrachloroethylene	17.09	11.0	190	17.3	6.4	95.4	14.9
15. Ethylbenzene	18.33	2.3	41.2	17.9	1.2	16.6	13.8
16. m&p-Xylene	18.54	9.0	142	15.8	5.1	65.8	12.9
17. Styrene	18.97	0.5	12.0	24.0	0.9	15.6	17.3
18. o-Xylene	19.08	3.1	56.1	18.1	1.8	26.8	14.9
19. 1,2,4-Trimethylbenzene	21.45	2.1	36.8	17.5	1.5	20.9	13.9
20. 1,4-Dichlorobenzene	21.67	0.5	9.0	18.0	2.8	44.0	15.7

*Contamination.

UPDATE ON CANISTER-BASED SAMPLERS FOR VOCs

William A. McClenny, Joachim D. Pleil, and Thomas A. Lumpkin
EMSL, U. S. EPA, Research Triangle Park, NC 27711

Karen D. Oliver
Northrop Services, Inc. - Environmental Sciences
Research Triangle Park, NC 27709

Over the past year, data interpretation from testing and comparison studies of canister-based VOC samplers has provided a basis for recommendations as to the better sampler components and sampling train configuration. Choice of components is of particular importance, since the sampled air must pass through the sampling train before it is collected and stored in the canisters. During this process, both additive and subtractive changes in the sample content are possible. Sample contamination from volatilized organics occurs without adequate cleaning of components. Contaminations, particularly from the Freons and tetrachloroethylene, have been noted, while losses of VOCs can occur from samples carried in a dry carrier gas, for example, from audit gas mixtures. This paper addresses the status of canister-based sampler design and use.

Introduction

Canister-based samplers for the collection of volatile organic compounds (VOCs) in whole air were designed as a possible alternative to the use of solid sorbents such as Tenax-GC. The development of canister-based samplers evolved from the use of SUMMA® polished canisters in VOC analysis.¹ Experience with these samplers in the field during the past year has pointed up the need for modifications to the original sampler configuration designed by the Environmental Monitoring Systems Laboratory (EMSL) at EPA.² Experience has also been gained in cleaning and certifying samplers before they are used in the field. This paper describes the updated sampler design, details of the certification procedures, and considerations relating to performing field audits.

Sampler Design

The updated sampler design is shown in Figure 1. The sampler includes an inlet, 2- μ m filter, mass flow controller, pump (optional), Magnelatch valve, pressure gauge, timer, and thermostatically controlled heater and fans. Modifications to the previous design include the addition of a blower to continually pull fresh sample through the inlet manifold at ~12 liters/min. The use of higher inlet flow rates dilutes any contamination originating in the inlet and reduces the chances that the sample will be altered by contacting active adsorption sites on the walls of the inlet. Another modification was the change from a heated inlet to an unheated inlet. As long as the interior temperature of the sampler is maintained at a higher level than the exterior temperature, the heated line was thought to be unnecessary when a high inlet flow rate is used. The sampler also contains an optional port for formaldehyde sampling with Sep-pak cartridges.

Figure 1 shows a vacuum-assisted sampler with an indication of the position of a pump in the pump-assisted sampler design option. In such a "vacuum-driven" sampler, the evacuated canister is used to provide the differential pressure needed to pull the sample. Usually, flow rates are maintained by an electronic flow controller, which compensates for the decreasing pressure differential between the canister and ambient air until this differential reaches about -2 in.Hg (-6.8 kPa). Removing the pump results in a quiet sampler, which is desirable when sampling indoors. If positive canister pressure is required for analysis, the sample can be further pressurized with zero air after receipt in the laboratory. In a pump-assisted sampler, whole-air is collected at a flow rate of 10 cm³/min for 24 h. This results in a final canister pressure of about 20 psig (138 kPa) in 6-L canisters. A pump-assisted sampler is useful when a larger sample volume is required, for example (1) for multiple analyses of the sample, or (2) when long-term, higher flow rate (as compared to a vacuum-assisted sampler), integrated samples are necessary for a particular study.

Certification of Samplers

During the past year considerable experience has been gained in cleaning sampler components and certifying samplers for use in the

field. GC-FID humid zero air test results of a badly contaminated sampler are shown in Figure 2 as an example of the problems encountered when sampler components are not clean. In addition, the possibility exists that some VOCs of interest may be removed from the sample through surface reactions within the sampling train.

In general, components are disassembled and cleaned before the sampler is assembled. Nonmetallic parts are rinsed with deionized water and dried in the vacuum oven at 50°C. Typically, stainless steel parts and fittings are cleaned by placing them in a beaker of methanol, which is then put in an ultrasonic bath for 15 min. Next, this procedure is repeated with hexane as the solvent. Then, the parts are rinsed with deionized water and dried in a vacuum oven at 100°C for 12 to 24 h. Once the sampler is assembled, we have found it helpful to purge the entire system with humid zero air for 24 h.

The cleanliness of the system is then tested by challenging the sampler with humid zero air. The humid zero air is pulled through the sampler and analyzed with an automated cryogenic trap and GC-FID/ECD or GC-MSD. The sampler results are then compared with control analyses. Generally, samplers contaminated with ~0.2 ppbv or greater of target VOCs are unacceptable. If the sampler passes the humid zero air tests, the next step is to challenge the sampler with ambient air spiked with selected VOCs at concentration levels expected in actual field sampling (i.e., 0.5 to 2 ppbv) to test the sample integrity of the system. A canister is filled with spiked ambient air from the sampling manifold while periodic control samples from the manifold are analyzed in real time. The canister sample is later analyzed and compared to control runs to determine whether any VOCs of interest were added or deleted from the sample.

Once the sampler has been tested with humid zero air and spiked ambient air, the sampler is subjected to a second round of spiked ambient air tests with the interior of the sampler warmed to ~110°F. The results of this test are examined to determine whether the elevated temperature affects sample integrity. For instance, elevated temperatures may possibly result in accelerated outgassing of certain VOCs from sampler components, and this should be investigated before the sampler is certified for field use.

Audit Procedures

Another problem encountered during the early field studies was the poor results of the existing audit procedure for field samplers. Field audits were performed over ~2 h at an elevated flow rate of 90 cm³/min with no conditioning of the sampler. The audit mixture consisted of 10 to 50 ppbv of VOCs in dry nitrogen. The FID results of a simulated audit are presented in Figure 3, and these results are similar to those of audits conducted in the field. When the sampler was challenged with a dry audit mixture, significant losses of a number of VOCs such as o-xylene and ethylbenzene were observed. When a humidifier was placed in line immediately following a dry audit, the subsequent humidified audit resulted in higher than expected concentrations of VOCs. These audit results were the same for the original sampler and an updated sampler containing a blower pulling sample at 500 cm³/min through the inlet. When an audit was simulated

in the laboratory with only a humidified audit standard, no losses of VOCs were observed.

Our interpretation of these results is the following: During normal ambient sampling, VOC concentrations are generally 7 orders of magnitude lower than the ambient water vapor concentration (i.e., 1 ppbv vs. 2-5%); thus, the excess water vapor occupies a high proportion of the available active adsorption sites in the sample path components, and the VOCs pass through the sampling train relatively undisturbed. However, when the dry audit gas is applied, the water vapor equilibrium shifts, and the adsorbed water is removed from the walls of the sampling path, thus greatly increasing the number of active sites available to trap VOCs. Because VOC molecules are less abundant than water molecules, equilibration is expected to take a long time. Also, when ambient air samples are subsequently taken, the ambient water vapor displaces the VOCs adsorbed during the dry audit, which then contaminate the sample. Currently, procedures for preparing humid audit standards are being developed by EPA.

Conclusions

The original canister-based sampler design has been updated and includes a blower to pull fresh sample past the VOC sampling port at elevated flow rates. The use of the heated inlet line has also been discontinued in favor of an unheated inlet. Use of the pump is optional on the basis of the user's need for a vacuum-driven sampler or a pump-based sampler. A certification procedure for samplers has been developed in which samplers are challenged with humid zero air and ambient air spiked with target VOCs. Poor results of field audits of canister-based samplers has led to the investigation of humidified audit standards.

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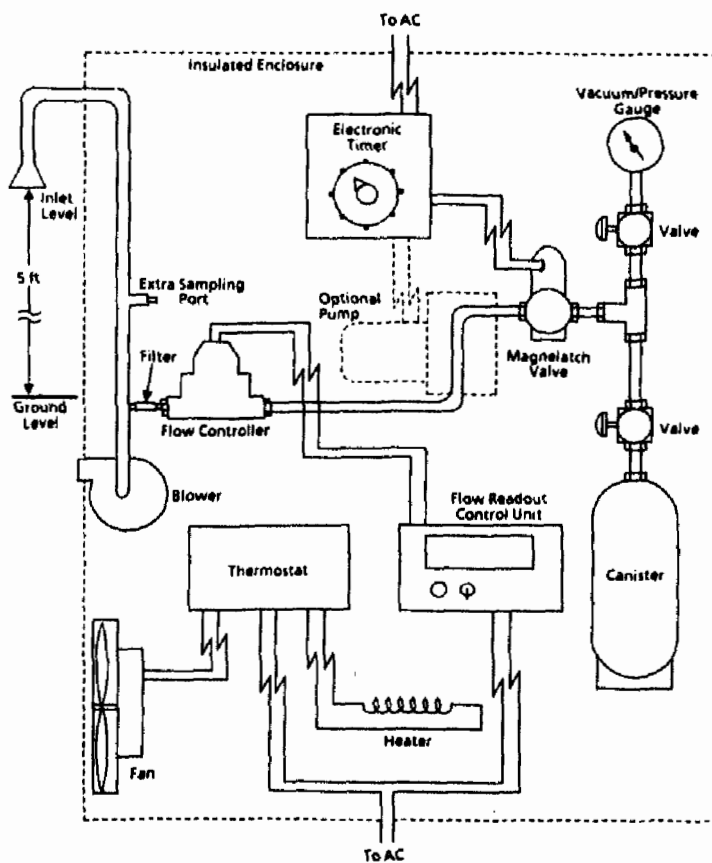


Figure 1. Updated sampler configuration.

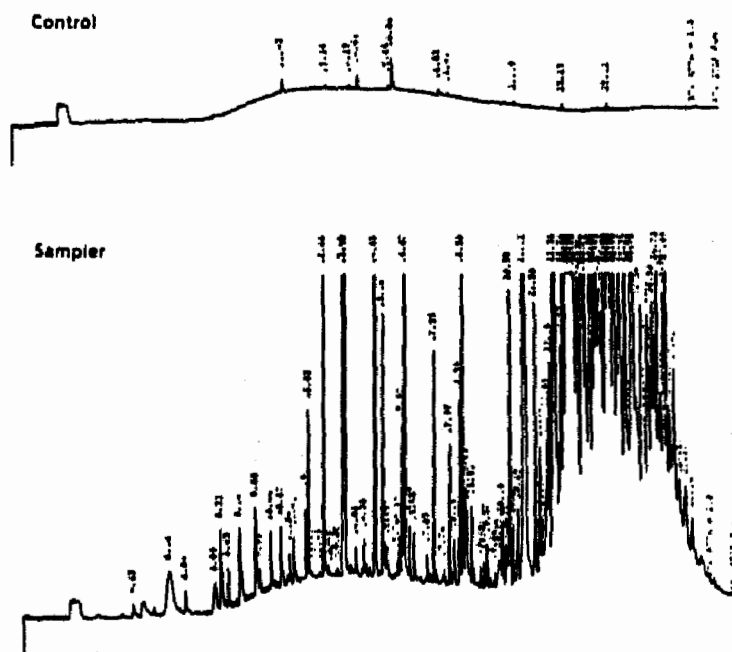
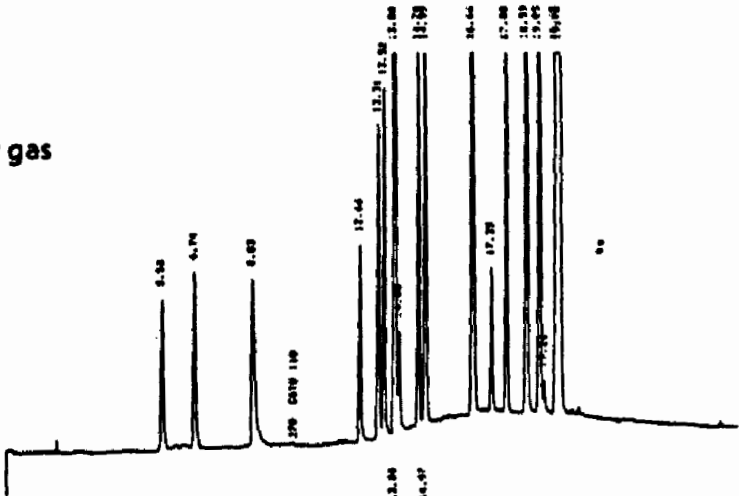


Figure 2. Example of gross contamination in GC-FID humid zero air tests of an uncertified sampler.

(a) Control – dry gas



NATIONAL AMBIENT VOC DATA BASE

Jitendra J. Shah, Emily Heyerdahl, and Ann Batson
Nero and Associates, Inc., Portland, OR 97204

Larry Cupitt, US EPA, Research Triangle Park, NC 27711
Hanwant Singh, Menlo Park, CA 94025

Every year a myriad of sources contribute to the growing body of literature on ambient Volatile Organic Chemical (VOC) concentrations. Due to the diversified nature of this information, researchers would be well served by a uniform data base. To this end, a national data base was prepared for EPA by collecting, evaluating and consolidating ambient concentrations of VOCs obtained in the United States for the years 1970 to 1980. It includes 151 potentially hazardous ambient VOCs. The data are evaluated for quality by a rating and ranking system. In late 1987, the updated data base will be available on IBM PC-compatible diskettes for use with dBASE III+, a commercially available data base management program.

Summaries of data from the existing data base and potential applications by other researchers will be presented. For example, it could provide a foundation for evaluating the implications of state and federal regulations. The sufficiency of data for a particular chemical(s) could be evaluated, allowing more efficient study design and allocation of resources. Measurements of specific chemicals can be compared as a function of sampling and analysis techniques. The data base also allows the comparison of air quality in urban, non-urban, source-dominated and indoor areas.

The assembled data base will be analyzed to answer basic questions such as:

- o What is the likely range and distribution of ambient concentrations for various chemicals?
- o Are there any detectable patterns or trends?
- o Are there detectable chemical "hot spots" or are the ambient concentrations relatively consistent over wide areas?

Introduction

The anticipation of new regulations for air toxics has placed added emphasis on the measurement of volatile organic compounds (VOCs) in most states. As a result, the knowledge about ambient concentrations of VOCs has increased considerably in the last decade. A significant amount of information is now available on many VOCs in the atmosphere. In 1983, a national data base on VOCs was prepared for and published by EPA.¹ This data base critically evaluated and consolidated published data on ambient concentrations of VOCs in the United States for the years 1970 to 1980. It is currently being updated to include ambient and indoor VOC data, and to include the years 1980 to 1986. The data base includes information on more than 150 potentially hazardous VOCs. In late 1987, the updated data base will be available on IBM PC-compatible diskettes for the use with dBASE III, a relational data base management system.

The objectives of the task to update the data base are:

- o Review EPA's existing VOC data base and correct any discrepancies found;
- o Identify new published and unpublished VOC data, critically evaluate it, combine it with the previous data, and analyze the resulting data base; and,
- o Provide the resulting VOC data base in a dBASE III format(s) designed to facilitate searching, sorting, editing, analysis and other manipulations.

Methodology

The existing VOC data base contains comprehensive information on ambient VOC levels in the U.S. from 1970 to 1980. This data base was checked for erroneous entries, and converted to dBASE III format to be included in the updated data base. The major elements of the update procedure are:

- o Contact individuals and organizations measuring VOCs
- o Perform literature search, obtain data
- o Develop data assessment criteria (ranking and rating)
- o Review reports, extract and critically evaluate data
- o Update the data base
- o Perform Quality assurance procedures
- o Analyze data base
- o Distribute data base

Contact Individuals and Organizations Measuring VOCs. A survey form was developed and an OMB clearance obtained. The survey form was sent to researchers who were identified as potentially having data. Data gathered through EPA sponsored programs were also obtained. A telephone follow-up to a small group of researchers was necessary to obtain adequate response.

Literature Search/Obtain Data. After several preliminary searches by EPA and NAI, a major on-line literature search was performed using the Chemical Abstracts data base of the Dialog on-line system. The data base was searched for each of the 151 chemicals in the original data base by Chemical Abstract Service (CAS) registry number combined with key words to limit retrievals to the ambient and indoor atmospheres in the U.S. during the years of interest (1980 to present).

The search yielded a list of 2769 references of which 600 were considered potentially useful and were reviewed for useful data. Table 1 lists some of the major databases which contain VOC information.

Develop Data Assessment Criteria (Ranking and Rating). To facilitate data evaluation, the data quality will be judged and reported in the form of ranking and rating. Ranking, a multi-digit number gives a quantitative evaluation of each of the chosen factors (Table II) affecting data quality. Ranking would be useful for data evaluation by researchers familiar with VOC measurements. Rating, a single letter code, on the other hand, is an overall measure of data quality. The rating is determined from the ranking of factors and their relative importance. The data quality evaluation will be performed during the review of reports.

Review Reports, Extract and Critically Evaluate Data. All reports and papers received from researchers or obtained from the literature were reviewed and evaluated for measurements of ambient concentrations of VOCs. The information listed on Table III was extracted from the useful reports and coded for data entry. Much of the information from EPA was obtained on diskettes, thereby reducing data entry time and errors.

Update The Data Base. The coded data from reports and from EPA diskettes were entered into dBASE III files contents as shown in Table III. DBASE III permits the specification of ranges of acceptable input values. This allows for immediate error checking and correction. The existing data base contains 18,000 records: the update is expected to include more than 70,000.

Quality Assurance Procedures. The following elements constitute the QA procedure.

- o Only experienced data entry personnel will be used
- o Much of the data will be obtained on diskettes and transferred directly into dBASE III format
- o Simple error checking techniques available in dBASE III will be used as appropriate
- o All software will be tested thoroughly before use
- o Scatterplots and other techniques for identifying "outliers" as potentially erroneous data will be performed
- o A certain number of reports (>10%) will be independently reviewed by two analysts, anomalies found will be discussed and corrected
- o A thorough review by prominent researchers in this field will be the most important QC element to insure data validity

Analyze Data Base. NAI will perform exploratory analysis on the master data file to address basic questions such as the following:

- o What is the likely range and distribution of ambient concentrations for the various chemicals?
- o Are there any detectable patterns or trends?
- o How does ambient concentrations compare with TLV, or other proposed ambient guideline levels?
- o Which chemicals are inadequately characterized?

The last data base was widely applied and the new data base is expected to have even wider applications. Some of the specific potential applications in receptor modeling have been discussed elsewhere.^{2,3}

Distribute Data Base. In order to maximize the usefulness of the resulting data base, it will be available on IBM PC-compatible diskettes in dBASE III format. The resulting data base will be available from EPA or NTIS or from NAI in late 1987.

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TABLE I. List of Data Bases Containing VOC Information

<u>Data Bases</u>	<u>Type of Data</u>	<u>Coverage</u>
National Ambient/Indoor VOC Data Base (This Work) J.J. Shah, E.K. Heyerdahl ⁴ & A. Batson, NAI	>70,000 after update*	Ambient/ Indoor *
National Ambient VOC Data Base H.B. Singh & R. Brodzinsky, SRI Int. ¹	17,700 data records	Ambient
Nonindustrial Sources of Pot. Toxic Subs. ⁵ G.E. Weant & G.S. McCormick, EPA	bibliographic citations	Source
Occidental Chemical VOC Database J.H. Mackey & D.L. Eichler Occidental Chemical Corp.	>10,000 data records	Ambient
Bibliographic Lit. Inform. System (BLIS) ⁷ J.M. Shackelford & W.R. Ott, EPA	621 abstracts	Indoor
Concentrations of Indoor Pollutants (CIP) ⁸ S. Brown, LBL	283 extended abstracts	Indoor
Indoor Air Information Retrieval (IAIR) ⁹ D. Chan & J.E. Howes, Jr., EPA	483 bibliographic citations	Indoor
Interim DB for State & Local VOC Meas. ¹⁰ W.R. Hunt, EPA	814 data records	Ambient/ Indoor

*indoor workplace excluded

**List of additional major studies to be included in this data base

TAMS

TEAM (Total Exposure Assessment Methodology) -- Pellizzari & Wallace

ATEOS

Indoor Study of 40 East Tennessee Homes -- Gammage & Hawthorne

EPA/EMSL Chlorinated Hydrocarbon Data

Houston Oxidant Modeling Study 1978

Versar Studies in Baltimore & Philadelphia (1984)

NMOC -- R.L. Seila, W. L. Lonneman

NE Corridor Regional Modeling Project (NECRMP)

SRI Data in EPA/600/3-86/047

Westberg: Milwaukee Ozone Study 1981, and Philadelphia Data Enhancement
Study 1980

Atmospheric Lifetime Study -- Rasmussen/Khalil

TABLE II. Ranking and Rating

<u>Weight</u>	<u>Factor</u>
10	Sampling and Analysis <ul style="list-style-type: none"> o appropriateness of sampling and analysis methods, storage, etc. o artifact or other problem with the methods
10	Quantification <ul style="list-style-type: none"> o QC o QA o calibration procedures o observed concentration relative to the quantitation limit o external lab QA o internal consistency
7.5	Representativeness <ul style="list-style-type: none"> o comparisons with others o internal consistency (ensemble data set) o spatial, temporal o quantity of data for purpose
5	Documentation <ul style="list-style-type: none"> o objective of monitoring o meteorology o comprehensiveness

TABLE III. dBASE III File Structure

<u>CONCENTRATION FILE</u>	<u>METHODS FILE</u>
Reference Number	Reference Number
Site Number	Site Number
Chemical Number	Chemical Number
Site Type	Sampling Method
City	Analysis Method
State	Minimum Quantitation Limit
Concentration	
Relative Standard Deviation	<u>SITES FILE</u>
Number of Samples	Reference Number
Minimum Concentration	Site Number
Maximum Concentration	Site Type
Number of Samples Less than	Latitude
Minimum Quantitation Limit	Longitude
Start Date	Site Address
Start Time	City
Stop Date	State
Stop Time	SAROAD Number
Hours Between Sampling and Analysis	
Ranking	<u>REFERENCE FILE</u>
Rating	Reference Number
Sampling Duration	Chemicals Measurement
Comments	Principal Investigator
	Authors
	Title
	Citation
	Year
	Objective

JUNE-SEPTEMBER, 6-9 AM, AMBIENT AIR BENZENE
CONCENTRATIONS IN 39 U.S. CITIES, 1984-1986

Robert L. Seila
Gas Kinetics and Photochemistry Branch
Atmospheric Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Ambient air samples from 44 sites in 39 U.S. urban areas were collected in electropolished, stainless steel canisters on week days from 6 to 9 am during June through September of 1984, 1985, and 1986. Not all sites were sampled all years. Samples were analyzed by capillary gas chromatography with flame ionization detection to determine C₂ to C₁₂ volatile hydrocarbon composition. Benzene, which is carcinogenic and present in automobile exhaust and gasoline, was present in every sample. Individual sample concentrations ranged from 1.0 parts-per-billion as carbon (ppbC) to 273 ppbC. The benzene median concentrations by site and year ranged from 4.8 ppbC to 35.0 ppbC with the overall median being 12.6 ppbC.

Introduction

Benzene is a known human and animal carcinogen (1) which has been designated as a hazardous air pollutant under Section 112 of the Clean Air Act (2). Benzene is present in gasoline and the emissions from gasoline fueled vehicles. Levels in gasoline range from 0 to 4% by volume with a national average of 1.3% (3). The major source of benzene in ambient air is mobile sources. In 1982, for example, mobile sources contributed 85% of benzene emissions. Of this 85%, 82% was due to exhaust emissions, 17% from evaporative emissions, and 1% from refueling operations. Gasoline-powered vehicles accounted for 95% of mobile source benzene (4). Stationary sources of benzene include fugitive emissions, coke by-products, chemical production, gasoline marketing, benzene storage, and solvent use. Benzene is ubiquitous in ambient air. Data on ambient air concentrations of benzene and other hazardous organic chemicals were assembled by Brodzinsky and Singh from 241 references covering primarily the years 1970 through 1980 (5). They reported a median concentration of 2.8 ppb by volume derived from 2292 measurements in urban/suburban areas of the U.S. Even with this large number of measurements, they were unable to perform trend analysis, because most concentrations were day-time measurements made during the warmer half of the year.

EPA initiated a multi-year project in 1984 to obtain 6-9 am total non-methane organic compound (NMOC) concentrations from selected U.S. cities. Between 10 and 15% of the samples were analyzed to determine speciated hydrocarbon compositions. Benzene was one of the hydrocarbons determined. Over the project's three years more than 900 samples were analyzed.

Experimental Methods

Ambient air was sampled daily from 6 to 9 am from June through September each year. Samples were pumped into evacuated, electropolished, stainless steel (ss) spheres and air freighted back to Research Triangle Park for analysis. The sampling protocol and equipment are described in detail elsewhere (6,7).

Benzene was determined on a Hewlett-Packard model 5880A gas chromatograph (gc) equipped with a flame ionization detector (fid) and outfitted with a dual valve cryogenic preconcentration system designed to condense 470-ml of air for injection onto a gc column. C₂ to C₁₂ hydrocarbons including benzene were condensed in an 18-cm by 3.2-mm o.d. ss trap containing 60-80 mesh glass beads at liquid oxygen temperature (-183° C) and separated on a 60-m, 0.32-mm i.d. fused silica column with a 1.0-um thick film of DB-1 bonded liquid phase. The column temperature program was -50° C for 1 min to 200° C at 8°/min. The fid was operated at 270° C. An IBM PC-XT with 640K RAM was used to receive and process the gc data. A National Bureau of Standards propane-in-air standard reference material was used for calibration of all hydrocarbons. The benzene limits of detection and quantification were estimated to be 0.04 and 0.12 parts-per-billion as carbon (ppbC) respectively. Benzene and other hydrocarbons were identified by retention time.

Results and Discussion

Table I is a statistical summary showing the number of samples, median, minimum, and maximum benzene concentration in ppbC by year for each site. During the three years of the study samples were analyzed from 44 sites in 39 cities. The five cities with two sites are shown with a "-1" or "-2" after the city in the table. Four of the Texas cities, Philadelphia, and Washington, DC were sampled all three years. The other four Texas cities, Atlanta, Birmingham, Kansas City, and Richmond were sampled during two of the three years. The remaining 25 cities were sampled only one year. The total number of analyses for all cities over all years was 812, although the number per city ranged widely from only three at Miami to 50 at Dallas.

The individual sample benzene concentrations ranged from a low of 1.0 ppbC at Orange in 1984 to 273 ppbC at Birmingham in 1986. The median concentrations ranged from 4.8 ppbC at West Palm Beach to 35.0 ppbC at Memphis, with an overall median of 12.6 ppbC for all sites. For 1984 and 1985, the median percent benzene fraction of NMOC ranged from 1.2 to 3.1 with an average of 1.9. The variation of benzene relative to NMOC was much less than the variation of the absolute or median concentrations. This suggests that benzene concentrations are highly correlated with total NMOC, which is consistent with the high percentage mobile source contribution to ambient air benzene concentrations. A high mobile source contribution to NMOC levels in urban areas is expected during the 6 to 9 am period.

The contribution of benzene from mobile sources can be estimated by multiplying measured ambient air acetylene concentrations by the benzene:acetylene ratio determined from a high mobile source area such as a tunnel (8). We calculated the vehicular benzene contribution for all of the 1984 and 1985 samples using the benzene:acetylene ratio (0.92) that we had determined for the Lincoln Tunnel in 1982. The results indicated that mobile source emissions contributed at least 90% of the benzene present in 92% of the 1984 and 1985 samples. The cities that showed significant evidence of sources other than mobile were St. Louis and Indianapolis in addition to four Texas cities, Beaumont, Clute, Orange, and Texas City. Texas City was the most prominent with 36% of its samples indicating at least a 10% contribution by stationary sources.

Conclusions

Ambient air benzene concentrations for 6 to 9 am in the 39 U.S. cities reported here were quite low. The site median concentrations ranged from 4.8 to 35.0 ppbC and the overall median was 12 ppbC. The data also indicated that mobile sources were the major source of benzene in the vast majority of samples.

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Table I. Statistical summary of benzene concentrations.

City	Year	N	Concentration, ppbC		
			Median	Min	Max
Akron OH	1984	10	6.0	4.6	15.2
Atlanta GA	1984	7	9.6	3.7	53.5
Atlanta GA	1986	14	11.2	4.0	27.8
Baltimore MD	1986	7	16.9	8.2	30.9
Baton Rouge LA	1985	16	8.3	2.4	23.5
Beaumont TX	1984	9	10.7	5.2	33.1
Beaumont TX	1985	19	14.1	6.8	49.4
Beaumont TX	1986	13	11.3	6.2	36.9
Birmingham AL	1984	6	8.4	7.8	185.7
Birmingham AL	1986	13	18.7	6.3	273.2
Boston MA	1985	8	6.0	3.9	15.9
Bridgeport CT	1986	16	8.9	3.5	33.4
Brooklyn NY	1986	16	13.7	5.0	38.5
Charlotte NC	1984	16	6.9	2.6	25.4
Chattanooga TN	1984	12	22.0	8.4	65.4
Chicago-1 IL	1986	8	27.3	14.1	48.4
Chicago-2 IL	1986	14	20.7	3.8	30.3
Cincinnati OH	1984	7	10.4	6.4	22.5
Cleveland OH	1985	17	23.7	5.2	60.9
Clute TX	1984	10	9.4	3.9	26.9
Clute TX	1985	17	12.0	1.3	34.8
Dallas TX	1984	13	10.0	4.5	24.4
Dallas TX	1985	23	12.6	5.7	34.9
Dallas TX	1986	14	11.5	4.2	21.3
Denver-1 CO	1986	12	16.7	6.3	39.6
Denver-2 CO	1986	13	24.5	17.9	39.5
El Paso TX	1984	8	18.8	6.0	39.2
El Paso TX	1985	17	16.0	6.3	39.4
El Paso TX	1986	9	20.0	6.9	41.6
Fort Worth TX	1984	13	14.2	8.6	37.4
Fort Worth TX	1985	19	13.0	5.8	26.0
Fort Worth TX	1986	16	10.5	6.2	40.4

Table I continued

City	Year	N	Median	Min	Max
Houston-1 TX	1985	22	16.1	5.2	50.9
Houston-1 TX	1986	14	22.5	7.5	112.3
Houston-2 TX	1986	12	22.7	10.9	31.7
Indianapolis IN	1984	10	18.9	9.1	76.2
Kansas City MO	1984	11	12.4	5.8	34.8
Kansas City MO	1985	18	9.7	4.1	22.6
Lake Charles LA	1985	16	11.9	3.8	18.2
Manhattan NY	1986	12	10.5	5.3	31.8
Memphis TN	1984	8	35.0	17.8	47.0
Miami FL	1984	3	12.9	7.6	17.3
New Haven CT	1986	16	10.5	2.6	57.5
Orange TX	1984	10	8.5	1.0	14.5
Orange TX	1985	16	7.8	1.8	46.4
Philadelphia-1 PA	1984	7	15.2	8.5	27.8
Philadelphia-1 PA	1985	13	15.6	6.3	31.0
Philadelphia-1 PA	1986	14	6.0	1.9	17.9
Philadelphia-2 PA	1985	11	19.6	6.9	51.0
Portland ME	1985	13	10.4	2.4	18.1
Richmond VA	1984	10	6.4	2.6	10.0
Richmond VA	1985	14	9.8	4.7	18.5
Salt Lake City-1 UT	1986	14	21.4	8.8	41.8
Salt Lake City-2 UT	1986	13	26.1	9.7	47.2
Scranton PA	1984	9	7.1	3.2	18.5
St Louis MO	1985	18	11.1	3.8	72.7
Texas City TX	1984	13	12.0	5.5	47.3
Texas City TX	1985	15	12.6	3.4	119.4
Trenton NJ	1986	16	13.1	8.0	36.6
Tulsa OK	1986	12	7.7	2.6	65.2
Washington DC	1984	10	17.8	13.8	33.5
Washington DC	1985	11	15.3	7.3	23.5
Washington DC	1986	11	5.6	3.7	25.3
West Palm Beach FL	1984	8	4.8	2.6	9.7

NONMETHANE ORGANIC COMPOUND SAMPLING AND
ANALYSIS PROGRAM

Robert A. McAllister, Dave-Paul Dayton,
Denny E. Wagoner
Radian Corporation
Research Triangle Park, NC 27709



Harold G. Richter
Office of Air Quality Planning and Standards
Office of Air and Radiation
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

The program to measure nonmethane organic compound (NMOC) concentrations in ambient air has completed its third year using the cryogenic preconcentration direct flame ionization detection (PDFID) method. Forty-four field sites were located in (or near) 39 metropolitan centers in the United States. Twenty-three states in eight EPA regions were involved. Twenty-two sites participated in the 1984 study, 19 in 1985, and 23 in 1986. Integrated ambient air samples were taken from 6:00 A.M. to 9:00 A.M. in electropolished stainless steel canisters Monday through Friday from June through September. Analyses were done at Radian Corporation's Research Triangle Park (NC) Laboratory within three days of sample collection.

Nearly 5000 separate ambient air NMOC concentrations are included in the three-year data base. Care was taken to determine the data quality in terms of precision, accuracy, and completeness. For most of the sites which participated in the study for more than one year, a lowering trend of the NMOC concentration with time was detected. In Philadelphia, PA, for example, the NMOC concentration averaged 1.02 parts per million carbon (ppmC) in 1984, 0.657 ppmC in 1985, and 0.450 ppmC in 1986. In 1985 ambient air samples were tested for their NMOC stability while being stored in canisters over fourteen days. No change in NMOC concentration was discerned over that time period.

Introduction

The gas chromatographic, flame ionization-detector (GCFID) method has been one of the most accurate methods for determining NMOC concentrations.^{1,2,3} The EPA-Quality Assurance Division (QAD) developed the PDFID method because it is faster, simpler, and less costly to operate than the GCFID method.

During the summers of 1984, 1985, and 1986, the PDFID method was used by Radian to measure 4773 NMOC concentrations in ambient air, and was shown^{4,5,6} to have an accuracy and precision comparable to the GCFID method. The EPA-QAD monitored the Radian NMOC measurements with a PDFID instrument. The EPA-Atmospheric Sciences Research Laboratory (ASRL), using the GCFID Method, measured the NMOC concentration of a number of the same ambient air samples collected for the NMOC monitoring program.

Data Summary

Table I shows NMOC concentrations at sites in the program for more than one year in terms of arithmetic averages (means), medians, and number (the count of valid samples received from the site in one year). The upper part of Table I shows six sites that participated in the NMOC program all three years. The lower part of the table lists the sites that were in the program for only two years. Table II gives the same data for those sites in the NMOC program for only one year.

Comparing the mean NMOC concentrations in 1984, 1985, and 1986 shows an overwhelming number of cases in which the average parts per million carbon (ppmC) decreased from year to year. There are 22 out of 26 comparisons in Table I showing a decrease of the annual mean NMOC concentration from year to year, or between 1984 and 1986. Many of the sites selected were in urban areas, or at locations where the major source of NMOC is internal combustion engines (automobiles, trucks, etc.), or industrial sources.

Precision

Precision was determined by repeated analyses of site samples.

Analytical Precision

Table III shows the results of repeated analyses of site samples in terms of % difference, and absolute % difference. The Radian-vs-Radian mean % is the average difference between the second and the first analysis by a Radian channel. At Radian, four PDFID channels were in use and designated Channels A, B, C, and D, respectively. Tests^{7,8} involving analysis of ambient air samples by all four Radian channels established that there were no significant differences between analyses among Radian channels. The mean % difference for the Radian-vs-Radian, 1984 through 1986 comparisons was -0.3536%, with a pooled standard deviation of 15.688%. Mean % difference for the Radian-vs-Radian comparison was similar to a bias for the second analysis compared to the first analysis. It was close to zero (= -0.354%), as expected. The EPA-QAD-vs-Radian comparison indicates that the difference averaged -8.875% of the mean of the individual EPA-QAD and Radian NMOC measurements. The negative sign indicates that the EPA-QAD NMOC measurements averaged higher than the Radian NMOC measurements.

The EPA-ASRL-vs-Radian comparison shows a positive mean difference of 2.015%, implying that the Radian measurements averaged higher than the EPA-ASRL measurements.

The mean absolute % differences given in Table III are important indicators of precision. They are the expected % differences for the three comparisons, Radian-vs-Radian, EPA-QAD-vs-Radian, and EPA-ASRL-vs-Radian NMOC measurements, without regard to sign. The Radian-vs-Radian mean absolute % difference comparison is a within-laboratory precision (or analytical precision) of the NMOC measurement by the PDFID technique. The EPA-QAD-vs-Radian mean absolute % difference comparison is an expected bias for the PDFID method including the between-laboratory bias and the within-laboratory bias. The EPA-ASRL-vs-Radian comparison is an expected absolute % bias between a GCFID method in one laboratory and the PDFID method in another laboratory, thus containing between-method bias and within-laboratory bias.

The standard deviations in Table III are all measures of precision, either of the % differences or of the absolute % differences. The standard deviation of the absolute % difference is always smaller than the standard deviation of the % difference. Note also that the Radian-vs-Radian overall (or pooled) standard deviations are less than the corresponding EPA-QAD-vs-Radian standard deviations or the EPA-ASRL-vs-Radian standard deviations. This follows because in the Radian-vs-Radian comparison, the standard deviations (or precisions) are the within-laboratory precisions. For the EPA-QAD-vs-Radian, and the EPA-ASRL-vs-Radian comparisons, the standard deviations include both the between-laboratory (or between-method) and the within-laboratory components of the precision.

The within-laboratory and between-laboratory components of bias and precision are fixed factors in this analysis; i.e., they apply to the particular laboratories involved, Radian (Perimeter Park, NC), EPA-QAD (Research Triangle Park (RTP) NC), and EPA-ASRL (RTP, NC) laboratories in particular, and not to all laboratories in general.

Table IV shows the separation of the between-laboratory standard deviations (precisions) from the standard deviations given in Table III for the EPA-QAD-vs-Radian and the EPA-ASRL-vs-Radian comparisons. In all cases the within-laboratory standard deviations (precisions) were assumed to be equal to the Radian-vs-Radian standard deviations (from Table III). The between-laboratory standard deviations are larger than the analytical precisions, the within-laboratory precisions.

The mean absolute % difference for repeated analyses in the Radian Laboratory was 9.8% with a standard deviation of 12.2%. The average % difference of successive analyses in the Radian laboratory averaged -0.354% with a standard deviation of 15.7%. These values were used for the analytical precision of the PDFID method.

Between-laboratory % differences were -8.9% for the EPA-QAD laboratory, and +2.0% for the EPA-ASRL laboratory, both compared to the Radian laboratory, with standard deviations of 16.3% and 19.5%, respectively. Between-laboratory absolute % differences were 15.0% for the EPA-QAD laboratory and 13.4% for the EPA-ASRL laboratory, both compared to the Radian laboratory, with standard deviations of 14.4% and 15.6%, respectively.

Sampling and Analytical Precision

Overall precision, including both sampling and analysis variability, was determined by analyses of duplicate samples, simultaneously collected in two identical canisters. The % differences between duplicate sample analyses and absolute % differences, means and standard deviations are given in Table V. The mean % difference is small (-0.263%), as expected, and the standard deviation of the % difference is 20.139%. The standard deviation of the % difference is a measure of precision of the duplicate samples and their analysis and include the between-duplicate variability and the within-duplicate variability, or analytical error. The expected absolute % difference for duplicates is 11.690% with a standard deviation of 16.433%, again including between-duplicate variability and analytical error (or analytical precision).

Separation of the between-duplicate variability and the analytical is indicated in Table V. The calculation for separating the between-duplicate variability from the analytical variability is similar to the calculations illustrated in Table IV. The assumption is made that the Radian analytical precision estimated in Table III applies also to the duplicate sample results. The between-duplicate variability (or precision) is slightly less than the between-laboratory and between-method variabilities estimated in Table IV.

Accuracy

Because the NMOC measurements encompass a range of mixtures of unknown compounds, it was not possible to define absolute accuracy. Accuracy was determined relative to propane standards with internal and external audit samples.

Accuracy for the Radian measurements was monitored throughout the program. Four days per week a propane sample was prepared in-house and analyzed. The propane used to prepare the in-house quality control (QC) standard was certified by the EPA-QAD and was referenced to the National Bureau of Standards, Standard Reference Material 1667b, propane. In-house propane QC samples were prepared by diluting the certified propane with cleaned, dried air. Percent difference between the measured NMOC concentration and the calculated NMOC concentration for the in-house QC standards showed an overall mean percent bias among Radian channels of 1.18%, ranging from 0.91% to 1.44% for the four Radian channels. Percent bias was defined as

$$\% \text{ bias} = ((\text{NMOC (measured)} - \text{NMOC (calculated)}) / \text{NMOC (calculated)}) \times 100$$

The results show excellent quality control for each channel considering that the bias results include errors caused by dilution of the QC sample in addition to the analytical error.

External audit results were referenced to the EPA-QAD PDFID instrument. Table VI shows bias figures for all three years of the program for Radian Channels A,B,C, and D, and for the EPA-ASRL GCFID channel. The Radian percent biases were all below 5% and were negative, showing the EPA-QAD NMOC measurement to average higher than the Radian measurements. The EPA-ASRL bias measurements are positive and are less than 6%. The EPA-QAD NMOC measurements for propane average greater than those for EPA-ASRL.

Completeness

Completeness was defined as the percent of the total scheduled samples that were successfully taken and analyzed, beginning with the first valid sample from the site. Completeness in 1986 from 23 sites ranged from 87 to 100%, averaging 96.8%. Completeness in 1985 averaged 95.8%, and 90.6% in 1984.

Other Results

In 1985, measurements were taken to determine whether the length of storage of the ambient air samples into the canisters affected the measured NMOC concentration. For time periods up to 14 days after sampling, no discernible concentration difference was detected in 26 site samples selected at random. In the NMOC program, samples were generally analyzed less than 50 hours after sampling, but never more than 80 hours after sampling.

Tables II through VI are available upon request by contacting Dr. Robert A. McAllister, Radian Corporation, P.O. Box 13000, Research Triangle Park, NC 27709. (919) 541-9100.

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TABLE I. NMOC CONCENTRATIONS AT SITES PARTICIPATING MORE THAN ONE YEAR

NMOC Ambient Air Concentration, ppmC										
Site	Code	Mean	1984		1985			1986		
			Median	Number	Mean	Median	Number	Mean	Median	Number
Beaumont, TX	BMIX	0.89	0.715	86	1.769	1.679	93	0.796	0.636	89
Dallas, TX	DLTX	0.97	0.905	74	0.856	0.731	82	0.724	0.648	57
El Paso, TX	ELTX	0.93	0.820	69	0.707	0.662	90	0.486	0.413	88
Fort Worth, TX	FWTX	0.97	0.830	69	0.742	0.612	84	0.630	0.568	87
Philadelphia, PA ^a	P1PA	1.02	0.920	63	0.657	0.490	71	0.450	0.342	69
Washington, DC	WDC	0.81	0.710	63	0.687	0.607	63	0.351	0.289	71
Atlanta, GA	ATCA	0.79	0.600	55	--	--	--	0.544	0.451	84
Birmingham, AL	BHAL	0.99	0.705	56	--	--	--	1.019	0.582	92
Clute, TX	CLTX	0.82	0.610	72	0.741	0.645	89	--	--	--
Houston, TX ^b	HITX	--	--	--	0.924	0.752	77	1.117	1.011	91
Kansas City, MO	KCMO	0.79	0.625	68	0.535	0.424	92	--	--	--
West Orange, TX	ORTX	0.69	0.650	71	0.586	0.539	92	--	--	--
Richmond, VA	RVA	0.53	0.495	64	0.539	0.450	67	--	--	--
Texas City, TX	TCTX	0.92	0.780	69	0.603	0.433	86	--	--	--

^aMuseum location.

^bCAMS 1.

AUTOMATED MEASUREMENT OF NONMETHANE
ORGANIC COMPOUND CONCENTRATIONS IN AMBIENT AIR

Dave-Paul Dayton, Joann Rice
Robert A. McAllister, Alston L. Sykes
Radian Corporation
Research Triangle Park, NC 27709



Frank F. McElroy, Vinson L. Thompson
Environmental Monitoring Systems Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

An automated preconcentration direct flame ionization detection (APDFID) method for measuring nonmethane organic compound (NMOC) concentrations in ambient air has been developed and tested in the Radian Laboratory. The prototype automated system incorporated the principles of the manual preconcentration direct flame ionization detection (PDFID) method and obtained and analyzed four 9-minute integrated ambient air samples per hour. Bias was determined on 17 field samples relative to the NMOC concentrations determined by the PDFID method. The average bias was -6.2%, with an absolute bias of 10.7%.

The relative responses of the APDFID and PDFID methods were determined for several types of organic compound standards, measured in terms of the ratios of the slopes of the calibration curves for the organic compounds to the respective slopes for propane. The ratios ranged from 0.953 to 1.422.

Dry standard propane (2.84 ppmC) was humidified by bubbling through HPLC-grade water. The concentration of the humidified propane was calculated, assuming that the dry standard had been saturated with water vapor. The concentration of the humidified propane standard, measured by the APDFID method showed a bias of -3.22% compared to the calculated concentration.

Introduction

Measurements of ambient NMOC concentrations are used by states to develop emission control measures needed to achieve compliance with the National Ambient Air Quality Standards for ozone. During the Summers of 1984, 1985, and 1986, analysis of nearly 5000 ambient air samples have confirmed the usefulness of the PDFID method.

Although accurate and efficient, the PDFID method is based on manual operation of the NMOC analytical system to analyze individual air samples. To monitor diurnal changes in NMOC concentration in ambient air and to help identify NMOC sources, an automated method is needed to permit repetitive, unattended analyses of ambient air for NMOC at field monitoring sites.

This paper describes the development of an automated PDFID instrument for measuring NMOC concentrations in ambient air. The instrument, operating procedures, and calibration results with propane and other organic compounds are described. The effect of water vapor on the system and a comparison of automated NMOC measurements to manual PDFID results are discussed. A number of problems have arisen in the course of the development of the instrument for the automated NMOC concentration measurement. One of the major problems and its possible solution is discussed.

Apparatus and Operating Procedures

While the automated instrument and its operating procedures are still under development, the initial studies demonstrated that current technology is available to enable automated NMOC measurements successfully and reliably.

The APDFID NMOC measurement is similar to the PDFID NMOC measurement, in that it is basically a cryogenic preconcentration direct flame ionization method. An objective of the APDFID development program was to sample ambient air 60% of each hour. The analysis instrument selected is a programmable VARIAN Model 3400 gas chromatograph utilizing a modified on-column injector. This instrument is operated with a cycle consisting of 9 minutes for ambient air sampling and 6 minutes for analysis, resulting in 4 cycles per hour and a sampling fraction of 60% of each hour.

A six-port valve, mounted in the oven of the chromatograph, routes the ambient air sample through the cryogenically cooled trap, during trapping, and routes the carrier gas through the electrically heated trap to the flame ionization detector during analysis. The APDFID system incorporates an on-column injector, modified to accept the trap assembly. The trap assembly consists of a brass block containing the trap, a heater, and a temperature sensor within the block. The trap assembly is located in an insulated housing. A solenoid valve controls the flow of liquid nitrogen to the nozzle directing cryogen spray to the outside of the trap assembly. Both the trapping temperature (-170°C) and the desorption temperature (130°C) are regulated using active temperature control.

A vacuum pump pulls the ambient air through the system, and a flow controller regulates the sampling rate.

The beginning of a sampling/analysis cycle may be chosen as the point at which the previous sample has emerged from the trap and analysis has been completed. At that point the trap/block temperature is being controlled at $130 \pm 1^\circ\text{C}$, and helium carrier gas passes through the trap to the flame ionization detector. At that time, cryogen (liquid nitrogen) is sprayed onto the trapping/desorption block, and the setpoint for temperature control is changed to -170°C . When the temperature of the trap has been controlled at -170°C for about 30 seconds, the six-port valve is switched to draw a sample of ambient air at 12.1 mL/min for 9 minutes into the trap, which is packed with glass beads.

The six-port valve is then switched to bring in the helium carrier gas, in the opposite flow direction, and at the same time, the setpoint of the trapping/desorption block temperature is changed to 130°C . The block temperature is increased at the rate of 150°C per minute and the released, revolatilized organic compounds are measured by the FID and the response is integrated. The block temperature is then held for about 30 seconds to be sure that all the organic compounds (and water) in the 9-minute sample have been flushed from the trap. A new cycle is then ready to begin.

Results

The APDFID instrument was calibrated daily with two propane standards and zero air. The propane standards were certified by the U.S. EPA, Quality Assurance Division (QAD), referenced to a National Bureau of Standards propane Standard Reference Material No. 1667b. Three types of tests were conducted. (1) Tests were done to compare the measured APDFID instrument response for several organic compounds with propane response. (2) Several canister air samples for which the NMOC concentration had been determined previously by the PDFID method were analyzed by the APDFID method to compare the results. Finally, (3) measured concentrations of dry propane and humidified propane were compared to determine the bias that the presence of moisture has on the APDFID instrument.

The organic species results are given in Table I. Calibration curves were generated for the six compounds shown in the table, using three concentrations of each (1.0, 3.0, and 6.0 ppmC) diluted from the original cylinder concentration. Each concentration was replicated three times. Table I gives the slopes of the linear regressions resulting from the calibration data for each compound. The third column in Table I gives the slope of the propane calibration curve that was done the same day as the compound calibration curve.

The ratio of the compound slope to the propane slope, given in the last column, compares the relative response of the compound with the response of propane in the APDFID system. Ideally, all of the ratios should be 1.000, indicating that all of the organic compounds produced a response equal to propane, which is the compound of choice for calibrating the NMOC PDFID instrument and the APDFID instrument. The ratios for propylene and butadiene were considerably higher than 1.0, which is not typical for the PDFID method. Further work is anticipated to determine the cause of these unexpected results.

Analyses of ambient air samples by both the PDFID method and the APDFID method are reported in Table II. Sample ID Numbers 2899 through 2933 were site samples collected during the 1986 NMOC Monitoring Program and analyzed first by a Radian PDFID channel in September 1986 and then analyzed by the APDFID between November 24, 1986 and December 12, 1986. Sample ID numbers with an "A" suffix were locally collected and analyzed first on an EPA PDFID instrument and then on the APDFID instrument. The NMOC concentrations are reported in parts per million carbon (ppmC) by volume. Percent bias in Table II averages -6.2, relative to the PDFID concentration measurement; absolute % bias averages 10.7.

To determine the effect of water vapor on the APDFID measurement, wet and dry propane were used in separate measurements. Dry standard propane with a concentration of 2.84 ppmC was used to determine a calibration factor for the APDFID instrument. Dry standard propane (2.84 ppmC) was then humidified by bubbling through HPLC-grade water. The concentration of the humidified propane was calculated, assuming that the dry standard had been saturated with water vapor. The concentration of the humidified propane standard, measured by the APDFID method showed a bias of -3.22%, compared to the calculated concentration.

Discussion and Recommendations

The preliminary results to date indicate the feasibility of an automated system to make measurements of NMOC concentrations in ambient air. Both the instrument and operating procedure are still in the development stage.

One of the biggest problems encountered in the operation of the instrument was that occasionally, liquid nitrogen would pool at the bottom of the brass injector block and would collect between the temperature sensor and its ceramic packing. This would permit the top of the brass block to heat to a temperature higher than the control setpoint of -170°C , while the temperature sensor and the bottom part of the column/block would remain at liquid nitrogen temperature (-195.8°C). It is felt that the temperature control problem can be solved by adding a second cryogen injection port 180° from the present injection point, by enlarging the venting port between the column block and the chromatograph's oven, and by adding a small heater in the bottom of the cavity where the liquid nitrogen is currently collecting.

The data quality may also be improved by optimizing the gas sampling rate to assure that enough sample is being trapped to give reproducible results with improved accuracy.

Table I. ORGANIC SPECIES RESULTS

Compound	Compound Slope	Propane Slope	Compound/Propane Slope Ratio APDFID
Propylene	468,426	334,665	1.400
Benzene	354,773	350,829	1.011
Ethane	327,805	344,117	0.953
m-Xylene	366,863	344,996	1.063
1,3-Butadiene	521,729	366,988	1.422

Table II. BIAS OF THE NMOC CONCENTRATION

Sample ID	PDFID NMOC, ppmC	APDFID NMOC, ppmC	% Bias ^a	Absolute % Bias
2899	0.459	0.497	8.3	8.3
2899	0.459	0.513	11.8	11.8
2900	1.679	1.407	-16.2	16.2
2924	1.319	1.324	0.4	0.4
2924	1.319	1.317	-0.2	0.2
2928	0.647	0.382	-41.0	41.0
2928	0.647	0.721	11.4	11.4
2930	1.053	1.095	4.0	4.0
2930	1.053	1.003	-4.7	4.7
2931	0.210	0.178	-15.2	15.2
2933	0.876	0.598	-31.7	31.7
2485A	0.512	0.502	-2.0	2.0
2899A	2.023	1.769	-12.6	12.6
2928A	2.024	1.798	-11.2	11.2
2929A	0.508	0.467	-4.1	4.1
2929A	0.500	0.515	3.0	3.0
2930A	0.496	0.472	-4.8	4.8
Average			-6.2	10.7

^a % Bias = [(APDFID NMOC - PDFID NMOC)/(PDFID NMOC)] x 100

ANALYSIS OF VOLATILE ORGANIC SAMPLING TRAIN SAMPLES
USING MEGABORE GAS CHROMATOGRAPHY/MASS SPECTROMETRY

T. A. Buedel, J. T. Bursey,
J. B. Homolya, R. L. Porch
Radian Corporation
Research Triangle Park, NC
27709

R. G. Fuerst, T. J. Logan, M. R. Midgett
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711



Analysis of volatile organic sampling train (VOST) samples by capillary gas chromatography results in increased chromatographic resolution for the characterization of products of incomplete combustion in stack emission samples. A megabore column was selected to provide the highest sample capacity for the wide dynamic range of compound concentrations encountered in VOST samples coupled with the best possible chromatographic resolution. VOST samples on Tenax[®] and/or Tenax[®]/charcoal cartridges are thermally desorbed onto the analytical trap of a commercial purge and trap apparatus, from which the organic compounds are desorbed directly to the head of a megabore column operated initially at subambient temperatures. The VOST target compounds are identified and quantified by a computerized gas chromatograph/mass spectrometer system. All of the VOST target compounds exhibited response factors with coefficients of variation of less than 25% when using triplicate analyses at four concentrations. The megabore column analysis time for the VOST target compounds is approximately 30 percent faster than the present VOST protocol where a packed chromatographic column is used.

Introduction

According to the Resource Conservation and Recovery Act (RCRA), owners or operators of hazardous waste incinerators must operate these facilities in a manner that does not endanger human health or the environment. The Code of Federal Regulation (CFR), Title 40, Part 264, states that an incinerator must achieve a Destruction and Removal Efficiency (DRE) of 99.99% for every Principal Organic Hazardous Constituent (POHC) described in the Trial Burn Permit. In the present methodology for the sampling and analysis of samples taken of the emissions from hazardous waste incinerators, samples of stack gas are collected on a set of sorbent cartridges, one containing Tenax GC^R and the other Tenax GC^R combined with charcoal. The cartridges are thermally desorbed through 5 mL of water and the organic compounds are collected on an analytical sorbent trap. The adsorbed organics are then desorbed onto the head of a 3.0 mm x 2 m glass column packed with 1% SP-1000 on Carbopack B and analyzed by a computerized gas chromatograph/mass spectrometer system.

The analytical methodology for VOST focuses on target compounds in order to determine the DRE. The key questions in a trial burn are, of course: Has the incinerator performed successfully in the combustion of the compounds of interest? Have these compounds been effectively removed (99.99% or better) from the emissions? For the limited number of compounds of interest, analytical standards can be analyzed to determine retention times accurately and, unless compounds with ions of exactly the same masses coelute exactly, the target compounds can be deconvoluted from potentially interfering species. However, when the question of possible formation of PICs is being addressed, the PICs are not target compounds, as their identity is not known in advance. The analyst is required to perform qualitative analysis and the quality of the mass spectrum obtained is critical to the success of the mass spectral interpretation. Automated deconvolution techniques can be untrustworthy and extensive use of manual mass spectral deconvolution techniques is time-consuming and requires extensive training and experience on the part of the analyst.

Improving the analytical process by improving the chromatographic resolution is one route to the production of mass spectra of better quality: improved chromatographic resolution decreases coelution of compounds and the mass spectra hence exhibit fewer interfering peaks. The megabore capillary column (0.53 mm diameter) has sample capacity approaching that of a packed column while retaining much of the peak resolution traits of a narrow or wide-bore capillary column. The resulting improvement in chromatography is dramatic: Figure I shows a typical VOST sample analysis using a packed column, while Figure II shows a comparable field sample analyzed on a megabore column. An additional benefit of the use of the megabore column is evident upon the examination of Figure II: in the same elution time as the packed column analysis, the megabore analysis shows the elution of naphthalene and dichlorobenzenes. Naphthalene will not elute from the packed column in analysis times of an hour or more; the dichlorobenzenes do not resolve completely on the packed column. On the megabore, the three dichlorobenzene isomers exhibit baseline resolution and naphthalene elutes in approximately 20 minutes. The ability to analyze compounds with good chromatographic resolution on the megabore is limited only by the ability to purge these compounds from the sorbent cartridges and the water successfully and quantitatively.

Experimental

Two GC/MS configurations were used to evaluate the megabore VOST methodology. Both systems used a quadrupole mass spectrometer. One system, the Finnigan-MAT 4500 has differential pumping, using diffusion pumps. The other system, the Finnigan-MAT 5100, has no differential pumping but uses a turbomolecular pump. The chromatographic column was the same on both systems, a DB-624 (J&W Scientific), 30 m long with a film thickness of 3 microns. The column was operated at a flow rate of 2-2.5 mL/min, over a temperature range of -20°C to 295°C, and coupled directly to the ion source of the mass spectrometer. The subambient temperatures are used to obtain chromatographic resolution of gaseous target compounds. Although the VOST method as presently formulated is restricted to compounds in the boiling point range of 30°C to 100°C, there is widespread interest in the quantitation of chloromethane, bromomethane, chloroethane, and vinyl chloride as POHCs and PICs. Therefore, a goal of the development of the megabore technique was to obtain analytical data for the gases with boiling points below 30°C. The composition of the analytical column of the purge and trap apparatus was varied as an experimental parameter, since the analytical trap described in the present VOST protocol entrained too much water for successful use with the megabore column. The analytical trap ultimately used was composed of 90% Carbotrap[®]/10% charcoal (w/w), using a 1 minute dry purge on the 5100 but no dry purge on the 4500 system.

Results and Discussion

Using the EPA Method 624 purgeable standards (commercially available), target compounds were loaded on and purged from a Tenax[®]/charcoal cartridge. Relative response factors were calculated for the compounds of interest relative to d_6 -benzene, in accordance with the present formulation of the VOST method. Bromofluorobenzene and d_4 -1,2-dichloroethane were spiked on the cartridges as surrogates. Reproducibility of these response factors, as expressed by the relative standard deviation of replicate determinations over the calibration range, was used to evaluate the acceptability of the method. Results for both systems, with the target analytes at a level of 100 ng, are shown in Table I. Coefficients of variation for the VOST target compounds are all in a reasonable range (5-22%). The coefficients of variation for the gases are higher but all of the gases are observed. Analytes, surrogates, and quantitation standards were again spiked onto VOST sampling cartridges (Tenax[®]/charcoal composition) and thermally desorbed into the analytical apparatus. The calibration curve was prepared using an EPA Method 624 standard in triplicate on both systems, with the analytes at concentrations of 25, 50, 100, and 150 ng; the results for both systems are shown in Table II. Reproducibility of the calibration curve for each mass spectrometer, expressed by the coefficients of variation, is comparable. The chromatographic peaks, even at the longer retention times, tend to be 8-14 seconds wide. The goal of improved chromatographic resolution is met with the use of the megabore fused silica capillary column, and the reproducibility of the VOST method using the packed column for chromatographic analyses has not been sacrificed for the improvement of chromatographic resolution. In addition, the time required for performance of the chromatography for the VOST assay is decreased by approximately 30%.

As a final test of the modified method, a blind quality control sample was prepared and analyzed in triplicate, using the VOST target compounds. The results are shown in Table III. Reproducibility for the triplicate analysis was acceptable and all values obtained were within 14% of the accepted value.

Conclusions

The VOST analytical methodology is enhanced by including megabore capillary analysis. Chromatographic resolution is improved, so the initial goal of improving the characterization of PICs should be attainable when the method is applied to the analysis of actual field samples. Analysis times using the megabore column are shorter by approximately 30% by comparison with the time required to perform the analysis using the packed column. Sensitivity, as determined by estimated limits of detection in both the packed column and megabore modes, is improved because the megabore column is coupled directly to the ion source, so the entire sample reaches the ion source of the mass spectrometer. Also, capillary chromatographic peaks are sharp, so the concentration of the compound of interest in the ion source is higher at the capillary chromatographic peak maximum. Reproducibility is acceptable for the analytes which are within the purview of the method (boiling point of 30°C to 100°C), and all of the gaseous compounds of interest are observed. Several field tests are essential to evaluate the modified methodology with actual field samples. Parallel tests with the standard methodology and the modified methodology would be desirable.

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Disclaimer

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References

1. E. M. Hansen, "Protocol for the Collection and Analysis of Volatile POHCs Using VOST," EPA Report 600/8-84-007, March, 1984.

TABLE I. PRECISION OF SELECTED METHOD 624 COMPOUNDS
DETECTED FROM TENAX-CHARACIAL CARTRIDGES

Compound	Ion	Finnigan-MAT 4300			Finnigan-MAT 5100		
		Mean Response Factor	Standard Deviation	Coefficient of Variation (%)	Mean Response Factor	Standard Deviation	Coefficient of Variation (%)
NOTE: Target Compounds							
Methylene chloride	84	0.8257	0.0805	11	1.198	0.170	14
Chloroform	83	0.6160	0.1321	22	0.747	0.078	10
1,1,1-Trichloroethane	97	0.4047	0.0852	21	0.534	0.061	8
Carbon tetrachloride	117	0.3177	0.0665	21	0.328	0.016	5
Trichloroethane	130	0.2660	0.0278	10	0.318	0.026	8
Benzene	78	1.4420	0.2743	19	2.235	0.486	20
Tetrachloroethylene	164	0.7267	0.0979	14	0.320	0.048	15
Toluene	92	0.3717	0.0366	10	0.815	0.118	14
Chlorobenzene	112	1.9050	0.1429	8	0.771	0.087	9
Ethylbenzene	106	1.0617	0.1079	10	0.436	0.032	8
m, p-Xylene	106	3.0300	0.3083	10	1.227	0.107	9
p-Xylene	106	1.4567	0.1128	8	0.525	0.078	15
Other Compounds							
Chloroethane	50	0.2180	0.1850	84	2.146	1.166	54
Bromoethane	94	0.0360	0.0203	56	0.274	0.083	23
Vinyl chloride	62	0.2090	0.0234	11	0.466	0.028	6
Chloroethane	64	0.0853	0.0370	43	0.272	0.074	27
1,1,2,2-Tetrachloroethane	83	0.7340	0.0367	5	0.225	0.067	30
Surrogate/Internal Standards							
d ₁ -1,1-Dichloroethane	63	0.2607	0.0095	4	0.2232	0.031	14
Deutrofluorobenzene	95	0.9482	0.0164	2	0.026	0.001	2
d ₆ -Benzene (IS)	84	1.0000	-----	-----	1.000	---	---

¹ Triplicate analyses at 100 ng of each compound.

² Coefficient of variation = Standard Deviation \times 100
Mean

Table II. RESPONSE FACTOR CALIBRATION CURVE FOR SELECTED METHOD 624 COMPOUNDS
DESORBED FROM TENAX/CHARCOAL CARTRIDGES

Compound	Florisil-MAT 1200			Florisil-MAT 2100		
	Mean Response Factor	Standard Deviation	Coefficient of Variation (%)	Mean Response Factor	Standard Deviation	Coefficient of Variation (%)
YEST Target Compounds						
Methylene chloride	84	1.076	0.182	17	1.178	0.215
Chloroform	83	0.544	0.096	15	0.565	0.108
1,1,1-Trichloroethane	97	0.412	0.039	14	0.382	0.075
Carbon tetrachloride	117	0.314	0.045	14	0.228	0.040
Trichloroethane	190	0.278	0.026	9	0.283	0.049
Benzene	78	1.598	0.257	13	2.046	0.672
Tetrachloroethylene	164	0.801	0.089	11	0.284	0.050
Toluene	92	0.394	0.071	18	0.740	0.128
Chlorobenzene	112	2.283	0.317	14	0.684	0.101
Ethylbenzene	106	1.248	0.178	14	0.559	0.093
m-Xylene	108	3.683	0.304	14	1.080	0.178
p-Xylene	106	1.747	0.276	14	0.448	0.083
Other Compounds						
Chloroethane	30	0.393	0.236	48	0.020	2.346
Bromoethane	94	0.077	0.451	16	0.597	0.289
Vinyl chloride	82	0.294	0.032	28	0.448	0.082
Chloroethane	64	0.497	0.088	26	0.247	0.054
1,1,2,2-Tetrachloroethane	61	0.087	0.137	24	0.186	0.048
Surrogate/Internal Standard						
d-1,2-Dichloroethane	63	0.273	0.017	4	0.214	0.037
Bromofluorobenzene	65	0.910	0.101	11	0.318	0.074
d-Benzene (IS)	84	1.000	----	1.000	---	---

¹ Triplicate analyses at four concentrations: 25, 50, 100, 150 ng.

² Coefficient of variation = $\frac{\text{Standard Deviation}}{\text{Mean}} \times 100$

Table III. BLIND QUALITY CONTROL RECOVERY TEST RESULTS

Compound	Amount Injected (ng)	Average ¹ Amount Recovered (ng)	Standard Deviation	Average ² Percent Recovery
m-Xylene	40	38	1.64	97
Toluene	45	51	5.21	114
Benzene	75	73	4.88	97
Chloroform	75	84	5.26	112
Trichloroethane	45	50	2.63	110

¹ Triplicate analyses.

² Percent recovery = $\left(\frac{\text{average amount recovered}}{\text{amount injected}} \right) \times 100$.

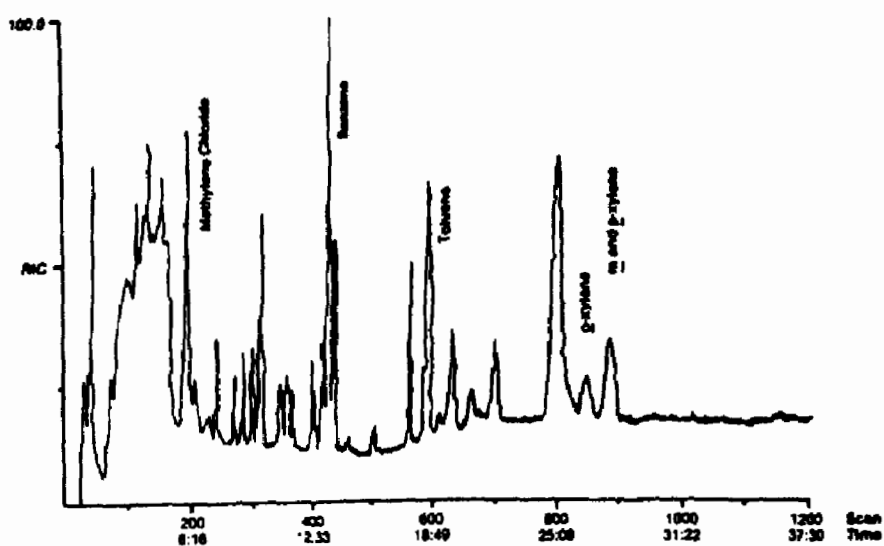


Figure 1. Typical Analysis of a VOST Sample Using an SP-1000 Packed Column.

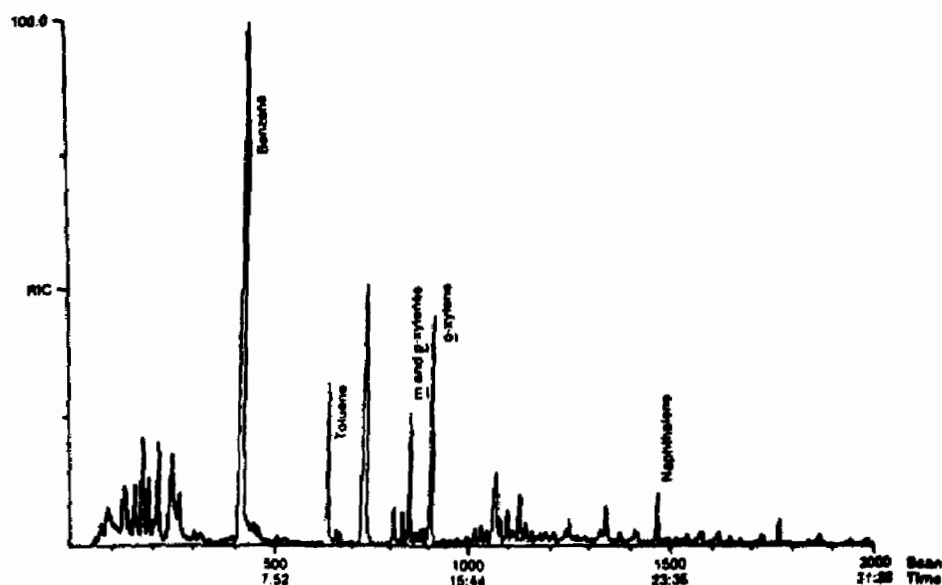


Figure 2. Chromatogram of a Field Sample Desorbed From a Tenax® /Charcoal Cartridge and Analyzed Using the Megabore in the 5100 GC/MS Analytical System

PRECONSTRUCTION MONITORING OF
AMBIENT AIR FOR TOXIC NON-CRITERIA
POLLUTANTS AT A MUNICIPAL
WASTE-TO-ENERGY SITE

Larry D. Ogle, David A. Brymer and
Maureen P. Kilpatrick
Radian Corporation
8501 MoPac Boulevard
P.O. Box 9948
Austin, Texas 78766



Ambient air monitoring for toxic compounds prior to the construction of a Waste-to-Energy facility was used to establish background concentrations. The data will be used in support of the design and permitting of the facility. Ambient levels were established by sampling six consecutive days each quarter for one year.

The non-criteria pollutants of particular interest in this study included metals, vapor phase chloride and fluoride, polychlorinated dibenzofurans and dibenzodioxins, polychlorinated biphenyls, polynuclear aromatic hydrocarbons, and volatile organics. Methodology used was designed to provide data at levels low enough to adequately define ambient concentrations. Multiple sampling and analysis techniques were compared to identify the most useful technique for each analyte. Field blanks and field spikes were used to define the applicability of each method for the target analytes.

Very low levels of the non-criteria pollutants were observed in the ambient air. Sample volumes and detection limits established during this project were sufficient to characterize the compounds of interest at ambient levels.

Introduction

Disposal of municipal waste is an area of increasing concern, particularly for larger municipalities. One of the options for disposal of combustible waste is incineration since incineration can reduce landfill demand by as much as 90%. The resulting heat energy then can be used to generate electricity providing an additional incentive for incineration. Waste-to-Energy facilities often are sited close to the source of refuse to minimize transportation costs, however, this proximity to heavily populated areas has raised concerns about the environmental impact of such a plant on the surrounding neighborhoods.

The objective of this study was to obtain information on the baseline (i.e., background) levels of non-criteria pollutants in the ambient air prior to construction of a waste-to-energy facility. A monitoring site was established approximately four blocks from the construction site of the Hennepin County Waste-to-Energy facility in Minneapolis, Minnesota. The collected data included meteorological, criteria pollutant and non-criteria pollutant measurements. These data will be used in support of the design and permitting of the facility.

Meteorological and criteria pollutant data were collected continuously for one year. Non-criteria data was collected during six consecutive days each quarter during that year. Quarterly sampling was desirable to determine if appreciable seasonal variations, both in content and concentrations, were observable. The non-criteria pollutants of prime interest in this study were: chlorides (as HCl), fluorides (as HF), metals (Sb, As, Be, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Se, Ag, Sn, V, Zn and Pb), polychlorinated dibenzodioxins and dibenzofurans (with emphasis on the 2,3,7,8-tetrachloro-isomers), polychlorinated biphenyls, polynuclear aromatics, and volatile organics (with emphasis on vinyl chloride, benzene, tetrachloroethylene and the dichlorobenzenes).

Experimental Methods

The design of the experimental methods for the measurement of the non-criteria pollutants was responsive to multiple objectives: 1) comparing the performance of ambient air monitoring techniques to determine which method was the best for the specific needs of this study; 2) obtaining sufficient data to determine if ambient levels of some parameters were low enough to delete them from further monitoring during the course of the program to effect some cost efficiency for the project; 3) utilizing screening techniques whenever possible to obviate the need for detailed and expensive analysis if analytes were not present at detectable levels; 4) utilizing methods which provided data on analytes not of specific concern to the project but of potential interest to the community at large (i.e., broad applicability of methodology); 5) utilizing methods which not only were generally accepted but also were capable of providing data at concentration levels low enough to adequately define the non-criteria baseline; and 6) defining an appropriate number of field and laboratory blanks and spikes that the limitations of the methods could be known.

A test plan was developed which provided sampling and analysis methods to address the objectives described above. A summary of the techniques used to measure the non-criteria pollutants is provided in Table I.

Results

The use of the methods (described in Table I) to monitor the non-criteria pollutants has resulted in a large amount of data. In general, very low levels of non-criteria pollutants were observed. Observations on the methodology are: the GC-ECD screening technique for PCBs was determined to be of limited use; the GC-FID screening technique for PAHs resulted in a number of false positive identifications; the XAD-2® resin was preferred for PCB collection over PUF® plugs due to spike retention; the impinger technique gave higher values for chlorides and fluorides than the sorbent tube technique; Tenax® or combinations of Tenax and Carbosieve S® were not effective in retaining low molecular weight organics and were very prone to contamination.

Field spikes were used to validate the collection and retention efficiencies of the methods. Field blanks were employed as a check of background contamination and to ensure the levels observed were above the background levels. From the instrument detection limits and the amount of sample collected, a lower limit of quantitation has been established. These levels and the field spike recoveries are presented in Table II.

Conclusions

The data collected during the course of this project have been sufficient to describe the baseline ambient air levels of non-criteria pollutants. Sample volumes and detection limits were sufficient to characterize the pollutants at or below levels of concern. In many cases, however, the best method was not established. This is particularly true in the case of fluorides and chlorides. Additional method development and evaluation is needed to establish methods for the measurement of such air toxics. This development will aid those working in the area of ambient air measurements, the agencies with the responsibilities to determine if new facilities will provide an environmental burden, and those designing the facilities and related technology.

TABLE I. SAMPLING AND ANALYTICAL TECHNIQUES FOR NON-CRITERIA POLLUTANTS

Target Compound Group	Sampling Method	Analytical Methods
Particulate Metals	Hi-Vol Filter	ICAP, GFAA
Mercury	Gold Amalgamation	Vapor Phase AA
Polychlorinated Biphenyls	Glass Fiber Filters/XAD-2	GC-ECD
	PUF Plugs	GC-MS
		GC-ECD
		GC-MS
Polynuclear Aromatic Hydrocarbons	Glass Fiber Filters/XAD-2	HPLC-UV and Fluorescence, GC-FID, GC-MS
Polychlorinated Dioxins and Furans	Glass Fiber Filters/XAD-2	GC-MS
Chlorides	Impinger Solutions } Silica Sorbent Tubes }	Ion Chromatography
Fluorides	Impinger Solutions } Silica Sorbent Tubes }	Ion Chromatography Ion Specific Electrode
Volatile Organics	Tenax } Tenax/Carbosieve S }	Thermal Desorption GC-MS
	Charcoal Tubes	GC-FID
	Stainless Steel Canisters	GC-FID, PID and HECD

TABLE II. AVERAGE METHOD EFFICIENCIES AND QUANTITATION LIMITS

Target Analytes	Spiking Compound	Amount Spiked (ug/sample)	Mean Recovery	Standard Deviation	Lower Limit of Quantitation (ug/m ³)
PAHs	Naphthalene-d ₈	15	88	9.0	0.1 - 160 ^a
	Pyrene-d ₁₀	15	68	6.7	
PCBs (KAD-2)	Monochloro ¹³ C ₆ biphenyl	0.10	65	24	0.004
	Tetrachloro ¹³ C ₁₂ biphenyl	0.25	68	21	
	Octachloro ¹³ C ₁₂ biphenyl	0.40	68	23	
	Decachloro ¹³ C ₁₂ biphenyl	0.50	68	23	
(PUF)	Monochloro ¹³ C ₆ biphenyl	0.10	63	7.3	0.0006
	Tetrachloro ¹³ C ₁₂ biphenyl	0.25	84	8.5	
	Octachloro ¹³ C ₁₂ biphenyl	0.40	83	13	
	Decachloro ¹³ C ₁₂ biphenyl	0.50	92	7.8	
Polychlorinated Dibenzodioxins	³⁷ Cl-2,3,7,8-TCDD	0.015	94	8.5	4 x 10 ⁻⁶
Volatiles					
(Tenax)	Benzene-d ₆	0.5	0	0	0.03 - 0.3 ^a
(Tenax/Carbosieve S)	Benzene-d ₆	0.5	0	-	0.03 - 0.3 ^a
(Charcoal)	Methylene chloride	15	106	- ^b	7 - 45 ^a
	Tetrachloroethylene	17.9	94	- ^b	
	1,3-Dichlorobenzene	13.5	83	- ^b	
Stainless Steel Canisters	-	-	-	-	2 - 7 ^a
Chloride	-	-	-	-	1.2
Fluoride	-	-	-	-	0.9
Metals	-	-	-	-	1.2 - 600 ^a
Mercury	-	-	-	-	1.0

^aCompound dependent - describes the range experienced for the various analytes.^bTwo determinations.

GRAB SAMPLING AS AN EFFECTIVE TOOL IN AIR POLLUTION MONITORING



Joseph P. Krasneo
Atmospheric Chemistry Research Group
Scientific Instrumentation Specialists
Moscow, Idaho

.....Grab sampling of gaseous chemical species has been utilized for a number of years. Various rigid containers, polymeric film bags and other devices are used manually, semi-automatically, or most recently with microcomputer control. The advantages are simplicity, low cost, easy field use and sample collection, and sample storability up to the analysis time. Disadvantages are high manpower cost for manual sampling in larger field experiments, sample degradation/contamination in some types of grab sampling devices, and lack of data on stability/storability of a number of species of interest such as VOC's.

.....The evolution of rigid grab sampling containers led to an increased use of sampling devices made from specialized materials, i.e. passivated stainless steel (PSS) resulting in successful sampling and storage of trace and toxic gases down to the low ppt (v/v) level for extended periods of time. Recent advances in the construction of PSS grab sampling containers and syringes coupled with the improvements in sampling procedures, and availability of solid research data on stability and storability of dozens of organic toxic air pollutants make this approach to air sampling increasingly attractive.

.....On-going automation of grab sampling procedures and subsequent use of sophisticated, yet readily available analytical techniques such as capillary gas chromatography (GC) using specific detectors (FID, ECD, PID, MSD), or GC-Mass spectrometry (MS) give the researchers and regulatory personnel a powerful tool for effective abatement and control of gaseous toxic air pollutants.

Introduction

.....The rapid industrial development during the past fifty years coupled with significant population increases brought about a significant deterioration of localized and global atmospheric environment. The onset of the era of smog also signifies growing interest and concern about the sources, fate and effects of various air pollutants. The early work in the 1950's involved relatively simple experiments, followed by a more thorough laboratory work geared toward pollutant identification, atmospheric reactions and transformations, and exposure/effects on humans and plants. This work, in the sixties and early seventies reached a momentum that brought about an increased public and regulatory agency awareness, concern, and a clear need for additional theoretical work, research, testing and more extensive field experiments.

.....One of the fundamental tasks facing researchers was the need to collect and analyze samples of ambient or industrial atmospheres. The requirements included minimal, or preferably no effect on sample composition and integrity, ability to contain and transport the sample to the laboratory (clearly the preferred choice to taking complex and delicate instrumentation to the field site), low cost and ease of use. Initial sampling work utilized rigid glass, metal and plastic containers, polymeric film bags and various adsorbents. As the need for more accurate measurements at lower (sub-ppm) concentrations intensified, some of the shortcomings of the commonly used sampling methods became quite apparent. Contamination, sample degradation, rapid loss of collected species thwarted attempts to carry out reliable, larger scale field experiments. The need to measure background concentrations of a number of trace atmospheric gases, low level air pollutants and complex gaseous mixtures found in urban atmospheres resulted in the prototyping and limited availability of new grab sampling devices. Specifically, several research organizations independently developed versions of a rigid, metal sampling container with different surface treatments, i.e. electropolishing, oxidation, coating and passivation (1). These were used with good to excellent results for ambient (10 ppt to 500 ppm v/v) sampling of halocarbons, hydrocarbons and a number of stable atmospheric gases such as CO₂, CH₄, N₂O, CO and others. By mid-seventies large number of electropolished and passivated stainless steel containers were used for stratospheric/tropospheric grab sampling of halocarbons from airborne (balloon, aircraft) and surface (ship, mobile laboratory) platforms. In this time period some shortcomings were encountered in the use of polymeric sampling bags made from polyethylene, teflon and mylar (2) and solid adsorbents (activated charcoal, molecular sieve, Tenax) for sampling of aliphatic and aromatic hydrocarbons (C₁-C₁₂). Passivated stainless steel containers provided very satisfactory performance for these species. Increased concerns about the ozone levels and its photochemical reactions affecting air quality in larger urban areas intensified the need for thorough sampling/monitoring of non-methane hydrocarbons (NMHC's). In the past several years number of detailed studies confirmed validity of grab sampling using passivated SS containers (3, 4, 5, 6).

Grab sampler design and construction criteria

.....Most tasks that require monitoring and/or measurement of gaseous pollutants involve sample collection, storage and subsequent analysis. Air pollution control authorities need measurements of a number of toxic gases, including volatile organic compounds (VOC's) to assure acceptable air quality levels. In addition, emission inventory, human exposure data, and industrial manufacturing process control is needed for the development and

implementation of proper control strategies. Frequently, in-situ monitoring and measurement of air pollutants is not feasible because of the cost and complexity of the field deployment of a number of sensitive analytical instruments. The grab sampling offers a viable alternative with lower cost, simplicity, and flexibility of use. Properly collected, appropriate size single grab sample provides important information on a host of atmospheric pollutants when analyzed in a well equipped, permanently based laboratory.

.....The most important requirements for the grab sampling containers are non-contaminating, non-reactive and inert contact surface; small surface to volume ratio; reusability/durability; optimal construction; relatively small size and weight; easy sample collection procedures; acceptable cost; safety and ease of transportation, and application for a wide variety of gaseous and liquid mixtures.

.....The construction and pre-deployment handling of the grab sampling containers, together with the user sampling/recycling procedures determine the degree of success in using them. While deceptively simple the grab samplers evolved over a number of years from simple, "home-built" units to sophisticated, commercially produced sampling instruments. The design approach, selection of quality components and stringent assembly procedures are of utmost importance. For example, proper forming of hemispheres from selected grade of stainless steel sheet stock determines the degree of success in subsequent preparation, cleaning and passivation prior to the assembly. The passivation procedure is the key step in the sampler manufacture. Much more effective than electropolishing the SUMMA passivation process removes surface scale, decreases the contact area by smoothing the SS surface, removes impurities from the stainless steel surface and effectively oxidizes chromium and nickel in the material itself. The cleanliness and inertness of the Summa passivated stainless steel surface has been demonstrated repeatedly by storing ppt levels of trace gases for several months or longer without any appreciable losses of the stored species. With proper cleaning the "blanks" of the grab samplers are below detectable limits of analytical techniques such as GC and GC-MS.

.....The welding procedure is another critical step in the grab sampler construction. Great attention to proper procedures needs to be exercised, i.e. amount of current/heat applied to the stainless steel hemispheres, proper shielding with inert purge gas, absence of oxygen from the welded area, penetration/uniformity of the welds, and care in attaching other components to the finished spherical or cylindrical sampling containers. Complete avoidance of elastomeric materials is an inherent feature of the all-welded, or fitting equipped grab samplers. An extensive quality control/quality assurance program must be an integral part of the entire manufacturing process to ascertain problem free use. Visual and mechanical inspection at every step is supplemented by special leak testing of the completed grab samplers with a sensitive (1×10^{-9} std. cc/sec.) mass spectrometer based helium leak detector. Final cleaning and preparation utilizes a quadrupole mass spectrometer residual gas analyser (RGA) with a mass range up to 200 amu. This instrument allows continuous monitoring and recording of the entire cleaning process with data on any contaminants present in the system, or degassing from the grab sampling containers. If necessary, temperature (100-400 C), and/or evacuation level (10^{-2} to 10^{-5} torr) can be adjusted to completely remove any undesirable species from the finished grab samplers. The final testing/blanking involves individual or batch ECD/FID-GC analysis of the sampling containers readied for shipment.

Grab sampling methods

.....The design of most of the available grab sampling containers allows

several sampling modes. The most common approach uses evacuated grab samplers (care has to be taken to assure zero blanks). A near instantaneous, or time-averaged sample is collected. Sampling stops at sub-ambient or ambient pressure. No pumps or additional hardware is required except a flow control device for the time-averaged sampling. Collected sample is either analyzed directly via an evacuated sample inlet manifold, or the grab sample is pressurized with zero air. The dilution factor has to be taken into consideration when low concentration species are sampled. The size of the grab sampling container determines the final sample volume. Commonly used grab samplers range in size from less than one liter to about fifty liters. The most versatile and widely used size is six liters. Sufficient sample is available for multiple analyses of low level VOC's utilizing cryogenic pre-concentration and GC or GC-MS analysis. The sample inlet, connecting tubing and other components (valves, gauges, regulators) must be meticulously checked for contamination to permit trouble-free sampling and valid data. Most frequently used cleaning procedures use elevated temperatures (dictated by the component material), evacuation (preferably with efficient high vacuum, cold-trapped pumps), or purging with zero air or clean inert gas. Combination of the above techniques can also be used.

.....Positive pressure grab sample collection is carried out with suitable, inert sampling pumps with stainless steel bellows, or combination of SS pump head and Viton diaphragm. The grab sampler can be equipped with a purge "T" assembly to allow dynamic flow in and out of the sampling container via an inlet and outlet valve. Sampling system surface equilibration is one of the benefits of this sampling approach. Other advantages are larger sample size, positive pressure (up to 40 psig) which facilitates sample transfer and analysis, and easy cleaning/recycling with the purge gas. These benefits are offset by somewhat higher cost, need for additional hardware and electrical power. However, considering the durability and flexibility of the grab samplers (particularly with the modular construction where valve(s), pressure/vacuum gauges and flow control devices can be easily added) the purge "T" assembly is a desirable addition to the "basic" grab sampler, outweighing the initial cost. Again, the users must pay great attention to the cleanliness of the sampling system components, and assure satisfactory "blanking" prior to deployment in the field.

.....Cryogenic pumping/enrichment is used infrequently. Great care and emphasis needs to be given to the proper cryogenic sampling system configuration including flow, pressure control and monitoring devices, and suitable material selection (most SS alloys become brittle at low temperatures). The primary advantage is the ability to greatly increase sample volume, or to pre-concentrate compounds of interest by a pumpless, cryogenically induced flow. Additional advantages are stability of reactive species at low temperatures, and ability to use similar approach for sample component separation and pre-concentration prior to analysis. Disadvantages include complexity, use of consumables (i.e. liquid nitrogen, oxygen or argon), and need for skilled personnel.

.....Successful use of grab sampling containers requires a suitable and reliable recycling system typically consisting of a heat source (oven), vacuum source (pump), and clean purge gas (zero air). Sampling system components must be contamination and leak free. Periodic checks are needed to determine the container condition to assure that there is no significant sample degradation, loss or other undesirable phenomena. A grab sampler use log is highly desirable.

.....Currently, the sampling requirements are shifting to longer term, integrated sampling for periods up to 24 hrs. Clearly, flow control in the 1-100 ml/min. range is required. Several approaches are available. Fixed

flow orifices provide a simple, inexpensive flow control but do not allow full utilization of the grab sampling containers. More sophisticated manual or electrically actuated flow controllers are available with better accuracy, reproducibility and ability to take full advantage of the grab samplers when used in conjunction with sampling pumps. Mass flow controllers are also available but their sensitivity to variations in ambient conditions (i.e. temperature) and high cost limit their usefulness. Automated operation of the entire sampling cycle is highly desirable. The timing and hardware (valves, pumps, controllers) actuation functions are easily controlled by a small, low cost microcomputer. The unit controls the sampling start-up time, pump operation, system purge, sequential switching of individual grab sampler inlet valves for up to twelve grab samplers and also operation of the flow or pressure control device(s). In addition, delay between samples, multiple sample collection (duplicates), and other features can be easily incorporated in the computer software. Sample collection parameters are stored and can be easily retrieved, transferred or printed out. The main advantages are full automation and integrated, long-term sequential collection of a number of grab samples. The disadvantages are higher cost and relative system complexity.

Conclusions

The grab sampling has evolved into a well tested and widely used alternative to other sampling methods such as polymeric bags and solid adsorbents. Because of its simplicity, reliability and flexibility of use for a great variety of sampled species ranging from high ppm level to low ppt concentrations the grab sampling is rapidly becoming the preferred method for VOC/NMOC and toxic gas sampling. The automation and significant sampling capability extension (i.e. long-term integrated sample collection), and the availability of sensitive and automated analytical methods (7) provide the researchers, control and regulatory personnel with comprehensive information necessary for effective gaseous air pollutant control and abatement.

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Table I. Passivated stainless steel grab sampler sampling compatibility list

Type or Group of Gases to be Collected	Concentration Range (Parts: Vol./Vol.)	Recommended Sampling Approach	Comments
Inert, man-made gases: SF ₆ , Fluorocarbons, etc.	-12 -6 10-----10	Ambient pressure	Glass/plastic also suitable
Fluorochlorocarbons, Halogenated Hydrocarbons	-11 -6 10-----10	Ambient or positive pressure	Elastomeric materials unsuitable
Hydrocarbons (VOC/NMOC)	-10 -5 10-----10	Positive pressure or cryogenic sampling	Elastomers and some adsorbents not recommended
CH ₄ , CO ₂ , N ₂ O, and most inert gases	-9 -3 10-----10	Ambient pressure	
Sulfur-containing gases (H ₂ S, COS, mercaptans)	-8 -4 10-----10	Positive pressure or cryogenic sampling	Some limitations because of signif. sample loss at low concentrat.
Toxic gases (per EPA classification)	-10 -5 10-----10	Ambient/positive pressure sampling	Some limitations w/ solid adsorb's.
Reactive process gases at elevated temperature	-8 -3 10-----10	Ambient pressure	Avoid condensation Collection @ amb. temp./press. only

NOTE: Collection of reactive gases such as HCL, HF, NO, NO₂, SO₂, and others should be done under controlled conditions.

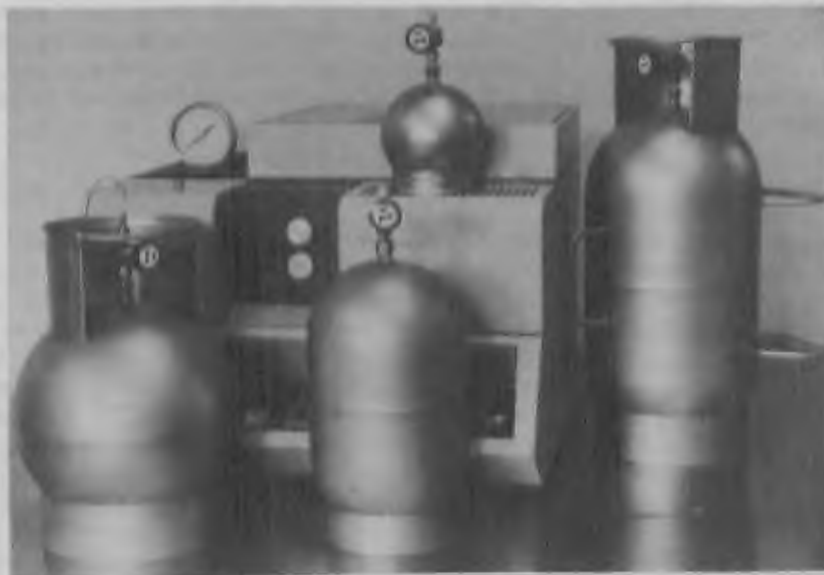


Figure 1. Illustration of grab sampler sizes, shapes and configurations

AMVAN: Delaware's Comprehensive
Air Toxics Monitoring Van

Terri V. Henry, Joseph J. Kliment
Air Surveillance Branch
Division of Air and Waste Management
Delaware Department of Natural Resources
and Environmental Control
New Castle, Delaware 19720

The State of Delaware utilizes a mobile air monitoring van (AMVAN) for sampling and analyses of non-criteria pollutants. The equipment involved in the analyses includes a gas chromatograph, meteorological instrumentation, data logger and computer terminal, radiological equipment and safety equipment. The van is currently used for surveys, emergencies, and radiological response. AMVAN has been effective in monitoring for compounds of interest including benzene and vinyl chloride. Future expansion of its monitoring capabilities is presently under consideration.

AMVAN: Delaware's Comprehensive Air Monitoring Van

Introduction:

AMVAN is Delaware's new mobile air monitoring van designed for rapid sampling and analyses of air pollutants in the field. The van is primarily utilized for short and long term surveys of both hazardous air pollutants and the traditional criteria air pollutants, thus providing the Division of Air and Waste Management with field data for development of air toxics monitoring methodologies and environmental risk assessment. Of particular interest are those air toxic pollutants which have been designated by the Environmental Protection Agency as detrimental to the health of humans.¹

The van was contracted during the winter of 1985 after air releases at a petro-chemical complex focused attention on the State's air toxics monitoring capability. It is the outgrowth of the fixed air monitoring program which has been operational in Delaware since the late sixties. Unfortunately, the major disadvantage of the fixed monitoring system is the inability to cover all air pollutant incidents because of the dependence on wind direction. During the early seventies a small van containing a sulfur dioxide monitor was utilized with considerable success, while plume chasing to determine ground level concentrations of sulfur dioxide. The van was subsequently upgraded to a trailer with an electrical generator and the ability to sample for several air contaminants simultaneously and continuously. The experience obtained from this initial work was incorporated into the design of AMVAN utilizing the latest state of the art instrumentation and data processing.

Along with the survey sampling, the van is also utilized for any air related environmental emergencies, radiological emergencies and upgrading of the emissions inventory for toxic air pollutants. AMVAN is utilized throughout Delaware with the initial effort being concentrated in the industrial areas.

Van Design

The van was designed by Environmental Measurement, Inc. around a Ford Econoline chassis and a specialized Grumman body. It contains instrument racks, a laboratory bench, and an operator's desk, along with a pressurized water system, microwave, refrigerator, and sanitation system to compliment on-board analyses. To provide temperature stability for the instrumentation, two high capacity air conditioner/heater systems are utilized. A unique internal air filtration system protects the operator from exposure to hazardous air pollutants and possible contamination when sampling in the field.² The system utilizes a combined particulate and carbon bed adsorption system to cleanse the air.

AMVAN is designed to operate independent of the normal electrical supply while in the field by utilizing a high capacity electrical ONAN generator. There is, however, the flexibility to connect to the regular electrical supply through an umbilical cord for extended sampling

periods, providing a special adapter is available. To prevent contamination of sampled air by the generator exhaust, the air inlet probe is pointed into the wind and a specially designed catalytic exhaust purifier reduces the hydrocarbon and carbon monoxide to carbon dioxide and water.

Sampling Equipment

The van's initial instrument complement consists of a Photovac 10570 photoionization (PID) gas chromatograph for detection and analysis of atmospheric organic pollutants and meteorological sensors for determining wind speed and direction. The wind sensors are mounted on a telescoping tower which is raised pneumatically to a height of 30 feet. There is the flexibility to raise the mast by a hand pump if the pneumatic system fails. Monitors for measuring criteria air pollutants such as sulfur dioxide, nitrogen oxides, ozone, carbon monoxide, and suspended particulates can be installed in a standard instrument rack.

Radiological monitoring instrumentation such as a Geiger-Mueller counter and Canberra Series 10 Gamma Spectrometer are utilized for radiological emergency sampling.

Consideration is also being given to the installation of a portable flame ionization gas chromatograph or a mass spectrometer or other state of the art instrumentation to compliment the PID gas chromatograph for rapid field analyses of additional organic compounds in the ambient air.

To facilitate field sampling, outside air is drawn through a special intake probe lined with Teflon and into a manifold system to provide sufficient outside air to the appropriate monitoring instruments. Gases for instrument operation and calibration are contained in cylinders in a special storage compartment inside the van.

Safety Equipment

To provide critical protection to the field monitoring team several pieces of safety equipment are supplied in the van. Included are self-contained breathing apparatus (SCBA's), anti-contamination equipment, full-face masks with canisters for organics and radionuclides, portable radiation detection kits, dosimeters, and a first-aid kit.

Data Processing and Communications

Data from the sensors are processed through an Environmental Systems Corporation on-board data logger and computer with direct read-out on a Qwint computer terminal. The computer can provide information on pollutant concentrations, wind speed and direction, along with necessary quality assurance data. Large volumes of data can be stored directly on an on-board magnetic tape for subsequent processing on a PDP 11/23 DEC air quality computer at the laboratory. The van operator has complete flexibility, through the data terminal, to make program or command changes or requests for special data output.

For purposes of emergency data reporting, a unique system for transmitting data utilizing a "cellular" car phone modem is being evaluated. Air pollution data would be sent via the cellular phone system directly to a

terminal thus providing emergency planners with finger-tip information. Data could also be sent directly to the air quality computer at the laboratory for subsequent storage and processing capability.

A cellular car phone presently provides direct communication capabilities with Department and State emergency management personnel through use of the standard telephone system. AMVAN also contains a state communications radio with the capability of communicating with the Department of Natural Resources and Environmental Control and Division of Emergency Planning and Operations should an emergency occur.

Field Applications and Experiences

The van is currently surveying a manufacturer who produces chlorinated benzenes. This involves locating the van upwind, downwind and in densely populated areas near the plant to monitor for benzene and monochlorobenzene. In the future, a comparison will be made between various plant processes with the results of the survey on the fugitive emissions. This will be incorporated into the State of Delaware's emission inventory program.

A second on-going seasonal study involves a company which produces asphalt concrete used as a paving material for surfacing roads. The plant produces both conventional and recycled asphalt. Odor complaints have been made by the local citizens during the manufacturing of recycled asphalt, and as a result a survey has been initiated utilizing AMVAN to compare the total ionizables calibrated as hexane between the conventional and recycle processes to determine any major emission differences between the two products.

AMVAN has also been incorporated into Delaware's radiological emergency plan.³ It is utilized as an analysis and communications base in support of radiological monitoring activities. For training purposes it is involved in a Nuclear Regulatory Commission/Federal Emergency Management Agency annual drill along with Delaware's Department of Emergency Planning and Operations (DEPO). These exercises prepare the Department for Emergency planning in case of an accidental release from a nuclear power plant located in New Jersey or for a radiological transportation accident.

The van has been called out on an emergency response incident involving a leaking underground gasoline storage tank. Gasoline fumes had been detected in a private citizens home which were linked to a local gasoline station. Gasoline from the station's underground storage tank seeped into the storm sewer and telephone conduit. Ventilation systems were placed on the storm sewers to relieve vapor pressure which was building up inside. Grab samples were taken above the ventilation systems in response to the local citizens concerns. These samples were injected into the gas chromatograph located in the AMVAN while on site. Benzene, toluene and xylene peaks were detected but were not significant.

These are only a few examples of the capabilities for a mobile air monitoring vehicle.

Summary

AMVAN provides needed surveys to establish environmental impacts and upgrade emission inventories. The van also is used during emergencies and for radiological response. AMVAN has been and will continue to be a valuable asset to the on-going development of the air toxics program for the State of Delaware.

Acknowledgement

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ESTIMATION OF VAPOR PRESSURES FOR NON-POLAR ORGANIC
COMPOUNDS FROM GAS CHROMATOGRAPHIC RETENTION DATA

T.F. Bidleman^{1,2}, D.A. Hinckley², and W.T. Foreman³
1. Department of Chemistry and 2. Marine Science Program,
University of South Carolina, Columbia, SC 29208.
3. Cooperative Institute for Research in Environmental
Sciences, University of Colorado, Boulder, CO 80309.

The vapor pressure of an organic chemical exerts a large influence on its dispersal in the environment, directly affecting volatilization from soils and adsorption to suspended particles in air. The Henry's Law constant, which can be calculated from the ratio of vapor pressure to water solubility, is a controlling factor in the air-water exchange of vapors. Vapor pressure also governs the ability of a solid adsorbent to collect organic vapors during air sampling.

Conventional methods of determining vapor pressures, effusion and gas saturation, are time-consuming and require fairly large quantities of material. Capillary gas chromatography (GC) offers an alternative method of estimating vapor pressures for non-polar compounds. Several compounds can be run per day, and only analytical standard quantities of chemical are required. The latter feature is an advantage when dealing with highly toxic or costly materials.

In a previous article (1) we presented the theoretical and experimental details for determining ambient temperature vapor pressures by GC. Briefly, test compounds and a reference compound having a known vapor pressure are chromatographed at a series of temperatures on a short fused silica column coated with a non-polar stationary phase. Vapor pressures of test compounds are calculated from the relative retention times of test to reference compounds and the reference compound vapor pressure.

When the GC method was applied to 24 test compounds having reported vapor pressures, we found that the initial estimate of vapor pressure, p_{CC}^0 , was well correlated with but not exactly equal to the compound's liquid-phase vapor pressure, p_L^0 . One reason for the discrepancy lies in the fact that many high molecular weight organic compounds are solids at ambient temperatures, and their (hypothetical) p_L^0 must be calculated from the vapor pressure of the crystalline solid, p_S^0 , using:

$$\ln p_L^0/p_S^0 = (\Delta S_f/R)(T_m - T)/T \quad \text{Equation 1.}$$

In Equation 1, T_m and T are the melting and ambient temperatures (kelvin), R is the gas constant, and ΔS_f is the entropy of fusion. Average values of ΔS_f are 13.5 and 13.1 cal/deg-mol for rigid aromatic hydrocarbons (2) and polychlorinated biphenyl (PCB) congeners (3), but substantial differences among compounds occur. For example, the range of ΔS_f for several PCB congeners is 10-17 cal/deg-mol (3). In this study we have improved and expanded the GC vapor pressure technique published earlier (1):

1. Instead of assuming an average $\Delta S_f = 13.5$ cal/deg-mol as done previously (1), we used experimental ΔS_f for as many test compounds as possible. Experimental p_{CC}^0 were then correlated to p_L^0 , calculated from the test compound's p_S^0 using Equation 1.
2. A new GC reference compound, p,p'-DDT, was selected to supplement the n-alkane references eicosane and octadecane previously used (1). The p_S^0 and ΔS_f of p,p'-DDT have been well established by several investigators. From average literature values and Equation 1, $\log p_L^0$ (torr) = $-4640/T + 10.20$. Moreover, p,p'-DDT is electron capture detector (ECD) responsive whereas a flame ionization detector (FID) is required with the n-alkanes. Use of an ECD is advantageous in that very small quantities of halogenated test compounds can be chromatographed, reducing the possibility of overloading the short capillary column.
3. Vapor pressures (p_L^0) of several organochlorine insecticides have been determined, including endosulfan and its metabolites, major constituents of technical chlordane, and two highly toxic components of technical toxaphene.
4. The limitations of the GC method when applied to somewhat polar molecules such as organophosphate and pyrethroid insecticides have been examined.

Experimental

Test and reference compounds were chromatographed on a polydimethylsiloxane bonded phase fused silica column (BP-1, SGE Inc.) 1.0-m long x 0.22 mm i.d. mounted in a Carlo Erba 4160 or Varian 3700 instrument. A series of 4-7 isothermal runs in the 70-180° range was made. An FID was used with hydrocarbons (PAH and n-C₂₀) and organophosphates; halogenated hydrocarbons (pesticides, PCB) were detected with an ECD. Conditions: carrier gas H₂ or He at 1-3 mL/min, injector 150-240°, detector 300-320°. Samples in n-hexane were injected at a 10-20:1 split ratio. Data treatment was as described in (1).

Results and Discussion

In our original study (1) compounds were chromatographed on a bonded phase (BP-1) column and a WCOT column containing n-C₈₇ (Apolane-87). The Apolane-87 column has since been discontinued by its only manufacturer (Quadrex, Inc.), so only the BP-1 column was used in the present investigation. We also switched from He to H₂ carrier about midway through the project, and observed improved column efficiency.

Seventeen hydrocarbons and halogenated hydrocarbons having known vapor pressures (Table 1) were chromatographed along with the p,p'-DDT reference, and p_{GC}^o were calculated from relative retention data (1). These p_{GC}^o were compared to p_L^o of the test compounds, which were calculated from literature p_S^o using Equation 1. In converting p_S^o to p_L^o, we used experimental ΔS_f values in Equation 1, taken from references (3-7). A plot of log p_L^o vs. log p_{GC}^o showed a close correlation between the two vapor pressures, with a small systematic difference, the regression equation being:

$$\text{Log } p_L^o = 0.991 \text{ Log } p_{GC}^o + 0.094, \quad r^2 = 0.953 \quad \text{Equation 2.}$$

Equation 2 was used to calculate p_L^o from measured p_{GC}^o for compounds of unknown vapor pressure.

Vapor pressures (p_L^o) of several organochlorine pesticides, determined by the GC method, are given in Table 2. Literature values were available for only two of these, and in both cases the agreement is reasonably good. The determination of p_L^o for Toxicants A and B illustrates an important application of the GC method. These toxic components of technical toxaphene are not available commercially, and could only be obtained in microgram quantities from laboratories involved in toxaphene research. Their vapor pressures probably could not have been determined in any other way.

In our previous article (1), p_L^o of several PCB congeners were determined using an eicosane or octadecane reference and a calibration curve based on 24 test compounds. The calibration curve was prepared using an average ΔS_f = 13.5 cal/deg-mol to convert literature p_S^o to p_L^o. These data have been recalculated using experimental ΔS_f for as many test compounds as possible, which resulted in slight changes in p_L^o for the PCB congeners. A selection of the recalculated congener data is given in Table 3, along with recent values determined by Murphy et al. using a static equilibration method (8). The agreement is generally very good, although the p_L^o derived from GC measurements are slightly higher. The p_L^o of Murphy et al. (8) were obtained from commercial Aroclor fluids, and adherence to Raoult's Law was assumed.

To test the accuracy of the GC method with moderately polar compounds, p_{GC}^o of ten organophosphate pesticides and flame retardants were determined vs. n-alkane references. The p_{GC}^o were generally higher than p_L^o of the organophosphates, by an average factor of 3.8. Since p_{GC}^o overestimated p_L^o, caution is suggested in applying the GC method to polar compounds. One could continue to use the n-alkane standards, derive a regression equation for organophosphates similar to Equation 2, and then calculate p_L^o from measured p_{GC}^o. Alternatively, an organophosphate of known vapor pressure could be used as a reference compound to determine p_{GC}^o, which should then correspond more closely to p_L^o, an approach preferred by

Kim et al. (9). Similar difficulties may be encountered with other polar compounds. The p_{GC}^o of four synthetic pyrethroid insecticides were determined vs. p,p' -DDT and p_L were calculated using Equation 2. The results showed a high bias when compared to literature values, by an average factor of 6.0 (Table 4).

In conclusion, the GC method can provide accuracy within a factor of two for the p_L^o of non-polar hydrocarbons and organochlorines. If a BP-1 or equivalent column is used to determine p_{GC}^o for other non-polar compounds, their p_L^o can be calculated using Equation 2. The technique should prove useful for other classes of non-polar air pollutants such as chlorinated dioxins and dibenzofurans.

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Table 1. Test Compounds for Vapor Pressure Calibration (Figure 2).

	$-\log p_L^0$, torr (25°C) ²		$-\log p_L^0$, torr (25°C) ²
HCBz	3.051	p,p'-DDE	4.625
PH	3.125	2,2',4,5,5'-PeCB	4.654
AN	3.153	EICH	4.706
ALD	3.246	o,p'-DDT	4.863
γ -HCH	3.321	p,p'-DDD	5.132
PY	3.967	BaA	5.390
DIEL	4.119	2,2',3,3',5,5',6,6'-OCB	5.404
2,2',5,5'-TeCB	4.222	DCB	6.967
FLA	4.322		

1. Abbreviations: HCBz = hexachlorobenzene, PH = phenanthrene, AN = anthracene, ALD = aldrin, HCH = hexachlorocyclohexane, PY = pyrene, DIEL = dieldrin, TeCB = tetrachlorobiphenyl, FLA = fluoranthene, PeCB = pentachlorobiphenyl, EICH = eicosane, BaA = benz(a)anthracene, OCB = octachlorobiphenyl, DCB = decachlorobiphenyl.

2. Calculated from literature p_g^0 (1,10) and experimental ΔS_f (3-7) using Equation 1.

Table 2. Vapor Pressures of Organochlorine Pesticides.

	p_L^0 , torr (25°)		p_L^0 , torr (25°)
<u>Chlordane Components</u>		<u>Endosulfans</u> ¹	
Heptachlor	2.6E-4	Endosulfan ether	4.4E-4
α -Chlordene	2.0E-4	Endosulfan lactone	8.1E-5
γ -Chlordene	1.4E-4	Endosulfan I	5.6E-5
trans-Chlordane	5.9E-5	Endosulfan II	3.5E-5
cis-Chlordane	4.3E-5	Endosulfan sulfate	1.5E-5
trans-Nonachlor	3.5E-5		
cis-Nonachlor	1.6E-5		
<u>Miscellaneous</u> ²			
α -Hexachlorocyclohexane	1.3E-3		
Toxicant B ₃	2.1E-5		
Toxicant A ³	1.2E-5		

1. Literature for Endosulfan I (10) = 2.9E-5

2. Literature for α -HCH (11) = 2.0E-3

3. Components of technical toxaphene

Table 3. Vapor Pressures of PCB Congeners

	p_L^0 , torr (25°)	
	This Work	Murphy et al. (8) ¹
2,2',5,6'-TCB	2.1E-4	1.4E-4
2,3',4,4'-TCB	5.3E-5	3.4E-5
2,2',4,4',5-PCB	2.7E-5	2.0E-5
2,2',3,4,5'-PCB	2.1E-5	1.6E-5
2,2',4,4',5,5'-HCB	6.9E-6	3.4E-6
2,2',3,4,4',5'-HCB	5.3E-6	2.0E-6
2,2',3,4',5,5',6-HCB	1.4E-6	1.3E-6
2,2',3,4,4',5,5'-HCB	5.7E-7	4.2E-7

1. estimated from values at 20°C.

Table 4. Vapor Pressures of Synthetic Pyrethroids

	p_L^0 , torr (25°C)		
	This Work	Literature(11,13,14)	Error Factor ¹
cis-Permethrin	1.9E-7	3.7E-8	5.1 +
trans-Permethrin	1.6E-7	2.5E-8	6.4 +
Cypermethrin	4.3E-8	5.2E-9	8.3 +
Phenvalerate	1.6E-8	3.7E-9	4.3 +

1. This work/literature.

ESTIMATES OF VAPOR-PARTICLE PARTITIONING FOR SOME INDIVIDUAL POLYCHLORINATED BIPHENYLS AND n-ALKANES IN DENVER AIR.

William T. Foreman^{1,3} and Terry F. Bidleman^{1,2}

1. Department of Chemistry.
2. Marine Science Program, and Belle W. Baruch
Institute for Marine Biology and Coastal Research.
University of South Carolina, Columbia, SC 29208.
3. Present address: Cooperative Institute for
Research in Environmental Sciences, Campus Box
449, University of Colorado, Boulder, CO 80309.

ABSTRACT

Polychlorinated biphenyls (PCB), n-alkanes, and other semivolatile organic compounds (SOC) are present in air in gaseous and particulate forms. Estimates of the vapor-to-particle (V/P) distribution for non-polar SOC can be obtained from high volume air sampling using a glass fiber filter to collect particles and an adsorbent trap to collect vapors. Apparent V/P distributions of 10 PCB congeners and 6 n-alkanes (octadecane to tricosane) from air samples collected in Denver, CO were estimated using the partition coefficient $A(TSP)/F$, where A and F are the adsorbent- and filter-retained SOC concentrations and TSP is the total suspended particle concentration. $A(TSP)/F$ were related to the average sampling temperature (T, Kelvin) through: $\log A(TSP)/F = m/T + b$. For both classes of compounds, fitted $\log A(TSP)/F$ at 5°C correlated well with the SOC liquid (or sub-cooled liquid) phase vapor pressure.

INTRODUCTION

Atmospheric residence times of trace organic pollutants depend on the chemical and physical properties of the constituents which control their removal. Removal processes include destruction mechanisms (i.e., reactions with oxidizing species or photolysis), precipitation scavenging, dry deposition of particles, and dry gas exchange with various surfaces. For semivolatile organic compounds (SOC), a critical consideration in modeling removal mechanisms is the distribution of these contaminants between the vapor and particle phases.^{1,2} Knowledge of this distribution

is also useful when developing sampling and pollution control equipment.

One method of estimating the vapor-to-particle (V/P) distribution, and factors influencing it can be obtained from high volume air sampling using a filter to collect particles and an adsorbent trap to collect vapors. In recent years, several research groups have used this approach to estimate the V/P ratio for selected SOC, including polycyclic aromatic hydrocarbons (PAH),³⁻⁵ n-alkanes,⁶ and organochlorine pesticides and total polychlorinated biphenyls (PCB).⁷ The present study was undertaken to estimate the apparent V/P distribution of selected individual PCB congeners and n-alkanes in Denver, Colorado air, and to test the influence of SOC vapor pressure on the partitioning process.

EXPERIMENTAL

A total of nine high volume air samples were collected in downtown Denver in October 1985 and January 1986, using a glass fiber filter-polyurethane foam (PUF) plug sampling system. Filters and PUF plugs were extracted in a soxhlet extractor for 24 h, and the extracts cleaned-up and fractionated using an alumina-silicic acid column chromatography procedure.⁸ n-Alkanes were quantified by GC-FID, and individual PCB congeners by GC-ECD using the method of Capel et al.⁹

RESULTS AND DISCUSSION

Apparent V/P distributions of 6 n-alkanes (octadecane to tricosane) and 10 cleanly separated PCB congeners (tetra- to heptachlorobiphenyls in the Aroclor 1254 fluid region) were estimated using the partition coefficient $A(TSP)/F$, where A and F are the adsorbent- and filter-retained SOC concentrations and TSP is the total suspended particle concentration. $A(TSP)/F$ of the individual SOC were related to the average sampling temperature (T, Kelvin) using an expression derived by Yamasaki et al.³:

$$\text{Log } [A(TSP)/F] = m/T + b \quad (\text{Equation 1})$$

Examples of Equation 1 plots for 5 PCB congeners are shown in Figure 1. Similar plots were constructed for the other 5 PCB and the n-alkanes. Most of the scatter in these plots is probably related to the use of an average sampling temperature for the 12-24 h sampling period when temperatures fluctuated by as much as 21°C. Temperature variations can produce changes in the partial pressure of SOC in equilibrium with particulate matter, resulting in blow-off losses or adsorption gains to the particles on the filter. Changes in SOC concentration would produce a similar effect. Samples were also collected during the fall and winter, and differences in particle size distribution, surface area, and content of carbonaceous material may have influenced the partitioning. The influence of relative humidity on SOC adsorption to particles is also unknown, and humidity conditions varied daily.

For both classes of compounds, log-log plots of the best fit $A(TSP)/F$ at 5°C versus the liquid (or subcooled liquid) phase vapor pressure (p_L^0) of the SOC were constructed. A/F partitioning of the n-alkanes (Figure 2) revealed a high degree of correlation with p_L^0 ($r^2 = 0.995$). Similarly, Figure 3 shows that partitioning of the 10 PCB congeners also correlated well with p_L^0 ($r^2 = 0.977$), and these results are in agreement with previous studies suggesting that A/F partitioning of non-polar SOC

is largely governed by the compound's liquid phase vapor pressure.^{7,8}

CONCLUSIONS

Despite the inability to control the critical variable of temperature and vapor concentration, field studies of PCB and n-alkane partitioning from high volume experiments have provided estimates of the apparent V/P distribution, as determined from the adsorbent- to filter-retained ratio. This study, along with other field⁷ and laboratory⁸ investigations of V/P partitioning, have revealed that SOC volatility, expressed by p_L^0 , is the dominating factor governing the adsorption of non-polar SOC to urban air particulate matter.

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Figure 1

Plots of $\log A(TSP)/F$ versus $1/T$ (Equation 1) for some Aroclor 1254 region PCB congeners in Denver air. 95% confidence bands for the predicted lines are included. Congener chlorine substitution patterns are PCB #175 = 2,3,4,6,2',3',5'; PCB #146 = 2,3,5,2',4',5'; PCB #70 = 2,5,3',4'; PCB #110 = 2,4,5,2',5'; PCB #180 = 2,3,4,5,2',4',5'.

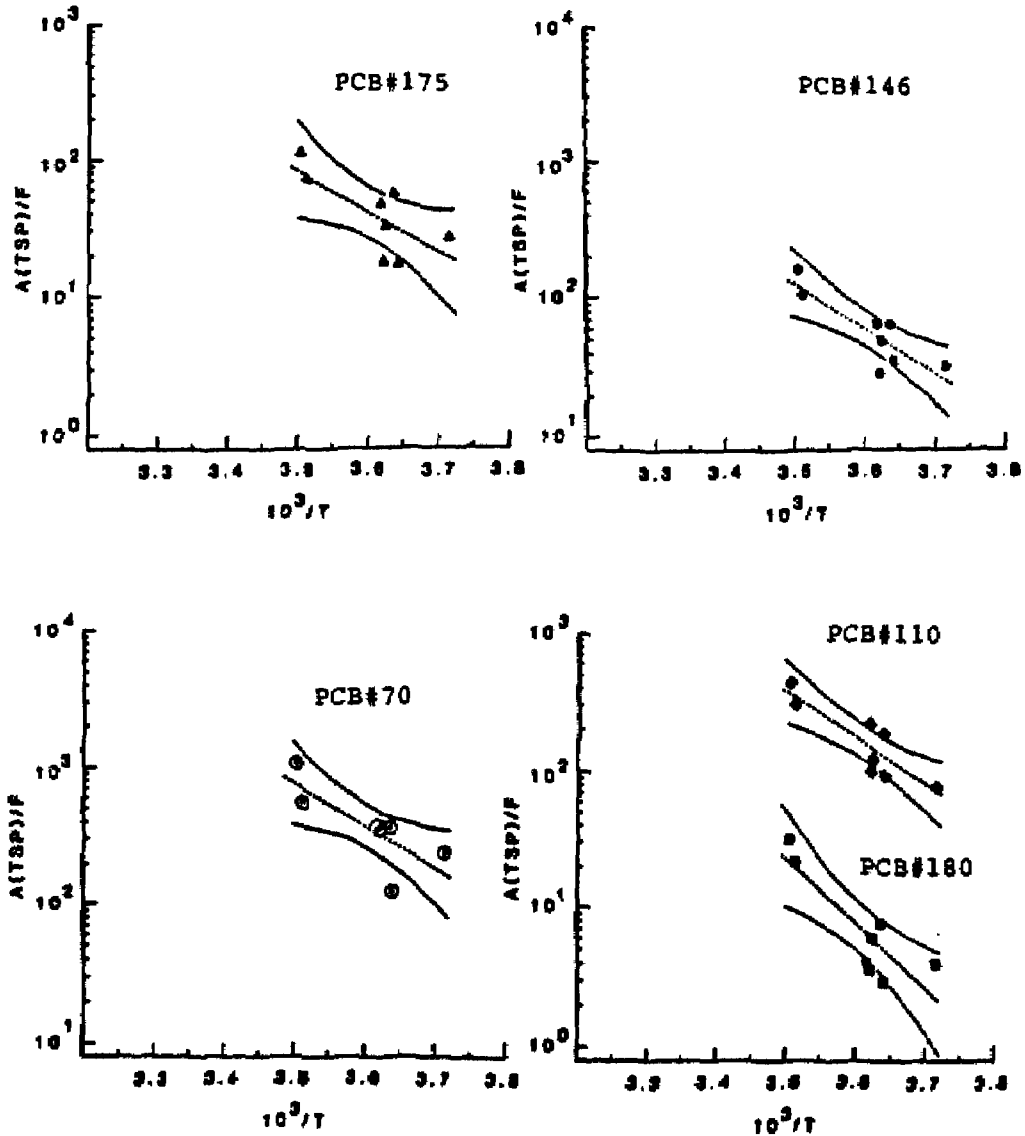


Figure 2

Plot of $\log A(TSP)/F$ at $5^{\circ}C$ versus $\log p_L^{\circ}$ for the n-alkanes. 95% confidence limits for the predicted points, derived from the Equation 1 plots, are shown. 18 = octadecane through 23 = tricosane are plotted.

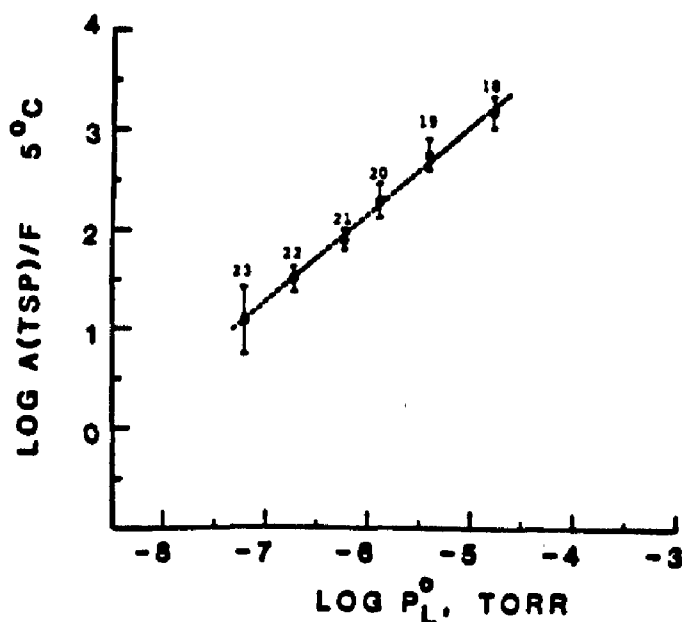
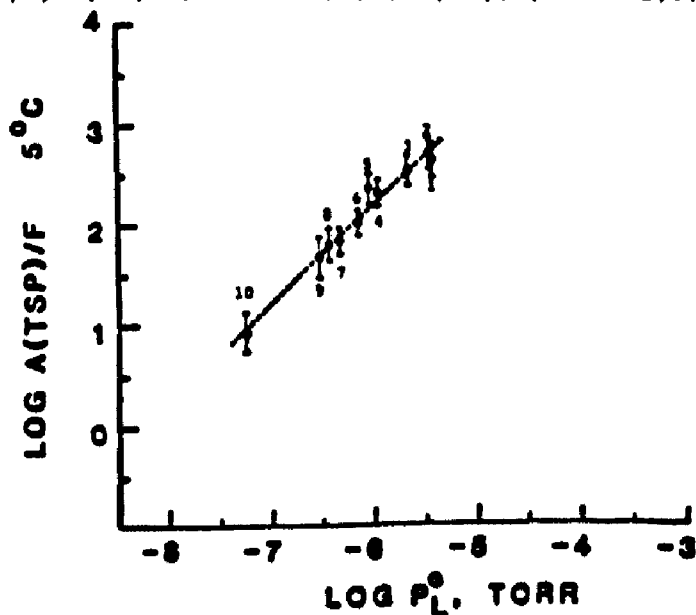


Figure 3

Plot of $\log A(TSP)/F$ at $5^{\circ}C$ versus $\log p_L^{\circ}$ for selected congeners in the Aroclor 1254 region. 95% confidence limits for the predicted points, derived from the Equation 1 plots, are shown. 1 = 2,5,3',4'; 2 = 2,4,3',4'; 3 = 2,4,5,2',5'; 4 = 2,3,6,3',4'; 5 = 2,3,4,2',3'; 6 = 2,4,5,3',4'; 7 = 2,3,5,2',4',5'; 8 = 2,4,5,2',4',5'; 9 = 2,3,4,6,2',3',5'; 10 = 2,3,4,5,2',4',5'.



MEASUREMENTS OF DIBENZODIOXINS AND DIBENZOFURANS IN AMBIENT AIR

Brian D. Eitzer and Ronald A. Hites
School of Public and Environmental Affairs
and Department of Chemistry
Indiana University
Bloomington, Indiana 47405

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are toxic compounds which are transported through the atmosphere. It has been shown by a comparison of sources and sinks that during the transport process there is a change, in the homolog profile of these compounds. To examine this change, a method of measuring these compounds in ambient air was developed. The method uses a high volume air sampler equipped with a glass fiber filter and polyurethane foam plug. This allows for the separate analysis of particulate and vapor phases. The filter and plug are spiked with isotopically labeled standards prior to extraction and clean-up. The purified extracts are analyzed by electron capture, negative ion, chemical ionization gas chromatographic mass spectrometry. The PCDD and PCDF are quantified as the total concentration of each homolog class for tetrachloro through octachloro homolog classes. Atmospheric concentrations and vapor to particle ratios (V/P) for each class have been determined; there is an inverse relationship between log V/P and temperature.

Introduction

The presence of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in remote lake sediments¹ indicates that these compounds are transported through the atmosphere to environmental sinks such as lake sediments or human fat.² The major sources of these compounds to the atmosphere are waste incineration³⁻¹⁰ or automobile exhaust.¹¹ The homolog profiles (the relative amount of the compounds grouped by chlorination level) in the sources and in the sinks are different. In the sources, there is a broad range of homolog classes; in the sinks, the pattern is dominated by octachlorodioxin with heptachlorodioxins and furans as minor components. In order to determine what factors are important during the atmospheric transport process, we have undertaken a study of PCDD and PCDF in ambient air. The concentrations of PCDD and PCDF in vapor and particulate phases have been determined and have been shown to be affected by temperature and level of chlorination.

Experimental Methods

Air samples were taken at four sites in Bloomington, Indiana. Air was sampled with a high volume air sampler modified with a 10 x 10 cm polyurethane foam (PUF) plug as a back-up to a 0.1 μ m glass fiber filter. Air was sampled at 0.5 m³/min for a two to three day period. The total suspended particulate matter was determined by equilibrating the filter in a desiccator for 24 hrs and weighing it both before and after sampling.

Prior to extraction, the glass fiber filter and the PUF plug were spiked with per-¹³C-octachlorodibenzodioxin and per-¹³C-1,2,3,7,8-pentachlorodibenzofuran as internal standards. It was assumed that any losses that occurred during extraction and clean-up were equal for the internal standard and the analytes. This pair of labeled standards was calibrated with unlabeled standards to develop response factors for each homolog class.

Air samples were Soxhlet extracted with 300 ml benzene for the glass fiber filters and 2 L petroleum ether for the PUF plug for a period of 24 hr. After extraction, the solvent was reduced and exchanged to hexane in a rotary evaporator and taken through a two-step chromatographic clean-up to remove interferences.

The extracts were passed through a 1.5 x 20 cm column packed with silica gel, activated at 160° C for 16 hr then deactivated with 1% by weight of water and equilibrated for 16 hr. The sample was eluted with 75 mL each of hexane, 15% methylene chloride in hexane, and methylene chloride. The dioxins and furans were collected in the second fraction. The solvent of this fraction was exchanged to hexane and reduced to less than 1 mL. This sample was then passed over a 0.5 x 6.5 cm micropipet packed with alumina, activated at 250° C for 2 hr, then deactivated with 1% by weight of water and equilibrated for 16 hr. The sample was eluted with 8 mL each of hexane, 2% methylene chloride in hexane, and 40% methylene chloride in hexane. The dioxins and furans were present in the third fraction which was collected in an 8 mL sample vial and concentrated to 100 μ L by slowly passing purified N₂ over the sample. The sample was then ready for gas chromatographic mass spectrometry (GC/MS).

The samples were analyzed on a Hewlett-Packard 5985B GC/MS system. A 30 m x 0.25 mm DB-5 fused silica column with helium as the carrier gas, was temperature programmed (splitless injection at 60° C, isothermal for

2 min., 300 C/min to 2100 C, 20 C/min to 2800 C, isothermal for 10 min) to separate the dioxins and furans. The mass spectrometer was operated in the electron capture, negative ionization mode with methane as the reagent gas. The ion source pressure was 0.4 torr, and the ion source temperature was 150° C. To enhance sensitivity, selected ion monitoring was used. Two ions from the most intense isotopic cluster of each homolog group were monitored for each of the dioxins and furans. If these ions were not present in the proper ratio, as predicted by the isotopic abundances, it was assumed that the peak was that of an interferent and was not quantified.

Samples were quantified by using response factors for each homolog class as compared to the labeled standards (one isomer per homolog class). Concentrations were then determined by ratioing the peak areas, multiplying by the amount of the internal standard added, dividing by the sample weight, and correcting for the response factor. Concentrations are reported as fg/m³ of each homolog class. It should be noted that the method might be significantly underestimating the concentration of 2,3,7,8-tetrachlorodioxin because this particular homolog does not respond well in the negative ion mode.

Results

Since the PUF plugs act as frontal chromatography columns, it is important that the air sample volume be below the chromatographic breakthrough volume. Although the breakthrough volume for these analytes and plugs was not rigorously measured, two experiments were performed to assure ourselves that the breakthrough volume was not exceeded. In the first experiment, a PUF plug was split in two halves (orthogonal to the flow) which were analyzed separately. No dioxins or furans were found on the back half of the plug. In the second experiment, two samples were obtained simultaneously at different flow rates; thus, different volumes of air were sampled. If the breakthrough volume was exceeded the higher volume sample should have lower concentrations. This was not the case, indicating that the sample volume was less than the breakthrough volume.

The average concentrations of PCDD and PCDF in a 40 measurement data set are shown in Figure 1. It should be noted that the vapor phase shows increased concentrations of the less chlorinated homologs as compared to the particulate bound phase. This is expected because these homologs are more volatile. Also note that the particulate bound homolog profile is quite similar to that seen in other environmental sinks.^{1,2,12} This suggests that this phase is important in the transport of these compounds from their sources to their sinks.

For any given homolog, the ratio of the vapor phase to the particulate bound phase is dependent on temperature. This can best be seen in Figure 2 which is a plot of the log of this ratio vs. inverse temperature for the hexachlorodioxins and furans. As the temperature rises, the vapor phase becomes more prevalent.

Conclusions

We have measured PCDD and PCDF in air at femtogram per cubic meter levels. The method we have developed can be used to study these compounds as they are transported from source to sink. The data suggest that the sorption of PCDD and PCDF to particulate matter plays an important role in the transport of these compounds to environmental

sinks. This sorption is temperature dependent as shown by the inverse relationship between the vapor/particulate ratio and temperature.

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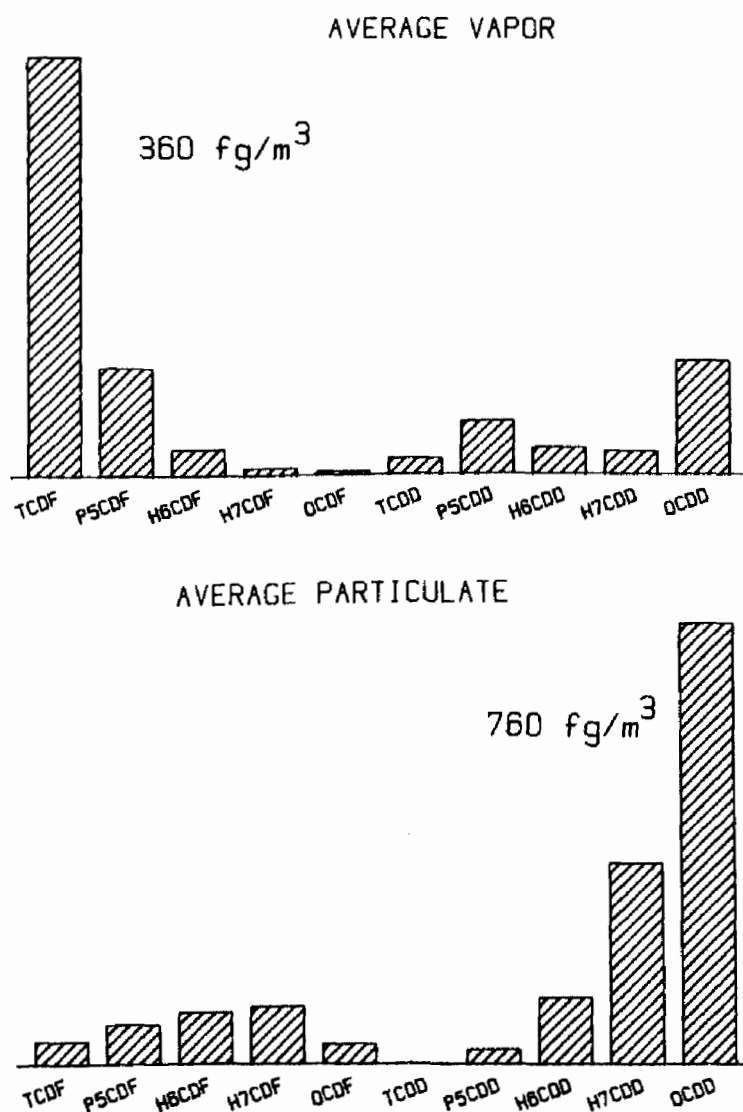
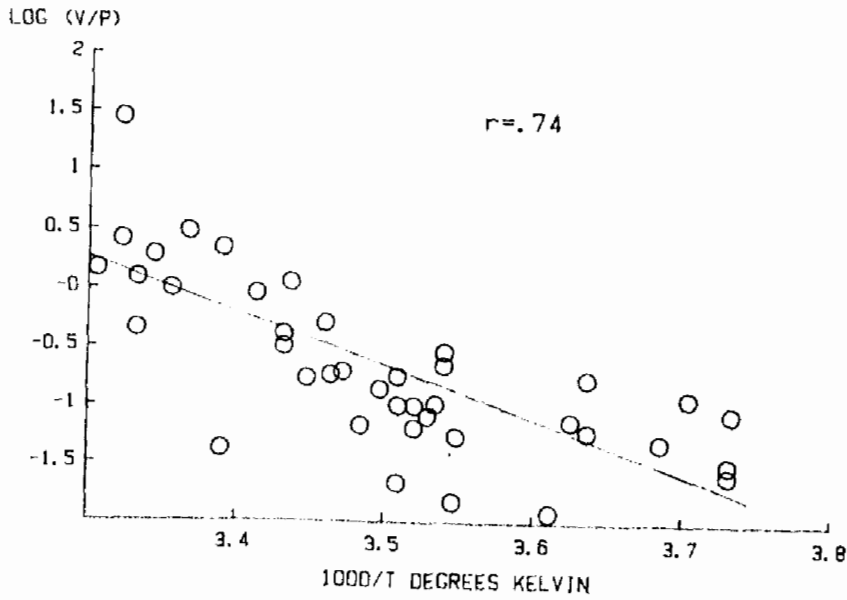


Figure 1. Average concentrations (in fg/m³) of PCDD and PCDF in air in Bloomington, Indiana. Top, the vapor phase; bottom, the particulate bound phase. Total concentrations of each homolog class of the tetra-, penta-, hexa-, hepta- and octachlorodibenzofurans (TCDF, P5CDF, H6CDF, H7CDF, and OCDF, respectively) and tetra-, penta-, hexa-, hepta-, and octachlorodibenzo-p-dioxins (TCDD, P5CDD, H6CDD, H7CDD, and OCDD, respectively) are shown. The concentration of the most abundant homolog class in each group is shown.

H6CDD



H6CDF

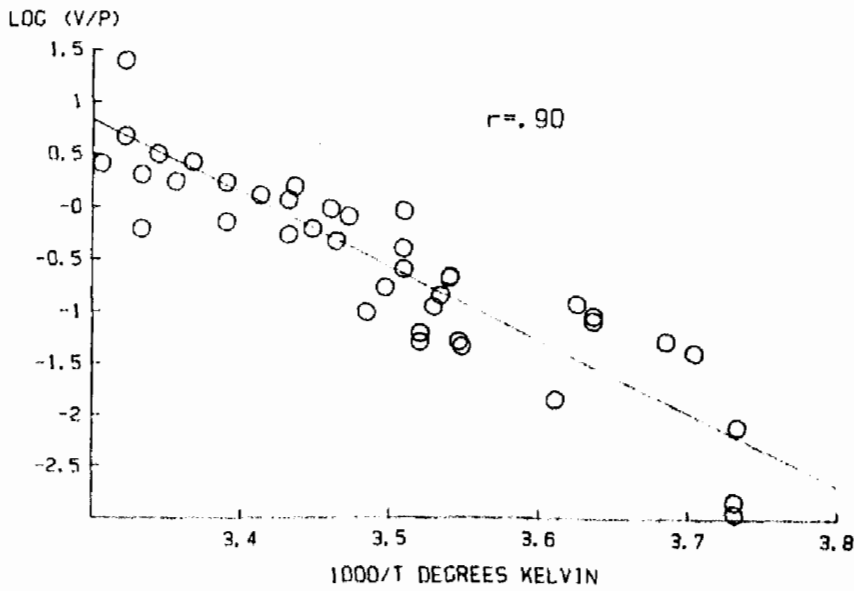


Figure 2. Log (vapor/particulate) plotted vs. inverse temperature for hexachlorodibenzo-*p*-dioxins and hexachlorodibenzofurans. The correlation coefficients (r) are shown.

MEASUREMENT OF HENRY'S LAW CONSTANT
FOR SELECTED HALOCARBONS IN
DILUTE AQUEOUS SOLUTIONS

Gary B. Howe
Tony N. Rogers
Research Triangle Institute
Research Triangle Park, North Carolina

Joseph E. Knoll
M. Rodney Midgett
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina

Henry's law constant is an important physicochemical property to consider in predicting the environmental fate of toxic organic compounds. Many environmental fate assessment models depend heavily upon Henry's law constants as measures of air/water equilibrium partitioning behavior. In addition, Henry's law constant is an important parameter in the design of handling and treatment processes for toxic organic contaminated water. In this work, Henry's law constants were measured for methylene chloride, chloroform, and 1,2-dichloroethane using two different techniques. The first technique used was a static headspace measurement technique known as Equilibrium Partitioning in Closed Systems (EPICS) in which equal masses of organic compound were loaded into different liquid volume systems and allowed to equilibrate overnight. The organic concentration in the headspace of each bottle was then measured by gas chromatography with flame ionization detection. Measurements were performed at five different temperatures ranging from 10-30°C. In addition, measurements were performed using EPICS for solutions of 0.5 M sodium chloride in water containing low concentrations of volatile organic compound. The second technique used was batch air stripping in which an organic compound in water solution was purged with air while monitoring the organic in air effluent concentration by GC-FID. Henry's law constant was determined from a linear regression of the logarithm of concentration versus time. Measurements using this technique were performed at selected temperatures for comparison with the EPICS results.

Introduction

In addition to the well established problem of groundwater contamination from toxic organic compounds, air emissions of volatile organic compounds (VOC) from hazardous waste treatment, storage, and disposal facilities has become a major environmental concern. In the case of surface impoundments, the VOCs are usually present in water at relatively low concentrations and thus Henry's law for ideal dilute solutions can be applied for vapor-liquid equilibrium calculations.

A technique frequently used to estimate Henry's law constant of a VOC in water is to calculate the ratio of the pure compound's vapor pressure to its aqueous solubility limit, as expressed in Equation 1.

$$H_C = \frac{p^{\text{sat}}}{X_s} \quad (1)$$

where: p^{sat} = vapor pressure of the pure VOC, atm

X_s = ultimate solubility of the VOC in water, mole fraction

This assumes that an incremental amount of VOC added to a saturated aqueous solution will form a second pure organic phase that has an equilibrium partial pressure above it equal to the pure component vapor pressure. To use this estimation technique, it also must be assumed that the Henry's law relationship is valid up to the ultimate solubility limit. And obviously, this technique will only provide an accurate determination of Henry's law constant when reliable vapor pressure and aqueous solubility data are available.

The objectives of this work were: (1) to explore some simple experimental techniques for directly measuring Henry's law constant for dilute solutions of VOC in water as an alternative to the potentially unreliable estimation technique, (2) to test the effects of solution ionic strength on the Henry's law constant of three VOCs, and (3) to compare experimentally determined values of Henry's law constant for chloroform, 1,2-dichloroethane, and methylene chloride with those calculated from the estimation technique described earlier.

Experimental Methods

The first technique used for directly measuring Henry's law constant is known as Equilibrium Partitioning in Closed Systems, or EPICS, which was originally proposed by Gossett and Lincoff in 1984. EPICS is based on a closed system mass balance for a given VOC distributed between liquid and gas phases. The component mass balance takes the form shown in Equation 2.

$$M = C_L V_L + C_G V_G \quad (2)$$

where: M = total organic mass in system
 C_L = liquid-phase organic concentration
 C_G = gas-phase organic concentration
 V_L = total liquid volume
 V_G = total gas volume

If the same mass of organic compound is introduced into two closed containers containing different volumes of pure water, a mass balance

expression can be written for each system. Equating these expressions and introducing Henry's law to substitute for the liquid phase VOC concentrations gives an equation relating Henry's law constant to headspace concentrations and known volumes. (Equation 3)

$$H_C = \frac{(C_{G1}/C_{G2}) V_{L1} - V_{L2}}{V_{G2} - (C_{G1}/C_{G2})V_{G1}} \quad (3)$$

where: H_C = dimensionless Henry's law constant

Absolute concentrations need not be measured because any proportional measure of concentration, such as GC peak areas, will yield the required headspace ratio for Equation 3.

Prior to performing EPICS measurements, a saturated stock solution for each compound was prepared by adding an amount of organic solute in excess of the solubility limit to pure water in one liter amber glass bottles. Stock solutions were allowed to equilibrate for several days before using.

In preparing samples, two pairs of 250 ml amber glass bottles were filled with 20 ml and 200 ml of pure water, respectively. The same volume of saturated stock solution was then added to each bottle and the bottles were sealed with a Teflon lined silicon rubber septum cap. The stock solution volume added was dependent upon compound solubility and was chosen to produce an initial liquid phase concentration of 10 milligrams per liter. This was to ensure that the measurements were made in the concentration range where Henry's law is obeyed. The loaded bottles were shaken vigorously by hand and placed in a constant temperature water bath for a minimum of 16 hours before analysis.

After equilibration, headspace samples were withdrawn from the bottles with a 1.0 cm³ gas-tight syringe and injected into a Varian 3700 gas chromatograph equipped with a flame ionization detector. The GC column consisted of a 14 in. long X 1/8 in. OD stainless steel tube packed with 60/80 mesh Porasil B. Peak areas were measured by electronic integrator and the results were transmitted to a personal computer data file. A mean Henry's law constant and relative standard deviation were determined from the four measurements by intercomparing the two sets of high volume/low volume results. Measurements were performed for each compound at five different temperatures beginning at 10°C and ranging to 30°C in 5°C increments.

Additional measurements were performed using EPICS with substitution of 0.5 M sodium chloride for pure water as diluent. Measurements were performed for all three compounds at temperatures ranging from 10-30°C.

A second technique investigated for measuring Henry's law constant is known as batch air stripping. The system we used is shown schematically in Figure 1 and consisted of a water-jacketed glass column with a glass fritted disc press-fit into the column inlet. Air was supplied to the column from a tank of high purity compressed air. Purge air was passed through a water-filled impinger prior to entering the column to prevent water evaporation from the column. A constant flow of temperature con-

trolled water was maintained through the column jacket to ensure isothermal operation.

Before beginning a run, the column was loaded with a known volume of pure water. After temperature equilibration, a quantity of saturated stock solution was pipetted into the column and gas flow was initiated at a preset rate. The column exit gas was pumped through a 0.5 cm³ stainless steel sample loop attached to a six-port rotary valve. The valve was actuated periodically to inject samples into a GC with a flame ionization detector. Sample peak elution time was typically 30-45 sec which allowed real-time analysis of column effluent gas instead of collecting liquid aliquots for later headspace analysis.

Henry's law constant was calculated by correlating concentration data against a solute mass balance equation for the column. The differential form of the mass balance is shown in Equation 4.

$$Y_0 G - Y(t)G = \frac{d}{dt} (C(t)V) \quad (4)$$

where: Y_0 = organic concentration at gas inlet, mol/m³
 $Y(t)$ = time-variable outlet gas concentration, mol/m³
 G = volumetric gas flow rate, m³/min
 $C(t)$ = time-variable liquid concentration, mol/m³
 V = total liquid volume, m³

By substituting Henry's law relationship into Equation 4 and integrating, the expression shown in Equation 5 results.

$$\ln C(t) = \ln C_0 + \frac{H_c G}{V} t \quad (5)$$

where: t = elapsed time, minutes

According to this equation, a logarithmic plot of liquid or gas-phase concentration as a function of elapsed time will yield a straight line with a slope directly related to Henry's law constant. It is not necessary to know the initial batch concentration, C_0 , or absolute concentrations in the gas phase since only the y-intercept will be influenced by these factors. Therefore, any proportional measure of gas phase concentration such as GC peak area can be inserted for $C(t)$. There are two primary assumptions in using the batch air stripping technique for measuring Henry's law constant: (1) the gas exiting the column must reach full concentration equilibrium with the organic laden liquid and (2) there must be complete mixing of the liquid within the column. These two requirements can create problems in column design since the first requirement of equilibrium is best achieved in tall columns whereas complete mixing is most easily achieved in shorter columns.

Results

Summarized in Table I are the Henry's law constants measured for methylene chloride, 1,2-dichloroethane, and chloroform using the EPICS technique. Good precision was achieved with the relative standard deviation less than 8 percent at all temperatures. As expected, the measured constants increased with the increasing temperature as solubility decreases and vapor pressure increases. The constants are reported in units resulting from expressing the gas phase concentration as a partial pressure in atmospheres and the liquid phase concentration in moles per cubic meter.

Shown in Table II are selected results from EPICS measurements performed with substitution of 0.5 M sodium chloride for pure water. The control results are those which were determined earlier for pure water diluent tests. The constants measured for 0.5 M NaCl systems were consistently higher than the results for pure water systems, indicative of the "salting out" effect that ionic species have on VOCs. The difference between the constants for pure water and salt water was statistically significant in all cases except methylene chloride at 20°C and chloroform at 30°C.

The 0.5 M salt concentration used is approximately that of seawater and thus can be considered a worst case situation for natural waters when assessing the influence of salt concentration on vapor-liquid equilibrium.

Table III shows results from measurements performed by batch air stripping for methylene chloride and chloroform at two different liquid depths compared with values for the same compounds at 25°C determined by EPICS and estimated from literature values of vapor pressure and solubility. The slight increase in measured constants by batch air stripping in increasing the liquid depth from 44 cm to 56 cm provides some evidence that full equilibrium was not achieved for either compound with this column design. It is not known whether these differences are statistically significant given the limited number of tests performed.

Literature estimates of Henry's law constant for both compounds are in relatively good agreement with measured values, suggesting that Henry's law is obeyed up to the solubility limit and literature values for both aqueous solubility and pure compound vapor pressure are accurate.

Conclusions

Both EPICS and batch air stripping are suitable techniques for direct measurement of Henry's law constant for hydrophobic organic compounds. Some advantages of EPICS are: (1) the mass transfer limitation of the batch air stripping technique is avoided since the equilibration of VOC between vapor and liquid phases can take place over several hours, and (2) the method is relatively simple-requiring only septum bottles, routine laboratory glassware, a constant temperature bath, and a gas chromatograph with flame ionization detector. Some limitations of EPICS are: (1) it is fairly time consuming since most compounds require at least overnight equilibration before measurements can be performed, (2) there is the potential for adsorption of VOC to the bottle or septum surfaces resulting in loss of mass and biasing of headspace concentrations, and (3) a limited range of sensitivity since at Henry's law constants greater than about 2.0 (dimensionless units), the headspace concentration ratio becomes nearly

constant. However, most VOC's of environmental interest have dimensionless constants of less than 1.0.

A definite increase was observed in Henry's law constants of the three compounds in systems containing 0.5 M NaCl, indicating a salting-out effect, and suggesting that ionic strength should be considered in determining vapor-liquid equilibrium behavior of VOCs.

Table I. EPICS Test Results

Temp., VC	<u>H_c, atm-m³/mol (RSD)</u>		
	<u>Methylene chloride</u>	<u>1,2-Dichloroethane</u>	<u>Chloroform</u>
10	1.40 x 10 ⁻³ (7.0)	7.05 x 10 ⁻⁴ (4.4)	1.72 x 10 ⁻³ (4.1)
15	1.69 x 10 ⁻³ (1.5)	8.79 x 10 ⁻⁴ (4.1)	2.33 x 10 ⁻³ (2.5)
20	2.44 x 10 ⁻³ (4.8)	1.21 x 10 ⁻³ (7.8)	3.32 x 10 ⁻³ (2.4)
25	2.96 x 10 ⁻³ (2.6)	1.46 x 10 ⁻³ (1.6)	4.21 x 10 ⁻³ (5.2)
30	3.61 x 10 ⁻³ (1.7)	1.75 x 10 ⁻³ (6.9)	5.54 x 10 ⁻³ (7.2)

Table II. Ionic Strength Test Results

<u>Compound</u>	<u>H_c (dimensionless)</u>		<u>Temp., VC</u>
	<u>Control</u>	<u>0.5M NaCl</u>	
Methylene chloride	0.0600	0.0792	10
	0.1015	0.1080	20
	0.1452	0.1566	30
1,2-Dichloroethane	0.0303	0.0432	10
	0.0504	0.0605	20
	0.0705	0.0832	30
Chloroform	0.0742	0.0889	10
	0.1380	0.1470	20
	0.2228	0.2348	30

Table III. Batch Air Stripping Results

	<u>Henry's law Constant, atm-m³/mol</u>	
	<u>Methylene Chloride</u>	<u>Chloroform</u>
Batch air stripping (44 cm depth)	2.64 x 10 ⁻³	4.43 x 10 ⁻³
Batch air stripping (56 cm depth)	2.71 x 10 ⁻³	4.62 x 10 ⁻³
EPICS	2.96 x 10 ⁻³	4.21 x 10 ⁻³
Lit. estimate	2.52 x 10 ⁻³	3.82 x 10 ⁻³

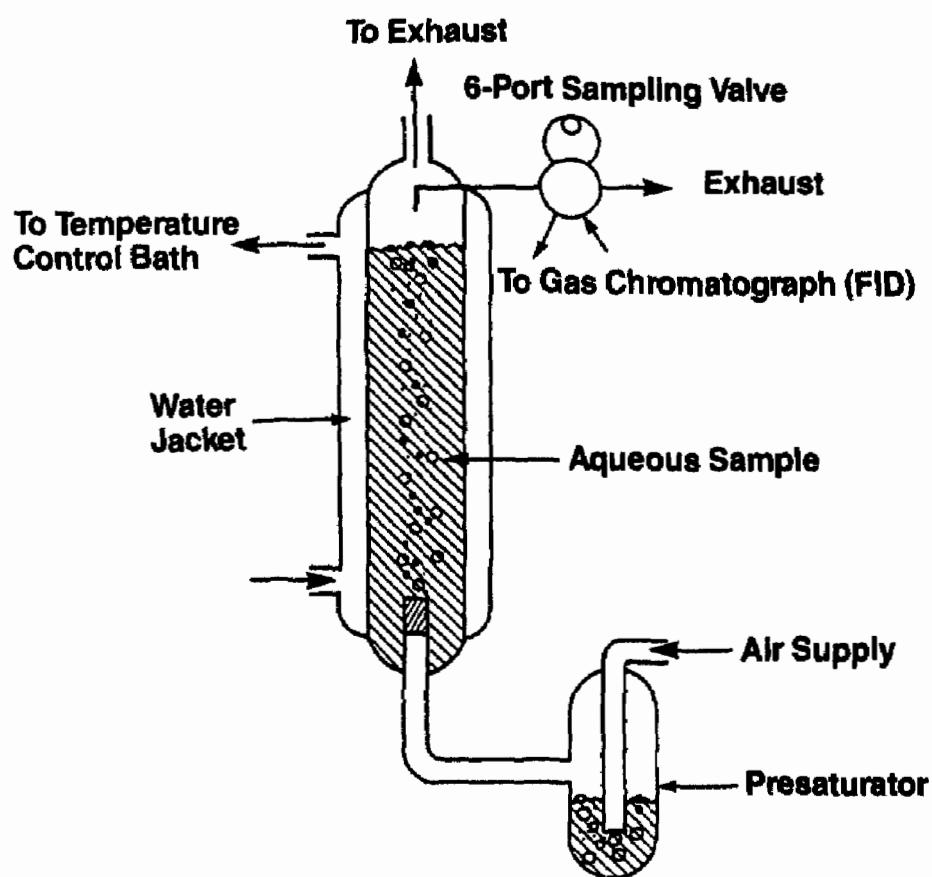


Figure 1. Batch air stripping column.

EXPERIMENTAL AND CALCULATED REACTIVITY
PARAMETERS OF POTENTIAL ENVIRONMENTAL
SIGNIFICANCE FOR NITRO-POLYCYCLIC
AROMATIC HYDROCARBONS

Arthur Greenberg
Chemistry Division
New Jersey Institute of Technology
Newark, New Jersey 07102

William J. Simonsick, Jr.
Marshall Research and Development Laboratory
E.I. DuPont de Nemours & Co.
3500 Grays Ferry Avenue
Philadelphia, Pennsylvania 19146

Joel F. Liebman
Department of Chemistry
University of Maryland Baltimore County
Catonsville, Maryland 21228

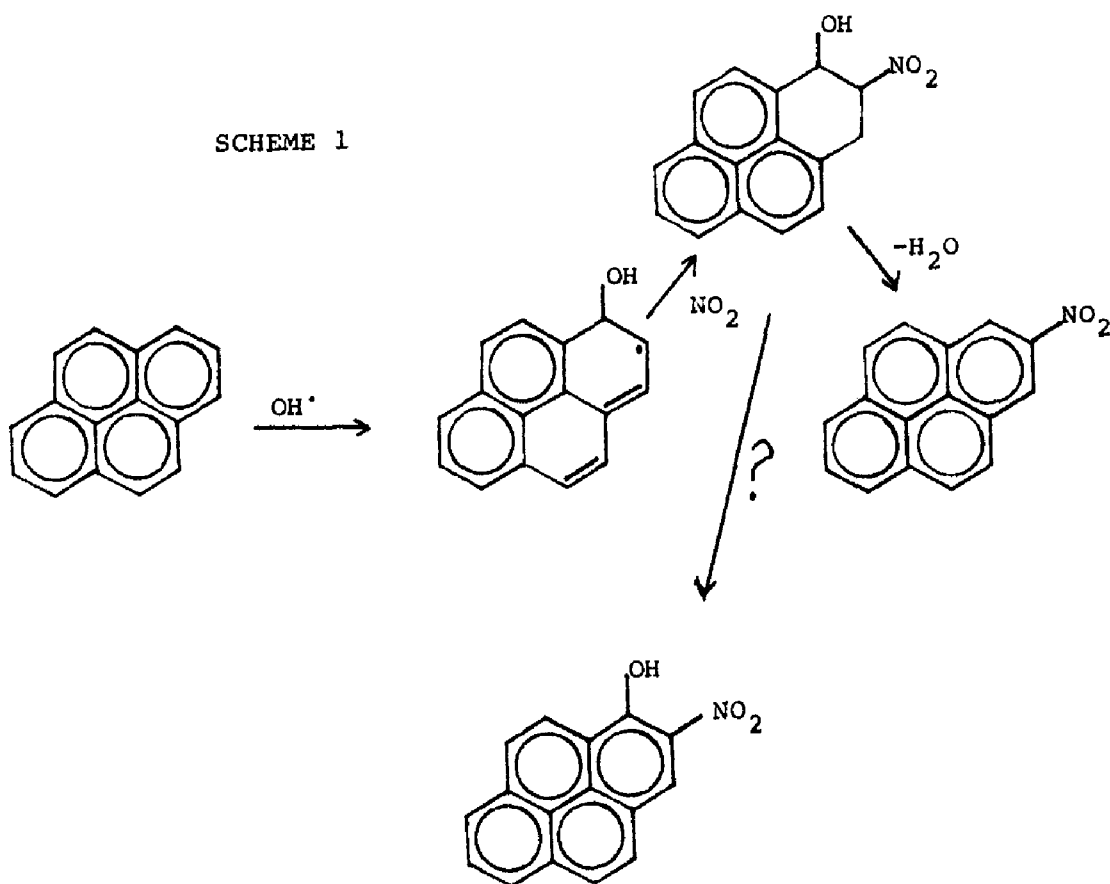
Abstract

Theoretical and experimental parameters related to the ambient stabilities of nitrated polycyclic aromatic hydrocarbons are presented. The calculational method is MNDO, a semiempirical technique development by Dewar and co-workers. Properties of interest include gas-phase enthalpies of formation, first and second ionization potentials (and their difference) and electron affinities as well as comparisons with PAH. It is apparent that ionization potentials are affected by the number of nitro groups rather than by position of substitution. There also appears to be a "saturation" effect on larger or more substituted molecules. The IP1 - IP2 difference for the nitro-PAH barely changes relative to the difference for the corresponding PAH possibly indicating no dramatic effects for reaction with singlet oxygen and possibly ozone.

EXPERIMENTAL AND CALCULATIONAL REACTIVITY PARAMETERS OF POTENTIAL ENVIRONMENTAL SIGNIFICANCE FOR NITRO-PAH

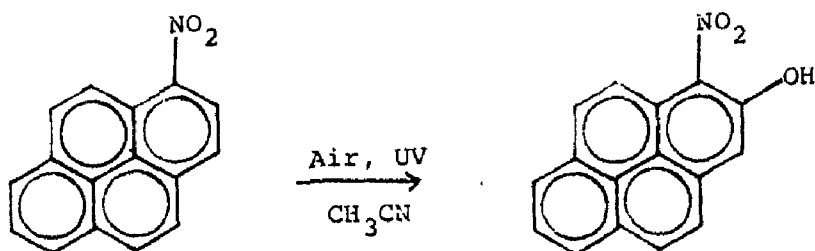
Introduction

During recent years there has been increased awareness of the potential health hazards associated with airborne nitro derivatives of polycyclic aromatic hydrocarbons(nitro-PAH).(1) Presently, interest has focused on more polar mutagenic compounds, many of which are apparently nitrated.(2) A specific group of compounds, hydroxynitropyrenes or nitropyrenols, have been identified in air samples and seem to be associated with significant biological activity.(3-5) In trying to understand how polar nitro compounds are formed, one can consider the reactivity of the PAH themselves. Thus, the formation of 2-nitropyrene is thought to proceed via initial attack of OH on pyrene in the presence of oxides of nitrogen as shown in Scheme 1.(6) 2-Nitrofluoranthene can be produced similarly.(6) It is also possible that 2-nitrofluoranthene may be produced during gas-phase reactions of fluoranthene with dinitrogen pentoxide (pyrene does not yield 2-nitropyrene under these conditions).(6)



The possibility that a compound such as 2-nitropyren-1-ol may be formed under these conditions does not appear to have been considered explicitly. In this case it is clear that hypothetical formation of this compound would depend on PAH, not nitro-PAH, reactivity. Photochemical reaction of 1-nitropyrene (Scheme 2) in solution yields the indirect mutagen 1-nitro-2-pyrenol.(7,8) However, this compound does not appear to be present in ambient airborne particulates although measurable amounts are observed in particulate matter associated with diesel emissions.(9,10)

SCHEME 2



It is not clear whether nitropyrenols observed in air and associated with aerosol aging are formed from the nitropyrenes or from pyrenols, nor is it clear that the other classes of more polar derivatives of nitro-PAH presumed to be present are formed from the nitro-PAH themselves. Nevertheless, it seems useful to summarize what is known experimentally about parameters related to nitro-PAH reactivity and add to the data set with calculation. There has been little uniform reported data on nitro-PAH decomposition. Table 1 reports selected examples of published data.

Presentation of Results

In Table 2 we present experimental and calculational data on nitro-PAH and related PAH. The calculational technique is MNDO developed by Dewar and co-investigators.(11) Calculations were performed at the Indiana University CDC Cyber 170/855 and some of these (PAH) have been reported elsewhere.(12) The experimental ionization potentials (IP, adiabatic) and electron affinities (EA) are from a compendium (13). It is clear from Table 2 that for the PAH, the calculated IPs are higher than the experimental values. Part of this is because the calculated values will correspond to vertical IPs if one assumes the validity of Koopmans theorem. Only four values for nitro-PAH (considering benzene a "PAH") are known experimentally and the values are also 0.6 - 0.9 eV too low but the trends are reasonable. Figure 1 illustrates that there is something of a "saturation effect" on placing nitro groups on PAH of increasing size. Thus, the difference in first IP between the nitro-PAH and the corresponding PAH appears to decrease as the PAH gets larger. In Table 3 are listed experimental IPs and EAs for a variety of substituted

nitrobenzenes. Although the other monosubstituted benzenes are not presented, again there is a "saturation effect" in that the difference in IP between benzene and nitrobenzene is greater than that between toluene and nitrotoluene. It is also clear that positional substitution of the nitro group has very little effect on ionization potentials. The largest effects are produced as one increases the degree of nitration. The nitroaniline IPs are qualitatively different from the rest of the set in that ionization is largely from the amino lone pair. It is still surprising that direct conjugation of the pi-donor amino with the pi-acceptor nitro has such a small effect. Generally, these results agree with the virtual equality of the IPs of 1-nitro and 2-nitronaphthalene. It is also clear from Table 3 that there are considerably large positive electron affinities for nitrated aromatics (they are strong charge-transfer acceptors) while, in contrast, benzene radical anion is unbound. In Table 4 we list the first and second IPs for some PAH and their nitro derivatives. It has been noted that PAH most reactive to Diels-Alder reactions, a model for reaction of some PAH with singlet oxygen or ozone, are the ones having the greatest difference between IP1 and IP2 even if the IPs are relatively high.(14) It is clear from Table 4 that nitro groups do not dramatically effect this difference (although one should keep in mind that these substituents are not coplanar with the ring). It is possible that 7-nitrobenz(a)anthracene may be less reactive toward singlet oxygen than the parent hydrocarbon.

In Figure 2 we have plotted charges and other data for the nitro-PAH investigated. There is evidence that, for alternant PAH at least, greater reactivity is associated with high relative positive charge.(12) If this follows for nitro-PAH, then 2-nitroanthracene, for example, should be more reactive than the other two isomers. It would also appear that 2-nitropyrene should be more reactive than the 1-nitro isomer. The nitro-olefinic nature of 1-nitroacenaphthylene is clear from this figure and some of this is present in 9-nitrophenanthrene.

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Table 1. Examples of reactivity studies on Nitro-PAH

COMPOUND	CONDITIONS	$t_{1/2}$	PRODS
9-Nitroanthracene ^a	part. carbon (dark)	--	--
	silica (dark)	--	--
	O ₃ , NO ₂	--	anthraquinone
1-Nitropyrene ^b	UV/DMSO soln	1.2 d	phenols, quinones
	UV/silica	6 d	" "
3-Nitrofluoranthene ^b	UV/DMSO soln	12.5 d	" "
	UV/silica	>20 d	" "
1,8-Dinitropyrene ^b	UV/DMSO soln	0.7 d	" " *
	UV/silica	5.7 d	" " *

*plus significant 1-nitropyren-8-ol

a. D.A. Saucy, R.M. Kamens, R.W. Linton, Polycyclic Aromatic Hydrocarbons, Ninth International Symposium, M. Cooke and A.J. Dennis (eds), Battelle Press, Columbus, 1986, pp. 811-825.

b. P.C. Howard, M.C. Biaglow, M.P. Holloway, E.C. McCoy, M. Anders, H.S. Rosenkranz, Presentation at Tenth International Symposium on Polycyclic Aromatic Hydrocarbons, Columbus, Ohio, October 21-23, 1985.

Table 2. Comparison of experimental IP and EA data for PAH and nitro-PAH (eV) with corresponding MNDO values

	IP(expt)	MNDO			MNDO EA
		IP1	IP2	Diff	
Nitrobenzene (1)	9.86	10.31	10.46	0.15	0.80 (0.97) ^a
1-Nitronaphthalene (2)	8.60	9.30	9.81	0.51	
2-Nitronaphthalene (3)	8.65	9.30	9.91	0.61	
9-Nitroanthracene (4)	7.87	8.72	9.57	0.85	1.59
1-Nitroanthracene (5)		8.60	9.51	0.91	1.47
2-Nitroanthracene (6)		8.62	9.59	0.97	1.49
9-Nitrophenanthrene (7)		9.16	9.24	0.08	1.24
1-Nitroacenaphthylene (8)		9.41	9.58	0.17	1.82
3-Nitroacenaphthylene (9)		9.40	9.54	0.14	1.67
4-Nitroacenaphthylene (10)		9.35	9.54	0.19	1.60
5-Nitroacenaphthylene (11)		9.37	9.58	0.21	1.66
1-Nitropyrene (12)		8.62	9.35	0.73	1.57
2-Nitropyrene (13)		8.58	9.40	0.82	1.47
2-Nitrofluoranthene (14)		9.03	9.21	0.18	1.55
7-Nitrofluoranthene (15)		9.00	9.25	0.25	1.58
5-Nitrotetracene (16)		8.27	9.39	1.12	1.81
7-Nitrobenz(a)anthracene (17)		8.73	9.11	0.38	1.52
6-Nitrobenzo(a)pyrene (18)		8.45	9.11	0.66	1.73
Benzene	9.25	9.39	9.39	0.00	
Naphthalene	8.15	8.58	9.11	0.53	
Anthracene	7.41	8.05	8.97	0.92	
Phenanthrene	7.86	8.48	8.70	0.22	
Acenaphthylene	8.22	8.53			
Pyrene	7.41	8.03	8.77	0.74	
Fluoranthene	7.95	8.47	8.72	0.25	
Tetracene	6.97	7.72	8.89	1.17	
Benz(a)anthracene	7.41	8.11	8.62	0.51	
Benzo(a)pyrene	7.12	7.83	8.65	0.82	

a. Experimental value

Table 3. Experimental IP and EA Affinities of selected nitroaromatics.

	IP(eV)	EA (kcal)
Benzene	9.25	---
Nitrobenzene	9.86	22.3
1,2-Dinitrobenzene	≤ 10.71	---
1,3-Dinitrobenzene	10.3	36.2
1,4-Dinitrobenzene	10.43	43.6
1,3,5-Trinitrobenzene	10.96	60.6
2-Nitroaniline	8.27	
3-Nitroaniline	8.31	
4-Nitroaniline	8.34	
3-Nitrobenzonitrile	10.29	
4-Nitrobenzonitrile	10.23	
2-Nitrotoluene	9.45	20.6
3-Nitrotoluene	9.48	21.3
4-Nitrotoluene	9.40	20.9
2-Nitro-o-xylene	9.17	
4-Nitro-m-xylene	9.10	
2-Nitroethylbenzene	9.39	
3-Nitroethylbenzene	9.64	
4-Nitroethylbenzene	9.71	
1,3,5-Trinitrotoluene	8.8	
Toluene	8.82	
Ethylbenzene	8.77	

Table 4. Relationships of IP₁ and IP₂ and their differences for PAH and nitro-PAH. (MNDO values in eV).

PAH	NITRO-PAH	IP ₁	IP ₂	DIFF
Benzene		9.39	9.39	0.00
	Nitrobenzene	10.31	10.46	0.15
Phenanthrene		8.48	8.70	0.22
	9-Nitrophenanthrene	9.16	9.24	0.08
Naphthalene		8.58	9.11	0.43
	1-Nitronaphthalene	9.30	9.81	0.51
	2-Nitronaphthalene	9.30	9.91	0.61
Benz(a)anthracene		8.11	8.62	0.51
	7-Nitrobenz(a)anthracene	8.73	9.11	0.38
Anthracene		8.05	8.97	0.92
	1-Nitroanthracene	8.60	9.51	0.91
	2-Nitroanthracene	8.62	9.58	0.96
	9-Nitroanthracene	8.72	9.57	0.85
Tetracene		7.72	8.89	1.17
	5-Nitrotetracene	8.27	9.39	1.12

Figure 1.

EXPERIMENTAL ADIABATIC IONIZATION POTENTIALS
OF AROMATICS AND CORRESPONDING NITROAROMATICS

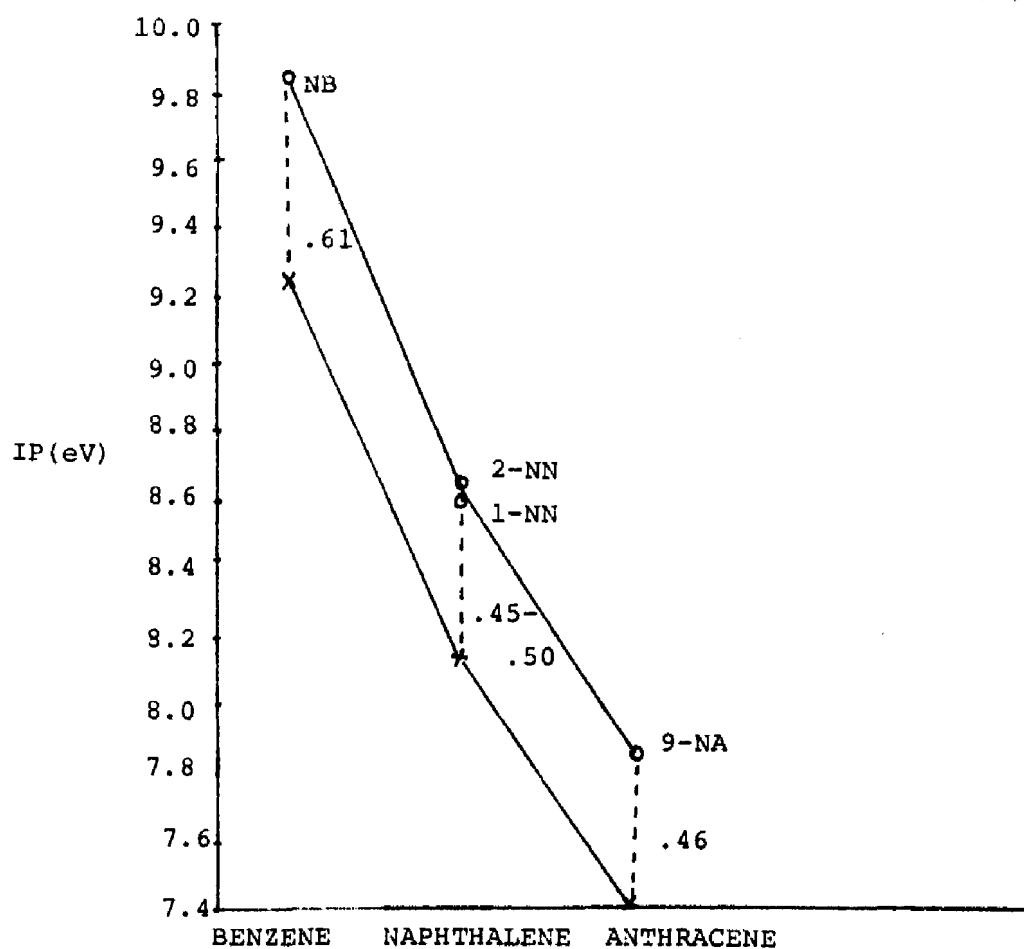


Figure 2.

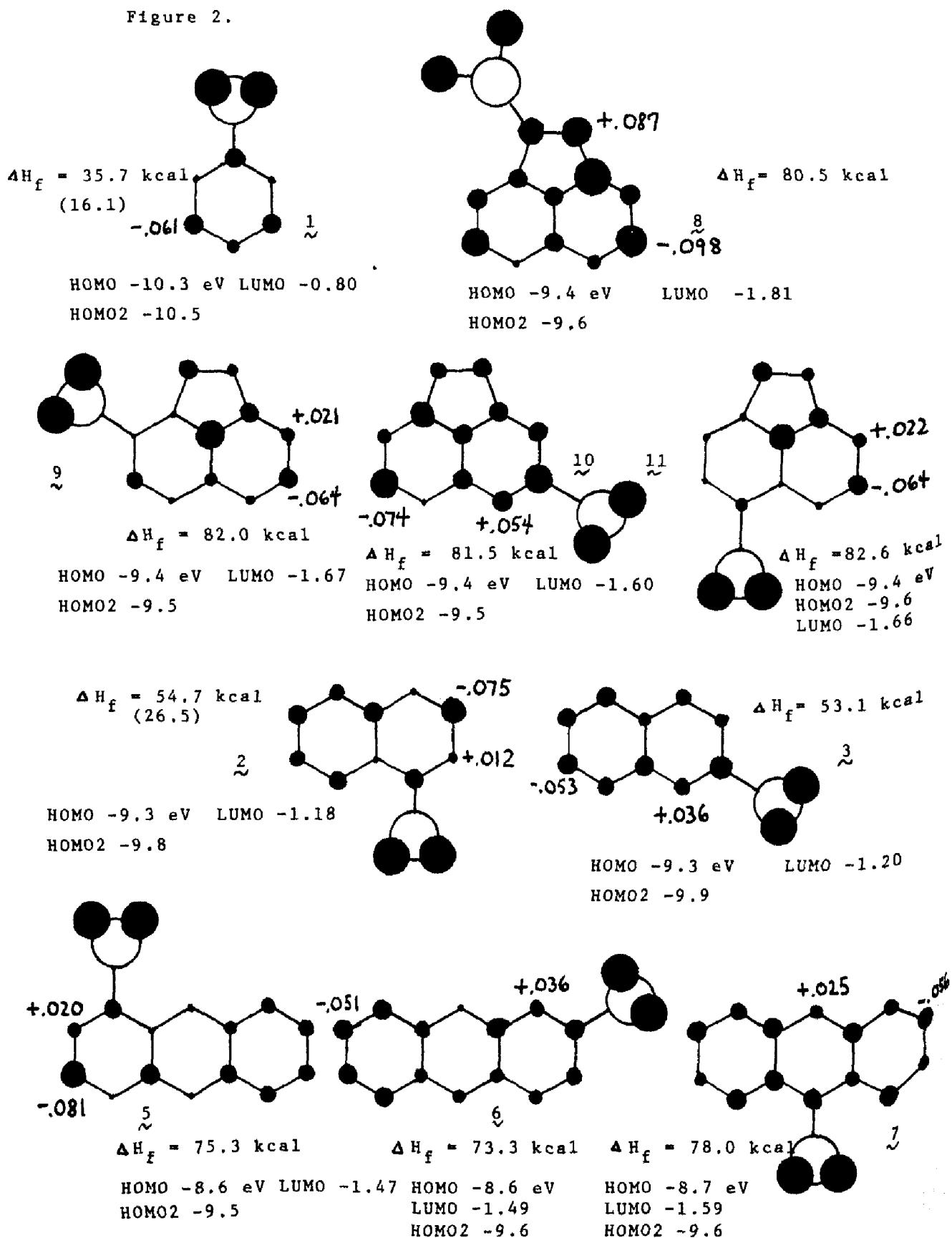
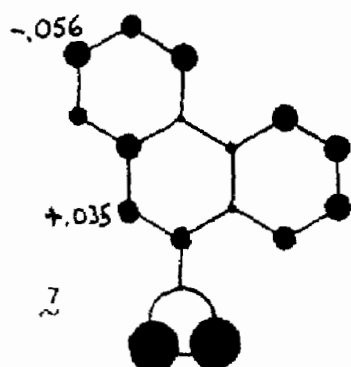
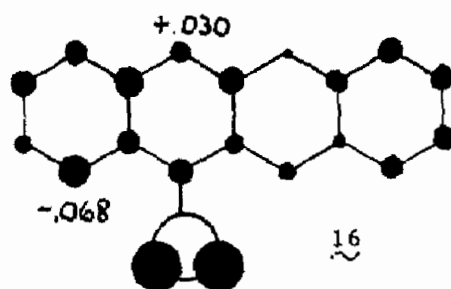


Figure 2 cont'd



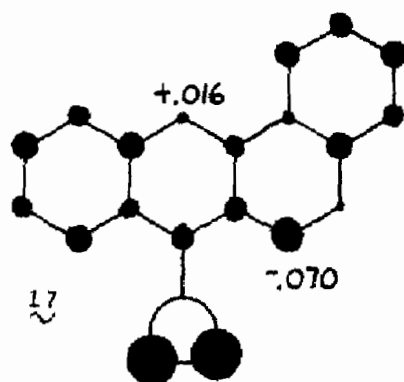
$$\Delta H_f = 72.7 \text{ kcal}$$

HOMO -9.2 eV LUMO -1.24
HOMO2 -9.2



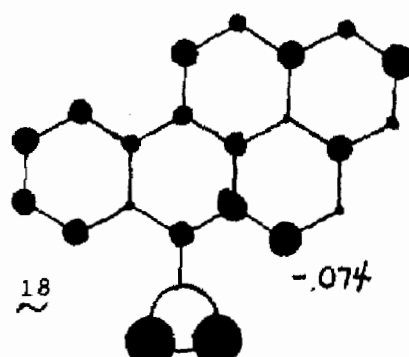
$$\Delta H_f = 100.1 \text{ kcal}$$

HOMO -8.3 eV LUMO -1.81
HOMO2 -9.4



$$\Delta H_f = 94.4$$

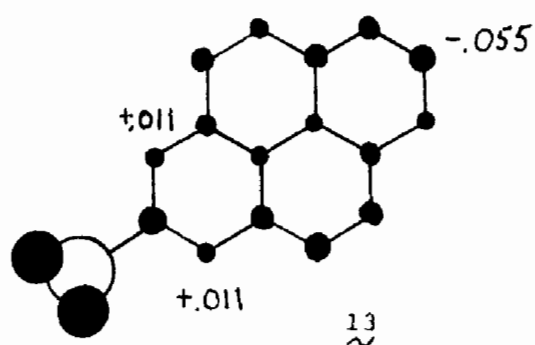
HOMO -8.7 eV LUMO -1.52
HOMO2 -9.1



$$\Delta H_f = 101.9$$

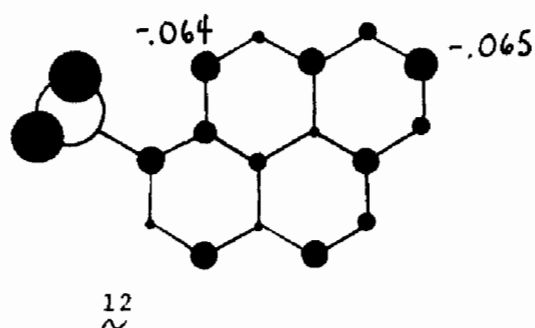
HOMO -8.4 eV LUMO -1.73
HOMO2 -9.1

Figure 2 cont'd



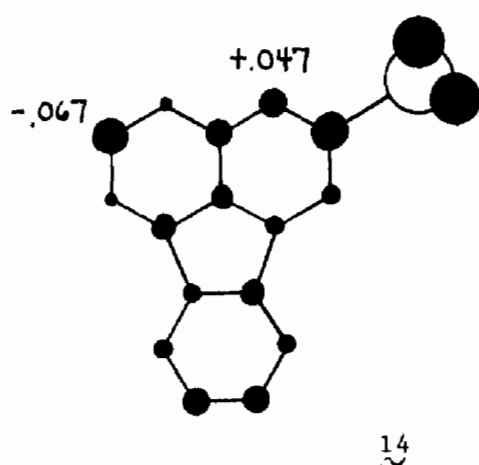
$$\Delta H_f = 75.33 \text{ kcal}$$

HOMO -8.6 eV LUMO -1.47
HOMO2 9.40



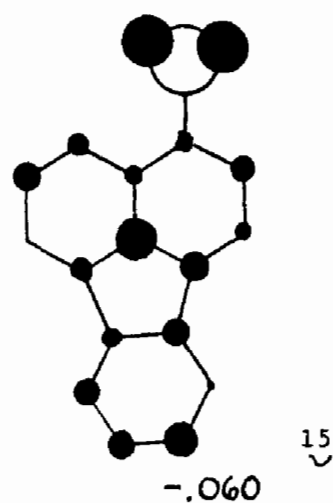
$$\Delta H_f = 77.9 \text{ kcal}$$

HOMO -8.61 eV LUMO -1.57
HOMO2 9.35



$$\Delta H_f = 87.2 \text{ kcal}$$

HOMO 9.0 eV LUMO -1.55
HOMO2 -9.2



$$\Delta H_f = 88.75 \text{ kcal}$$

HOMO 9.0 eV LUMO -1.58
HOMO2 -9.2

A PERSONAL COMPUTER DATABASE FOR THE CHEMICAL,
PHYSICAL AND THERMODYNAMIC PROPERTIES OF THE
POLYCYCLIC AROMATIC COMPOUNDS.

Douglas A. Lane
Environment Canada,
Atmospheric Environment Service,
4905 Dufferin Street,
Downsview, Ontario, M3H 5T4, Canada.

Donna M.A. McCurvin
Ontario Ministry of the Environment,
125 Resources Road,
P.O. Box 213,
Rexdale, Ontario, M9W 5L1, Canada.



A Database for the chemical, physical and thermodynamic properties of the Polycyclic Aromatic Compounds (PAC) has been compiled for use on an IBM XT or AT (or compatible) microcomputer using the commercially available SCIMATE data management software. Data, both experimental and calculated, have been culled from journals, text books, theses and government and industry reports for 729 PAC including the unsubstituted, parent Polycyclic Aromatic Hydrocarbons (PAH), and their alkyl, amino, oxygenated, and nitro derivatives. Each class of substituted PAH occupies a separate floppy disk. A separate references disk contains over 440 references.

No attempt has been made to assess the data for accuracy, no data have been omitted because they appeared to be outlier data, nor has any data been recommended. In addition, data have been listed as presented in the literature publications, and where possible, the method used to determine the value of a property has also been indicated.

From this effort, several observations can be made: (i) there is a great paucity of information for many properties for most PAC; (ii) the data reported for a single property for a single compound may vary by several orders of magnitude; (iii) where several experimental methods exist to determine a single property, the different methods yield consistent, but different data; (iv) there are a number of errors in the literature arising from the incorrect translation of data (reported in a previous publication) from one set of units to another.

Introduction

In order to assess the potential chemical and biological threat of the PAC to the environment, to follow their migration through the biosphere, to perform effective analytical determinations and to characterize their behaviour in natural and synthetic fuels, it is necessary that the chemical, physical, thermodynamic, spectral and biological properties of the PAC be available and readily accessible. Unfortunately, there is a great paucity of such information in the literature and, that which does exist, is often widely scattered through journals, textbooks and government reports (many of which are difficult, if not impossible, to obtain). In some instances, data from one report has been incorrectly quoted (through mistranslation from one set of units to another) in another publication.

It was for the above reasons that work was started to create a comprehensive PAC database.

Hardware and Software

The PAC database, to be most useful and most accessible, was created on an IBM XT personal computer using the SCIMATE (1) data management software.

Before data can be stored in a record, a template must first be created to overlay the data which will be input to the records. Each template may contain from one to twenty fields of data within the record. After the fields have been defined, there is no limit to the number of characters per field other than the total record limit of 1894 characters. If it is anticipated that a record will contain more than 1894 characters, two records may be linked together before data is entered. Linking of records cannot occur after the first edit.

Data in the database may be searched in several ways. Searches may be conducted on a key word or phrase and the Boolean operators AND, OR and ANDNOT may be used to facilitate the search procedure. In addition, field directed searches enable one to search for data in one specific field only. While the SCIMATE system has some limitations, it has proven to be quite satisfactory for the purpose at hand. Searched data may be manipulated directly or transferred to a work file for further processing. Columnar reports may be generated from the entire user file or from records retrieved from a search.

The Database

The PAC database currently contains (on 7 floppy disks) over 800 Kbytes of information on 729 PAC taken from over 440 references. A compilation of data for the aza-arenes has been started but that data is not covered in this discussion. The fifty-two properties included in the database are listed in Table I.

It would appear, at first glance, that there is a great quantity of data about the PAC. However, upon closer examination, one finds that there is considerable data for a few properties for a very few PAC. This is well demonstrated in Table II which shows, for 23 of the properties, the number of compounds in each PAC class for which any data, at all, has been found. In the final column, the total number of compounds for which data has been found for a specific property is listed. For example, of

729 compounds in the database, melting point data has been found for only 548 (or 75%) of the compounds. Vapour pressures have been found for only 16 (2.2 %) compounds and aqueous solubility data for 47 (6.4 %) compounds. What is most revealing is the number of zeros appearing in the table. There is an obvious need for more data in many areas.

A closer inspection of the data for a particular property for a specific compound reveals some potential problems. For example, consider the vapour pressure data, shown in Table III, for anthracene. The reported values range from 2.71 E-04 KPa to 4.02 E-07 KPa . Over three orders of magnitude separate these 20 values. Which one, if any, is correct? Further inspection of the vapour pressure data for other PAC shows that the data reported depends upon the measurement technique used. Solid phase measurements give results one or two orders of magnitude lower than those made from sub-cooled liquid phase measurements. HPLC measurements usually agree quite well with the solid phase measurements while values obtained from the Antoine calculation are usually higher than those obtained from solid phase measurements. All of this can lead to confusion if only one or two values are available. Indeed, the more data that is available, the more difficult it is to decide which value to use.

Occasionally errors do occur in the journals. The vapour pressure for Benz(a)anthracene cited in atmospheres (20) was incorrectly translated to KPa and reported as 6.67 E-13 KPa (2). Six other literature values averaging $1.99 (\pm 0.8) \text{ E-08 KPa}$ show this result to be erroneous. It is, therefore beneficial to have several measured values from which to choose a preferred value.

Conclusions

A computer database for the PAC has been initiated. It has demonstrated the great lack of chemical, physical and thermodynamic data available for the PAC. It has revealed a great variation in data for particular properties of some compounds and has detected some outliers which turned out to be errors of translation from one set of units to another.

It is the hope of the authors that this compilation will be useful to those who require such data and to those who wish to perform experiments to fill in some of the many gaps in the database.

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TABLE I

List of properties covered in the PAC database.

1. Appearance	27. Free Energy of Proton Transfer
2. Aqueous Solubility	28. Free Energy of Solubilization
3. Boiling Point	29. Heat Capacity
4. Carcinogenic Potential	30. Heat Capacity of Solubilization
5. Chemical Abstracts Number	31. Henry's Law Constant
6. Chemical Formula	32. Hydrogen Affinity
7. Critical Density	33. HMO Delocalization Energy
8. Critical Pressure	34. Ionization Potential
9. Critical Temperature	35. Melting Point
10. Critical Volume	36. Molar Refractivity
11. Density	37. Molecular Connectivity Index
12. Dielectric Constant	38. Molecular Weight
13. Dipole Moment	39. Name
14. Electron Affinity	40. Organic Solubility
15. Enthalpy of Combustion	41. Partition Coefficient
16. Enthalpy of Formation	42. Phosphorescence Spectra
17. Enthalpy of Fusion	43. Photochemical Half-Life
18. Enthalpy of Ionization	44. Proton Affinity
19. Enthalpy of Proton transfer	45. Refractive Index
20. Enthalpy of Solubilization	46. Saturation Vapour Concentration
21. Enthalpy of Sublimation	47. Singlet Energy
22. Enthalpy of Vaporization	48. Synonyms
23. Entropy at 298 K	49. Thermal Reactivity
24. Entropy of Solubilization	50. UV Maxima
25. Equilibrium Vapour Concentration	51. Vapour Pressure
26. Fluorescence Spectra	52. Van der Waals Volume

TABLE II

The Number of compounds within each class for which data has been found for selected data fields.

Parameter	Parent	Alkyl	Amino	Keto	Nitro	Quinone	Total
Compounds per class	109	355	30	62	92	81	729
Aqueous Solubility	26	21	0	0	0	0	47
Boiling Point	41	92	7	2	10	5	157
Carcinogenic Potential	70	154	1	1	4	5	235
Density	14	26	6	1	1	4	52
Electron Affinity	16	0	0	0	0	0	16
Enthalpy of Combustion	14	5	2	0	0	0	21
Enthalpy of Formation	36	4	2	0	0	0	42
Enthalpy of Fusion	7	2	1	0	0	0	10
Enthalpy of Ionization	14	6	0	0	0	0	20
Enthalpy of Sublimation	25	0	0	0	0	0	25
Enthalpy of Vaporization	30	60	0	0	0	0	90
Heat Capacity	5	3	0	0	0	0	8
Henry's Law Constant	8	2	0	0	0	0	10
HMO Delocalization Energy	7	2	2	0	1	0	12
Ionization Potential	59	26	0	0	0	0	85
Melting Point	75	300	30	5	78	60	548
Molecular Connectivity Index	30	13	0	0	21	0	64
Organic Solubility	30	48	23	23	21	7	131
Partition Coefficient	23	20	2	0	0	0	55
Proton Affinity	14	4	0	0	0	0	18
Refractive Index	3	5	0	0	0	0	8
Van der Waals Volume	9	0	0	0	0	0	9
Vapour Pressure	14	2	0	0	0	0	16

Table III
Vapour Pressures for Anthracene

Vapour Pressure in KPa at 25°C	Comments	Literature Reference
2.71 E-04	from Antoine Equation	Zwolinski (3)
2.09 E-05	from Antoine equation	Mortimer (4)
2.31 E-05	from Antoine equation	Nelson (5)
2.60 E-05		NRC (6)
2.60 E-05		OME (7)
1.04 E-06		Stevens (8)
3.17 E-05	from liquid phase	Weast (9)
1.44 E-06	from solid phase	Macknick (10)
8.34 E-07	from solid phase	Bradley (11)
8.30 E-07	effusion method	Bradley (11)
8.60 E-07	effusion method	Kelly (12)
2.40 E-06	effusion method	Wiedermann (13)
1.11 E-06	microcalorimeter method	Malaspina (14)
7.99 E-07	HPLC method	Wasik (15)
4.90 E-07	said to be literature average	API (16)
4.27 E-07	(solid at 20°C)	OME (7)
1.00 E-06	(at 20°C)	Grayson (17)
5.01 E-07	(at 20°C)	Taylor (18)
3.10 E-06	(at 20°C)	Power (19)
4.02 E-07	(at 20°C)	OME (7)

**GC/PID Analysis of Headspace for Volatile Organics Over
Drinking Water**

J. Jerpe, EPA Regional Laboratory, Maryland

G. Heston, EPA/ERS, Philadelphia, PA

L. Wilder, Roy F. Weston, New Jersey

Introduction

Head space analysis as defined as the static sampling of the vapor phase in thermodynamic equilibrium with the aqueous phase⁽¹⁾ is a technique which contrasts with isolation methods of trace gas analysis from water such as the dynamic organic analysis of gas stripping (purge and trap) procedure of Bellar and Lichtenberg⁽²⁾.

It has been shown in a lengthy and systematic study⁽³⁾ that the partition effect may be greatly modified by addition of salts (sodium sulfate), temperature, and pH fluctuations. It is therefore possible to choose an optimum condition for head space analysis whereby drinking water may be profiled.

The situation exists, however, where potable water contaminated with trihalomethanes in quite varying amounts presents an immediate and substantial health hazard. It may be necessary to sacrifice rigorous quality assurance procedures and the time and effort associated with dynamic volatile organic analysis for results of a screening analysis of samples as received. With a portable gas chromatograph of suitable sensitivity, these testing procedures may be performed in the field with a minimum of time to reporting concentrations.

It was our intention to evaluate such a method of head space analysis of organic vapor above drinking water with a minimum of sample preparation. These results reported as volume by volume were systematically compared with results reported by other laboratory operators using flame ionization detection and ion-trap mass spectrometry. Residential well water (groundwater) in many areas of Region III have volatile organic contaminants with levels above the drinking water standards and acceptable human health risk levels. Once detected, these problems must be addressed in the quickest manner possible. Initial sampling is extensive and, to ensure safety of the public health, must continue even after temporary solutions are implemented (the installation of carbon filtration units). Because of the large amount and the frequency of sampling required, and because of the fast turnaround time needed for results, Region III EPA/TAT employed a portable GC with a photoionization detector (Photovac, Inc.) for on-site volatile organic analysis.

Field analysis was first used at a Superfund site after receiving preliminary sampling results sent to a private laboratory. Eleven residences at this site were shown to have groundwater contaminated with various levels of trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA). In this way, the technique of a rapid and sensitive field method could be evaluated with attendant precision and accuracy. These water samples were being consumed by local residents and immediate screening results were needed even on a semi-quantitative basis.

When trichloroethylene and or 1,1,1-trichloroethane were found in appreciable concentration by photo-ionization portable gas chromatography in the field, the specific sample was sent to the laboratory for confirmation by injecting head space vapor above the solution into a Finnigan Ion-Trap Mass Spectrometer to confirm the screenings analysis.

Furthermore, the mass-spectrometer was calibrated with a fabricated gas mixture of 1,1,1-trichloroethane, benzene, and trichloroethylene in order to report as an external standard auto-quantitative mode concentrations in parts-per-billion. Through the use of these techniques, all residential well water samples were analyzed within 24 hours of collection. Quick

turnaround time was necessary for several reasons. First, initial sampling results indicated which residences were affected and required immediate attention. Extent of contamination results also gave a rough indication of the area of the source of the contamination and the flow direction of the contamination plume. Knowing plume direction, one could estimate which homes were most likely to become contaminated in the future. These homes were sampled periodically to check for the presence of contamination.

Secondly, once carbon filtration units were installed in individual homes, periodic sampling and analysis was required to ensure that contaminant breakthrough had not occurred. Samples collected before the filters (to monitor changes in groundwater contamination), between the filters, and at the residential taps were analyzed within 24 hours of collection. If contaminant breakthrough had occurred at the tap, both filters were changed immediately. If breakthrough was detected between filters but not at the tap, the contaminated filter was removed and replaced by the filter nearest to the tap, and a new filter was put inline nearest the tap.

Photovac detection limits were found to be significantly below EPA approved methods. In addition, EPA's Central Regional Laboratory (CRL) in Annapolis, MD, also analyzed several samples using EPA Method 624 as a QA/QC measure.

When samples were collected, each VOA bottle was filled half full, allowing the volatile organics to equilibrate in the headspace/air space above the sample. Standards of each contaminant were made in a similar fashion. Known concentrations of compounds were injected into known volumes of water and allowed to equilibrate with the headspace. By comparing Photovac analytical results with those of EPA Methods 601 and 624, the Photovac headspace method has proven to be a quick, accurate field method of analysis.

EXPERIMENTAL METHODS

Sample Collection and Preservation:

To rid residential water systems of standing water, each well was purged by allowing the cold water to run for 10-20 minutes. After purging, the water flow rate was reduced significantly and samples were taken. For EPA 601 analysis, 40ml VOA bottles of the same lot number were completely filled with cold water and capped. For headspace analysis, a 40 mL VOA bottle was half-filled with cold water and capped. A field blank (distilled, deionized water) was included with each sampling round.

After collection, samples were labelled (date, location, and sampling), placed in ziploc baggies, and then sealed in tin cans and placed on ice. Samples were analyzed by the lab within 3 days of collection, and with in 48 hours by the headspace method.

Headspace Analysis:

Instrumentation:

A Photovac Model 10A10 (a portable GC with a PID detector) with a Hewlett Packard 5990A Integrator was employed for headspace analysis. A 4' x 1/8" SE-30 column was used with zero grade air (Linde Specialty Gas UN 1022) as the carrier gas.

Standards:

The following Supelco standards were used:

- 1) 1,1,1-trichloroethane (TCA), 1 ml
200 ug/ml in methanol
Lot No LA14565
Cat No 4-8614
- 2) Trichlorethylene (TCE), 1 ml
0.2 mg/ml in methanol
Lot No LA13702
Cat No 4-8606

Previous sampling results revealed that concentrations of these compounds found in residential well water ranged from less than 1 ppb to greater than 7500 ppb, making several concentration ranges of standards necessary. Standard concentrations were prepared to encompass less than 1 to 10 ppb, 10-100 ppb, and 100-500 ppb. Any sample that contained greater than 500 ppb of any of the target compounds was diluted until it fell within the standard concentration ranges.

A known concentration of the Supelco Standard was injected into a known volume of water and allowed to equilibrate with the headspace. A minimum of three different concentrations (with three injections each) of a compound were used to make a standard curve. 0.1 uL of the 2 ppb standard was injected into a 40 mL VOA bottle containing 20 mL of water to yield a concentration of 1.0 ppb.

$$(0.2\text{ug/L} \times 0.1\text{ul std}) / (20\text{ml water}) = 0.001\text{ug/ml} = 1.0\text{ug/L}$$

Samples:

Before injection, samples were removed from ice and allowed to reach room temperature (the same temperature of the standards). No preconcentration of samples was necessary, as the headspace technique analyzes the headspace above the water sample. The headspace concentrations are proportional to the contaminant concentration in water. Once samples reached room temperature, a known volume of headspace was injected into the column. Each sample was analyzed in duplicate to ensure accurate injection techniques. If a sample contained contaminant concentrations greater than the standard concentration ranges, it was taken from the full VOA bottle and diluted.

Sample Splits:

Initially, a duplicate of each sample collected was also sent to a private lab for analysis (volatile organic analysis by EPA Method 601). After private laboratory results proved comparable to those of the Photovac, approximately one out of three samples were sent to a private laboratory as a QA/QC measure.

To positively identify the gas chromatography peaks of the target compounds, random samples were injected by the same techniques into a Finnigan GC/Ion-Trap Mass Spectrometer and programmed to search and quantitate in an automatic mode. The same standard solutions used for Photovac screening were intentionally used to generate calibration statistics for the quantitative analysis.

A formal fabricated gas standard from 99% pure neat solutions of 1,1,1-trichloroethane, trichloroethylene and benzene prepared in a 1 liter gas bottle was suitably diluted and injected into the GC/MS system as a cross-referenced standard to compare the Supelco methanol solution standard responses.

RESULTS and DISCUSSION:

Sample concentrations were calculated using peak areas of compounds eluting with the same retention time as the standards. Concentrations of each multiple injected sample were averaged to yield the final sample concentration. These results were then compared with analytical results of EPA Methods 601 and 624. Typical headspace analysis calibration curves are displayed in Figure 3. A typical chromatograph of standard injections, accompanied by several chromatographs of headspace injections of samples are shown in Figures 1 and 2.

Over two hundred samples were analyzed using the headspace method: an average of 30 samples day. Typical results of the headspace method are shown below.

Tables 1 and 2 display the percent differences between the positive values of the Photovac headspace method and private laboratory analysis (EPA Method 601) for 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE). The mean relative percent difference and the standard deviation for 1,1,1-trichloroethane are 50.1 and 28.2, respectively. Corresponding TCE values are 76 and 55.3.

These results compare favorably with those found in the enclosed Performance Evaluation Study and Interlaboratory Method Evaluation Study (Method 601) results performed by the EPA Environmental Monitoring and Support Laboratory Quality Assurance Branch in Cincinnati, Ohio. Results from their interlaboratory study reveal a standard deviation of 23 and 93 from the mean (based on 100 ppb and 400 ppb), and 12.4 and 61 for TCE (based on 41.6 ppb and 200 ppb).

The standard deviation of the mean percent differences calculated for the affected residences are in good comparison with the standard deviations from the mean of the study (refer to Table 3).

When comparing the variation between Photovac and private laboratory results, it should also be noted that different instruments and methods of analysis were used. The private laboratory utilized EPA Method 601 which involves a purge and trap sample extraction technique followed by temperature-programmed GC analysis, while the Photovac method involves headspace analysis and no temperature programming.

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TABLE 1. Comparison of Photovac and Private Laboratory Split Sampling Data for Trichloroethylene (Positive Values).

<u>Photovac (ppb)</u>	<u>Private Lab (ppb)</u>	<u>Relative % Difference</u>
137.2	120	13.4
144.5	120	18.5
15.7	6.8	79.1
20.3	6.8	99.6
150	94	45.9
194	94	69.4
174	100	54.0
224	100	76.5
13.2	5.8	77.9
75.1	69	8.5
2.2	1.3	51.4
35.4	29	19.9

Average Relative Percent Difference: 50.1

Standard Deviation \pm 28.2

TABLE 2. Comparison of Photovac and Private Laboratory Split Sampling Data for Trichloroethylene (TCE).

<u>Photovac (ppb)</u>	<u>Private Lab (ppb)</u>	<u>Relative % Difference</u>
0.3	0.5	50
3.6	0.5	151
2.2	0.5	125
3.8	4.7	21.0
5.0	5.0	0
1.0	9.0	160
9.0	7.0	25

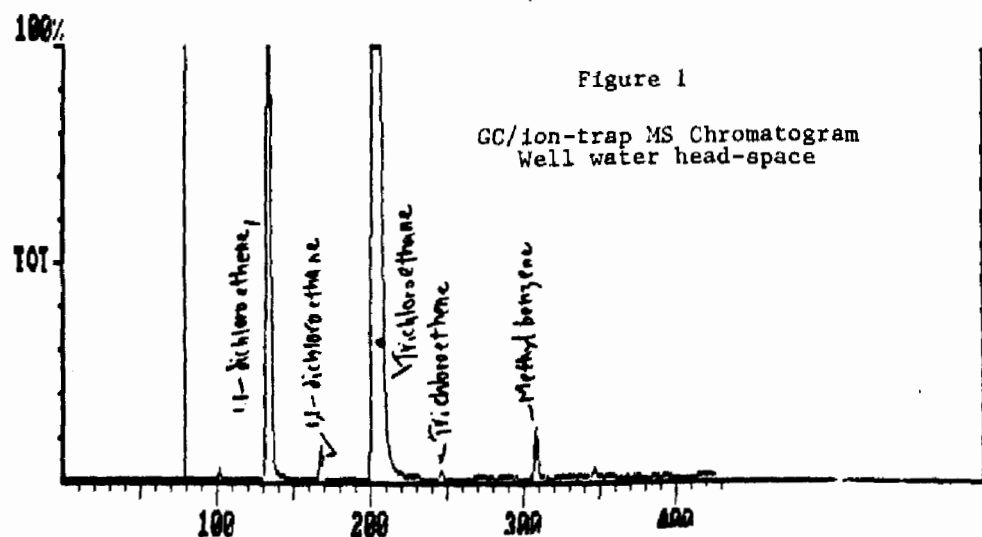
Average % Difference: 76

Standard Deviation: \pm 55.3

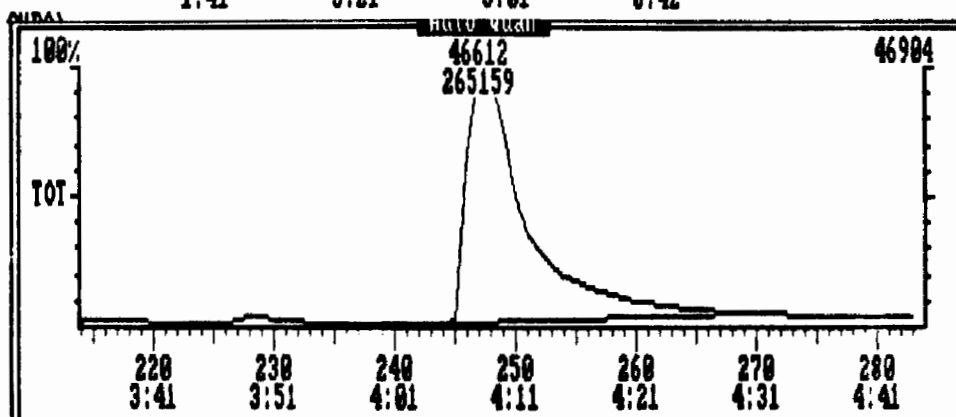
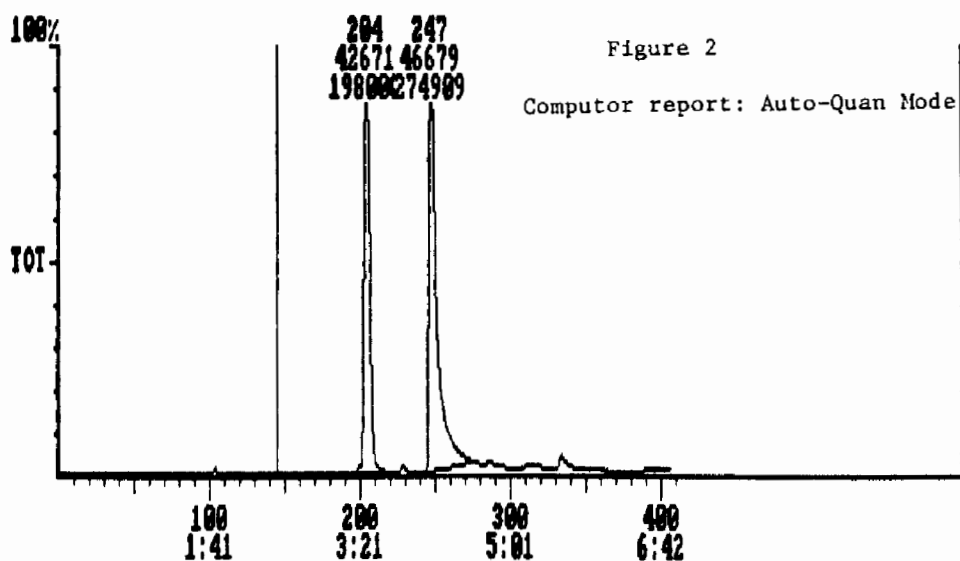
TABLE 3. Comparison of Photovac and Private Lab Results With the EPA Performance laboratory Study.

<u>Compound</u>	<u>EPA (Standard Deviation)</u>	<u>Concentration (ug/L)</u>	<u>Photovac/Martel Comparison Standard Deviation of % Difference</u>	<u>Concentration Range (ug/L)</u>
1,1,1-Trichloro- ethane	23 93	100 400	28.2	0 - 200
TCE	12.4 61	41.6 200	55.3	0 - 200

Chromatogram Datafile: ADAMSTON Acquired: Sep-04-1986 07:20:20
Comment: C. HANES-WELL 4M HEAD-SPACE PHOTO-VAC COMPARISON /3-C STANDARD
Scan Range: 1 - 426 Scan: 79 Int = 0 @ 1:20 RIC: 100% = 16846

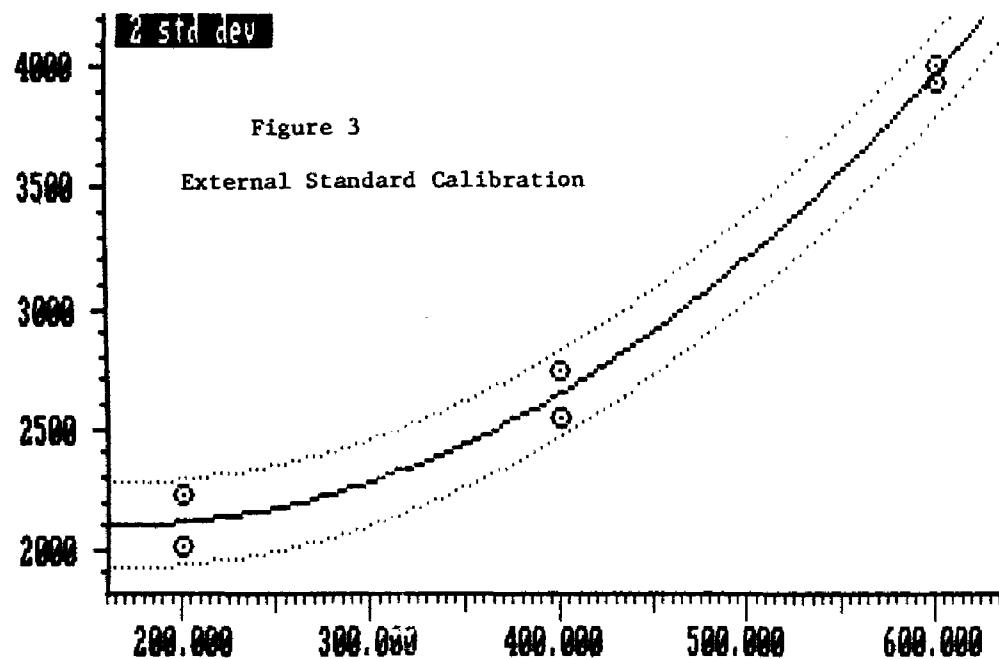


Chromatogram Datafile: ADAM Acquired: Aug-26-1986 11:38:41
 Comment: 31.0 KPa 275 PPM SPLIT:1,1,1-TCE/TRICHLOROETHYLENE EACH PER L
 Scan Range: 1 - 486 Scan: 145 Int = 72 @ 2:26 RIC: 100% = 46904



No	Compound/Standard Name	Exp RT	Thrsh	Act RT	Fit S/N	Scan#	Peak Area
1	1,1,1-TRICHLOROETHANE	3:27	700	3:25	995	204	198576
2	TRICHLOROETHYLENE	4:11	700	4:08	986	247	265159

Calibration Plot (Ext Stds) Filename: TCE Correlation Coeff: 0.964
1,1,1-TRICHLOROETHANE Compound: 1 of 1 Standard Deviation: 0.088
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin/Lin)



OVERVIEW OF THE EMSL METHODS COMPARISON STUDY

by

W. A. McClenny

Environmental Monitoring Systems Laboratory, U. S. EPA
Research Triangle Park, NC 27711

The question of which of several candidate sampling systems to use for multicomponent collection at dry deposition network sites has been addressed by a methods comparison study. The study took place over a thirteen-day period from 29 September to 12 October 1986. The three leading candidates for multicomponent collection, i.e., the Canadian filter pack, the transition flow reactor (TFR) and the annular denuder system (ADS), were operated on a daily and weekly basis. A tunable diode laser (TDL) system was used as the reference technique for measurements of nitric acid (HNO_3) and nitrogen dioxide (NO_2). Passive sampling devices were used for daily and weekly measurements of NO_2 while the Luminol NO_2 chemiluminescence monitor was used for real-time monitoring. The study site was located at a prototype dry deposition monitoring site at the US EPA facility in the Research Triangle Park, North Carolina, U.S.A.

Introduction

The EMSL developmental and evaluation effort for dry deposition monitoring has recently been focused on the selection of instrumentation for sampling selected ambient gases and particles. Multicomponent samplers designed for continuous collection of targeted species, such as sulfate-containing particulate, SO_2 , HNO_3 , etc., are being considered for long-term use in the 100-station national network to be implemented through an EMSL contractual effort. Specifically, the factors influencing selection of sampling units for weekly and sub-weekly multi-component collection are under study. These factors include accuracy, artifact-free collection, reliability and expense. Chief among the candidate sampling units are: (a) the filter pack (FP) system (usually referred to as the Canadian filter pack because of their extensive usage¹); (b) the transition flow reactor (TFR)^{2,3}; (c) the annular denuder system (ADS) as altered from the earlier Italian version⁴ to meet dry deposition monitoring constraints⁵. These systems plus a tunable diode laser system⁶ for providing reference measurements of HNO_3 and NO_2 during common sampling periods, were brought together for a field monitoring comparison study over a thirteen-day period from 29 September to 12 October 1986. Supplemental measurements of NO_2 were made with the commercially available Luminol® Model LMA3 continuous point monitor⁷ and with passive sampling badges coated with triethanolamine.⁸ These systems were assembled at the site of EMSL's dry deposition site in the Research Triangle Park, North Carolina. Routine measurements of meteorological parameters and ozone were also being recorded at this site.

Discussion

The five research groups that were assembled for this study are listed in Table I. Each of these is represented in the program for this session for the purpose of presenting and discussing the results of their individual experiments

and the reference measurements. The last presentation in the session is intended to provide a comparison of results across different methods and an identification of conclusions and of unresolved issues.

Table 1. Participants and Measurement Methods

<u>Research Group</u>	<u>Measurement Method; Measured Species</u>
Unisearch Associates, Inc Toronto, Canada; G. MacKay	Tunable Diode Laser: NO ₂ and HNO ₃
Atmospheric Environmental Service, Downsview, Ontario, Canada; K. G. Anlauf, H. A. Wiebe, D. C. MacTavish	Filter Packs with several sampling periods: NO ₂ , SO ₂ , sulfate, nitrate, ammonium, HNO ₃
Research Triangle Institute; J. E. Sickles, II, L. L. Hodson, E. E. Rickman, Jr., M. L. Saeger, D. L. Hardison, A. R. Turner, S. K. Sokol, E. D. Estes	Annular Denuder System (ADS), Transition Flow Reactor (TFR); ADS: SO ₂ , HNO ₃ , HONO, NH ₃ , sulfate, nitrate, ammonium; TFR: SO ₂ , HNO ₃ , NO ₂ , NH ₃ , sulfate, nitrate, ammonium
U.S. EPA and Northrop Services J. D. Mulik (EPA) and D. E. Williams (Northrop Services)	Triethanolamine-coated filter in holder (PSD); NO ₂
Northrop Services; D. K. Bubacz, E. H. Daughtrey, J. D. Pleil and K. G. Kronmiller	Luminox Model LMA ₃ real-time measure- ments; NO ₂

The original sampling schedule is shown in Table 2. Daily sampling periods were chosen as the basis for statistical comparisons among the multicomponent samplers. Only two instruments were run on a weekly sampling schedule. These were the ADS and the passive sampling badges. The originally planned TFR and filter pack weekly samples were to be made by personnel providing the routine operation of the dry deposition station. However, these samples were not valid because of problems encountered during a change in operational responsibility from one group to another. ADS and PSD weekly sample results were compared to the sum of the daily values for the seven-day period from 30 September until 7 October and for the five-day period from 7 October until 13 October. Both Luminox and diode laser measurements were averaged on a hourly, daily and also weekly basis for appropriate comparisons. Daily runs began at 10:30 a.m. and ended at 8:30 a.m. the following day. The two hour interval from 8:30 to 10:30 was reserved for flow audits, calibration and data processing.

Table 2. SAMPLING SCHEDULE

	September					October							
	29	30	1	2	3	4	5	6	7	8	9	10	11
TFR (daily)	x	x	x	x	x	x	x	x	x	x	x	x	x
ADS (daily)	x	x	x	x	x	x	x	x	x	x	x	x	x
Filter Pack (daily)	x	x	x	x	x	x	x	x	x	x	x	x	x
Luminox (continuous)	-----												
Passive Badges (daily)	x	x	x	x	x	x	x	x	x	x	x	x	x
Diode Laser (continuous)	-----												
TFR (weekly)	+-----+-----+												
ADS (weekly)	+-----+-----+												
Filter Pack (weekly)	+-----+-----+												
Passive Badges (weekly)	+-----+-----+												

The placement of the Unisearch van (housing the tunable diode laser) and the AES van, with respect to the station, is shown in Figure 1. Figure 2 shows duplicate daily TFR, ADS, and FP samplers, as well as weekly ADS and TFR units, on the roof of the station. Triplicate PSDs were located on the roof also, while a second set of triplicate PSDs were placed inside the station and exposed to ambient air brought into the station through a large diameter manifold. Two Luminox NO₂ monitors and the TDLAS were located inside the Unisearch van. Inlets for these units were positioned adjacent to the station near the TFR and ADS inlets. Short-term filter pack sampling units using an automated sequencer were located on the roof of the AES vans.

A summary of the results to be compared for each of the methods is given in Table 3.

TABLE 3. SUMMARY OF STUDY RESULTS

Species	ADS	TFR	FP	TDLAS	Luminox	PSD
NO ₂		x	x	x	x	x
SO ₂	x	x	x ^b			
HNO ₃	x	x, x ^a , x ^d	x ^b	x		
NH ₃	x	x				
Total NO ₃ ⁻	x	x	x			
Total NH ₄ ⁺	x, x ^c	x, x ^c	x			
Total SO ₄ ²⁻	x	x	x			

^a HNO₃ computed from TFR results assuming it functions similarly to a FP; it considers the sum of NO₃⁻ recovered from the nylon strip and filter as an upper limit estimate of HNO₃.

^b HNO₃ from the FP assumes no particle NO₃⁻ volatilization and that the NO₃⁻ on the nylon filter represents only HNO₃.

^c Total gaseous and particulate ammonia and ammonium (Total NH₃ + NH₄⁺) are also considered.

^d HNO₃ was independently measured by Tom Ellestad of the Atmospheric Sciences Research Laboratory (ASRL) of the US EPA using equipment that was nominally identical to the equipment used by RTI (supplied to RTI by Ellestad).

Quality control for the study included both flow checks and calibrations during the daily break in sampling. Standards for HNO₃ and NO₂ were taken from calibration systems (permeation tubes) on board the Unisearch van. RTI personnel coordinated sample exchanges between their laboratory and the AES laboratory for normalization of instrument response with respect to analyses of extracts from filters and denuders.

Disclaimer

The research described in this article does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Figure 1. Location of sampling stations for the study.

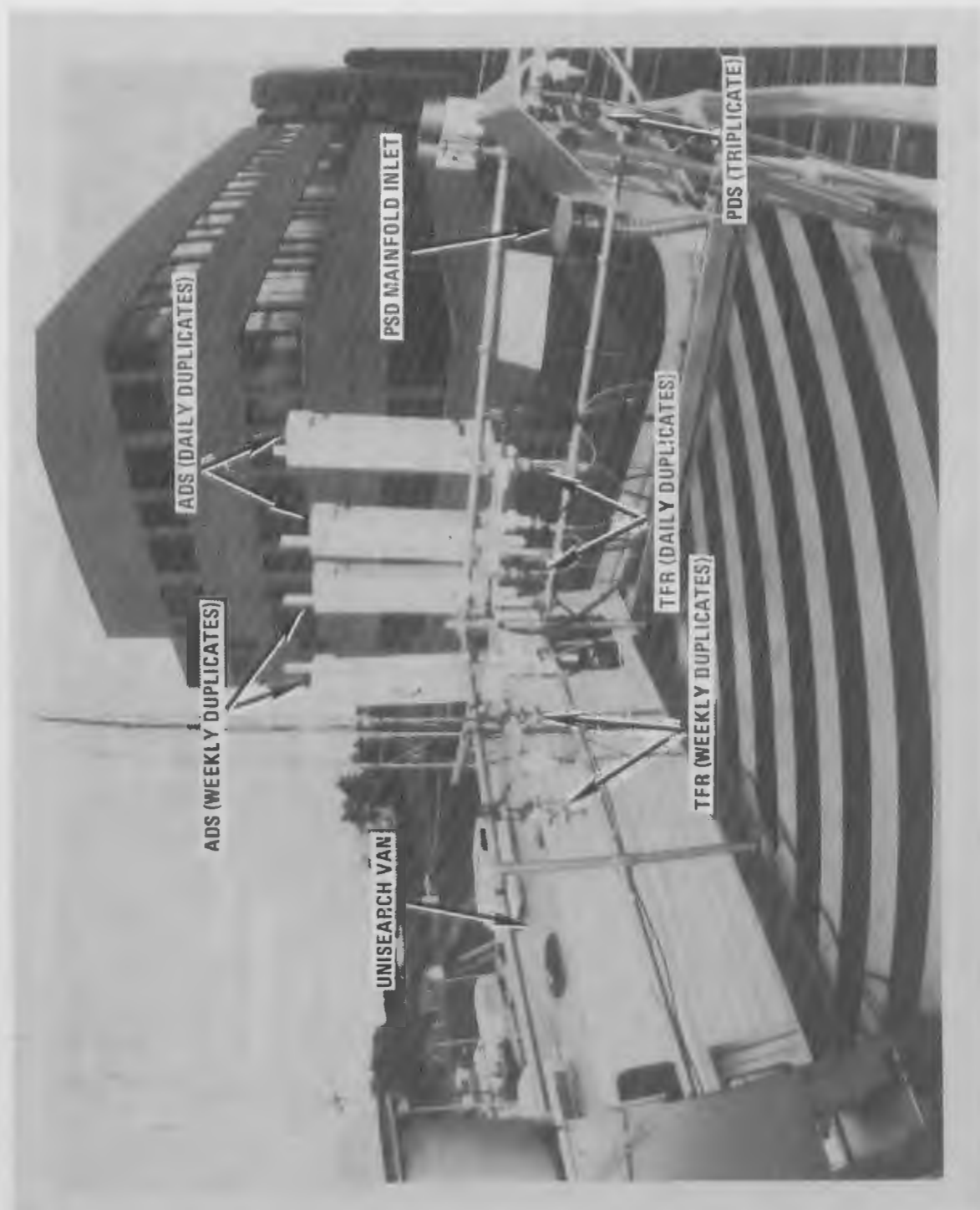


Figure 2. Annular denuder system, transition flow reactor, and personal sampling device placement on dry deposition station.

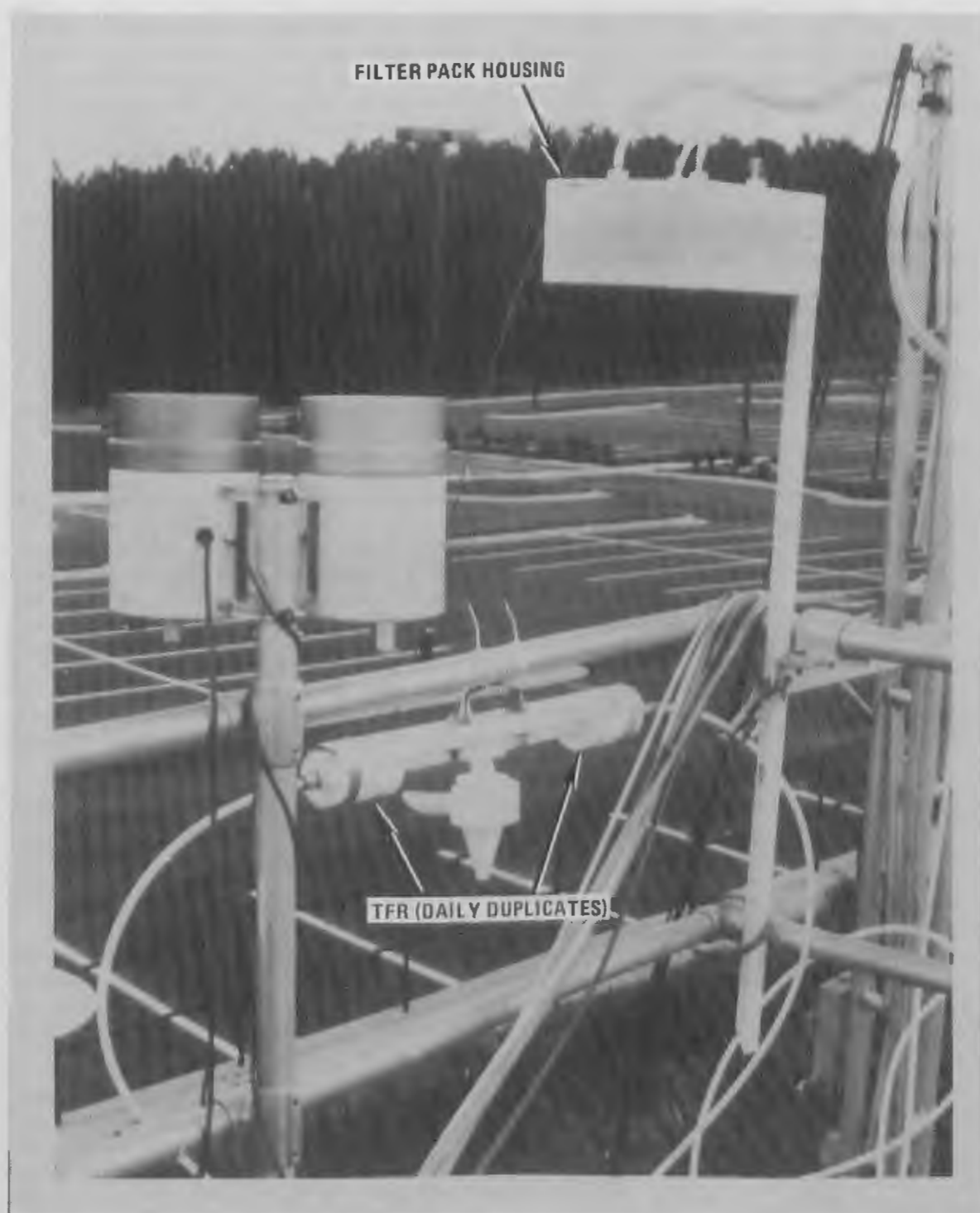


Figure 3. Filter pack and transition flow reactor (second daily sample) placement on dry deposition station

REFERENCE MEASUREMENTS OF HNO_3 AND NO_2
BY TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY

G.I. Mackay and H.I. Schiff
Unisearch Associates Inc.,
222 Snidercroft Rd.,
Concord, Ontario, L4K 1B5
Canada



ABSTRACT

Measurements of HNO_3 and NO_2 in ambient air were made using a Tunable Diode Laser Absorption Spectrometer (TDLAS). This system was used as a reference technique for the two gases because of the unequivocal identification and sensitivity achievable with the TDLAS technique. The two gases were measured simultaneously under automatic computer control with detection limits better than 100 pptv and response times of 5 minutes or less.

Average values of HNO_3 and NO_2 were 0.57 ppbv and 8.7 ppbv respectively and greater than 95% data coverage of the two week study was achieved. The system was calibrated using permeation devices for both gases. Potentiometric titrations before and after the study and ion chromatograph measurements of nitrate collected in bubblers containing KOH solutions during the study indicated that the HNO_3 device was stable to within $\pm 5\%$. The NO_2 permeation rate was determined by weighing before and after the study and was stable to within 3%. Overall accuracy is estimated to be $\pm 15\%$ for NO_2 and $\pm 20\%$ for HNO_3 .

Key word index: trace gas measurements, nitrogen dioxide, nitric acid, tunable diode lasers.

Introduction

Tunable diode laser absorption spectrometry (TDLAS) offers a number of advantages for measuring atmospheric gases¹. It is a universal method applicable, in principle, to all gases of atmospheric interest. Its high spectral resolution provides unequivocal identification of the target gas. When operated with a long path cell it can measure most atmospheric gases at sub part per billion (ppbv) concentrations. Real time, in situ, measurements can be made with time resolutions of less than one minute.

It is also ideally suited to serve as a standard against which less definitive methods, such as filter and denuder techniques, can be compared and calibrated^{2,3}. Its relatively rapid response permits measurements of concentration fluctuations not possible with most other methods.

This paper describes an improved version of the instrument and measurements of NO_2 and HNO_3 made during the Environmental Protection Agency sponsored Dry Deposition Study at Research Triangle Park North Carolina, during September-October 1986.

Description of the TDLAS System

Figure 1 shows a schematic of the TAMS-150, an improved version of the system described previously^{1,4}. Temperature control of the Pb salt diodes in their operating range of 20 to 80 K is provided to ± 0.005 K by the combination of a closed cycle helium cryocooler, a heater and a servo temperature system. Two cryostats are used, each having a laser source assembly containing 4 laser diodes. One laser diode from each assembly can be chosen to permit two gases to be measured simultaneously. The emitted radiation from each of the diodes is scanned over the selected absorption feature by changing the current through the diode.

The laser beam from each head is collected and focussed by all-reflective optics into the White cell. Mirror, S flips back and forth to select the beam from each of the diodes in turn.

The beam enters the 1.5 m base path Teflon-lined White cell containing a corner cube reflector⁵ and undergoes 102 passes before exiting to the detector. Absorptions down to about 10^{-4} can be measured which correspond to detection limits in the range 25 to 100 parts per trillion by volume for most atmospheric gases.

About 5% of the beam is reflected by the 45° angle of the White cell entrance window through a cell containing high concentrations of the target gases onto a separate liquid nitrogen cooled HgCdTe infrared detector. The output from this detector is used to lock the laser radiation wavelength to the center of the absorption line.

Sampled air enters through an inlet, flows continuously down the tube and is exhausted at the other end. A constriction at the inlet end and a servo valve at the exhaust end maintains a constant flow rate and pressure in the cell. Maintaining the cell at 25 Torr reduces pressure broadening of the absorption line which both increases the sensitivity of the measurement and minimizes the likelihood of interferences from other gases.

The absorption is measured in the frequency modulated, 2f, mode⁶ which results in an increased signal-to-noise ratio compared to using direct absorption.

The system is under computer control. Laser temperature and current selections for each species are input to the computer. The system is then switched to automatic mode and operates unattended for at least 24 hours.

The computer signals the selection mirror to position itself so that one of the beams enters the White cell. The line is scanned under computer control at a rate of ~30 Hz for 3 sec (the approximate residence time of the gas in the White cell) and an accumulated 2f line shape is acquired.

At the end of the 3 sec averaging period the signal on the reference detector, D2 is checked. If the reference channel indicates that the line is not exactly at the center of the line the computer adjusts the laser temperature to bring the line back to the center.

The selection mirror is then commanded to bring the second beam into the White cell and the measurement procedure is repeated for species B. Each species is thus measured once every 6 sec. Data is accumulated in this way for a period of, for example, 3 min providing an average value for the 2f line shapes over that time frame. The data set, which provides one mixing ratio for each species, is then stored on computer disk.

The computer manipulates solenoid valves and flow controllers to perform measurement and calibration sequences automatically. In a typical sequence the valve system is commanded to flow either zero (bottled) air or scrubbed, ambient air through the White cell. Background spectra of the components are obtained by scanning over the wavelength regions of the selected absorption lines. A typical example is shown in Figure 2a.

Calibration gas is then added to the zero (or scrubbed) air flow and allowed to stabilize for ~1 min. An averaged calibration spectrum is then obtained for 3 min which also serves as a reference spectrum and the raw data is archived (Figure 2b).

The background spectrum is subtracted (channel by channel) from the reference spectrum. This procedure removes any frequency dependent structure in the background from the reference spectra provided it remains stable for the averaging period. The result of this subtraction is shown in Figure 2c.

Valves are then reset to admit ambient air, and after another stabilization period an ambient air spectrum is acquired for 3 min (Figure 2d) and the background spectrum subtracted (Figure 2e). The net ambient spectra is least square fitted to the net reference spectrum. The same calibration sequence is followed for both gases being measured.

The frequency of calibration and the time duration of the various stages of the sequence can be altered by the operator. The choice depends on the mixing ratios of the species being measured; low ambient concentrations require more frequent determination of the background and reference spectra.

Application of the TDLAS System to the Measurement of NO_x and HNO_x

The use of the system to measure an atmospheric component has 3 requirements: 1) selection of a laser and an absorption feature; 2) establishment of a calibration procedure; 3) ensuring sampling integrity.

The selection of a laser and an absorption feature represents a compromise between the absorption line strength, the characteristics of the laser emission at the wavelength of the line, and absence of interferences at this wavelength from other atmospheric gases⁷. Suitable lines were selected in the 1720 cm^{-1} region for HNO_x and in the 1600 cm^{-1} region for NO_x .

The calibration philosophy calls for the addition of a known amount of the calibration gas to the sampled air stream at the entrance to the sampling line. The concentration of the "spike" is chosen to provide an increase in measured mixing ratio comparable to the mixing ratio of the gas in the ambient air. In this way, any surface effects that may occur will be the same for the sampled and spiked air and should, therefore, compensate.

In contrast to NO_2 , which has a response time equivalent to the residence time of the sample gas in the White cell, the response time to additions of HNO_3 is about 5 min to reach 75% of steady state. To permit more rapid calibration for HNO_3 , an alternative method was used. During the calibration period the calibration gas mixture was redirected into a 15 cm cell (C in Figure 1) situated in the laser beam in front of the detector. The pressure in the cell was maintained at 25 Torr to match the conditions in the White cell and the flow was controlled at a level to provide an equivalent mixing ratio in the White cell of 6 ppbv. At the beginning and end of the study the HNO_3 spike was introduced at the inlet to sampling line (our preferred method of calibration) to check validity of the optical calibration. The agreement between the two methods was within 10%.

Permeation devices were used as the calibration sources. The NO_2 source was a Metronics wafer device calibrated by weighing before and after the study to be permeating at a rate of $144 \pm 2 \text{ ng} \cdot \text{min}^{-1}$. The HNO_3 source was manufactured by Unisearch Associates and was a special design in which the carrier gas passes through a length of Teflon tubing immersed in a tube containing a mixture of HNO_3 and H_2SO_4 . The permeation rate was determined by pH titration before and after the study and by ion chromatography on the extract from KOH bubblers during the study. From all determinations, an average value of $267 \pm 13 \text{ ng} \cdot \text{min}^{-1}$ was obtained for the HNO_3 permeation rate.

Results

Data coverage, as expressed as percentages of the total measurement period were better than 95% for both species. The standard measurement period was 10:30 through 08:30. The period 08:30 through 10:30 was set aside for calibrations and maintenance of the instrumentation.

Figures 3 and 4 show respectively, the one hour averaged values of NO_2 and HNO_3 taken on October 2. These observations are typical of the study period. NO_2 had two daily maxima, morning and evening which coincided with the peak automobile traffic in the area. 3 min data points ranged as high as 40 ppbv and down to 1 ppbv. HNO_3 showed a single maximum in early afternoon which is more typical of photochemical production. 3 minute data points reached maximums of ~3 ppbv during the early part of the study and nighttime minimum were generally in the 0.1 to 0.3 ppbv range with some periods below the detection limit of 0.1 ppbv.

Figures 5 and 6 show the corresponding measurements for the entire study. After the 6th of October the weather deteriorated, becoming mostly overcast with heavy rain occurring on the 11th. This is evidenced by the decrease in the HNO_3 maximum during the latter part of the study. Average values for HNO_3 and NO_2 over the two weeks were 0.57 ppbv and 8.7 ppbv respectively.

Conclusions

The tunable diode laser absorption spectrometer has been shown to be capable of providing real time measurements of the diurnal behaviour of NO_2 and HNO_3 in relatively clean air under field conditions. Its high specificity, good sensitivity and rapid response time makes it a very suitable standard against which other less definitive methods can be compared.

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Figure Captions

Figure 1. Schematic of the optical system and control electronics

Figure 2. Computer screen printouts for NO_2 : a) raw background spectrum; b) raw calibration spectrum; c) calibration spectrum, background subtracted; d) raw ambient spectrum; e) ambient spectrum, background subtracted

Figure 3. Hourly averaged NO_2 mixing ratios at RTP, NC on Oct 2, 1986

Figure 4. Hourly averaged HNO_3 mixing ratios at RTP, NC on Oct 2, 1986

Figure 5. Hourly averaged NO_2 mixing ratios at RTP, NC; Sept 29-Oct 12, 1986

Figure 6. Hourly averaged HNO_3 mixing ratios at RTP, NC; Sept 29-Oct 12, 1986

FIG. 1

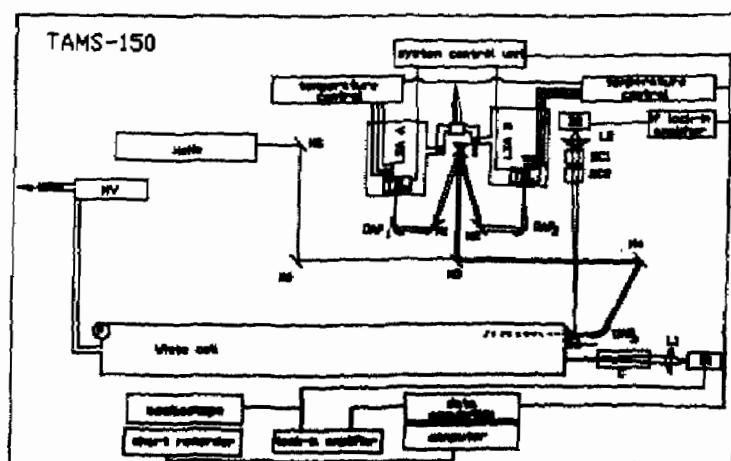


FIG. 2

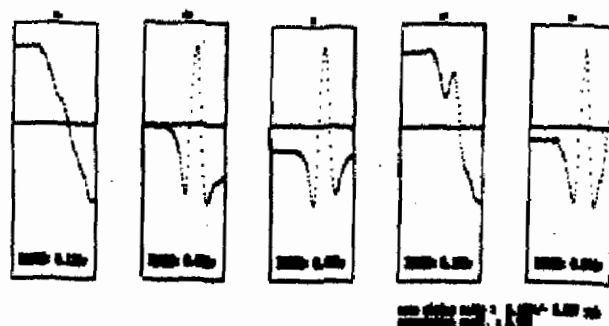


FIG. 3

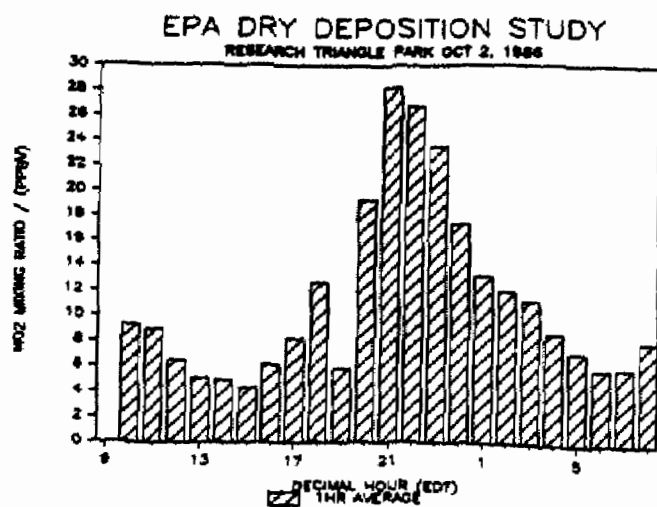


FIG. 4

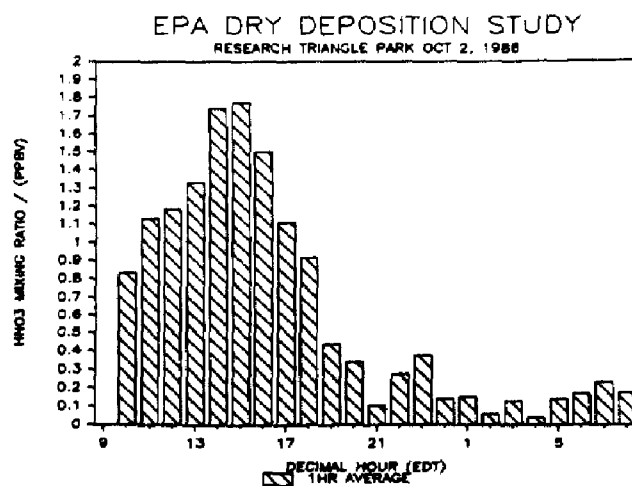


FIG. 5

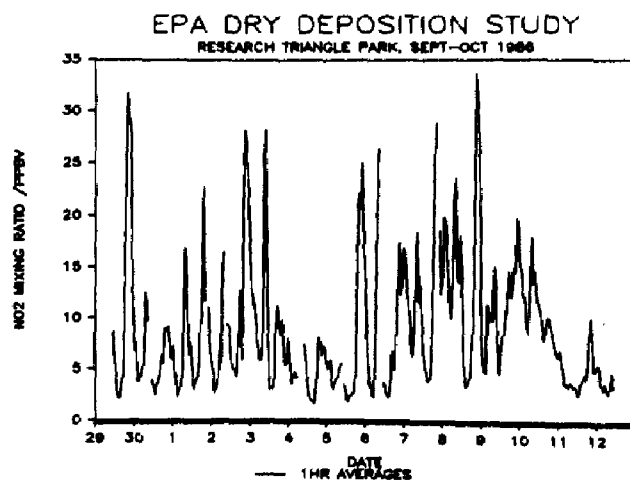
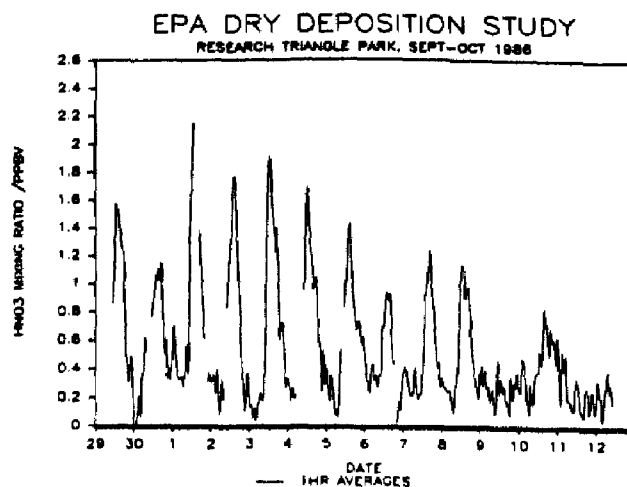


FIG. 6



MEASUREMENT OF ATMOSPHERIC NITRIC ACID AND AMMONIA BY THE FILTER METHOD AND A COMPARISON TO THE TUNEABLE DIODE LASER METHOD

Kurt Anlauf, David MacTavish and Alan Wiebe
Atmospheric Environment Service
4905 Dufferin Street
Downsview, Ontario, Canada, M3H 5T4

Gervase Mackay
Unisearch Associates Inc.
222 Snidercroft Road
Concord, Ontario, Canada, L4K 1B5

ABSTRACT

The measurement of atmospheric nitric acid by nylon filters is compared to that by tuneable diode laser spectroscopy over the range 0-2.5 ppb. 1h/2h and 22h sampling periods are compared. Furthermore, the effect of sampling period (up to 22h) on artifact nitric acid is also discussed - any such effects were within experimental error and hence were minimal under the study conditions. The results of measurements of atmospheric ammonia (1h-12h sampling periods) by citric acid-impregnated W41 filters are also presented. The results of this comparison study have shown that filter methods for measurement of atmospheric nitric acid and, probably ammonia, may be adequate and reliable for rural conditions in N.E. America.

INTRODUCTION

Measurement of water soluble nitrogen and sulfur compounds in air can be readily and economically made by means of filtration methods. By using combinations of filters, atmospheric species such as particle -NH_4 , -NO_3 and -SO_4 and gaseous SO_2 , NH_3 and HNO_3 can be routinely measured in monitoring networks. An eight-station regional network (CAPMON), employing filter methods is currently being operated in Canada by the Atmospheric Environment Service for measurement of atmospheric particles, SO_2 and HNO_3 .

There are potential artifact effects in measurements of the particles and gases when using filter methods, since particles can have gaseous precursors that exist in equilibrium with the particles. These artifacts are caused by displacement of equilibrium conditions when

changes occur in gas concentrations, temperature or humidity during sampling. For example, the collection and subsequent evaporation of NH_4NO_3 during long sampling periods (24 hour) could be an important process when filter measurements are made at locations with high concentrations of NH_3 and HNO_3 , high temperature and low relative humidity. Furthermore, reactions with particles can result in the evolution of reactive gases, which can be lost from particle filters and collected by subsequent impregnated filters.

Comparisons of nitric acid and particle- NO_3 measurements by filter and denuder difference methods¹ over 24h sampling periods have shown that in urban atmospheres, filter measurements were, on average, about 25% higher than those by the denuder difference method. This difference was attributed to systematic artifact particle- NO_3 volatilization during 24-hour sampling periods.

A comparison study of methods for measurement of atmospheric nitrogen and sulfur species was held at Research Triangle Park, N.C. from September 29 to October 12, 1986. This study provided an opportunity to evaluate volatile nitrate losses during filter sampling of regional, rural air masses. For this study, short duration (1h and 2h), extended duration (4h - 12 h) and daily (22h) filter samples were collected. Comparison of the averaged short duration with the extended period daily filter samples should provide information on artifact processes during filter sampling for HNO_3 . It is expected that artifact processes will be minimized for the short duration samples, since concentrations and composition of particles, precursor gases, temperature and humidity are unlikely to change dramatically during sampling. Besides the filter measurements, a diode laser was operated by Unisearch Associates Inc.² and provided an independent measurement for comparison with HNO_3 collected by nylon filters. Results of HNO_3 and NH_3 measurements by the filter method and HNO_3 measured by the diode laser will be compared.

EXPERIMENTAL

Filter Holder and Sample Analyses. For filter sampling, triple-stack filter holders of inner fluorocarbon polymer and outer polyethylene construction were used. Atmospheric particles were collected on the front Teflon filter (1 micron pore size, Gelman Sciences, Inc.). The second filter, made of nylon ('Nylasorb', Gelman Sciences Inc.) was used for collection of nitric acid. Ammonia or SO_2 was collected on a third, impregnated Whatman 41 filter. For ammonia, the impregnation solution was an aqueous mixture of 10% v/v glycerol and 25% w/v anhydrous citric acid (Baker, reagent grade). Details of operation of the filter holder system and analyses of the collected samples are reported in another publication³. The only variation to these procedures was that 6 mL extraction volumes were used for the 1h and 2h samples and 20 mL for the 22h samples. The 22h filter samples were originally extracted and analyzed at the Research Triangle Institute (Research Triangle Park, N.C.). Remaining solutions were then returned to the Atmospheric Environment Service for re-analysis. The latter set of results were used for calculations of atmospheric concentrations used in this report.

Filter Blanks. Two different levels of water soluble nitrate and chloride were found in the 13 nylon filters used as field blanks during the study. These were evaluated as two separate sets. Seven of the filters contained low levels of chloride (3-5 $\mu\text{g}/\text{filter}$) and an average

of $0.43 \mu\text{g}/\text{filter}$ of NO_3 (standard deviation = $\sigma = 0.10$). The other set of six contained $25\text{--}40 \mu\text{g}/\text{filter}$ Cl^- and an average of $1.82 \mu\text{g}/\text{filter}$ NO_3 ($\sigma = 0.37$). Each of the samples collected on the nylon filters was corrected by using the appropriate average blank value according to the level of chloride found in the filter. For the high chloride containing filters, the standard deviation corresponds to 0.06 and 0.03 ppb HNO_3 for 1h and 2h sample periods respectively (nominal 2.5 and 5 m^3 air volumes).

The average NH_3 found in 13 citric acid-impregnated filters used as field blanks was $0.47 \mu\text{g}/\text{filter}$ ($\sigma = 0.17$), with a range of 0.23 to $0.77 \mu\text{g}/\text{filter}$. For the 1h and 2h samples, the Standard Deviation of the average blank corresponds to 0.10 and 0.05 ppb NH_3 .

RESULTS

Results of filter measurements are expressed in ppb and were calculated from air volumes referenced to 20°C and 1 atm . Figure 1 shows HNO_3 and NH_3 concentrations as obtained from the $1\text{h}/2\text{h}$ filter samples. The photochemically formed HNO_3 shows the typical diurnal pattern for regional air masses, reaching a maximum in the mid-afternoon. NH_3 generally showed the opposite behavior, reaching a maximum during night-time hours and declining to minimum during the day (although there were some exceptions).

The results of a linear least squares regression comparison between the filter and laser measurements are presented in Table I. The 95% confidence intervals about the regression slopes and the intercepts are included.

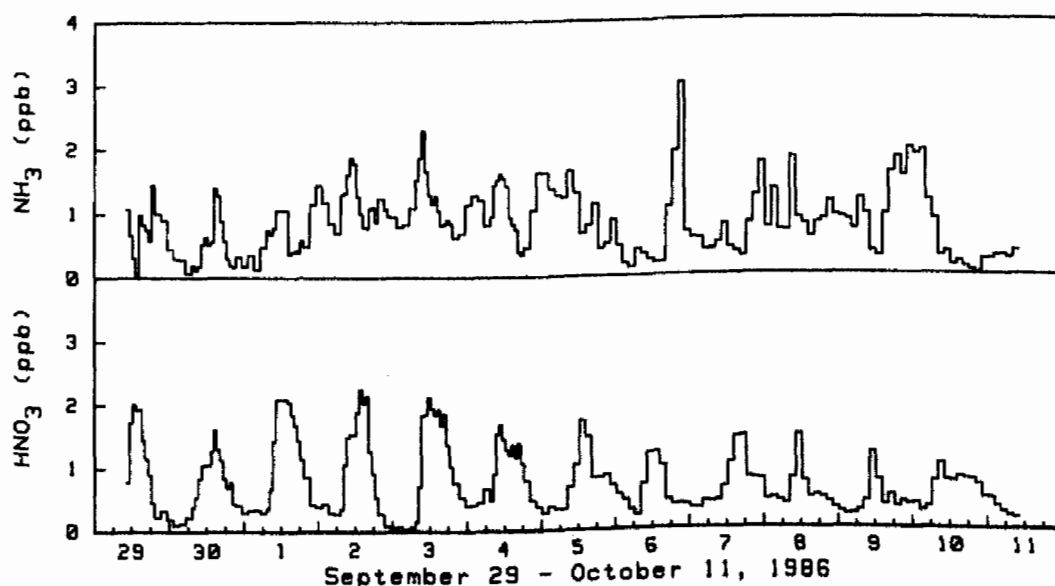


Figure 1. 1h and 2h concentrations (ppb) of atmospheric nitric acid and ammonia during the comparison study period at Raleigh, N.C.

Table I. Linear least squares regression statistics on filter and tuneable diode laser measurements of HNO_3 and NH_3 (concentrations in ppb).

n	r^2	slope	CI	y-int	CI	mean x	mean y	$S_{y,x}$
<u>1h/2h filter samples (y) vs laser (x) HNO_3</u>								
148	0.82	1.12	± 0.08	0.06	± 0.07	0.66	0.80	0.24
<u>22h filter samples (y) vs laser (x) HNO_3</u>								
11	0.66	0.85	± 0.46	0.09	± 0.26	0.58	0.59	0.10
<u>22h (y) vs 1h/2h (x) filter samples HNO_3</u>								
12	0.95	0.86	± 0.13	0.01	± 0.10	0.72	0.63	0.03
<u>4-12h (y) vs 1h/2h (x) filter samples HNO_3</u>								
16	0.99	1.00	± 0.07	-0.04	± 0.07	1.00	0.96	0.07
<u>4-12h (y) vs 1h/2h (x) filter samples NH_3</u>								
16	0.79	0.87	± 0.26	-0.01	± 0.30	1.10	0.95	0.20

n = no. of samples, r^2 = square of the correlation coefficient, CI = 95% confidence interval, $S_{y,x}$ = standard error of estimate of y on x

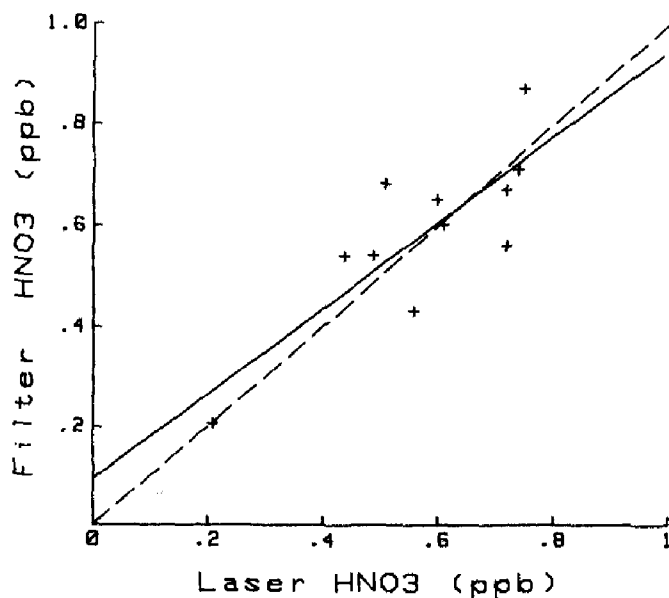


Figure 2. Linear least squares regression plot of measurement of nitric acid by the nylon filter (22h sampling period) and the tuneable diode laser (averaged over 22h).

1h/2h filter samples vs laser HNO_3 . Over the range of 0-2.5 ppb HNO_3 , there was more reasonable agreement and the degree of scatter was considerably less than in a previous comparison³. The detection limit of the tuneable diode laser was about 0.1 ppb and its accuracy was estimated to be better than 20% over most of the measuring range². This uncertainty, and those in the filter blanks probably account for the observed differences.

22h filter samples vs laser HNO_3 . Although there is excellent agreement in the means of concentrations, there are considerable uncertainties in the slope and intercept of the regression line. This is not unexpected, given the few data points and the fact that all, except one, were in a limited concentration range of about 0.4-0.8 ppb (see Figure 2).

22h vs 1h/2h filter samples HNO_3 . The average HNO_3 concentration as obtained by the 22h filters was somewhat lower than for the 22h-averaged 1h/2h filters; likewise the slope was somewhat less than one. If volatilization of particle nitrate were important to our measurements, an HNO_3 concentration difference in the opposite direction would have been observed. The observed difference may be related to two causes: (1) unlike other samples, the 22h samples were re-analyzed at AES about 3 months after extraction and analysis at RTI, N.C., and some sample deterioration may have occurred; (2) variability in blank corrections for the 1h/2h filters.

4-12h vs 1h/2h filter samples HNO_3 . In contrast, to the previous case, there is excellent agreement between filters from two sets of sampling periods. In this case, all filters had been extracted and analyzed at AES. Again, volatilization of particle nitrate is not evident.

4-12h vs 1h/2h filter samples NH_3 . Over the range of 0-2 ppb, there was little difference in measured NH_3 concentrations (see Table I for details). Some of the difference may be attributed to variability in blanks. As observed before for HNO_3 , the measured NH_3 difference does not suggest volatilization of particle ammonium nitrate as being important during our study.

CONCLUSIONS

A comparison of 1h/2h and 22-h nylon filter measurements of atmospheric nitric acid with those from a tuneable diode laser have shown on average, good agreement at the low concentrations encountered (0-2.5 ppb). Varying the sampling period for the filters did not reveal any significant differences; that is, artifact effects due to volatilization of particle nitrate could not be detected. The technique of using Whatman 41 filters impregnated with citric acid for measurement of atmospheric ammonia seems promising - again, sampling periods of 1h-2h gave similar results as those for longer periods. All the findings, so far, support the use of filter methods for measurement of atmospheric nitric acid (and probably ammonia) in N.E. America.

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MEASUREMENTS OF NITRIC ACID AND OTHER DRY
DEPOSITION COMPONENTS USING THE ANNULAR DENUDER
SYSTEM AND THE TRANSITION FLOW REACTOR



J. E. Sickles, II, L. L. Hodson, E. E. Rickman, Jr.,
M. L. Saeger, D. L. Hardison, A. R. Turner,
C. K. Sokol, and E. D. Estes
Research Triangle Institute
Research Triangle Park, North Carolina

R. J. Paur
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina

An intensive field study was conducted in the Research Triangle Park, North Carolina in the fall of 1986. The main objectives of this study were to conduct measurements of nitric acid and selected other airborne gaseous and particulate acidifying species using different types of samplers and to compare their performance under field sampling conditions. This paper presents and compares results collected using the annular denuder system (ADS) and the transition flow reactor (TFR).

Ambient concentrations of the following constituents were obtained: nitric acid, nitrous acid, nitrogen dioxide, sulfur dioxide, ammonia, strong hydrogen ion, and particulate nitrate, sulfate, and ammonium. Concentration and precision results from both samplers are compared. Statistical analyses of selected results are also presented.

Introduction

The phenomenon of acid deposition has received considerable public, political, and media attention. Dry deposition includes all processes where airborne contaminants are removed from the atmosphere at the earth's surface, excluding those processes aided by precipitation. Since dry deposition may contribute substantially to the acidic deposition burden, the U.S. Environmental Protection Agency (EPA) plans to implement a dry deposition monitoring network. Several constituents, including HNO_3 , HNO_2 , NO_2 , SO_2 , NH_3 , NH_4^+ , NO_3^- , SO_4^{2-} , and H^+ may be important contributors to ecosystem acidification. Currently, three multiple-constituent sampling systems are available for sampling selected acidifying constituents from ambient air. They are the filter pack (FP), the transition flow reactor (TFR), and the annular denuder system (ADS). The objective of the current study was to collect data that would permit the comparison of the performance of the ADS and the TFR under field sampling conditions.

Experimental

A 2-week intensive study was conducted at the EPA dry deposition monitoring site in the Research Triangle Park, North Carolina. Daily sampling was performed over 13 consecutive days beginning 09/29/86 and ending 10/12/86. RTI operated two ADSs and two TFRs each day (22-hour sample duration) and two ADSs each week (7- and 5-day sample durations) of the study.

The ADS is described in Reference 1. In this device, sampled air passes in series at 14 SLPM through: a cyclone to remove large particles ($D_{50} = 3.3 \mu\text{m}$); two Na_2CO_3 coated annular denuders to collect HNO_3 , HNO_2 , and SO_2 ; one citric acid coated annular denuder to collect gaseous NH_3 ; one Teflon filter to collect fine particles; and one nylon filter to collect volatilized nitrate.

The TFR is described in Reference 2. Air is sampled at 33 SLPM through a cyclone of the same design employed in the ADS ($D_{50} = 1.8 \mu\text{m}$); the sample is then split into two identical trains. A 1 SLPM bleedstream is drawn from the cyclone base to prevent particle accumulation. This stream passes through a Na_2CO_3 coated filter to permit resolution of nitrates and sulfates. Each 16 SLPM stream passes through a tube lined with a 3.2 cm long strip of nylon to collect 8.5 percent of the gaseous nitric acid and a similar strip of Nafion to collect 17 percent of the gaseous NH_3 . The sample then passes through a Teflon filter to collect fine particles, a nylon filter to collect the remaining HNO_3 and volatile nitrate, and an oxalic acid coated filter to collect the remaining NH_3 and volatile ammonium. At this point a 1.6 SLPM stream is drawn through two triethanolamine (TEA) coated filters to collect SO_2 and NO_2 . This 1.6 SLPM stream and the remaining 14.4 SLPM stream then pass through mass flow controllers and are exhausted through a pump.

The samples collected in the ADS and TFR are extracted into solution where the recovered nitrate, nitrite, and sulfate are determined by ion chromatography (IC). Ammonium is determined by a colorimetric method, indophenol blue. Hydrogen ion concentration is determined as pH. The measured mass of each species is used along with the sampled volume of air to infer the airborne concentration.

Results

Concentration and Precision Results

Concentration and precision results for the ADS and TFR samplers are summarized in Table 1. The tabulated parameters include: total gaseous and particulate ammonia and ammonium ($\text{Total NH}_3 + \text{NH}_4^+$); fine particle ammonium (Fine NH_4^+); ammonia (NH_3); hydrogen ion collected on the Teflon filter (H^+ Teflon); total gaseous nitric acid and particulate nitrate (Total NO_3^-); fine particle nitrate (Fine NO_3^-); nitric acid (HNO_3); nitrous acid (HNO_2); nitrogen dioxide (NO_2); total particulate sulfate (Total SO_4^{2-}); fine particle sulfate (Fine SO_4^{2-}); and sulfur dioxide (SO_2). The term "total" indicates that the cyclone catch for that species is included. The term "fine" refers to particles passing the cyclone and entering the Teflon filter in the particulate phase. Studywide estimates of mean and standard deviations (SD) of each parameter are given for each sampler. It should be noted that tabulated SDs represent day-to-day variability. Within day median coefficients of variation are also given for the two samplers.

The TFR Fine NO_3^- results are negative in 24 of 26 cases. As a result, they do not permit meaningful comparisons and are not considered in subsequent data analyses.

In general, both the ADS and TFR show good precision for all the remaining parameters. In all cases, the median difference between the paired ADS daily samples is less than $0.2 \mu\text{g}/\text{m}^3$, and with two exceptions, the corresponding results for the TFR are less than $0.5 \mu\text{g}/\text{m}^3$. With only two exceptions, TFR HNO_3 and TFR H^+ Teflon, the median CV's are less than 20 percent. The median CV's for the $\text{Total NH}_3 + \text{NH}_4^+$, Total NO_3^- , and Total SO_4^{2-} are all less than 5 percent. This shows excellent within sampler precision for both the ADS and TFR.

Since the colorimetric ammonium analysis was more variable than the IC analyses, the relatively high median CV's for NH_3 in each sampler may be reflecting the large analytical variability for NH_4^+ at the low concentrations associated with ambient NH_3 .

The pH analysis of Teflon filter extracts resulted in appreciable variability of the H^+ Teflon in both samplers. This is not surprising when it is noted that a difference in pH of 0.25 at a pH of 5.00 can propagate a difference of $7.8 \text{ n mol H}^+/\text{m}^3$.

Sample Stability

Weekly average concentrations were computed using results from the appropriate daily ADS samples. These results were then ratioed to the results of the appropriate weekly samples. Ratios near unity suggest sample stability across sampling durations of 22 hours to 7 days.

Most of the computed to measured results are near unity. The ratio for HNO_2 is high and thought to be so because collected nitrite is oxidized to nitrate to a larger extent in the ADS over the 1-week sampling duration than over 1-day periods. The low ratio for HNO_3 may also be reflecting this enhanced conversion of nitrite to nitrate in the weekly samples.

Statistical Analysis of ADS and TFR Results

Correlation coefficients from linear regression analysis of ADS and TFR daily mean values for the 13-day study are given in Table 2. The average ratios of daily mean ADS to TFR results for each parameter are given in Table 2. Differences between the daily mean ADS and TFR values were used in t tests to determine if the observed differences between the results from the two samplers are significant at the 95 percent confidence level. Results of these tests are also given in Table 2.

Behavior of Stable Species. Results of the ADS and TFR are highly correlated in most cases. In six of seven cases, correlation coefficients (r) exceed 0.85. For the two stable species, total particulate sulfate and total gaseous nitric acid and particulate nitrate, the results from the two samplers are highly correlated, with average ratios of concentrations near unity. There is no apparent difference between the results from the two samplers. This provides strong evidence that both samplers were operating under known flow conditions. It also suggests that across-sampler differences in the partitioning of portions of the Total NO_3^- or Total SO_4^{2-} must depend on unique characteristics of the samplers employed.

Total NO_3^- . As noted above, the measures of total gaseous nitric acid and particulate nitrate from the ADS and TFR are in agreement. They are highly correlated (i.e., $r = 0.96$). The average of the ADS to TFR ratios is 1.00 ± 0.08 , and the t test does not indicate a significant difference between the two measures.

HNO_3 . The ADS and TFR measures of HNO_3 are well correlated (i.e., $r = 0.88$). The average of the ADS to TFR ratios is 0.54 ± 0.12 , and the t test indicates that the difference between the measures is significant at the 95 percent confidence level. The sum of the nitrate on the TFR nylon strip and filter was used to obtain upper bound HNO_3

estimates which were also compared to ADS measures of HNO_3 . Although not shown in Table 2, these parameters are highly correlated (i.e., $r = 0.98$), the average of the ADS to TFR ratios is 0.88 ± 0.08 , and the two measures are again significantly different at the 95 percent confidence level. These results show better agreement between TFR and ADS measures of HNO_3 when the TFR HNO_3 is computed under the assumption that the TFR functions similarly to a filter pack rather than according to TFR theory.

Total SO_4^{2-} . As noted previously, the measures of total particulate sulfate from the ADS and TFR are in agreement. They are highly correlated (i.e., $r = 1.00$), the average of the ADS to TFR ratios is 1.03 ± 0.04 , and the t test does not indicate a significant difference between the measures from the two samplers.

SO_2 . The ADS and TFR measures of SO_2 are also highly correlated (i.e., $r = 0.98$). The average of the ADS to TFR ratios is 1.32 ± 0.30 (reciprocal = 0.76), and the t test indicates that the difference is significant. Tests of the recovery of SO_2 from TEA-coated filters conducted in our laboratory have shown approximately 80 percent recovery under humid conditions. The observed discrepancy between the ADS and TFR SO_2 concentrations may be related to reduced sulfate recovery from the TEA-coated filters in the determination of SO_2 with the TFR.

Total $\text{NH}_3 + \text{NH}_4^+$. Total gaseous and particulate ammonium as measured by the ADS and TFR are highly correlated (i.e., $r = 0.95$). Although the average of the ADS to TFR ratios is 0.86 ± 0.13 , the t test does indicate that the results of the two samplers are significantly different. A portion of this difference may be attributed to under-sampling of particulate ammonium by the ADS since there was no provision in this sampler to collect any volatilized ammonium downstream of the Teflon filter. The discrepancy may also be associated with the previously noted variability in the ammonium determinations.

NH_3 . The ADS and TFR measures of ammonia are poorly correlated (i.e., $r = 0.49$), and the average of the ADS to TFR ratios is 1.17 ± 0.41 . The variability of the results prevents detection of a difference between the ADS and TFR measures of this parameter.

H^+ Teflon. Strong hydrogen ion is determined from the measured pH of the extract of Teflon filters in both the ADS and TFR. ADS and TFR measures of H^+ are well correlated (i.e., $r = 0.86$), and the average ratio is 1.59 ± 0.66 . In spite of the large variability, the t test indicates that the results of the two samplers are different at the 95 percent confidence level. The ADS H^+ concentration may exceed the corresponding TFR value in part because undetected ammonia in the TFR neutralizes a portion of the H^+ in that sampler.

Conclusions

Conclusions and findings drawn from this study are given below.

- o Both ADS and TFR show good precision for all measured species concentrations except fine particle NO_3^- (Fine NO_3^-).
- o For the two stable species, total particulate sulfate (Total SO_4^{2-}) and total gaseous and particulate nitrate (Total NO_3^-), the results from the ADS and TFR are highly correlated, have average ratios near unity, and are not significantly different. These findings indicate that both samplers were operating under known flow conditions.
- o Statistical comparisons of ADS and TFR results show no significant differences for Total NO_3^- , Total SO_4^{2-} , and NH_3 ; the ADS estimate to exceed that of the TFR for SO_2 and H^+ ; and the TFR estimate to exceed that of the ADS for HNO_3 and Total $\text{NH}_3 + \text{NH}_4^+$.
- o Weekly average concentrations computed from measured daily samples were ratioed to measured weekly results to assess sample stability in the ADS. The ratio was near unity for most species. High ratios for HNO_2 may be reflecting enhanced NO_2 oxidation on the denuders over 1-week versus 1-day sampling periods. The conversion of nitrites to nitrates over extended sampling periods (i.e., weekly periods) may result in an overestimate of ambient HNO_3 concentrations and an underestimate of ambient HNO_2 concentrations with the ADS.
- o H^+ concentrations measured with the ADS exceed those with the TFR because undenuded NH_3 in the air sample reaching the TFR Teflon filter neutralizes a portion of the H^+ collected on the Teflon filter with that sampler.
- o SO_2 concentrations measured with the ADS exceed those measured with the TFR by approximately 30 percent. Tests in our laboratory suggest that the TFR results require a correction for reduced SO_4^{2-} recovery efficiency (i.e., 80 percent) under humid conditions.

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TABLE 1. SUMMARY OF CONCENTRATION AND PRECISION RESULTS FOR ADS AND TFR SAMPLERS

	Daily (9/29/86 to 10/12/86)			
	Mean \pm SD ^a		Median CV, % ^b	
	ADS	TFR	ADS	TFR
Total $\text{NH}_3 + \text{NH}_4^+$	2.545 \pm 1.153	2.911 \pm 1.191	3.3	4.6
Fine NH_4^+ (as NH_4^+)	1.794 \pm 1.055	2.174 \pm 1.091	3.2	9.1
NH_3	0.717 \pm 0.246	0.632 \pm 0.176	10.0	13.5
H ⁺ Teflon	29.61 \pm 15.31 ^c	22.82 \pm 16.74 ^c	11.2	21.8
Total NO_3^-	3.086 \pm 0.586	3.141 \pm 0.739	4.2	1.3
Fine NO_3^-	0.602 \pm 0.559	-0.728 \pm 0.688 ^d	15.7	46.6 ^d
HNO_3 (as NO_3^-)	1.509 \pm 0.627	2.715 \pm 0.847	7.7	20.6
HNO_2 (as NO_2^-)	0.911 \pm 0.466	--	4.8	--
NO_2 (as NO_2^-)	--	19.17 \pm 6.94	--	3.2
Total SO_4^{2-}	6.687 \pm 3.332	6.528 \pm 3.238	2.4	1.7
Fine SO_4^{2-}	6.275 \pm 3.446	5.972 \pm 3.282	2.2	1.9
SO_2 (as SO_4^{2-})	8.490 \pm 5.460	7.197 \pm 5.676	1.8	12.8

^aUnits: $\mu\text{g}/\text{m}^3$ except where noted otherwise; SD represents day-to-day variability.

^bRepresents median within day precision for 13 days of paired measurements for each sampler.

^cUnits: $\text{n mol}/\text{m}^3$ (uncorrected for blanks).

^dTFR Fine NO_3^- results are negative in most cases. They do not permit meaningful comparisons.

TABLE 2. STATISTICAL COMPARISON OF ADS AND TFR RESULTS

	r^a	Average Ratio of ADS to TFR ^b	t Test Results ^c
Total NO_3^-	0.96	1.00 ± 0.08	no difference
HNO_3	0.88	0.54 ± 0.12	ADS < TFR
Total SO_4^{2-}	1.00	1.03 ± 0.04	no difference
SO_2	0.98	1.32 ± 0.30	ADS > TFR
Total $\text{NH}_3 + \text{NH}_4^+$	0.95	0.86 ± 0.13	ADS < TFR
NH_3	0.49	1.17 ± 0.41	no difference
H^+ Teflon	0.86	1.59 ± 0.66	ADS > TFR

^aCorrelation coefficient for linear regression of mean daily ADS on TFR results, $n = 13$.

^bAverage of ratio of daily mean results for ADS and TFR (\pm one standard deviation).

^cResults of t test for 13 paired results at 95 percent confidence level.

Passive Sampling Device Measurements of NO₂ in Ambient Air

James D. Mulik
Environmental Monitoring Systems Laboratory
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

and

Dennis E. Williams
Northrop Services, Inc.
Research Triangle Park, NC 27709

Abstract

Passive sampling devices (PSDs) using triethanolamine-coated glass fiber filters as the collection surface and stainless steel mesh as a diffusion barrier between the air and the collection surface were deployed as part of the methods comparison study. The PSDs do not require a pump, and are small (2" diameter cylindrical sections), inexpensive sampling devices. The sampling rate for the devices with both surfaces of the device collecting has been established as approximately 154 cc/min under typical ambient conditions.

Three PSDs were placed in the ambient air and were therefore subject to any sampling rate variations due to wind, humidity and temperature changes. An additional three devices were placed inside the local dry deposition shelter within a glass cylinder through which ambient air was drawn at a controlled rate. The outside and inside PSDs averaged 8.84 ppbv and 9.92 ppbv, respectively, and a significant degree of variability was noted among triplicates.

Introduction

Several years ago the EPA began a modest program to develop passive sampling devices (PSDs) for the collection and analysis of both organic and inorganic air pollutants. More recently, however, the EPA has become more interested in personal exposure monitoring to support the ambient air quality

standards set under the Clean Air Act. Passive sampling devices are ideally suited for personal exposure monitoring because of their relatively low cost and small size. Commercially available NO₂ passive sampling devices, such as the Palmes tube (1), lack the sensitivity needed to obtain 8 to 24 hr time weighted average (TWA) measurements in non-occupational air. The sampling rate for the Palmes tube is $\sim 1.0 \text{ cm}^3/\text{min}$, which affords a sensitivity of 300 ppbv-hr when analyzed spectrophotometrically. Consequently, 5- to 7-day exposures are required to determine much lower levels of NO₂ found in ambient and indoor air.

PSDs have been used extensively by industrial hygienists to assess the effects of respiratory exposure to hazardous pollutants of workers. Since ambient air levels of most pollutants are several orders of magnitude lower than those normally found in the workplace, more sensitive monitoring systems are required. These systems are generally not portable and are usually located at fixed, outdoor sites. Such fixed-site monitoring may not accurately reflect the average daily exposure of the general populace to air pollutants. This is particularly true in the United States, where the average person spends an estimated 90% of the time indoors (2).

To obtain an accurate estimate of individual exposure to air pollution, the person must carry or wear the monitor. Therefore, the device must be unobtrusive, and lightweight. It should operate quietly, and place little or no burden on the individual. It must also be inexpensive, since many more units may be required for personal monitoring than for fixed-station monitoring. Active (pump-based) sampling systems used for occupational exposure assessment can and have been used successfully outside of the workplace (3). However, the pumps weigh from 0.5 to 1.5 kg and may not be comfortable to wear,

especially for small persons. In addition, they must be battery-powered and most cannot be continuously operated for more than 6 to 12 hr. Passive devices, which require no pump, are much lighter in weight and are not power limited.

EPA's initial efforts in developing passive sampling devices resulted in several publications and EPA final reports (4-8). Four NO_2 passive sampling methods were studied and were described in detail at the 1986 EPA-APCA Meeting. Two of the four methods that showed the most promise were:

1. AG/AGO coated on Chromosorb P followed by thermal desorption into a chemiluminescent NO_x monitor.
2. Modified EPA-PSD using triethanolamine coated on glass fiber filter paper as the sorbent, followed by extraction and ion chromatographic analysis.

Experimental

Further evaluation of the AG/AGO chemiluminescent NO_2 method showed that water vapor was a serious interferent. At relative humidities higher than 30% the overall sampling and recovery efficiency declines sharply and approaches 30% recovery at 80% relative humidity. The interference by water vapor would prevent the use of the sorbent in a passive sampling device, but when used in an active sampling device, this effect could be avoided by removing the water vapor ahead of the sorbent tube by means of a Nafion dryer. Because of the water vapor problem with AG/AGO in the passive mode, this work was dropped to focus on the modified EPA-PSD with Palmes tube chemistry and ion chromatographic analysis.

The EPA PSD that was originally designed for volatile organic compounds was converted to a PSD for NO_2 simply by replacing the Tenax® sorbent with triethanolamine-coated glass fiber filter paper. Ion chromatography was em-

ployed for analysis. The effective sampling rate of the modified EPA-PSD is 154 cm³/min making it potentially 150 times more sensitive than the Palmes tube.

The PSD has recently become commercially available from Scientific Instrumentation Specialists, Inc. (SIS) of Moscow, Idaho. An exploded view of the device is shown in Figure 1. The PSD is 3.8 cm in diameter, 1.2 cm in depth and weighs 36 g. Pairs of 200-mesh wire screens and perforated plates placed on each side of the sorbent bed serve as diffusion barriers.

The SIS-PSD for NO₂ was shown to have a minimum detectable quantity of 30 ppb-hr; to show no interference from NO and relative humidities as high as 80%; and to respond linearly from 20 µg/m³ to 460 µg/m³ (9).

All passive sampling devices have a minimum face velocity above which they must be used to maintain a constant sampling rate. The curve shown in Figure 2 is a plot of the response of the SIS-PSD to NO₂ versus face velocity (cm/sec.). From a practical standpoint, it appears that the SIS-PSD for NO₂ samples at reasonably constant rates at face velocities above 30 cm/sec.

The SIS-PSDs for NO₂ were tested in ambient air by direct comparison with a tunable diode laser system (10) during a field study in the EPA Annex parking lot at the Research Triangle Park, NC in October 1986. The PSDs were exposed outdoors in triplicate at ambient conditions of wind velocity, temperature and humidity and were located near the tunable diode laser sampling line. They were exposed for 22 hours each day of the 13-day study. Table I shows the excellent comparability between the two methods. In addition to the direct outdoor exposures, another set of 3 PSDs was simultaneously exposed inside a chamber through which outside air was passed at a constant known face velocity (100 cm/sec). While these measurements were generally slightly higher than those made outside the chamber, they agreed within experimental error.

Conclusions

Prior to this work, commercially available passive sampling devices for NO_2 could not be used as personal exposure monitors because they lacked the sensitivity needed for concentrations found in non-industrial settings, such as indoor air and ambient air. The results presented in this paper demonstrate that the SIS-PSD can be successfully applied to 8 to 24 hr time weighted average (TWA) measurements of NO_2 in ambient air. Although there was some variability between the 22 hr daily averages of the PSDs and the tunable diode laser daily average, the 13 day average agreed within a part per billion.

It should be noted that the PSDs were not meant to provide data that is accurate to plus or minus a few percent of the real value. They were designed to provide semi-quantitative data inexpensively and to be user friendly so that they could be used as personal exposure monitors to obtain the data that health effects researchers and statisticians need for their models.

The agreement between the two methods is even more remarkable when considering the complexity and high cost of the tunable diode laser (~ 0.2 million) and the simplicity and low cost of the SIS-PSD (less than \$200). The cost of the SIS-PSD for NO_2 could be reduced drastically by making the device out of a moldable plastic material. This passive sampler must be further evaluated for potential interferences from nitrous acid (HONO) and peroxyacetyl nitrate (PAN). HONO is not expected to be a significant interferent because of recent work by Biermann et al. (11) on measuring HONO in both indoor and outdoor air environments. Biermann found that the observed HONO/NO_2 ratio was only 2.5% indoors and 5% outdoors. PAN is also not expected to interfere with the SIS-PSD for NO_2 for the following reasons:

1. Diffusion coefficient of PAN is probably very low.

2. PAN would probably not get through the stainless steel diffusion barrier.
3. The ion chromatographic technique separates nitrate from nitrite.

The SIS-PSD described herein provides a personal exposure monitor that has the sensitivity and selectivity to monitor NO_2 in non-occupational environments, thus making it possible to perform large-scale monitoring at a relatively low cost. It is envisioned that such devices can be tailor-made for other pollutants, such as formaldehyde, ethylene oxide, ozone, etc.

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TABLE I. Comparison of SIS-PSD with a tunable diode laser for NO₂ in ambient air.

Day	Modified PSD						Tunable Diode Laser		
	Outside			Inside Chamber ^A					
	Conc, PPB	Uncertainty		Conc, PPB	Uncertainty		Conc, PPB	Uncertainty	
1	11.1	±	1.3	12.4	±	3.8	10.2	±	1.5
2	9.0	±	1.1	9.3	±	2.9	6.0	±	0.9
3	10.9	±	1.3	11.2	±	3.5	7.8	±	1.2
4	9.6	±	1.2	11.2	±	3.5	11.3	±	1.7
5	9.3	±	1.1	8.3	±	2.6	6.2	±	0.9
6	6.2	±	0.7	5.9	±	1.8	4.5	±	0.7
7	9.1	±	1.1	8.4	±	2.6	8.4	±	1.3
8	10.3	±	1.2	10.3	±	3.2	9.2	±	1.4
9	12.1	±	1.4	14.5	±	4.5	13.4	±	2.0
10	7.3	±	0.9	11.1	±	3.4	12.0	±	1.8
11	7.1	±	0.9	10.6	±	3.3	12.2	±	1.8
12	9.4	±	1.1	9.9	±	3.1	7.8	±	1.2
13	3.5	±	0.4	5.1	±	1.6	4.7	±	0.7
Avg	8.8	±	1.1	9.9	±	2.8	8.8	±	1.3

^A Ambient outside air passed through chamber at 100 cm/sec.

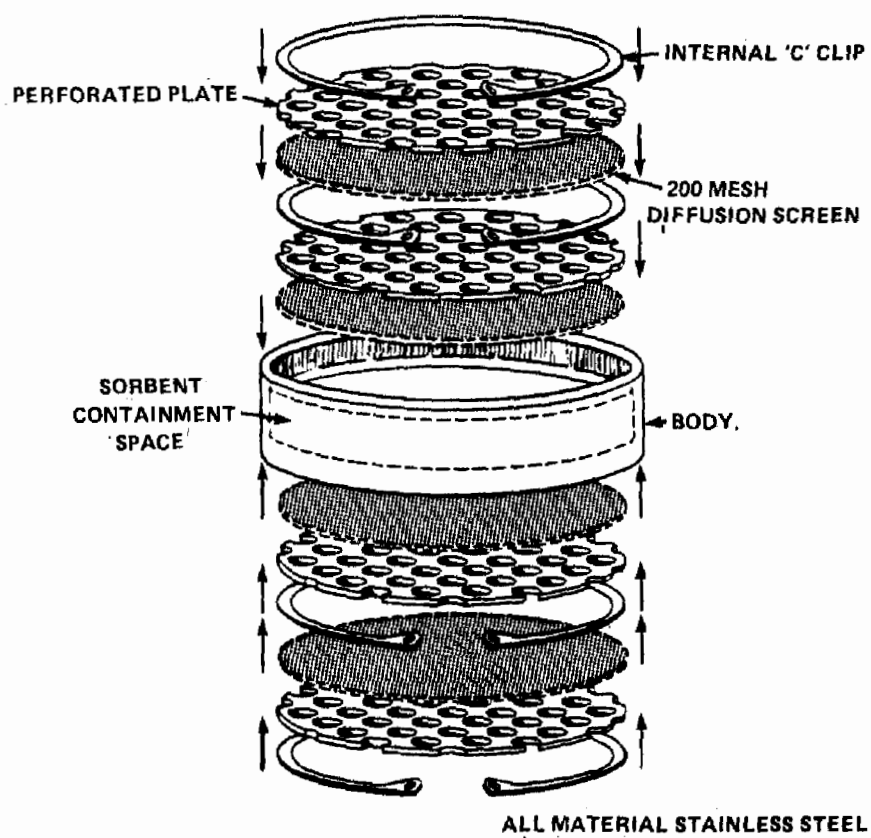


Figure 1 -- SIS Passive Sampling Device

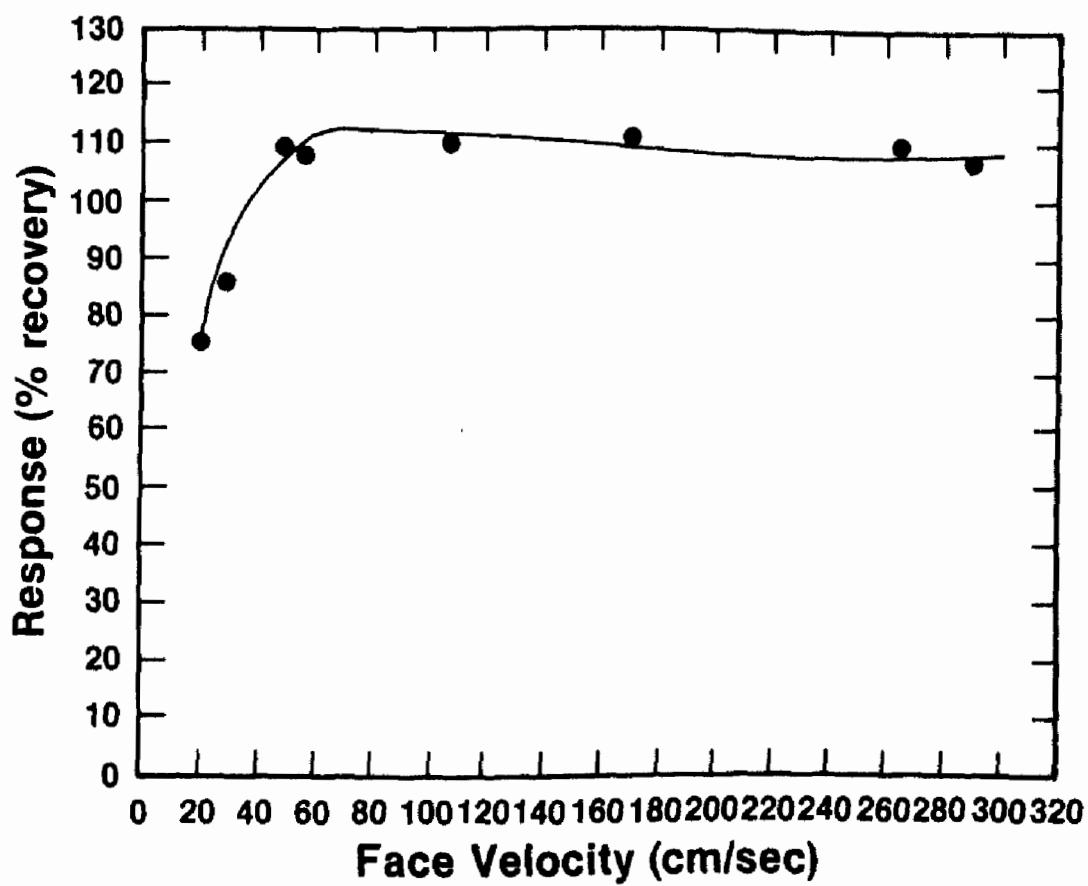


Figure 2 -- NO₂-PSD:Response vs. Face Velocity

LUMINOX MEASUREMENTS OF AMBIENT NO₂

D.K. Bubacz, E.H. Daughtrey, J.D. Pleil, and K.G. Kronmiller
Northrop Services, Inc. - Environmental Sciences
Research Triangle Park, NC 27709

Abstract

Two Luminex LMA-3 monitors were run simultaneously to measure real-time fluctuations of ambient NO₂. This was done as a part of the Fall 1986 Methods Comparison Study for measurement of compounds related to acidic deposition, conducted at the U.S. EPA Environmental Research Center Annex, Research Triangle Park, NC, from September 29 through October 13, 1986. Although they were purchased from the same manufacturer (Scintrex, Ltd., Ontario, Canada), the two instruments employed different temperature-dependence correction methods. One used temperature-sensing electronics to compensate the output signal; the second used feedback-controlled heating to maintain the reaction chamber of the instrument at a fixed temperature.

Data from both LMA-3 instruments were collected in real time by a Keithly-Compaq data acquisition system, which stored and printed hourly and daily averages. In this paper we describe our system and experimental methods, and we use our test results to compare the two monitors with one another and with the NO₂ reference system, a diode laser operated by another group.

Introduction

Between August 29 and September 12, 1986, as part of the methods comparison study held at the U.S. Environmental Protection Agency (EPA) Annex in Research Triangle Park, NC, two Luminox LMA3 NO₂ monitors (Scintrex, Ltd; Ontario, Canada) measured real-time NO₂ gas concentrations in ambient air. The two luminol-based instruments simultaneously sampled outside ambient air in a performance study of instruments equipped with different temperature compensation devices. The modifications were implemented to remedy a substantial temperature-sensitive response problem observed in earlier model instruments.¹ One LMA3 instrument (#1LMA3) was equipped with a temperature-controlled (30°C) reaction cell, whereas the other (#2LMA3) contained signal-correction circuitry to compensate for ambient temperature fluctuations. The data sets from the two instruments were compared with each other and with the tunable diode laser (TDL), the instrument used as the reference method for NO₂ measurement.

Experimental Methods

Ambient NO₂ measurements were made from inside a mobile laboratory situated next to the dry acid-deposition station in the rear parking lot of the EPA Annex in Research Triangle Park. The two Luminox LMA3 instruments sampled ambient air through separate 0.25-in.-i.d. Teflon lines extending from each instrument to a Teflon tee. From the tee a common sample line extended to the top of the dry-deposition station to a vertical height of approximately 10 ft. At the inlet of each Luminox instrument, 47-mm Teflon filters were installed to prevent fouling by dust and dirt. Sample air was drawn into each instrument by a small d.c.-driven, flying-vane-type air pump operating at a nominal flow rate of 1.5 L/min. Luminol solution was moved into and out of the reaction cell of each instrument by means of a peristaltic pump operating at approximately 0.05 mL/min.

Real-time ambient monitoring was maintained continuously for 22 h/day, throughout the study. The 2-h downtime each day was used for equipment maintenance, data transferal, and instrument calibration. Real-time data were collected and stored on a Keithly-Compaq (Keithly Instruments, Inc.; Cleveland, OH) data acquisition system. The system calculated and stored hourly averages, which were then manually reduced to daily, 22-h averages.

Multipoint calibration curves generated both before and after the comparison study were used to arrive at the final average daily concentrations of ambient NO₂.

Results and Discussion

Ambient NO₂ values versus time for the two Luminox instruments and the TDL are plotted in Figure 1. A qualitative comparison of data from the two Luminox LMA3 instruments indicates that the instruments tracked each other on a day-to-day basis, showing good agreement on increasing and decreasing trends. Similarly, good agreement is evident in the comparison of the Luminox instruments with the TDL with the exception of day 7 to day 8, when the Luminox instruments both

indicated a decrease while the TDL showed an increase in the NO₂ daily averages. On the eleventh day of the study, the #2LMA3 instrument showed a substantially higher average daily value than either of the other two instruments.

Quantitative comparisons are shown in Figures 2 and 3. Figure 2 is a comparison of NO₂ daily averages of Luminox instruments #1LMA3 and #2LMA3. A 1:1 correlation line drawn on the plot shows that #2LMA3 measured higher daily averages than #1LMA3 nearly two-thirds of the time. Two daily averages from the Luminox monitors show agreement to within 5% of each other.

Figure 3 compares the daily averages of the #1LMA3 instrument to those of the TDL instrument. Results indicate excellent agreement between the two instruments for approximately three-fourths of the study. In Figure 4, data from the #2LMA3 instrument and the TDL instrument are compared. Although the #2LMA3 instrument yielded daily NO₂ averages that were consistently higher than averages calculated for the reference method (TDL), the results roughly parallel those of the TDL, indicating a possible calibration offset in the Luminox instrument.

An overall comparison of the two temperature-corrected Luminox instruments from this preliminary investigation was made in terms of agreement with the reference method and in terms of versatility in field operation. Both Luminox instruments approximated ambient NO₂ concentration to a degree comparable to the TDL's performance. The #1LMA3 instrument showed an overall average concentration of 8.98 ppbv NO₂ while the #2LMA3 instrument showed 10.2 ppb NO₂. These values agreed within 99% and 86% of the value obtained with the TDL, respectively.

The advantages and disadvantages of each temperature modification design should be weighed before a design is selected for field use. An advantage of the #1LMA3 design is that the reaction cell temperature remains constant, thereby reducing interference of ambient temperature fluctuations with reaction kinetics. On the other hand the #2LMA3 instrument design incorporates signal-processing electronics, which may introduce calibration-shift problems.

Portability must be considered for operation of instruments in the field. When sampling requirements do not exceed 2-3 h, the Luminox instruments may be operated on a single battery charge. In this respect the thermostatic control of the #1LMA3 instrument is limited by its 110-V a.c. power requirement, whereas the #2LMA3 instrument is capable of independent operation up to 2-3 h. However, the advantage of independent operation becomes negligible when one considers that the data recording devices require an external power source to operate. In addition, most field monitoring studies far exceed the maximum 2- to 3-h operating time of a single battery charge.

Based on the data from the study, both temperature-correction modifications show comparable results to those of the reference method, TDL, with the exception of a slight calibration offset in #2LMA3. Thus, the temperature-correction design employed in the field

should be chosen on the basis of the suitability of its design for the conditions under which the instrument is to be operated.

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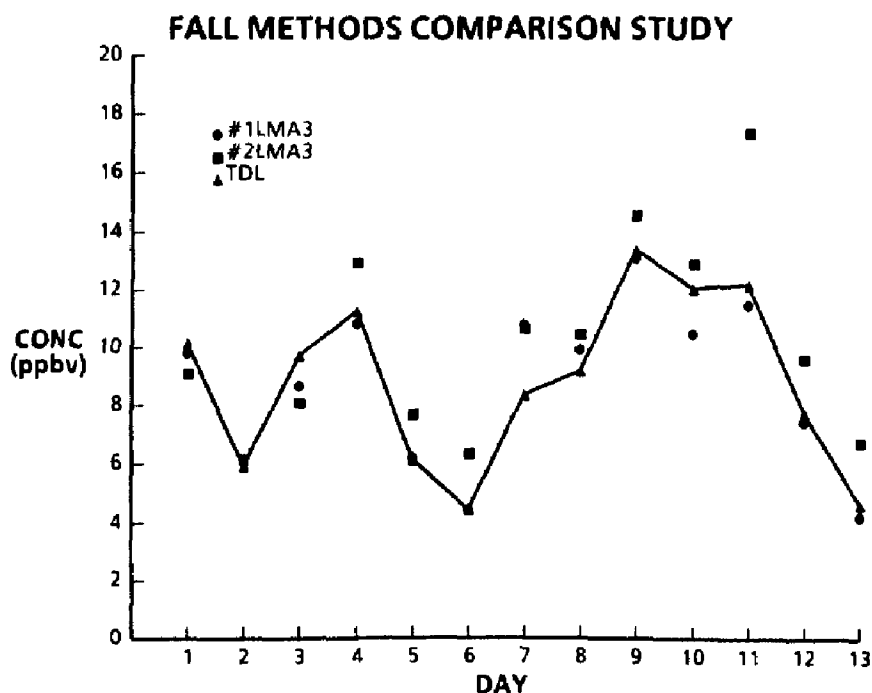


Figure 1. Plot of daily (22-h) NO₂ averages measured with Luminox NO₂ monitors and the tunable diode laser, Aug. 29-Sept. 12, 1986.

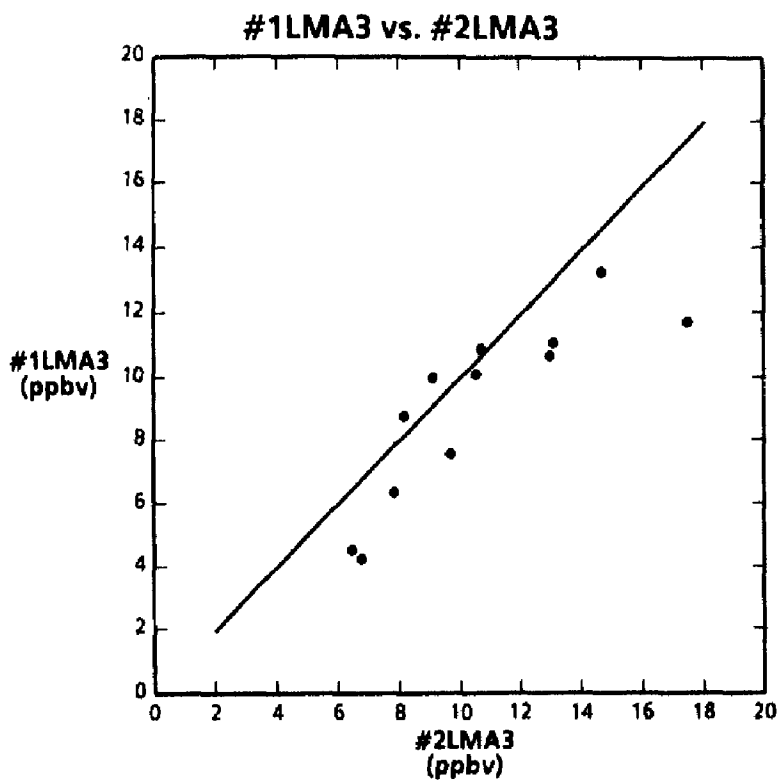


Figure 2. Comparison plot of #1LMA3 vs. #2LMA3 daily NO₂ averages.

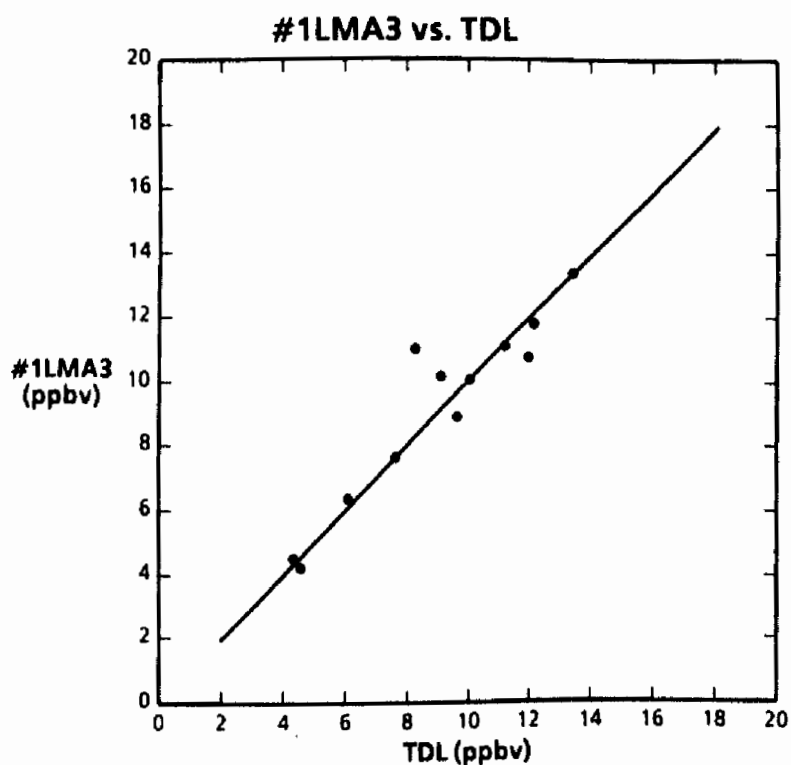


Figure 3. Comparison plot of #1LMA3 Luminox monitor vs. tunable diode laser daily NO_2 averages.

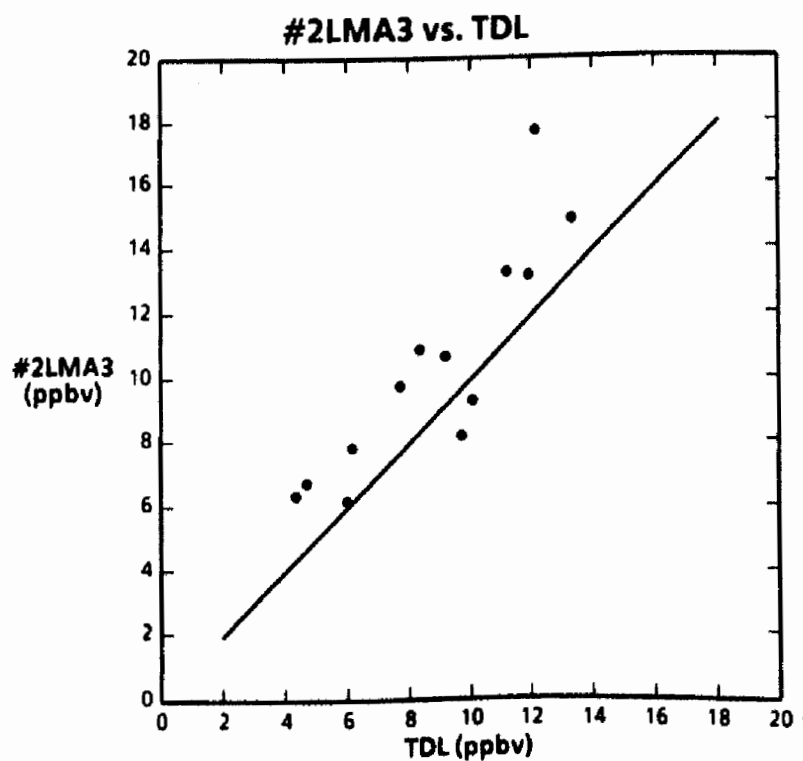


Figure 4. Comparison plot of #2LMA3 Luminox monitor vs. tunable diode laser daily NO_2 averages.

Comparison Across Different Methods and Interpretation of Results

Richard J. Paur and William A. McClenny

Environmental Monitoring Systems Laboratory
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

Abstract

A thirteen day comparison study of samplers/methods for estimating concentration of various sulfur and nitrogen containing species was conducted in Sept/Oct 1986 in Research Triangle Park, NC. The primary objective of the comparison was to determine whether results obtained from multicomponent samplers, each representing a candidate method for use in acid deposition networks, were equivalent, and to further determine whether those results were in agreement with an independent spectroscopic method for gaseous nitric acid and nitrogen dioxide. This paper presents selected results from the study and compares the performance of the various methods.

Introduction

The Environmental Monitoring Systems Laboratory (EMSL) of the US EPA has been conducting a methods development program for measurement of the atmospheric concentration of the chemical species that are important in acid deposition monitoring. These species include nitrogen and sulfur containing species such as SO_2 , NO_2 , NO_3^- , SO_4^{2-} , HNO_3 , NH_3 , and NH_4^+ , and other contributing species such as ozone and H_2O_2 . The acidity of particulate matter collected on Teflon filters can be estimated by measurement of the pH of aqueous extracts of the filters; however, the significance of the measurement is unclear due to problems in maintaining the integrity of the sample.

One of the methods examined in the study, the annular denuder system (ADS), collects acidic species on a carbonate coated denuder assembly. One of the materials observed during ion chromatographic (IC) analysis of the denuder extract is NO_2^- ion; the NO_2^- ion is present in concentration greater than that expected for partial collection of NO_2 , NO or PAN. The source of the excess nitrite has been tentatively identified as HONO. The ambient concentrations of HONO, HNO_3 and NO_2 is compared to provide some insight into the potential role of HONO as a nitrogen donor to biological systems and to examine the plausibility of the identification of the species as HONO by its correlation with the concentration of NO_2 , one of the precursors of HONO in the troposphere.

Many of the results presented here are presented in more detail in the previous papers given in this session. The intent of this paper is to provide comparisons between similar measurements from different methods.

The data obtained in the study was reduced to 22 hour average values for each pollutant and sampler. Replicate values were averaged together to permit

statistical analysis of the data in terms of linear regression treatments of 5 or 13 22-hr values from individual samplers, or, in the case of nitric acid, from a composite average of 4 different samplers. The uncertainties presented are those associated with the least squares linear regression and do not include the uncertainties associated with the chemical analysis or flow rates (see the preceding papers for estimates of these uncertainties). The error bounds are calculated for 95% confidence intervals.

In the following discussion the methods for sampling and/or the corresponding measurement results after sampling will be referred to as:

ADS	-- annular denuder system
TFR	-- transition flow reactor
FP	-- filter pack
-F suffix	-- denotes measurement results for particle species collected downstream of an inlet.
-T suffix	-- denotes sum of measurement results for particle species collected on inlet and downstream of inlet
TFR-RTI	-- TFR results obtained by Research Triangle Institute personnel
TFR-ASRL	-- TFR results obtained by Atmospheric Sciences Research Laboratory personnel
TFR-RTI-FP	-- TFR results interpreted as a filter pack instead of as recommended by originator's standard operating procedure
TDLAS	-- tunable diode laser spectrometer measurements
COMP	-- composite average of measurements from ADS, FP, TFR-ASRL and TFR-RTI-FP

Results and Discussion

Sulfate

The sulfate results presented in Table 1 indicate generally close agreement between the ADS and TFR samplers for both fine fraction and total particulate sulfate. For the TFR-ASRL subset of five sampling runs, the inlet was not extracted, so only TFR-ASRL-F can be reported. The FP results were 10-15% greater than ADS or TFR results in terms of the regression line slope; this difference is probably not significant when flow and analytical errors are considered. The implication of such good agreement for sulfate results is that flow rates were accurately known and that any disagreement in results for other species must be due to causes other than uncertainty in flow rates.

Total sulfate values are evenly distributed over the concentration range of 4-14 $\mu\text{g}/\text{m}^3$. The difference between fine and total sulfate is incremental, averaging about 5% of the total sulfate; hence, all inlets used were adequate.

Sum of gas phase and particle nitrate

The sum of gas phase and particle phase nitrate obtained by the ADS, TFR-RTI and FP are in agreement. The relatively large uncertainties associated with the slope and intercept values are in large part due to the narrow range of concentrations (2-4 $\mu\text{g}/\text{m}^3$) observed during the comparison.

Nitrate

The size range of particles containing nitrate extends from fine particles to particles well above the cutpoint of the inlets on the ADS and TFR samplers (3.3 μm and 1.8 μm aerodynamic diameter, respectively). Therefore, comparisons are complicated and conclusions are less certain than for sulfate. Table 1 shows that the total particulate nitrate from the ADS and FP are in agreement. The relatively narrow concentration range observed during the study is largely responsible for the large uncertainty associated with the slope. The comparison of ADS-F with FP is not meaningful, since FP results include large particle nitrate and, without exception, are considerably higher than the corresponding ADS-F values. The comparison between ADS-F and TFR-RTI-F is not meaningful due to unexplained differences between the nominal and observed collection efficiencies of the TFR for HNO_3 and the fact that fine nitrate is calculated (not measured) using TFR measurements of HNO_3 .

The 0.79 ratio between the ADS and TFR-ASRL is likely due to the different cutpoints for the two inlets.

Sulfur dioxide

The sulfur dioxide data shows that the FP, ADS, and TFR-RTI agree well in terms of slope but that the FP and TFR show an offset of 0.5 and 1.5 $\mu\text{g}/\text{m}^3$, respectively, compared to the ADS. The capture of some of the sulfur dioxide by nylon filters in the FP and TFR was taken into account. The offset may be due to extraction problems, matrix effects with the IC, or blank problems; however, a cursory examination of the pertinent data does not offer strong support for any of these hypotheses.

Nitrogen dioxide

Comparison of the TFR-RTI with the tunable diode laser (TDLAS) shows favorable agreement. The relatively greater estimates provided by the TEA treated filter in the TFR are somewhat surprising in view of laboratory studies indicating less than 100% collection/extraction efficiencies for the TEA filters.

Nitric Acid

Nitric acid measurements from the various methods were compared to a composite average of measurements from the ADS, FP, TFR-ASRL, and TFR-RTI-FP. Table 1 shows that 4 of the 5 integrating sampler methods agreed with the composite average to within 0.1 in terms of slope and with less than 0.1 $\mu\text{g}/\text{m}^3$ intercept value. The slope of the TFR-RTI vs the Comp regression was 1.17 and the intercept value was large. This combination causes the TFR-RTI to average 63% higher than the composite average. The cause of the anomalous behavior of that sampler is not understood, in spite of a detailed investigation of its performance.

Ammonium ion

The TFR and ADS comparison yields unity slope but the data shows a significant intercept. This may be due to positive artifact in the TFR or loss of ammonium ion from the Teflon filter in the ADS. Limited (4) tests to determine the losses in the ADS suggest smaller losses than would be required to explain the observations. Both mechanisms suggested above may be operating.

Ammonia

The results for ammonia show little correlation between the measurements. The low concentration of ammonia might be expected to produce measurement difficulties; however, the coefficient of variation of replicates measurement with the ADS and TFR would suggest that the measurements should agree better than was observed.

Nitrogen

An interesting aspect of the use of carbonate coated denuders in the ADS is the observation of nitrite ion in the denuder wash solution. Some nitrite may be expected from reaction of NO_2 and PAN with the surface; the second denuder tube is used as a field blank to correct for this artifact. The excess nitrite left after correction for known interferences has been tentatively identified as due to collection of HONO .

Figure 1 is scatter plot showing the concentration of nitrogen available from nitric acid vs the concentration of nitrogen available from HONO . For the site and sampling period of this comparison, the amount of nitrogen available from the two sources is roughly equivalent at about $0.3 \mu\text{g}/\text{m}^3$. In view of the considerable interest in determining HNO_3 concentrations for purposes of understanding plant response and delay of winter hardening in forests, the above results suggest that an effort should be made to verify the source of the excess nitrite. The only information available from this comparison study concerning a possible source of the nitrite is a plot of the excess nitrite vs nitrogen dioxide (see Figure 2). The nitrite concentration is roughly equal to 5% of the NO_2 concentration. This is in general agreement with results presented by Biermann et al.¹; however, the samples reported here were taken over a 22-hr period and interpretation of the data is very difficult since the day/night concentrations are merged. It must also be noted that a similar relationship might also be due to imperfect correction for nitrite interference from nitrogen dioxide conversion to nitrite in the denuder tubes.

Conclusions

The various methods agree well in terms of sulfate estimates. Measurements for nitrate are complicated by particle size/inlet size selection and nitrate volatility, but are in generally good agreement when these factors are taken into account. The sulfur dioxide measurements suggest some blank and/or extraction problems still exist; these problems may be primarily problems in samplers which pass the gas stream through nylon filters prior to collection of

the sulfur dioxide. The limited nitrogen dioxide comparison showed close agreement between the TDLAS and TFR-RTI.

The nitric acid measurements showed close agreement among the FP, ADS, TFR-ASRL, and the TFR-RTI when treated as a filter pack. When operated according to recommended operating procedures, the TFR-RTI gave results which exceeded the composite average by 63% when averaged over the 13-day comparison period. For ammonium ion, the FP result are about 30% high relative to the ADS and TFR in terms of regression line slopes. The TFR has a positive offset of about 0.5 $\mu\text{g}/\text{m}^3$ relative to the FP and ADS. The TFR and ADS ammonia results were in very poor agreement over the concentration range observed.

The excess nitrite observed in the ADS contains nitrogen in concentrations approximately equal to the nitrogen present in HNO_3 .

Disclaimer

The research described in this article does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Table 1. Linear Regression Parameters for Comparison of Selected Methods/
Chemical Species

Method	n	R ²	Slope*	Intercept*
<u>Sulfate</u> ; range = 4-14 $\mu\text{g}/\text{m}^3$				
TFR-ASRL-F vs ADS-F	5	.993	1.00 \pm 0.15	- 0.05 \pm 1.36
TFR-RTI-F vs ADS-F	13	.993	0.95 \pm 0.06	0.05 \pm 0.45
ADS-T vs FP	13	.961	0.86 \pm 0.12	0.74 \pm 0.90
TFR-RTI-T vs FP	13	.953	0.84 \pm 0.12	0.77 \pm 0.96
<u>Sum of gas phase and particle nitrate</u> ; range = 2-4 $\mu\text{g}/\text{m}^3$				
FP vs ADS	13	.769	0.88 \pm 0.32	0.30 \pm 1.01
TFR-RTI vs ADS	13	.914	1.20 \pm 0.25	- 0.57 \pm 0.77
<u>Nitrate</u> ; range = 2-4 $\mu\text{g}/\text{m}^3$				
FP vs ADS-T	13	.769	0.88 \pm 0.32	0.30 \pm 1.01
TFR-ASRL vs ADS-F	5	.993	0.79 \pm 0.12	0.13 \pm 0.13
<u>Sulfur dioxide</u> ; range = 2-14 $\mu\text{g}/\text{m}^3$				
FP vs ADS	13	.994	0.94 \pm 0.05	- 0.41 \pm 0.48
TFR-RTI vs ADS	13	.966	1.02 \pm 0.13	- 1.48 \pm 1.27
<u>Nitrogen dioxide</u> ; range = 8-30 $\mu\text{g}/\text{m}^3$				
TDLAS vs TFR-RTI	13	.938	1.11 \pm 0.19	- 0.68 \pm 3.58
<u>Nitric acid</u> ; range = 0.3-3 $\mu\text{g}/\text{m}^3$				
FP vs Comp	13	.982	1.02 \pm 0.09	0.02 \pm 0.16
ADS vs Comp	13	.976	0.95 \pm 0.10	- 0.08 \pm 0.17
TFR-ASRL vs Comp	5	.996	1.08 \pm 0.13	0.04 \pm 0.24
TFR-RTI vs Comp	13	.804	1.17 \pm 0.38	0.77 \pm 0.68
TFR-RTI-FP vs Comp	13	.988	0.98 \pm 0.07	0.07 \pm 0.13
TDLAS vs Comp	12	.731	0.65 \pm 0.28	0.53 \pm 0.51
<u>Ammonium ion</u> ; range = 0.5-5 $\mu\text{g}/\text{m}^3$				
TFR-RTI vs ADS	13	.987	0.97 \pm 0.07	0.44 \pm 0.15
FP vs ADS	13	.933	1.32 \pm 0.23	0.02 \pm 0.48
<u>Ammonia</u> ; range = 0.3-1.2 $\mu\text{g}/\text{m}^3$				
TFR-RTI vs ADS	13	.239	0.35 \pm 0.41	0.38 \pm 0.31

* 95% confidence intervals for slope and intercept.

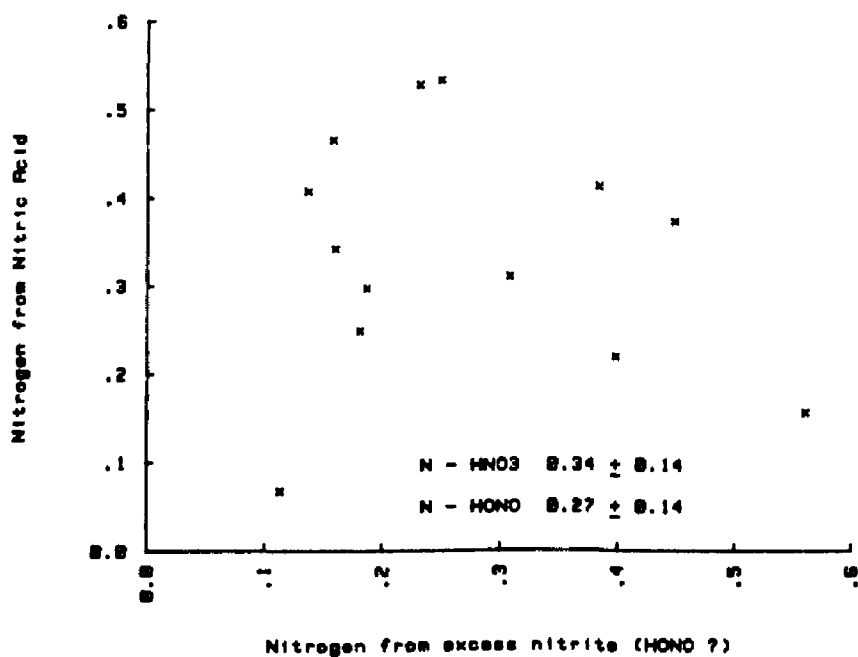


Figure 1. Nitrogen ($\mu\text{g}/\text{m}^3$) from nitric acid and from excess nitrite.

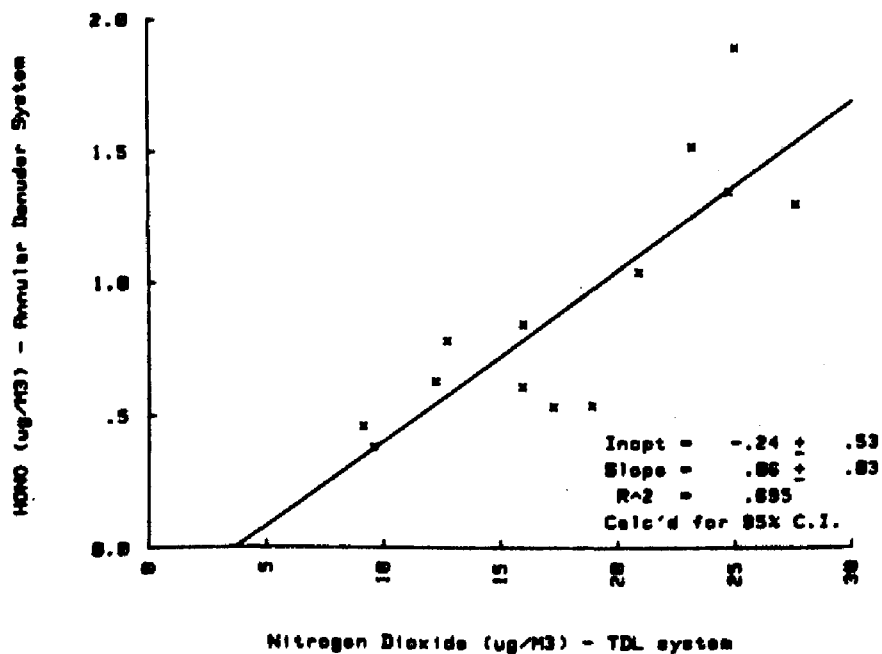


Figure 2. Plot of excess nitrite vs. nitrogen dioxide.

THE BEHAVIOR of OXY-PAH and NITRO-PAH on
ATMOSPHERIC SOOT PARTICLES

Richard Kamens¹, Hani Karam¹, James Fulcher¹,
Zhishi Guo¹, Jean Perry¹,
Daniel Saucy², and Leonard Stockburger³
¹Dept of ESE, Univ. of North Carolina, Chapel
Hill, North Carolina, 27514;
²Arizona State University, Tempe Arizona,
85287; ³US Environmental Protection
Agency, RTP, NC, 27709

ABSTRACT

A preliminary investigation of the relative atmospheric stability of selected oxygenated polyaromatic hydrocarbons (Oxy-PAH) and nitrated polyaromatic hydrocarbons (Nitro-PAH) on airborne soot particles exposed to sunlight was undertaken. Diesel soot particles were used as a source for Nitro-PAH and wood soot particles as a source of Oxy-PAH. Dilute particle systems were exposed to midday natural sunlight for periods of 3-4 hours in 25m³ outdoor Teflon film environmental chambers. Aromatic oxygenates such as 9,10-anthracenedione and cyclopenta(def)phenanthrene appear to be stable on wood soot particles, while polyaromatic hydrocarbons such as benzo(a)pyrene and benzo(ghi)perylene decay on fresh wood or diesel soot particles in sunlight; 1-nitropyrene and 6-nitrobenzo(a)pyrene on freshly emitted diesel soot particles also exhibit decay under certain outdoor conditions.

THE BEHAVIOR of OXY-PAH and NITRO-PAH on ATMOSPHERIC SOOT PARTICLES

INTRODUCTION

A significant portion of the extractable organic matter from airborne soot particles is composed of semi-polar and polar oxygenated compounds. Currently, however, there is almost no information on the stability of these compounds in the atmosphere. In this paper we will describe preliminary outdoor chamber experiments which address the stability of selected oxygenated polyaromatic hydrocarbons (Oxy-PAH) and nitrated polyaromatic hydrocarbons (Nitro-PAH) on airborne combustion soot particles.

EXPERIMENTAL

Chamber Experiments

Wood soot particles were added to two 25m³ outdoor teflon film chambers in the manner which has been described in previous documents⁽¹⁻³⁾. Diesel soot particles were added to the chambers directly from the tail pipe of a 1967 Mercedes 200D sedan. Injection occurred for approximately 6 seconds, after warm engine startup, with a slight load on the engine. Diesel soot particles (purchased from the National Bureau of Standards, SRM #1650) also were injected into the chambers using a liquid nitrogen injection system, previously described by Saucy and co-workers⁽⁴⁾. The resulting aerosol systems, ranging in concentration from 400 to 2500 ug/m³, were aged for periods of 3 to 4 hours in mid-day sun.

Sample Workup Procedures

Particles were collected at various times during the experiments on 47 mm Pallflex Teflon-impregnated glass fiber filters. In selected experiments, an XAD-2 cartridge (4 x 0.9 cm id SS tube) was placed downstream of the filter to assess the collection distribution of selected oxygenated PAH between the particle filter and the XAD trap. The sample flow rate was 18 l/min.

Filters were extracted with 25 ml of dichloromethane (MeCl₂) in micro soxhlet extractors. Material collected on XAD traps was removed by passing 10 ml of MeCl₂ through the XAD cartridge. Extracts were concentrated to approximately 200 ul and fractionated on a Waters semiprep Poracil column with a mobile phase flow rate of 2 ml/min⁽³⁾. The solvent program started with 95% hexane, 5% MeCl₂. At 12 minutes it was programmed to 100% MeCl₂ at 5% min⁻¹, held at 100% MeCl₂ for 1 minute, and then quickly programmed to 100% ACN and held there for 24 minutes. The PAH fraction was collected from 8-23 minutes, the Nitro-PAH from 23-29.5 minutes and the Oxy-PAH fraction from 29.5-42.5 minutes. Recoveries through the fractionation ranged from 60 to 98% depending on the compound and concentration of the sample.

Analysis of Oxy-PAH and Nitro-PAH

Analysis of the semipolar Oxy-PAH fraction was performed with Carlo Erba model #4130 gas chromatograph (FID) with a 30 m fused silica J&W 1701 column. This column gave better resolution of the compounds of interest when compared with a less polar 30 m fused silica J&W DB-5 column. A 30 m J&W carbowax 20 m column also was evaluated, but its upper temperature limit of 220 to 240 °C and high column bleed prevented analysis of peaks eluting after 9,10-anthracenedione(9,10-anthraquinone). Identification of selected Oxy-PAH were determined from GC/MS analysis of the Oxy-PAH fraction on either a Hewlett Packard 5992 GC/MS or a Finnigan Mat 4500 GC/MS system. Repeated GC/MS analyses of chamber soot samples of the Oxy-PAH fraction indicated that compounds identified from authentic standards or compounds tentatively identified by comparison with library spectra, were free from contamination by artifact phthalate peaks. All tentatively and authentic standard identified compounds had an correlation coefficients greater than or equal to 0.9 when matched against the eight most intense mass spectral peaks from library spectra. The structure and names of seven different Oxy-PAH typically monitored in a chamber experiment are shown in Table 1. A reconstructed ion chromatograph of an Oxy-PAH fraction from a chamber wood soot sample is shown in Figure 1.

Nitro-PAH were analyzed by reverse phase HPLC with fluorescent detection, using a method originally developed by Tejada and co-workers⁽⁵⁾. A Supelco PAH 5um column was used for chromatographic separation. The eluting Nitro-PAH were then reduced to corresponding Amino-PAH in a 20 mm x 4 mm id column which contained ground automobile Pt/Rh catalyst. The size of the catalyst particles was estimated to be 40 to 100 um and the reducer column was maintained at 60 °C. 1-nitropyrene (1N-P) was monitored at excitation and emission wave lengths of 360 & 430 nm; 7-nitrobenz(a)anthracene (7N-BaA) at 300 & 475 nm; 6-nitrochrysene (6N-Chry) at 273 & 437 nm; and 6-nitrobenzo(a)pyrene (6N-BaP) at 420 & 495 nm.

RESULTS AND DISCUSSION

PAH and Oxy-PAH Stability on Soot Particles

To determine the recovery of Oxy-PAH compounds from XAD-2 sampling, clean air, at a flow rate of 18 l/min for 20 minutes, was drawn through XAD cartridges which contained a preloaded mixture of Oxy-PAH. The Oxy-PAH concentrations were 100 ng per species, and the compounds ranged from napthaquinone to 7,12-benz(a)anthracenedione. Elution with MeCl₂ gave recoveries for most compounds in the range from 81 to 96%. The exceptions were anthrone and 1-hydroxyanthraquinone. These compounds were recovered at 23 and 70% after the 20 minutes of air flow. Similar recoveries were obtained when using acetone as an eluant solvent but much lower recoveries were observed when acetonitrile was used (43-56%).

During experiments with wood smoke (ave temp = 21 °C), partitioning between the filter and the XAD cartridge was observed for lower molecular weight oxygenates. For example 34.1% (sd =15.2; n=10) of the recovered 9-fluorenone (mw = 180, bp = 341.5 °C) was found in the XAD-2 extracts. For 9,10-anthraquinone (mw = 208, b.p. = 379.8 °C) 91.1% was recovered from the filter extracts (sd=7.5%; n=10).

Thus in this paper we have assumed that compounds with boiling points and molecular weights similar to or greater than that of 9,10-anthraquinone have a tendency to exist primarily in the particle phase and are not appreciably stripped from our filters during sampling.

Wood soot systems aged for several hours in the dark show that PAH and Oxy-PAH concentrations (ng of compound per mg of collected soot) are stable. When wood smoke with PAH and Oxy-PAH loadings in the thousands ng/mg was aged in the presence of midday sunlight ($\text{NO}_x < 0.07\text{ppm}$, photochemical $\text{O}_3 < 0.08\text{ppm}$), PAH concentrations slowly declined. Oxy-PAH concentrations however, appeared to be more stable (Figure 2). At lower organic particle loadings and moderate humidities, PAH tend to degrade more quickly in sunlight. By analogy, we speculate that under such lower concentration conditions, Oxy-PAH species also would be more stable than PAH. A possible exception is 7-benzanthrone. In all of the sunlight experiments it exhibited some decay while other Oxy-PAH appeared to be more stable.

Based on these experiments it is not possible to determine the extent to which simultaneous Oxy-PAH synthesis and destruction processes are occurring as airborne soot particles age in the presence of sunlight. Our results suggest that if significant synthesis occurs, then it must be offset by a loss process in order to maintain the relatively stable time-concentration profiles that are observed.

NITRO-PAH Behavior

A diesel soot-particle aerosol free from combustion gases was established in one chamber using the NBS diesel soot particulate standard (SRM #1650) and the liquid nitrogen injector. Chamber Nitro-PAH concentrates from SRM #1650 diesel soot aged in the presence of sunlight are illustrated in the bottom graph of Figure 3. The average temperature for this run was 34.9 °C, the dew point was 17.4 °C and the average total solar intensity was $0.81\text{ cal cm}^{-2}\text{ min}^{-1}$. The chamber contained rural background NO_x and NMOC concentrations. Photochemically generated O_3 accumulated to a maximum concentration of 0.06ppm. Figure 3 suggests that most Nitro-PAH are stable on these soot particles under the noted experimental conditions, although some compounds (6-NBap) may decay.

Simultaneously, in the second chamber, we conducted an experiment with automobile diesel emissions. The initial NO and NO_2 concentrations were 0.31 and 0.16 ppm. The NMOC was 0.6 ppmc, and 0.03 ppm of O_3 accumulated. PAH and Nitro-PAH on these particles exhibited a rapid decay (Figure 3, top graph). We were unable to determine if nitro compounds that can be generated

from secondary photochemical reactions, (e.g., if 2-nitropyrene or 2-nitrofluoranthene), were formed during these experiments.

Particle measurements taken with a laser optical particle instrument (LAS-X, PMS, Boulder, CO.) indicate that the Mercedes diesel particles had a symmetrical particle size distribution with a mean mass diameter of 0.196 μm . This size distribution did not change significantly over the course of the experiment. The NBS SRM #1650 particles had a broader mass size distribution (mean = 0.293). The calculated surface to volume ratios (assuming smooth, spherical particles) for both the fresh and the NBS diesel soot particles did not change appreciably with time during the course of an experiment. The surface to volume ratio of NBS diesel soot was approximately 40% lower than the fresh Mercedes soot (assuming that the Lasser particle counter responded to both types of soot particles in the same manner). It is additionally possible that as NBS diesel soot particles aged (in their sealed vial containers) prior to use in these experiments, the surface morphology changed appreciably as volatile compounds were lost. This may have formed channels and interstices on the particle surface. The net result would be an additional reduction in the effective surface available for reaction with light and other reactive gases in the immediate environment of the particle. Lastly, we do not know if suspension of the NBS diesel particles in the liquid nitrogen injector altered the surface of the particles.

SUMMARY

The preliminary results reported in this study suggest that high Oxy-PAH loadings on airborne wood soot particles and ambient air ($\text{NO}_x < 0.07\text{ppm}$) appear to be stable in sunlight. Similarly high PAH concentrations slowly decline. When fresh diesel soot particles were exposed to sunlight, ($\text{NO}_x = 0.47\text{ ppm}$) Nitro-PAH decreased in concentration. However, PAH and Nitro-PAH present on NBS pre-collected diesel soot particles were stable in sunlight under the same outdoor conditions. Differences in 1) particle surfaces between freshly emitted and stored particles or 2) photochemical environments, may explain the difference in behavior between the same Nitro-PAH on these two types of diesel soot particles.

ACKNOWLEDGEMENTS

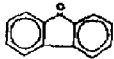
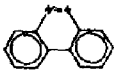
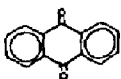
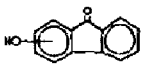
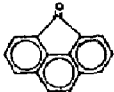
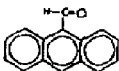
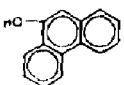
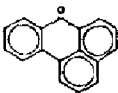
The authors would like to thank Mr. Joe McElwee and Ms. Kelly Dix for their technical assistance. This work was sponsored by a grant, #R812256, and cooperative agreement #CR 812820-02-0 from the US EPA to the University of North Carolina. This paper has not undergone US EPA review for publication and the contents do not necessarily reflect EPA views or policy. Mention of trade names or commercial products does not constitute EPA endorsement or recommendation for use.

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Table 1

Structures of Compounds Monitored in Oxy-PAH Fraction

NAME		MOLECULAR WT.
9-FLUORENONE		180
BENZO-C-CINNOLINE		180
9,10-ANTHRAQUINONE		208
HYDROXY-FLUORENONE		196
CYCLO PENTA-def- PHENANTHRONE		204
9-ANTHRACENE- CARBOXALDEHYDE		206
9-PHENANTHROL		194
BENZANTHRONE		230

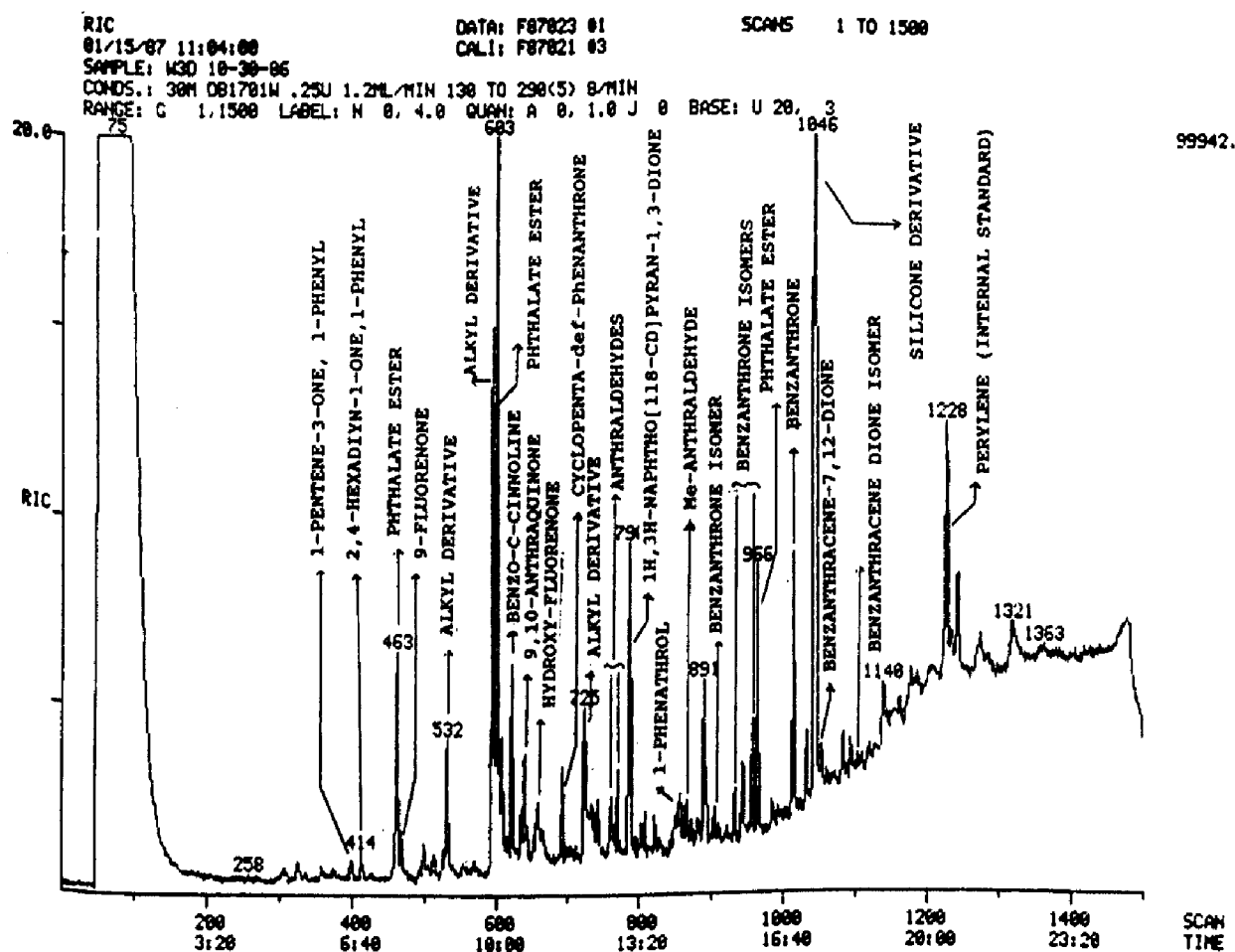


Figure 1. Reconstructed ion chromatograph of Oxy-PAH fraction from a Chamber wood soot extract. 30 m 1701 0.25 u fused silica column(J&W). 50 sec split/splitless inj at room temp; program from 130 °C to 290 °C. Finnigan Mat 4500 GC/MS. Authentic standards were available for 9,10-anthraquinone, 9-fluorenone, 7-benzanthrene, and benzanthracene7-12,dione. Other peaks tentively identified by library matching.

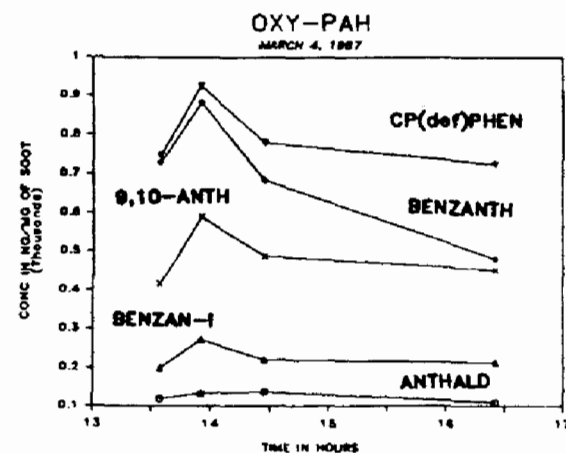
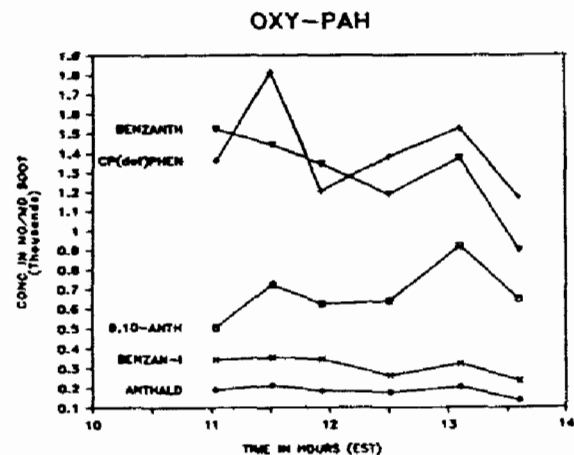
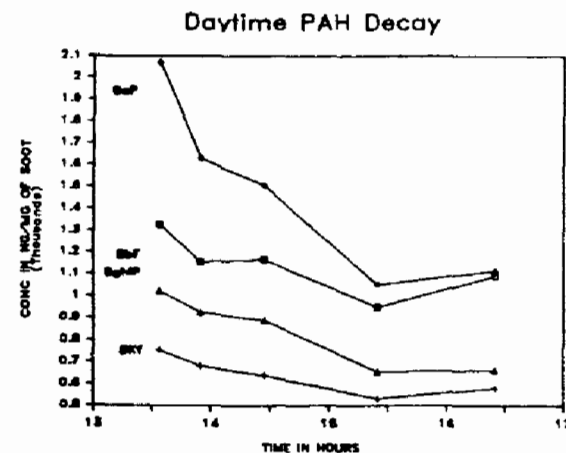
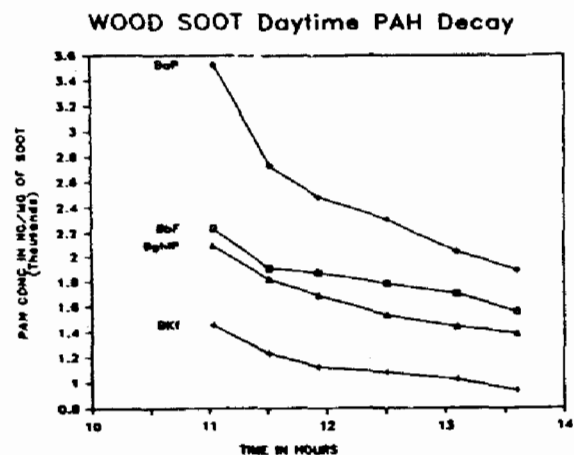
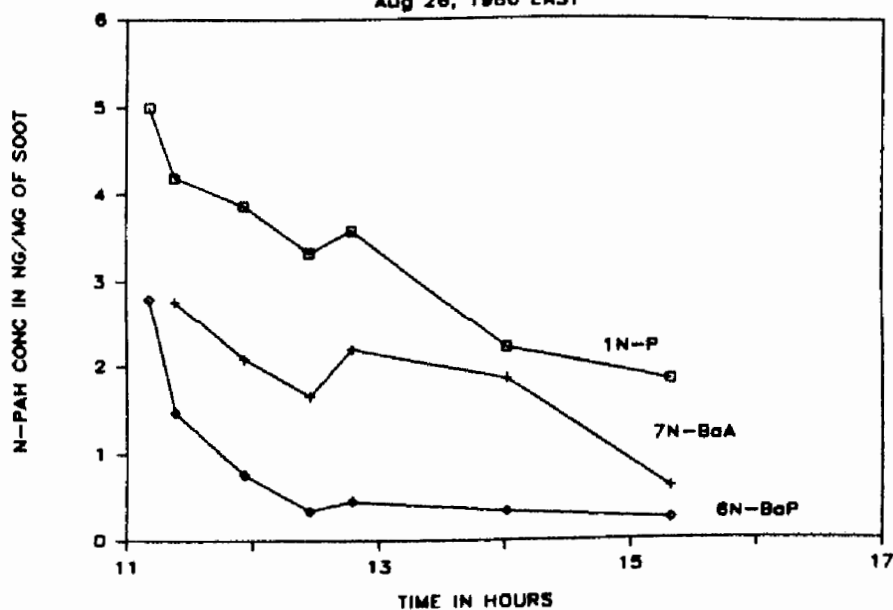


Figure 2. Daytime Decay of Oxy-PAH and PAH in Sunlight. Left; Experiment on February 8, 1987, ave temp = 21 °C; Right, March 4, 1987, ave temp = 16 °C;

Mercedes DIESEL nitro-PAH IN SUNLIGHT

Aug 26, 1986 EAST



NBS DIESEL nitro-PAH IN SUNLIGHT

Aug 26, 1986

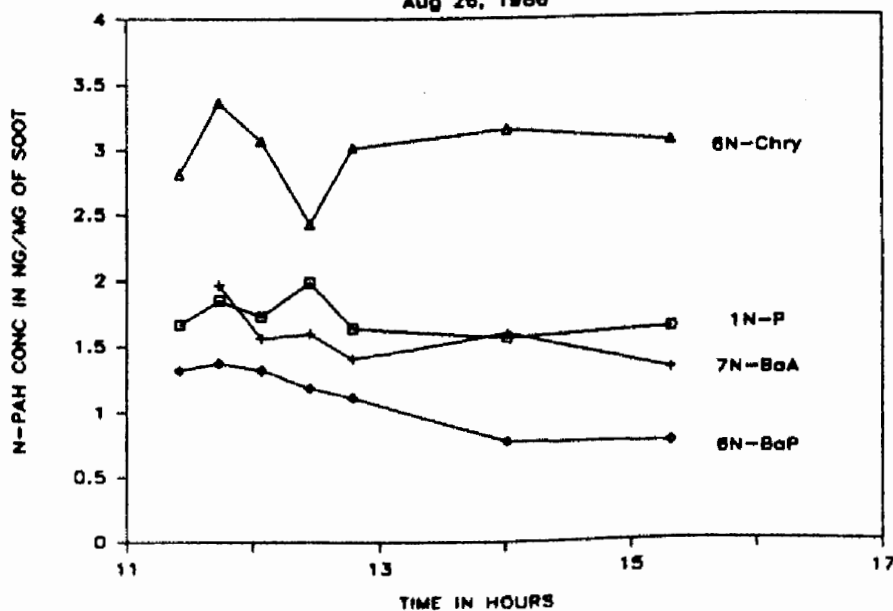


Figure 3. Stability of Nitro-PAH on Diesel soot Particles in Sunlight; 1N-P particle loading divided by 10 in NBS diesel soot experiment(bottom graph), and tentative identity of 6N-Chry assigned on the basis of retention time.

COMPARATIVE MUTAGENIC ACTIVITIES OF SEVERAL PEROXYACYL NITRATES

T.E. Kleindienst, P.B. Shepson, C.M. Nero, E.E. Hudgens
Northrop Services, Inc. - Environmental Sciences
Research Triangle Park, NC 27709

L.T. Cupitta, J.J. Bufalini^a, L.D. Claxton^b
^aAtmospheric Sciences Research Laboratory
^bHealth Effects Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Salmonella typhimurium strain TA100 was exposed to a series of peroxyacyl nitrates including peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN), peroxybutyryl nitrate (PBN), peroxybenzoyl nitrate (PBzN), and chloroperoxyacetyl nitrate (CPAN). Gas-phase concentrations for the individual exposures were in the high ppbv range. The deposition rate (i.e., the dose) could be determined from the measured decrease of the gas-phase concentration in the exposure chamber and the exposure time. The mutagenic activity of each compound was determined from linear dose-response curves. Values for the mutagenic activity ranged from 250 (PBN) to 7350 (PBzN) revertants/ μ mole. The mutagenic activity of PAN as a function of initial gas-phase concentration showed nonlinear effects that could not be attributed to Henry's Law considerations.

Introduction

Peroxyacyl nitrates (PNs), $RC(O)OONO_2$, represent oxidants formed in the polluted troposphere. Aldehydes, except for formaldehyde, serve as important precursors to PN formation following their reaction with OH. The peroxyacyl radical formed combines with NO_2 to produce PNs. Thus, acetaldehyde leads to peroxyacetyl nitrate (PAN) formation, propionaldehyde to peroxypropionyl nitrate (PPN) and butyraldehyde to peroxybutyryl nitrate (PBN). PAN has long been associated with possible physiological damage, and it has been shown to be mutagenic in the Ames Test with *Salmonella typhimurium*, strain TA100.¹ However, quantitative data on the toxicity and genotoxicity of PAN are fairly limited. Of the PNs only PAN, PPN,² and peroxybenzoyl nitrate (PBzN) (vide infra) have been observed in ambient air.³ PAN concentrations in polluted air generally range from 1-20 ppb with the others one to two orders of magnitude lower in concentration.

Over the past four years, we have examined the mutagenic activities of mixtures of hydrocarbons (e.g., propylene, toluene) and oxides of nitrogen that have been irradiated in a smog chamber. In a number of these mixtures, strong mutagenic activities have been observed from the products of these oxidations. Although the mixtures were complex, we have been able to determine that PAN was one of the primary contributors to the total mutagenic activity in TA100.⁴ We are currently examining the mutagenic activities of a series of peroxyacyl nitrates. These include PAN, PPN, PBN, PBzN, and chloro-peroxyacetyl nitrate (CPAN). (The last two compounds arise as products from the oxidation of benzaldehyde and chloroacetaldehyde, respectively.) The results of these measurements are of significance with respect to assessing the human health hazards associated with exposure to urban air.

Experimental Methods

The experimental method involved flowing dilute mixtures of the test compound in air into an exposure chamber that houses the test bacteria, *S. typhimurium*. Several timed exposures were performed for each compound in order to obtain dose-response curves. The mutagenic activities were determined from the measured deposition of each PN and from the dose-response curves. Two methods were employed to generate the PNs: (1) the appropriate aldehyde was oxidized by NO_3 in the presence of NO_2 and air, and (2) a solution-phase synthesis was used that involved the nitration of a peroxyorganic acid to give the peroxyacyl nitrate.

In the first technique (which has been previously described with respect to the formation of PAN⁴), the appropriate aldehyde, NO_2 , and O_3 in air were mixed in a 22.7-m³ Teflon reaction chamber. The chamber was operated in a dynamic mode, which allowed steady-state concentrations of PNs to be generated in the chamber. The effluent from the reaction chamber was then fed into a 190-L chamber where the bacteria were exposed to the gas-phase PNs. This procedure was

employed to generate CPAN, PBzN, and PAN. For CPAN and PBzN, chloroacetaldehyde (50% in water) and benzaldehyde (neat), respectively, were added in the vapor-phase to a mixing manifold by bubbling N₂ through the liquid. For the PAN preparation, acetaldehyde was taken from a dilute tank mixture in N₂ (0.8%). The aldehydes were introduced into the manifold to give an initial concentration of 1 ppm. O₃ was added to the manifold from the output of a commercial ozonizer, and NO₂ from a concentrated tank mixture in air at concentrations of 1 and 2 ppmv, respectively. Dilution air was provided using an Aadco zero-air generator. All flows were regulated using mass flow controllers to give the desired chamber concentration. The average residence time of gases in the chamber was 6.7 h. There was no evidence of major product formation other than the desired PN. In addition, there was no evidence of appreciable decomposition of the PNs.

The PNs were measured directly from the reaction and exposure chambers by GC as has been previously described for PAN.¹ The GC used to measure PAN was calibrated with a standardized solution of PAN in dodecane (vide infra). A known quantity of this solution was injected into air in a Teflon bag to make the gas-phase standard. These solutions were not synthesized for PBzN and CPAN. For these two cases it was assumed that the decrease in the aldehyde concentration measured between the inlet and the effluent of the reaction chamber represented the concentration of the PN formed. This assumption was tested for PAN and found to be valid within 15%.

The biological assay used in this work employed the bacteria *S. typhimurium*, strain TA100. Tester strains were obtained from Dr. Bruce Ames, University of California, Berkley, CA, and maintained by the Genetic Toxicology Division of the Health Effects Research Laboratory, U.S. EPA Environmental Research Center. The test procedures were those of Ames *et al.*⁵ with modifications as described earlier (1).

Each exposure chamber (clean air control and effluent) was filled with 45 petri dishes containing the tester strain and five survivor plates used as a qualitative check for toxicity. The exposure chamber was then brought up to the same steady-state concentration of the PN as in the reaction chamber. The covers on the petri dishes were then removed to begin the exposure. The total mass of PN deposited into the plates was determined by measuring the concentration in the exposure chamber before and after the covers were removed. Exposures were performed for various lengths of time to obtain a dose-response curve. We have found that re-covering a dish effectively stops the deposition of material and that the deposition is linearly related to the exposure time for PAN. Exposure periods ranged from 15 to 600 min. Following the exposures, the bacteria were incubated for 48 h at 37°C, and the number of revertant colonies/plate was counted. The exposure of the bacteria to clean air served as the control.

The second experimental method (i.e., the nitration of the peroxyorganic acid) was employed for PPN and PBN. These PNs were prepared according to the procedure outlined by Gaffney *et al.*⁶ The synthetic procedure ultimately yielded a solution of the PN in dodecane. This solution could then be used as a steady source of

vapor-phase PN. PAN was also synthesized for analytical purposes. The concentration of PAN in dodecane could be determined by hydrolyzing PAN to give $\text{CH}_3\text{C}(\text{O})\text{O}^-$ and NO_2^- and measuring NO_2^- by IC. For PBN and PPN, the analogous conversion to NO_2^- was significantly slower, and reproducible results could not be obtained. Thus, the solution concentration was not determined.

The electron capture GC could not be calibrated directly for PPN and PBN in air. Thus, these PNs were measured on the NO_x channel of a calibrated NO_x analyzer. It was assumed that the response of the analyzer to PPN or PBN was equivalent to NO_2 on a molar basis. Although this assumption could not be tested for PPN or PBN, it was tested for PAN since gas-phase standards in air could be generated. In this case, the magnitude of the response generated by PAN was identical to that from an equivalent concentration of NO_2 .

To perform the exposure, the PN in dodecane was added in sufficient quantity to a bubbler. N_2 was bubbled through the solution, which was thermostatted to 0°C . The N_2 stream containing a equilibrium concentration of the PN was added to a 150-L manifold where it was mixed with zero air. The contents of the manifold were flushed through the exposure chamber containing the biological assay. All further experimental techniques for this method were identical to those described above, except that the exposure chamber concentrations were measured with the NO_x analyzer rather than by GC.

Results

In each of the experiments, the primary data (i.e., the number of revertants/plate and the difference in concentration of the test compound before and after the plates were uncovered) leads to the calculation of two quantities, the mutagenic activity (revertants/h) and the deposition rate of the test compound ($\mu\text{moles/h}$). The mutagenic activity was obtained directly from the slope of the dose-response curve. One such plot has been presented previously for PAN.⁴ The number of revertants/h (per plate) was determined from the linear portions of the dose-response curves. Effects of toxicity can lead to nonlinear plots with negative curvature. All plots obtained in this study were linear, although PPN did give depressed survivor levels at the longer exposure times.

The fraction of the gas-phase test compound that deposits into the plates is used to determine the deposition rate, which is calculated from the following equation

$$\frac{\Delta[\text{PN}]}{\Delta t} \left(\frac{\mu\text{moles}}{\text{h}} \right) = \frac{\alpha[\text{PN}]_0 \Delta V}{RT N_p} \quad (1)$$

where $[\text{PN}]_0$ is the initial concentration of the peroxyacyl nitrate in ppmv, α is the fraction of the PN depositing into the medium, V is the flow rate through the chamber (850 L/h, in all cases), and N_p is

the total number of plates. The fraction (α) is independent of concentration, but can vary with flow rate through the chamber.

The results of these experiments have been tabulated in Table I. The table lists the compounds tested along with the procedure used to perform the exposure. $[PN]_0$ and (α) were measured during the exposures, whereas $\Delta[PN]/\Delta t$ was calculated from equation (1). The slope from the dose-response curves is given in the second to last column. The mutagenic activity (revertants/ μ mole) is given in the last column and was obtained by dividing the (revertants/h) by (μ moles/h).

For the PAN, PBzN, and CPAN exposures, significant concentrations of the reactants were present in the effluent mixture. The reactants were thus tested for mutagenic activity by performing an exposure of the initial unreacted mixture. For PAN and PBzN, the initial mixture was nonmutagenic. This was not the case for CPAN, because the initial mixture contained $ClCH_2CHO$, which is a mutagen of TA100. Thus, the mutagenic activity for the effluent mixture of CPAN needed to be corrected for the contribution of $ClCH_2CHO$. However, the $ClCH_2CHO$ contribution to the mutagenic activity was greater than that due to CPAN, because $ClCH_2CHO$ is significantly more soluble in the test medium than is CPAN. Thus, only the upper limit for the CPAN mutagenic activity was calculated.

In previous studies^{1,4} we have examined the mutagenic activity of PAN and found various measurements to differ by up to an order of magnitude. It was originally suggested⁴ that PAN decomposition products might be the cause of the discrepancy. Subsequently, a series of exposures was performed at a number of different gas-phase PAN concentrations. It was found that while the mutagenic activity (revertants/h) increased linearly with exposure time (i.e., dose), the activity was largely independent of the gas-phase concentration over the 100-3000 ppbv range. This observation would imply that the test medium had reached saturation (i.e., Henry's Law conditions) for PAN. However, as previously observed (ref 1, Figure 1) even at a gas-phase concentration of 1 ppmv there is no evidence of PAN saturation in the medium after a 20-h exposure. In addition, for relatively large PAN concentrations, the dose-response curve is linear throughout the exposure, implying that the rate of deposition remains constant and Henry's Law conditions are not being approached. Therefore, it is currently unclear why the measured reversion rate should be independent of the gas-phase concentration. For the present, however, a reversion rate of 14 rev/h represents an average mutagenic activity over a wide range of gas-phase concentrations (104-850 ppbv).

Conclusions

Mutagenic activities for a series of PNs have been presented. PBzN gave the greatest activity being nearly an order of magnitude greater than any other tested. However, the values for the mutagenic activity in Table I should be considered preliminary values until it is determined what effect changing the gas-phase concentration has on the mutagenic activities.

Disclaimer

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Table I. Summary of Experimental Results and the Mutagenic Activities for the Exposure of Peroxyacetyl Nitrates (PNs) to *S. typhimurium*, Strain TA100

PN	Method	[PN] ₀ ppbv	a	Δ[PN]/Δt (μmoles/h)	Mutagenic Activity (rev/h)	Mutagenic Activity (rev/μmole)
PANa	CHO/NO ₃	850	0.161	0.0374	14	a
PPN	SOLTN	332	0.133	0.0306	10.8	353
PBN	SOLTN	287	0.160	0.0320	8.1	254
PBzN	CHO/NO ₃	138	0.070	0.0067	49	7350
CPAN	CHO/NO ₃	106	0.210	0.0155	<10	<645

^aSee discussion.

AN EXPERIMENTAL TECHNIQUE FOR MEASURING THE OH RATE OF ATTACK ON PARTICLE BOUND PAH

Zhishi Guo, Richard Kamens and Harvey Jeffries

Department of Environmental Sciences and
Engineering, University of North Carolina
Chapel Hill, North Carolina 27514

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An experimental technique for studying OH rates of reaction with particle-bound polyaromatic hydrocarbons (PAH) is described. PAH on combustion soot particles were reacted directly with OH radicals in a 200 liter continuous stirred tank reactor (CSTR). To provide a relatively stable source of particles for reaction in the CSTR, wood soot particles were injected into a 25 m³ outdoor Teflon film chamber. Soot particles were drawn at a constant flow into the CSTR. The large chamber in effect served as a storage tank or reservoir for combustion soot particles.

The photodissociation of methyl nitrite inside the CSTR was used to provide a source of OH. PAH concentrations at the inlet, $[PAH]_{in}$, and outlet, $[PAH]_{out}$, of the CSTR were monitored along with vapor phase species, such as propylene or ethylene, $[Ref]_{out}$, which have established literature OH rate constants (k_0). The OH rate constants for selected PAH (k_1) was then be determined from the expression given below if the rates of reaction with in the CSTR (r_1 for PAH and r_0 for the reference compound) can be determined.

$$\frac{r_{PAH}}{r_{ref}} = \frac{k_1}{k_0} \frac{[PAH]_{out}}{[Ref]_{out}}$$

Non steady state CSTR equations were developed to calculate r for both particle bound and gas phase reactants. Other reactants in the CSTR which result in a loss of PAH (i.e. O_3 , NO_2 , $HONO_2$, photolysis, etc) were considered in the PAH-OH rate constant estimates.

AN EXPERIMENTAL TECHNIQUE FOR MEASURING THE OH RATE OF ATTACK ON PARTICLE BOUND PAH

INTRODUCTION

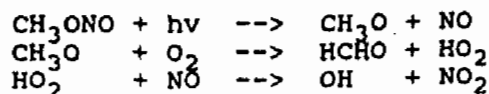
The reaction of vapor phase organic compounds with hydroxyl radicals(OH) is one of the most significant reaction pathways of both tropospheric and stratospheric chemistry. The relatively high OH rates of reaction for two and three ring PAH^[1] suggest that OH attack may be the major loss process for these compounds in the atmosphere. However, virtually nothing is known about the reactions of OH radicals and polyaromatic hydrocarbons (PAH) with more than four rings. This is because there has been difficulty in developing a technique for studying the reaction of particle bound PAH with gas-phase OH radicals.

GENERAL APPROACH

In this work PAH on soot particles were reacted with OH radicals in a continuous stirred tank reactor (CSTR). To provide a relatively stable source of particles for reaction in the CSTR we injected into one of our large outdoor chambers(25m³), combustion soot particles from a residential wood stove. The large chamber was a reservoir for the feed aerosol which could then be introduced at a constant flow rate into the CSTR (Figure 1). Real soot particles were used because we have found that compounds coated onto substrates (silica, alumina, carbon black) do not necessarily exhibit the same atmospheric reactivity as these same compounds do on real soot particles.

We have previously shown that particle size distributions do not change appreciably with time in our outdoor chambers^[2,3], and that the slow loss of particles to the chamber walls can be characterized. We have also shown that in the dark, particle bound PAH, nitro-PAH, and aromatic carbonyl mass as measured in ng per mg of soot are very stable over a period of many hours^[3,4].

The photolysis of methylnitrite (CH₃ONO) inside the CSTR was used to provide a source of OH according to the following reactions:



To inhibit the formation of O₃, N₂O₅ and NO₃, excess NO was added to the inlet flow. PAH concentrations at the inlet and outlet of the CSTR were monitored along with vapor phase species, such as propylene or ethylene, which have established literature OH rate constants. These vapor phase compounds were used as reference compounds. The OH rate constants for selected PAH was

determined by comparing the relative loss of a PAH with that of the reference compound. This approach is similar in concept to the relative rate technique developed and used in batch reactors at the University of California at Riverside^[5-7]. In the case of CSTR, as will be discussed later, the equation for rate constant calculation is different, but one still need measure only the decay of the reference compound and compare that to the decay of a selected PAH to determine the unknown rate constant.

EXPERIMENTAL

The 200-liter CSTR used in this pilot study has been previously described by Gery and co-workers^[8]. It is surrounded by thirty-four long-wave UV lamps (GE, F20 BLB). Gas and filter samples were taken at both the inlet (large chamber) and the outlet of the CSTR. To aid in the transfer of material from the large chamber to the CSTR, an airtight in-line fan was used between outdoor chamber and the CSTR inlet. The inlet/outlet flow was maintained at 9.24 liters per minute, corresponding to a residence time of 21.6 minutes. The in-line fan and CSTR outlet pump were balanced so that one atmosphere of pressure existed in the CSTR. Particle size measurements (0.09 to 3.0 μm) were performed with a laser optical particle counter (Model Las-X, Particle Measuring Systems, Boulder, CO). The effects of the in-line fan on CSTR particles size distributions were negligible.

The method of MeONO preparation in our laboratory has been previously described^[9]. Calculated volumes of ethylene and/or propylene were directly injected into the chamber and were monitored by a on-site GC (Carle model 211, isothermal at 60°C, porapak Q 50-80 mesh 1/8" SS col, FID). NO_x was monitored with a Bendix model 8101-B chemiluminescent analyzer (Ronceverte, WV 24970, USA). O₃ was monitored with a Bendix model 8002 chemiluminescent analyzer.

To avoid any adverse light effect in the large chamber reservoir, all the experiments were conducted after dark. Wood smoke emissions were added directly from the chimney of a residential wood stove to the 25 m³ outdoor Teflon film chamber. Split pine logs (6 cm x 10 cm x 50 cm) were used as a fuel and these were burned at a rate of 2 to 6 kg/hr. The resulting dilute wood smoke had initial particle concentrations of 1500 to 3000 $\mu\text{g}/\text{m}^3$. A calculated volume of methylnitrite (500 to 800 c.c.) was flushed into the outdoor chamber by a nitrogen stream. When the addition of particles from the feed reservoir began, the lights around the CSTR were turned on. Sampling began 90 minutes later.

Particle samples were taken from both the large chamber and the CSTR outlet. Soot particles were collected on 47 mm teflon-impregnated glass fiber filters (Pallflex T60A20) at a flow of 9.24 liters/min. Particulate masses on the filters were ranged from 0.2 to 1.0 mg.

Filter samples were extracted in 25 ml micro soxhlet extractors with methylene chloride (Burdick and Jackson, HPLC grade) 3-4 hours after collection. Sample work up procedures and analytical techniques used for PAH analysis have been described elsewhere^[2-4].

THEORETICAL CONSIDERATIONS

A CSTR consists of a well-stirred tank into which there is a continuous flow of reacting material and from which the partially reacted material passes continuously. The theory of CSTR in steady state has been well established^[10,11]. The mathematics that describes the behavior of the CSTR are based on the assumption of perfect mixing. A fair approximation to perfect mixing is not difficult to attain in a CSTR provided that the fluid phase is not too viscous. The rate expression for a CSTR in the steady state is:

$$r = \frac{[C]_{in} - [C]_{out}}{\tau} \quad (1)$$

where:

r = the reaction rate for the chosen reactant with the units of concentration per unit volume per unit time;

$[C]_{in}$ = the inlet reactant concentration;

$[C]_{out}$ = the outlet reactant concentration;

τ = the residence time or holding time, which is defined as $\tau = V/F$; where f is the inlet/outlet flow rate in volume per unit time, and V the volume of CSTR; After seven residence times at a constant inflow, the CSTR will attain 99.9% of its steady state concentration.

CSTR in Non-Steady State

In this work gas and particle phase species in the large reservoir were slowly decreasing. This occurs because the large reservoir is being slowly diluted by drawing samples into the CSTR, and because particles are being lost to the reservoir walls. These loss mechanisms slowly change the rate at which reactants enter the the CSTR. It is necessary therefore, to consider the situation of a CSTR under non-steady state. For this purpose, we have developed two rate expressions.

For gas-phase species, the rate can be determined by

$$r = \frac{[C]_{in} - [C]_{out}}{\tau} - s \quad (2)$$

where $[C]_{in}$, $[C]_{out}$, and r are the same as in Eq.(1); term s here is defined as, $s = d[C]_{out}/dt$, the rate of change of concentration in the CSTR. The value of s can be determined by finding the slope of $[C]_{out}$ vs. time curve. This equation looks very similar to Eq.(1) except an extra term s . As one can see, Eq.(1) is actually a special case of Eq.(2). This expression may be used for reactions of any order.

The behavior of reactant molecules on the particle surface differ from that of gas molecules. Although particles entering the CSTR can freely move about, the molecules on particle surface can not. They cannot leave the surface and intermix with other gas molecules. Each particle retains its identity and acts as a tiny batch reactor. We call this type of mixing *macromixing*^[10]. For particle bound species and first-order PAH (or pseudo first-order) reactions, the rate can be determined by

$$r = \frac{(A)_{in} - (A)_{out}}{\tau^*} P \quad (3)$$

where:

$(A)_{in}$ and $(A)_{out}$ are the inlet and outlet concentrations of particle bound species respectively, measured in molecules per mg of particles, and P the particle concentration in the CSTR during sampling period, measured in mg of particles per m³ of air.

τ^* is the average residence time for particles collected from the outlet flow. τ^* may not necessarily equal τ , and its value is affected by the change of inlet particle concentration and the particle loss rate in the CSTR. The experimental determination of τ^* is not difficult. The step-by-step derivation of Eq.(2) and Eq.(3) will be discussed elsewhere. However, our computer modeling has shown that both equations are correct and accurate.

Calculation of the OH-PAH Rate Constant

We have assumed that OH attack on PAH and a reference compound is a first order reaction with respect to OH and the reactants of interest. In actuality, k_1 may be a pseudo secondary order rate constant which embodies other features on the particle surface which, in turn, promote the reaction of OH with a surface PAH molecule.

According to the perfect mixing assumption, the CSTR effluent stream should have the same composition as its contents. r_{pah} is the rate of reaction of a specific PAH and r_{ref} is the rate of reaction of a the reference compound.

Thus:

$$r_{pah} = k_1 [OH] [PAH]_{out} \quad (4)$$

$$r_{ref} = k_0 [OH] [Ref]_{out} \quad (5)$$

Combining these two equations gives:

$$\frac{r_{PAH}}{r_{ref}} = \frac{k_1}{k_0} \frac{[PAH]_{out}}{[Ref]_{out}} \quad (6)$$

Note that the $[OH]$ terms were canceled out in the above equation, which means OH concentrations need not be known and need not remain constant during the experiment. The reference

rate constant, k_0 , is known from established literature values. By utilizing Eq.(3) to calculate r_1 and Eq.(1) or Eq.(2) to calculate r_0 , the OH rate constant, k_1 , can be determined. In the determination of r_1 , all reaction rates which lead to a loss of PAH must be subtracted from r_1 .

PRELIMINARY EXPERIMENTS AND FEASIBILITY TESTS

To estimate the OH rate of attack of a given PAH on a soot particle surface, we must also know the reaction rate from other processes which might result in a PAH loss. These include PAH reactions with light, O_3 , NO_2 , $HONO_2$, $HONO$, and N_2O_5 . In the OH experiment to be described we estimated that 0.05 ppm O_3 , 8.6 PPM of NO_2 , 9.0 PPM of $HONO_2$, 0.4 ppm $HONO$, 0.003 N_2O_5 formed in the CSTR. Since the data to be presented are very preliminary, we will report for illustration purposes only the rate data for benzo(a)pyrene (BaP). It is important to reemphasize that these data are very preliminary.

In characterization test of the CSTR we determined the photolysis loss constant of BaP due to CSTR lights to be $1.24 \times 10^{-4} \text{ min}^{-1}$. Base on previous work^[3], the half-life of BaP at 0.05 ppm O_3 is in excess of 10 hours and thus the loss due to O_3 was not considered important. With 23 ppm of NO_2 + wood soot in the CSTR (dark), we determined the k_{NO_2} to be $1.28 \times 10^{-20} \text{ cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1}$. Separate CSTR experiments with 4 ppm of nitric acid did not show a loss of BaP. This is consistent with the work reported by Lindskog et al.^[12] and Pitts et al.^[7]. BaP on wood soot particles passively exposed to 0.1 ppm $HONO$ did also not result in any BaP loss^[12].

When $4.28 \times 10^{-4} \text{ [mg cm}^{-3}]$ wood soot particles, 10 ppm of NO and 24 ppm of CH_3NO_2 were fed into the CSTR with the lights on, a 33% reduction in BaP resulted in the CSTR. The CSTR temperature was 296 K and the residence time in the CSTR was 1296 seconds (21.6 minutes). The inlet BaP was $1.06 \times 10^{15} \text{ [molecules mg}^{-1}]$ and the outlet was 7.07×10^{14} . This give a BaP concentration in the CSTR of $3.03 \times 10^{11} \text{ [molecules cm}^{-3}]$. Ethylene was used as a reference with a rate constant of $8.5 \times 10^{-12} \text{ [cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}]$.

The calculated gross reaction rate for BaP using Eq.(3) was 1.67×10^8 . Parenthetically, it is useful to add, that when just ethylene and propylene were separately run in the CSTR with CH_3ONO , the OH rate constant of propylene was 3.08 times greater than that of ethylene. This is very good agreement with literature OH rate constants for these two compounds.

In the calculation of rate constant for BaP above losses due to photolysis, NO_2 were not excluded. The OH rate may be calculated however as follows:

$$\begin{aligned} \text{OH rate} &= \text{Overall rate} - \text{Photolysis rate} - \text{NO}_2 \text{ rate} \\ &= \text{Overall rate} - k_{\text{photo}} [\text{BaP}] - k_{\text{NO}_2} [\text{NO}_2] [\text{BaP}] \\ &= 1.67 \times 10^8 - 1.24 \times 10^{-4} \times 3.03 \times 10^{11} \\ &\quad - 1.28 \times 10^{-19} \times 7.38 \times 10^{13} \times 3.03 \times 10^{11} \end{aligned}$$

$$= 1.67 \times 10^8 - 3.75 \times 10^7 - 2.86 \times 10^6$$

$$= 1.27 \times 10^8 \text{ [molecules cm}^{-3} \text{ sec}^{-1}\text{]}$$

It can be seen that OH rate takes 63% of the overall rate. This value can be translated to an OH rate constant of $k = 7.8 \times 10^{-11} \text{ [cm}^3 \text{ molecule}^{-1} \text{ second}^{-1}\text{]}$. At an assumed atmospheric OH radical concentration of $1 \times 10^6 \text{ molecules per cm}^3$ [1], the atmospheric half-life for BaP due to reaction with OH radicals is 146 minutes. Daytime wood soot PAH experiments in our outdoor chambers (solar radiation = $1 \text{ cal/cm}^2/\text{sec}$, $\text{NO}_x = 0.06 \text{ ppm}$), typically exhibit (under midday sunlight and moderate humidities and temperatures) PAH half-lives at 293 K which range from 35-50 minutes [4,5]. It is reasonable to assume that OH concentrations from photochemical smog processes are higher than $1 \times 10^6 \text{ [molecules/cm}^3\text{]}$ in these outdoor runs. If this is the case, then a significant portion of the previously observed photo-induced decay may be attributed to OH attack. We have observed in trying to characterize the photo-induced PAH loss on soot particles in our large chambers that this process is influenced by the intensity of sunlight, humidity, particle loading, and temperature. Future work will address these factors with respect to OH-PAH reactions.

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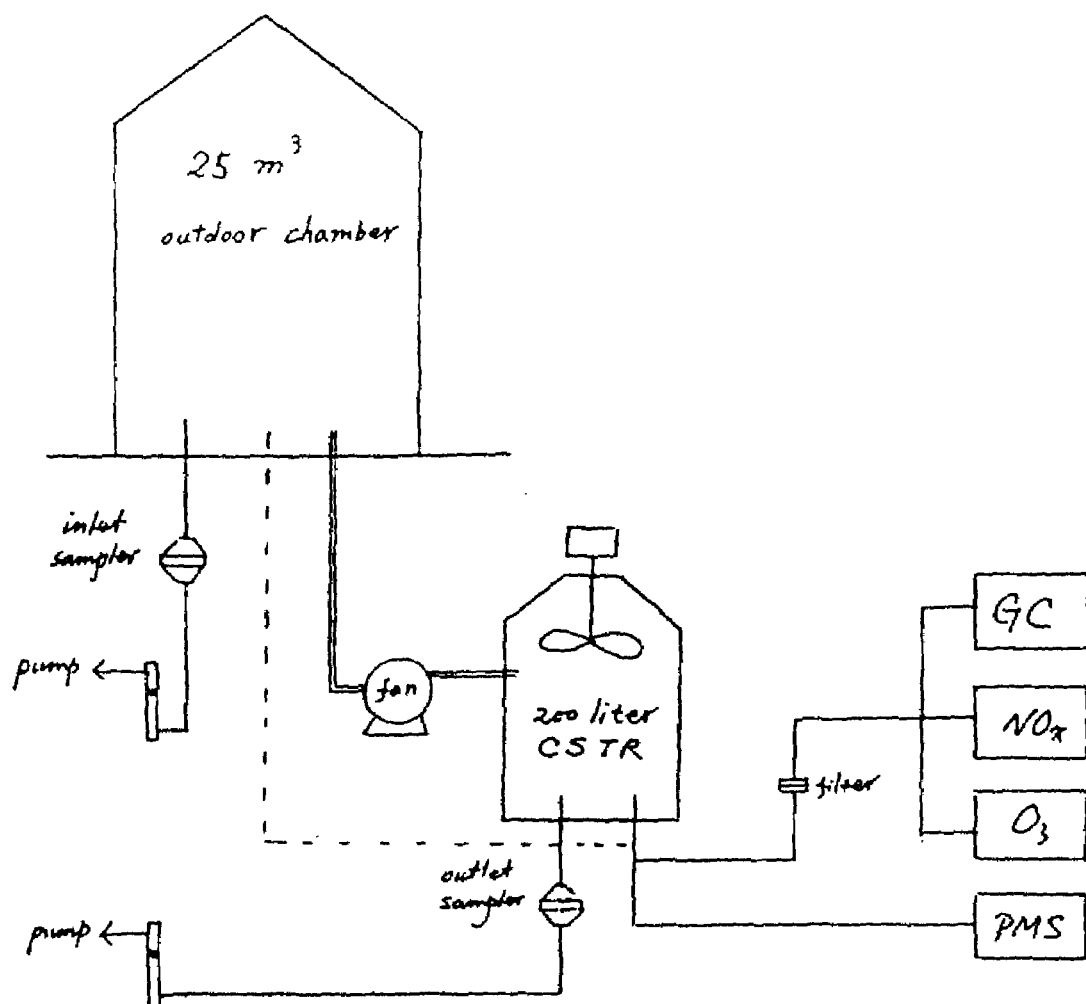


Figure 1. The Experimental System Used in Pilot Study

CHARACTERIZATION OF ORGANIC SPECIES ON JET ENGINE EXHAUST PARTICLES

by

Michael R. Kuhlman, Jane C. Chuang, and Surendra B. Joshi*

BATTELLE
Columbus Division
505 King Avenue
Columbus, Ohio 43201-2693

Introduction

The aerosol particles emitted by jet engines operated by the U.S. Air Force are predominantly of submicron diameter and composed of unburned carbon. Components of this aerosol which are very minor, on a mass basis, may, however, assume great importance in the occupational and ambient environment. Trace elements, especially heavy metals, which may be present at very low concentrations in the jet fuel will be concentrated in the small particle fraction of the emitted aerosol due to the very low volatility of these materials. Reactive hydrocarbons, such as polycyclic aromatic hydrocarbons (PAH) and nitro-PAH may also be present in condensed form on the particles emitted due to the low vapor pressures of these compounds. The very small size of the emitted particles permits them a relatively long residence time in the atmosphere and enables them to be deposited in the innermost portions of the respiratory tract.

The objective of the current study being performed by Battelle for the U.S. Air Force is the characterization of the chemicals found on engine exhaust particles and assessment of their environmental significance. This type of measurement of these particle emissions from military jet engines has not been previously reported.

In this study, the gaseous and particulate-bound organic species in the exhaust from three different jet engines operated at several power settings were analyzed. The engine exhaust was also injected into 25 m³ Teflon-walled outdoor chambers and the evolution of the resulting photochemical system was followed with periodic measurements of NO_x, O₃, and total hydrocarbon concentrations. During the multi-hour photochemical experiments, samples of the chamber contents were collected for subsequent analysis of gaseous and particle-bound organics using gas chromatography-mass spectrometry (GC/MS). In a companion study, the engine emissions were characterized at various power settings for a more detailed

*Affiliated with Tyndall AFB, Florida.

analysis of the hydrocarbon species present, especially for the lower molecular weight compounds.

Experimental Method

Three Teflon-walled chambers were used in these experiments. Two of the chambers were used to age engine exhaust under different conditions, and the third chamber was used as a control, containing either ambient air or ambient air plus a mixture of reactive hydrocarbon gases and NO_x , but no jet engine exhaust. The chambers were cylindrical in cross section with a conical top, and the interior surfaces were Teflon or aluminum to minimize surface reactivity. The chambers had a diameter of 3 m and a height of the peak of 4 m, which provided a volume of approximately 30 m^3 . Each chamber was equipped with a low rpm impeller for mixing, with heated injection and sampling lines, and with a blower and air inlet for purging.

Prior to use in the engine exhaust study, the chambers were "conditioned" by injection by high concentrations of O_3 repeatedly. Chamber characterization experiments subsequently performed included measurements of leakage rates and O_3 decay under dark and light conditions, examination of chamber background reactivity by performance of ambient air photochemical runs and matched runs of reactive HC- NO_x systems.

The matrix of experiments performed which involved injection of jet engine exhaust into the chambers included three engines operated at a total of three different power settings of interest. A total of six engine exhaust tests was run, with 12 chamber conditions. The following factors were examined in the aging experiments: the influence of photochemical reactions in the light versus dark chamber experiments, the effect of engine power setting, and the differences between the engine types.

For each experiment the chambers were purged overnight with charcoal scrubbed, filtered, shop air which was turned off prior to 0600. Chamber background measurements and SF_6 injections were performed during the time from 0600 until the chambers were moved to the engine test cell to be charged with engine exhaust. During the period that the exhaust-containing chambers were not being sampled, the control chamber was injected with either ambient air or a reactive hydrocarbon/ NO_x mixture and monitored exclusively until the exhaust containing chambers were repositioned for the aging experiment.

For characterization of the organic compounds in the engine exhaust, samples of the engine exhaust were collected on quartz fiber filters and XAD-2 sorbent

traps. For these samples the sampling line was heated to 50 C from the sample probe to beyond the exit from the test cell. The exhaust gas sample was then permitted to cool by contact with the walls of a stainless mixing chamber and drawn through the filter and sorbent trap at a measured flow rate and temperature. In this manner the aerosol sample was obtained at nearly ambient temperature.

Samples of the chambers contents were collected for later analysis at several times during the aging experiments. These samples were obtained by withdrawing approximately 1 m³ of the chamber air through a quartz fiber filter and XAD-2 sorbent trap. At the end of each aging experiment, a 5 m³ sample was withdrawn in the same manner. Selected XAD traps were spiked immediately after sampling to assess the losses of PAH due to sample handling. The XAD traps were sealed and enclosed in aluminum foil after sample collection to protect the collected sample from light, and the traps and filters were maintained below 0 C on site until they were shipped to the laboratory for extraction and analysis.

The chambers were monitored at 20-minute intervals for NO, NO_x, O₃, THC, and SF₆ concentrations. The temperature and relative humidity of the air in each chamber was monitored as well. To monitor these parameters, the air was drawn through a switching valve which permitted air to be withdrawn from any of the three chambers or from an ambient air intake located above the mobile analytical laboratory. The sampling lines were either Teflon or glass and were maintained above ambient temperature to prevent condensation within the sampling lines. Each chamber was sampled for a 5-minute interval, and the measurements made during last 3 minutes were averaged by the data collection/system control software. Table 1 lists the instruments which were monitored by the Apple IIe-based data collection system.

TABLE 1. INSTRUMENTATION USED FOR CHAMBER ATMOSPHERE MONITORING

Parameter	Instrument
Total hydrocarbons	Beckman 402
Ozone	Bendix Model 8002
Solar intensity	Eppley UV radiometer
Oxides of nitrogen	Monitor Labs Model 8440
Temperature/humidity	EG&G Model 911
Chamber temperature	Type K thermocouples

Analysis of Samples for PAH and nitro-PAH

Certain filter and XAD-2 samples from the chambers and engine exhaust were extracted separately with methylene chloride by Soxhlet technique. The remaining filters were extracted together with their corresponding XAD-2 sample to maximize the mass in the extract. Prior to extraction, a standard solution of perdeuterated PAH was spiked onto selected filters and XAD-2 to determine PAH losses attributable to sample preparation. The extracts were then concentrated by Kuderna-Danish (K-D) evaporation. Aliquots of the concentrated extracts were removed to determine the total extractable organic mass. Selected extracts were fractionated using open bed silica gel column chromatography. This procedure has been successfully used to separate the extracts from diesel exhaust particles and ambient air particles into four compound classes including aliphatic, aromatic, moderately polar, and highly polar compounds. Three of the fractions (aromatic, moderately polar, and highly polar) were analyzed by gas chromatography/mass spectrometry (GC/MS) in the full scan mode. The preliminary information obtained from the GC/MS analyses includes the estimated extraction efficiency, the extractable organic mass of the jet engine particles, the PAH distribution between filter and XAD samples, and the classes of compounds present in the filter and XAD-2 samples.

The analyses were conducted on a Finnigan 4500 quadrupole mass spectrometer (MS) equipped with a gas chromatograph (GC) and an INCOS 2300 data system. A fused-silica capillary GC column and on-column injection (45 C) with negative chemical ionization at 150 eV were used for determination of NO_2 -PAH. The conventional splitless injection (300 C) with electron impact mode at 70 eV was used for PAH analysis. The multiple ion detection mode was employed in both EI and NCI analyses.

Results and Discussion

The results presented here are preliminary and include only a portion of the experiments performed and have been selected to indicate the range of results obtained and analyzed up to this time. The results indicate the nature of the influences of engine operating power, engine type, and photochemical activity on the PAH and nitro-PAH determined in the initial and final filter samples collected in several of the experiments.

The XAD-2 samples of engine exhaust contained much higher masses of extractable organic matter than did the corresponding filter samples. Full scan GC/MS analyses of the XAD-2 samples showed the major components to be aliphatic

hydrocarbons, while alkyl benzenes, 2- to 4-ring PAH, and oxygenated PAH were also present. Similar classes of compounds were detected in the filter samples, although the more polar compounds dominated the mass found in these extracts.

Table 2 presents the concentrations of the PAH and nitro-PAH found in the filter samples collected at the start and at the end of the experiment in which exhaust from a J-79C (smokeless) engine was aged in the chamber exposed to sunlight. These values are expressed as concentration of each compound associated with the suspended particulate matter in the chamber. The initial values in the chambers represent the engine exhaust diluted by approximately a factor of five. It is readily seen that these concentrations are quite low and that the decay of these compounds during the experiment reduces their concentration by one to two orders of magnitude, in general.

This table also presents the PAH and nitro-PAH concentrations measured at the start and end of the "light" aging experiment for the TF33-3 engine operated at idle power. The idle operating power produces the most hydrocarbon laden exhaust of the power settings examined in this study and the TF 33-3 was seen to emit higher hydrocarbon concentrations than the other engines studied. Comparison of the "initial" concentrations seen here with those in Table 2 permits a relative comparison of the TF33-3 and J-79 engines to be made. The very extensive decay of the PAH compounds seen above is repeated here.

A final set of results is presented in the table for the TF33-3 engine operation at 30 percent power. There is an obvious reduction in the exhaust concentrations of these compounds. There also appears to be a significant lessening of the extent of decay of these compounds relative to those seen elsewhere in the table. The explanation for this result requires further analysis of the gas concentrations measured in the chambers in these experiments. Summary values such as these may mask the actual dynamics of the formation and decay of the individual compounds. Only by making comparisons across experiments and with intermediate values of compound concentrations can one deduce the processes leading to the changes observed in tables such as these.

Conclusions

The analysis of samples obtained and the interpretation of the experimental results of these experiments are currently under way. The results assessed to date permit us to conclude that the concentration of PAH and nitro-PAH associated with particulate phase of the engine are quite low, due, no doubt, to the very large volumes of air processed through these engines. There is an apparent increase in the decay rate of the PAH for the chambers exposed to sunlight,

relative to those kept darkened, and obvious evidence of the formation of various nitro-PAH during the experiments. Differences in the results for the different engines and power settings have been noted at this time and will be better defined as the analysis proceeds.

Acknowledgments

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TABLE 2. INITIAL AND FINAL CONCENTRATIONS (ng/m³) OF COMPOUNDS IN AEROSOL SAMPLE FROM CHAMBER CHARGED WITH EXHAUST FROM J79 AT IDLE, TF33-3 ENGINE AT IDLE AND 30 PERCENT POWER

Compound	J79 (Idle)			TF33-3 (Idle)			TF33-3 (30%)		
	Initial	Final	Ratio	Initial	Final	Ratio	Initial	Final	Ratio
<u>Polynuclear Aromatic Hydrocarbons</u>									
Naphthalene	8.41	0.68	0.081	12.90	1.25	0.104	3.5	0.3	0.09
Dibenzothiophene	32.15	0.54	0.017	82.10	0.45	0.005	11	1.0	0.09
Phenanthrene	153.3	3.49	0.023	757.0	6.45	0.0085	304	15	0.05
Anthracene	11.62	0.56	0.048	101.0	0.41	0.0041	24	2.3	0.10
Fluoranthene	119.0	1.74	0.015	294.0	1.83	0.0062	217	4.8	0.02
Pyrene	138.5	0.98	0.007	410.0	0.97	0.0024	280	2.5	0.01
Benz[a]anthracene	3.96	0.98	0	47.30	<0.22	0.0047	14	<.3	<.02
Chrysene	9.89	0.21	0.021	25.60	0.37	0.014	22	0.7	.03
Cyclopenta[c,d]pyrene	0.25	ND	0	41.00	--	0	47	ND	--
Benzo[fluoranthenes	4.70	ND	0	94.70	0.22	0.0023	22	ND	--
Benzo[e]pyrene	2.08	ND	0	34.70	0.26	0.0075	9.4	ND	--
Benzo[a]pyrene	1.14	ND	0	37.90	0.22	0.0058	8.4	ND	--
Indeno[1,2,3-c,d]pyrene	2.05	ND	0	56.80	<0.22	0.0039	4.7	ND	--
Benzo[g,h,i]perylene	5.19	ND	0	78.90	<0.22	0.0028	10	ND	--
Dibenzo[a,h]anthracene	ND	ND	0	1.86	ND	0	<.2	ND	--
<u>Nitrated Polynuclear Hydrocarbons</u>									
2-Nitro-1-naphthol	37.1	0.87	0.023	133.0	0.77	0.006	14	1.3	0.09
4-Hydroxy-3-nitrobiphenyl	1.86	0.31	0.17	5.37	0.12	0.022	2.8	0.25	0.09
1-Nitronaphthalene	2.10	0.059	0.028	2.05	0.17	0.083	2.3	0.38	0.17
Nitronaphthalene isomer	1.24	0.049	0.040	0.31	0.045	0.15	0.35	0.16	0.46
9-Nitroanthracene	0.57	0.071	0.12	0.57	0.016	0.028	3.0	0.26	0.09
9-Nitrophenanthrene	0.30	0.024	0.08	0.15	0.37	2.5	0.49	0.09	0.18
Nitroanthracene/phenanthrene isomer	0.27	0.021	0.078	0.27	0.011	0.041	0.33	0.04	0.12
3-Nitrofluoranthene	0.13	0.012	0.092	0.30	0.0071	0.024	0.54	0.57	1.06
1-Nitropyrene	0.69	0.0033	0.0048	0.15	0.0049	0.033	0.18	0.02	0.11
6-Nitrochrysene	0.07	ND	0	ND	ND	--	ND	ND	--
Di-Nitropyrene isomer	ND	ND	--	ND	ND	--	ND	ND	--

ND = Not detected.

Prediction of Photochemically Produced Formaldehyde With Chemical Mechanisms Developed for Urban Ozone Systems

Kenneth G. Sexton

Dept. of Environmental Sciences and Engineering
School of Public Health, University of North Carolina
Chapel Hill, NC 27514

Abstract

Chemical mechanisms developed for use in Air Quality Simulation Models for photochemically produced ozone may be used as a method to estimate formaldehyde yields from the hydrocarbon and nitrogen oxides precursors. Two chemical mechanisms are compared in their ability to simulate smog chamber experiments conducted at the University of North Carolina where formaldehyde was measured as a photochemical product. A wide range of experimental conditions are used including simulated automobile exhaust, simulated urban-like mixtures, and specific hydrocarbons which are predominant in the atmosphere.

Introduction

Chemical mechanism models have been developed for simulation of photochemistry leading to the formation of ozone in the troposphere. Formaldehyde is an important compound in this chemical system (1). Although successful simulation of the ozone chemistry requires including the chemistry of formaldehyde, the mechanisms primary development goal has been the prediction of ozone. There is concern that these chemical mechanisms developed for ozone, may be used to estimate formaldehyde concentrations in the atmosphere. The chemical mechanisms have not been evaluated as thoroughly for formaldehyde as they have been for ozone.

There is reasonable concern that the simulation and prediction of formaldehyde may be less successful than simulation of ozone. This arises from several problems.

Formaldehyde is formed as a product from the oxidation of hydrocarbons in the atmosphere. The amount depends on the type of hydrocarbon and the type of reaction. Often many chemical intermediates and reactions are involved. Formaldehyde also photolyzes to yield radicals and carbon monoxide. Many details of these processes are still uncertain or unknown. The experimental database of formaldehyde measurements in either the atmosphere or smog chambers is much less developed and certain than for ozone and its primary chemical precursors. The successful simulation of formaldehyde has been only a secondary goal in the development of these types of chemical models, mainly to assure the prediction of ozone. Because of limited resources imposed on mechanism developers, development of a chemical mechanism often stops when reasonable successful prediction of ozone is achieved.

The goal of this study was to perform a limited modeling program to determine how successful two mechanisms developed for ozone in the urban atmosphere are in simulation and prediction of formaldehyde.

Chemical Mechanisms, Test Conditions and Methods

Two recent chemical mechanisms were used to illustrate the ability to simulate formaldehyde in two types of photochemical systems: UNC Outdoor Dual Smog Chamber experiments and an "EKMA-type" urban scenario with continuous emissions and meteorological dilution. The new ERT, Inc. chemical mechanism developed by Carter, Atkinson, Lurmann and Lloyd (CALL) (2) and the recently distributed SAI Carbon Bond IV chemical mechanism developed by Whitten and Gery (CB4) (3) were used.

The code for the computer-based model PC-PKSS, used to implement the chemical mechanisms and simulate the different photochemical systems was written by Harvey Jeffries (4). It is capable of not only simulating outdoor smog chamber-type experiments with varying temperature and photolytic rates, but also EKMA-type simulations with continuous emissions and meteorological dilution (5). It reproduces EKMA-type simulations performed by the OZIPM3 (6). The photolytic rates used are discussed in (7).

The UNC Outdoor Dual Smog Chamber has been used to study the photochemistry responsible for ozone formation in urban systems since 1974 (8,21). Experimental data including the measurements of chemical precursors and products, and physical parameters throughout the experiment have been obtained for a wide range of conditions of interest to chemical model developers. Over 300 dual-smog chamber experiments have been processed and distributed (16,19). The description of the chamber and the analytical methods are in several reports. The formaldehyde monitor is an automated reversed West-Gaeke method sold by CEA Instruments. At its normal operating range (0 to 1 ppm) it has a minimal detection sensitivity of ~20 ppb. Preliminary results show that it compared reasonably well with other formaldehyde methods in this range in a Intercomparison study conducted in 1986 (22).

Several experiments from the UNC Smog Chamber set were selected which study the reactivity of individual important hydrocarbons in the atmosphere. These are also either explicitly represented in the chemical model or are the representative compound used in the model to represent a class of compounds. Experiments conducted with hydrocarbon mixtures developed to be equivalent to autoexhaust in reactivity, or structured from ambient measurements were also selected.

In modeling smog chamber experiments, assumptions need to be made concerning the effect of the chamber on photolytic rates and type and magnitude of background chamber reactivity. Discussions of these concerns are in several reports (16,18,21).

The chamber teflon material attenuates solar radiation which is a function of wavelength; and the reflective chamber floor also must be considered. The area around the chamber also needs to be considered. Spectral irradiance measurements made inside the chamber have been used to derive a preliminary set of photolytic rates for the UNC chamber. These are shown in Table 1. Research in this area is continuing. Background chamber reactivity has been studied (1,23,24) and is also continuing. The surface to volume ratio is lower than most smog chambers because of the large size. Each side of the dual chamber has a volume of 150,000 liters. Background reactivity assumed by most modelers is much less than assumed for other chambers. Normal assumptions include 0 to 50 ppb of formaldehyde (25 ppb average) and 0 to 25 ppb of NO₂ source material (10 average) on the walls which off-gas as a function of light intensity. Also initial HONO levels of 0 to 3 ppb are normally used: with a maximum of 5 ppb used for experiments performed after a long series of very reactive experiments have been conducted. The protocol followed in modeling a set of experiments is to maintain reasonable consistency in chamber assumptions through the entire set, using the same assumptions for both sides of the dual chamber pair of experiments performed on a given day. The benefit of the dual-nature of the smog chamber is that the instruments are time-shared and both chamber sides are prepared (vented and dehumidified) the same. Both sides are subject to the same light and temperature; chamber assumptions should be similar. Even if there is a question of calibration of an analytical method, at least the relative differences in measured chemical reactivity should be simulated by a chemical mechanism model.

Results - Smog Chamber Comparisons

Formaldehyde is explicitly represented in both chemical mechanisms. Four formaldehyde/NO_x experiments were simulated. The dual experiment performed on July 8, 1986 is a matched initial NO_x (~0.17 ppm) and different initial formaldehyde: 1.02 vs 0.54 ppmC. This type of experiment illustrates the benefit of the dual-nature of the chamber design in that two levels of reactivity (HC/NO_x), with the same chamber physical conditions and assumptions are provided for testing. The time-concentration profile results are shown in Figure 1. The ozone maximum is better simulated on the 1.02 ppmC side but the formaldehyde is better simulated on the lower 0.54 ppmC side. This experiment was part of the formaldehyde intercomparison study. The other two experiments July 18, 1977 and August 12, 1980 were also simulated reasonably well. These results are not shown for space considerations.

Ethylene is an dominant hydrocarbon in the atmosphere and is explicitly represented in each mechanism. Propylene is also important in the atmosphere. It is the surrogate in the CALL mechanism for terminal olefins and is the basis for the CB4 olefin chemistry. Four ethylene and two propylene experiments conducted in three dual-chamber experiment combinations were modeled: low HC/NO_x ethylene vs propylene on July 13, 1986, low vs high HC/NO_x ethylene on July 9, 1986, and high HC/NO_x ethylene vs propylene on October 4, 1984. These cover a range of reactivity. The two 1986 experiments were also part of the

formaldehyde intercomparison study (22) and the formaldehyde measurements compared well. A consistent set of chamber background assumptions were used.

In general, the success of simulating these experiments was a function of HC/NOx, especially for ethylene. The ozone maxima were simulated fairly well in general but both mechanisms were late in predicting ozone especially in the lower HC/NOx runs. Both mechanisms underpredicted ozone for the lowest HC/NOx ethylene experiment: one side of the July 9, 1986 experiment. The CALL mechanism overpredicts ozone for the high HC/NOx ethylene runs. For both mechanisms for all experiments the hydrocarbon predictions were good to excellent. Formaldehyde predictions were best for the high HC/NOx experiments for both mechanisms although both mechanisms underpredicted (15 to 25% CB4 and 20 to 30% CALL). See Figure 2. For the lower HC/NOx experiments both mechanisms underpredicted about 45% (see Figure 3). That is, neither mechanism simulated the relative change in formaldehyde produced in the delta HC/NOx ethylene experiments of July 9, 1986. It should be pointed out that the model simulations of the formaldehyde concentration profiles of the July 8, 1986 experiment shown in Figure 1 were much more successful. The formaldehyde monitor was checked for span calibration at least twice a day. It was very stable during the entire intercomparison study.

Toluene and m-xylene are the basis for these two classes of aromatics for both mechanisms. A dual experiment conducted June 27, 1984 compares matched initial NOx conditions with 2 ppmC m-xylene on one side and 5 ppmC Toluene on the other. Both mechanisms simulate the m-xylene NOx, O3 and xylene concentration-time profiles very well, with the CALL mechanism just a little slower in reactivity passed the midpoint of the experiment. Both mechanisms overpredict ozone on the toluene side (~25% CB4, ~33% CALL), but the CB4 mechanism reproduces the proper shape. While the CB4 mechanism simulates the toluene profile, the CALL mechanism does not oxidize enough. The CALL mechanism predicts the measure amount of formaldehyde on the toluene side and overpredicts about 40% on the xylene side. The CB4 mechanism overpredicts by a factor of 2 for both systems. The differences between the chemical mechanism predictions is from the different representations of the still uncertain aromatics chemistry. The CB4 mechanism is still under development with a new release projected for September 1987. Changes to the toluene chemistry representation are currently being made (25).

Four hydrocarbon mixtures were used for testing. Mixtures are good for testing a chemical mechanisms ability to respond correctly to composition variation. On August 31, 1981, two matched initial NOx and hydrocarbon concentration conditions with two different compositions were compared. These are two olefin/paraffin compositions of different complexity. These mixtures contain no aromatics. Two experiments with two mixtures designed to be reasonable approximations of autoexhaust

(SYNAUTO) and an urban atmosphere (SYNURBAN) were also modeled. The design of these mixtures are described in detail (18,20). The SYNAUTO has been shown to be reasonably equivalent to the reactivity of real autoexhaust (19).

Both mechanisms underpredict the ozone and formaldehyde maxima of the SIMMIX side by 20%. CB4 simulates the UNCMIX ozone to within 10% while the CALL mechanism underpredicts by 25%. Both mechanisms however underpredict the formaldehyde concentration by 45 to 50%. The SYNAUTO experiment of August 8, 1984 is simulated relatively well for both ozone and formaldehyde with both mechanisms with CB4 overpredicting the measured formaldehyde by ~10% and the CALL mechanism underpredicting by ~12% (see Figure 4). The SYNURBAN experiment of August 22, 1984 is overpredicted for ozone by both mechanisms with the CALL mechanism predicting ozone better although it is too reactive initially. The formaldehyde is underpredicted by 26 (CB4) to 35 (CALL) percent (see Figure 5).

Results - Urban Simulation

An "EKMA-type" urban simulation is the example 1 in the "Guidelines for OZIPM3" document (6). This example was selected for the comparison because it is published and demonstrates the ability to reproduce the photochemical simulation. This is a simple trajectory model with initial chemical precursors including formaldehyde, emissions along the trajectory path, and with meteorological "characteristic-curve" dilution. The conditions are listed in Table 3.

The original example 1 simulation utilized a default composition determined by the Carbon Bond mechanism developers. Since then a new database from 41 cities and rural sites has been used to determine new default composition for CB4 (26). The same database was used to determine a default composition by the developers of the CALL mechanism for urban simulations with the CALL mechanism (2). Speciation is different for each mechanism, and some interpretation is necessary: the developers of CALL assume 3% formaldehyde in the emissions composition and 2.2% is used for the CB4. For the entrained aloft hydrocarbon composition assumptions: 5% formaldehyde is used for CALL and 6% is used for CB4. These default compositions were used with each mechanism.

The results of these simulations with both mechanisms for five levels of control are shown in Figure 6. The agreement between mechanisms is better for ozone than for formaldehyde, although the shapes of the ozone profiles are apparent. The absolute predictions of formaldehyde are shown in Figure 7. These final concentrations for both pre-control and 100% control are in agreement with published ambient measurements (27). The relative effect of control is also shown. This is also different.

Shown in Figure 8 are the production and loss flowcharts for formaldehyde for the two mechanisms. These are computed from the integrated rates giving total mass through each of the different reactions. The reactions shown are often incomplete for space considerations. The formaldehyde yields from certain reactions such as the oxidation of principal hydrocarbons is misleading also since other intermediates produced in the same reaction go on to produce formaldehyde. The main reason for showing these flowcharts is for showing the differences in the representation of the chemistry in the two mechanisms and to compute the relative sources of formaldehyde between direct input and chemical production. Notice that the direct injection source accounts for 35 to 40 percent of the formaldehyde; only 10 to 13% are from direct emissions and entrainment of aloft formaldehyde. More than half of the formaldehyde in this particular urban system is photochemically produced during the day.

Conclusions and Recommendations

In general, these chemical mechanisms simulate O₃ better than they simulate formaldehyde. Although the simulations were good for the synthetic autoexhaust and perhaps passable for the synthetic urban mixtures, the fact that different mechanisms show different success for simulating the formaldehyde yield from different important individual hydrocarbons suggest that the general success with these mixtures is a result of fortuitous averaging. Other reasonable hydrocarbon mixture compositions not yet tested may be even less successful. These mechanisms have not been evaluated for formaldehyde as thoroughly as they have been for ozone. The formaldehyde/smog chamber database is not as good or extensive as the general ozone/smog chamber database. Research is needed to better understand the aromatics chemistry. As these new kinetic details are incorporated into the chemical mechanisms, formaldehyde predictions will become more successful over a wider range of conditions.

The atmospheric modeling examples illustrate some of the problems and issues that will arise from different modelers using different mechanisms and different input assumptions. Predictions of formaldehyde and control strategies for the atmosphere are subject to the same uncertainties of the underlying experimental database used to develop and test chemical mechanisms.

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Table 1. Photolytic Rates for UNC Smog Chamber

UNC Chamber Rates, ES=Aug, A=0.08, Rho=0.4, Tau=0.75--0.45, Sky=0.8

ZA	0	10	20	30	40	50	60	70	78	86
NO2			L1							
	0.5731	0.5661	0.5427	0.5045	0.4500	0.3788	0.2887	0.1788	0.0830	0.0153
HCHOR x 1000			L2							
	1.6522	1.6176	1.5093	1.3364	1.1043	0.8282	0.5297	0.2517	0.0916	0.0227
HCHOS x 1000			L3							
	2.1693	2.1345	2.0221	1.8398	1.5856	1.2655	0.8874	0.4835	0.2030	0.0547
Old x 1000			L4							
	1.6878	1.6243	1.4372	1.1576	0.8259	0.4979	0.2294	0.0657	0.0131	0.0016
CCHO x 1000			L5							
	0.1973	0.1917	0.1747	0.1484	0.1150	0.0786	0.0438	0.0169	0.0048	0.0009

Table 2. Conditions for Urban Simulation Example 1.

Latitude: 39.9 Longitude: 75.1 Date: 6/24/80

Mixing Heights: 250m at 0800, 1235m at 1500, Characteristic Curve

O3 aloft: 0.07 ppm, NMOC aloft: 0.04 ppmC, NMOC surface: 0.038

Initial Values: NMOC = 1.1 ppm, NOx = 0.12 ppm

Future NOx: No change

Emission Fractions of Initial Values:

Hour	8	9	10	11	12	13	14	15
	----	----	----	----	----	----	----	----
NMOC	0.17	0.17	0.17	0.10	0.02	0.02	0.02	0.02
NOx	0.35	0.35	0.35	0.19	0.03	0.03	0.03	0.07

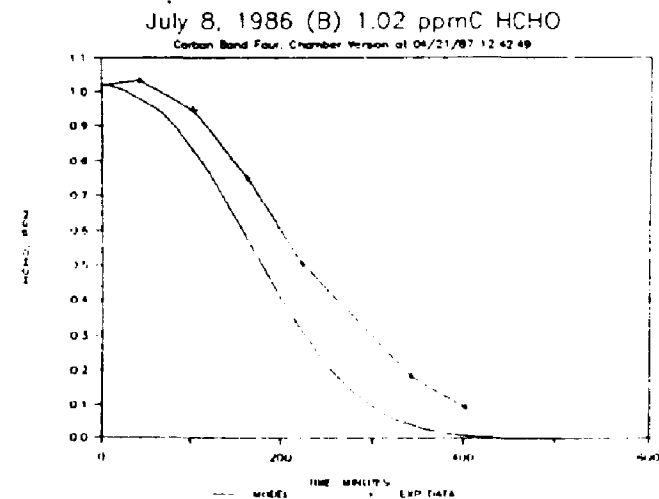
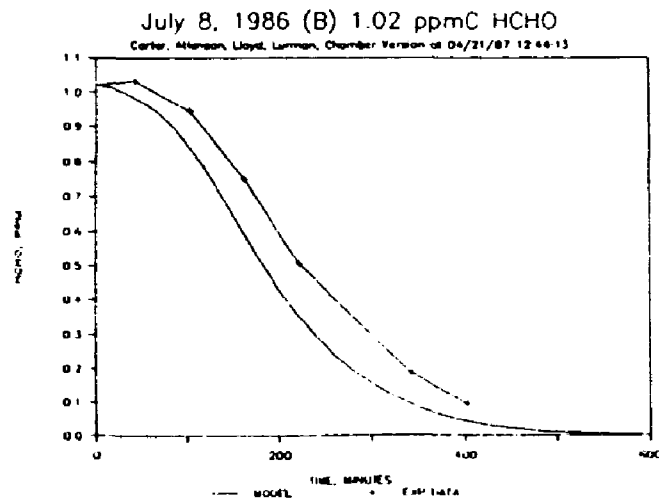
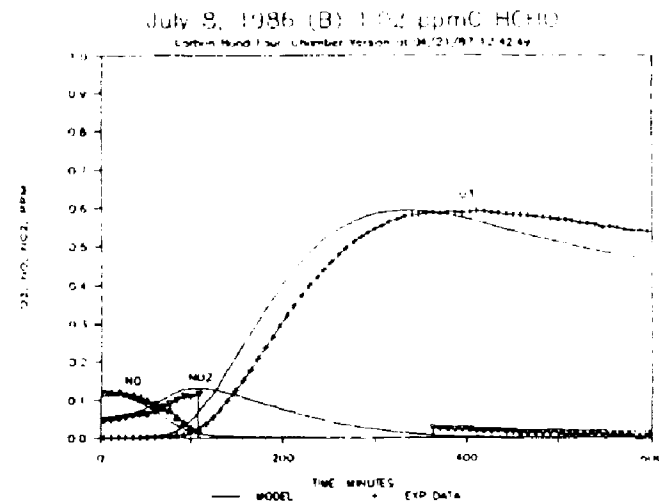
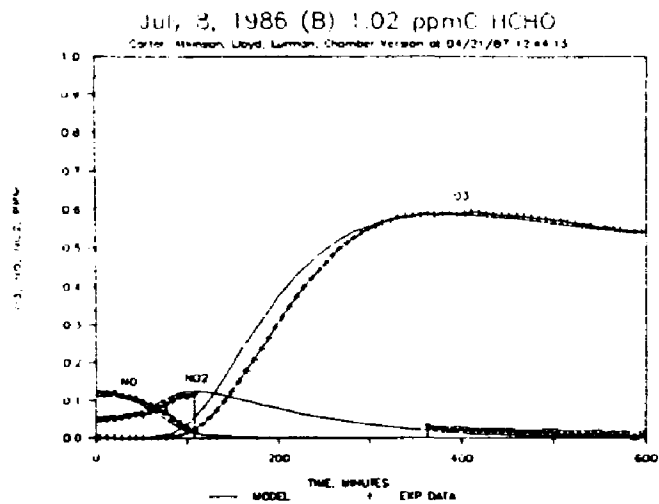


Figure 1a. Simulations of July 8, 1986 1.02 ppmC HCHO.

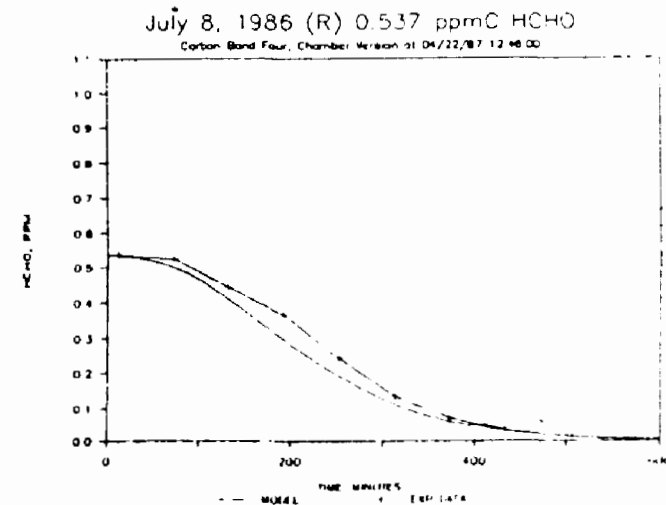
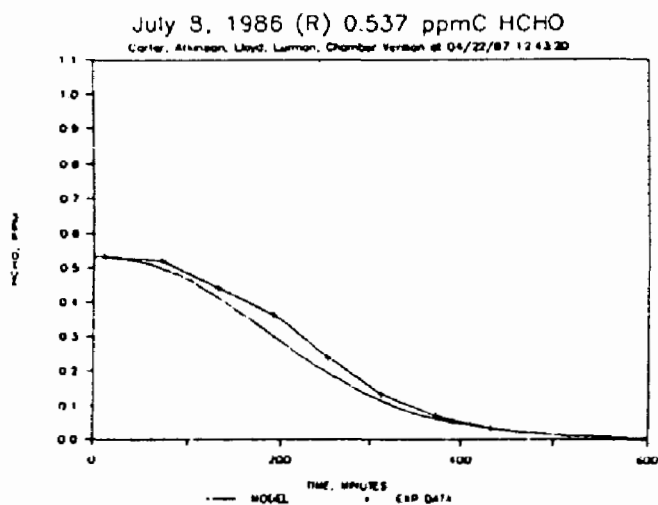
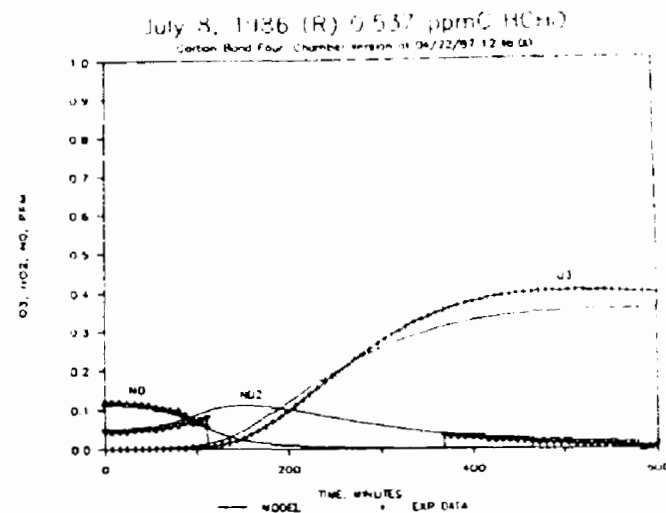
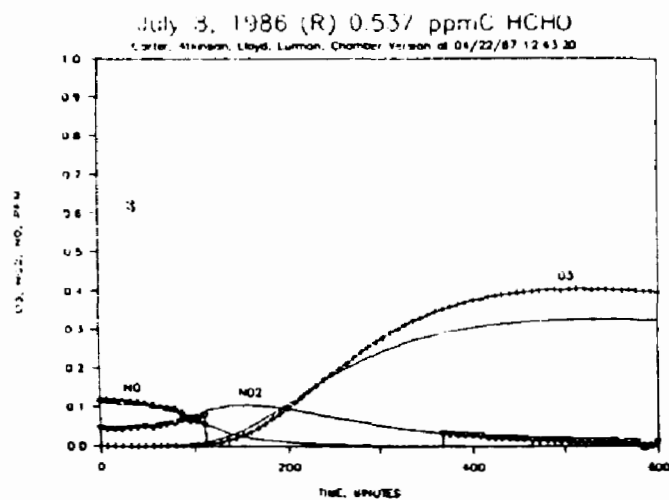


Figure 1b. Simulations of July 8, 1986 0.54 ppmC HCHO.

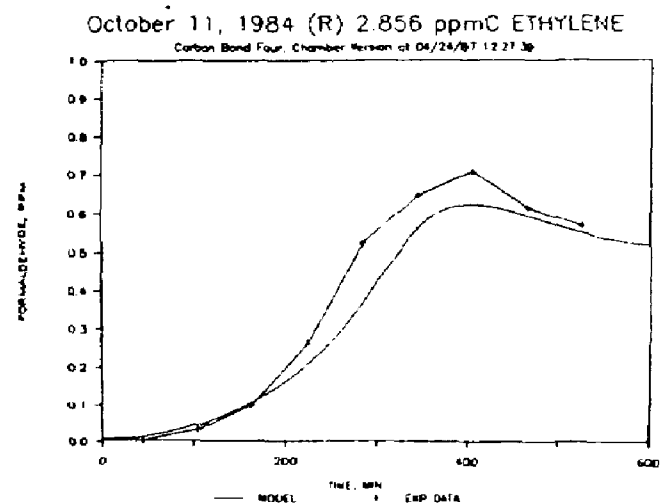
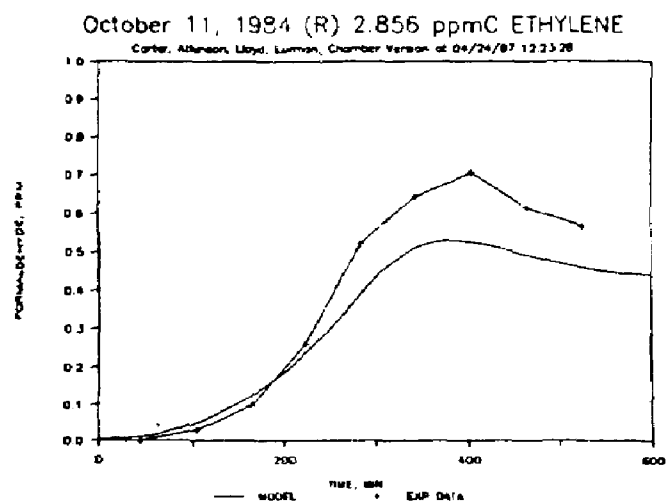
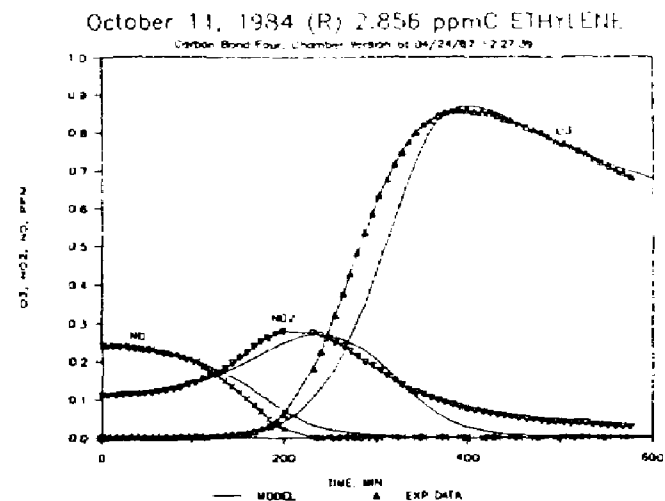
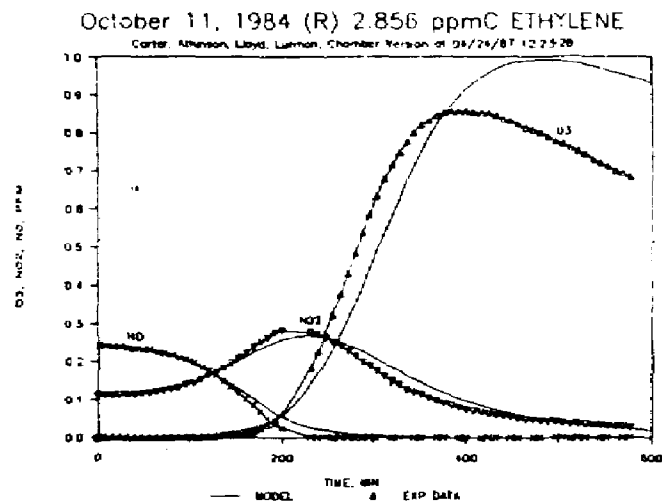


Figure 2. Simulations of October 11, 1986 (High Ethylene).

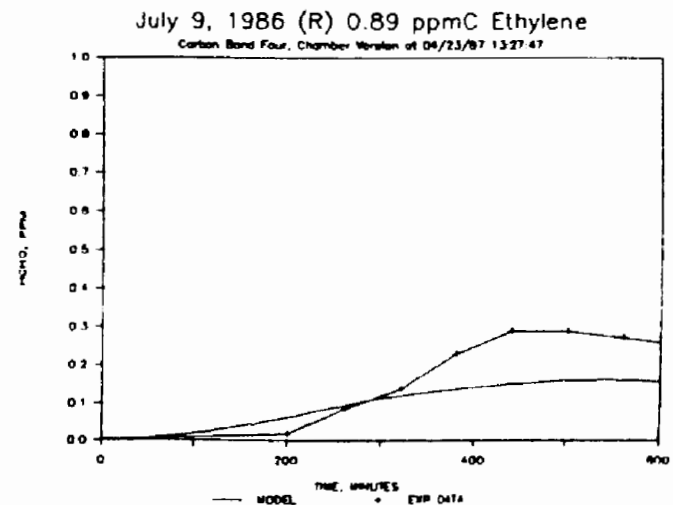
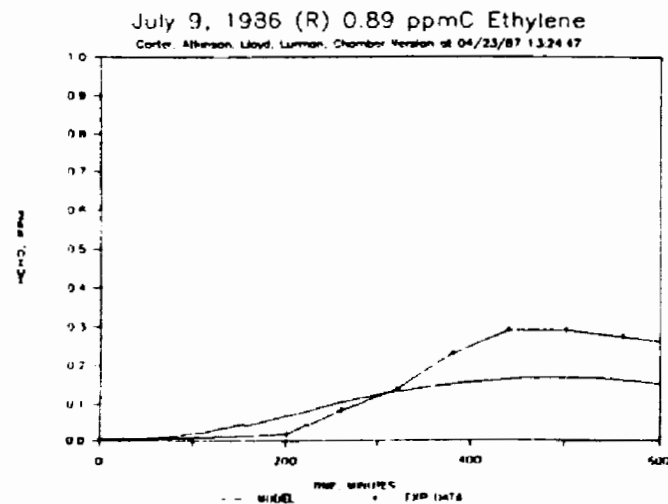
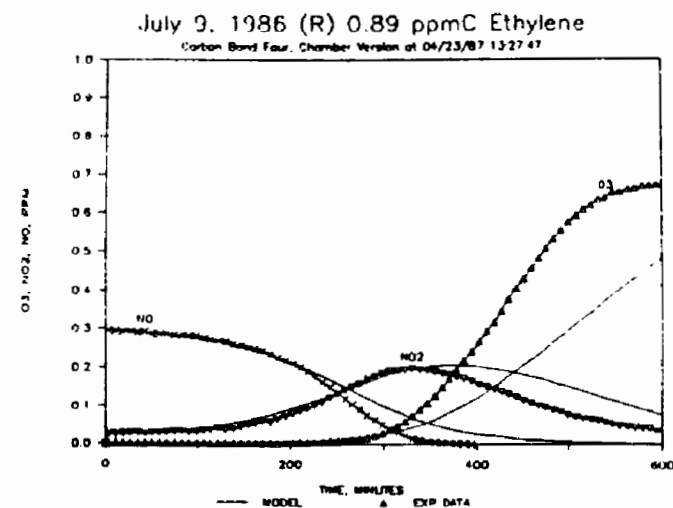
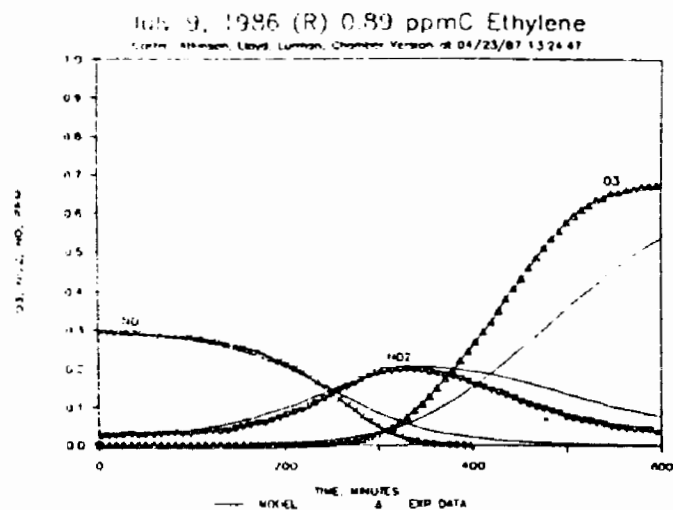


Figure 3. Simulations of July 9, 1986 (Low Ethylene)

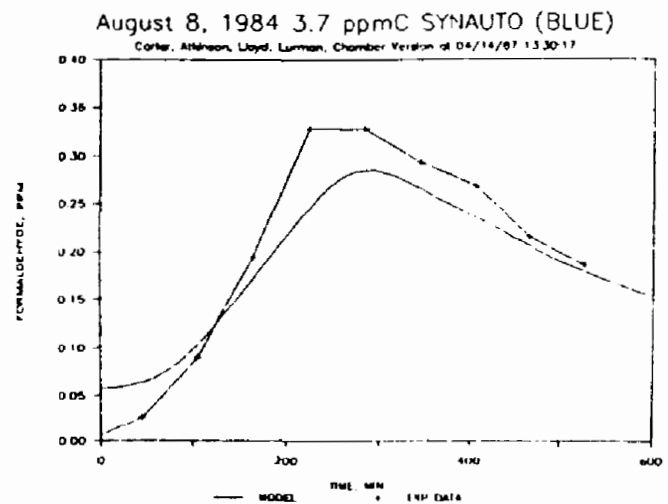
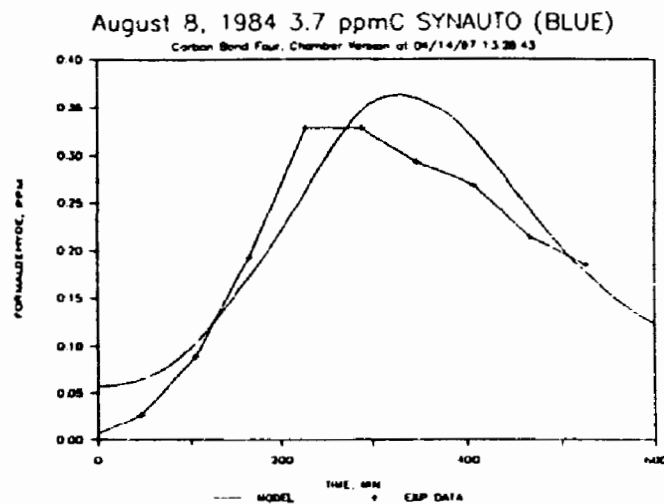
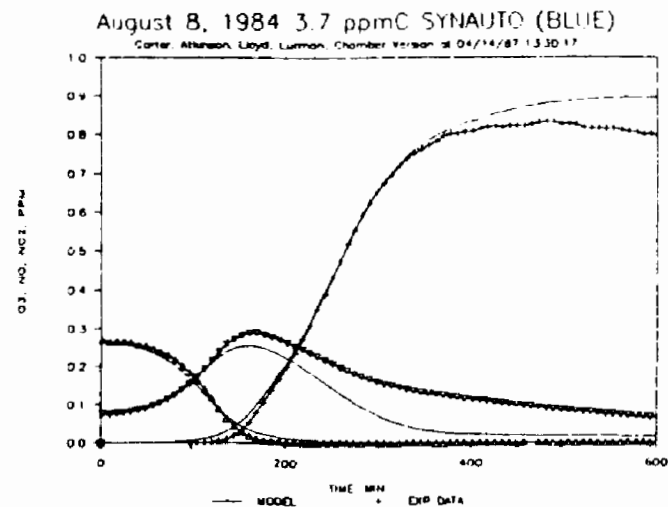
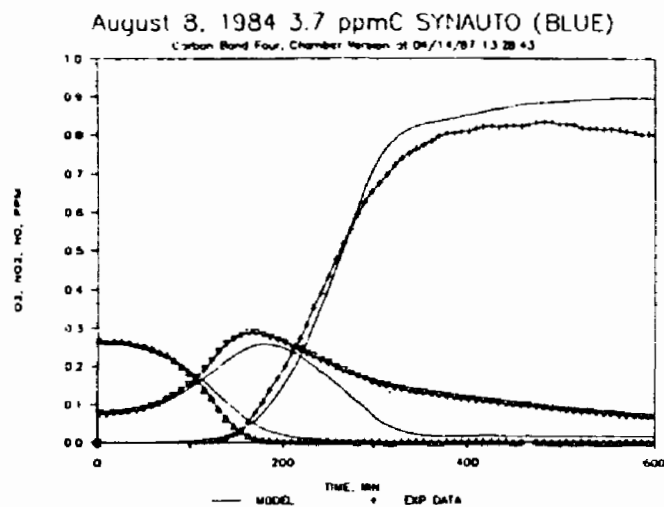


Figure 4. Simulations of Synthetic Autoexhaust.

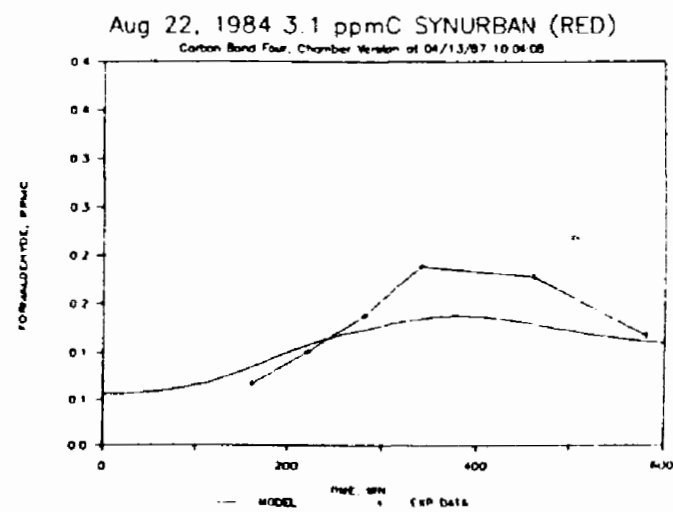
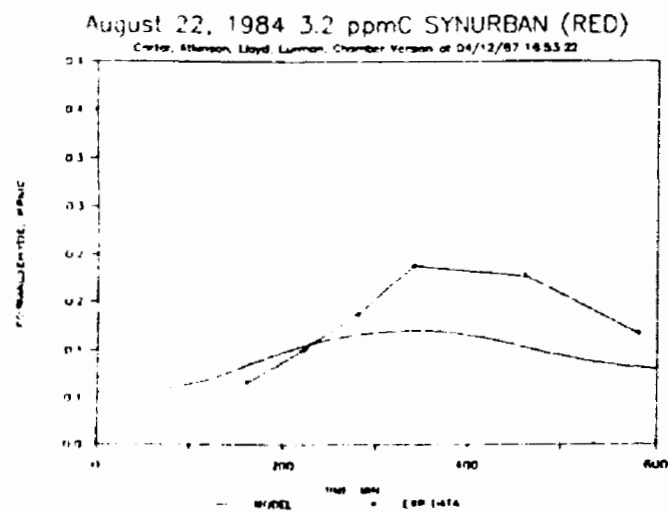
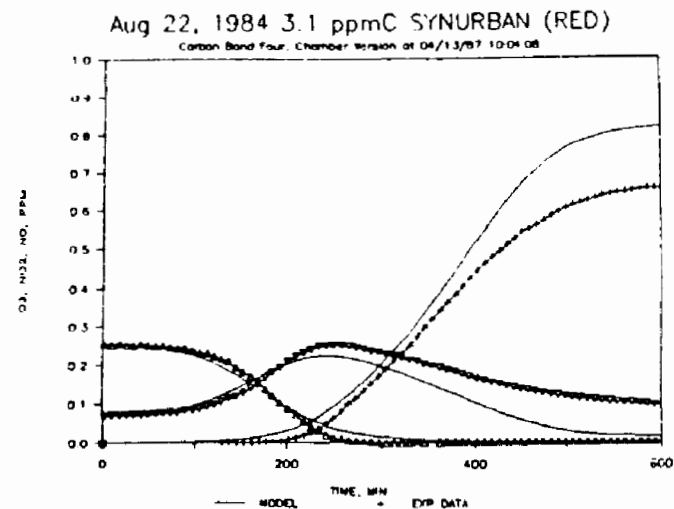
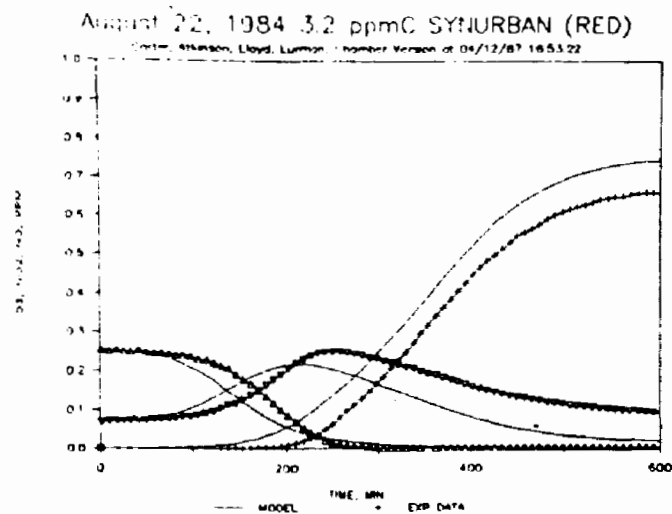


Figure 5. Simulations of Synthetic Urban Atmosphere.

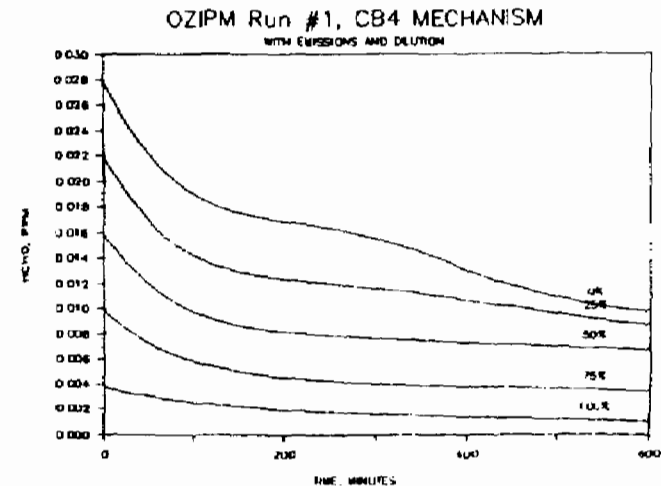
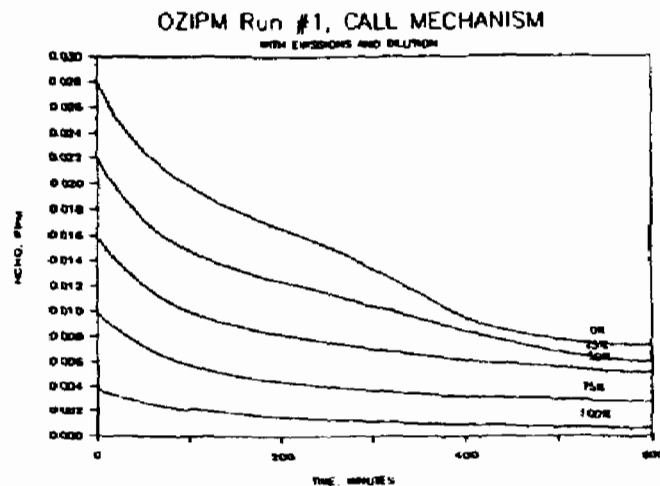
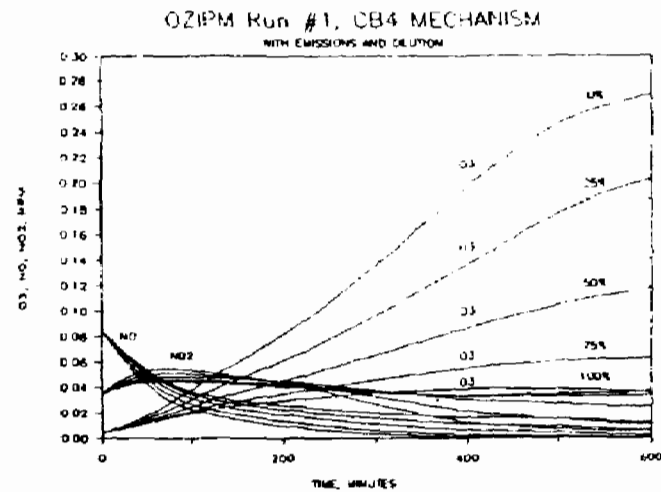
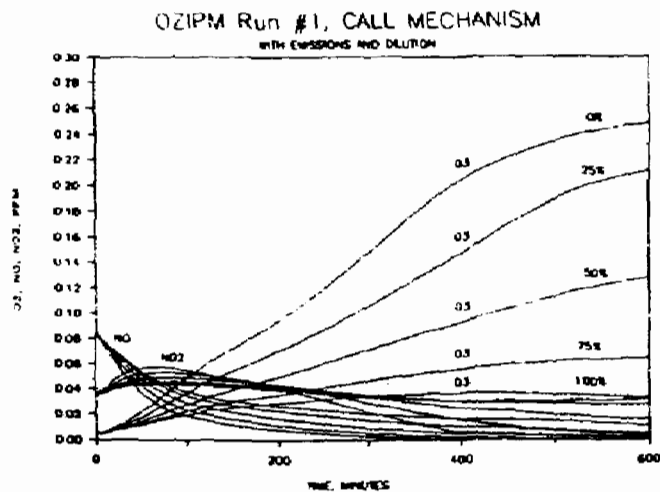


Figure 6. Urban Simulation Example 1.

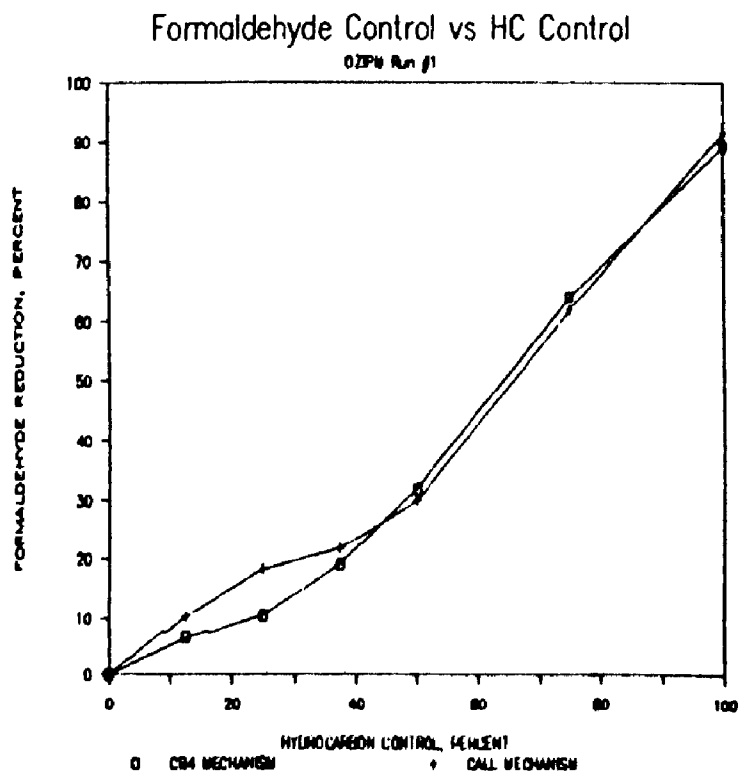
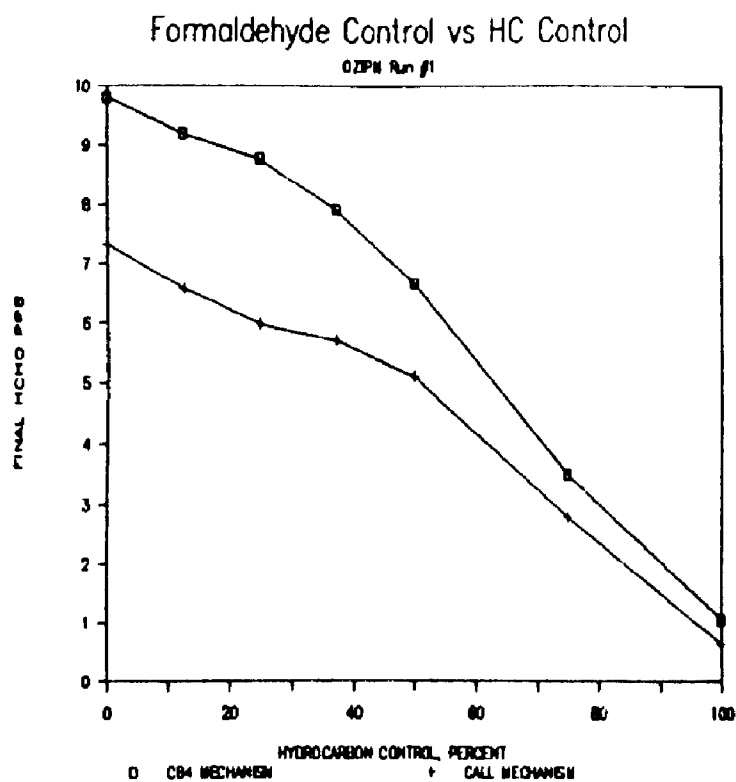
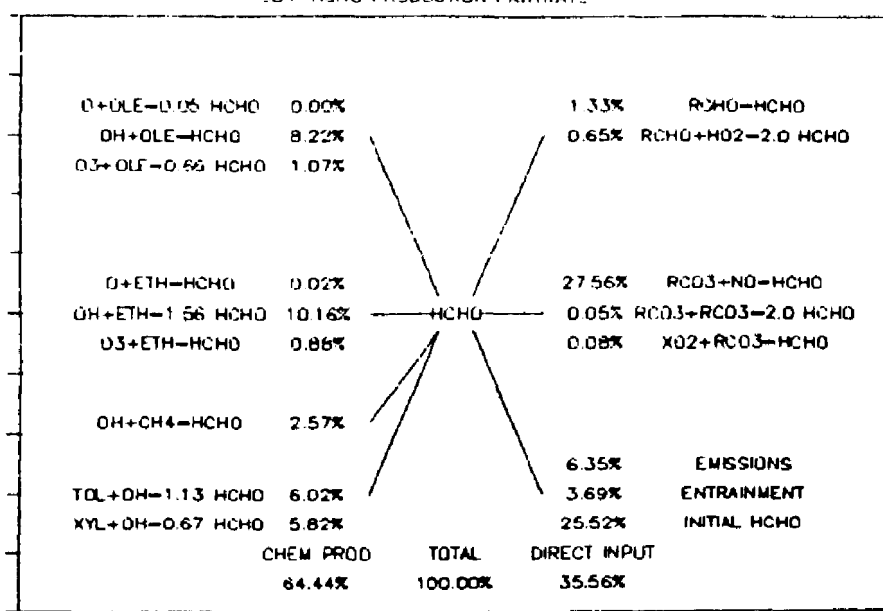


Figure 7. Formaldehyde Control vs HC Control

OZIPM Run #1, CB4 MECHANISM

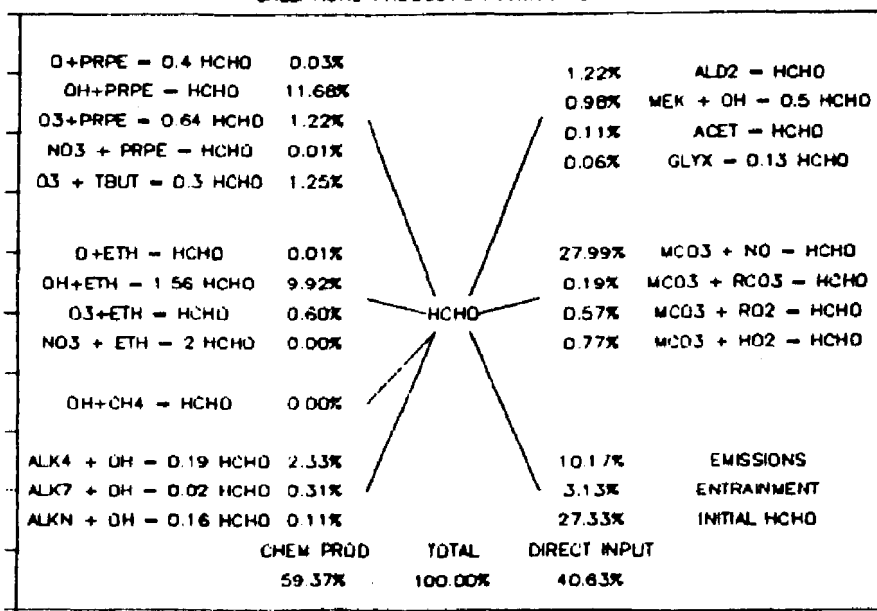
CB4: HCHO PRODUCTION PATHWAYS



WITH EMISSIONS AND DILUTION

OZIPM Run #1, CALL MECHANISM

CALL: HCHO PRODUCTION PATHWAYS

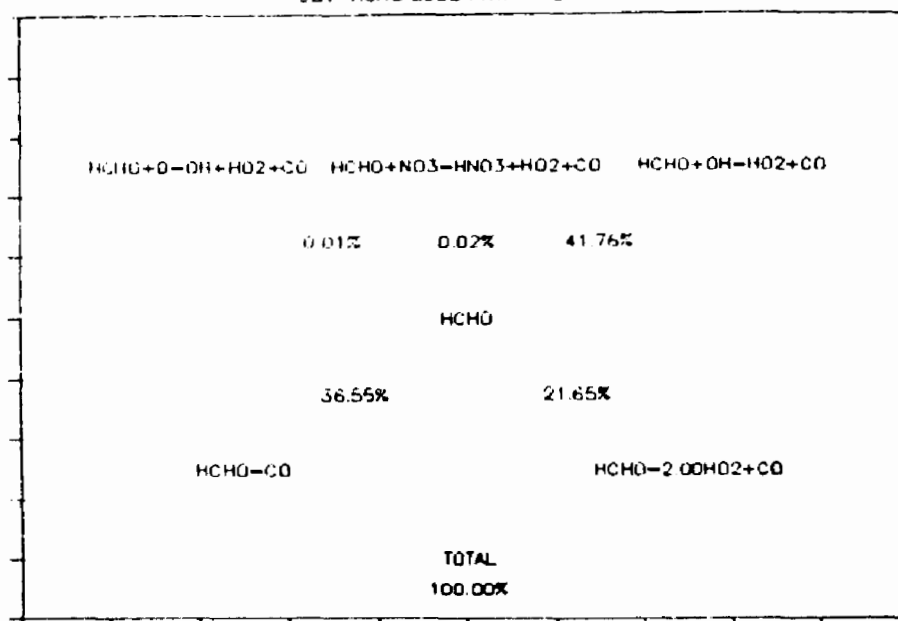


WITH EMISSIONS AND DILUTION

Figure 8a. Formaldehyde Production Flowcharts

OZIPM Run #1, CB4 MECHANISM

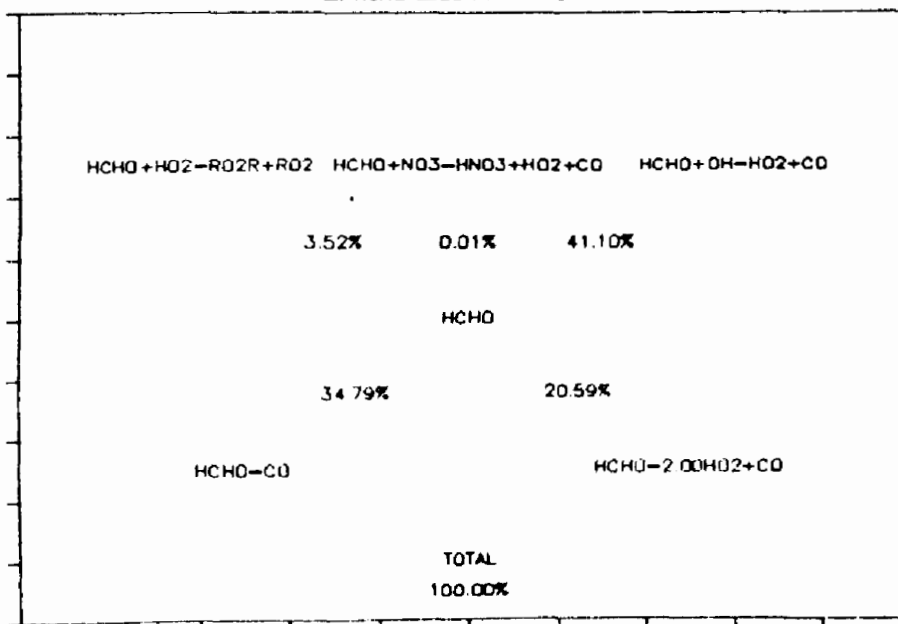
CB4: HCHO LOSS PATHWAYS



WITH EMISSIONS AND DILUTION

OZIPM Run #1, CALL MECHANISM

CALL: HCHO LOSS PATHWAYS



WITH EMISSIONS AND DILUTION

Figure 8b. Formaldehyde Loss Flowcharts

THE INHIBITION OF PHOTOCHEMICAL SMOG--X.
MODEL CALCULATIONS OF THE EFFECT OF
(C₂H₅)₂NOH ON NO_x-C₂H₄-C₄H₈-2 ATMOSPHERES

Julian Heicklen
Department of Chemistry and
Environmental Resources Research Institute
The Pennsylvania State University
University Park, PA 16802



Model calculations are made on the effect of (C₂H₅)₂NOH on NO_x-C₂H₄-C₄H₈-2 atmospheres. The critical initial DEHA concentration needed to keep the maximum O₃ and PAN concentrations <1 ppb is 100-200 ppb for slightly or moderately smoggy days. It is independent of [NO]₀, [H₂O]₀ and nearly independent of [NO₂]₀/[NO_x]₀. It increases dramatically with dilution rate and increases linearly with hydrocarbon concentration. The cost for using DEHA as an anti-smog agent would be about \$1 per car per day used.

Introduction

In a previous paper,¹ I have modelled a C_2H_4 -NO atmosphere to test the inhibiting effect of diethylhydroxylamine (DEHA). The mechanism used reproduced well the data of Schaal et al.² In the present paper, the calculations are extended to see what critical initial concentrations of DEHA, $[DEHA]_c$, are needed to keep the maximum O_3 , $[O_3]_{max}$, and PAN, $[PAN]_{max}$, concentrations to <1 ppb for a 12-hour run under typical Los Angeles sunny-day conditions (sun declinations of 10.53° and latitude of 34°) for a variety of reaction conditions.

Most of the model runs have been done with C_2H_4 as the hydrocarbon. The mechanism used was that used earlier¹ with some updating of rate coefficients. Some calculations were also done with 2- C_4H_8 as the hydrocarbon. The rate coefficients were drawn from the same sources as before with the updating from Finlayson-Pitts and Pitts.³

The updated and added reactions and their rate coefficients are given in Table I. An explanation of the parameters in Table I is given in my earlier paper.¹ As before NO, NO_2 , and H_2O are assumed to be in a rapid heterogeneous equilibrium with HONO. The HONO photodissociation acts as a homogeneous HO radical source. There are 135 reactions and 60 reaction species plus N_2 , which is not reactive but acts as a chaperone.

Results

The results of the model calculations are given in Figures. 1-5. Figure 1 shows the effect of initial NO concentration on a C_2H_4 -NO- H_2O atmosphere with a dilution rate of 7% per hour. The diluent air contains 10^4 ppm H_2O and 25 ppb O_3 . In the absence of DEHA, the maximum O_3 concentration, $[O_3]_{max}$, goes through a maximum value of 181 ppb as the initial NO concentration, $[NO]_0$, increases. The critical initial DEHA concentration, $[DEHA]_c$, needed to keep $[O_3]_{max}$ and $[PAN]_{max} < 1$ ppb remains unchanged at 120 ppb, independent of $[NO]_0$.

Figure 2 shows the effect the initial ratio of $[NO_2]$ to $[NO_x]$ at constant total NO_x concentration. There is no effect on $[O_3]_{max}$ which is ≈ 170 ppb, but $[DEHA]_c$ increases from 120 to 160 ppb as $[NO_2]_0/[NO_x]_0$ increases from 0 to 0.50. This occurs because the NO_2 can oxidize some of the DEHA by generating odd oxygen (O or O_3).

The effect of water vapor concentration is given in Figure 3. Neither $[O_3]_{max}$ nor $[DEHA]_c$ is significantly affected by water vapor composition, as long as it is above 0.3% so that HONO is present to generate HO radicals.

In Figure 4 we see the effect of dilution rate, which is significant. With no dilution $[O_3]_{max}$ in the absence of DEHA is 287 ppb, but it drops rapidly with increasing dilution rate, reaching the U.S. federal standard of 120 ppb at a dilution rate of 14%/hour. On the other hand, $[DEHA]_c$ rises sharply from 100 ppb for stagnant air to 165 ppb at a dilution rate of 14%/hour.

The effect of hydrocarbon concentration is shown in Figure 5. Three series of runs are depicted there. In one C_2H_4 is the hydrocarbon and

$[C_2H_4]_0/[NO]_0$ is kept constant at 2.25. Both $[O_3]_{max}$ in the absence of DEHA and $[DEHA]_c$ increase linearly with $[C_2H_4]_0$ with $[O_3]_{max}$ being 75 ppb greater than $[DEHA]_c$. Two series of runs were done with 2-C₄H₈ as the hydrocarbon. One of these also contained C₂H₄. The results are plotted vs $[C_2H_4]_0 + 7.46 [2-C_4H_8]_0$ because the HO radical reaction is 7.46 times faster with 2-C₄H₈ than with C₂H₄. Since the DEHA scavenges HO radical, it was anticipated that the HO-radical reactivity is the critical parameter in determining $[DEHA]_c$. For the run with only 2-C₄H₈ as the hydrocarbon, the ratio $[2-C_4H_8]_0/[NO]_0$ was kept constant at 0.56. $[O_3]_{max}$ in the absence of DEHA was much lower than in the C₂H₄ runs, but still exceeded the U.S. federal standard of 120 ppb in all runs. It increased with hydrocarbon concentration. Similar results were observed with the series containing both C₂H₄ and 2-C₄H₈. $[DEHA]_c$ increased linearly with hydrocarbon concentration, but $[DEHA]_c$ was lower for comparable HO reactivity than for the runs containing only C₂H₄.

Conclusions

In summary about 100-400 ppb of DEHA are needed initially to completely suppress photochemical smog production, at least for C₂H₄ and 2-C₄H₈ as the hydrocarbons. The amount needed is independent of $[NO]_0$, $[H_2O]_0$, and is nearly independent of $[NO_2]_0/[NO_x]_0$. It increases dramatically with dilution rate and increases linearly with hydrocarbon concentration. For slightly or moderately smoggy days where $[O_3]_{max}$ is less than 200 or 250 ppb, $[DEHA]_c = 100-200$ ppb. Only for very heavy hydrocarbon loadings, where the effective equivalent C₂H₄ concentration exceeds 1 ppm, does $[DEHA]_c$ become larger than this.

With the assumption that about 200 ppb of DEHA are needed to prevent a typical smoggy day, we can estimate the cost of such a program. Typically the morning inversion height at the beginning of a smoggy day is 100 meters. Thus the amount of DEHA needed is 161 pounds per km². At a cost of about \$3 per pound for the DEHA and its distribution, the cost becomes \$483 per km². Typically urban centers have a motor vehicle density of about 500 per km². The cost for using DEHA as an anti-smog agent becomes about \$1 per car per day used. This can be compared to the cost of pollution control devices which exceed \$100 per car per year including the price of the device, annual inspections, repairs, regulation, and the use of unleaded gasoline.

References

1. J. Heicklen, "The inhibition of photochemical smog--IX. Model calculations of the effect of (C₂H₅)₂NOH on C₂H₄-NO_x," Atmos. Environ., **19**: 597 (1985).
2. D. Schaal, K. Partymiller, and J. Heicklen, "The inhibition of photochemical smog--VII. Inhibition by diethylhydroxylamine at atmospheric concentrations," Sci. Total Environ., **9**: 209 (1978).
3. B. J. Finlayson-Pitts and J. N. Pitts, Jr., Atmospheric Chemistry, Wiley Interscience, New York, (1986).

Table I: Rate coefficient parameters for updated and additional rate coefficients*

REACTION	A (cm ³ /sec)	n	E _a (KJ)	R(1/2) (1/cm ³)	Coeff (1a, 1, R)
O ₂ + HNO = NO ₂ + NO	1.0E-13	0	0	0	0
HO + C ₂ H ₄ = HOC ₂ H ₄	2.19E-13	0	-411	0	0
HO + CH ₂ O = H ₂ O + HCO	9.0E-12	0	0	0	0
O + C ₂ H ₄ = CH ₃ + HCO	0.77E-11	0	840	0	0
O ₂ + CH ₃ O = NO ₂ + CH ₂ O	8.9E-14	0	1273	0	0
NO + CH ₃ O = CH ₃ ONO	1.44E-11	0	0	0	0
NO + CH ₃ O = HNO + CH ₂ O	8.3E-12	0	0	0	0
NO ₂ + CH ₃ O = CH ₃ ONO ₂	1.11E-11	0	0	0	0
NO ₂ + CH ₃ O = HNO ₂ + CH ₂ O	8.9E-12	0	0	0	0
CH ₃ CHO = CH ₄ + CO	0.2600E-04	0.2000E-04	0.1000E-04	0.1000E-04	0.0000E+00
O ₂ + C ₂ H ₄ = CH ₂ O + HCO ₂	0.2000E-04	0.1000E-04	0.1000E-04	0.0000E+00	0.0000E+00
O + CH ₂ O = HO + HCO	1.2E-14	0	2432	0	0
HO + 2-C ₄ H ₈ = 2-HOC ₄ H ₈	2.3E-11	0	0	0	0
2-HOC ₄ H ₈ + O ₂ = 2-HOC ₄ H ₈ O ₂	1.0E-11	0	-349	0	0
O ₂ + CH ₃ CHO = NO + NO ₂ + CH ₃ CHO + CH ₃ CHO	7.0E-12	0	0	0	0
O ₂ + CH ₃ CHO = CH ₃ CHO + NO ₂	1.0E-11	0	0	0	0
HO ₂ + 2-HOC ₄ H ₈ O ₂ = HOC ₄ H ₈ O ₂ H	7.7E-14	0	0	0	0
HOC ₄ H ₈ O ₂ H = H ₂ O + 2-C ₄ H ₈ + O ₂	1.0E-13	0	0	0	0
O + C ₂ H ₄ = H + CH ₂ CHO	0.43E-11	0	840	0	0
CH ₂ CHO = CH ₂ O + HCO	1.0E-13	0	0	0	0
O + 2-C ₄ H ₈ = PRODUCTS	2.3E-11	0	-10	0	0
CH ₂ CHO = CH ₂ O	0.40E-12	0	0	0	0
CH ₂ O = CO ₂ + H ₂	0.12E-12	0	0	0	0
CH ₂ O = CO + H ₂ O	0.42E-12	0	0	0	0
CH ₂ O = H + HCO ₂	0.66E-12	0	0	0	0
O ₂ + HCO ₂ = NO ₂ + CO	9.0E-12	0	0	0	0
O ₂ + 2-C ₄ H ₈ = CH ₃ CHO + CH ₃ CHO ₂	9.0E-13	0	1136	0	0
CH ₃ CHO ₂ = CH ₃ CHO	0.40E-12	0	0	0	0
CH ₃ CHO ₂ = CH ₃ + CO + HO	0.19E-12	0	0	0	0
CH ₃ CHO ₂ = CH ₃ + CO ₂ + H	0.34E-12	0	0	0	0
CH ₃ CHO ₂ = HCO + CH ₃	0.05E-12	0	0	0	0
CH ₃ CHO ₂ = CH ₄ + CO	0.12E-12	0	0	0	0
CH ₂ O + NO = CH ₂ O + NO ₂	7.0E-12	0	0	0	0
CH ₂ O + NO ₂ = CH ₂ O + NO ₃	7.0E-13	0	0	0	0
CH ₃ CHO ₂ + NO = CH ₃ CHO + NO ₂	7.0E-12	0	0	0	0
CH ₃ CHO ₂ + NO ₂ = CH ₃ CHO + NO ₃	7.0E-13	0	0	0	0
HO + CH ₃ ONO = HNO ₂ + CH ₃ O	6.0E-13	0	0	0	0
HO + CH ₃ ONO = H ₂ O + CH ₂ O + NO	6.0E-13	0	0	0	0
HO + CH ₃ ONO ₂ = HNO ₂ + CH ₂ O	6.0E-13	0	0	0	0
HO + CH ₃ ONO ₂ = H ₂ O + CH ₂ O + NO ₂	6.0E-13	0	0	0	0

*See Heicklen¹ for a list of other reactions and descriptions of the various parameters.

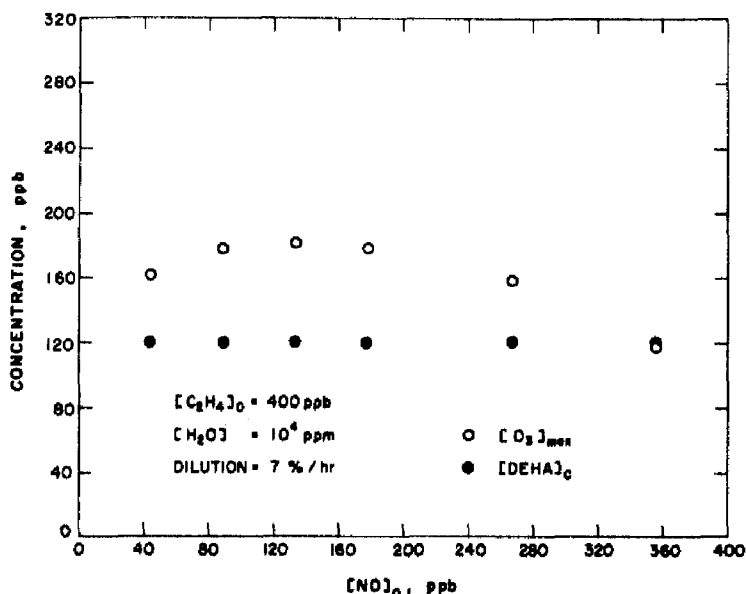


Fig. 1: Plots of concentration vs initial NO concentration for a 12-hour run at 294K and 1 atm total pressure for a sun declination of 10.53° and a latitude of 34°. Initial concentrations at 8:00 a.m. of C₂H₄ and H₂O are 400 ppb and 10⁴ ppm, respectively. The dilution factor is 7% per hour with air containing the same composition of H₂O vapor and O₃ at 25 ppb: O, [O₃]_{max} in absence of DEHA; ●, [DEHA]₀ at 8:00 a.m. to keep [O₃]_{max} and [PAN]_{max} < 1 ppb.

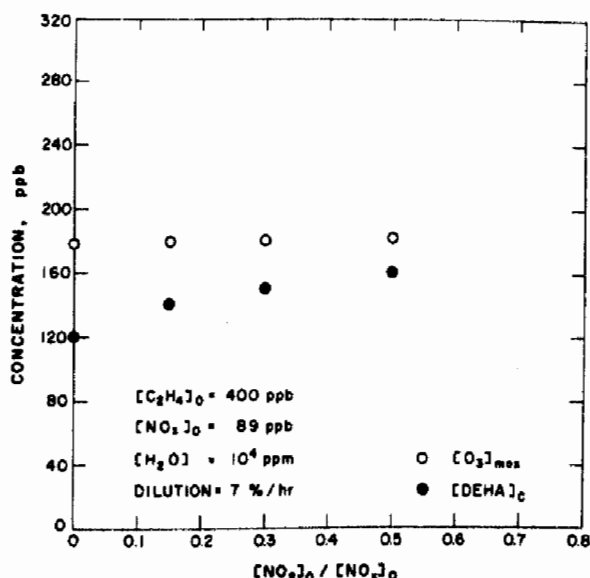


Fig. 2: Plots of concentration vs initial fraction of NO_2 in the NO_x for a 12-hour run at 294K and 1 atm total pressure for a sun declination of 10.53° and a latitude of 34° . Initial concentrations at 6:00 a.m. of C_2H_4 , NO_x , and H_2O are 400 ppb, 89 ppb, and 10^4 ppm, respectively. The dilution factor is 7% per hour with air containing the same composition of water vapor and O_3 at 25 ppb: \circ , $[O_3]_{max}$ in absence of DEHA; \bullet , $[DEHA]_c$ at 6:00 a.m. to keep $[O_3]_{max}$ and $[PAN]_{max} < 1$ ppb.

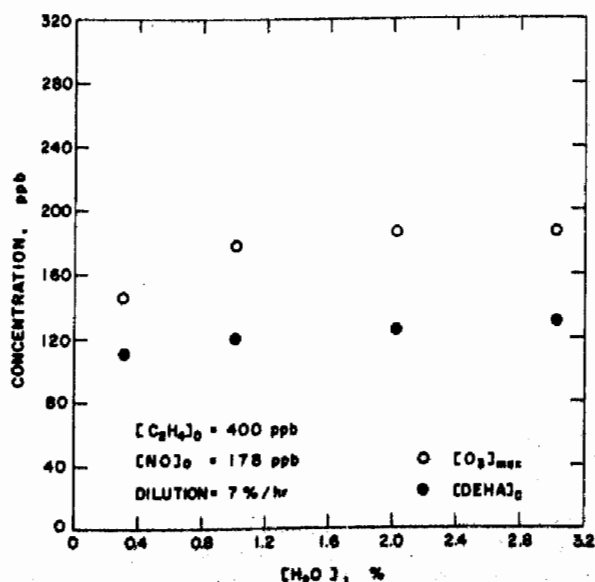


Fig. 3: Plots of concentration vs percent H_2O in air for a 12-hour run at 294K and 1 atm total pressure for a sun declination of 10.53° and a latitude of 34° . Initial concentrations at 6:00 a.m. of C_2H_4 and NO are 400 ppb and 178 ppb, respectively. The dilution factor is 7% per hour with air containing the same composition of water vapor and O_3 at 25 ppb: \circ , $[O_3]_{max}$ in absence of DEHA; \bullet , $[DEHA]_c$ at 6:00 a.m. to keep $[O_3]_{max}$ and $[PAN]_{max} < 1$ ppb.

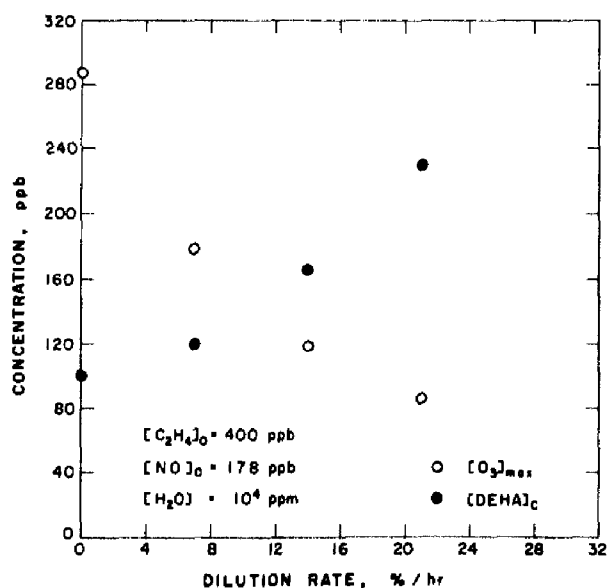


Fig. 4: Plots of concentration vs dilution rate for a 12-hour run at 294K and 1 atm total pressure for a sun declination of 10.53° and a latitude of 34° . Initial concentrations at 6:00 a.m. of C_2H_4 , NO, and H_2O are 400 ppb, 178 ppb, and 10^4 ppm, respectively. Dilution is with air of the same water composition and O_3 at 25 ppb: O, $[O_3]_{max}$ in the absence of DEHA; ●, $[DEHA]_c$ at 6:00 a.m. to keep $[O_3]_{max}$ and $[PAN]_{max} < 1$ ppb.

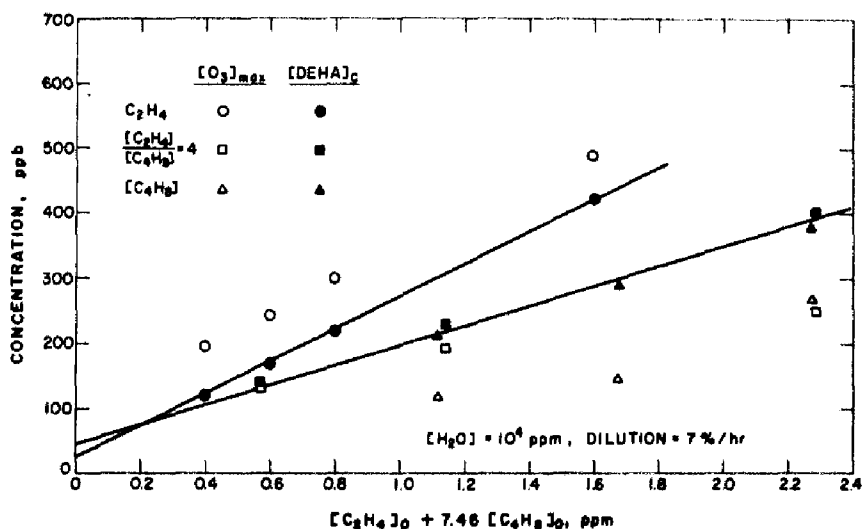


Fig. 5: Plots of concentration vs $[C_2H_4]_0 + 7.46[2-C_4H_8]_0$ for a 12-hour run at 294K and 1 atm total pressure for a sun declination of 10.53° and a latitude of 34° . Initial concentrations at 6:00 a.m. of H_2O vapor is 10^4 ppm. The dilution factor is 7% per hour with air containing the same composition of water vapor and O_3 at 25 ppb: O, ●, $[C_2H_4]_0/[NO]_0 = 2.25$, $[2-C_4H_8]_0 = 0$; □, ■, $[C_2H_4]_0/[2-C_4H_8]_0 = 4.0$, $NO = 178$ ppb; ▲, △, $[2-C_4H_8]_0/[NO]_0 = 0.56$, $[C_2H_4]_0 = 0$. The open points give $[O_3]_{max}$ in the absence of DEHA. The filled points give $[DEHA]_c$ at 6:00 a.m. to keep $[O_3]_{max}$ and $[PAN]_{max} < 1$ ppb.

INTERCOMPARISON OF METHODS FOR THE MEASUREMENT OF
AMBIENT LEVELS OF H₂O₂

T.E. Kleindienst, P.B. Shepson, C.M. Nero
Northrop Services, Inc. - Environmental Sciences
Research Triangle Park, NC 27709

R.R. Arnts
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

G.I. Mackay, L.K. Mayne, H.I. Schiff
Unisearch Associates, Inc.
Concord, Ontario, Canada L4K 1B5

G.L. Kok, J.A. Lind, A.L. Lazrus
National Center for Atmospheric Research
Boulder, CO 80303

P.K. Dasgupta, H. Hwang
Department of Chemistry and Biochemistry
Texas Tech University
Lubbock, TX 79409

A study was conducted to perform simultaneous measurements of H₂O₂ concentrations using several techniques, including (1) tunable diode laser absorption spectroscopy, (2) resonance fluorescence from an enzymatically produced complex, and (3) chemiluminescence from reaction with luminol. Sources of H₂O₂ included surrogate samples in zero air in the presence and absence of common interferences, that produced by irradiating hydrocarbon (e.g., C₂H₄ or CH₃CHO)/NO_x mixtures in a smog chamber, and that found in ambient air. The techniques from four groups were compared with respect to sensitivity, selectivity, and dynamic range for measuring H₂O₂ concentrations.

Measurements of H₂O₂ in zero air were performed for concentrations ranging from 0.062 to 130 ppb. The agreement for the four sets of

measurements ranged from 14 to 23% when compared to standard values for the H_2O_2 concentration. For each technique, there was no indication of interferences from O_3 , NO , NO_2 , HCHO , CH_3OOH , and SO_2 , except for the luminol technique, which showed a negative SO_2 interference. Agreement among the techniques was considerably worse for the irradiated hydrocarbon mixtures. In these mixtures, significant concentrations of organic hydroperoxide were also detected by the enzymatic techniques. For the ambient measurements, agreement of approximately 30% with the mean values was achieved on average.

Introduction

Hydrogen peroxide (H_2O_2), an oxidant formed in the troposphere, has received recent attention due to its proposed role in the formation of acid precipitation. Produced from the recombination of hydroperoxyl radicals, H_2O_2 is extremely soluble in water as it has a Henry's Law constant of $1.5 \times 10^5 \text{ M atm}^{-1}$ at 25°C . It is currently believed that H_2O_2 is the primary species in the atmosphere that oxidizes sulfur (IV) (e.g., SO_2) to sulfur (VI) compounds in the condensed phase.¹ This has been suggested not only due to the high aqueous solubility of H_2O_2 , but also because its rate of reaction with sulfur (IV) increases with increasing acidity. Although *in-situ* mechanisms exist for forming H_2O_2 in the aqueous phase, absorption from the gas phase represents the major source of aqueous-phase H_2O_2 . Thus, to assess quantitatively the role of H_2O_2 in acid precipitation, accurate measurements of H_2O_2 in the gas phase are required.

Few measurements of atmospheric H_2O_2 in the gas phase have been reported. Until recently, most attempts have been plagued by techniques having poor sensitivity or lack of specificity. Most of these techniques have relied on trapping soluble air components in a liquid scrubbing medium followed by analysis of the resultant solution. Many of the previous difficulties have been met with the use of improved liquid methods.^{2,3} Direct gas-phase measurements of atmospheric H_2O_2 *in situ* have now also been reported. These recent developments make it possible to measure H_2O_2 accurately under a variety of atmospheric conditions.

This paper describes an intercomparison study of various techniques to measure H_2O_2 at ambient concentrations. The study was conducted to measure H_2O_2 in zero air and in the absence and presence of several interfering compounds. Measurements were also made for H_2O_2 formed in surrogate photochemical mixtures and H_2O_2 produced in ambient air. Four techniques, three of which were recently developed, are compared with respect to sensitivity, selectivity, and dynamic range.

Experimental Methods

The intercomparison study was conducted at Northrop Services, Inc. - Environmental Sciences (NSI-ES) during the period June 16-26, 1986. Participants in the study included groups from the National Center for Atmospheric Research (NCAR), Texas Tech University (TTU), Unisearch Associates, Inc. (UNI), and NSI-ES. The techniques each of the groups employed during the study have been presented in the literature and

only a brief description is given here. NCAR employed a continuous scrubbing, fluorometric detection (CSFD) technique in which a fluorescent dimer of p-hydroxyphenylacetic acid is formed by an enzymatically mediated reaction with H_2O_2 .² TTU used a diffusion scrubbing, fluorometric detection (DSFD) technique³ that employs the same basic chemistry as in the NCAR technique to produce a fluorescent dimer. The method of collecting H_2O_2 represents the major difference between the techniques. In each of these enzymatic techniques the total hydroperoxide and organic hydroperoxide concentrations were measured. The H_2O_2 concentration was determined from the difference of these two measurements. Unisearch employed tunable diode laser absorption spectrometry (TDLAS) for the direct measurement of H_2O_2 in the gas phase.⁴ NSI-ES used the luminol technique based on methods that were previously presented.⁵

In the initial phase of the study, pure samples of H_2O_2 were generated and mixed with zero air. Vapor-phase H_2O_2 was generated by passing zero air through microporous tubing submerged in a solution of H_2O_2 in water. The gas-phase concentration of H_2O_2 emanating from the generator could be continuously maintained at its Henry's Law concentration at the flow rates employed. To maintain stability, the entire generator was immersed in a thermostatted bath. The concentration in the gas stream was dependent only on the solution molarity and temperature. The concentrated H_2O_2 gas stream was fed into a 1-L mixing manifold where it was diluted with zero air at 30 Lpm. The concentration in the mixing manifold could be set by regulating the H_2O_2 flow feeding the manifold. The diluted mixture was fed directly into a second manifold where sampling took place. The generator, manifolds, and connecting lines were composed of PFA Teflon, which has proved to be extremely inert to H_2O_2 loss, and were shielded from light.

Undiluted, vapor-phase H_2O_2 concentrations from the generator were measured by impinger collection through 28 mM solutions of TiCl_4 at pH 1. Upon reaction with H_2O_2 , TiCl_4 forms a yellow complex with a maximum absorbance of 415 nm. The solution concentration was then determined spectrophotometrically using a measured extinction coefficient of $739 \text{ M}^{-1} \text{ cm}^{-1}$ at 415 nm. This technique can accurately determine gas-phase H_2O_2 concentrations in the high ppbv to ppmv range. With the use of two H_2O_2 generator solutions (i.e., 0.010 and 1.0 M) and a 0-1000 ccpm mass flow controller, gas-phase H_2O_2 concentrations in the range 0.050 to 200 ppbv could essentially be dialed in.

Several experiments were performed in which one or more compounds serving as possible interferences could be added quantitatively to the mixing manifold. The interferences included common atmospheric pollutants: NO_2 , SO_2 , O_3 , and formaldehyde (HCHO). Methyl hydroperoxide (CH_3OOH), a minor component of polluted atmospheres, was also added as a possible interfering species. The concentrations of these compounds in the sampling manifold was determined using continuous gas monitors (NO_2 , O_3 , SO_2), impinger collection (HCHO), or by calculation (CH_3OOH).

In the second phase of the study, gas mixtures (ethylene/ NO_x and acetaldehyde/ NO_x) were irradiated in a smog chamber that was operated

in a dynamic mode. These types of dynamic systems provide steady-state concentrations of H_2O_2 in the presence of many inorganic and organic species found in polluted air including peroxyacetyl nitrate (PAN) produced in the $\text{CH}_3\text{CHO}/\text{NO}_x$ system. The residence time of gases in the chamber can be varied to allow various extents of reaction to be obtained. For these experiments, effluent from the smog chamber passed through 19-mm PFA Teflon tubing and into the sampling manifold.

In the last phase of the study, ambient air sampling was performed on three consecutive nights and for a 24-h period. The ambient sampling port, located 4 m above the ground, was connected directly to the sampling manifold (19-mm PFA Teflon tubing) to ensure that all measurements were taken from the same air parcels.

Results and Discussion

For the first phase of the study (H_2O_2 in zero air and in the presence of possible interferences) the individual sampling periods were 1 h in length. Collection of CSFD samples involved continuous collection over the entire period while the DSFD, TDLAS, and luminol samples were taken in a discrete measurement mode. Measurements were obtained from a total of 23 sampling periods. In 10 periods, pure samples of H_2O_2 in zero air (0.062 to 128 ppbv) were taken. In another 10 sampling periods, one or more of the interferences were added to approximately 5 ppbv H_2O_2 . In the other three periods, background samples from zero air were obtained including one in which 500 ppbv O_3 was added to zero air.

A plot of the H_2O_2 measurements in zero air against standard H_2O_2 values (from the TiCl_4 measurements) shows good linearity for each of the techniques over several orders of magnitude. A DSFD value of 70 ppbv for a standard value of 128 ppbv is approximately 40% low. This can be attributed to the fact that calibrations for this system could only be performed in a range less than 3 ppbv. A luminol value of 2.4 ppbv at a standard value of 1.1 ppbv appears high since the technique (as it was used in this study) was operated at its detection limit (1 ppbv) in this case. A comparison of the individual H_2O_2 measurements with the standard values gives the following average percent deviations: CSFD - 18.3%; DSFD - 21.4%; TDLAS - 14.3%; and luminol 23.4%. When averaged together the H_2O_2 data from the four techniques showed less than a 3% systematic difference with the standard values.

The concentration ranges for compounds serving as interferences are given as follows: O_3 , 118-456 ppbv; SO_2 , 6-32 ppbv; HCHO 18-58 ppbv; NO_x at 125 ppbv; and CH_3OOH at 7 ppbv. The CSFD and TDLAS H_2O_2 data showed no effect for the addition of the interferences either alone or in combination. The luminol data showed a negative interference due to the presence of SO_2 although the interference was removed when SO_2 and O_3 (150 ppbv) were present together. The TTU data showed a positive H_2O_2 interference due to O_3 as determined in a run with 500 ppb O_3 in zero air. This signal was apparently due to a surface effect, and subsequent investigation of this problem has indicated that contaminated surfaces in the scrubber can lead to artifact formation of H_2O_2 by O_3 .

The photochemical systems produced a mixture of species in the presence or absence of H_2O_2 . The CH_3CHO/NO_x irradiated system represents one of the simplest photochemical mixtures, particularly at small extent of reaction. Under these conditions in which 10-20 ppb of NO remain in the mixture, only HCHO, PAN, O_3 , NO_2 , CH_3ONO_2 , and HNO_3 are produced⁶ in significant concentrations. At a larger extent of reaction for which radical-radical reactions are much more probable, H_2O_2 , organic peroxides, and organic nitrates are formed in addition to the products of small extent of reaction. The C_2H_4/NO_x irradiation at a large extent of reaction produces NO_2 , O_3 , HCHO, and H_2O_2 . For each of the three photochemical mixtures, H_2O_2 concentrations in the low and sub ppbv range were observed. The H_2O_2 measurements taken from these photochemical mixtures generally showed poor agreement (i.e., often worse than a factor of two). However, in all of these mixtures, organic hydroperoxides (ROOH), as measured using the enzymatic technique, were produced in yields much higher than H_2O_2 itself. According to the DSFD measurements, ROOH concentrations were nearly an order of magnitude higher in concentration than H_2O_2 for each system (assuming R is CH_3). Since the H_2O_2 concentration in the enzymatic systems is obtained from the difference between the total peroxide signal and the organic component, small relative uncertainties in each of these values can lead to large uncertainties in the H_2O_2 concentration. This probably accounts for the poor agreement in the photochemical systems.

The C_2H_4/NO_x irradiated mixture showed a large organic peroxide component even though most current chemical mechanisms for C_2H_4 photooxidation indicate formation of inorganic peroxide only. It has been suggested⁷ that hydroxymethyl hydroperoxide (HMP), $HOCH_2OOH$, could form via the addition of water to the CH_2OO radical formed in the ozonolysis of ethylene. To test this hypothesis, a C_2H_4/O_3 mixture under dark conditions was tested. In this system, the organic hydroperoxide as measured by the DSFD apparatus was a factor of seven greater in concentration than the inorganic component. While the measurements do not confirm the presence of HMP, there were no observations inconsistent with its formation.

The ambient measurement of H_2O_2 generally showed better agreement between methods than that obtained from the photochemical mixtures. This is not surprising since the organic hydroperoxide component in the atmosphere is generally much lower than H_2O_2 itself. Mean H_2O_2 concentrations ranged from 0.1-2 ppbv. Agreement between data sets was on the order of 30%.

Conclusions

This study has confirmed that reliable methods for measuring H_2O_2 in the gas phase with high sensitivity now exist. Detection limits of better than 0.060 ppbv were obtained using the CSFD and DSFD enzymatic techniques and approximately 0.10 ppbv for the TDLAS. For the luminol system the detection limit was approximately 1 ppbv, though this system was probably not optimized. The techniques were generally free of interferences, although a negative interference was observed with SO_2 with the luminol technique. The ambient measurements indicate

that the sensitivity of the DSFD, CSFD, and TDLAS is probably sufficient to measure H_2O_2 under rural as well as urban conditions.

Disclaimer

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Multivariate Calibration Using the
Partial Least Squares (PLS) Method

W. J. Dunn III

College of Pharmacy
University of Illinois at Chicago
833 S. Wood Street
Chicago, Illinois 60612

ABSTRACT

The calibration of the gas chromatograph for quantitating the components of complex mixtures observed in the air quality monitoring program can lead to difficulties due to nonlinearity of detector response and colinearity in the calibration data itself. It is difficult to deal with these two problems with the software resident on most gas chromatography systems as most calibration software is based on multivariable regression techniques. The recently developed partial least squares (PLS) in latent variables (1) method has been shown to work quite well when either or both of these conditions are present in a calibration problem. This approach and the algorithm on which it is based will be discussed below.

Introduction

The problem of quantitative analysis of gas chromatography data obtained from samples of complex mixtures is generally a calibration problem. In samples in which the number of components is 30 or more it is not practical to calibrate for the components as frequently as required since more than 30 calibration samples should be done in order to reduce collinearity problems. If the detector response is nonlinear in the concentration ranges of interest the problem is further

compounded. A procedure has recently been proposed which can handle both of these problems (1). This technique is the partial least squares (PLS) regression method (1) which has been recently proposed as a method well-suited for multivariable calibration problems, such as the one discussed here. As the result of preliminary applications of the method to gas chromatography data of Aroclor mixtures (2) we have found it to work extremely well.

a. Multivariable calibration

A typical gas chromatography calibration sample is shown in Figure 1. This reconstructed ion chromatogram was obtained in the routine calibration of a GC/MS analysis of air quality data. The known concentrations of the analytes are called the chemical data and the GC responses are the response data. The chemical data will be referred to as the dependent variables or Y-block and the response data are the independent variables or the X-block. The number of calibration samples in a given experiment is n , the number of components in calibration sample is m and the number of chemical responses is p . In the case of GC data, $m = p$, while in the case of uv/ir data $m < p$.

Calibration is the process of developing a model which will allow the prediction of the Y-block from the X-block. This is sometimes referred to as determining the sensitivity of the method.

There are two general steps involved in the calibration process. The first is called calibration and the second is called testing. There are several data analytic methods which can be applied in the first, or calibration, step. The method most commonly used is multivariate regression since it is the method resident in the computers present on most commercial instruments. Another method, principal components regression, has also been used, and more recently, the partial least squares in latent variables, (PLS) regression has been proposed as a robust method for this problem.

In the ideal calibration problem, the chemical data are linear with instrument response. If the problem is multivariable in nature, there can be multicollinearity in the data. If there is nonlinearity in the data and/or if there are collinearities in the data, multivariable regression is not appropriate for application. Principal components regression can deal with the collinearity problem but the PLS regression technique gives more robust results. A discussion of this technique follows.

b. Partial least squares (PLS) regression

The PLS regression method operates by extracting principal components-like vectors from the X- and Y-blocks. This is shown in Figure 1 where the T and U vectors are derived to simultaneously explain the systematic variation in the chemical and response data be optimally correlated through the inner

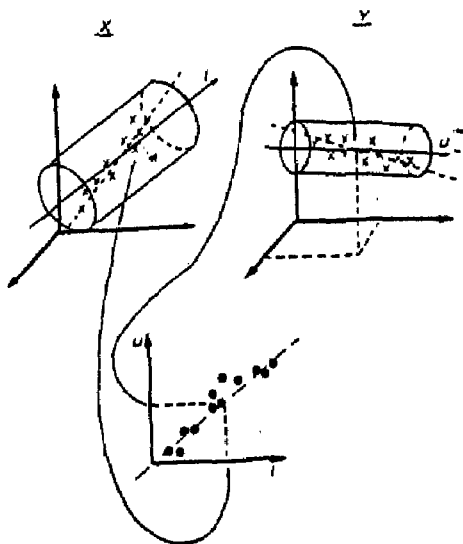


Figure 1. Diagram of the PLS regression methods

relation, $T = UB$. This is also shown algebraically in equations 1 - 4, below. Here, i is the chemical data index and j

$$\begin{aligned} x_{ki} &= x + \sum t_{ka} p_{ai} + e_{ki} & 1) \\ y_{kj} &= y + \sum u_{ka} q_{aj} + f_{kj} & 2) \\ u &= b t & 3) \\ \hat{y} &= b t q & 4) \end{aligned}$$

is the response index. The summations are over the number of components A where $a = 1, 2, \dots, A$. Equation 3 is the inner relation between the t 's and u 's which leads to the predictive relationship in equation 4.

The PLS method uses the Nonlinear Iterative Partial Least Squares, or NIPALS, algorithm to extract the T 's and U 's. The algorithm is a 7-step iterative procedure which is given below.

- Step 1. let $u_{\text{start}} = \text{some } y_j$
- Step 2. $p' = u'X/u'u$ ($w' = u'X/u'u$)
- Step 3. normalize p' (normalize w')
- Step 4. $t = Xp/p'p$ ($t = Xw/w'w$)
- Step 5. $q' = t'Y/t't$
- Step 6. normalize q'
- Step 7. $u = Yq/q'q$

On reaching Step 7, compare u with that in Step 1. If they are equivalent stop, otherwise move the u in Step 7 to Step 1 and repeat until convergence. After convergence calculate the weights as shown in steps in parentheses to give orthogonal t 's. Usually the algorithm converges quickly. The t 's can then be used to derive predictive inner relations.

Note that in Step 2, the vector p' is calculated so as to contain information from the X-block and in Step 5 q' is calculated so as to contain information about the Y-block. The result is that the t 's and u 's extracted are correlated.

After a component has been extracted, and the y 's and x 's predicted, blocks of orthogonal residuals result. From these addition PLS components can be calculated. Cross-validation (3) can be used to estimate the number of predictively significant PLS components that are optimal for a given problem.

Once the t 's have been calculated they can be used in the prediction step to estimate the concentrations. This is done through the relations shown in equations 3 and 4, above.

PLS regression is a rather new approach to the calibration problem. It is not well described in the literature but numerous papers are beginning to appear of its applications in this area. The method has a number of advantages which make it suitable calibration problems associated with complex mixtures. One of its advantages is that it is computationally straight forward and can be programmed to run on desk top computers.

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MULTIVARIATE QUALITY ASSURANCE PROGRAM FOR DIOXINS AND FURANS

Stephen E. Swanson, Martin Nygren, Lars-Owe Kjeller and
Christoffer Rappe
Department of Organic Chemistry
University of Umeå
Umeå, Sweden

A quality assurance program has been initiated in this department which uses multivariate statistics to monitor daily mass spectrometer performance. With this program, instrument performance can be determined through the simultaneous evaluation of all 28 analytes in each quantitation standard. This multi-element calibration is simplified through the use of a peak detection and quantitation program combined with the SIMCA multivariate statistics package. This peak detection program uses peak detection algorithms available in the Finnigan INCOS software, then evaluates those peaks using techniques developed in this department. Through the use of these techniques, peaks are evaluated based on relative chromatographic retention and relative ratio of ions in molecular ion clusters. Dioxin and furan peaks can be quantitated or evaluated using multivariate statistics. Thus instrument response can be accurately evaluated regardless of how many different operators are using the instrument.

Introduction

Frequent monitoring of instrument response is a basic quality assurance technique which is common practice in most analytical laboratories and is a minimum requirement of most standard procedures.¹ In most laboratories, this is accomplished through maintenance of calibration curves and instrument response charts for quantitation standards. Frequently these quantitation standards can contain upwards of 20, 30 or more

analytes which must be monitored individually. When instrument response records are based on methods of linear regression analysis, a separate response curve and response chart must be maintained for each analyte. Thus with 20 or more quality control charts to monitor after every 8 hours of operation, this minimum quality assurance technique can become quite tedious. With the use of multivariate statistical methods, however, the response of these several analytes can be combined into one instrument file. The result is that response of all analytes can be monitored simultaneously, this simplifying record-keeping aiding in interpretation.²

If multivariate statistical methods are to be used routinely, the standard response data for all analytes must be processed and combined into a single file for multivariate analysis. This procedure may require specialized software. The organic analytical chemistry group at the University of Umeå has developed a procedure which allows multivariate analysis of instrument response data collected from a Finnigan 4500 mass spectrometer using an INCOS data system. This software was specially developed for evaluation and processing of MID (multiple ion detection) results from analyses of Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzo Furans (PCDFs).

Experimental Methods

The Finnigan 4500 mass spectrometer in the organic chemistry department at the University of Umeå is routinely used for analysis of PCDDs and PCDFs in a variety of samples. To achieve maximum sensitivity and selectivity, the mass spectrometer is operated in the negative chemical ionization mode and the mass spectral responses are monitored using the MID technique on the INCOS data system. The masses monitored and their theoretical ratios are given in table I.

Special application software has been written by this group to evaluate and process this MID data. The general procedure for data processing is shown in Figure 1. Following GC/MS analysis for PCDDs and PCDFs, the INCOS data system prints out the chromatograms of ions selected by the MID program, shown in Table I. This INCOS procedure also quantitates each chromatographic peak and stores the peak heights and areas in "*.QL" files. The "*.QL" files are then transferred to an IBM AT personal computer. The IBM then sorts the peak heights and areas by relative retention times to pair responses for the molecular ion (M) and the M+2 ion (see Table I). The pairs of heights and areas are then evaluated. First, the pairs are evaluated based on the ratio of M and M+2 and then on the relative retention time of the peaks compared to the established retention time of the PCDD and PCDF isomers. The identification of TetraCDFs is shown as an example.

TetraCDF is monitored by response of its molecular ion (M=303.9) and the M+2 ion (305.9), as shown in Table I. The peak heights and areas are sorted by the IBM based on relative retention time so that each peak for mass 303.9 is paired with a 305.9 peak of the same retention time. These paired peaks are

then evaluated based on the following PCDD/PCDF identification criteria. First the areas of the 303.9 peaks are compared with the 305.9 peaks. This area ratio is then compared to the theoretical ion ratio (76%), shown in Table I. The same comparison is made for the heights of the 303.9 and 305.9 peaks. Next, the pairs of peaks are evaluated based on their relative retention times compared to actual retention times of the TetraCDF isomers established by analysis of a retention time standard. Peaks are then flagged as TetraCDFs which meet all three identification criteria: 1.) peaks which appear at the same retention time for both M and M+2 (303.9 and 305.9); 2.) peaks which have the correct ratio of height and area ($76 \pm 10\%$) and 3.) peaks which are within 10% of the established TetraCDF retention times. The results of this sorting and evaluation are printed out by the IBM computer so the analyst can review the computer's evaluation. This resulting file may be edited if the analyst disagrees with the printed evaluations. After the file is edited, only the PCDD and PCDF peaks are saved.

This PCDD/PCDF raw data file can be of three types; quantitation standard, unknown, or retention time standard, as shown in Figure 1. Each type of file is processed differently. In quantitation standards, the relative response of the peak height and area of each compound is calculated compared to the internal standard response. This information is stored for later use in calculation of unknowns. This data can also be stored in a format which can be taken up for multivariate statistical analysis using the SIMCA-3B program. In the second type of data file, samples of unknown concentration, the PCDD and PCDF responses are corrected for internal standard response, then are compared with measured responses for the quantitation standard and final concentrations are calculated. These concentrations can be printed out in an annotated data report or can be saved in a format which can be taken up for multivariate statistical analysis using the SIMCA-3B program. The third type of data file, results of analysis of a retention standard, is used to create a new retention time template which is then stored for evaluation of subsequent data files.

Principal component (PC) analysis and the SIMCA-3B system have been described in detail elsewhere.³ Thus a brief summary of the features of this system will be given here. The PC model of the data set is calculated, as shown by the following equation:

$$x_{ik} = \bar{x}_k + \sum_{a=1}^A t_{ia} * p_{ak} + e_{ik}$$

Where x_{ik} is the measured value of the variable k (the height or area of mass peak k) of object i (the ion chromatogram i). The parameters \bar{x}_k are the averages of the variables k. The PC parameters t_{ia} , scores, and p_{ak} , loadings, are calculated so that the residuals e_{ik} are minimized using the least squares method. The loadings describe the multivariate relation between variables and the scores describe the multivariate relation between objects. The number, A, of statistically significant components (product terms) is determined by cross validation.³

Results

The average time for GC/MS analysis of all Tetra- through OctaCDDs and CDFs is approximately one hour. Subsequent to that analysis, the printing of the results and creation of "*.QL" files on the INCOS system takes 45 minutes to one hour. The remaining steps in the process: transfer of data, sorting, evaluation, editing and final PC analysis of the standards data takes another 15 to 20 minutes. In general, little or no additional editing of the data files are required when quantitation standards are analyzed.

Figure 2 shows a calibration curve which was generated using this procedure. The results presented are a 6-point calibration curve which with standards 1 through 6 representing a concentration range of two orders of magnitude. Though this appears to be a linear calibration curve, the graph shown in Figure 2 is actually created from the responses of all M and M+2 heights and areas, a total of 128 variables.

Conclusion

Through the use of this data processing package, the results of PCDD and PCDF analysis can be quickly evaluated and the concentration calculated. This data processing package also provides the capability for formatting these results in manner which allows subsequent multivariate statistical analysis using the SIMCA-3B package. Multivariate statistical analysis of mixed quantitation standards allows simultaneous evaluation of the responses of all compounds in the mixed standard, thus simplifying the evaluation of instrument response.

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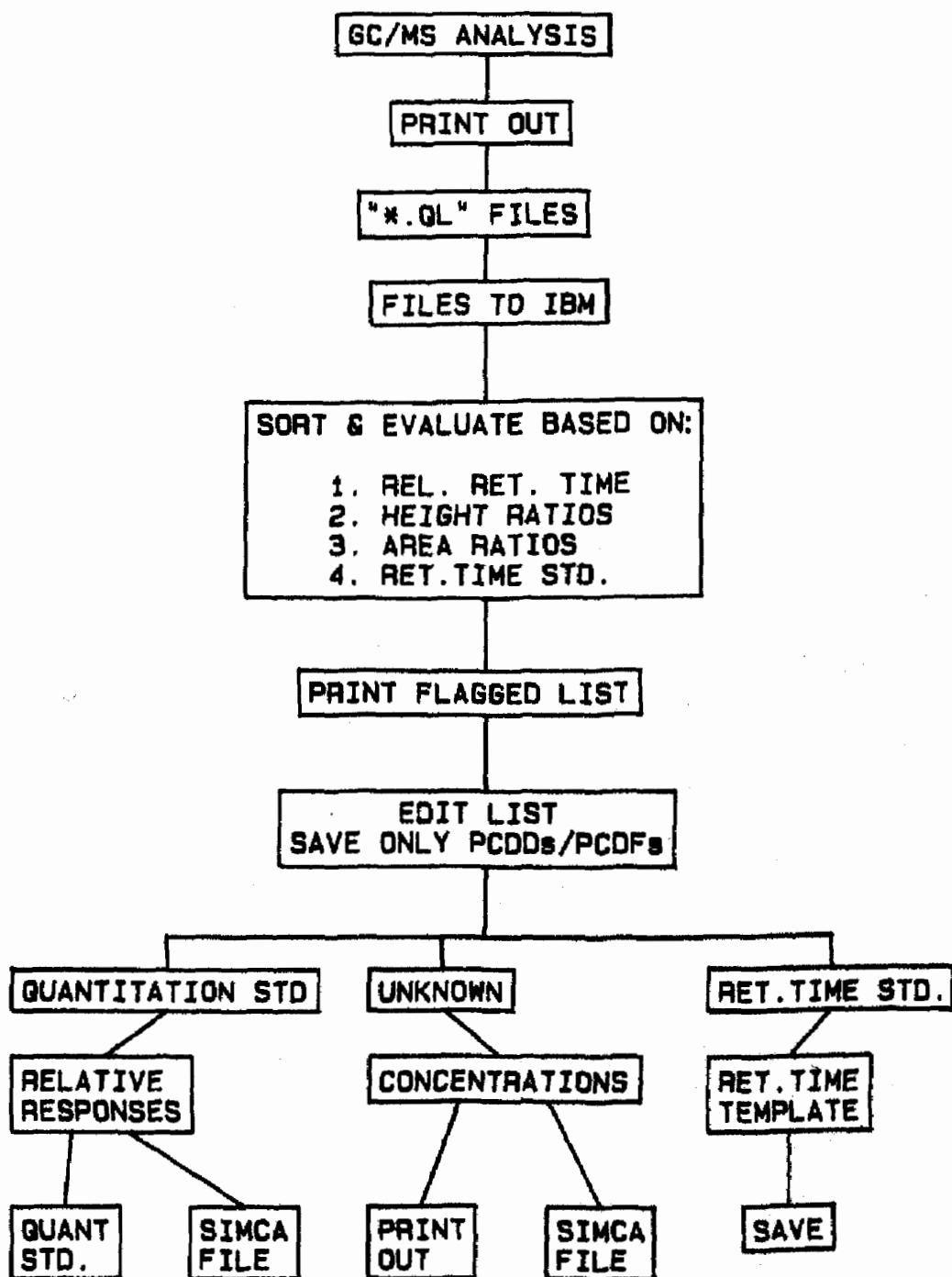
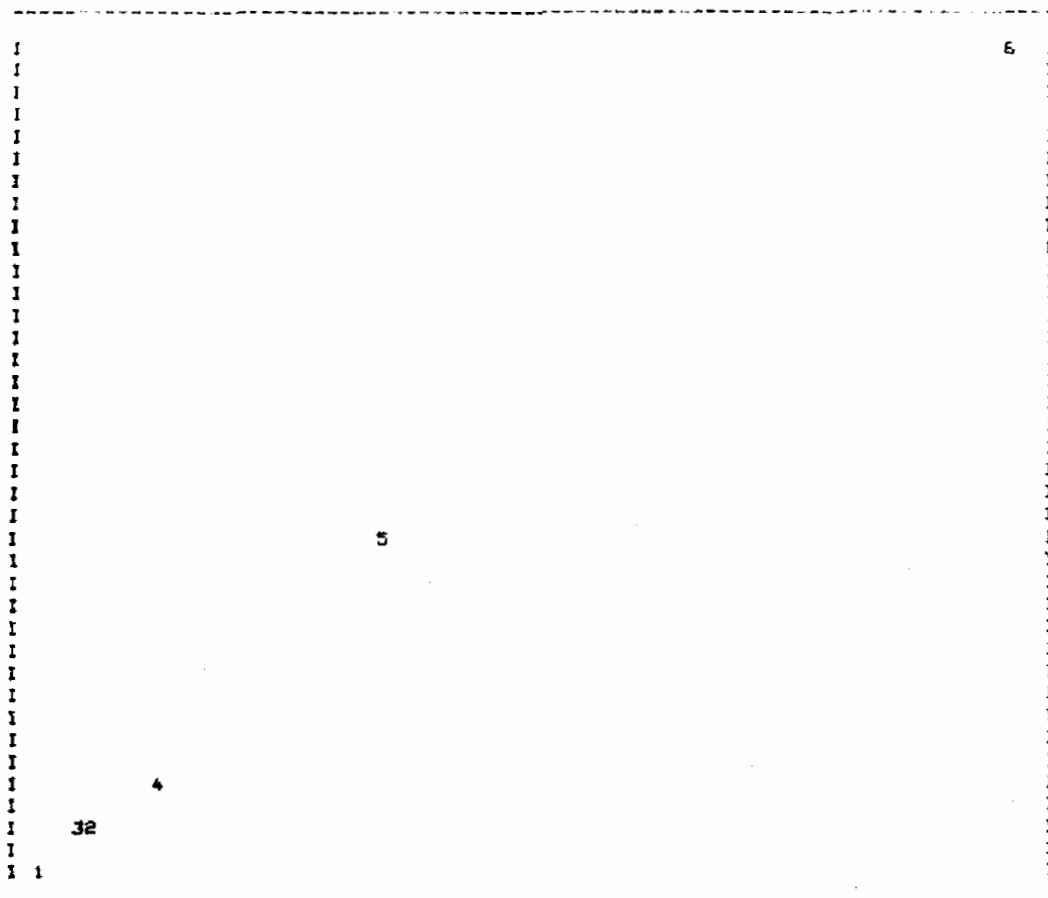


Figure 1. Procedure for evaluating, quantitating and storing PCDD/PCDF data.

Table I. PCDD and PCDF Ions Monitored and Their Theoretical Ratios

Homolog	Masses Monitored (Theoretical ratio)	
TetraCDF	303.90/305.90	(100/76)
PentaCDF	337.86/339.86	(100/61)
PentaCDD	353.86/355.86	(100/61)
HexaCDF	371.82/373.82	(100/51)
HexaCDD	387.82/389.82	(100/51)
HeptaCDF	405.78/407.78	(100/43)
HeptaCDD	421.80/423.78	(100/43)
OctaCDF	441.75/443.74	(100/87)
OctaCDD	457.74/459.74	(100/87)



IDENTIFYING POLYCYCLIC AROMATIC HYDROCARBON SOURCES
FROM AMBIENT AIR DATA COLLECTED IN URBANIZED
AREAS OF NEW JERSEY

R. Harkov - Office of Science and Research, New Jersey Department of
S. Shiboski Environmental Protection, Trenton, New Jersey.
A. Greenberg - Department of Chemistry, NJIT, Newark, New Jersey.
F. Darack

ABSTRACT - A large ambient air data base for polycyclic aromatic hydrocarbons has been analyzed to identify potential combustion source contributors to the measured concentrations. Two related multivariate procedures, principle factor analysis (PFA) and principle component biplot (PCBi), were utilized to analyze data collected at three urban New Jersey sites; Newark, Elizabeth and Camden. Results from this study identified three to four potential source groupings for the PAH. However, only two specific source categories were tentatively linked to PAH levels at Newark and Camden. A major difficulty in the present study is the lack of adequate PAH emissions data.

INTRODUCTION - Polycyclic aromatic hydrocarbons (PAH) have been measured in the air environment for more than twenty five years (NAS 1983). In addition, different profiles of PAH have been developed for various combustion sources such as motor vehicles, space heaters, power plants, coke ovens and agricultural and forestry residue removal operations (Grimmer 1983, Daisey et al 1986). Although source and ambient data on PAH have been available for a period of time, estimating the relative contribution of the various combustion sources to the measured atmospheric concentrations has been difficult. This observation is in contrast to the significant progress that has been made in the apportionment of source contributors for other pollutants such as particulates (Copper and Watson 1980).

Some of the problems in utilizing ambient air PAH data to apportion the contribution from various combustion sources include: a) relatively small data sets, b) incomplete knowledge of emission profiles of various PAH and the consistency in the emitted profiles, c) poor precision associated with ambient PAH measurements, d) weak correlations with potential source tracers such as metals and e) high degree of correlation between PAH within a data set (Harkov et al 1986a, b, Daisey et al 1986). In spite of this situation a number of workers have attempted to identify PAH sources utilizing ambient air data (Daisey et al 1979, Harkov et al 1984, Thrane 1984, Cretney et al 1985, Harkov et al 1986c). Cretney et al (1985) were successful in resolving transformed PAH data analyzed by principle components analysis (PCA) into the two most important PAH sources in New Zealand. Using principle component biplot (PCBi), Harkov et al (1986c) were able to tentatively identify PAH sources at four New Jersey locations. Generally, most workers have met with a modest level of success in identifying PAH source contributors, but have been unsuccessful in quantitative PAH source apportionment. The present report utilizes a large PAH data base from three urban sites in New Jersey to identify combustion source contributors to the measured ambient PAH levels. In this analysis

two related multivariate techniques, principal factor analysis (PFA) and PCBi are utilized to help resolve PAH sources at the three urban New Jersey sites.

METHODS -

Sample Collection/Analysis - The PAH data was collected at the three urban sites (Newark, Elizabeth, Camden) utilized during the New Jersey ATEOS project (Harkov and Fischer 1982). During the ATEOS project, PAH samples were collected with size-selective inlet (SSI) PM15 samplers equipped with pre-ignited glass fiber filters (Gelman-A) through four separate, 6 week campaigns from 1981-1983 (Greenberg et al 1985). As a follow up study, PM10 samples were collected using Wedding inlets and pre-ignited quartz fiber filters (Whatman-QMA) every sixth day from 10/83-10/84 at the same three urban sites. All samples were analyzed in an identical fashion using soxhlet extraction with cyclohexane, followed by TLC and HPLC. The complete ATEOS PAH and quality assurance (qa) data and the analytical procedures have been presented elsewhere (Greenberg et al 1985, Harkov et al 1986a), as have the subsequent PM10 PAH data with qa results (Harkov et al 1986b).

Data Base Description - By combining both data bases between 200-220 observations are available for analysis for each site. However, since PAH data sets contain a large number of missing values due to numbers below detection limits or noise in the analysis (Harkov et al 1986a,b), multivariate statistical techniques are difficult to perform and interpret for this pollutant class. Eight PAH were selected for analysis because they represented the most complete data set of the twenty six compounds measured. These compounds are shown in Table-1 with some physical characteristics. Levels of data quality (Harkov et al 1986a,b) and reactivity indices (Greenberg and Darack 1985) indicate that no systematic patterns exist within this data base. The multivariate analyses are thus assumed to reflect source contributions and meteorological changes, rather than the atmospheric, sampling or analytical fate of the various pollutants.

Statistical Approach

A - Principle Factor Analysis - Principle factor analysis was carried out with the personal computer software STATGRAPHICS (STSC 1981) utilizing listwise deletion of missing values and varimax rotations. The Hotelling T^2 test available in STATGRAPHICS was utilized to identify potential outliers, and from those observations identified each one was individually removed to demonstrate its importance on the final model development.

B - Principle Component Biplot (PCBi) - This exploratory data analysis tool was developed by Gabriel and coworkers at the University of Rochester (Gabriel 1982, Cox and Gabriel 1982) and was first applied to air pollution data by Harkov et al (1986c). It is a graphical display of both rows and columns of a data matrix, i.e. of observations (rows) and individual pollutants (columns) in the present case. Biplots are useful for visual inspection of data matrices so that outliers or unusual distributions of the observations or pollutants can be readily observed. For PCBi, the sample data is approximated by the first two principal components, which generally

account for 70-90% of the variance in the model. In the present case, GH' PCBi has been utilized, since this biplot procedure gives a better fit to the variables (pollutants) than to the observations (Gabriel 1982). The theory behind the biplot representation rests on the fact that only matrix x of n rows and p columns with rank r can be factorized into a product of a matrix G with n rows and r columns a matrix H with p rows and r columns, such that $X = GH'$. The principal component biplot starts with a standard principal component analysis of the correlation matrix of the data matrix X and bases G and H on the first two principal component scores and first two eigenvectors respectively (i.e. $r=2$). The actual plot is produced by plotting G and H in the space of the first two principal components. The n points in the resulting plots represent the n observations, while the p sectors represent the p variables of the data matrix X . For the PCBi display, the angles between any two vectors are inversely proportional to their correlation and the length of a vector is proportional to its contribution to the principal components. The personal computer version of the statistical package MINITAB (Ryan et al 1982) was utilized to produce PCBi. This analysis was accomplished utilizing a series of algorithms available in the MINITAB package.

RESULTS

Principle Factor Analysis (PFA) - In the present analysis, PFA identified three to four similar factors at each site and only final factor solutions will be presented (Tables 2-4). Outliers were confirmed for only the Elizabeth site ($N=3$) and the Camden site ($N=1$). The total number of complete observations for the Newark, Elizabeth and Camden sites, after listwise deletion, were 83, 52, and 79 respectively. The first factor accounted for approximately 80% of the variance in the model of each site and was primarily associated with BkF, BaP, B₁F and BbF, with lower loadings of BghiP and ICDP. The next factor was associated with Cor and BghiP and accounted for approximately 10% of the variance at each site. A third factor was associated with BeP and accounted for approximately 5% of the variance in the models. Finally, at Elizabeth and Camden a fourth factor was associated with ICDP and accounted for about 4% of the variance in the model.

Principle Components Biplot (PCBi) - Since principle components analysis is based on sample correlation or covariance matrices, we have elected to employ pairwise correlation matrices to increase the amount of information utilized in the PCBi analysis. The use of pairwise correlation matrices increases the number of samples considered in the analysis by using all the complete observations on any pair of variables in the computation of correlation coefficients. However, to actually compute the principle component scores only the complete observations could be utilized. The effect of this approach is that the correlation matrices are based on approximately twice the number of data points when compared with the observations with no missing values. This method was thought to more closely approximate the true relationship between variables and provide a contrast to the approach utilized in PFA.

As described earlier, the PCBi technique can allow visual identification of outliers in a data set. In the present analysis, each potential outlier was removed from the data set to test its influence on the biplot results. The testing of outliers from the PCBi technique for the current data produced the following number of outliers; two at Newark, three at Elizabeth and five at Camden. Final complete observation numbers for Newark, Elizabeth and Camden in the biplot analysis were 81, 52 and 75 respectively. Those outliers identified in both PFA and PCBi were identical, but it appears that the PCBi method is more sensitive to outliers than the PFA screening procedure utilizing the Hotelling T^2 test. The information in Figures 2a and 2b provides a comparison of PCBi results with and without outlier removal at the Camden site.

All three sites had a common cluster of PAH (BkF, BaP, B₁F, BbF), (Figures 1-3). At Newark and Camden a common cluster occurred for BghiP/Cor and at both these sites BeP was separated from the other seven PAH compounds. On the Elizabeth biplot BeP/Cor and BghiP/ICDP produced separate clusters.

Discussion - Profiles of PAH emissions from combustion sources have been compiled by Grimmer (1983) and most recently by Daisey et al (1986). Analysis of these compilations indicates that the current state of knowledge on PAH emission profiles is not adequate for use in receptor modelling. Because the state-of-the-art for PAH fingerprinting is very immature the present analysis will rely heavily on additional information pertaining to the specific airsheds utilized in the current study and previous apportionments of PM₁₀, EOM and BaP in New Jersey (Morandi 1985, Harkov and Shiboski 1986, Harkov and Greenberg 1985).

Both PFA and PCBi identified a group of PAH (BkF, BaP, B₁F, BbF) that were clustered together at the three sites. Since additional PAH had reasonably high loadings on this factor in PFA and because this factor accounted for a very significant portion (~80%) of the variance in the PFA models, it is possible that this cluster was related to general meteorological conditions and/or a number of non-specific (area) PAH sources. However, the PCBi identified this cluster as being clearly separate from the other PAH at all three sites. A review of data concerned with diesel and spark ignition motor vehicle exhaust, industrial, and oil and coal combustion emissions does not yield any potential source category for this cluster (NAS 1983, Grimmer 1983, Daisey et al 1986, Hangebrauck et al 1967). Relatively high levels of benzo[fluoranthene] have been detected in communities impacted by wood combustion and in wood smoke soot (Manning et al 1983, Soderberg et al 1983, Cretney et al 1985, Sexton et al 1985). A source apportionment for BaP in New Jersey (Harkov and Greenberg 1985) identified wood combustion as the major source of this contaminant during the heating season (Nov.-March). Because the monitoring locales utilized in the present study are inner-city sites, any impacts of wood combustion emissions would probably be small. Since our heating season data set is insufficiently large after listwise deletion, we could not explore a winter/summer comparison of this PAH cluster. Thus the actual source identification for this cluster is uncertain.

The PFA identified a Cor/BghiP factor at each site and this factor accounted for about 9% of the variance in the model. Both Cor and BghiP have been used as indicators of motor vehicle contributions to ambient PAH levels, since PAH profiles from this source category indicates that relatively high levels of these two compounds are emitted to the atmosphere (Grimmer 1983, NAS 1983, Daisey et al 1986). The PCBi analysis also produced a Cor/BghiP cluster at two of the three sites. In the Elizabeth PCBi BeP was clustered with Cor and ICDP with BghiP. This result is contrary to what was expected since the Elizabeth site was thought to be the most heavily impacted by motor vehicles (Harkov and Shiboski 1986, Harkov et al 1984). The PAH clusters at a site should reflect; a) source emission densities and profiles in the vicinity of the locale, b) environmental fate of the PAH and c) local meteorology. While previous studies in New Jersey indicate that motor vehicles are a major source of BaP and extractable organic matter (Harkov and Greenberg 1985, Harkov and Shiloski 1986), the poor resolution of motor vehicles in the Elizabeth PCBi may be caused by two sources which are located in the same general direction and/or as a result of strong alternate PAH sources that emit Cor or BghiP. The only potential source category near Elizabeth which can meet these requirements is a large oil refinery that is located to the south and west of the site.

Benzo(e)pyrene was identified as a factor at all three urban sites and independent of the other PAH in the PCBi at Newark and Camden. At the Elizabeth site, BeP was associated with Cor in the PCBi. Although we cannot definitely attribute a source category to BeP, we are tentatively linking it to fuel oil combustion. Relatively high levels of BeP emissions from oil combustion have been reported in the literature (Brockhaus and Tomingas 1976, Hangebrauck et al 1967, Bennett et al 1979), although this emissions information is far from being mature. Fuel oil is an important energy source in inner city areas of New Jersey, although the actual amount of PAH produced from this source category appears to be small (Harkov and Greenberg 1985).

The factor analysis has produced a factor with high loadings of ICDP at Elizabeth and Camden. Since PCBi generally indicated that ICDP is associated with clusters of other PAH and the amount of variance explained by ICDP in the PFA models is very small (~4%), at the present time we are considering this factor as an artifact of the specific statistical technique and not related to a potential source category.

By utilizing two different multivariate techniques, it has been possible to provide some internal checks on the determination of sources of PAH from this data set. Generally, both methods provided similar results, with some notable exceptions. One potential advantage of the PCBi procedure is that the problem of status of pollutants and factor inclusion in the final models for PFA is avoided. Identifying the correct number of viable factors in PFA is difficult because of the problem of the lack of rigorous factor cut-off criteria. The problem of factor or cluster identification appears to be small or nonexistent in the PCBi technique. However, compared with PFA outlier rejection is a more important step in cluster resolution in PCBi.

Without more complete information of source emissions of PAH it will remain difficult to utilize ambient data to accomplish source apportionment for this class of air pollutant. Currently there is a small program evolving in New Jersey to characterize stationary combustion source emissions profiles of PAH, NO₂-PAH, Quinones and other substituted PAH to help in both source resolution from ambient data and to understand the potential impacts from increasing the amount of waste combustion in the New Jersey environment.

CONCLUSIONS

A multivariate statistical analysis of ambient PAH data was carried out to identify potential source contributors to the measured concentrations. Both PFA and PCBi produced very similar results in that some three to four potential groups of PAH were found to explain most of the variability in the data from three urban New Jersey sites. Only one grouping of PAH (BkF, BaP, B₁F, BbF) was common to all three sites. Identification of a combustion source contributor to the ambient levels of these PAH was not possible utilizing current emissions data. A Cor/BghiP and a BeP group was identified at Newark and Camden and was thought to reflect motor vehicle and oil combustion contributions respectively. At Elizabeth two groupings of PAH, Cor/BeP and BghiP/ICDP, were thought to be produced by the influence of an additional source co-located in the direction of high source strength areas for motor vehicles and oil combustion. This source was tentatively identified as a large oil refinery. Without better emissions information, source resolution of ambient PAH data sets will be very difficult to perform successfully.

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TABLE-1
PHYSICAL DATA

<u>COMPOUND</u>	<u>MW</u>	<u>MP(°C)^{a,b}</u>	<u>BP(°C)^{a,b}</u>	<u>VP (ATM, 25°C)</u>
Benzo(k)fluoranthene	252	215	-	1.3×10^{-13} ^a
Benzo(j)fluoranthene	252	166	481	1×10^{-11} ^c
Benzo(b)fluoranthene	252	167	480	1×10^{-11} ^c
Benzo(a)pyrene	252	179	496	7.2×10^{-12} ^a
Benzo(e)pyrene	252	179	493	7.2×10^{-12} ^a
Indeno(c,d)pyrene	275	-	534	-
Benzo(g,h,i)perylene	276	273	542	1.3×10^{-13} ^a
Coronene	300	438	590	1.9×10^{-15} ^a

a - Santodonato et al (1981)

b - Grimmer (1983)

c - Calculated from Mackay et al (1982)

TABLE-2
FINAL FACTOR ANALYSIS MODEL - ELIZABETH
(ROTATED FACTOR LOADINGS ≥ 0.60)

	<u>FACTOR 1</u>	<u>FACTOR 2</u>	<u>FACTOR 3</u>	<u>FACTOR 4</u>
BkF	0.79			
BaP	0.67			
BghiP		0.67		
ICDP			0.83	
Cor		0.84		
BeP				0.92
BjF	0.93			
BbF	0.72			

N=112

TABLE-3
FINAL FACTOR ANALYSIS MODEL-CAMDEN
(ROTATED FACTOR LOADINGS, ≥ 0.60)

	<u>FACTOR 1</u>	<u>FACTOR 2</u>	<u>FACTOR 3</u>	<u>FACTOR 4</u>
BkF	0.85			
BaP	0.87			
BghiP	0.61	0.67		
ICDP				0.60
Cor		0.83		
BeP			0.94	
BjF	0.89			
BbF	0.83			

N=79

TABLE-4
FINAL FACTOR ANALYSIS MODEL-NEWARK
(ROTATED FACTOR LOADINGS, ≥ 0.60)

	<u>FACTOR 1</u>	<u>FACTOR 2</u>	<u>FACTOR 3</u>
BkF	0.91		
BaP	0.91		
BghiP	0.76	0.55	
ICDP	0.83		
Cor		0.93	
BeP			0.90
BjF	0.92		
BbF	0.88		

N=83

Figures

Figure 1 - Principle component biplot - Elizabeth

Figure 2 - Principle component biplot - Camden
a. without outlier removal
b. with outlier removal

Figure 3 - Principle component biplot - Newark

Key for Figures

- 1 - Benzo(k)fluoranthene
- 2 - Benzo(j)fluoranthene
- 3 - Benzo(b)fluoranthene
- 4 - Benzo(a)pyrene
- 5 - Benzo(e)pyrene
- 6 - Indeno(1,2,3-cd)pyrene
- 7 - Benzo(g,h,i)perylene
- 8 - Coronene

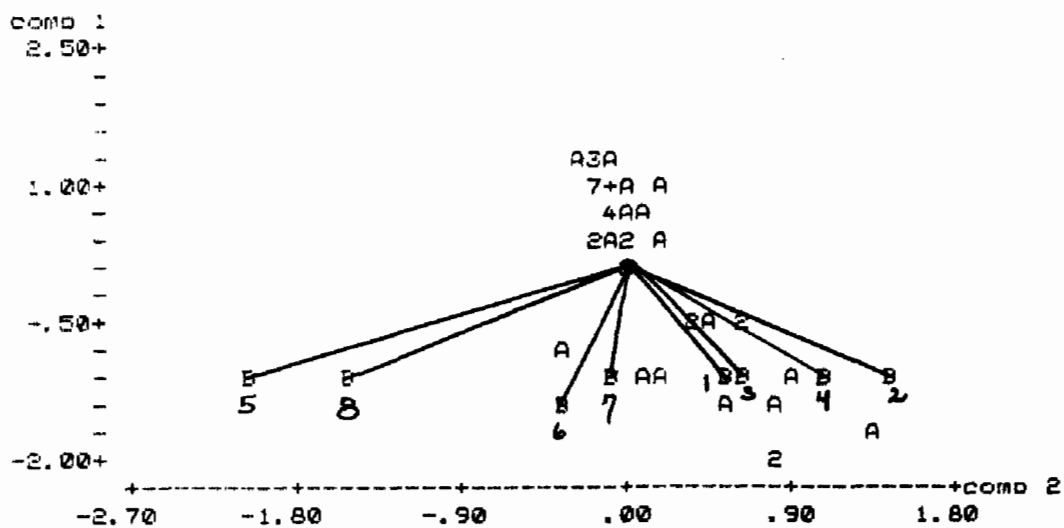


Figure 1

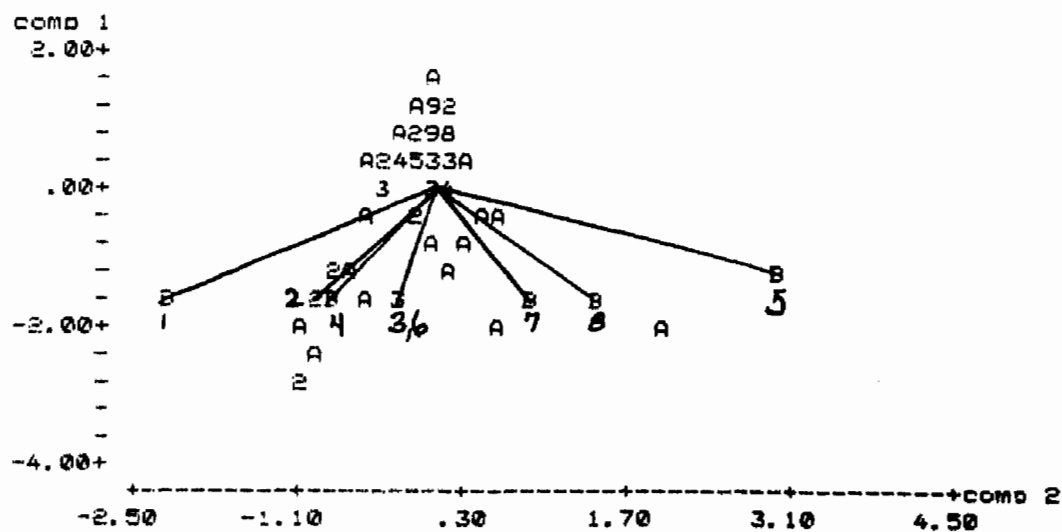
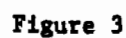


Figure 2a



**Use of a Rule-Building Expert System for Classifying
Single Particles Based on SEM Analysis**

P.K. Hopke and D.S. Kim
Institute for Environmental Studies
University of Illinois at Urbana-Champaign
1005 W. Western Avenue, Urbana, IL 61801
and
R. Lee and G.S. Casuccio
Energy Technology Consultants
350 Hochberg Road, Monroeville, PA 15146



Computer-controlled scanning electron microscopy (CCSEM) permits the characterization of size, shape, and composition of individual particles and thus provides a rich source of data to identify the origin of ambient airborne particles. The problem is how to make best use of this information. The general procedure has been to assign each particle to a class of similar particles based on its x-ray fluorescence spectrum. The initial efforts developed the class characteristics and classification rules in an empirical fashion. Recent studies have suggested that greater specificity and precision in the subsequent class balance analysis can be obtained if particle classes are more homogeneous. To obtain the classification of large numbers of particles in an efficient manner, the x-ray intensity data have been subjected to an agglomerative hierarchical cluster analysis. The resulting groups of samples are then used as candidate examples for a rule-building expert system that provides a decision tree that can be used for subsequent particle classification. An error analysis approach based on jackknifing has also been developed. The use of this approach to characterize particle source emissions will be presented.

Introduction

Receptor modeling generally apportions airborne particulate matter to sources through various statistical methods based on the bulk chemical analysis of ambient samples. These methods have been important tools for particulate control strategy over the past 15 years. Among these techniques, the Chemical Mass Balance (CMB) has been known as a conceptually powerful technique. However, it cannot be implemented until accurate source profiles are available. In practice, a CMB analysis loses power when the sources of particulate matter have similar compositions. This limitation can be solved by measuring additional variables to obtain distinct differences among the source profiles.

Microscopic methods have been used to characterize individual particles and to identify sources of ambient aerosol mass. Recently, innovative computer-controlled scanning electron microscopy (CCSEM) has provided individual particle information, including size parameters and chemical compositions within a short analysis time so that a large number of particles can be analyzed. A particle class balance (PCB), analogous to CMB, is the combination of the statistical and the microscopic methods and assumes a linearly additive sum of class mass fractions times a fractional contribution of aerosol mass by the particulate sources. Johnson and McIntyre¹ used this technique for aerosol apportionment study in Syracuse, N.Y. They used twelve source types from 47 possible source signatures and fitted to the 23 ambient samples measured. To do this, they created only 25 separate classes of particles based on the observed relative net x-ray intensities. As they mentioned, there is a possibility of overlap among 25 particle classes when comparing signatures of similar sources. Casuccio and Janocko² also suggested a particle balance model based on the segregation of the source and the ambient samples into classes within various aerodynamic size categories.

The most important thing in the PCB model is to create homogeneous particle classes to characterize the source profiles. To define the particle class membership, an agglomerative hierarchical clustering analysis was used to determine the potential class membership. Then chemically homogeneous particle classes were created using a rule-building expert system by removing outliers from each particle class. The mass fraction of particles belonging to these homogeneous particle classes can then be used as the source profile.

El Paso Airshed

The City of El Paso is located at the tip of western Texas, with the state of New Mexico to the west. There are problems of noncompliance with both the TSP and lead ambient air quality standards³. The Rio Grande River flows south of the city, which is the boundary between the United States and Mexico. The city of Ciudad Juarez lies just to the south in Mexico across the river. El Paso also has the Franklin Mountains intruding from the north.

CCSEM was selected as the primary analytical method to study source and ambient particle samples. Several other methods, including proton-induced x-ray emission, ion chromatography, and atomic absorption were used to verify the CCSEM results. Each source or ambient sample had more than 700 particles analyzed and each particle is characterized by 25 variables; 6 size variables and 19 x-ray intensities. Twenty-one source samples were used to obtain source composition profiles. More

detailed descriptions for analytical methods are available in the literature^{4,5}.

Cluster Analysis

The basic concept of classification is to identify the objects (cases) that are similar in a pattern space based on a measure of dissimilarity or distance. The agglomerative hierarchical algorithm, AGCLUS⁶, was selected for the classification of the CCSEM data since the hierarchical method is simple in terms of computational scheme, and is flexible in terms of decision of significant clusters when comparing it with non-hierarchical methods. The agglomerative method starts from the individual objects in separate clusters and ends with a single cluster containing all of the objects. Larger clusters are constructed by merging smaller clusters. This method requires that once an assignment of objects to a cluster is made, those objects will remain together at higher and higher clustering levels. Hierarchical clustering is represented in the form of tree-shaped dendrograms. Non-hierarchical clustering was used to confirm the agglomerative analyses⁷.

It is then necessary to define a "homogeneous" particle class. A class is determined to be homogeneous by examining the presence or absence of the related chemical elements for all particles. When all particles in a class show only the same elements, this class is referred to as homogeneous. A particle in Al-Si-Fe class will show only Al, Si, and Fe x-ray intensities. In the sense of this concept, all particles initially clustered together from cluster analysis can be examined, and thus it is possible to remove outlier particles for each class.

Expert System as a Classification Tool

A knowledge-based expert system, a class of high performance computer programs in the area of artificial intelligence, was used to build a decision tree from examples of particle classes following classification studies. EX-TRAN⁸ is a series of programs designed to generate a set of rules based on examples for which various variables are known and which have known outcomes. It produces a self-contained FORTRAN program that can implement these rules. EX-TRAN searches the features one at a time to identify the one for which it can "best" separate one class from the others based on an extension of Quinlan's ID3 algorithm⁹.

To perform this study, "representative" examples were obtained from the homogeneous particle classes. From the AGCLUS cluster analysis, each data set representing one of source samples was split into 23 to 67 homogeneous particle classes. A total of 11,294 (73%) out of 15,499 particles were placed into one of the homogeneous classes so that they could be used as examples for expert system implementation. Table I shows the total number of particles, the total number of particles placed in homogeneous classes, and the number of homogeneous classes for each source data set.

In order to create a classification rule from the expert system, the 283 homogeneous particle classes from the 21 source data set were created after deleting outlier particles. Table II shows only a portion of the homogeneous classes, those which are all the sodium containing particle classes observed in the individual source samples. As can be seen, some classes were unique, i.e., observed in only a particular source, and other classes were observed in two or more sources. Among the whole 283

classes, some classes such as Na-Al-Si-Ca, Mg-Al-Si-Ca, Mg-Si-Ca, Al-Si-K, Al-Si-K-Ca, etc. were frequently observed in more than 12 sources. Particularly, the Al-Si-K class was the most commonly observed class in 17 out of the 21 source samples.

The derived rules were extensively tested by examining all 15,499 particles of source samples. Only two (0.01%) out of the total particles were misclassified. These misclassifications occurred when the number of representative examples in a class was much less than that of the active variables. During the test of the decision rule, it was found that the classification rules could also detect the misclassification of the hierarchical cluster analysis, AGCLUS. In the sample T240 from Table I, 501 particles were assigned to homogeneous classes. However, three unassigned particles were revealed to belong to one of the homogeneous classes. In this manner, the total 48 particles from the 21 source samples were misclassified by the hierarchical cluster analysis. The misclassified examples were reassigned to homogeneous particle classes and the information for each class was corrected.

Mass fractions for each source sample were calculated. The full set of source profiles are available on request from the authors. A simple correlation study showed that profiles for the 21 sources were highly independent of each other, even for the 7 fugitive soil samples. An ambient aerosol mass apportionment study will be performed using these source profiles.

The uncertainties of each class for all the source samples were calculated. The jackknife approach has been applied in order to estimate the uncertainties in the mass fractions. One data point at a time is omitted for all the data points, and the mass fraction is then determined. From the standard deviation of these values an uncertainty is estimated. The method can give a measure of variability regardless of its distribution function¹⁰. Tukey's jackknife estimate of standard error¹¹ was used to estimate the uncertainty of mass fraction in each class.

Generally, as the number of particles in a certain class increased, the uncertainty decreased. For a class containing one or two particles, 100% of mass fraction was used arbitrarily since the method of omitting one data point cannot be applied. The determination of uncertainty is essential in the sense of providing credibility of each class membership.

Conclusion

Twenty-one source samples from the El Paso Quantitative Microscopy Study were explored to define the homogeneous particle classes. Following cluster analysis, 283 classes were created after deleting outliers. A decision rule was developed by an expert system and used to check and correct particle membership. A PCB can give increased source resolution over that available with bulk chemical data since there are many more variables available. It reduces the possibility of collinearity problems.

Acknowledgements

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Table I. Source Characterization Results for the El Paso Classification Study

Sample ID	Description	No. of Particles	No. of Classified Particles	No. of Classes
T219	UTEP (soil near monitor)	735	622	31
T220	American Minerals Sample (Mn Smelter)	735	438	52
T221	Highway Emission (San Antonio)	735	401	40
T234	El Paso Rock Quarry	735	651	34
T235	ASARCO Zinc Baghouse	735	595	48
T236	ASARCO Copper Reverberatory Furnace	720	471	47
T237	ASARCO Converter Baghouse	735	378	53
T238	ASARCO Zinc Plant Baghouse	735	586	23
T239	IB & MC (near monitor)	735	621	43
T240	ASARCO Lead Blast Furnace	735	501	33
T242	Dirt Road, Azacate/Valencia	735	608	41
T248	Parkers Brothers (Slag Crushing Operation)	735	584	43
T256	Dixie Ethyl Refinery (old gas refinery)	750	610	41
T263	ASARCO Coke Storage Hoppers	750	453	67
T264	ASARCO Sinter Plant (front)	750	431	60
T266	Newell Salvage (salvage yard)	750	578	59
T268	IB & MC (near monitor)	735	619	38
T270	ASARCO Sinter Plant	750	432	60
T271	ASARCO Lead Sinter Plant	750	453	62
T272	Phelps Dodge (copper refinery)	709	615	31
T273	Southwest Portland Cement	750	647	33
Total		15,499	11,294	949

Table II. Sodium containing homogeneous particle classes and those number of particles for each source.

Na-Mg-Al-Si- S-Fe	t265(3)
Na-Mg-Al-Si- K-Ca-Fe	t242(2) t268(5)
Na-Mg-Al-Si-Ca	t239(8) t242(4) t268(2)
Na-Mg-Si- S- K	t263(4)
Na-Mg-Si- K-Ca	t234(2)
Na-Mg-Si-Ca	t219(4) t234(2) t239(4) t242(2)
Na-Mg-Si-Ca-Pb	t270(2)
Na-Mg-Si-Pb	t263(4) t264(7) t270(8) t271(11)
Na-Mg-Ca	t234(8)
Na-Mg-Pb	t264(5) t270(7) t271(8)
Na-Al-Si	t219(7) t220(5) t239(10) t242(6) t248(4) t256(6)
	t268(9) t272(10)
Na-Al-Si- S	t266(8)
Na-Al-Si- S- K-Fe	t266(4)
Na-Al-Si- S-Ca	t221(7) t266(2)
Na-Al-Si- S-Ca-Fe	t266(5)
Na-Al-Si- S-Fe	t266(6)
Na-Al-Si- K	t219(4) t220(5) t221(2) t234(9) t239(11) t242(13)
	t248(4) t256(8) t266(7) t268(9) t272(14)
Na-Al-Si- K-Ca	t219(7) t239(11) t242(6) t256(4) t268(8) t272(4)
	t273(5)
Na-Al-Si- K-Ca-Fe	t221(3) t239(7) t242(7) t248(4) t268(3) t272(6)
Na-Al-Si- K-Fe	t221(5) t239(10) t242(7) t256(8) t268(3) t272(3)
Na-Al-Si-Ca	t219(19) t220(4) t221(4) t234(6) t239(16) t242(15)
	t248(6) t256(3) t266(4) t268(13) t272(15) t273(8)
Na-Al-Si-Ca-Fe	t219(3) t239(4) t242(2) t248(3) t256(5) t273(4)
Na-Al-Si-Fe	t239(6) t256(5) t266(2)
Na-Al-Si-Fe-Mn	t220(3)
Na-Al-Si-Pb	t221(3) t271(5)
Na-Si- S	t236(6) t263(4)
Na-Si- S- K-Ca	t270(4)
Na-Si- S-Ca	t242(3) t256(4) t263(4) t266(6) t272(3)
Na-Si- K-Ca	t234(2)
Na-Si- K-Pb	t235(5) t270(3)
Na-Si-Ca	t219(12) t221(4) t234(17) t239(15) t256(2) t272(4)
	t273(4)
Na-Si-Ca-Fe	t248(9)
Na-Si-Ca-Fe-Mn	t220(3)
Na-Si-Fe-Mn	t220(5)
Na-Si-Pb	t236(5) t237(4) t263(7) t264(4) t266(3) t270(10)
	t271(10)
Na- S-Ca	t263(10) t266(10) t271(5)
Na- S-Fe	t263(2)
Na- K-Pb	t235(8)
Na-Fe-Mn	t220(2)
Na-Fe-Pb	t263(2)

A COMPOSITE RECEPTOR METHOD APPLIED TO PHILADELPHIA AEROSOL

Thomas G. Dzubay and Robert K. Stevens
Atmospheric Sciences Research Laboratory
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

Glen E. Gordon, Ilhan Olmez*, and Ann E. Sheffield
Department of Chemistry and Biochemistry
University of Maryland, College Park, MD 20742

William J. Courtney**
Northrop Services Inc., Research Triangle Park, NC 27709



A new receptor method that is a composite of chemical mass balances (CMB), multiple linear regression, and wind trajectory receptor models was developed to apportion particulate mass into source categories. It was applied to 156 aerosol samples collected in dichotomous samplers at three sites in the Philadelphia area and analyzed by x-ray fluorescence (XRF), instrumental neutron activation (INAA), ion chromatography (IC) and pyrolysis. Major components of mass of $\leq 10\text{-}\mu\text{m}$ diam particles were 50-55% sulfate plus related water and ions, 16-27% crustal matter, and 4-7% vehicle exhaust. Less than 5% was attributed to primary emissions from stationary sources. Wind-stratified data indicated that $80 \pm 20\%$ of the sulfate was from a regional background. Multiple linear regression attributed 72 ± 8 and $16 \pm 5\%$ of S to coal- and residual oil-fired power plants, respectively.

Introduction

The CMB model is useful for apportioning the mass concentration of suspended particles. However, a difficulty is that the required signatures are not known accurately for sulfate and vehicle exhaust. For sulfate, there is an uncertain amount of water. For vehicle-exhaust, the Pb-abundance is difficult to specify in the United States because measurements are sparse, and the Pb content in gasoline has been declining rapidly in recent years.

We explore the feasibility of using a composite receptor method to overcome this difficulty. It was tested using data from a summer, 1982, study when ambient aerosol was collected for 52 12-h periods in the PM-10 size range at three sites (Figure 1) in the Philadelphia area¹. The ambient samples were collected by dichotomous samplers and analyzed by XRF, INAA, IC and pyrolysis. Emission source and resuspended soil samples were also collected by dichotomous samplers and analyzed^{2,3}.

We present a mass apportionment based on the following steps: (a) Wind-trajectory analysis⁴ was used to identify sources to include in the CMB. (b) A new method consisting of a composite of CMB and multiple linear regression (MLR) was used to determine abundances of Pb in vehicle exhaust and S in regional sulfate. (c) CMB, based in part on results of the composite method, was used to apportion mass into 9 components. (d) Wind-direction stratification was used to detect the relative influences of local and regional sources of S. (e) MLR of S vs Se and V was used to estimate particulate S contributions from coal and oil.

Results and Discussion

Precision and Accuracy. Table I shows correlation coefficients and a comparison of mean values obtained by XRF, IC and INAA. The paired data are highly correlated, and the ratios of means agree within overall errors for S, Mn, Fe, Zn, and Sb. The agreement between IC and XRF results for S indicate that sulfate, the species measured by IC, occurred as S.

Wind-Trajectory Method. We used a wind trajectory method⁴ to select sources to include in our CMB. Resultant wind direction θ and standard deviation $\delta\theta$ were computed for each 12-h period from hourly data on surface winds. Also, the mean concentration \bar{x} and standard deviation s were calculated for each species. The wind-trajectory method selected events having $\theta \leq 20^\circ$ and $x \geq \bar{x} + 2s$. Emission sources were identified when element abundance ratios matched those in source signatures². Sources selected were a paint pigment plant and a Sb roaster, both south southwest of Site 28, and municipal incinerators northwest of Site 28. Also selected were residual oil-burning and catalytic cracker emissions².

Composite of CMB and MLR. In a study in Denver during winter, Levis et al. used MLR to determine abundances of elements in vehicle exhaust, wood smoke, sulfate, and crustal matter⁵. Because atmospheric K, their tracer for wood smoke, included a contribution from soil, they used the measured K concentration minus a correction for soil as a wood-smoke tracer. We applied a modified form of that technique to Philadelphia aerosol. Modification was needed for Pb from vehicle exhaust because a significant portion of Pb originated from at least two additional sources: incinerators and combustion of residual oil. In our method, non-vehicular Pb was determined by CMB and was subtracted from the measured Pb to yield a tracer for vehicle exhaust.

The CMB method expresses concentration C_i of species i as

$$C_i = \sum_j A_{ij} M_j, \quad (1)$$

where A_{ij} is the abundance of species i in component j , and M_j is the total mass concentration attributed to component j . The unknown values M_j are found by a least-squares method that minimizes the expression⁶,

$$\chi^2 = \sum_j [(C_i - O_i)/E_i]^2 \quad (2)$$

where O_i is the observed concentration of species i , and E_i^2 is the effective variance, which includes the uncertainties in O_i and A_{ij} .

For each species i in eq 2, two criteria must be met: (a) all major sources j of the species must be included in eq 1, and (b) its abundance in each component must be known. For our data these criteria were met for a fine-particle CMB based on Al, Si, Ca, Ti, V, Ni, Zn, Cd, Sn, Sb, La, Ce and Sm in the following six components: municipal incinerators², catalytic crackers², residual oil combustion², Sb roaster², paint pigment manufacturing⁴, and local dust³. Using these 13 elements and 6 source we applied the CMB model to data for each 12-h sampling period to obtain 156 sets of M_j . Then, for mass, S and Pb we calculated O_i' as

$$O_i' = O_i - \sum_j A_{ij} M_j \quad (3)$$

where O_i' represents $[M']$, $[S']$, and $[Pb']$ which are the portions of observed concentrations due only to vehicle exhaust and sulfate. We applied MLR to all 156 observations and obtained $R = 0.95$ (multiple correlation) and

$$[M'] = 3592 \pm 775 \text{ ng/m}^3 + (4.92 \pm 0.13)[S'] + (15.0 \pm 3.2)[Pb'] \quad (4)$$

We interpret the reciprocal of regression coefficient of $[S']$ in eq 4 as the abundance of S in the regional sulfate component, $20.3 \pm 1.4\%$. Water retained on acidic sulfate particles during laboratory mass analysis may explain S abundances lower than 24.2% and 26.1%, for S in pure $(NH_4)_2SO_4$ and NH_4HSO_4 , respectively. Likewise, eq 4 indicates a $6.7 \pm 1.5\%$ abundance of Pb in vehicle exhaust. This falls within the range of results obtained by other investigators: 6.9% for a Pennsylvania Turnpike tunnel during 1977⁷, and $4.4 \pm 0.6\%$ for Denver during winter, 1982⁵.

Mass Apportionment. Fine particle mass was apportioned by CMB into 8 components as in Table II. In addition to the 6 components used in the preliminary CMB, vehicle exhaust and regional sulfate were included. For vehicle exhaust, the Pb abundance of $6.7 \pm 1.5\%$ was derived from eq 4. Abundances of other elements in vehicle exhaust (S, Cr, Mn, Fe, Ni and Br) were taken from Pennsylvania Turnpike tunnel data⁷ adjusted for the vehicle mix in Philadelphia. The regional sulfate component included the $20.4 \pm 1.4\%$ S-abundance derived from eq 4. Concentrations of other elements were from the regional sulfate signature of ref 8 normalized to our S value.

Except for Cl, Br, As and Se, the measured and calculated element concentrations agree fairly well. The model overestimated Cl and Br values because it does not account for losses by volatilization. The regional sulfate component represents most of the calculated As and Se, but the signature derived from Shennandoah Valley data⁸ appears not exactly to represent As and Se Philadelphia. Deviations for such elements has little effect on our apportionment of mass.

We applied CMB as in Table II to each sample. Averages for each site were computed and are shown in Table III. Also indicated are estimates of possible bias due to uncertain abundances of key elements in the source signatures. Results for the dust signature are labeled "minerals and coal fly ash" in Table III because such subcomponents were not resolved. The dust signature³ that we used is a preliminary one, and, therefore, a large value of possible bias is shown in Table III. The component labeled "other" is the intercept in eq 4 and may represent components not included in the CMB.

The coarse fraction CMB results are based on five components shown in Table III. Because, we did not constrain our CMB solutions to positive values, negative values below detection limit were sometimes obtained as coarse particle results in Table III indicate.

Sources of Particulate Sulfur. Average species concentrations were calculated for cases of steady wind from NNE and SSW along our line of samplers. Sampling periods were included if data were available for both Sites 12 and 34 and if at least 75% of the hourly wind directions were in the SSW (165° to 255°) or NNE (245° to 75°) quadrants. The ratio of average upwind to downwind S-concentrations for Sites 12 and 34 was 0.80 ± 0.18 . Because Sites 12 and 34 are at the edges of the Philadelphia urban area, such ratios suggest that local sources contribute about 20% of the particulate S and sources beyond the Philadelphia area contribute 80%. In an earlier study, local and regional components were deduced from sulfate measured at 45 stations in eastern U. S. between 1963 and 1978⁹. Early in that period, local sources contributed 45% of total sulfate during summer months. By 1978 the local component had decreased to 25% due to controls on S emissions applied mainly in urban areas⁹.

Emission inventories for Eastern states indicate that about 90% of the SO_2 , the precursor for particulate S, is emitted from coal- and residual oil-fired power plants. Assuming that Se and V are tracers for coal- and residual oil-fired power plants, respectively, we used MLR to express fine particle S as

$$[S] = 380 \pm 355 \text{ ng/m}^3 + (1791 \pm 201)[\text{Se}] + (67 \pm 21)[V] \quad (5)$$

Multiple correlations were $R = 0.67$ for 156 samples. Because S is emitted mainly as SO_2 , atmospheric reactions are required to produce particulate S. Variability in the fraction of SO_2 converted to SO_4^{2-} could account for correlations that are only moderately high. Results obtained by dividing the mean of each term in eq 5 by the mean fine particle S concentration indicate that the particulate S-contributions from coal- and oil-fired power plants are $72 \pm 8\%$ and $16 \pm 5\%$, respectively.

Summary

The composite method was a valuable supplement to the CMB model for analyzing the Philadelphia data set. The composite method enabled us to estimate the average Pb abundance in vehicle exhaust when incinerators and residual oil combustion contributed a portion of the Pb. The combined use of XRF and INAA enabled us to resolve more sources than possible if only one of those methods were used. The former provided essential data on Si, S, Ni, and Pb; the latter provided essential data on Al, V, Se, La, Cs, and Sm. The wind-trajectory method identified four categories of stationary sources to include in the CMB. Interpretations reported here are a few of the possibilities other investigators may attempt. One may obtain our data on IBM-PC readable disks by sending one 1.2-Mbyte or two 360-kbyte floppy disks to the principal author.

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*Present address: Massachusetts Institute of Technology, Cambridge, MA

**Present address: International Business Machines Corporation, Dallas, TX

Table I. Comparison of XRF, INAA, and IC Results for 50 Paired Fine Particle Samples from Camden, NJ (Site 28) between July 14 and August 13, 1982^a.

	XRF mean ng/m ³		Other mean Results ng/m ³	Ratio of means (XRF/other)	R
S	4063 ± 20	IC	3719 ± 70	1.09 ± 0.09	0.97
S	4196 ± 20	INAA	3863 ± 900	1.09 ± 0.14	0.92
K	101 ± 3	INAA	144 ± <15	0.70 ± 0.10	0.94
Ca	40 ± 5	INAA	49 ± 18	0.81 ± 0.11	0.65
V	19 ± 4	INAA	13 ± <1	1.43 ± 0.18	0.86
Mn	6 ± 2.3	INAA	6 ± <0.6	1.09 ± 0.15	0.72
Fe	91 ± 3	INAA	94 ± <10	0.97 ± 0.12	0.89
Zn	82 ± 1.5	INAA	92 ± <9	0.89 ± 0.11	0.997
Se	1.2 ± 0.6	INAA	1.8 ± <0.2	0.67 ± 0.10	0.70
Br	29 ± 0.8	INAA	23 ± <2	1.27 ± 0.16	0.97
Sb	73 ± 5	INAA	79 ± <8	0.93 ± 0.11	0.998

Table II. Mass Balance of Average Fine Particle Composition at (Site 28)^a

	Calculated	Meas- ured.	Dust	Res. Oil	Paint Pig.	Cat. Crack.	Munic. Incin.	Veh. Exh.	Sb- Roast	Regional S
V-C	1027 ± 1128	2046	67	15	0	1	4	939	1	0
NV-C	1153 ± 584	1867	10	29	0	0	25	1089	0	0
Na	94 ± 30	146	12	21	0	1	44	16	0	0
Al b	46 ± 10	53	23	5	2	14	2	0	0	0
Si b	137 ± 32	103	65	16	0	43	12	0	0	0
S b	4197 ± 403	4196	1	87	0	27	21	47	1	4012
Cl	224 ± 33	3	1	0	0	0	194	30	0	0
K	63 ± 18	101	6	1	2	0	54	0	0	0
Ca b	38 ± 8	40	12	20	4	0	2	0	0	0
Ti b	17 ± 9	15	2	1	13	1	0	0	0	0
V b	11 ± 3	13	0	11	0	0	0	0	0	0
Mn	4 ± 1	6	1	0	0	0	0	1	0	2
Fe	122 ± 11	91	92	11	9	0	2	8	0	0
Co*	684 ± 141	483	11	669	0	3	2	0	0	0
Ni b	13 ± 3	11	0	12	0	0	0	0	0	0
Zn b	83 ± 18	82	1	7	0	0	70	3	0	1
Br	69 ± 35	29	0	0	1	0	2	67	0	0
As*	209 ± 219	632	0	30	0	0	47	0	0	132
Se*	954 ± 233	1800	67	14	0	2	29	0	0	842
Mo*	645 ± 396	900	1	372	0	0	272	0	0	0
Cd	2 ± 1	2	1	0	0	0	1	0	0	0
Sn b	6 ± 4	5	0	0	0	0	5	0	1	0
Sb b	79 ± 9	79	0	0	0	0	1	0	77	0
La*	871 ± 187	1120	13	195	0	662	1	0	0	0
Ce* b	712 ± 160	609	26	152	0	534	0	0	0	0
Sm* b	45 ± 9	40	3	8	0	34	0	0	0	0
Pb b	249 ± 62	249	3	10	0	0	42	179	0	14
Mass	24910	28282	742	723	59	214	717	2683	104	19668

^aAn asterisk (*) denotes data in pg/m³; all other data are in ng/m³.

^bElements included in least-squares fit.

Table III. Average Mass Balance for July 14 to August 13, 1982, Deduced by Composite of CMB and MLR Methods.

Component	Size Fraction	Site 12	Site 28	Site 34	Possible Bias, %
Minerals and coal fly ash	fine	1066	751 ± 36	597	40
Residual oil fly ash	fine	489	685 ± 20	427	30
Ti-rich paint pigment	fine	40	54 ± 6	4	30
Fluidized catalyst cracker	fine	144	199 ± 6	96	30
Municipal incinerators	fine	503	651 ± 31	190	30
Antimony roaster	fine	4	94 ± 3	2	10
Motor vehicle exhaust	fine	2388	2757 ± 163	1511	20
Sulfate, cations and water	fine	18635	19396 ± 318	18537	10
Other (MLR intercept)	fine	3592	3592 ± 775	3592	
Minerals and coal fly ash	coarse	7264	9033 ± 192	4730	40
Marine	coarse	160	228 ± 26	113	50
Sulfate	coarse	440	595 ± 67	718	30
Municipal incinerators	coarse	54	-38 ± 26	-42	50
Antimony roaster	coarse	15	231 ± 14	7	10
Calculated total	fine	26862	28179 ± 855	24958	
Calculated total	coarse	7934	10048 ± 207	5527	
Calculated total	PM-10	34796	38227	30485	
Measured total	PM-10	34868	39715	33858	

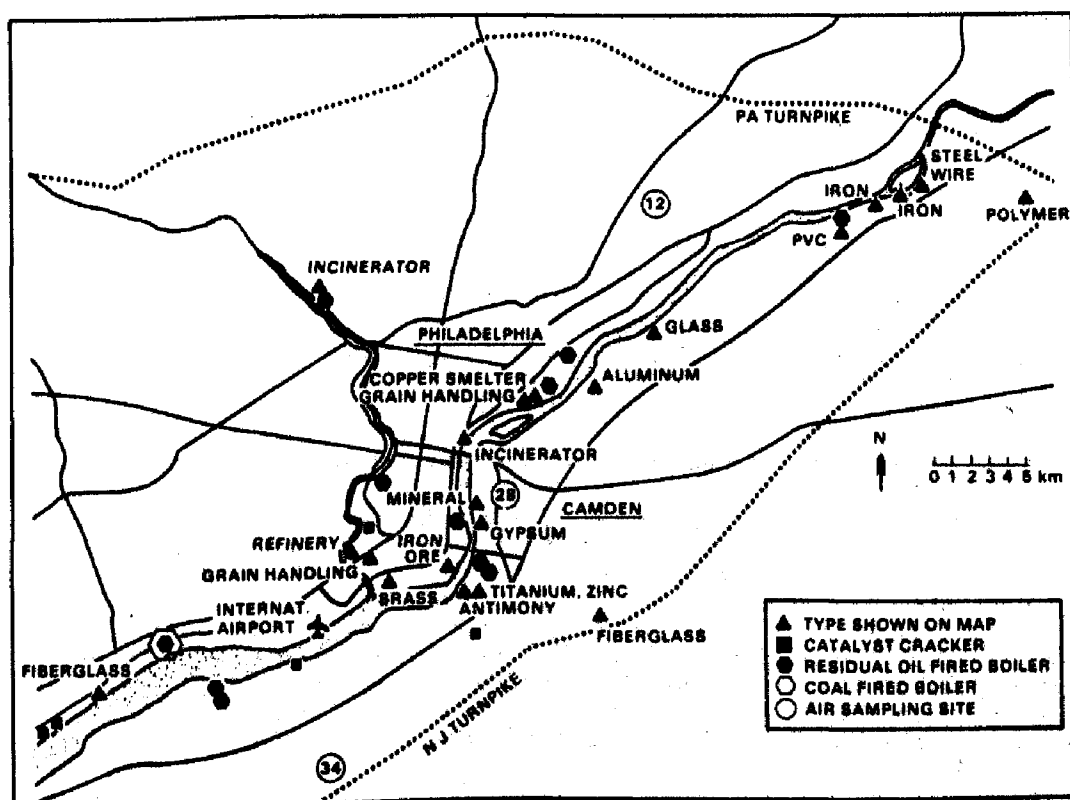


Figure 1. Map showing sampling site locations and point sources having particle emission rates above 50 Hg/y.

DIFFICULTIES AND EFFICIENCIES ENCOUNTERED WITH A
BULK-AIR SAMPLING SCHEME FOR CHARACTERIZING
HEAVY GAS RELEASES OVER A GRASS-COVERED SITE

Glen A. Marotz Department of Physics
 and Astronomy
 University of Kansas
 Lawrence, KS 66045

Dennis D. Lane Department of Civil
 Engineering
 University of Kansas
 Lawrence, KS 66045

Ray E. Carter, Jr. Department of Civil
 Engineering
 University of Kansas
 Lawrence, KS 66045

Richard Tripp U.S. Environmental
 Protection Agency
 Region VII, 25 Funston Rd
 Kansas City, KS 66115

John Helvig U.S. Environmental Protection Agency
 Region VII, 25 Funston Rd
 Kansas City, KS 66115



Assessing atmospheric composition using most currently available techniques is often difficult and time consuming. Difficulties work against detection and determination of possible toxic gas signatures from industrial processes, landfills and other release situations. Time constraints mitigate against rapid response in actually or potentially dangerous circumstances. Recent work has shown that a bulk air technique can be used to gather and characterize ambient air samples relatively rapidly. When coupled with cryogenic-focused GC analysis, qualitative and quantitative data can be obtained. An approach to characterization of heavy gas releases using a combination of the whole-air technique, portable meteorological equipment coupled with a fixed sampling network, and modeling was formulated and evaluated on a grass-covered site over a six month period. In previous work, preliminary results from two sample runs were described in which downwind surface concentrations of two heavy gases were assessed (volatilized toluene and methyl chloroform emitted at a fixed rate over short time periods). In this paper, the analysis approach is extended to data from two additional sample runs that were conducted under different meteorological conditions. The goal is to further evaluate the three-part approach as a rapidly deployable scheme for assessing toxic gas releases.

Key Words: Heavy Gas, Whole Air Sampling, Field Data, Toluene, Methyl Chloroform

INTRODUCTION

Characterization of potentially harmful gaseous releases from industrial activities, or accidental emissions, require a timely response by organizations with public health responsibilities. The species must be known or identifiable, and some judgements about spatial and temporal patterns must be made in the shortest time period practicable. The problem becomes more difficult if the gases released have known acute or toxic effects; yet another layer of complexity is added if the emissions are heavier than air. While trace gas releases can be modeled using approaches based upon generally accepted characterizations of the turbulent structure of the atmosphere, heavier than air gases (HTAG) pose an additional problem because they modify atmospheric flow characteristics for a period of time. Few approaches are established for dealing with HTAG situations.

We have conducted evaluations of a possible set of sampling procedures based on results from controlled HTAG releases. This set consists of a gaseous analysis technique that utilizes whole-air sampling and cryogenic-focused gas chromatography (GC), and possible applications of two HTAG models for temporal and spatial release description. The results to this point are summarized, and then the approach is extended to a second set of release conditions and sampling/analysis/modeling evaluations.

PRIOR WORK

Lane, et al.¹, Pfiel and McClenny², and Tripp³ have shown that whole-air sampling (based on stainless steel spheres) and cryogenic-focused GC analysis yields accurate and precise characterization of ambient volatile organic compound (VOC) releases. Marotz, et al.⁴ hereafter referred to as MLCTH) used the whole-air sampling/GC analysis technique, combined it with a meteorological instrument package and a fixed-grid sampling network, and conducted field evaluations of the approach using a known HTAG source composition and release rate. Gases used were toluene and methyl chloroform in a 50/50 liquid mixture by volume. Volatilized emissions were produced from a generator designed to operate at different emission rates. The emission rate was varied between 110 and 200 ml min⁻¹ for a series of eleven evaluation runs of 30 minutes each spread over a six month period (July through December, 1986) at a short-grass-covered site in eastern Kansas.

Meteorological and source strength/composition data from two of the eleven test cases were used as input for HTAG model runs, which formed the third part of the approach evaluated in MLCTH. Model output was briefly compared with values obtained from the bulk-air sampling technique.

Based on preliminary analysis of principally surface-collected samples and model runs, MLCTH concluded that, overall, the approach yielded relatively quick and precise results. Questions relative to extension of the approach to a different set of meteorological conditions, the usefulness of multiple spheres arrayed at locations other than the gaseous plume centerline, the capability to model measured concentrations at "breatheable height", and the usefulness of the available models themselves remain open and are partially treated in this paper.

METHODOLOGY

The tripartite approach (whole-air sampler deployment, meteorological instrumentation appropriateness, and modeling of results) was evaluated at a large (approximately 250m by 250m), level, short grass-covered open area situated to the northwest of two principal transportation arterials.

Meteorological instrumentation consisted of the fewest devices necessary for provision of needed model input data. Assessed were wind speed (2m), wind direction (2m), air temperature (1m), surface temperature, relative humidity (2m), and barometric pressure. Additional data included soundings (00/12 GMT) from Topeka, KS (40 km from the study site), upper air (850 mb) and surface synoptic charts.

Available spheres (Demaray Scientific Instrument, Ltd, Model 0647, 6.0L equipped with Whitey Microvalves, Model SS-21RS2) numbered 13, and were positioned on the surface at distances of -25, 50, 75 and 100m from the VOC generator at the intersections of a 30°/60° ray/arc combination (Fig. 1). Ray directional orientation and angle were determined by the plume centerline direction.

Two models were used, CHARMTM (version 4.0) and DEGADIS, to extend field sample-based characterization of the plume. Both have been tested against field data, are written in computer interactive form, and are commercially available. The theory and description for both are presented in MLCTH, Ooms and Tennekes⁵ and Spicer and Havens⁶.

Conditions for Runs 4 and 5 described here are shown on Table 1. Stability conditions in both 4 and 5 were neutral to stable, and synoptic conditions were similar.

RESULTS

Field Data

Surface concentrations ranged from background values to a maximum of 625 and 705 ppb for methyl chloroform and toluene, respectively (Fig. 2a-2d); in both Runs the plume showed the semi-elliptical shape characteristic of HTAG releases⁶. The larger minor axis, higher centerline concentrations in Run 4 versus 5 for both gases appeared to be a function of four factors: (a) wind directional variability, which amounted to about a sixty percent greater standard deviation value in 4 versus 5; (b) average wind speed, which tended to maintain concentration along the centerline; (c) a greater generator emission rate in 5 versus 4; and (d) ambient temperature differences that may have assisted volatilization (Table 1). Both tests occurred under similar stability regimes, and surface heating was not a factor in aiding plume mixing.

Model Runs With Surface Data

Several points are pertinent to the comments in this section. Although model estimates are presented in Table 2, they are meant for general reference only. Neither model's predictive capabilities were evaluated in a proper, complete, and rigorous manner; to do so would have required much more intensive sampling, a different sampler array, additional meteorological information, and many more replications. The sampling network was intended to provide data principally for the whole-air samplers,

not for modeling purposes. The sampling site was large enough for the former objective, but the limited fetch available may have prevented complete adjustment of the wind profile to surface conditions, thereby creating turbulence within the network itself, which could have altered dispersion in an unpredictable manner. Furthermore, the sampling points were all relatively close to the source given the way in which HTAG plumes are gradually modified and disperse.⁶ Indeed, the sampler locations fell within the distance range where concentration values changed most rapidly (eg., in Run 5 observed ppb concentrations for toluene fell 68 percent in 50M; Table 2). Rather, interest was in simply taking a brief look at the role models and modeling might play as part of the approach described in this paper. Experience does suggest that, overall, both HTAG formulation efforts are flexible, sensitive to small changes in input values, and that the potential user has wide latitude in directing the nature of the output product. The user's application needs, knowledge, and experience with a particular model will determine its ultimate value.

The user supplies data on a number of meteorological variables for both models. DEGADIS requires direct input of the stability class, CHARM will allow the same choice, or will estimate stability from cloud cover and solar heating estimates. Stability class choice is significant because all atmospheric mixing conditions are calculated from the stability conditions selected. The user also must know what gas is being emitted in order to either select from a list, substitute one with similar properties, or provide physical constants if the first two options are unavailable. Physical constants were supplied to DEGADIS for both gases, a necessity because the internally supplied values hold only for liquid natural gas.

CHARMTM had toluene on its internally compiled list, but ethylene dichloride was chosen to represent methyl chloroform, because the latter gas was not on the internal list. Finally, the source strength and physical characteristics must be known accurately, or very good estimates must be made.

Several DEGADIS runs were completed using input choices that varied slightly but were based on reasonable judgements about release conditions; the numbers in Table 2 were the lowest we could obtain without compromising the model constraints. Ancillary data suggest that the plume shape is accurately represented, and that concentration gradients are reasonable, although values show consistent over prediction. DEGADIS provides plume half width, deviation values, and other information about the emitted plume, but it does not provide a graphic display.

CHARM yielded predicted values that were closer to observed values near the source generator in Run 4 for both gases; the displayed concentrations were larger than observed past 50m for methyl chloroform (ethylene dichloride). CHARM also produced a graphic output display of plume width and length, along with superimposed, user-chosen concentration isoplethic values. The latter were set at, or close to, observed values at specific points of interest for this paper, but such an approach mitigates against a view of the concentration value range in the entire plume. The smallest diameter area that can be displayed consists of a circle of 0.2 km radius, which forms a background for the predicted plume overlay. Details at one-fourth the latter radius were obtained by requesting specific concentration value locations.

CONCLUSIONS

The results of this paper lead to the following conclusions:

- The whole-air technique based on data collection using stainless steel spheres fitted with microvalves appears to work well; results can be obtained reasonably fast, and produce accurate and precise representations of the release situations.
- The sampling network is easy to set-up and take-down, and the arc/ray/height arrangement possibilities allow much flexibility; the number of samplers and the field arrangement directly effect the time spent in the field data collection phase, and a balance must be subjectively reached between quick response and adequate characterization of the release.
- The meteorological equipment needed to provide model input data need not be complicated or sophisticated; a good continuous visual display of wind speed and directional data is helpful as the sampling network is deployed.
- In order to better address the applicability of models to HTAG releases, more investigation of model approaches to the HTAG problem, the critical information needed for model input, and the appropriate sampling ray all required.

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Table 1. Selected Data for Sample Runs

Variable	Run Number	
	4	5
Date	7-23	11-6
Air T (°C)	29.1	8.6
Surface T (°C)	27.3	7.8
RH (%)	69	80
Pressure (atm)	1.007	1.003
Wind Direction	345	191
°WD	25	15
Wind Speed (m/sec)	1.4	2.5
Start Time (CST)	9:10	9:12
Arc Angle with centerline (°)	30/60	30/60
Emission Rate	110 ml/min	150 ml/min

Table 2

Model Estimated Versus Measured Surface
Concentration Values (ppb) at Centerline Location

Toluene

Location	Run 4			Run 5		
	DEGADIS	Measured	CHARM TM	DEGADIS	Measured	CHARM TM
100 M	3182 ¹	84	>10, 967M ²	2012	225	>200, 74M
75M	5584	150	>100, 195M	3498	371	>300, 55M
50M	12450	321	>300, 84M	7721	705	>700, 34M

Methyl Chloroform³

Location	Run 4			Run 5		
	DEGADIS	Measured	CHARM TM	DEGADIS	Measured	CHARM TM
100 M	3388	70		1874	193	>100, 69M
75M	5960	125		3276	322	>300, 41M
50M	13319	277	>300, 544M	7523	625	>600, 21M

¹ Interpolated ppb values

² A specified concentration value was used as an input to CHARMTM and the linear occurrence of that value along the centerline is indicated in meters

³ Ethylene dichloride was substituted for methyl chloroform in CHARMTM

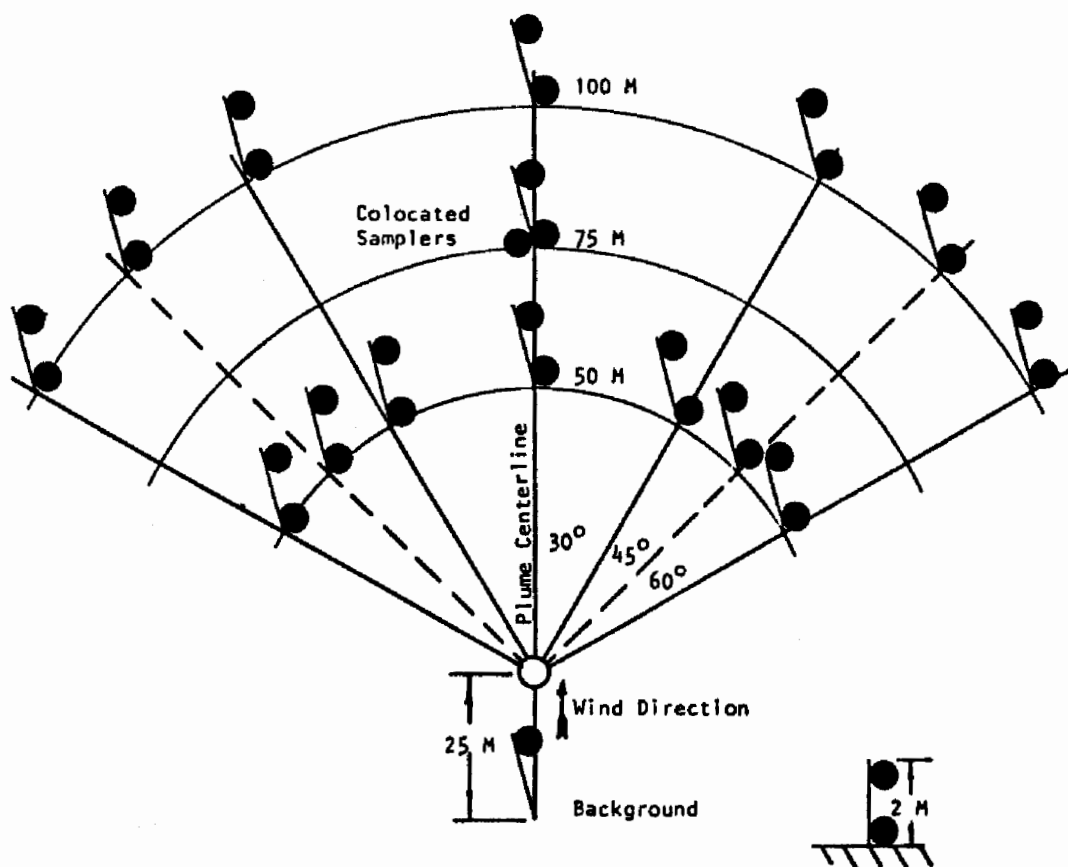


Fig. 1. Schematic Diagram of the Sampling Network

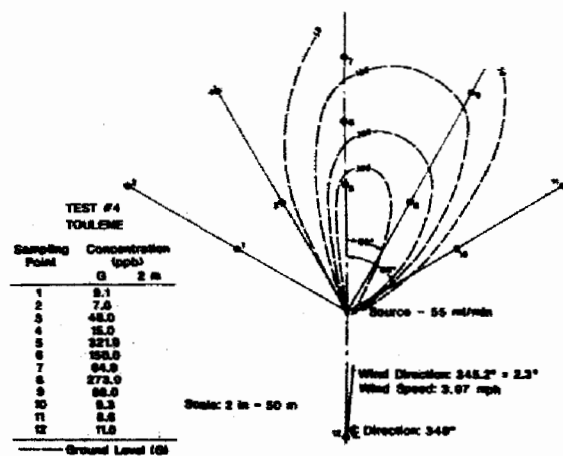


Figure 2 a.

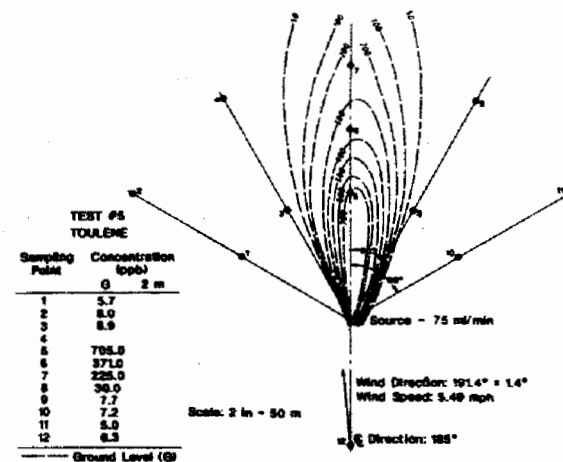


Figure 2 c.

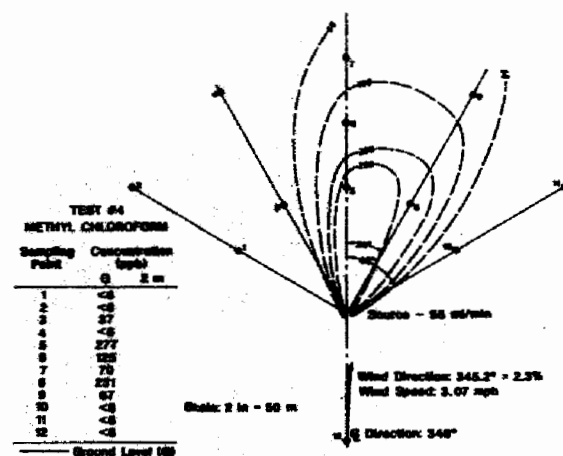


Figure 2 b.

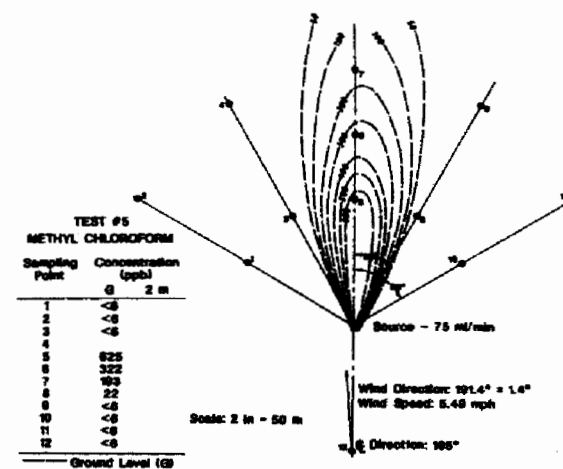


Figure 2 d.

MEASUREMENT, ASSESSMENT AND CONTROL OF HAZARDOUS (TOXIC)
AIR CONTAMINANTS IN LANDFILL GAS EMISSIONS IN WISCONSIN

Julian D. Chazin, Mark Allen and Dennis D. Pippin
Air Monitoring Section
Bureau of Air Management
Wisconsin Department of Natural Resources
Madison, WI 53707



Vinyl chloride, a known human carcinogen, was found to be present in landfill gas (LFG) emitted from almost all closed cells at active landfills or closed landfills which handled municipal waste. Landfills which handled industrial wastes only (including pulp and papermill sludge residues) were free of vinyl chloride in the LFG. The concentrations of vinyl chloride were found to be significant regardless of the type of venting system employed. Benzene, another known human carcinogen, was detected in the LFG of only 3 of 22 landfills studied and at much lower concentrations. Other noncarcinogenic hazardous air contaminants were detected but at emission rates well below those being proposed for regulation under Wisconsin's Air Management rules.

Measurement of the concentrations of vinyl chloride in ambient air adjacent to the landfills was not possible due to limitations in the ambient monitoring procedures used. However, modeling of the emissions from the vents of several active gas extraction systems indicated ambient impacts on adjacent populations to be from 2 to 400 times greater than the ambient exposure levels for vinyl chloride recommended by the Wisconsin's Division of Health. As a result, a change in Wisconsin's rules for land disposal of municipal solid waste is being proposed which would require the collection and combustion (or adsorption on activated charcoal) of hazardous air contaminants in landfill gas. The rule, in the series governing solid wastes and landfills, essentially brings landfills emitting gas under the same requirements as are being proposed for all point sources of toxic air contaminants. The rule requires landfills to essentially meet the requirements of Wisconsin's proposed new air toxics regulations.

INTRODUCTION

Landfill gas, composed predominantly of carbon dioxide and methane, is a byproduct of the decomposition of organic wastes deposited in landfills. In addition to the major fixed gases, other trace gases are released from decomposition of (or directly from) the waste itself (for example, solvents, materials of composition of the waste, hydrogen sulfide in anaerobic decomposition, etc.). Analysis of landfill gas has been undertaken across the nation and reports have been issued on the results of such analysis within Wisconsin as well as from other states.¹

In 1985, the City of Madison Division of Health, responding to concerns of citizens living in the vicinity of its landfills, conducted some tests for trace contaminants in the landfill gas at four landfills utilizing length-of-stain (pull) detector tubes. Due to the indicated presence at some landfills of vinyl chloride, a known human carcinogen, the City of Madison sought the assistance of the Wisconsin DNR. Tests were conducted utilizing Tenax sorbent tubes. Unfortunately, problems were encountered in the lab analyses of the Tenax tubes and no data could be obtained. However, because Tenax does not adsorb vinyl chloride, separate tests utilizing tubes containing activated charcoal were also conducted. The charcoal tube results confirmed the observations made by the City. Following the initial tests, it was decided to do a full-blown analysis of one of the City of Madison landfills as well as a survey of all the landfills in the city. The study was completed and the results indicated a more general problem than was originally believed.

In May, 1983, a Hazardous Emissions Task Force was appointed to provide guidance to the Department on the regulation of "hazardous air emissions" (toxic air pollutants). In July, 1985, they published a report designating specific air contaminants for control and recommending a mechanism to do so.² Soon after, the Bureau of Air Management began to develop regulations based on the recommendations of the task force; the rule development was occurring simultaneously with the conduct of this study.

PHASE I - MONITORING STUDY

Study Design

In response to our request for assistance, DNR's Residuals Management Section of our Bureau of Solid Waste Management submitted a list of possible landfills for a statewide survey of landfills. The (municipal and industrial) landfills selected were: (1) either closed landfills or had closed cells; (2) were known to be generating landfill gas; (3) were within 1/2 mile of homes; and (4) the cells were closed within the last 30 years. The area covered included most of the populated areas of the state.

In addition, a comprehensive study was performed at one landfill in Madison, the Mineral Point Road landfill. A sampling was conducted over a period of five days, with the flow being lowered each day in the stack vent at the tail end of the gas extraction system (by lowering the blower velocity), from a maximum of about 800 DSCFM to a minimum of 400 DSCFM on the fifth day. In addition, once flow was stabilized, six one-hour samples were collected (some in duplicate) each day at the blower stack. For all other landfills in the survey, only two to three samples (with some duplicates) were collected at each sampling point with the sampling period ranging from 60 to 80 minutes.

Monitoring and Laboratory Analysis Methodology

It was decided that only source sampling would be conducted, whether from active or passive sources of landfill gas. The sample collection method included the use of Gillian personal sampling pump and activated charcoal tubes and was further detailed in an internal memorandum. The analysis of samples was conducted by the State Laboratory of Hygiene's Occupational Health Lab following the NIOSH methods⁷ with solvent extraction of front and back halves of a primary and a backup tube, followed by gas chromatography retention time with a flame ionization detector (FID). The FID was periodically replaced by mass spectrometry as the detector for confirmatory analysis for each species. In addition to charcoal tube samples, a combustible gas meter was employed to detect the presence and relative level of methane as an indicator of LFG. At select sites where active extraction systems are vented through stacks, stack velocities were measured using a standard Pitot tube (for dispersion modeling purposes).

Quality assurance for the sampling and analysis was provided by: replicate sampling and analysis; the use of field and laboratory blanks; the assessment of "breakthrough" on the sorbent tubes by front and back half analysis (and the use of a "backup" tube); and the confirmatory analysis by Mass Spectrometry. Flows on the personal sampling pumps were calibrated by the specified method and were traceable to a primary standard.

Monitoring Results and Discussion

Between April 6, and August 22, 1986, 22 landfills were monitored throughout Wisconsin. The results of the monitoring were presented in a series of reports beginning on September 22, 1986. A summary of the results was presented in a report dated September 26, 1986.⁴ If the detailed results for a specific landfill are desired, copies of the individual reports for each site are available upon request from the authors.

The results which included a wide range of volatile organic compounds, indicate that for noncarcinogens, the source concentrations are not expected to exceed emission limitations established in the proposed rule and when extrapolated to ambient concentrations (by using an arbitrary 1/500 dilution factor) are not expected to exceed 1% of the TLV. The limiting contaminants were believed to be the carcinogens, benzene and vinyl chloride. Benzene was found in very few landfills (3 out of 22) and the concentrations detected were very low ranging from 0.4 ppm (just above the 0.3 ppm detection limit) to 3 ppm (for a sample pulled directly from a gas monitoring probe sunk into the waste mass). Further consideration of benzene was put aside pending an evaluation of vinyl chloride.

Table I presents the results for vinyl chloride. The data are presented in more or less descending order of concentration (while retaining the classification system presented by the Bureau of Solid Waste Management). Municipal landfills handling municipal (household) wastes are the primary emitters of vinyl chloride. Some of these landfills emit no vinyl chloride or the concentrations are very low. All the others had very significant concentrations of vinyl chloride in the LFG. In addition, municipal landfills which accepted predominantly industrial wastes, and industrial landfills which accepted predominantly industrial wastes or papermill sludge (but no municipal wastes) were free of vinyl chloride emissions.

Conclusions - Phase I

It was concluded that vinyl chloride was the limiting hazardous air contaminant in LFG. It was also concluded that vinyl chloride was present only in municipal wastes. It was also concluded that, based on the direct emissions measured and the preliminary estimates of ambient impact for one landfill, VC posed a potential threat to human health for persons living in the vicinity of landfills where LFG was being emitted.

This was based on the CAG risk concentration of 2.6 ug/m^3 (1 in 1 million risk)⁵ as well as some of the acceptable ambient concentrations listed in the NATICH data base⁶. There however seemed to be some discrepancy between the available sources. The advice of the Wisconsin Division of Health was sought because of the discrepancy and because VC was a known human carcinogen. The interim policy being used in Wisconsin (before the promulgation of regulations dealing with hazardous air emissions) required emissions to be limited to ambient impacts which had a risk of one cancer death per one million persons exposed to a hazardous air contaminant over a 70-year lifetime.

PHASE II - HEALTH ASSESSMENT

A request for a health assessment was made by the DNR to the Wisconsin Division of Health and on December 1, 1986, the DOH published (in summary form) its findings⁷. The full report was still in preparation at the time this report was written. The report presented a list of ambient vinyl chloride guideline levels derived from various sources, ranging from 0.6 to 235 parts per trillion (1.5 to 600 ng/m^3), with the lowest value (derived from U.S. EPA data) and one other (39.2 ppt , 100 ng/m^3) representing one-in-a-million cancer risk concentrations. The DOH concluded:

"The conclusion of the DOH risk assessment is that vinyl chloride venting from landfills would represent a public health threat at the one excess cancer in one million population level if ambient air concentrations to nearby residents exceeded 0.0006 ppb as a 24 hour per day average exposure. The DOH believes that the WI/EPA-CAG cancer risk model is the most appropriate method for the cancer risk analysis. It is the most recent assessment and best reflects the prevailing cancer state-of-the-art risk assessment process."

It is obvious that the one-in-a-million risk ambient concentration was well below that submitted by Region V U.S. EPA [2.6 ug (2600 ng)/ m^3] or any currently being used by other states - from a high of 238 ug/m^3 (95 ppb), 8-hour average, for Nevada, to a low of 20 ug/m^3 (8 ppt), annual average, for Illinois⁸.

One author of the report, Dr. John Olson of DOH, indicated that recent literature indicates onset of the cancers associated with vinyl chloride are now observed at an earlier age and that "lifetime" exposure to VC may not be a good predictor of cancer onset. This could mean that shorter term exposure at higher concentrations could have adverse effects.

PHASE III - MODELING OF SOURCE EMISSIONS

While concentrations measured at closed landfill sites (to which the general public has access) were above the recommended level, it was not clear that persons living some distance from the LFG source might be continuously exposed to harmful levels. Therefore, it was decided that dispersion modeling should be performed for landfills which had active

extraction systems with conventional sources (stacks) which could be modeled. In that fashion estimates of ambient concentrations could be predicted. To perform modeling requires measurements other than VC concentrations, i.e. gas flow through the stack, temperature of the gas and stack dimensions (in addition to information on the surrounding impacted terrain). Only four sources were selected for modeling. The other landfills with active extraction systems contained no VC in the LFG. However, when the monitoring team attempted to measure flow at one of the landfills selected, they were unable to do so using conventional flow measurement methods. Therefore, modeling could not be performed for that source. The modeling exercise therefore was restricted to only three landfills.

Modeling Methodology

Conventional stack test techniques were used to obtain the necessary stack parameters, i.e., flow (with a standard Pitot tube), temperature (with a laboratory grade thermometer), and length (with a standard meter rule). The measurements obtained for those parameters were in addition to the average VC concentration obtained from a number of stack samples which were analyzed by the methodology described earlier under Phase I - Monitoring. Two different modeling exercises were performed utilizing several different models: 1) U.S. EPA's Climatological Dispersion Model (CDMOC) for Mineral Point annual VC concentrations; 2) the single source (CRSTR) dispersion model for Mineral Point 1-hour and 24-hour "worst case" concentrations; 3) the Multiple Point Gaussian Dispersion Algorithm with Optional Terrain Adjustment (MPTER) model for Delafield and Verona; 4) preliminary modeling with the CDMOC and ISLCST models for Delafield and Verona (not reported).

Modeling Results and Discussion

The results of the modeling were presented in three memorandum reports (available from the authors upon request). It appeared obvious that homes in the vicinity of Landfill #1 may be exposed to levels exceeding even the CAG limit. For Landfill #2, which is immediately adjacent to the Dane County Hospital and Homes, it appeared as if the level of exposure is 13 to 33 times the DOH limit for residents within the perimeter of the area modeled. Finally for Landfill #3, with a large numbers of homes within 500 meters, it appeared as if the level of exposure is 2 to 7 times the DOH limit for residents within the modeled area.

Conclusions - Phase III

Based on the results of modeling for the three landfills, it was concluded that residents in the vicinity of closed landfills or landfill cells which contain municipal wastes (and which are relatively close to populations) are being exposed to potentially harmful levels of vinyl chloride. While the number of landfills modeled was relatively small compared to those tested (16 municipal landfills), the levels of VC detected at almost all of those was believed to be of great concern due to the comparatively low DOH limit. The difference is several orders of magnitude, i.e. 1.00 ppm (lowest detected level) versus the 0.0000006 ppm limit or one to about 10 million. For emissions from probes or wells on site, the dilution factor to the fence line for most landfills would not be expected to come close to that ratio i.e. would be a much smaller ratio. Certainly many of these closed landfills are unfenced and people have access directly to many of them. Therefore, there was general consensus between Air Management, Solid Waste and Division of Health personnel that

there was a need to control landfill gas emissions. Fortunately, almost all of the largest landfills in Wisconsin already are capturing the landfill gas and either flaring the gas or are combusting the gas for heat or for energy.

PHASE IV - CONTROL OF LFG EMISSIONS

Soon after the initial monitoring performed in Madison, the question of control came to the fore. Is combustion an adequate method for destruction of VC? DNR's Engineering and Surveillance Section determined that it was. Carbon absorption as an alternative control technique was later determined to be adequate for removal of vinyl chloride as an alternative. (Reports available upon request.)

Concurrently, development of administrative rules requiring the control of Hazardous Air Contaminants (HAC's) was proceeding. Those rules require the use of best available control technology (without regard to cost) for known human carcinogen emissions. Since for VC in LFG the control technology exists, it was decided by mutual agreement between the respective DNR sections that the specific concepts for LFG be incorporated into revisions of the solid waste rules in the process of being adopted.

The changes in the solid waste rules include incorporation of the definition of HAC's (toxic air pollutants), prohibiting landfills from emitting HAC's, requiring new landfills to be designed to control HAC's, and requiring that closure of landfills include systems for collection and control (combustion or absorption on activated carbon). The rules restrict the requirements to landfills greater than 500,000 cubic yards (medium size landfills and larger). They provide for exemption from collection and control if the landfill owner can demonstrate (by sampling and analysis of source emissions and modeling or other methods) that ambient impacts would meet the HAC rule requirements.

REFERENCES - Due to space limitations could not be included but are available from the authors upon request.

Due to APCA requirements limiting this paper to six pages, tables, figures and additional discussion could not be included; the full text of this paper is available directly from the authors by writing c/o Box 7921, Madison, WI 53707-7921.

EVALUATION OF THE FLUX CHAMBER METHOD FOR MEASURING AIR EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM SURFACE IMPOUNDMENTS

Alex R. Gholson, John R. Albritton, and R.K.M. Jayanty
Center for Environmental Measurements
Research Triangle Institute
Research Triangle Park, North Carolina

Joseph E. Knoll and M. R. Midgett
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina

Enclosure methods have been used to measure air emissions of a variety of compounds from soils, water, sediments, and living organisms. A flux chamber method, which employs the enclosure method, recently has been used to measure organic air emissions from hazardous waste treatment, storage, and disposal facilities. Using a simulated surface impoundment facility (SIS), this flux chamber method was evaluated. The liquid surface of the SIS was enclosed so that the total emission rate from a liquid surface could be determined experimentally. Emission measurements using the flux chamber method made at several points on the surface were compared with the emission rate measured for the total surface inside the enclosure. Both the accuracy and precision of the flux chamber method were predicted from these measurements. The influence of sweep flowrate, emission rate, and different organic compounds on precision and accuracy were investigated.

The results of this study show that a consistent negative bias exists for all the flux chamber measurements. This bias became significantly more negative at a low sweep flowrate (2 L/min). The bias also was found to be compound dependent. Precision was less than 5 percent under all conditions for the single component studies and between 6 and 13 percent for the three component study.

Introduction

The U.S. Environmental Protection Agency (USEPA) has been instructed to set air emission standards for hazardous waste treatment, storage, and disposal facilities (TSDF) by the 1984 Resource Conservation and Recovery Act amendments. In order to determine the potential health and environmental effects of these air emissions, methods to measure or predict them are required. The flux chamber method has been developed and is being used to measure air emission from TSDF to provide a data base for regulatory decisionmaking and to validate proposed models used to predict air emissions^{1,2,3,4}.

In an attempt to define the quality of the data being produced by the flux chamber method, this study was made to determine the accuracy and precision of the flux chamber method for use on surface impoundment facilities. The influence of the experimental parameter of sweep

flowrate and the environmental parameters of emission rate and volatile organic composition on accuracy and precision was investigated.

Experimental Methods

The flux chamber design used for this evaluation was developed for the USEPA by Radian Corporation.⁵ It consists of a stainless steel cylinder with an enclosure area of 0.13 m². The top is enclosed with a clear acrylic dome fitted with ports for sweep flow inlet, sample outlet, temperature probes, and a gas exit. The volume of the enclosure with a 1 in. insertion depth is approximately 30 L.

The design for the surface impoundment simulator (SIS) is shown in Figure 1. The surface area of the liquid is 1.86 m² with an average depth of 0.46 m. The surface is enclosed in a shell covered with Teflon with one end opened and the other end attached to the inlet of a blower. Sampling ports are provided for two flux chambers, flow monitoring, and sampling the air before the blower.

The volatile organic compounds (VOC) measured for this study were 1,1,1-trichloroethane for single component studies and a mixture of 1,1,1-trichloroethane, toluene, and 2-butanone for the three component study. The organic components were added to the bottom of the tank. The density of the compounds or mixtures was always greater than 1.0 g/mL to prevent forming an organic layer on the surface. Two immersion heaters were located just above the organic layer to control the tank temperature and increase the convective mixing inside the tank. A pump was used periodically to increase the aqueous concentrations of the organic components.

All analyses were performed using a gas chromatograph (GC) with a flame ionization detector (FID). Flux chamber samples were collected in a syringe and injected into a gas sampling valve with a 2-mL loop. SIS air samples were collected in syringes or aluminum gas cylinders and preconcentrated on Tenax that was thermally desorbed. SIS water samples were collected in glass vials with no headspace and analyzed by syringe injection.

Results

Single Component Study

Accuracy and precision of the flux chamber method were calculated from a series of colocated flux chamber measurements made inside the SIS containing a single VOC, 1,1,1-trichloroethane. A series of nine initial emission measurements were made under similar emission conditions and the same flux chamber conditions. The sweep flowrate was set at the 5 L/min recommended by Radian's study. Table I shows the variance found between each duplicate measurement. The coefficient of variance (CV) was less than 5 percent for all the measurements except for two. Using a pooled standard deviation, the precision was predicted from these data to be 3.0 percent. This value was chosen to be the control condition precision.

Colocated measurements, conducted at night, were made at an emission rate approximately one tenth of the control condition measurements. Table II compares the precision calculated for these conditions with the earlier conditions. No change in the precision was found for the low emission rate conditions. The variance found at night was half that found for the control conditions. The improved precision at night could be due to an effect of sunlight on the performance of the flux chamber or the effect of the sunlight on the real emission rate. Emission rates made in full sunlight were found to be highly variable both from flux chamber measurements and SIS measurements. All measurements reported here were made in the shade or on overcast days.

The precision and accuracy of the method also were determined at a sweep flowrate of 2 L/min and 10 L/min. Table II show the results for three colocated tests at each flowrate. A decrease in the precision value (improved precision) was found at the higher flowrate, and a slight increase in the precision value (poorer precision) was found for the lower flowrate. These results indicate that precision is improved by increasing the sweep flowrate possibly due to improved mixing at the higher flowrate.

The average emission rate calculated from a colocated flux chamber study was compared with the average emission rate calculated before and after from the total SIS measurement to predict the accuracy of the method. Table III lists the average percent bias found between the flux chamber and SIS values for the control conditions and the other flux chamber conditions studied. The bias was consistently negative (the flux chamber values lower than the SIS values). The average bias values were not significantly different within the 90 percent confidence limit (CL) for all the measurements except the low sweep flow study, which had a significantly more negative bias. This suggests that the accuracy of the method decreases at the lower sweep flowrate.

Three Component Study

The precision and accuracy study was repeated with three VOC in the tank. These included 1,1,1-trichloroethane, 2-butanone, and toluene. Comparing the results of nine colocated duplicate flux chamber measurements with the control of the single component study reveals several apparent differences. Table IV shows the precision estimated for each compound. The values are greater than for the single component control and vary by almost a factor of two between themselves. The increased variance may be due to the large difference in emission rates being pooled.

The accuracy of the three component results showed similar differences when compared with the single component study. Table V shows the results of bias calculations between the flux chamber and the SIS emission results. Three significantly different average bias values were found, and each one except toluene varied significantly from the single component results. Of special interest is that 1,1,1-trichloroethane in the mixture had an average bias of less than one-half of 1,1,1-

trichloroethane in the single component mixture. The total emission measurement bias showed no significant difference from the single component results.

Conclusions

The results of the precision and accuracy study indicate that precise emission measurements can be made using the flux chamber method. The consistent negative bias found indicates that the flux chamber method may underestimate the emission rate from a surface impoundment. Either the flux chamber depresses the emission rate over the area it covers or the total emission rate may not be equally distributed over the surface with higher emission at the sides.

Of the experimental parameters investigated, only daylight and sweep flowrate was found to affect the accuracy or precision significantly. Results suggest that sunlight may affect the variance between two color-coded flux chambers and lower sweep flowrate (2 L/min) increases the variance between measurement and increases the bias. Both precision and accuracy appear to be compound dependent and are dependent on the matrix.

Studies are recommended to determine the effect of solar intensity on both the emission rate and the flux chamber method, the cause of the compound dependency of the flux chamber accuracy, and the reason for the consistent negative bias found in the results. Plans for determining the flux chamber precision in the field currently are being made.

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TABLE I. FLUX CHAMBER PRECISION AT 5 L/MIN FOR
SINGLE COMPONENT SOURCE

Sample No.	Average surface temperature	Surface liquid concentration	Average emission rate, (g/min/m ²)	% CV
1.	23	130	14,300	2.1
2.	23	130	12,100	0.14
3.	22	130	13,200	1.5
4.	21	16.2	9,730	4.6
5.	21	16.2	9,750	6.0
6.	21	16.2	8,910	0.46
7.	23	93.6	7,470	4.8
8.	24	93.6	7,350	11
9.	24	93.6	7,630	4.8

CV = Coefficient of variance.

TABLE II. RESULTS OF FLUX CHAMBER PRECISION STUDY
FOR SINGLE COMPONENT

Variable parameter	Number of replicates	Precision ^a
Control	9	3.0
Low emission rate	3	2.9
Nighttime	3	1.5
2 L/min sweep flow	3	4.1
10 L/min sweep flow	3	1.4

$$^a \text{Precision} = \frac{\sqrt{\frac{(x_1 - x_2)^2}{2n}}}{\bar{x}}$$

TABLE III. RESULTS OF FLUX CHAMBER ACCURACY STUDY FOR SINGLE COMPONENT

Variable parameter	Number of replicates	Average bias, % + 90% CL
Control	9	-45.1 ± 6.4
Low emission rate	3	-67.1 ± 16.6
2 L/min sweep flow	3	-81.5 ± 9.6
10 L/min sweep flow	3	-49.3 ± 8.3
Nighttime	3	-57.2 ± 21.3

CL = Confidence limit.

TABLE IV. RESULTS OF PRECISION STUDY FOR THREE COMPONENT MIXTURE

Compound	Number of duplicate measurements	Range of emission rates	Precision, %
2-Butanone	9	11,000 → 42,000	6.7
1,1,1-Trichloroethane	9	46,000 → 100,000	10.6
Toluene	9	5,100 → 14,000	13.1
Total	9	65,500 → 160,000	8.6

TABLE V. RESULTS OF ACCURACY STUDY FOR THREE COMPONENT MIXTURE

Compound	Number of measurements	Average bias, % + 90% CL
2-Butanone	9	-68.1 ± 3.1
1,1,1-Trichloroethane	9	-21.0 ± 6.0
Toluene	9	-38.2 ± 4.4
Total	9	-40.7 ± 3.3

CL = Confidence limit.

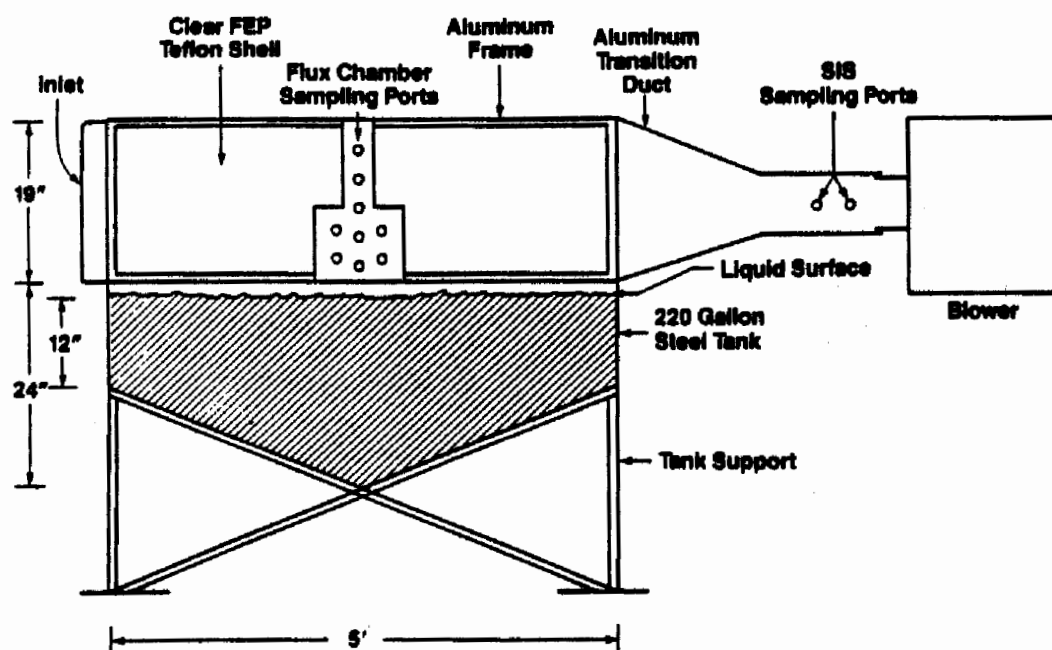


Figure 1. Side view of surface impoundment simulator (SIS).

DEVELOPMENT OF A SAMPLING METHOD
FOR MEASURING VOC EMISSIONS FROM
SURFACE IMPOUNDMENTS

Bart Eklund, Michael R. Kienbusch, and David Ranum
Radian Corporation
Austin, Texas

Terry Harrison
U. S. EPA, OAQPS/EMB
Research Triangle Park, North Carolina

This paper presents the results of an EPA-sponsored program to develop a sampling method to quantify air emissions of volatile organic compounds (VOCs) from surface impoundments and other liquid surfaces. The chosen sampling method used an enclosure device, or flux chamber, to isolate a defined surface area and collect the gaseous emissions to allow a direct emission rate measurement. The development program included four distinct tasks: 1) identify the pertinent design and operation factors of the emission isolation flux chamber (EIFC) which may significantly affect the measured emission rate, 2) conduct a pilot-scale study to evaluate and optimize the performance of the flux chamber, 3) develop a standard sampling protocol, and 4) demonstrate the method at a field site. Results from each task are presented. The average percent recovery for the EIFC was 96.7% for a seven-component standard and the reproducibility was $\pm 7.5\%$.

Introduction

The U.S. EPA is interested in measuring the volatile organic emissions from surface impoundments. Measurement of organic emissions from surface impoundments has been studied from several different perspectives. Three general perspectives are: 1) to indirectly measure ambient air concentrations at downwind locations and use meteorological data in conjunction with dispersion modeling to calculate the emission rate; 2) to measure liquid phase concentrations and use mass transfer theories and emission rate models to estimate the emission rate; and 3) to directly measure the emission rate using an emission isolation flux chamber (EIFC) approach.

The direct approach was chosen for further investigation because it is relatively inexpensive and offers increased precision estimates over the modeling and indirect approaches. At the same time, if acceptable, the EIFC procedure could be applicable in confirming mass transfer and emission rate modeling theories.

Development of the method consisted of performing four tasks: 1) identify the pertinent design and operational factors of the EIFC; 2) conduct a bench-scale pilot-study to evaluate each design and operational factor; 3) write an operations protocol for EIFC applications on surface impoundments; and 4) demonstrate the EIFC technique, in this case, at an industrial wastewater facility.

The purpose of this paper is to present the results from each of the four tasks performed to develop this technique.

Experimental Design

As previously discussed, four tasks were performed during the method development study. Each task is briefly discussed below, after a general introduction to the flux chamber sampling method.

EIFC Theory of Operation

The emission isolation flux chamber is a device used to make direct emission rate measurements from land or liquid surfaces such as landfills, spill sites, and surface impoundments. The enclosure approach has been used by researchers to measure emission fluxes of a variety of gaseous species, including sulfur and volatile organic species. The approach uses a flux chamber to sample gaseous emissions from a defined surface area. Clean, dry sweep air is added to the chamber at a fixed controlled rate. The volumetric flow rate of sweep air through the chamber is recorded and the concentration of the species of interest is measured at the exit of the chamber after equilibration (steady state). The emission rate is expressed as:

$$E_i = C_i R / A \quad (1)$$

where: E_i = emission rate of component i ($\mu\text{g}/\text{m}^2\text{-min}$),
 C_i = concentration of component i in the air flowing from the chamber ($\mu\text{g}/\text{m}^3$),
 R = flow rate of air through the chamber (m^3/min), and
 A = surface area enclosed by the chamber (m^2).

All parameters in Equation 1 are measured directly.

Design and Operational Factors

The first task was to identify the design and operational factors of the EIFC which may affect the measured emission rate.¹ The chamber design and operating procedures used by previous researchers were noted, along with prior evaluative and theoretical studies. The theoretical basis for the applicable emission processes was also discussed in terms of how it impacts the EIFC design and operation. The design and operation factors chosen for further evaluation were insertion depth, sweep air flow rate, impeller rotation rate, internal pressure, sampling duration, line length, and construction materials. These were selected based upon judgment, prior field sampling studies, and results from a validation study of EIFC techniques for soil surfaces.²

Pilot-Scale Testing

Once the design and operational parameters were defined, a pilot-scale evaluation of selected factors was performed.³ A large (1.5 m x 1.5 m x 0.6 m) galvanized tank was constructed to act as an artificial surface impoundment. Emission tests were performed using aqueous solutions of toluene. Toluene represents a typical, moderate-to-low solubility, highly volatile compound found in many surface impoundments. Four sets of tests were conducted. A series of calibration tests were performed to set the operating procedures for the test facility. A set of parametric tests evaluated the effect of design and operating parameters on measured emission rates. A third set of tests examined the reproducibility of the EIFC sampling method. The fourth set of tests evaluated sample recovery using the preferred design and operating conditions.

Protocol Development

After the pilot-scale validation studies, an operations protocol was developed.⁴ The protocol documents the preferred design and operation of the EIFC method. It provides step-by-step sampling and analytical procedures and provides detailed information on fabrication, sampling strategy, and data reduction. The sampling strategy is designed to determine an average emission rate for a given zone that is $\pm 20\%$ of the true value at a 95% confidence interval. The current strategy divides the emission source into homogenous zones, the zones are then each gridded, and a statistically

determined number of grid points are randomly sampled. The protocol is currently under review by the U.S. EPA/ RTP.

Field Demonstration

The EIFC sampling protocol was demonstrated at an industrial wastewater lagoon.⁵ This study was done in conjunction with another study on the degree of stratification present at this site. Consequently, the sampling locations were not randomly selected.

Emission rate measurements were made at five locations on the lagoon. The EIFC was fitted with three flotation pods to provide buoyancy. The EIFC was lowered in place using a cherry-picker and operated remotely from the shore using an umbilical containing the inlet and exit gas lines. At each point, grab samples of the chamber atmosphere were collected and immediately analyzed on site for total non-methane hydrocarbons (TNMHC) by gas chromatography (GC). Gas samples were also collected in evacuated, stainless steel canisters for subsequent off-site GC analysis to determine the emission rates of individual compounds. Liquid grab samples were collected at each point for correlation to compound-specific emission rates to calculate field mass transfer rates.

Results

The results of the pilot-scale testing are summarized in Table I. The interpretation of results was complicated by the inherent spatial variability in emissions of the artificial surface impoundment. The design parameters, material of construction and sample line length were each found to affect the emission rate measurement by less than 10%. The operational parameters generally did have a significant effect on the emission rate measurement. The emission rate was found to increase with an increase in sweep air flow rate. Use of an impeller increased emissions by about 20%. Adequate mixing could be achieved through the design of the sweep air inlet manifold. Therefore, the use of an impeller has been discontinued for the sake of simplicity. Positive pressure build-up within the EIFC was found to affect the emission rate, so a pressure relief valve (opening) was added to the EIFC. Emission rates were found to decrease somewhat with time, probably due to surface depletion in the column of liquid isolated by the flux chamber. Results for reproducibility and standard recovery tests indicated the accuracy and precision of the method are good. A figure of the EIFC as currently conceived is shown in Figure 1.

The results of the field study are summarized in Table II. The major compounds emitted were benzene and toluene. Approximately a dozen compounds per sampling point could be detected at 1 ppbv or greater in the flux chamber atmosphere. For TNMHC, the average sampling variability was +25% and the average analytical variability was +12% for the gas-phase analysis. This ratio of sampling to analysis variability compares favorably with other air sampling methods.

Conclusions

Each of the four elements of the study was successfully completed. The pilot-scale examination of the design and operational factors identified several factors that must be controlled to ensure a reproducible sampling technique. These included the sweep air flow rate, induced mixing via sweep air inlet, the sampling time, and internal pressure. The design of the flux chamber is also of importance because the sweep air flow rate and induced mixing are both dependent upon the design. A protocol was developed that discussed in detail the design and operations of the EIFC for liquid surfaces. The protocol is currently under Agency review. A field demonstration of this method was performed using the protocol as a guide. The field project showed that the method is feasible for making emission rate determinations.

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TABLE I. SUMMARY OF RESULTS FOR PILOT-SCALE TESTS

Test	Test Range/ Result	Significance of Test on Emission Rate Measurement	Recommended Design/Operating Value
Parametric Tests			
Depth of Penetration	1.27-7.62 cm	None	1.27-2.54 cm
Sweep Air Flow Rate	1.4-21.2 L/min	Yes	5-10 L/min
Impeller Rotation Rate	0-135 rpm	Yes	No impeller
Internal Pressure	0-0.762 cm H ₂ O	Yes	$\Delta P < 0.127$ cm H ₂ O
Sampling Duration	0-6.6 hrs	Yes	<30 min
Sample Line Length	1.52-30.5 m	None	<30.5 m
Construction Material	Steel/Teflon, Plexiglas/Teflon	None	---
Precision Tests			
Reproducibility	+7.5%	None	---
Recovery Tests^a			
1.52 m Sample Line	96.7%	None	---
30.5 m Sample Line	104%	None	---

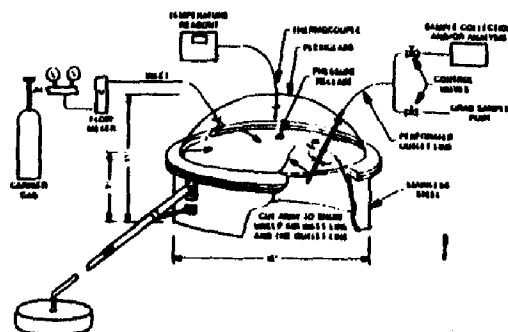
^aMulti-component standard.²

Figure 1. A cutaway design of the emission isolation flux chamber and support equipment.

TABLE II. SUMMARY OF RESULTS FOR FIELD STUDY

Compound	Emission Rate (g/m ² -day) ^a					Mean
	Grid 1	Grid 2	Grid 3	Grid 4	Sludge	
Methyl Chloride	0.338	0.00480	0.0271	0.0290	0.0369	0.0872
Benzene	9.42	6.69	3.86	6.92	0.758	5.53
Toluene	5.14	2.87	0.851	1.12	0.269	2.05
Total NMHC	27.6	11.6	5.35	9.25	1.36	11.0

LABORATORY AND FIELD EVALUATION OF THE SEMI-VOST
METHOD FOR MEASURING EMISSIONS FROM HAZARDOUS
WASTE INCINERATORS

J. T. Bursey, J. L. Steger, M. A. Palazzolo,
D. J. Benson, R. L. Porch, J. Rice,
J. B. Homolya, R. A. McAllister,
J. F. McGaughey, D. E. Wagoner
Radian Corporation
Research Triangle Park, NC 27709



J. H. Margeson, J. E. Knoll, M. R. Midgett U. S. Environmental Protection
Agency Research Triangle Park, NC 27711

Laboratory studies and two field evaluations have been completed to assess the formulation and performance of the Semi-Volatile Organic Sampling Train (Semi-VOST) method for measuring concentrations of principal organic hazardous constituents (POHCs) with boiling points greater than 100°C emitted from hazardous waste incineration. Laboratory experiments were performed initially to design and test a dynamic spiking system to allow spiking of test compounds in the field for a reliable procedure to assess method precision and bias. Additional laboratory tests were performed to determine analytical method detection limits to estimate the levels at which deuterium labeled compounds should be spiked under field conditions. Compounds representative of a variety of chemical and physical properties were selected as test compounds to be spiked in a field test executed at a hazardous waste incinerator. After collection of the samples in the field, train components were extracted with methylene chloride, the extracts concentrated, and compounds of interest were quantified using high resolution gas chromatography coupled with low resolution mass spectrometry. The first field test showed that method precision and bias are compound specific, and the distribution and recovery of POHCs in the various components of the sampling train are related to the compound chemical functionality, water solubility, and boiling point.

Subsequent to the first field test, an extensive series of laboratory experiments was performed to modify the dynamic spiking apparatus and procedures for use in the field. Also, since previous experiments had shown recoveries of certain compounds to be poor or variable, laboratory experiments were performed to determine the extent and nature of compound interactions with components of the sampling train. Water soluble compounds may form salts by reaction with the wet and acidic environment normally encountered in stack emissions. These water soluble compounds are also collected in the aqueous portions of the sampling train and may be poorly recovered by solvent extraction. The analytical procedure was revised by pH adjustment to improve recovery of basic and water soluble compounds. A screening procedure was also developed to determine the optimal extraction solvent and to estimate the

recovery of test compounds obtained from acidic water condensates using the sample preparation methodology presented in the Semi-VOST protocol.² tert-Butyl ether was selected as the optimum solvent for the extraction of water soluble compounds. For the second field test, five deuterium labeled gaseous compounds were dynamically spiked into four simultaneously-operating Semi-VOST trains at a hazardous waste incinerator equipped with a wet scrubber. Results from the laboratory experiments and the second field test provided precision and bias estimates for the test compounds, and compound retention volumes on the solid sorbent were evaluated through a series of distributive volume experiments. Data were evaluated from gaseous dynamic spiking and liquid spiking of the test compounds on XAD-2[®] resin, and³ the effects of sample storage time on sample stability were investigated. Conclusions reached from the second field test are : 1) the data from the dynamic spiking of a variety of POHCs exhibiting a range of boiling points, water solubilities, and chemical functionalities support the findings of the previous field test and laboratory studies, 2) the experimental data give the basis for the use of laboratory-determined retention volumes of POHCs to predict field breakthrough volumes through XAD-2[®] resin, and 3) the experimental results support the selection of the Semi-VOST method as the method of choice for sampling flue gas emissions of organic compounds with boiling points greater than 100°C.

Introduction

The Solid Waste Disposal Act, amended by the Resource Conservation and Recovery Act of 1975 (RCRA), requires that EPA establish a national regulatory program to ensure that hazardous wastes are managed in a manner which does not endanger human health or the environment. The statute requires EPA to promulgate performance standards for hazardous waste management. Included in the regulations are provisions for waste disposal by incineration and requirements that hazardous waste incinerators be so operated that principal organic hazardous constituents (POHCs) are destroyed and/or removed with minimum efficiency of 99.99%. To determine destruction and removal efficiency (DRE), EPA has designed the Semi-VOST Method as the method to measure flue gas concentrations of POHCs with boiling points greater than 100°C. The Quality Assurance Division of the EPA Environmental Monitoring Systems Laboratory (EMSL) has responsibility for evaluating and standardizing EPA source test methods. In the application of Semi-VOST methodology, gaseous and particulate components are isokinetically withdrawn from an emission source and collected in a multicomponent sampling train. Under contract to EMSL, Radian Corporation is providing technical assistance in evaluating the Semi-VOST Method. The objective of the Semi-VOST program is to provide data necessary to determine bias, precision, applicability, and limitations of the method. The technical approach used to collect these data is a multi-task effort involving literature, laboratory, and field studies. An initial field test, utilizing a quad-train approach, provided preliminary data on method bias and precision. As a result of recommendations which evolved from the first field study, additional laboratory studies and a second field test at a hazardous waste incinerator were performed.

On the basis of experience gained from the first field test and laboratory experiments both before and after the field test, a second field test again utilized a quad-train to evaluate method performance by sampling flue gas from

a full scale incinerator while spiking test compounds into the sampling trains. The objectives of the laboratory and field program were:

- 1) evaluate the effect of water solubility and compound functionality on recovery of selected test compounds;
- 2) develop a screening procedure for selection of the optimum extraction solvent and estimation of recovery of water soluble compounds from acidic water condensate;
- 3) design, construct, and evaluate the performance of a dynamic spiking system for introduction of deuterated test compounds;
- 4) execute a second field test to provide additional data on method precision and bias for additional test compounds; and
- 5) determine the utility of using laboratory determined retention volumes to predict field breakthrough.

Results and Discussion

In the field studies, the sampling system used four simultaneously operating Semi-VOST trains. To obtain identical samples of the stack gases at a point of average velocity for each train, a common fixed heated probe system (quad-probe) was used. In the first field test, three test compounds (toluene, chlorobenzene, and tetrachloroethane) were used for dynamic spiking experiments to determine method bias. Bias values obtained for toluene and tetrachloroethane were +1 and -16%, respectively. Bias could not be determined for chlorobenzene since the dynamic spike concentration was low relative to high levels measured in the stack gas. Method precision for chlorobenzene could be calculated from unspiked sample train data in three components: sampling, sample preparation, and analysis, with results of 17.6, 2.3, and 8.9%, respectively. Overall method precision was 19.9% for chlorobenzene uncorrected for deuterated spike recovery. Distributive volume experiments performed to determine sample train breakthrough used chlorobenzene concentrations of the stack gases; 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) may react with the acidic environment to form salts insoluble in the extraction solvent and soluble in water present in the sampling system. Recovery of resorcinol, an extremely water soluble compound, requires a more polar extraction solvent. Based on data obtained from the laboratory experiments, if no modification is made to the Semi-VOST methodology, compound losses due to salt formation/water solubility can range from 34 (pyridine) to 75% (resorcinol). In addition, laboratory experiments showed that it is imperative to extract adsorbent resin samples immediately after removal from the resin cartridge, as volatilization of compounds from the resin may occur if extraction is not initiated immediately. Since aqueous components of the sampling train may contain organic salts and water soluble compounds of interest, analysis of any water present by high performance liquid chromatography as well as an additional resin extraction using methanol is

recommended to retrieve any of these salts or water soluble compounds which may have been left on the resin after extraction of the resin with methylene chloride. To assess interferences due to solvent interaction, stabilities of aniline, pyridine, phenol, and resorcinol in methylene chloride were evaluated. Concentrations of these four test compounds remained within ten percent of the original value for up to 118 days; thus, no major solvent-compound interactions were observed for the usual Semi-VOST sample storage time.

Breakthrough or specific retention volume is the sample volume required to elute a compound (adsorbate) introduced onto a resin (adsorbent) bed. Before breakthrough occurs, the amount of spiked material adsorbed on the bed is directly proportional to the volume sampled. Therefore, the adsorbate-sample volume relationship must pass through the origin. After breakthrough occurs, the amount of adsorbate is no longer proportional to sample volume, but approaches a horizontal asymptotic value equal to equilibrium loading. When solid adsorbents are used for trapping and concentrating organic materials, it is desirable to have some means to estimate the efficiency of the procedure, to determine the maximum volume of gas that may be sampled before significant breakthrough occurs. The retention volume determination consists of packing a chromatographic column with the adsorbent and measuring the retention times of the analytes at various temperatures (see data shown in Table I). This procedure was used in the laboratory for comparison with results obtained in actual field testing. In the second field study, three quad-probe tests were conducted to compare results of laboratory breakthrough volume studies to data obtained in the field. During these tests, three trains were spiked with deuterium labeled compounds using the dynamic spiking system and one train was operated unspiked. The three spiked trains provided a triplicate set of samples for the breakthrough analysis and the unspiked train provided a background sample. Figure 1 shows the results of the distributive volume study for d_8 -toluene. Note that once breakthrough has occurred, the adsorbate versus sample relationship is no longer linear because it leveled off to an equilibrium adsorbed concentration.

Five tests in the second field study were performed with the quad-probe to assess method precision and bias. Five deuterated compounds were spiked into the sampling trains at 100 times the method detection limit level during the tests to provide data on precision and bias. For the five test compounds, the following results were obtained: d_5 -pyridine, precision 17.7 %CV, bias -29.0%; d_8 -toluene, precision 14.6 %CV, bias -14.9%; d_{10} -o-xylene, precision 8.1 %CV, bias -0.9%; d_2 -tetrachloroethane, precision 32.9 %CV, bias -18.5%; d_5 -chlorobenzene, precision 13.7 %CV, bias -13.8% (results are summarized in Table II). Two quad-probe samples were collected to provide information on sample stability. Dynamically spiked samples were stored for five weeks and nine weeks and then analyzed. Results for the stored samples were compared with results for liquid spiked samples to assess compound loss due to sample storage. The overall conclusion after analysis of these samples is that holding time (up to 63 days) between sampling and analysis does not significantly affect the results obtained. In the field study, the between set variance in compound recoveries was greatest for duplicate liquid spikes. The variances obtained when comparing two sets of duplicate dynamic spikes and dynamic spiking to liquid spiking were smaller. In the field study, all samples received were spiked in the laboratory with surrogate standards prior

to any sample preparation. The surrogate compounds were deuterium labeled compounds used to monitor the efficiency of the sample preparation process for recovering compounds from the matrix. Corrections can validly be made to allow for less than 100% recovery of surrogates and corrected values for compounds of interest will reflect recoveries of the surrogates.

Conclusions

The second field test demonstrated that dynamic spiking of the Semi-VOST train using deuterated compounds is a viable approach for determination of method bias under field conditions. In the absence of measurable stack emissions of POHCs, dynamic spiking can be used to measure method precision. Experimental data from the field test support the use of laboratory determined retention volumes to predict field breakthrough volumes. A difference in holding time before extraction for dynamically spiked resin samples does not result in a significant difference in recoveries for all of the compounds spiked. The use of surrogate standards during sample preparation and analysis is necessary to obtain the best representation of test compound recoveries. Deuterated analogs, when available, are the best possible surrogates because they behave exactly the same as the compounds of interest and will be truly representative of test compound recoveries. Use of deuterium labeled surrogate compounds is highly recommended. A comparison was made between observed values and expected levels of five compounds spiked onto resin as quality control samples provided by the Research Triangle Institute. Bias ranged from -1.8% to -8.9% with reference to the RTI values. Average % bias was -4.7%. The agreement is excellent, showing that the recovery of organic compounds from XAD-2® resin using the Semi-VOST methodology is favorable.

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Disclaimer

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TABLE I. RETENTION VOLUME

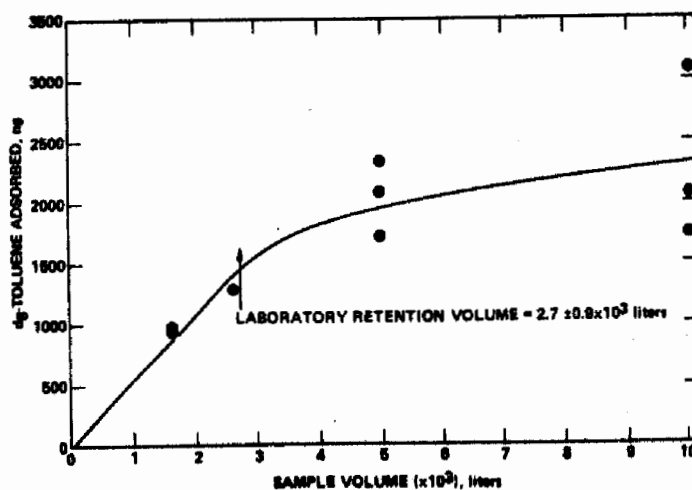
Compound	Retention Volume mL/g at 20°C	Sampling Flow Rate cfm ¹	Breakthrough Volume m ³ (ft ³)	Time for Breakthrough h
toluene	137,277	0.50	2.72 (96)	3.2
1,1,2,2,-tetra- chloroethane	1,430,672	0.50	28.6 (1011)	33.7
chlorobenzene	450,473	0.50	9.00 (318)	10.6
pyridine	68,896	0.50	1.36 (48)	1.6
o-xylene	1,021,676	0.50	20.4 (720)	24.0

¹0.50 cubic feet/minute (cfm) is equivalent to 0.01416 m³/min

TABLE II. SUMMARY OF PRECISION AND BIAS RESULTS

Compound	Number of Valid Samples	Mean S Recovery	Percent Bias ¹	Precision	
				Standard Deviation	Percent Coefficient of Variation
d ₅ -pyridine	16	71.0	-29.0	12.6	17.7
d ₈ -toluene	13	85.1	-14.9	12.4	14.6
d ₅ -chloro- benzene	13	86.2	-13.8	11.8	13.7
d ₁₀ -o-xylene	13	99.1	-0.9	8.0	8.1
d ₂ -tetrachloro- ethane	13	81.5	-18.5	26.8	32.9

¹Percent bias = Mean S recovery - 100

Figure I. Retention Volume Studies for d₈-Toluene

EVALUATION OF MICROWAVE TECHNIQUES TO
PREPARE COMBUSTION SOURCE SAMPLES

David A. Binstock, Peter M. Grohse, Percy L. Swift, and Alvia Gaskill, Jr.
Research Triangle Institute
Research Triangle Park, NC 27709

Thomas R. Copeland
ERCO/A Division of ENSECO, Inc.
Cambridge, MA 02138

Paul H. Friedman, Office of Solid Waste
U. S. Environmental Protection Agency
Washington, D.C. 20460

The use of microwave energy to facilitate sample decomposition prior to elemental analysis is now receiving considerable attention. Both wet and dry digestions are achievable. When microwave energy is used in combination with acid mixtures in closed vessels, the combined pressure and rapid heating can reduce digestion times to a few minutes from hours or days that may be required for open beaker digestions. This savings in time and labor is significant and has prompted the Office of Solid Waste to evaluate this technology as a preparation tool for solid wastes. Of particular interest are used oils and other fuels slated for incineration, incinerator ash and particulates from these processes.

This study reports on the evaluation of a commercially available microwave oven sample preparation system for this application. The effect of sample preparation conditions, including the acid matrix, heating time, and pressure were evaluated for fifteen toxic or hazardous elements in particulates and ashes. Analyses were carried out by inductively coupled plasma emission spectroscopy.

Introduction

The techniques that are typically used to prepare Resource Conservation and Recovery Act (RCRA) wastes for analysis for metals and other elements are relatively time consuming, requiring several hours to several days to complete. They also often involve the use of acid digestions and thermal decomposition steps which may result in analyte losses, incomplete recoveries, or sample contamination. These limitations are well known to the analytical community and to the end users of these data in EPA, states, and industry. The resulting inefficiency of these techniques reduces laboratory sample throughput, drives up the cost of analytical testing and impedes decision-making. Given these concerns, the USEPA Office of Solid Waste is interested in developing cost effective sample preparation techniques for metals and other elements in environmental and process waste samples. Once developed, these techniques can then be written as methods for inclusion in "Test Methods for Evaluating Solid Waste, SW-846" and made available to the user community.

One particularly attractive sample preparation technique that is now receiving considerable attention is microwave assisted sample dissolution. The use of microwave energy to facilitate sample decomposition prior to elemental analysis has received considerable attention in recent years. Both wet and dry digestions are achievable. When microwave energy is used in combination with acid mixtures in closed vessels, the combined pressure and rapid heating can reduce digestion times to a few minutes, from hours or days that may be required for open beaker digestions. This savings in time and labor is significant and has prompted the Office of Solid Waste to evaluate this technology as a preparation tool for solid wastes. Of particular interest are used oils and other fuels slated for incineration, incinerator ash, and particulates from these processes.

Previous evaluative work in this area was carried out by Nadkarni¹. Using a commercial microwave oven and an HF/aqua-regia digest, National Bureau of Standards (NBS) Coal 1632a and NBS SRM 1633a Fly Ash were solubilized. Copeland² (1985) used a $\text{HNO}_3/\text{H}_2\text{O}_2$ microwave procedure to prepare waste oils for determination of As, Be, Cd, Ni, and Pb.

This study reports on the evaluation of a commercially available microwave oven sample preparation system. The effect of sample preparation conditions, including the acid matrix, heating time, and pressure were evaluated for toxic or hazardous elements in particulates and ashes. Analyses were carried out by inductively coupled plasma emission spectroscopy.

Experimental Methods

Microwave Oven

The MDS-81D Microwave system (CEM Corporation, Indian Trail, NC) was used for this study. The oven resembles a standard microwave oven, but is equipped with additional features to facilitate sample preparation. For example, the Teflon-coated microwave cavity has a variable speed corrosion resistant exhaust system. The main element of the system couples a precise microwave variable power system with a programmable micro-processor digital computer. Other elements include a rotating turntable, Teflon vessels with caps and a patented pressure relief valve, a capping system, and a cooling tank.

The Teflon sample vessels and caps are designed to withstand pressures up to 100 psi and temperatures up to 200°C.

Inductively Coupled Plasma Emission Spectrometry (ICPES)

All analytical measurements were performed using an Instrumentation Laboratory 200 ICAP.

Reagents

All inorganic acids used were of "Ultrex" quality, from J. T. Baker Chemical Co. Other chemicals were of analytical reagent grade quality. Deionized water of 18 MΩ/cm specific resistivity was used.

Combustion Source Materials

The evaluation of microwave methods was carried out using NBS Coal 1632a and Fly Ash 1633a. Elemental values for these standards were obtained from their certificates of analysis.

Microwave Preparation Procedures

Total Digestion Procedure: A 300 mg sample is placed in a 60 mL Teflon digestion vessel equipped with a relief valve and treated with 1 mL concentrated HNO_3 , 3 mL HF, and 0.5 mL HClO_4 . The vessel is sealed and heated in the microwave oven at 15 percent power for 5 minutes, followed by 30 percent power for 15 minutes. The vessel is cooled, the cap removed, 3 mL HF added, resealed and heated at 20 percent power for one hour. The cap is then removed and the contents evaporated until fuming ceases. Six mL of 20 percent HNO_3 are added and evaporated to dryness; 15 mL 20 percent HCl added, the vessel sealed and heated at 10% power until dissolution of the residue is achieved. The vessel is uncapped, evaporated to dryness, and 15 mL 5 percent HCl is added and heated until the solution clears. The vessel is cooled and diluted with deionized water to 50 mL. Total digestion time is two hours.

HF/Aqua-Regia Procedure: A 300 mg sample is placed in a 60 mL Teflon digestion vessel equipped with a relief valve and treated with 6 mL aqua-regia ($3\text{HCl}:1\text{HNO}_3$) and 2 mL HF. The vessel is sealed and heated in the microwave oven at 100 percent power for 3 minutes. The vessel is cooled, the cap removed, the digestate filtered and transferred to a 50 mL volumetric flask with deionized water.

Results

Total Digestion Procedure

A total digestion ($\text{HClO}_4/\text{HF}/\text{HCl}$) microwave procedure was used to prepare NBS SRM 1633a Fly Ash. With the exception of Mn and Pb, recoveries were all within 25 percent of the NBS values (Table I). In addition, results for most elements are comparable to those from a more time-consuming conventional open-beaker digestion of the same material.

A modified total digestion procedure was used to prepare NBS SRM 1632a coal. Due to the potential explosion hazard of the HClO_4 /coal mixture, the digests were not taken to dryness. Good agreement was obtained for all elements with the exception of Mn, Pb, and Co (Table II).

HF/Aqua-Regia Procedure

NBS SRM 1632a coal was digested using three modifications of the HF/Aqua-Regia microwave procedure (Table III). The modified conditions were 3 minutes at 100% power (column A), 6 minutes at 75% power (column B), and a dry ash of 4 hours, followed by 3 minutes at 100% power (column C).

Microwave digestion for 6 minutes at 75% power yielded higher recoveries for Co, Cr, Mn, Pb, and V than the other variations, whereas digestion for 3 minutes at 100% power gave highest recoveries for Ni and Zn. Dry ashing followed by microwave HF/aqua-regia gave the lowest recoveries, with the exception of Fe, which was higher.

Conclusions

Our preliminary work indicates that substantial time/cost savings can be achieved using microwave digestion--particularly with closed vessel procedures. Table IV illustrates the considerable time savings for the three procedures used in this study compared to conventional techniques. There is also a potential reduced need for reagents such as HClO_4 and HF.

Future work will involve refining the acid digestion/microwave conditions for combustion source samples and other RCRA wastes.

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Table I. Analysis of NBS SRM 1633a Fly Ash
(Total Digestion Procedure)
(ug/g)

Element	Mean \pm S.D. (n = 3)	NBS Values	% Bias	Conventional ³ Digestion
Al	160,000 \pm 28,000	(140,000)	+14	148,000
Be	11.9 \pm 0.6	(12)	-1	15
Ca	9360 \pm 1060	11,000 \pm 100	-15	11,200
Co	49.5 \pm 0.3	(46)	+8	---
Cr	169 \pm 59	196 \pm 6	-14	160
Cu	90.3 \pm 3	118 \pm 3	-24	110
Mn	133 \pm 2	(190)	-30	175
Ni	130 \pm 25	127 \pm 4	+2	130
Pb	45.1 \pm 20	72.4 \pm 0.4	-38	82
V	313 \pm 3	(300)	+4	310
Zn	205 \pm 8	220 \pm 10	-7	210

n = number of replicates
() - uncertified value

Table II. Analysis of NBS SRM 1632a Coal
(Total Digestion Procedure)
(ug/g)

Element	Mean \pm S.D. (n= 2) RTI	NBS Values	% Bias
Al	30,200 \pm 5900	(31,000)	-3
Ca	2050 \pm 340	2300 ⁴	-11
Co	9.72 \pm 0.19	(6.8)	+43
Cr	31.2 \pm 2.8	34.4 \pm 1.5	-3
Cu	15.6 \pm 0.6	16.5 \pm 1	-5
Fe	10,400 \pm 600	11,100 \pm 200	-6
Mg	1030 \pm 180	---	---
Mn	19.6 \pm 0.6	28 \pm 2	-30
Ni	17.3 \pm 1.8	19.4 \pm 1	-11
Pb	ND	12.4 \pm 0.6	---
Sc	5.45 \pm 0.56	(6.3)	-14
V	44.2 \pm 0.7	44 \pm 3	+0.4
Zn	34.9 \pm 0.3	28 \pm 2	+25

n = number of replicates
() - uncertified value

Table III. Analysis of NBS SRM 1632a Coal
(Modified HF/Aqua-Regia Procedures)
Mean \pm S.D. (n = 3)
(ug/g)

Element	A ^a	B ^b	C ^c	NBS Values
Al	24,600	22,700 \pm 1600	19,600 \pm 3500	31,000
Cd	<0.5	<0.5	<0.5	0.17 \pm 0.02
Co	ND	7.37 \pm 0.73	5.77 \pm 0.74	(6.8)
Cr	20.1	24.6 \pm 2.7	23.8 \pm 5.3	34.4 \pm 1.5
Cu	10.3	11.4 \pm 1.0	10.5 \pm 4.0	16.5 \pm 1
Fe	7270	8940 \pm 267	9180	11,100 \pm 200
Mn	19.6	28.2 \pm 1.9	20.7 \pm 1.9	28 \pm 2
Ni	18.3	12.9 \pm 2.2	16.6 \pm 0.4	19.4 \pm 1
Pb	7.2	15.4 \pm 3.2	9.68 \pm 3.00	12.4 \pm 0.6
V	33.0	47.6 \pm 3.1	38.9 \pm 2.2	44 \pm 3
Zn	23.7	15.1 \pm 2.3	13.7 \pm 5.5	28 \pm 2

^aHF/Aqua-Regia, microwave 3 minutes @ 100% power, n = 1

^bHF/Aqua-Regia, microwave 6 minutes @ 75% power

^cAshed at 400°C 4 hours-HF/Aqua-Regia, microwave 3 minutes @ 100% power

n = number of replicates

() - uncertified value

Table IV. Comparison of Digestion Time of
Microwave and Conventional Techniques

Acid Digestion	Microwave	Conventional
Nitric acid	40 minutes	4 to 6 hours
Hydrofluoric/aqua-regia	3 to 10 minutes	6 to 8 hours
Total digestion	2 hours	16 hours

DEVELOPMENT AND EVALUATION OF ANALYTICAL TECHNIQUES FOR TOTAL
CHLORINE IN BURNER FUELS

Alvia Gaskill, Jr.

Eva D. Estes, David L. Hardison
Research Triangle Institute,
Research Triangle Park, North Carolina and
Paul H. Friedman, Office Of Solid Waste,
U.S. Environmental Protection Agency,
Washington, DC



A current EPA regulation prohibits the sale for burning in non-industrial boilers of used oils and oil fuels 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 4000 ppm total chlorine.

Analytical techniques for determination of total chlorine were evaluated or developed to provide regulatory agencies and the regulated community with appropriate chlorine test methods. The techniques evaluated included chemical titrations following oxygen bomb combustion, disposable field test kits, instrumental microcoulometry, and x-ray fluorescence spectrometry.

These candidate techniques were subjected to interlaboratory testing to estimate their precision, accuracy, sensitivity, and susceptibility to matrix effects. Information on ease of use and analysis costs was also collected. Based on this pilot study, test methods will be written for the most promising techniques and subjected to a formal collaborative study to generate precision and accuracy data for each method. These methods are to be proposed in the Federal Register as mandatory for compliance with the existing used oil regulation.

DEVELOPMENT AND EVALUATION OF ANALYTICAL TECHNIQUES FOR CHLORINE IN BURNER FUELS

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 a 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 hazards to exposed individuals. This concern has lead EPA to promulgate a regulation prohibiting the sale for burning of used oil contaminated at levels in excess of those given in Table 1.² 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 (40 CFR Parts 261 and 266) establishes a rebuttable presumption that used oil containing > 1000 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 chlorine³). 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 (4000 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.

To rebut the presumption, 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.

As a consequence of this regulation, the regulated community and the enforcement authorities will need to determine total chlorine in used oils and oil fuels. The ideal analytical technique for this determination should meet several performance criteria. The technique should be accurate such that it can determine if the chlorine content is above or below 1000 ug/g. It should also be precise such that replicate analyses of a well mixed sample yield reproducible results. It should be rapid, field portable and inexpensive. The used oil-to-fuel industry is somewhat dynamic, requiring in many cases onsite decisions as to acceptability of oil shipments. Ideally, the analytical determinations should be carried out in the field to quickly identify contaminated oil and oil fuel. Finally, the testing procedures should be simple enough so that users over a wide variety of skill and experience levels can perform the analyses. These can be expected to include generators, burners, truck drivers, laboratory technicians, and enforcement personnel.

To provide the regulatory community and regulatory agencies with appropriate chlorine test methods, the EPA Office of Solid Waste (OSW) and its contractor, Research Triangle Institute (RTI) have conducted a pilot study to identify and evaluate candidate analytical techniques for determination of chlorine in used oils and oil fuels. The results of this study, which are reported here, will be used to develop written test methods for the most promising techniques. These test methods will then be subjected to a formal collaborative study to generate precision and accuracy data for each method. These methods will then be proposed in the Federal Register as mandatory for compliance with the existing used oil regulation.

2. Approach.

2.1 Selection of Techniques for Evaluation

Candidate techniques were identified from reviews of the literature and from discussions with testing laboratories, equipment vendors and the oil industry. A broad spectrum of analytical approaches was considered. These ranged from published analytical test methods to prototype instrumentation and test kits for which development was incomplete. This complicated the evaluation of results, but inclusion of these varied methods, techniques, and instruments was necessary to assess the options available to EPA and the regulated community. A brief summary of each technique is provided below. Details are given in the final report on this study⁴.

The bomb combustion technique is based on ASTM Method D808-81. The oil sample is pressure oxidized by combustion in a stainless steel cylinder containing oxygen. The liberated chloride is absorbed in a sodium carbonate/bicarbonate solution contained in the bomb. The ASTM Method uses a gravimetric precipitation of chlorine as silver chloride as the analytical finish. However, this finish was found to lack adequate sensitivity at the 1000 ug/g level. For this study several alternative analytical finishes were evaluated. These included ion chromatography, mercurimetric titration, silver nitrate titration, and a ferricyanide colorimetric method.

Instrumental microcoulometry (MCT) is an automated technique in which an oil sample is first burned in a combustion chamber under oxygen to convert the chlorine to chloride. The chloride is then reacted with silver ions in a titrating cell, where the silver ions are replaced coulometrically. The total current required to replace the silver ion is a measure of the chloride present in the injected sample. Three MCT instruments currently available were evaluated. These are the COSA/Mitsubishi TSX-10, and the Dohrmann DX-20B and MCTS-20 analyzers.

An automatic instrumental chlorine determinator from LECO Corp., the Cl-35 was evaluated. It combusts oil samples under oxygen in a resistance furnace. The liberated hydrochloride gas is absorbed and measured by a chloride specific ion electrode.

A prototype field portable instrument based on the Beilstein test for chloride was evaluated. A probe containing copper wool is immersed in the sample and heated in a hydrogen flame. If chlorine is present, copper chloride emission will occur. The concentration of chlorine in the sample should be directly proportional to the intensity of this emission and can thus be quantified.

Two field portable disposable test kits were evaluated. Both kits operate by first dehalogenating chlorine from chlorinated organics (solvents, PCBs, etc.) by reacting the oil sample with a sodium naphthenate mixture in a diglyme catalyst. The chloride released by this reaction is then extracted into an aqueous buffer and titrated to the mercuric nitrate endpoint.

In the Dexsil Corp. kit, called Chlor-D-Tect 1000, the amount of sample and reagents are fixed such that a dark blue color results if the chlorine content is below 1000 ug/g and a yellow color results if the concentration exceeds 1000 ug/g. There is a relatively narrow transition zone over which the color change occurs.

The Chemetrics Inc. kit called Quanti-Chlor, involves largely the same chemistry as the Dexsil kit with the exception that the extracted chloride is titrated into an evacuated ampule containing mercuric nitrate solution to a yellow or colorless endpoint. The chlorine concentration in the oil over a range of 750-7500 ug/g is read from a scale on the ampule.

The final technique evaluated was x-ray fluorescence (XRF) spectrometry. This is a nondestructive technique in which the sample is placed in a disposable plastic cup covered with an x-ray permeable membrane and irradiated with x-ray radiation from a source within the instrument. The irradiated sample will then emit fluorescent element specific x-rays whose intensity can be quantified and correlated with the element's concentration in the sample.

Several types of XRF systems were evaluated. These included one field portable energy dispersive (EDXRF) system (the CSI XMET-840), several laboratory EDXRF systems (Oxford Analytical Lab X-2201, Horiba MESA 200, Tracor Spectrace 5000, Philips PV 9000), and two wavelength dispersive (WDXRF) systems (Philips 1400 and Oxford ChemX). These systems ranged in complexity from a system dedicated to determining only chlorine and sulfur to multielement systems capable of determining up to 60 elements.

2.2 Selection and Preparation of Test Samples

Both virgin and used oils and oil fuels representative of those subject to this regulation were obtained and characterized for chlorine content. These included crankcase, industrial hydraulic, metalworking and No. 6 fuel oil. Blends of No. 6 fuel oil with used oil were also created to simulate the final product of the used oil-to-fuel market.

These oils were then spiked with volatile, semivolatile, nonvolatile and inorganic chlorine over the range 0 to 10,000 ug/g, with most of the spike levels between 500 to 2000 ug/g, to cover the range of greatest interest. Chlorinated solvents were the volatile organics spiked, chlorinated benzenes the semivolatile organics and sodium chloride, the inorganic chlorine compound. Chlorooctadecane, a long chain paraffin hydrocarbon was selected as the nonvolatile spike compound to simulate similar compounds present as extreme pressure additives in metalworking fluids.

A total of 40 samples were supplied to each of nearly 20 volunteer laboratories from industry, equipment vendors, government and commercial testing laboratories. RTI acted as the referee laboratory and performed some of the testing by the bomb, test kit and XRF techniques.

Each laboratory was requested to analyze a total of 3 aliquots from each sample bottle and to report the chlorine content measured in each.

3. Results and Discussion

The accuracy of each technique was assessed on the basis of percent bias of the average of the three results for each sample from that of the expected value based on spiking and background level characterization.

Typical results for several of the techniques are given in Table II for a used crankcase oil and a 1:9 blend of used crankcase and No. 6 fuel oil. The LECO and Beilstein techniques were dropped from further consideration. It was determined that the LECO device has a detection limit near the 1000 ug/g level and thus suffered from poor accuracy at this level. The Beilstein device was determined to be unsuitable for determining chlorine in used oils, apparently due to an interference due to water. It was also insensitive to all forms of chlorine except chlorinated solvents.

The bomb technique with these analytical finishes and the MCT technique all gave results with ± 10 percent of expected. The test kits results were generally within ± 25 percent of expected with few false positives or negatives for the Dexsil kit.

XRF results varied somewhat, although the complexity of the instrument was apparently not a factor. In general, the biases were around 30 percent low, probably due to absorption of X-rays by water in the oil sample. This is sometimes compounded if the sample begins to stratify in the cell during the X-ray counting period. It is thought to be technique and not instrument related. One instrument, the MESA 200 suffers from an interference due to calcium in crankcase oils which results in high biases near 1000 ug/g.

In summarizing the performance of these techniques (Table III), additional factors such as susceptibility to matrix effects, analysis time, cost per analysis and field portability were determined or estimated.

The bomb/wet analytical techniques, the test kits, and the MCT all gave similar analytical performances. The basic difference is one of analysis time/sample, and cost/analysis. The bomb methods are tedious and labor intensive, while the test kits are rapid, have a fixed analytical cost that is somewhat lower and can be used in the field. The MCT systems are also rapid and in theory provide relatively low cost analyses.

The XRF technique is subject to matrix effects primarily due to water. However, the analysis time per sample, and the nondestructive nature of the technique make it attractive for high sample throughput.

4. Conclusions and Future Work

Techniques have been identified to determine the chlorine content in used oils in the field and in the laboratory. Based on this pilot study, written test methods are being developed for the bomb, test kit, MCT, and XRF techniques. These will be subjected to a formal collaborative study to generate precision and accuracy data for each method. These methods are to be proposed in the Federal Register as mandatory for compliance with this used oil regulation.

As part of this continuing evaluation, a cost effective used oil screening program is being developed which will combine field and laboratory testing to minimize costs, turnaround time, and ensure that the sale of solvent contaminated oil as fuel is prevented.

6. Acknowledgments

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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

^aLevel presuming mixing with hazardous waste.

^bLevel above which burning is not permitted if presumption can be rebutted.

TABLE II. TYPICAL RESULTS, % BIAS

Technique	Used oil 1320 ug/g	Used oil fuel blend, 998 ug/g
1. Bomb		
IC	-8	-4
Mercuric nitrate	-2	-8
Silver nitrate	-7	-13
Ferricyanide	+2	-5
2. Test kit		
Fixed point	-25	+10
Variable endpoint	-24	+35
3. Microcoulometry	+11	+9
4. EDXRF		
Portable	+5	+6
Nonportable	-21	-16
5. WDXRF	-30	+31

TABLE III. TECHNIQUE PERFORMANCE SUMMARY

Evaluation criteria	Bomb/Wet	Test kits	MCT	XRF
% Bias	<10%	±25%	±10%	-30%
% RSD	<10%	10%	5%	10%
False positives, negatives? ^a	Never	Seldom	Seldom	Sometimes
Matrix effects?				
Water	Never	Seldom	Never	Often
Oil type	Never	Never	Never	Sometimes
Chlorine form	Never	Never	Never	Sometimes
Analysis time/sample	45 min	10 min	10 min	<5 min
Cost/analysis ^b	\$25	\$11-14	\$3-5	\$3-5
Portability	No	Yes	No	XMET-840

^aresult not within ±25% of the expected value was considered a false positive or negative determination

^bbased on theoretical sample throughput with a technician working full time (8 hours/day)

OVERVIEW OF THE INTEGRATED AIR CANCER PROJECT

Joellen Lewtas and Larry Cupitt
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

The Integrated Air Cancer Project (IACP) is an interdisciplinary research program designed to develop the scientific methods and data sets needed to identify the major carcinogenic chemicals in the atmosphere; to characterize the emission sources and chemical precursors which give rise to the identified chemicals; and to improve the methodology and data available for assessing human exposure and risk due to exposure to airborne carcinogens. The research effort is focused primarily on characterizing the impact of complex mixtures of products of incomplete combustion, including the gaseous, semi-volatile, and particle-bound organic species.

These objectives will be approached in a stepwise manner by conducting a series of field studies in areas of increasing complexity. The initial work has concentrated on relatively simple airsheds where residential wood combustion and automobile emissions are the only significant combustion sources. Future efforts will add other residential combustion sources (e.g., fuel oil) and industrial sources.

The first phase of this project was conducted at Raleigh, NC and Albuquerque, NM during the winter of 1984-85. The focus of these initial efforts was: (1) to develop, evaluate, validate, and document the sampling and analysis methods necessary to accomplish the technical research, and (2) to attempt to extend current source apportionment techniques to account for the observed mutagenicity of the collected ambient aerosol samples. During FY-86/87 an extensive field program was conducted in Boise, ID.

Introduction

Major scientific questions regarding the relationship between air pollution and human cancer remain unanswered. This is due, in large measure, to the fact that estimates of human cancer caused by air pollution are highly refractory to the traditional techniques of epidemiology and exposure and risk assessment. The length of time (decades) that may pass between exposures to airborne carcinogens and diagnosis of cancer has precluded both meaningful prospective epidemiological studies of human populations and quantitative estimates of the risk from exposure to mixtures of airborne carcinogens. Retrospective studies are also difficult to perform since one does not know when the observed cancer was initiated. Because most nonoccupational cancers are not specific and could have multiple causations, the process of associating an observed cancer with a given putative agent has not met with great success. In 1977 and again in 1982, international experts concluded that air pollution arising from combustion products of fossil fuels, probably acting together with cigarette smoke, have been responsible for 10% of all cancers for the United States^{1,2}. This estimate is really a "best guess" based on studies of the urban versus rural cancer rates. Doll and Peto³, in a review of causes of cancer in the U. S., suggest that a much lower rate of 2% of cancer deaths could be attributed to pollution. Karch and Schneiderman⁴ on the other extreme suggest that past analyses of this problem have overestimated the contribution of smoking and underestimated the multicausal nature of cancer. They estimate that at least 11% and more likely 21% of lung cancer is related to air pollution.

Regardless of which of these estimates proves to be the most accurate, there is certainly reason to believe that the carcinogenic potential of air pollution may be a serious public health problem. EPA has undertaken a major research program directed specifically at clarifying the exposure, risk and sources of carcinogens in the air. This relatively long-term research program, initiated in 1985, is the Integrated Air Cancer Project (IACP). As a part of the IACP, a methodology is being developed to allow an estimate of the future cancer risk associated with human exposures to the direct and transformed emissions from identifiable sources. The Environmental Protection Agency has the responsibility and authority to regulate the emission of carcinogens into the air (e.g., Section 112, Clean Air Act), however, the identification of which carcinogens and which emission sources are of greatest potential human risk is not known and remains a high-priority research effort. The IACP adopts an approach which focuses on identifying those species actually present in the air which are most likely to be carcinogenic and attempts to determine how they came to be present in the environment. The accomplishment of this research requires the IACP to bring together the multi-disciplinary talents of chemists, physicists, engineers and toxicologists to conduct a series of coordinated field and laboratory studies of the emission sources, the atmospheric transport and transformation, human exposures, and the toxicological effects, in order to address the complex issues involved.

Integrated Air Cancer Project Goals and Strategy

Goals

Identify the Principal Airborne Carcinogens. Airborne carcinogens may exist as gaseous or volatile organic compounds (VOCs), as semi-volatile organic species (SVOCs), or as particulate-bound organic compounds [e.g., polycyclic organic matter (POMs)]. The identities and relative contributions to the total atmospheric burden of carcinogens by many of the organic chemicals present in the atmosphere are not yet known. The IACP is develop-

ing the methods and data necessary to begin to characterize many of these species. Within each of these groupings (e.g., VOCs, SVOCs, and POMs), the specific chemicals or chemical classes which contain mutagenic and carcinogenic compounds need to be identified, and their concentration in the environment needs to be measured. These carcinogens may be direct emissions from the sources, or they may be the transformation products produced from reactions of simple hydrocarbons or complex polynuclear aromatic hydrocarbons with acidic and oxidizing gases in the atmosphere. The complexity of the problem requires that an integrated approach be used to address these goals. Not only must the emissions from the various sources be identified, but the transformation products from those emissions must also be determined.

Determine Which Emission Sources Are the Major Contributors of Carcinogens to Ambient Air. Before one can reduce human exposure to hazardous air pollutants, the sources of the carcinogenic compounds themselves, or their precursors, have to be identified. Field studies with simultaneous emission characterizations and ambient monitoring, followed by source apportionment calculations, will be conducted to determine which emission sources are the major contributors of carcinogens to the ambient air. Characterization of emissions and ambient samples will be by both chemical and biological (mutagenicity and carcinogenicity) testing.

Improve the Estimate of Human Exposure and Comparative Human Cancer Risk from Specific Air Pollution Emission Sources. In order to improve the estimate of relative human cancer risk from specific air pollution emission sources, a comparative methodology is being developed to evaluate and utilize short-term mutagenesis and animal carcinogenesis data on emission sources. In addition, better total human exposure estimates will be developed for these complex emission products and individual carcinogens including transformation products.

Strategy

The long range goals of this project will require many years to attain. Approaching the long term goals through field studies of relatively simple airsheds will, in a stepwise fashion, yield the methodology to understand the more typical complex airsheds containing emissions from multiple sources experienced by the general population.

Current data indicate that motor vehicles and residential home heating sources make a significant contribution to the mutagenic activity of ambient air samples. Therefore, the initial phases of IACP were aimed at quantifying carcinogens emitted from residential woodstoves and motor vehicles. Communities were selected with relatively simple airsheds where a significant percentage of the homes use wood as the major heating fuel. The initial IACP studies conducted in Raleigh, NC and Albuquerque, NM emphasized field and laboratory evaluation to select sampling and analysis methodologies for a major field study initiated in Boise, ID in the winter of 1986-87. Transformation studies in laboratory simulations are assessing the role of atmospheric chemistry in altering the chemical composition and mutagenicity of the emitted chemicals. Simulations of the field study conditions will be used to determine the critical factors and chemical processes which transform the species between the source and the receptor.

Technical Approach

Integrated Field Studies

The field studies were designed to simultaneously sample and charac-

terize the emissions at the source (e.g., woodstoves or motor vehicles) in the ambient air near to specific sources and in the ambient air distant from an aggregate of sources⁵. Sampling indoors and outdoors of homes both with and without woodstoves was designed to provide an indication of the total human exposure. In general, source and ambient emission measurements were made during heating and nonheating periods as well as separate daytime and nighttime sampling periods to differentiate between wood combustion emissions and those from motor vehicles. Indoor, ambient, and source emissions were collected comparably and analyzed identically to provide a valid comparison between the fresh emissions and the chemicals at the receptor. Neighborhood survey data of motor vehicle and residential heating use was also recorded. Meteorological measurements and tracer studies were conducted throughout field tests as input to the source apportionment and atmospheric transformation studies.

The initial IACP field study in Raleigh, NC included major components of methods development and evaluation. Factors such as face velocity, sample integrity, and sample extraction and preparation methods were evaluated, and standard procedures developed for subsequent studies. Sampling methods were developed so that comparable samples could be taken simultaneously from woodstove sources and ambient air (indoors and outdoors). In order to collect large (gram) quantities of ambient air particulate matter for bioassay directed fractionation/characterization and carcinogenesis studies, new high volume samplers have been designed⁶. The sampling protocols take into consideration techniques necessary to collect particulate material as well as volatile, semi-volatile, and condensable organic material. New sampling and analysis methods were developed to prepare, sample, and extract large quantities of XAD-2 resin for organic characterization and bioassay studies. The results of the study included sampling protocols for source, ambient, and microenvironment air collection.

Analysis Strategies

Source Apportionment. Source apportionment is a combination of mathematical and analytical procedures which are used to determine the contribution of specific emission sources to measurements of air pollution. Several methods have been used to apportion the contributions of source emissions to ambient air quality including emission inventory methods, source dispersion models and receptor models. The receptor-model approach to source apportionment which is being used in the IACP is especially effective where the number of sources are small and well characterized. In addition, emissions from mobile sources and wood burning contain unique elemental tracers which improve the accuracy of the source apportionment calculations.

Source apportionment of mutagenic activity and the use of organics as tracer species in receptor model studies have not been extensively evaluated and are a major component of the IACP⁷. The unique feature in the receptor modeling studies in the IACP are that several types of information will be available. The receptor modeling will use a combination of elemental tracers (e.g., K and Pb), radiocarbon⁸, organic tracers⁹, and mutagenicity¹⁰ in the source apportionment calculations.

Bioassay Directed Fractionation/Characterization. This approach has been successfully used to identify potential carcinogens in complex mixtures including synthetic fuels, diesel emissions, and urban air particles¹¹. The complex mixtures are fractionated and each fraction is bioassayed. Mutagenically active fractions are further fractionated, bioassayed, and characterized until the major class or specific compounds responsible for the muta-

genicity are identified. The IACP is using the standard Ames Salmonella typhimurium plate incorporation mutagenicity assay, together with new micromutagenesis bioassays, coupled directly to analytical fractionation procedures¹⁰.

Atmospheric Transformation. A growing number of laboratory and field studies have suggested that there are unidentified compounds present in ambient air which cause increased mutagenic responses in both the vapor and aerosol phases. Chemical analysis has not fully identified many of these compounds, but the chemical class information suggests that the target compounds may be the partially-oxygenated or -nitrogenated reaction and transformation products of emitted organics. Recent studies have demonstrated that exposure of many organic source emissions to photochemical reaction conditions increases the mutagenicity of the emissions, especially the gaseous components¹².

The transformation studies carried out as part of the IACP will utilize a large reaction and atmospheric simulation chamber to produce irradiation products of air mixtures like those found in typical U.S. environments and in the IACP field study. The simulation chamber will produce consistent conditions which will permit exposure of bioassay test systems and will provide large quantities of the transformation products for chemical sampling and analysis. Bioassay studies are conducted on the starting materials and the irradiation products¹³.

Human Exposure Assessment. Since the initial phases of the IACP are focusing on characterizing the principal organic mutagens and carcinogens from products of incomplete combustion (PICs) the exposure assessment component of the program is designed to characterize the important human exposure environments indoors and outdoors which are impacted by PICs. Characterization of the total organic exposures will include measurement of VOCs via both canister and Tenax sampling and GC analysis¹⁴, SVOCs via XAD-2 sampling and analysis, and total particulate organic analysis. Specialized sampling and analysis of aldehydes was conducted using the 2,4-dinitrophenylhydrazine (DNPH) cartridge method¹⁴. Specific analyses are being conducted to quantitate exposures to polycyclic aromatic hydrocarbons (PAHs)⁹ and selected polar oxygenated and nitrated organics.

Comparative Carcinogenesis and Mutagenesis Assessment. In order to develop a comparative data base for risk assessment, a battery of bioassays will be used to evaluate the complex mixtures from the field study filter samples. A comparative potency method has been developed for cancer risk assessment based on a constant relative potency hypothesis and using data from a battery of short-term mutagenesis bioassays and animal tumorigenicity studies on a series of diesel vehicle emissions¹⁵. The same bioassays have been used to evaluate complex emissions for which human lung cancer risk estimations are available from occupational and relatively high dose exposures (emissions from coke ovens, roofing tar pots, and cigarette smoke) thereby providing a comparative basis for estimating lung cancer risk from emissions for which human data are not available. Recent EPA studies have expanded the combustion emission data set for which comparative mutagenesis and carcinogenesis data are available to include gasoline vehicle emissions, coal, oil, and wood combustion¹⁶. The IACP will further extend this data base to include comparative mutagenesis and carcinogenesis studies of composites of ambient particulate organics from the airsheds under study.

Summary

The IACP is a long-term research project with goals of (1) identifying the principal airborne carcinogens, (2) determining which emission sources are major contributors of carcinogens to ambient air, and (3) improving the estimate of human exposure and comparative human cancer risk from specific air pollution emission sources. Ultimately, this research will provide the methodology and data to estimate the comparative risks associated with human exposure to various combustion emissions sources and other sources.

Although accomplishment of the long-range goals of the IACP will require many years to attain, the IACP concept is to approach the goals in a stepwise fashion to provide short-term data on specific source categories. Studies are aimed at understanding both the chemistry and toxicology of complex mixtures of air pollutants focusing first on relatively-isolated airsheds, and progressing to more-typical and more-complex environments, with multiple source contributions. During the initial phases of the IACP, emphasis has been placed on the source categories of residential wood combustion and motor vehicles. Subsequent phases of this project will add other residential combustion sources (e.g., oil) and industrial sources.

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THE COLLECTION OF NEIGHBORHOOD AIR SAMPLES
IMPACTED BY RESIDENTIAL WOOD COMBUSTION IN
RALEIGH, NC AND ALBUQUERQUE, NM

V. Ross Highsmith and Charles E. Rhodes
Environmental Monitoring Systems Laboratory
Roy B. Zweidinger
Atmospheric Sciences & Research Laboratory
Raymond G. Merrill
Air & Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Pilot field studies were simultaneously conducted in Raleigh, NC, and Albuquerque, NM, from January through March 1985. Consecutive twelve-hour sampling (7AM - 7PM and 7PM - 7AM) was conducted at two fixed monitoring sites in both cities. In each city, the primary fixed sampling site was located in a residential neighborhood heavily influenced by residential wood combustion emissions. State-of-the-art sampling equipment and procedures were developed and tested for the collection, storage and shipment of field samples. Semi-volatile and volatile organic samples were collected and analyzed in Raleigh. Routine criteria pollutant and meteorological parameters were also monitored at each site. Indoor, outdoor, and source sampling was conducted at three Raleigh residences with operating woodstoves. Sample analysis included mass loadings, inorganic ions, volatile/elemental carbon, carbon-14, mutagenic activity, and organic characterization.

Both Raleigh and Albuquerque nighttime FINE particle (0-2.5 micron) mass loadings were more than twice the daytime FINE mass loadings. Approximately 60% of the nighttime FINE samples were extractable organics. The nighttime potassium concentrations from samples collected in both cities were more than twice the daytime potassium concentrations, suggesting significant impact by RWC emissions. The FINE loadings immediately outside the residences correlated well with the fixed site measurements but were approximately twice the FINE mass collected inside the residences. Overall, the residential data demonstrates the variability expected with differences in residence construction and individual activity.

INTRODUCTION

Advances in airtight woodstove technology and the relatively low cost for wood have combined to make residential wood combustion (RWC) an attractive alternative for home heating. Laboratory studies¹⁻⁴ have shown RWC emissions to be rich in polycyclic organic material (POM) and products of incomplete combustion (PIC's). The concentrations of these potentially carcinogenic compounds depend on the woodstove size, fuel source and operating conditions. Many homeowners operate their woodstoves at very low burn rates for two reasons: the purchased stove is too large for the installed area, or in an attempt to maintain overnight stove operation. The PIC's contributed to the ambient air from residential woodburning significantly increase under these oxygen-starved conditions. Communities dominated by residential woodburning report ambient outdoor air quality degradation directly corresponding to RWC emissions.⁵⁻⁷ In addition, recent residential studies contribute increases in indoor air pollutants to the use of woodstoves and fireplaces for home heating.^{8,9} The potential total human exposure to RWC emissions, both indoors and outdoors, is a primary area of concern to the scientific community.

The Integrated Air Cancer Project (IACP) is a long term US Environmental Protection Agency (EPA) program with three major objectives: identifying principal airborne carcinogens; determining the major emission sources for these carcinogens; and improving the estimate of comparative human cancer risks from specific air pollution emission sources. Initial IACP studies were planned for simple airsheds in order to develop the procedures needed to characterize complex airsheds typical of more industrialized urban areas. Residential Wood Combustion (RWC) was selected as the first source for evaluation based on its relative use and overall impact on the national air quality.¹⁰ RWC impacted samples, high in mass and organics, would also support the initial IACP sampling and analytical methods development initiatives.

Pilot field studies were simultaneously conducted during 1985 in Raleigh, NC and Albuquerque, NM to evaluate state-of-the-art monitoring for air carcinogens. The Raleigh study served as the major sampling location allowing maximum EPA personnel involvement while focusing on sampling and analytical methods development. Both ambient fixed site monitoring as well as residential indoor monitoring were conducted in Raleigh. The residential study was designed to evaluate methodologies for the simultaneous collection of indoor, outdoor, and RWC source samples. Source apportionment/receptor model analysis procedures outlined by Lewis and Einfield¹¹ was the primary focus of the Albuquerque study. Routine particulate and gaseous samples were collected at each sampling location. The majority of the ambient particulate samplers were modified to collect only the FINE (0-2.5 μ m) particle size fraction. Gas and particle phase semi-volatile organic compounds (SVOC's) and volatile organic compounds (VOC's) were collected indoors and outdoors in Raleigh but were not collected in Albuquerque. Criteria pollutant and meteorological parameters were also monitored at the fixed sampling sites.

EXPERIMENTAL

Fixed site ambient monitoring was conducted at primary and secondary locations in both Raleigh, NC and Albuquerque, NM from January 1985 through March 1985. The Raleigh airshed is not significantly impacted by major local sources but tends to reflect regional source contributions. Local topographical and meteorological conditions assist in minimizing the impact of automotive emissions on the Raleigh airshed. Albuquerque, at more than twice

the population of Raleigh, is a high elevation city located in the Rio Grande river basin and backs up against the Sandia mountain range to the East. As with Raleigh, Albuquerque has no local major industrial sources but has been shown to be impacted by RWC and mobile source emissions.¹¹ Regional contributions to the local airshed from the Western desert are minimal. The topography and meteorological conditions in Albuquerque favor the retention of local emissions especially during the intense winter inversions.

The Raleigh primary woodsmoke site was located in a residential neighborhood valley away from major roadways. A background site was located at a rural site approximately 10 miles North of Raleigh to evaluate regional source contributions to the airshed. Each of the three Raleigh residences selected for the study had nonsmoking occupants and were located within one quarter of a mile from the Raleigh primary sampling site. The Albuquerque primary woodsmoke site was located at the site of the earlier study.¹¹ A second Albuquerque site was located approximately two miles Northwest of the primary site at a major roadway intersection. Both Albuquerque sites were in close proximity (ca. 3/4 mile) of interstate highways.

Each fixed monitoring site was established in accordance with Inhalable Particulate Network (IPN)¹² and NAMS/SLAMS criteria.¹³ The types and numbers of samplers operated at each site are shown in Table I. Uniform sampling procedures were developed and employed in both cities. Twelve-hour ambient sampling (changeovers at 7AM and 7PM) was conducted to evaluate daytime versus nighttime source contributions. Samples for mass and inorganic analysis were collected on preweighed quartz or Teflon® media. Samples for bioassay and carbon analysis were collected on Pallflex T60A20 Teflon® impregnated glass fiber (TIGF) and IPN equivalent quartz filter media. Vapor phase SVOC's passing through particulate filters were collected on XAD-2 absorbent filled canisters installed immediate downstream of the filter. Cartridges impregnated with 2,4-dinitrophenylhydrazine (DNPH) and evacuated SUMMA® polished canisters were used to collect aldehydes and VOC's, respectively. Denuder equipped samplers were operated at the two primary sites for NO₃ and HNO₃ collection. Criteria pollutant and meteorological parameters were monitored using reference procedures. SVOC, bioassay and carbon samples were stored at -80° C immediately following sampling. Particulate samples for mass determination were conditioned for twenty-four hours followed by standard gravimetric analysis. Aldehyde and denuder samples were stored at -4°C.

Residential sampling followed the ambient procedures outlined above. Samples were collected on two consecutive nights at each residence, sampling one residence at a time. Table II lists the samples collected simultaneously indoors, outdoors, and at the Raleigh primary site. Particulate and SVOC samples were also collected directly from the operating woodstove flue using the Woodstove Dilution Sampling System (WSDSS).¹⁴⁻¹⁵ All the XAD-2 cartridges were placed outdoors during sampling to ensure comparability between residential, ambient, and source samples. Standard SF₆ tracer release techniques were used to measure residential air exchange rates.

ANALYSIS

The analytical procedures used in this study are referenced in Tables I and II. A set of fifty ambient site sampling periods (combination of day and night periods) were selected from each city for detailed analysis. Particle bound SVOC's were solvent extracted using dichloromethane. Aliquots were evaporated to dryness for gravimetric determination. Additional aliquots were solvent exchanged with dimethylsulfoxide (DMSO) and stored at -80° C

in preparation for bioassay analysis. The Ames bioassay, with and without the activation agent S9, was used to determine sample mutagenic activity. Residential samples for bioassay analysis were independently processed by the laboratory within 48 hours after sample collection. Particle and gas phase SVOC's were independently extracted with dichloromethane. Aliquots of each particulate extract was evaporated to dryness and quantitatively determined. The quantity of XAD-2 extracts were determined by gas chromatography and gravimetric analysis. Aliquots of the sample extracts were DMSO solvent exchanged and stored at -80°C pending bioassay analysis. Since the indoor sample mass was small, the mutagenic activity of all the residential samples was determined using the forward mutation assay method.

RESULTS AND DISCUSSION

The data for FINE particle mass collected in the 90 Raleigh and 103 Albuquerque ambient sampling periods are shown in Figures 1 and 2, respectively. FINE mass loadings exceeded $35\text{ }\mu\text{g}/\text{m}^3$ (ca. twice the Raleigh background level) during 17 Raleigh nighttime, 20 Albuquerque nighttime, and 4 Albuquerque daytime periods. No Raleigh daytime FINE level exceeded $35\text{ }\mu\text{g}/\text{m}^3$. In both cities, the two highest FINE mass loadings were recorded during weekend periods (Raleigh $135\text{ }\mu\text{g}/\text{m}^3$ and $130\text{ }\mu\text{g}/\text{m}^3$; Albuquerque $170\text{ }\mu\text{g}/\text{m}^3$ and $140\text{ }\mu\text{g}/\text{m}^3$).

Table III summarizes the ambient site particulate data. Daytime FINE mass loadings were approximately one half the nighttime levels in both cities. Daytime to nighttime concentrations of FINE potassium, a known tracer for woodsmoke, are 1:3 for Raleigh and 1:2 for Albuquerque. Plots of the nighttime potassium concentrations versus mutagenicity (TA98 plus S9) yield good linear correlations for both cities and suggest the influence of nighttime RWC emissions. The slope of the Raleigh data shown in Figure 3 is approximately five times that of Albuquerque (Figure 4), which is consistent with the reported proportions of potassium in hardwoods and softwoods. Woodburning in Raleigh is comprised primarily of hardwoods while softwoods are almost exclusively burned in Albuquerque.

Lead levels increased slightly during nighttime periods in both cities. More important, Albuquerque lead levels were three times the corresponding Raleigh lead levels as a result of a greater vehicle population and proximity to nearby roadways. Linear regressions of nighttime lead versus mutagenicity yielded good agreement in Albuquerque ($r = .83$), but poor agreement in Raleigh ($r = .68$), highlighting the influence of mobile source emissions in Albuquerque.

The Raleigh background data agrees well with the daytime primary site values and reflects regional source contributions. These data indicate that during the day the Raleigh primary site was not influenced by RWC or mobile source emissions.

Particle bound SVOC's increased from 40% during the day to more than 60% during the night corresponding to increased RWC emissions. The results of the Ames bioassay without the addition of the activation agent S9 show an increase in mutagenic activity with corresponding increase in FINE mass. The addition of S9 doubled the activity of the Albuquerque nighttime samples but did not influence the Raleigh samples. Based on the reported activity¹⁶ and relative potency¹⁷ of automotive emissions, the elevated lead levels in Albuquerque ($\text{max} = 1.37\text{ }\mu\text{g}/\text{m}^3$), and knowledge of the Albuquerque meteorology suggest that this increased activity may be associated with increased mobile source emissions. Ambient aldehyde and VOC results show increased total

concentrations with increased RWC emissions. Napthalene, a key component in woodsmoke, was elevated during RWC impacted periods.¹⁸

The impact of increased RWC emissions on pollutant concentrations is shown in Figure 5. Twelve-hour sampling periods and corresponding FINE mass loadings are also shown. Although daytime lead and potassium levels were equal (ca. .07 $\mu\text{g}/\text{m}^3$), nighttime potassium levels increased by a factor of 7.5 compared to a fourfold increase in lead levels. This data suggest that during this period of inversion, the Raleigh residential airshed was impacted not only by high RWC emissions, but also by other emission sources being concentrated by the local meteorological conditions.

The analysis data for the residential measurements are summarized in Tables IV and V. Four key factors impacted on the data reported. Residence 1 was noted as having a leaking woodstove which could be detected from the occasional odor throughout the house. The woodstove plume from the woodstove chimney at Residence 2 was observed periodically downwashing on the outdoor samplers. Residence 3 had an operational electrostatic precipitator in the cold air return duct during sampling. Electrical constraints at Residence 1 did not allow the operation of the outdoor dichotomous sampler or CO analyzer.

At the three homes monitored, indoor FINE and PM_{10} loadings were significantly less than the corresponding outdoor loadings, which differs from previous studies.^{8,9,19} The minimal FINE loadings observed in Residence 3 are attributed to the electrostatic precipitator. Outdoor and primary site FINE and PM_{10} loadings agreed well and indicate uniform distribution of emissions over the neighborhood. Indoor COARSE/FINE ratios were larger than corresponding outdoor values and are attributed to homeowner activities (i.e., vacuuming, walking, pets, etc.) causing reentrained coarse particles. Other key inorganic components were uniformly distributed between indoors and outdoors. The tracer gas studies suggest a complete exchange between indoor and outdoor air once every two hours. The WSDSS source samples compared well with laboratory test samples and are reported by Merrill and Harris.¹⁵

Residence 1 samples yielded the highest levels of gas phase extractable organics and napthalene, a key component for RWC. These are attributed to the leaky woodstove. A slight increase in outdoor extractable organics observed at Residence 2 is contributed to the downwashed plume. Overall, the mutagenicity of the outdoor residential particulate samples was 3-4 times greater than the corresponding indoor sample activity. Contaminated RAD-2 field blanks prevented a similar comparison between indoor and outdoor gas phase mutagenicity. Aldehyde and VOC concentrations were slightly elevated indoors. In the three homes sampled, the distribution of VOC's did not change from indoor to outdoor samples nor with increased FINE mass loadings. The distribution of aldehydes indoors differed from the outdoor levels with elevated formaldehyde concentrations being observed indoors.

CONCLUSIONS

Many of the procedures tested in these studies for collecting, storing and analyzing ambient, residential and source samples can be used to support future IACP objectives. The ambient data documented the impact of RWC emission on both Raleigh and Albuquerque during the 1985 winter heating season as well as the influence of mobile source emissions on the Albuquerque airshed. The residential study results provide observations that can be used to plan future indoor studies. FINE and PM_{10} levels were lower indoors

than outdoors suggesting that when operated correctly, an airtight woodstove should not directly influence indoor air quality. Leaks in the stove or flue allowing RWC emissions to enter the home will, however, elevate the indoor pollutant concentrations. The data suggest that the homes evaluated in this study were also influenced by other sources such as materials used to build or furnish the home and homeowner activities. This emphasizes the importance of preliminary questionnaire information and comprehensive data collection during exposure studies.

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DISCLAIMER

The research described in this paper has been reviewed by the Environmental Monitoring Systems Laboratory, US EPA and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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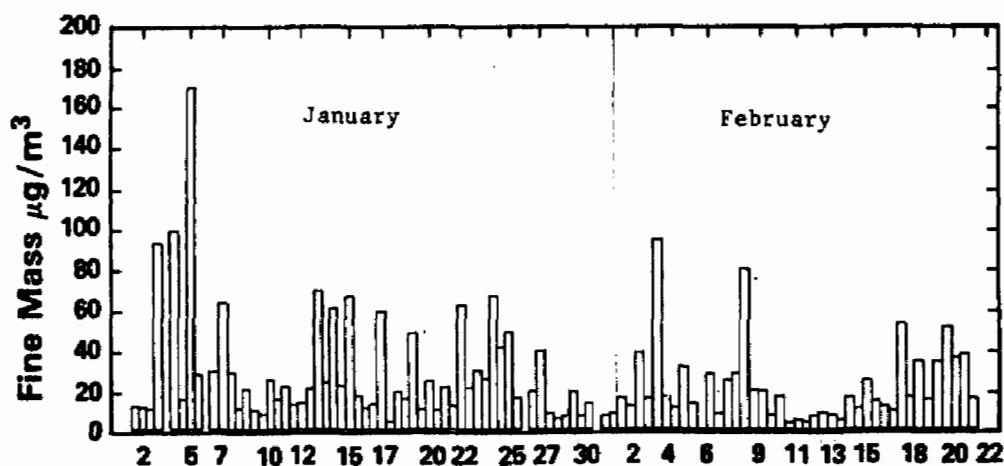


Figure 2. Albuquerque Fine Mass Loadings

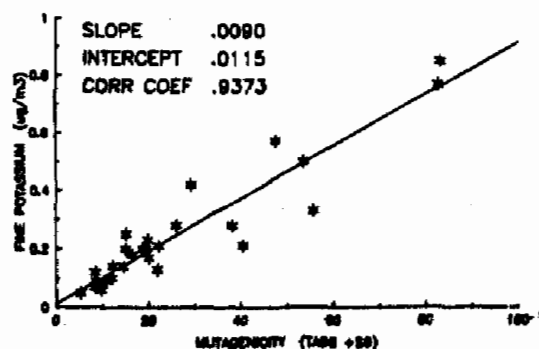


Figure 3. Raleigh Fine Potassium Versus Mutagenicity

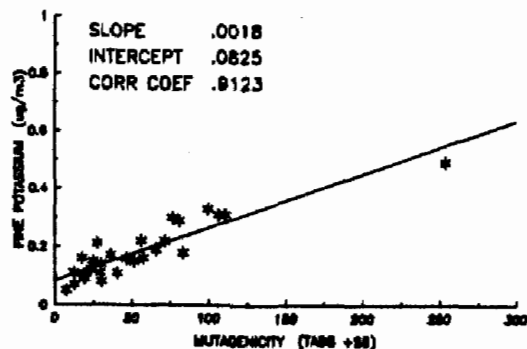


Figure 4. Albuquerque Fine Potassium Versus Mutagenicity

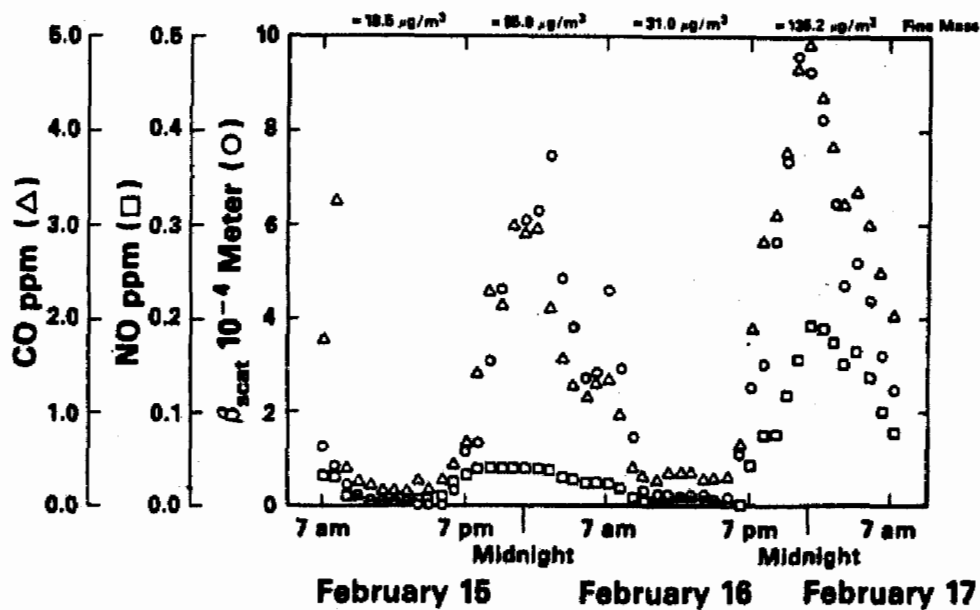


Figure 5. Time plot of a woodsmoke impacted weekend.

Analysis	Residence								
	1			2			3		
	In	Out	Ambient	In	Out	Ambient	In	Out	Ambient
Fine Mass, $\mu\text{g}/\text{m}^3$	18.0		22.4	27.2	57.2	55.4	2.8	16.8	14.8
Coarse/Fine Ratio	0.46		0.10	0.28	0.20	0.13	0.70	0.36	0.28
Fine K, $\mu\text{g}/\text{m}^3$	0.08		0.12	0.22	0.29	0.31	BD	0.05	0.04
Fine Pb, $\mu\text{g}/\text{m}^3$	0.04		0.08	0.22	0.31	0.25	BD	0.05	0.04
CO ppm			0.5	2.2	2.1	2.0	0.9	0.9	0.8
Air Exchange Rate	0.42			0.38			0.57		

TABLE IV. RESULTS OF INORGANIC ANALYSIS ON RESIDENTIAL SAMPLES

Analysis	Residence								
	1			2			3		
	In	Out	Ambient	In	Out	Ambient	In	Out	Ambient
Fine Mass, $\mu\text{g}/\text{m}^3$	18.0		22.4	27.2	57.2	55.4	2.8	16.8	14.8
XAD-2									
GRAV mg/sample	4.8	2.1	1.3	BD	BD	BD	BD	BD	BD
TCO mg/sample	21.1	8.8	8.3	18.8	17.5	14.0	8.3	3.0	1.0
Bioassay (+ SD)	15.8	47.7	47.0	38.2	108.3	95.1	5.5	18.9	18.4
Filters mutants/ m^3									
Total VOC $\mu\text{g}/\text{m}^3$	224	285	188	824	418		381	204	82
Total Aldehydes $\mu\text{g}/\text{m}^3$	48	14	10	41	34.3		84	18	5

BD = below detection

TABLE V. RESULTS OF ORGANIC ANALYSIS ON RESIDENTIAL SAMPLES

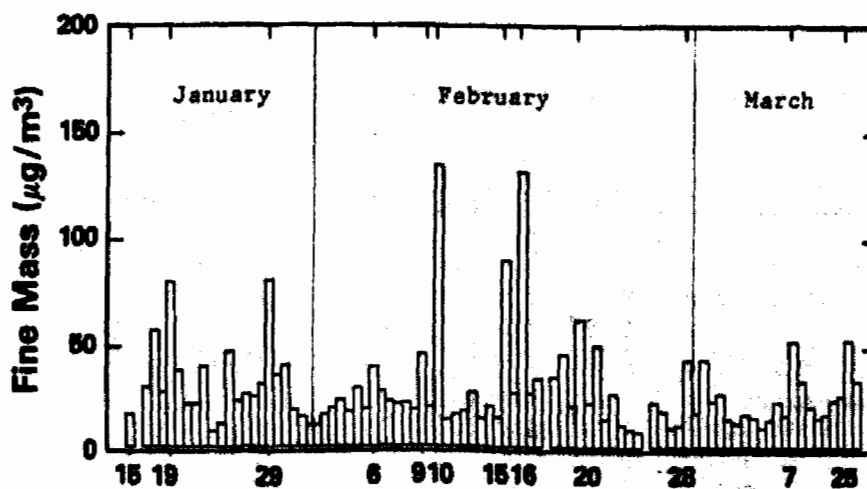


Figure 1. Raleigh Fine Mass Loadings

ANALYSIS	SAMPLER	RALEIGH		ALBUQUERQUE		ANALYSIS REFERENCE
		PRIMARY	BACKGROUND	PRIMARY	ROADWAY	
MASS	TSP	1	-	-	-	12
	Dichotomous	2	1	1	1	
BIOASSAY	PM _{2.5} Hi-vol	4	2	2	1	20,21
	PM ₁₀ Hi-vol	2	-	-	-	
RESIDENTIAL	4 CFM with XAD-2	2	-	-	-	30,31 22,23
SEMI-VOLATILES XAD-2	PM _{2.5} Hi-vol	2	-	-	-	22,23
	PM ₁₀ Hi-vol	2	-	-	-	
¹⁴ C	PM _{2.5} Hi-vol	2	1	2	1	24,25
C _v /C _e	Modified Dichotomous	-	-	1	-	26
NO ₃ , HNO ₃	Denuder	1	-	1	-	27
ORGANICS	VOC	1	1	-	-	28
	Aldehyde	1	1	-	-	29
CONTINUOUS	CO, NO _x , O ₃ , SO ₂	YES	YES	YES	CO	
	β scat.	YES	YES	YES	YES	
	Meteorology	YES	YES	YES	YES	

TABLE I. AMBIENT SAMPLERS

ANALYSIS	INDOOR	OUTDOOR	PRIMARY	ANALYSIS REFERENCE
MASS	Dichotomous	Dichotomous	Dichotomous	12
BIOASSAY	4 CFM	4 CFM	4 CFM	30,31
SEMI-VOLATILE	XAD-2	XAD-2	XAD-2	22,23
ORGANICS	VOC	VOC	VOC	28
	Aldehyde	Aldehyde	Aldehyde	29
CRITERIA	CO	CO	CO	
AIR EXCHANGE RATE	BAG	-	-	32

TABLE II. RESIDENTIAL SAMPLERS

	Raleigh			Albuquerque	
	Primary		Background	Primary	
	Day	Night	Total	Day	Night
Sample Periods	31	44	62	50	53
Fine					
Mass $\mu\text{g}/\text{m}^3$	18.4	42.7	18.3	27.2	57.1
K $\mu\text{g}/\text{m}^3$	0.08	0.24	0.07	0.10	0.18
Pb $\mu\text{g}/\text{m}^3$	0.08	0.13	0.08	0.30	0.38
Bioassay					
EOM $\mu\text{g}/\text{m}^3$	7.4	25.0		8.8	34.7
- S9 rev/ m^3	10.2	22.1		15.5	21.3
+ S9 rev/ m^3	8.5	24.8		21.2	52.1

TABLE III. RESULTS OF ANALYSIS ON AMBIENT SAMPLES

"THE SOURCE APPORTIONMENT OF CARBONACEOUS
COMBUSTION PRODUCTS BY MICRO-RADIOCARBON
MEASUREMENTS FOR THE INTEGRATED AIR CANCER
PROJECT (IACP)"



G.A. Klouda, L.A. Currie, A.E. Sheffield,
S.A. Wise, B.A. Benner
National Bureau of Standards,
Gaithersburg, MD 20899

R.K. Stevens and R.G. Merrill
U.S. Environmental Protection Agency,
Research Triangle Park, NC 27711

Abstract

Atmospheric particle samples were collected during the winter of 1984-1985 in Albuquerque, NM and Raleigh, NC by the EPA for the Integrated Air Cancer Project (IACP). Selected chemical fractions were analyzed for ^{14}C to apportion mobile (motor vehicles) and stationary (residential wood combustion) sources. In addition, these results were used to validate the EPA Single Tracer Regression Model (STRM), also a technique for the source apportionment of aerosols.¹ Preliminary ^{14}C results for the Albuquerque residential site at night showed 79% Contemporary Carbon (CC) compared to 95% CC for Raleigh at night for the total carbon; 88% and 94% of the total-C was organic, respectively. The Albuquerque traffic site during the day showed 1.4 to 3.9 times less CC compared to the daytime residential site for total-C. The elemental carbon fraction in all cases showed a lower percentage of contemporary carbon than the total carbon, which indicates that this chemical fraction may be an excellent tracer of mobile sources. These results are consistent with a daytime mobile source at the traffic site and a nighttime Residential Wood Combustion (RWC) source at the residential site. Also, the results from the EPA STRM technique for this study were in good agreement with those obtained by the ^{14}C Direct Tracer (^{14}C -DT) technique for source apportionment of these aerosols.¹

Introduction

Concentrations of carbonaceous pollutants in urban atmospheres have typically been measured over time and space to quantify the impact of total emission sources at receptor (collection) sites. For apportioning fossil and contemporary carbon source emissions, the ^{14}C Direct Tracer (^{14}C -DT) technique has been applied to bulk air particle samples, which are frequently size segregated ($<2.5\ \mu\text{m}$).² Application of the ^{14}C -DT technique to important chemical classes extracted from the bulk material, e.g. the polycyclic aromatic hydrocarbon (PAH) fraction, has shown a potential for improving the process of deconvoluting emission sources.^{2,3} Also, the origin of biologically active (mutagenic or carcinogenic) compounds and/or chemical classes, e.g. the PAH's, is important from a toxicological standpoint and is one of the prime objectives of the Integrated Air Cancer Project (IACP).

Additional source information may be gained by comparing the molecular "fingerprint" pattern of chemical fractions determined from source samples with that obtained from the ambient samples. Some compounds may be unique to the combustion source of interest.⁴ These chemical patterns coupled with ^{14}C -DT would potentially discriminate different combustion processes that utilize identical (in ^{14}C abundance) fuels, e.g. coal versus auto emissions. This additional discrimination in source apportionment is important for complex airsheds involving many sources.

The Integrated Air Cancer Project, with a focus on the Albuquerque, NM, and Raleigh, NC, airsheds (1985-86), has afforded an excellent opportunity to utilize the ^{14}C -DT technique on select chemical classes for the apportionment of stationary (RWC) and mobile (motor vehicle) sources. Advances in ^{14}C measurements by accelerator mass spectrometry (AMS) have improved sensitivities to ca. $50\ \mu\text{g-C}$ quantities⁵ and have, therefore, extended the capabilities of this technique to include chemical selectivity and time resolution in sampling for environmental pollutants. Total carbon (C_T) and elemental carbon (C_e) from day and night time samples were isolated for ^{14}C measurements. Preliminary ^{14}C results are presented along with a brief discussion of the chemical fractionation procedures for isolating the fractions of interest.

Experimental Methods

^{14}C - Direct Tracer Model (^{14}C -DT)

The ^{14}C measurement yields a quantitative measure of both fossil and contemporary carbon sources which contribute to the chemical fraction of interest for a given receptor site. For source apportionment of these particles, knowledge of some critical variables is required, such as the age of the fuels, usage patterns, time of sample collection and meteorological patterns. Since one objective was to evaluate the ^{14}C -DT technique for a simple two-source situation, it was important to design the sampling for source specificity. Once evaluated, the ^{14}C -DT technique would be used to validate the results

of EPA's STRM. The two techniques would then be applied to samples collected during the winter of 1986-1987 in Boise, Idaho.

The ^{14}C -DT technique involves the measurement of the $^{14}\text{C}/^{13}\text{C}$ ratio in the sample for AMS or the $^{14}\text{C}/^{12}\text{C}$ ratio for the low-level gas proportional counting (llc) technique. The sample isotope ratio is compared to the isotope ratio determined for modern carbon, $0.95 \times \text{NBS SRM 4990B Oxalic Acid}$. These isotope ratios define the fraction of modern carbon, f_M (Eq. 1). The fraction of contemporary carbon (f_C) is calculated by adjusting f_M to correct for bomb ^{14}C , which is a result of nuclear weapons testing in the atmosphere during the 1950's and 1960's (Eq. 2).

$$f_M = \frac{(^{14}\text{C}/^{13}\text{C})_{\text{sample}}}{0.95 \times (^{14}\text{C}/^{13}\text{C})_{\text{SRM 4990B}}} \quad (\text{Eq. 1})$$

$$f_C = f_M / 1.20 \quad (\text{Eq. 2})$$

$$f_C (\text{meas.}) = \Phi_{\text{auto}} f_C^{\text{auto}} + \Phi_{\text{RWC}} f_C^{\text{RWC}} \quad (\text{Eq. 3})$$

Equation 3 summarizes the "Two-Source Model" for the Albuquerque/Raleigh study where Φ represents the fractional source contributions. Assuming that no other sources contribute significantly to the measured f_C , this quantity yields the fractional contribution from RWC emissions ($f_C^{\text{auto}} = 0$).

Sample Collection

Samples were collected on quartz fiber filters with a high volume sampler equipped with an impactor to remove particles $>2.5 \mu\text{m}$ in diameter. Two receptor sites were chosen in Albuquerque for maximum impact of: 1) motor vehicles; San Mateo site and 2) RWC, Zuni Park site. Samples were collected on a 12-hour schedule beginning at 7:00 am and 7:00 pm. Both day and night samples from Zuni Park, day only samples from San Mateo, and nighttime samples from Raleigh were chemically fractionated for ^{14}C measurements. Prior to chemical fractionation, samples were stored at ca. 1°C .

Chemical Fractionation

Filter aliquots were taken for isolation of total carbon (C_T) and elemental carbon (C_E). Total carbon was isolated by thermal oxidation from: 1) 3-24 cm^2 aliquots for AMS ^{14}C measurements and 2) 100-280 cm^2 aliquots for llc; the filter area chosen was based on the particle loading and the concentration of total carbon. The CO_2 produced was cryogenically collected, distilled and quantified by manometry in a calibrated volume. Elemental carbon was isolated by first removing organic carbon by wet oxidation (using HNO_3) followed by thermal oxidation of the insoluble residue and quantification of the CO_2 by manometry as described above. The wet oxidation of organic matter was taken from the work of Schultz⁶ and modified by Sheffield et al.⁷ for treatment of air particle samples. Filter aliquots of 9 to 34 cm^2 were treated to recover C_E for ^{14}C measurements by AMS.

Sample CO₂ Preparation and ¹⁴C Measurements

The procedures for chemical purification of CO₂ and ¹⁴C measurement by *l1c* for fractions containing >5 mg-C are described by Currie et al. (1983). A few C_t fractions and all C_e fractions contained only microgram quantities and, therefore, required transformation to graphitic carbon for ¹⁴C measurement by AMS.^{5,9,10}

Results

Albuquerque, NM

Preliminary results based on ¹⁴C measurements of the total and elemental carbon fractions are summarized in table I. Nighttime samples collected at the residential site in Albuquerque showed 79% Contemporary Carbon (CC) for total carbon and about an equal mix of fossil and contemporary carbon in the elemental carbon fraction. This result reflects a predominant RWC source during the night as expected. The daytime samples reflect a decrease in contemporary carbon, which would be expected for typically warmer periods (less RWC) and an increase in automotive activity.

The traffic site during the day was more strongly influenced by auto emissions as demonstrated by lower f_C values. The elemental carbon fraction may be more sensitive to variations in fossil source contributions and, therefore, be an excellent tracer of mobile sources.

Raleigh, NC

Only nighttime Raleigh samples were measured. These results showed a high contribution from RWC in both the total and elemental carbon fractions, similar to that identified at the nighttime residential site in Albuquerque, NM.

Conclusions

The ¹⁴C-DT technique applied to samples collected for high source specificity has demonstrated its power to resolve auto and wood smoke emissions in Albuquerque, NM and Raleigh, NC given knowledge of likely sources, usage and meteorological patterns. ¹⁴C results showed that the elemental carbon fraction in all cases contained more fossil carbon and, therefore, may be a more useful tracer of mobile sources. These results have been used to validate the Single Tracer Regression Model (STRM) reported in this same proceedings by Stevens et al. (1987).

Additional ¹⁴C results for C_t and C_e are pending and are expected to yield more information about source variations for the study. We are currently isolating the PAH fraction from a few of the Albuquerque samples which will give more specificity in establishing the origin of this toxic chemical fraction produced from both auto and RWC sources. The chemical composition of the PAH fraction coupled with ¹⁴C will reveal the predominant species and their origins. The

application of the ^{14}C -DT technique to important chemical fractions, e.g. the PAH's, has only recently become possible through advances in accelerator mass spectrometry ^{14}C measurements on 50 $\mu\text{g-C}$ samples.⁵

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Table 1. Carbon concentrations and the fraction of Contemporary Carbon in samples collected in Albuquerque, NM and Raleigh, NC.*

<u>Albuquerque, NM</u>		
"Residential Site"	<u>Carbon ($\mu\text{g}/\text{m}^3$)**</u>	$f_C \pm \text{SE}^{***}$
Night		
Total (n=4)	34 to 71	0.79 ± 0.04
Elemental (n=3)	4.6 ± 0.7	0.46 to 0.72
Day		
Total (n=2)	11 to 24	0.66 ± 0.01
Elemental (n=1)	4.8 ± 0.7	0.25 ± 0.02
 "Traffic Site"		
Day		
Total (n=3)	14 to 24	0.17 to 0.47
Elemental (n=1)	6.1 ± 1.0	0.18 ± 0.03
 <u>Raleigh, NC</u>		
 "Residential Site"		
Day		
Total (n=4)	23 to 80	0.95 ± 0.06
Elemental (n=1)	3.2 ± 0.2	0.68 ± 0.04

* Results are reported either as an average of "n" observations or a range when results differ by greater than ca. 10%.

** Average carbon concentrations and standard errors (in $\mu\text{g}/\text{m}^3$) for total carbon were determined by thermal combustion of particles to CO_2 and detected by NDIR. Measurements were made in triplicate on $\sim 1 \text{ cm}^2$ filter aliquots. Elemental carbon concentrations were determined by combustion of the carbon residue, remaining from the wet oxidation treatment, to CO_2 . The CO_2 was quantified by manometric measurement in a calibrated volume.

*** f_C is the fraction of Contemporary Carbon and the standard error (SE) is 1σ-Poisson counting statistics. In the case where "n" is greater than 1, the error represents the dispersion among the data points. (Percent contemporary carbon = $f_C \times 100$.)

VOLATILE ORGANIC HYDROCARBON AND ALDEHYDE COMPOSITION
IN RALEIGH, N.C. DURING THE 1985 WOODSMOKE STUDY

Roy Zweidinger, David Dropkin, Fred Stump, and Silvestre Tejada
Atmospheric Sciences & Research Laboratory
Ronald Drago
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina

Initial field tests for collection of volatile organic hydrocarbons and aldehydes under EPA's Integrated Air Cancer Project (IACP) were held in Raleigh, NC during the winter of 1985. Sampling was conducted during 12 hour (7:00-7:00) daytime or nighttime periods. Hydrocarbons were collected by pressurizing 6 liter "Summa polished" stainless steel cylinders. Aldehydes were collected as 2,4-dinitrophenylhydrazone (DNPH) derivatives using impingers and cartridge collection methods. Sampling locations included the primary outdoor site located in a residential neighborhood, a rural background site and inside and outside three homes operating wood stoves. Non-methane hydrocarbon levels at the primary site ranged from 150 to 850 ppbc while total carbonyls ranged from 3 to 35 ppb (v/v). Benzene levels ranged from 5 to 32 ppbc while formaldehyde levels ranged from 2-14 ppb. Hydrocarbon levels and distributions in the homes were similar inside and outside with a few noted exceptions. Carbonyl levels, however, generally were much higher inside than outside. The elevated carbonyl levels observed inside the homes is likely due to factors other than the presence of a wood stove.

Introduction

The Integrated Air Cancer Project (IACP) is a long term interdisciplinary research program to develop scientific methods and databases for identifying the major sources of carcinogenic chemicals emitted into the air and/or arising from atmospheric transformation of chemicals emitted into the air.¹ Initial field studies² were conducted during the winter of 1985 in Raleigh, NC. Raleigh represented a simplified air shed impacted mainly by residential wood combustion and motor vehicle sources both of which can contribute substantially to the mutagenic activity found in ambient air samples. A limited amount of volatile organic hydrocarbon and aldehyde sampling was conducted during February and March 1985 while methods and protocols were being developed. Most samples were collected at the primary outdoor site located in a residential neighborhood and both inside and outside three homes operating wood stoves. A few samples were also collected at a rural background site. All sampling was conducted during 12 hour (7:00-7:00) daytime or nighttime periods.

Experimental Methods

Gas phase hydrocarbons were collected in 6 L "Summa" polished stainless steel canisters using a sampling apparatus similar to that described by Oliver.³ The initially evacuated canisters were filled by pumping the sample through a flow controller at about 20 cc/min. resulting in a final pressure of about 21 psig after 12 hours. The canister samples were quantitatively analyzed by GC/FID using a modified Nutech model 320 cold-trap thermal-desorption system for sample concentration and injection. Typically, a 1.5- to 3.0-L sample was injected. The C2's and C3's were separated on a 12 foot by 1/8 inch stainless steel silica gel column maintained at 30°C while the rest of the hydrocarbons were separated on a Quadrex 100m by 0.5 mm soft glass capillary coated with 7.5% hydrophobic silica using a temperature program from -80 to +140°C.⁴ Details of the hydrocarbon analytical procedures are available elsewhere.

Aldehydes were trapped as their 2,4-dinitrophenylhydrazine (DNPH) derivatives and analyzed by high performance liquid chromatography (HPLC). While a few aldehyde samples were initially collected using classical impinger techniques (acidified solution of DNPH in acetonitrile) for comparison, the majority of samples were collected using a cartridge technique. Briefly, prepacked silica gel cartridges were coated with an acidified solution of DNPH in acetonitrile (ACN) and excess solvent removed by blowing carbonyl-free nitrogen through the cartridges. The cartridges were used as direct probes and traps for sampling ambient air when the temperature was above 10°C, and a heated glass probe and manifold used when ambient temperatures were below 10°C. Sampling flow rates of 1L/min. were controlled using mass flow controllers or needle valves and a recording mass flow meter. The cartridges were eluted with 5 mL of ACN for analysis. Details on the cartridge sampling and analysis procedures have been reported.⁵

Results

The majority of sampling took place at night (7 P.M.-7 A.M.) at the Raleigh primary site. The primary sampling site (Quail Hollow Swim Club) was located in a residential neighborhood about one mile from two major roadways. Sampling periods encompassed a variety of meteorological conditions which affected the impact of wood stoves on air quality. Figure 1 shows the total NMHC levels in ppbc measured for several sampling

periods and hydrocarbon distribution by compound class. Both are plotted against the fine dichot particulate levels which varied from 19-129 $\mu\text{g}/\text{m}^3$. The fine particle loadings are an indication of wood smoke impact, with normal ambient levels in Raleigh being $<25 \mu\text{g}/\text{m}^3$. (An atmospheric inversion leading to high wood smoke particulate levels does not of course necessarily mean that the vapor phase was also mostly wood smoke related. Mobile sources might also be expected to contribute substantially. The current data set, however, is too small to perform apportionment calculations on the vapor phase.) Total NMHC levels ranged from 150 to 840 ppbc but did not show any particular correlation with particulate levels although both did exhibit maxima for the same sample period. Paraffins are the most abundant class of hydrocarbons for all samples ranging between 49 to 60% of the total NMHC. Aromatic hydrocarbons were generally the second most abundant class ranging from 18 to 26% of total NMHC. Olefins ranged from 7 to 24% of total NMHC. Unidentified compounds typically averaged about 5% of the total NMHC. In general, the distribution observed for Raleigh is similar to those observed in 29 other urban areas across the country (sampling during summers of 1984 and 1985 between 6 A.M.-9 A.M.).⁶ Benzene levels for these same sample periods ranged from 5 to 32 ppbc and averaged 3.1% of total NMHC.

Carbonyl concentrations observed at the primary site ranged from 3 to 35 ppb (v/v). Figure 2 shows the average distribution of carbonyls observed at the primary site. Formaldehyde, acetaldehyde, acetone, butyraldehyde, acrolein, propionaldehyde and x-butyraldehyde make up 95% of the total carbonyls. All the carbonyls in figure 2 which are preceded by an "x" indicate the summation of one or more unknown carbonyl derivatives which have retention times similar to known standards, e.g., one or more unknowns eluting near butyraldehyde between crotonaldehyde and benzaldehyde have been summed and labeled as x-butyraldehyde. Actual carbonyl levels observed on a ppb (v/v) basis were: formaldehyde 2 to 14; acetaldehyde 1 to 8; acetone 2 to 4; and acrolein 0.1 to 2.8. All other aldehydes generally were less than 1 ppb. Several aldehydes which we normally monitor were not detected at the primary site, i.e., hexanaldehyde, 2,5- dimethylbenzaldehyde and the three tolualdehydes.

Only a few hydrocarbon and aldehyde samples were concurrently obtained from the background site and primary site. The background site was located about 20 miles from the primary site in a rural area near Falls lake. All sampling periods at both sites corresponded to particulate levels $<25 \mu\text{g}/\text{m}^3$. Class distribution of the NMHC's were about equal, but the total NMHC at the primary site averaged twice the background site. Total carbonyl levels were similar at the both sites for two of three sampling periods while the primary site level was twice the background site for the third sampling period. Background formaldehyde levels ranged from 0.9 to 1.4 ppb while the primary site values ranged from 1 to 2 ppb.

Three homes with wood stoves were selected for indoor microenvironment studies as part of the Raleigh effort. Concurrent samples were taken inside and outside each home to estimate exposures which may result from an inside source as opposed to intrusion of wood smoke from outside. All the homes in the study were occupied by non smokers. Residence #1 had a top loading free standing stove while residences #2 and #3 both had fireplace inserts. The air exchange rates for residences #1- #3, determined by SF_6 release were 0.42, 0.39, and 0.57 hr^{-1} respectively.

Table I lists some of the carbonyl and hydrocarbon data for the residence study. All samples were taken during the nighttime sampling period. Interferences were experienced with the chromatography of residence #3 hydrocarbon samples which prevented determining accurate distributions. The NMHC class distributions were similar for residences #1 and #2 except for the aromatics inside residence #1. This increase is

essentially due to a high concentration of naphthalene. Residence #1 had a noticeable smokey odor inside and the naphthalene levels may be related to wood stove emissions. Formaldehyde, acetone and acetaldehyde were the most prevalent carbonyls in all three homes except for residence #3 which had notably higher levels of two unknowns, x-valeraldehyde and x-dimethylbenzaldehyde. All three residences had much higher formaldehyde levels inside than out while both residence #1 and #3 generally had higher inside levels of all carbonyls relative to the concurrent samples from outside. Carbonyl samples obtained inside residences #2 and #3 during the daytime sample period (stoves not in active use) were similar to the nighttime sample period. This would seem to indicate inside carbonyl levels may not be effected by wood combustion as much as by other domestic activities such as cooking and/or particular furnishings or construction materials.

CONCLUSIONS:

The Raleigh IACP study relative to hydrocarbons and aldehydes resulted in some general observations with the caveat that the data set is limited.

1. The distribution of NMHC at the Raleigh primary site was similar to other U.S. cities.

2. Over 95% of the carbonyl levels measured were due to only 6 compounds of which formaldehyde, acetaldehyde and acetone were the most prevalent.

3. Carbonyl levels definitely appear higher inside homes and may not be related to wood combustion.

4. Elevated levels of naphthalene inside one home coincided with a noted smokey odor.

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TABLE I. HYDROCARBON AND CARBONYL DATA FROM RALEIGH RESIDENTIAL STUDY

	RESIDENCE #1		RESIDENCE #2		RESIDENCE #3	
	IN	OUT	IN	OUT	IN	OUT
% Paraffin	51.66	61.65	54.39	53.42	---	---
% Olefin	13.69	14.00	16.65	17.94	---	---
% Aromatic	26.81	14.05	19.84	21.36	---	---
Total NMHC (ppbc)	434.31	525.99	1081.14	911.28	---	---
Benzene (ppbc)	7.65	8.77	22.01	23.02	8.20	8.73
Naphthalene (ppbc)	30.05	1.57	3.03	2.88	0.36	1.54
Carbonyls (ppb, v/v)						
Formaldehyde	13.07	2.86	14.53	7.27	21.98	2.18
Acetaldehyde	5.16	1.34	4.80	4.44	8.46	1.25
Acrolein	1.94	0.31	0.63	1.47	0.74	0.18
Acetone	7.95	1.70	4.72	4.32	6.99	1.81
Propionaldehyde	0.67	0.22	0.54	0.67	0.91	0.21
Butyraldehyde	0.83	0.41	0.93	1.08	1.40	0.78
Benzaldehyde	0.13	0.05	0.11	0.27	0.41	0.12
x-Butyraldehyde	0.20	0.51	0.55	0.70	0.01	0.23
x-Valeraldehyde	0.37	0.26	0.33	0.40	3.97	0.19
x-Dimethylbenzaldehyde	1.07	0.20	0.97	0.65	4.30	0.43
Total Carbonyls	32.50	8.21	28.18	22.31	49.45	7.78

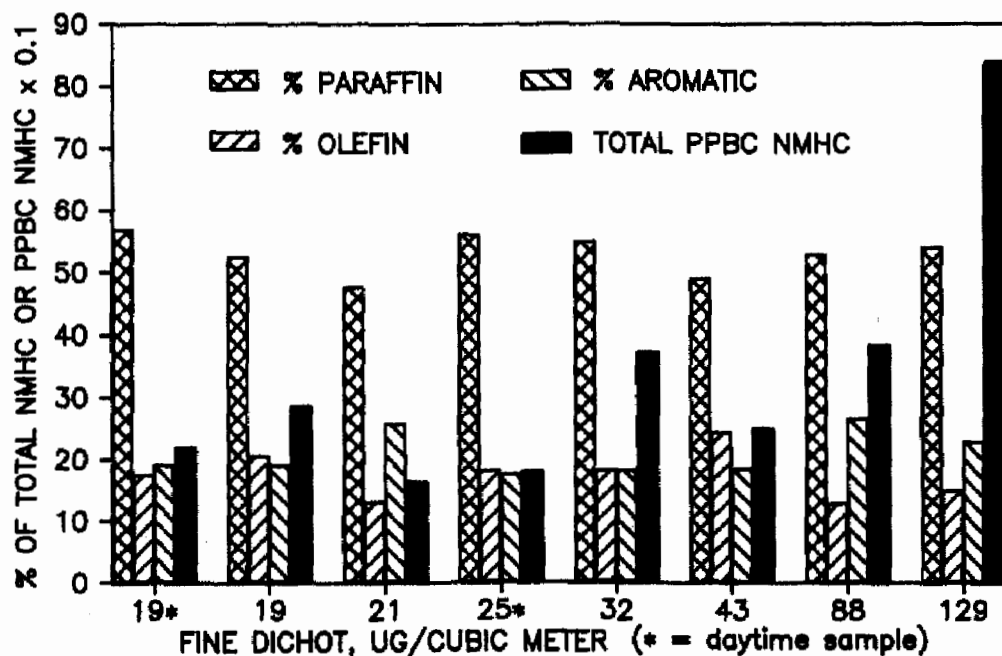


Figure 1. Total ppbc NMHC and class distribution vs fine dichot particulate concentrations observed at the Raleigh primary site.

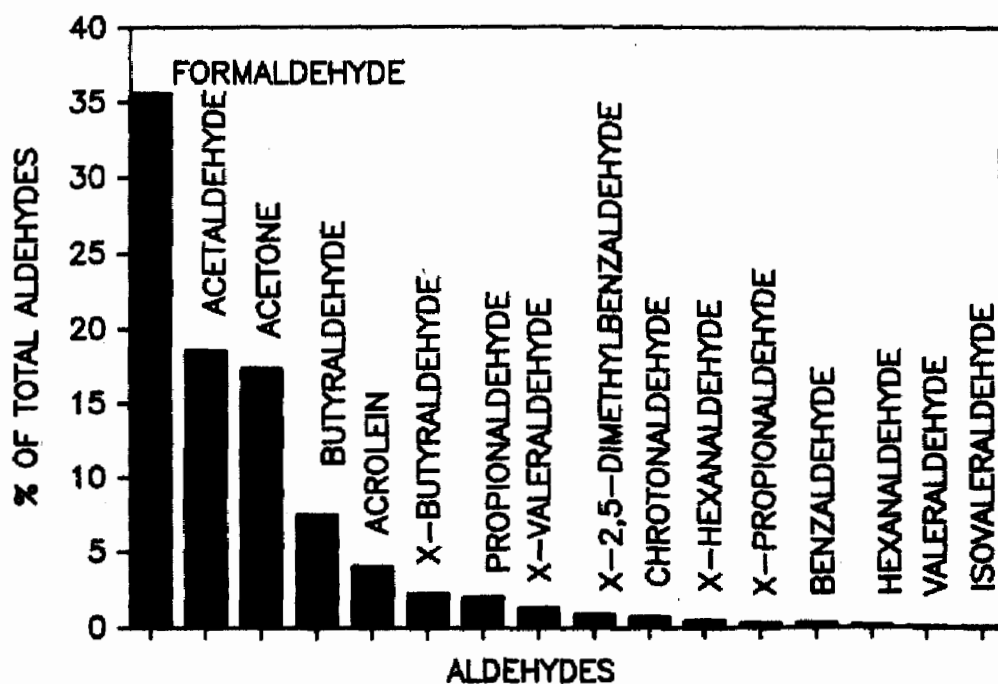


Figure 2. Average distribution of carbonyls at Raleigh primary site

Progress Toward Identifying Source Specific Tracers

Raymond G. Merrill Jr.
Roy B. Zweidinger, and Randall Watts
United States Environmental Protection Agency
Research Triangle Park, North Carolina 2711

Susan Razor
Acurex Corporation
Research Triangle Park, North Carolina 27709

Identifying organic source specific tracers is important to any integrated approach to human exposure. Several efforts to find source specific tracers have been conducted starting in earnest in the early 1970's. Emissions from wood heating appliances have been the most difficult to trace. Using literature data on the concentration of commonly analyzed compounds such as those from the class known as Polycyclic Aromatic Hydrocarbons (PAH) has met with little success because too few of the members of the class are reported quantitatively or because only one compound was used to establish the relationship between the source and its emissions. Two approaches are currently being pursued in the Integrated Air Cancer Program to identify source specific organic tracers. The use of commonly sought compounds, such as PAH, is being reevaluated using multivariate mathematical techniques. There appears to be a high correlation between individual PAH compounds in samples acquired directly from wood stoves. These correlations also appear to occur in ambient air samples dominated by residential wood combustion emissions. A second approach involves identification of organic compounds unique to the combustion source of interest. Several compounds from wood combustion appear to be candidates for unique tracers. Current progress toward identifying source specific tracers and quantitative relationships between them will be discussed.

Introduction

As part of EPA's Integrated Air Cancer Program (IACP) and EPA's Wood Stove Emissions program, several approaches are being investigated to find source specific parameters and if possible source tracers from wood stove emissions. Emissions from wood stoves have been difficult to relate to human exposure due to the complexity of the source operation characteristics. Two approaches are being followed to identify source tracers from wood stoves. One involves the apparent association or correlation between members of the class of compounds known as Polycyclic Aromatic Hydrocarbons. The other involves identification of compounds unique to the wood combustion process. In either case, one of the major goals of this aspect of IACP is to find a unique mathematical relationship which will allow the contribution of wood stove emissions to be evaluated in a complex air shed.

Experimental Methods

Source samples were collected from various types of wood stoves. The types included catalytic and conventional noncatalytic as well as high technology noncatalytic. Several fuel types were also evaluated including pine (cured and uncured), oak (cured and uncured), and douglas fir. Multiple tests were performed to evaluate the effect of burn rate on the emissions. For the pine and oak fuel was added to the stove twice during each burn. At the low burn rate each fuel charge was approximately equal to one third of the firebox volume. At the high burn rate the fuel charge was increased to two thirds of the firebox volume. (1) The douglas fir burn rate was established by the proposed New Source Performance Standard method for wood stove certification. (2) A single charge was placed into the hot stove and burned at one of 4 rates: one low, two medium and one high over a range of BTU output rates specific to each stove.

Samples were collected from wood stove sources using either of two methods, Modified Method 5 (MM5)(4) or Wood Stove Dilution Sampling (WSDSS)(4). Ambient samples were collected using a 10 um Hi-Vol sampler (5). Sample preparation was performed by soxhlet extraction of filters (from all sampling methods) and porous polymer (from MM5 and WSDSS)(6).

For samples taken directly from the wood stove flue gas by MM5 the combination of filter and sorbent extract was analyzed as a single sample without the aid of a cleanup step. For WSDSS samples PAH were isolated from extracts using solvent elution through silica and analysis was conducted on the filter and sorbent extract separately. Results for WSDSS are reported as the combined amounts found in both train components.

Analysis for PAH was performed on source samples using gas chromatography/mass spectrometry (GC/MS)(7) and on ambient samples using high performance liquid chromatography (HPLC) with fluorescence detection.(8,9) Calibration of each technique was performed with analytical standards for 16 specific PAH over a range of concentrations encompassing the sample concentration. GC/MS was chosen for the source samples because the concentration of PAH from typical samples was well within the range of sensitivity for this technique. HPLC/fluorescence was used for the ambient samples to allow quantitation of PAH compounds as much as a factor of 1000 less than the source samples.

Results

Screening of wood stove emission samples generated a list of tentative tracer compounds (not including PAH) shown in Table 1. Evaluation of the presence and concentration of these compounds in field collected source and ambient samples is ongoing. Two classes, benzfurans and methoxy phenols, seem to contain the best candidate tracer compounds.

Combined data from all source sample analyses are shown in Figures 1 and 2. Data from the ambient air samples collected in Alaska are shown in Figure 3. Data for the ambient air samples collected in Raleigh are shown in Figure 4.

Relations were determined between PAH in a pair wise manner using linear regression statistics. Values for significance were determined by the number of data points and the correlation coefficient of the regression line. Values greater than .15 were significant above random;

however, only correlations with correlation coefficients greater than or equal to 0.8 were used to select individual pairs of PAH presented here.

Conclusions

PAH Relationships

Combustion of wood, which contains lignin, produces several compounds which appear to be characteristic of woodstove emission. In addition there appears to be a high association among several of the PAH in samples acquired directly from wood stoves. These PAH compounds are formed in ratios that seem to be independent of stove type, wood species or burn rate. Using linear correlations between members of the set of PAH provides a better measure of the relationships than simple ratios. The same PAH ratios found in source samples also occurs in ambient air samples dominated by residential wood combustion emissions.

The findings have several potential uses. If the specific tracer compounds such as the methoxy benzenes prove to be unique tracers for wood combustion emissions then the concentration of these compounds can be used in classic source receptor/source apportionment modeling.

If the ratio of selected PAH are constant from wood stoves as they appear to be, and if different ratios exist for different sources then mathematical techniques are available to apportion the contribution of wood stoves in a complex airshed sample. They can be used to predict the concentration of several health related compounds in wood stove emissions with only the data on one in the group. Risk estimates can be refined by the ability to use the ratio of one PAH to predict the concentrations of other potentially hazardous PAH compounds in the class. Demonstrated control of one member of the PAH class can also be used to predict the control for other members where the relation or ratio exists.

End Notes

References

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Table 1

Tentative Identification of Major Compounds/Compound Classes Found in Wood Stove Emissions		
Furans	Ketones	Alcohols
methylfuran	furanyl-	phenol
benzofuran	ethanone	cresol
methylbenzofuran	butanedione	alkyl-
furfural	hexanedione	phenols
dihydro-dimethyl	propanone	ethyl-
furan	methyl furanone	benzenediol
furanone	ethyl furanone	methoxypropenyl-
bifuran	dimethylbenzo-	phenol
methylfuran-	furanone	hydroxymethoxy-
carboxaldehyde	acetophenone	phenylacetic acid
dibenzofuran	alkyl	methylbenzenediol
naphthofuran	acetophenones	biphenylol
methyl-dibenzofuran	hydroxy	nonanediol
acetophenones	methoxypropyl-	pentadecanol
	alkyl cyclo-	dodecanediol
	penteneone	
	pyranone	
	hydroxymethyl-	
	pyranone	
	fluroenone	
	phenanthrenedione	

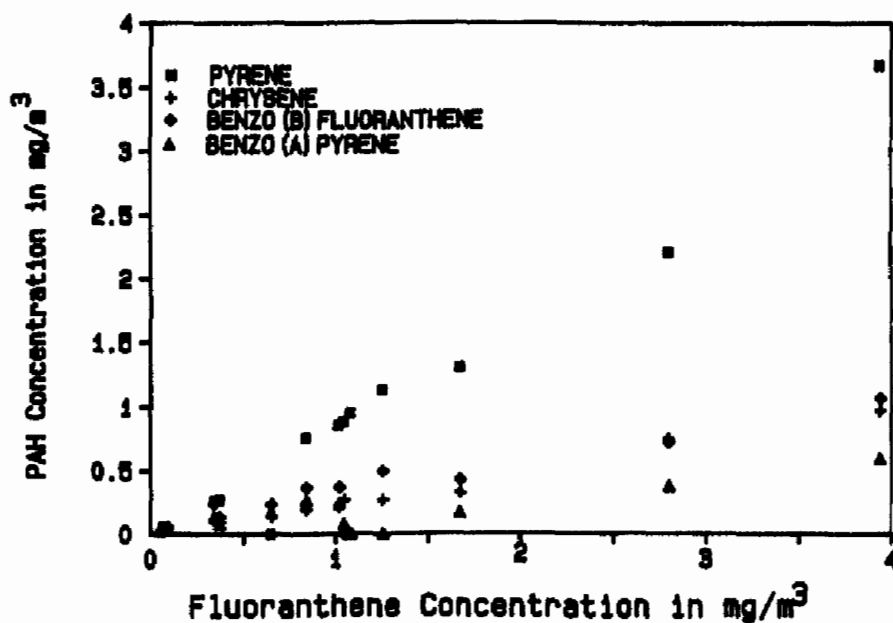


Figure 1. Fluoranthene vs selected PAH

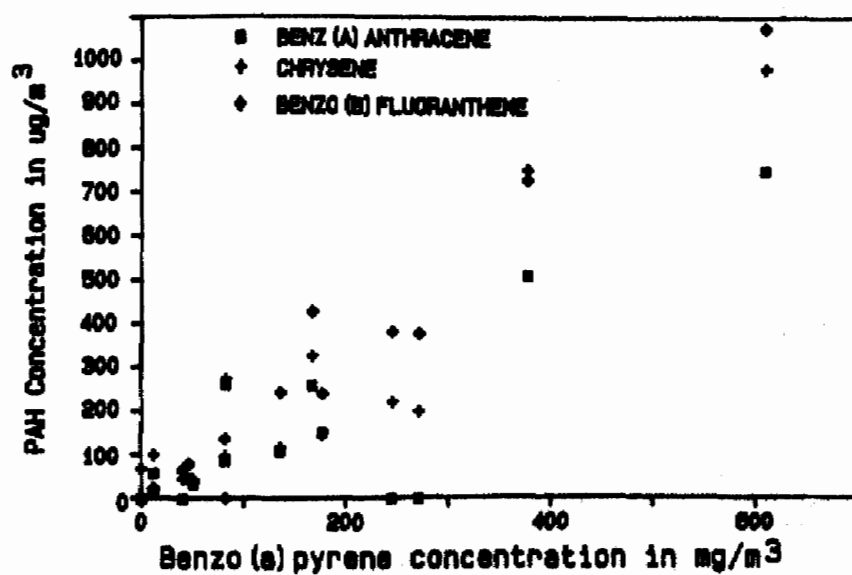


Figure 2. Benzo (a) pyrene vs selected PAH

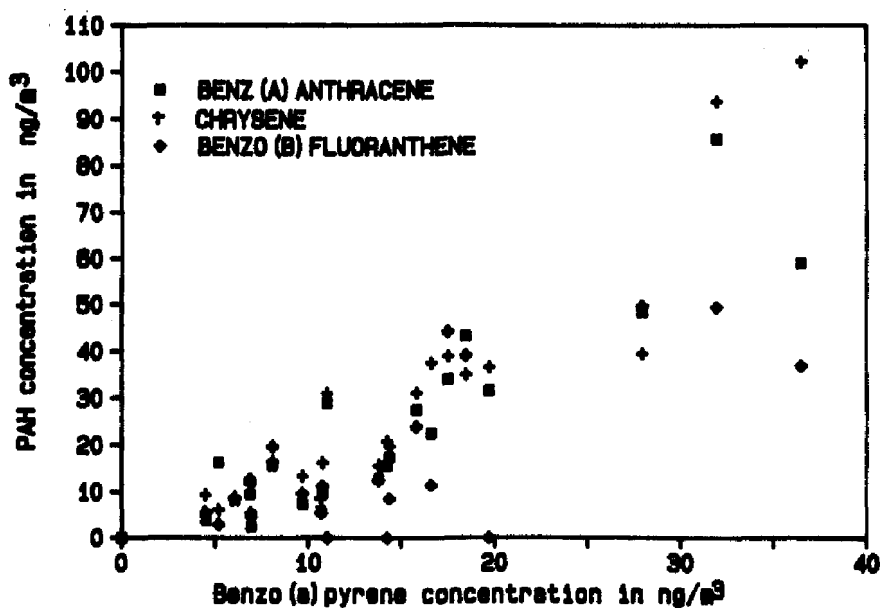


Figure 3. Benzo (a) pyrene vs selected PAH
Alaska night data

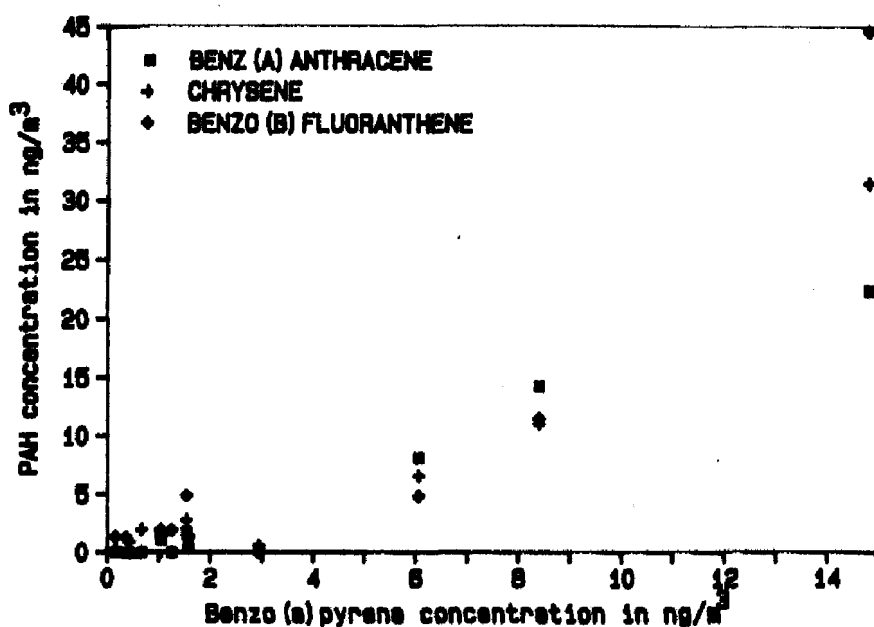


Figure 4. Benzo (a) pyrene vs selected PAH
Raleigh night data

THE MUTAGENICITY OF AMBIENT AND SOURCE SAMPLES FROM
WOODSMOKE-IMPACTED AIR SHEDS

Larry D. Claxton¹, Sarah H. Warren², Virginia S. Houk¹, Joellen Lewtas¹

¹Genetic Bioassay Branch
Health Effects Research Laboratory
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina

²Environmental Health Research and Testing
Research Triangle Park, North Carolina

Objectives of the U. S. Environmental Protection Agency's Integrated Air Cancer Project include the identification of major sources that emit genotoxins into the air and the identification of these genotoxins. As part of the project conducted in Raleigh, NC and Albuquerque, NM, ambient and source samples from woodsmoke-impacted air sheds were collected, extracted, and bioassayed for mutagenicity. The assay used was the Salmonella typhimurium plate incorporation assay using strain TA98 both with and without exogenous metabolic activation (S9). In contrast to roadway and background samples, woodstove source and woodsmoke-impacted ambient samples that were mutagenic increased in mutagenic response when S9 was present. The mutagenicity of the laboratory woodstove source samples was very comparable to woodstove source samples collected directly from the homes within the study. In general, woodsmoke-impacted ambient samples showed more mutagenicity per cubic meter air when sampled in the evening than when sampled in the morning hours.

Introduction

Air pollutants in the form of particles, vapors, and gases can exist in any urban environment. It has been recognized for a number of years that such pollutants, which are often the end products of combustion processes, are of health concern^{1,2,3}. In the 1960s, it was shown that organic extracts of urban particulate matter caused skin cancer when painted on mice^{3,4}. The major anthropogenic sources of this bioactive organic matter in urban areas appears to be heating sources, power generation, transportation, waste incineration, and industrial processes^{5,6,7}. Since prokaryotic bioassays require only a fraction of the material necessary for mouse skin carcinogenicity studies, these systems (e.g., the Ames *Salmonella* mutagenicity assay) have been used extensively in recent years in the evaluation of airborne particulate organic matter, especially for the evaluation of potential carcinogenicity⁸. The Integrated Air Cancer Project (IACP)⁹ has taken advantage of the correlation between the bacterial mutagenicity and animal carcinogenicity of combustion organics¹⁰ by using *Salmonella typhimurium* bioassays for mutagenicity in order to compare the genotoxicity of woodsmoke-impacted airborne particulate samples. This study has compared the mutagenicity of laboratory source samples, residential source samples, and ambient air samples.

Experimental Methods

The samples bioassayed were those collected and processed as part of the IACP studies in Raleigh, North Carolina and Albuquerque, New Mexico. The collection and preparation of samples is described more fully in a companion publication¹¹. The types of ambient air (AA) and source samples (SS) collected and their designations are as follows: 1) laboratory woodstove source samples (laboratory SS), 2) residential (home) woodstove source samples (residential SS), 3) woodstove-impacted ambient air samples used for source apportionment studies (woodsmoke AA), 4) automotive emission-impacted roadway samples (roadway AA), and 5) ambient air samples from a site not highly impacted by woodsmoke (background AA). Samples to be bioassayed were collected on Teflon-coated glass fiber filters, extracted with dichloromethane, and solvent exchanged into dimethylsulfoxide. Samples were bioassayed using the *Salmonella typhimurium* plate incorporation bioassay for mutagenicity as described by Ames, *et al.*, (1975)¹² and Claxton, *et al.*, (1987)¹³. Samples that were to be directly compared were assayed simultaneously in the same experiment. Each sample was tested at a minimum of 5 doses with duplicate plates per dose. Each experiment was replicated. A strain study demonstrated that *S. typhimurium* TA98 was the most responsive strain to each sample type; therefore, results are reported for this strain. All samples were tested with and without an exogenous activation system which consisted of 9000-g CD-1 rat liver homogenate (S9) as described by Ames, *et al.*, (1975)¹². All data was analyzed visually and by using two statistical packages designed for bacterial mutagenicity data. The two systems used were those of Stead, *et al.*,¹⁴ and Bernstein, *et al.*¹⁵ Since most of the data was linear at the lower doses, all slope values for comparative purposes were calculated using the method of Bernstein, *et al.*,¹⁵ and are reported as either revertants per μg of organic extract or revertants per m^3 air sampled.

Results

The woodsmoke AA samples were those outdoor ambient air samples collected at a woodsmoke-impacted site in each city. Figure 1 summarizes the results for the Raleigh daytime and nighttime woodsmoke AA samples tested with S9. In general, higher mutagenic activity levels per cubic meter of

air were seen for the nighttime (7P.M.-7A.M.) samples than for the daytime samples. The range of mutagenic activity seen for weekend samples (Figure 1) was very similar to the range seen for weekday samples. In Figure 2, the Raleigh woodsmoke AA samples are compared to the Albuquerque woodsmoke AA samples and to the Raleigh roadway AA and background AA site samples. For Raleigh, the activity seen with and without S9 was very comparable. For Albuquerque, however, the addition of S9 provided nearly a doubling of the mutagenic activity level. This may indicate that the Raleigh sample was impacted by sources of directacting mutagens (e.g., automobiles) to a greater extent than the Albuquerque samples. Alternatively, it may indicate, that atmospheric conditions in Raleigh produced a different spectrum of atmospheric transformation products. Whether examining mutagenicity on a μg of extractable organic basis or on a per cubic meter of air basis, the Raleigh woodsmoke AA samples were clearly more mutagenic than the background and roadway site samples. Source samples were collected directly from the woodstove stack outlets of 3 homes in Raleigh and from a woodstove tested under laboratory conditions using the woodstove source dilution sampler. The range of activity, on a revertant per μg organic material basis, was very similar for the home and laboratory source samples (Figure 3). Again, it is quite apparent that the mutagenic response is enhanced when S9 is added to woodstove organic emissions.

Conclusions

These studies indicate that the particle-bound organic emissions from woodstoves are mutagenic in a bacterial screening assay. The mutagenicity of these organics is enhanced by the addition of a microsome-containing exogenous activation system. In general, woodsmoke-impacted ambient air sampled at night was more mutagenic (revertant per m^3) than air sampled in the daylight hours. These airsheds, in turn, were more mutagenic than the roadway AA and background AA airsheds. The mutagenicity of ambient air in Raleigh and Albuquerque during woodburning periods were similar; however, the Raleigh data demonstrated less indirect (S9-requiring) mutagenic activity. The study also showed that laboratory and home source samples, simultaneously tested, gave similar results.

Disclaimer

The research described in this paper has been reviewed by the Health Effects Research Laboratory, U.S. Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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FIGURE 1. RALEIGH SOURCE APPORTIONMENT,
DAYTIME (AM) AND NIGHTTIME (PM) SAMPLES

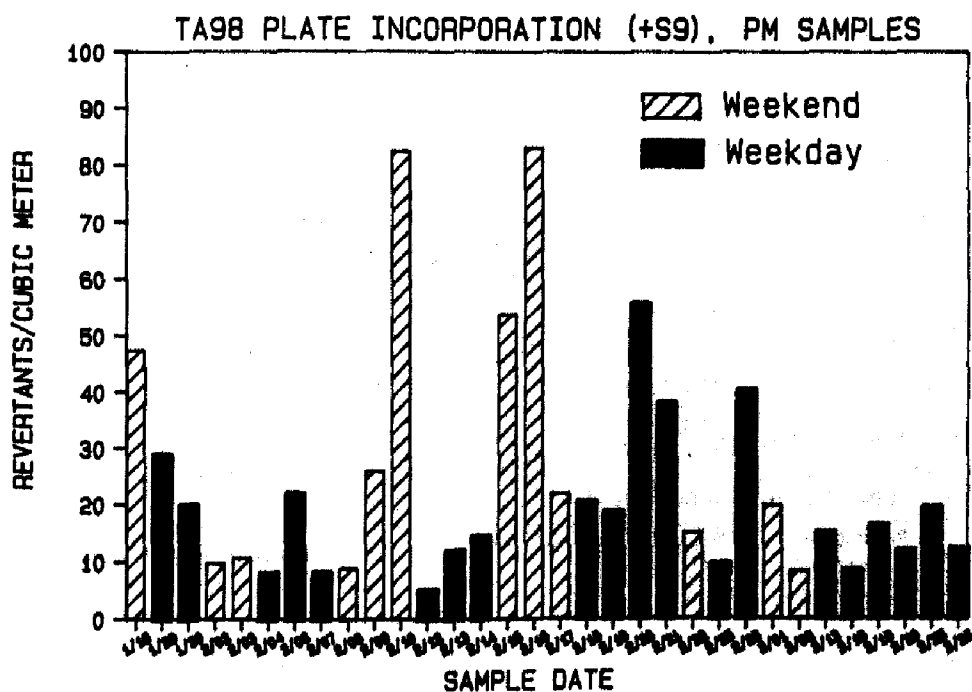
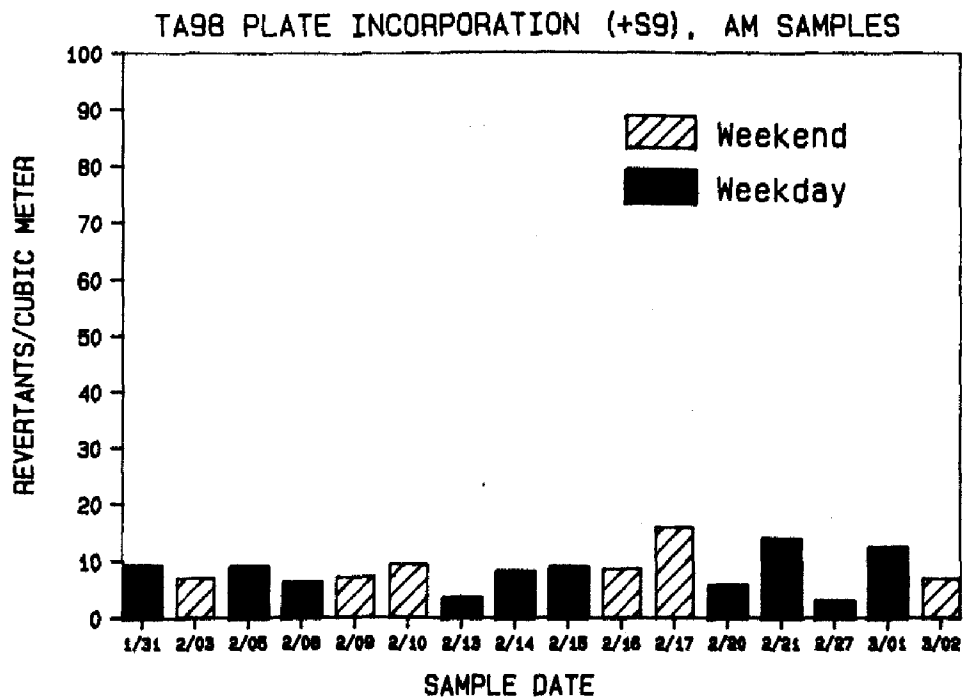
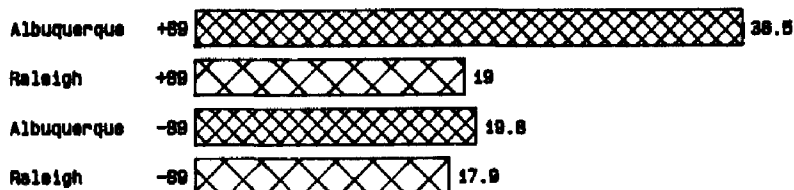


FIGURE 2. SALMONELLA REVERTANTS PER CUBIC METER AIR
FOR SOURCE APPORTIONMENT, ROADWAY,
AND BACKGROUND SAMPLES

S. typhimurium TA98 Plate Test

SOURCE APPORTIONMENT SAMPLES



ROADWAY & MAINSITE SAMPLES

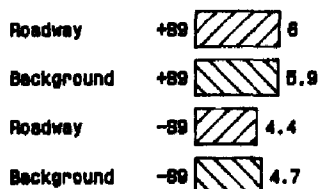
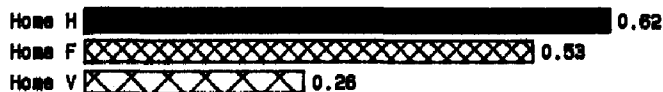


FIGURE 3. COMPARISON OF HOME SOURCE SAMPLES AND
LABORATORY SOURCE SAMPLE MUTAGENICITY

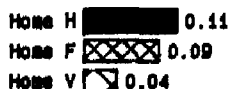
Home Source Samples +S9



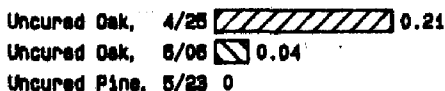
Laboratory Source Samples +S9



Home Source Samples -S9



Laboratory Source Samples -S9



S. typhimurium TA98
Plate test

IACP EMISSIONS: TRANSFORMATIONS AND FATE

L. T. Cupitt and L. D. Claxton
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

P. B. Shepson and T. E. Kleindienst
Northrop Services, Inc.
Research Triangle Park, NC 27709

Diluted emissions from wood stoves and automobiles were irradiated in a Teflon smog chamber to simulate their photochemical transformation in the atmosphere. Throughout the experiments, the chemical composition and physical properties of the gaseous and aerosol-bound complex mixtures were monitored. The mutagenicity of the gas-phase components and of the aerosol-bound chemicals were measured both before and after irradiation. Transformation of the dilute wood smoke occurred readily under all conditions tested: with and without added NO, with artificial illumination and with natural sunlight, at outdoor temperatures or at room temperature. As the photochemical reactions progressed, the volume of the aerosol-bound organics was seen to increase, suggesting that transformation products were condensing to form additional aerosol-phase materials.

The gas-phase reactants and products were tested for mutagenic activity by exposing Salmonella typhimurium, strains TA 98 and TA 100, to the filtered effluent. Filter samples of the starting materials and the transformed products were collected, extracted, and tested for mutagenic activity in the same bacterial strains by using a standard plate incorporation test. The transformations caused a dramatic change in the mutagenic activity of the gas-phase components. Comparisons of the mutagenic activity between the gas-phase and aerosol-bound chemicals have been estimated. When the mutagenicity is expressed in units of revertants per cubic meter of air, the gas-phase reaction products are found to be the most mutagenic.

Introduction

The Integrated Air Cancer Project (IACP) has focused on emissions from residential wood combustion (RWC) and from automobiles. As a part of the IACP, simulation experiments were conducted to characterize the atmospheric transformations of these complex mixtures. This research effort focused on three main questions: (1) Are transformations likely to occur? (2) If transformations do occur, what changes in chemistry and mutagenicity are induced? and (3) What is the relationship between gaseous and aerosol-bound mutagens?

Experimental Methods

A schematic diagram of the 22.7 m³ reaction chamber used for most of these experiments is shown in Figure 1. The chamber is housed in a truck trailer and consists of a 7.5 m long cylinder of Teflon film suspended between two aluminum end plates, each of which is coated with fluorocarbon paint. Irradiation is accomplished by means of blacklight and sunlamp fluorescent bulbs which surround the chamber. Oak logs, from the Research Triangle Park area of North Carolina, were burned in a commercially available wood stove. A portion of the wood smoke was introduced into a dilution tunnel and mixed with ambient air to cool the mixture. The diluted emissions were then used to fill the chamber to the desired concentration.¹ A few, preliminary experiments have recently been conducted using automobile emissions. The experimental set up is identical to Figure 1, except that the wood stove was replaced by a 1980 catalyst-equipped Toyota Corolla operating at high idle conditions and burning a "super unleaded" grade of gasoline. For a few wood smoke irradiations, a 9.0 m³ outdoor Teflon smog chamber was used. The outdoor chamber was at ambient temperatures and used only natural sunlight.

Four chambers were used for exposure of Salmonella typhimurium, strains TA 98 and TA 100, to the various gaseous mixtures. The chambers are 190-L, rectangular, Teflon-coated containers capable of holding more than 50 test plates. "Survivor" plates were routinely included for detection of toxicity effects. The test mixtures were flushed through the bioassay exposure chambers at 14 L min⁻¹, and exposures of the bacteria to the gaseous mutagens was accomplished simply by uncovering the glass Petri dishes containing the bacteria and permitting the mutagenic materials to dissolve into the plates. If one assumes that the "dose" is proportional to the exposure period, a type of dose-response curve can be generated conveniently by allowing various groups of plates to remain uncovered for differing periods of time. The details of the mutagenicity testing have been described elsewhere.¹⁻³ Particulate samples from each of the test streams were collected on Teflon-coated glass fiber filters identical to those used in the ambient IACP field study. Mutagenicity testing of the particulate extracts was accomplished using the Ames standard plate incorporation test.⁴ Four distinctive air streams were tested: the clean air used to replenish the chamber as samples were withdrawn, the ambient air used in the dilution tunnel, the reactants (i.e., the diluted wood smoke or auto exhaust prior to irradiation), and the chamber effluent (i.e., the diluted emissions after irradiation).

In several experiments, two bioassay exposure chambers were used in series to test the effluent from the reaction chamber. Not all of the gaseous mutagens entering the first bioassay exposure chamber are removed by the test plates. Data from the second chamber permits a better estimate of the total vapor-phase mutagenicity in the test air stream. The calculated gaseous mutagenicity may still be a lower limit estimate, however, since non-polar mutagens are not likely to be efficiently removed, even by two chambers in series.

The experiments were conducted by filling the reaction chamber with the wood smoke or automotive emissions to the desired concentration ("15 ppm Carbon), adjusting the NO_x concentration, if necessary, and then irradiating the mixture until an ozone maximum was reached. The lights were then turned off, and the effluent bioassay exposures were begun. For most of the wood smoke irradiations, additional NO was added to the system to increase the extent of reaction and to bring the hydrocarbon to NO_x ratio more in line with those measured in urban and suburban areas.⁵ Additional NO was not needed for the experiments involving automotive exhaust. Irradiation of the outdoor chamber was controlled by removal and re-installation of an opaque cover. The wood smoke irradiations usually took from one to two hours to reach the ozone maximum, while the automotive exhaust experiment was irradiated for about 5 hours. The bioassay exposures typically lasted up to 10 hours. Throughout the bioassay exposure period, the sample withdrawn from the reaction chamber had to be continuously replaced with clean air. This meant that the mutagens in the reaction chamber became more and more dilute with time ("4.5% per hour). An "effective" exposure time was calculated for the effluent bioassay chamber to account for the effects of dilution.

Results

Changes in the chemical composition and mutagenic potency were readily observed for all irradiation conditions. Table I lists the initial and final concentrations of a variety of chemicals observed during three of the wood smoke irradiations. Experiment A was conducted with dilute wood smoke alone, while experiments B and C contained additional NO_x . The addition of NO_x to the dilute wood smoke irradiations caused the system to react more completely and to produce even more mutagenic products than did Experiment A. Similar experiments conducted in the outdoor chamber gave essentially identical results for both chemistry and mutagenicity, despite differences in the light intensity and distribution and the somewhat lower (by 9x C) temperatures. Irradiation of the wood smoke mixture caused the aerosol volume distribution to increase, suggesting that transformation products may be condensing out on the aerosols. The mutagenicity of both the gas-phase and the aerosol components were measured before and after irradiation. When two bioassay exposure chambers were used in series to measure the gas-phase mutagenicity, the response in the second chamber was about 30% of that in the first chamber. This implies that the bioassay exposure chamber is around 70% efficient at removing the mutagens.

Figure 2 shows the comparison of the mutagenicity associated with the gas-phase and the aerosol-bound organics, both before and after irradiation. The mutagenicity in Figure 2 is reported in revertants m^{-3} and is shown for direct acting mutagens (i.e., without metabolic activation) in two bacterial

strains (TA 98 and TA 100). Prior to irradiation, the bulk of the mutagenicity was found in the particulate phase. After irradiation, however, the gaseous transformation products contribute significantly (80 to 99%) to the total mutagenic burden in the air. It should also be noted that the mutagenic products proved to be very stable in the reaction chambers. As described in the previous section, dose response curves were derived from exposures which lasted as long as 10 hours after the lights were turned off. The dose response curves remained linear over this time period, implying that the mutagenic vapor-phase products are long lived.

Insertion of an XAD-2 trap into the line between the irradiation chamber and the bioassay exposure chamber caused the mutagenic response to decrease by more than 80%. Unfortunately, only about 10% of the removed mutagenicity was recovered in the XAD-2 extract. Many of the vapor-phase mutagens removed by XAD-2 may either be unstable on the adsorbent, or may be lost during the extraction and concentration procedures.

A series of preliminary experiments were also conducted using diluted exhaust from an idling automobile to fill the simulation chamber. Once again, the gas-phase transformation products dominated the total mutagenic burden after irradiation.

Conclusions

Irradiations of complex mixtures involving both wood smoke and automobile exhaust have demonstrated that chemical reactions are probable and that the gas-phase products which result from these chemical reactions can constitute the major portion of the total atmospheric mutagenic burden. Chemical and mutagenic changes were observed for all tested conditions (with and without added NO_x ; artificial or natural illumination; controlled indoor environment or cooler outdoor temperatures), but the mutagenic response seems to increase with increasing chemical reaction. The mutagenic gas-phase products have been shown to be quite stable in the simulation chambers, with lifetimes considerably longer than many residential exchange rates.⁶ These results suggest that transformation of the gas-phase and aerosol components of complex mixtures may contribute significantly to the total burden of mutagens or carcinogens in the environment and should be considered in assessing risk.

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Table I. IACP Transformation Study: Gas Phase Concentrations of Chemicals During Wood Smoke Irradiations (ppb, v/v)

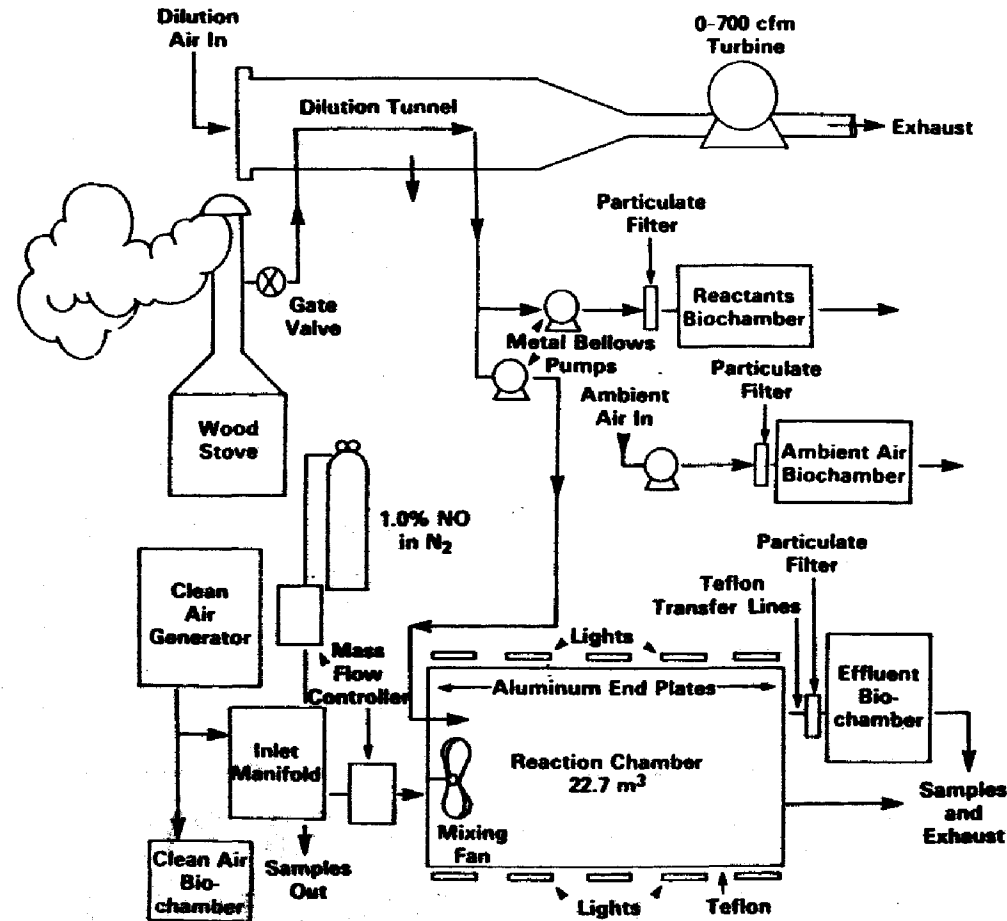
Species	Experiment A (No NO _x Added)		Experiment B (NO _x Added)		Experiment C (NO _x Added)	
	Initial	Final	Initial	Final	Initial	Final
Nitric Oxide	75	0	454	0	461	0
NO _x	135	64	657	252	576	259
Ozone	0	79	0	467	0	696
CO (ppm)	33.5	32.0	38.0	33.4	38.7	35.5
Ethylene	702	652	537	313	847	439
Benzene	68	62	62	50	102	68
Toluene	27	16	62	15	24	10
Formaldehyde	325	381	269	365	229	383
Acetaldehyde	140	106	88	109	57	75
PAN	0	52	0	174	0	232
HC (ppm-C)	20.6	19.1	16.4	13.2	17.2	15.0
HC/NO _x	153		25		30	

Figure Captions

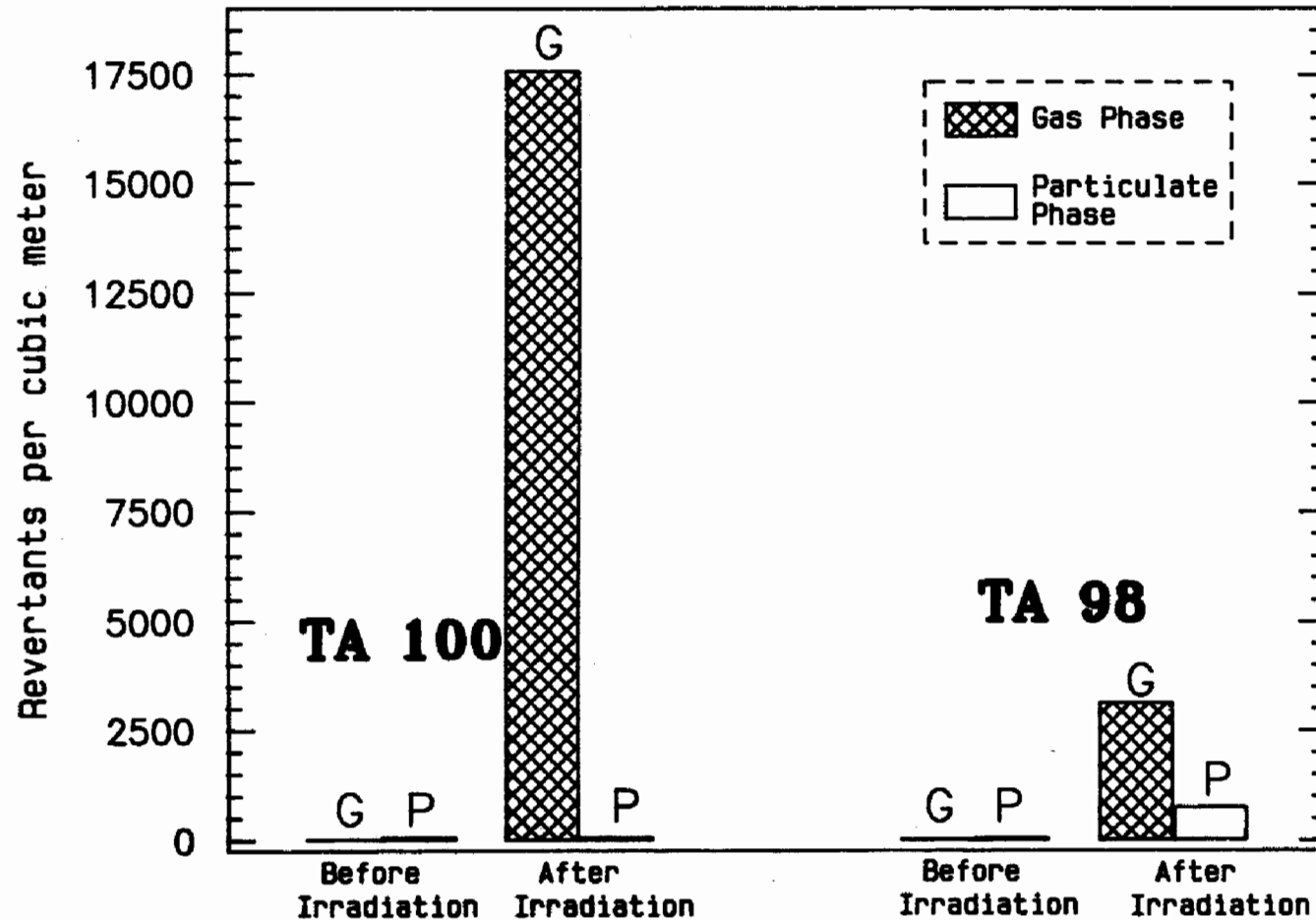
Figure 1. Schematic diagram of the experimental apparatus used in the IACP wood smoke study.

Figure 2. Graphical comparison of the mutagenicity of the gas- and particulate-phase components of wood smoke, before and after irradiation. (The mutagenicity was measured without metabolic activation and is expressed in units of revertants per cubic meter.)

Experimental Schematic of the Wood Stove, Reaction Chamber, and Exposure Apparatus



Gas and Particulate Phase Mutagenicity of Dilute Wood Smoke + NO_x in Air



CHEMICAL SPECIATION OF NICKEL
IN AIRBORNE DUSTS



Vladimir J. Zatka
Inco Limited
J. Roy Gordon Research Laboratory
Mississauga, Ontario L5K 1Z9

David Maskery
Inco Limited
Central Process Technology
Copper Cliff, Ontario POM 1N0

J. Stuart Warner
Inco Limited
1 First Canadian Place
Toronto, Ontario M5X 1C4

Responsible management of nickel-related health hazards in an industrial environment requires analytical knowledge, both qualitative and quantitative, of the various nickel species present in the airborne dust of the workplace. A wet-chemical procedure is described which apportions the airborne nickel species into four categories: (1) water soluble; (2) sulfidic; (3) metallic; and (4) oxidic. The procedure involves subjecting the dust to three sequential leaches with (1) ammonium citrate, (2) hydrogen peroxide-ammonium citrate, and (3) bromine-methanol, each of which selectively dissolves a number of related nickel compounds. The three leachates and the final residue are then analyzed for nickel and possibly for other elements. Since real samples usually contain a limited number of compounds, this categorization is often adequate to speciate the sample. The potential ambiguity of this approach is compensated by the fact that it can be readily implemented in regular analytical laboratories. The underlying chemistry of each leaching step is discussed and its selectivity and completeness are evaluated. The peroxide-ammonium citrate mild oxidative leach is time-intensive (2 h) and requires pH control and small sample size (<50 mg). The individual leaching methods were tested in an international interlaboratory program and the results are discussed briefly.

In the past, an increased incidence of respiratory cancer was associated with certain nickel refining operations. The compound(s) that may have been responsible for this risk has not been identified but some researchers and regulators have hypothesized that all forms of nickel should be considered to be potential carcinogens. However, extensive epidemiological studies have shown no nickel-related risk of cancer in the nickel-using industries or in the great majority of occupations in the nickel-producing industry. Furthermore, laboratory experiments indicate significant differences in the carcinogenic potential of different nickel compounds. Given the important role nickel plays in our technology, the efficient management of risk requires the ability to distinguish quantitatively between the different species of nickel in airborne dusts.

No universal analytical technique capable of quantifying as well as identifying all nickel species present in minute dust samples is known. Researchers are currently trying to solve the problem by instrumental and wet-chemical methods. Instrumental approaches deal with physical characteristics of atoms, less often of molecules, and usually require a powerful data processing capability. Nearly all of these techniques examine only a small area of the sample to the depth of a few micrometers. This limitation can cause problems during calibration and speciation as minute amounts of airborne dust are often not distributed uniformly on filters. Last, but not least, few laboratories have access to the sophisticated instruments and the researchers with the experience and skills needed to correctly interpret results. Speciation by wet-chemical methods, on the other hand, exploits the differences in chemical properties of the various phases found in nickel bearing dusts. Such methods utilize all of the dust on the filter so non-uniform deposition is not a problem. However, the overriding advantage of a chemical approach to speciation is that it can be used by the majority of normal chemical laboratories.

To be sure, wet-chemical speciation is seldom as simple and accurate as conventional wet-chemical determinations of total elemental contents. Speciation has problems of its own especially on a micro scale, such as in the analysis of personal monitor filters. Of primary concern is finding conditions which result in highly selective separations. If this is not possible, some ambiguity in speciation will result. However, knowledge of the process in the workplace often helps rule out some phases identified as possibilities by the speciation. Furthermore, the toxic properties of the compounds of a given metal are probably related to their wet-chemical behaviors.

Experimental Approach

We developed a procedure for the speciation of nickel-containing phases based on multiple sequential leaching of a dust sample with reagents of increasing chemical "power". Three selective leaches were used - ammonium citrate, hydrogen peroxide-ammonium citrate, and bromine-methanol solutions - followed by a final decomposition of the insoluble leach residue by nitric and perchloric acids. The four solutions so obtained were analyzed for nickel by normal atomic absorption or plasma emission methods. Nickel compounds present in the sample were thus divided into the four groups which are identified in Table I. The procedure was tested on small samples (<50 mg) of fine dusts (<45 μ m) from the mill, smelter, and refinery, individually and in mixtures. The simple four-fold categorization of the great variety of industrially important nickel compounds seems adequate as real dust samples usually contain only a limited number of different nickel-bearing species and these can usually be deduced from the origin and history of the sample.

Results

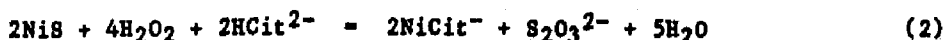
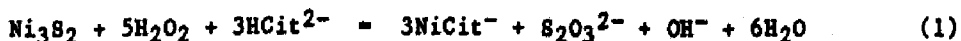
Soluble Nickel

Soluble nickel compounds are leached with a 0.1M solution of ammonium citrate (pH 4) rather than water. The citrate solution acts as a buffer and so ensures leach reproducibility by minimizing effects caused by foreign hydrolyzable salts. At the same time, complexing ability of the citrate ion toward higher-valent elements, such as iron(III), prevents unwanted precipitation of hydrolytic products. Citrate complexes of nickel are relatively weak, the most stable being NiCit^- ($\log K = 5.4$), and thus do not change the water solubility of "insoluble" nickel compounds.

The dissolution of nickel from basic nickel salts, for instance $\text{Ni}_x(\text{OH})_y(\text{SO}_4)_z \cdot \text{aq.}$ with water or ammonium citrate is incomplete and decreases with increasing basicity. Up to half of the contained nickel has been found to be leached from nickel carbonate and nickel hydroxide.

Sulfidic Nickel

This category comprises a large variety of nickel compounds, the most important of which are sulfides. Leaching with mild oxidizing solutions, all containing hydrogen peroxide, was proposed^{1,2,3} for the selective determination of nickel sulfide in binary mixtures with oxidic nickel. Others⁴ reported poor results and incomplete sulfide extractions with one such mixture of hydrogen peroxide and ammonium citrate¹. By extensive study, we found that a mixture of 1 volume of 30% hydrogen peroxide and 2 volumes of 0.1M ammonium citrate produced consistent results provided the solution pH was kept near 4. A minimum of two hours was usually necessary to ensure complete leaching of the sulfide phase from a 10-20 mg portion of dust. The reaction proceeds with formation of thiosulfate as the product of oxidation:



Of the two nickel sulfides, $\beta\text{-NiS}$ dissolves more slowly. It is worth noting that as the sulfides dissolve, the pH would increase if not for the buffering ability of the leach solution.

Nickel compounds other than sulfides which fall into this category include arsenides, selenides and tellurides. All were found leachable by the peroxide-citrate solution, though at varying rates, as shown in Table II. Ten mg samples of NiAs , $\text{Ni}_{11}\text{As}_8$ and NiSe dissolved within two hours. Ni_5As_2 and NiTe reacted at a much slower rate and almost 20 hours were needed to dissolve 10 mg portions. Fortunately, these compounds are present in small amounts, if at all, in dusts from the nickel industry.

Tests with pure metallic nickel showed that at pH 4 it was not attacked by the peroxide-citrate solution. However, it was deemed necessary to verify that this selectivity was not impaired by side reactions, such as cementation or surface activation, caused say by the leaching of copper and Ni_3S_2 from plant dusts. An in-depth leaching study of metallic phases (carbonyl nickel and ferronickel powder) showed that only 0.3 to 0.6% of the nickel dissolved after four hours. The leaching of metallics was not increased by the addition of either copper(II) or thiosulfate. Similarly recoveries of leachable sulfidic nickel from synthetic mixtures made of Ni_3S_2 , chalcopyrite concentrate, nickel or ferronickel powders and soluble cupric salt were satisfactory (92-96%) after two hours of leaching.

Metallic Nickel

Separating metallica from oxides by selective leaching has been a long established practice. A variety of oxidizing solutions ranging from silver, mercuric or cupric salts to chlorine⁵ or bromine⁶ in alcohol were used. Metallic nickel, pure or as ferronickel, readily dissolves in a solution of bromine in methanol (3% v/v). Sulfidic nickel species which have not been removed by a prior peroxide-citrate leach will also dissolve. Precipitated nickel hydroxide or carbonate should be absent as they are attacked to varying extents (0.2-5% Ni leached) depending on the history and composition of the specimen.

Oxidic Nickel

All oxidic forms of nickel remain in the final residue. They are solubilized by fuming with nitric and perchloric acids. We prefer collecting dust on PVC acrylic copolymer filters, such as the Gelman DM Metrical membrane, because they are insensitive to humidity fluctuations and, unlike plain PVC, are easily wet-ashed during oxide dissolution. Complete dissolution of the oxidized nickel phases can be assured only by fuming with perchloric acid assisted, in extreme cases, by added hydrofluoric acid. Analysts occasionally underestimate the refractory nature of oxidized nickel phases and, upon leaching the sample with aqua regia only or not heating the perchloric acid to high enough temperatures, report nickel values which suffer from an extensive low bias.

First Interlaboratory Test Program

The first interlaboratory program for the determination of diverse nickel phases in airborne dusts was sponsored in 1985 by the Nickel Producers Environmental Research Association (NiPERA). Twenty laboratories from eight countries evaluated the individual selective leach procedures on four bulk samples of dust: two synthetic mixtures and two plant dusts. Each of the four procedures was tested on two days using duplicate 10 mg sample portions. The small sample size was chosen so as to operate under conditions more closely resembling those involved in the analysis of loaded filters. The raw data reported by the participating laboratories was treated statistically according to ISO 5725⁷, and the outliers identified at the 95% probability level were removed. A final summary is presented in Table III⁸.

Considering the small portions analyzed and the inherent problems with phase analysis, repeatability "r" and reproducibility "R" of the reported results was generally acceptable. A few results, particularly for total nickel in the high grade sample ES-12, appeared to suffer from high bias which could be related to weighing or instrument calibration problems. More than 85% of all reported data sets passed the statistical tests. It was concluded that, with due attention by the analyst to the demands of microanalytical work, the four leaching methods tested provide a reasonable basis for the speciation of airborne nickel phases into four categories.

A second international program is now underway to test the sequential leach procedure using three bulk samples of plant dusts.

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Table I. Separation of nickel-containing phases by a sequence of selective leaches.

Group	Leach solution	Leached nickel phases
1	0.1M ammonium citrate	Normal salts (sulfate, chloride, sulfamate, etc.)
2	H ₂ O ₂ - citrate	Sulfides (Ni ₃ S ₂ , NiS, Ni ₃ S ₄ , [Ni, Fe] ₉ S ₈) Arsenides (NiAs, Ni ₃ As ₂ , Ni ₁₁ As ₈) Selenide (NiSe) Telluride (NiTe)
3	Bromine-methanol	Metallic (pure Ni, ferronickel)
4	Nitric-perchloric acids	Refractory oxide (NiO, Ni ferrite, silicate)

Table II. Leaching with hydrogen peroxide-ammonium citrate solution (pH 4).

Compound	XRD	Recovered by leaching 10 mg samples, %Ni	
		2 hrs	20 hrs
Sulfides	Ni ₃ S ₂	98	100
	β-NiS	94	99
	(Fe,Ni) ₉ S ₈	93	100
Arsenides	NiAs (72%)	100	—
	Ni ₁₁ As ₈ (28%)		
	Ni ₅ As ₂ (major)	62	98
	Ni ₁₁ As ₈ (major)	100	—
	Ni ₅ As ₂ (v.minor)		
Selenide	NiSe (major)	100	—
	Ni ₆ Se ₅ (v.minor)		
Telluride	NiTe (major)	73	100

Table III. Interlaboratory testing of the individual selective leach procedures on bulk dust samples.

Leach solution:		Citrate	H ₂ O ₂ + citrate	Br ₂ + methanol	HNO ₃ + HClO ₄
		% Nickel			
Sample		Soluble	Soluble+ sulfidic	Soluble+ sulfidic+ metallic	Soluble+ sulfidic+ metallic+ oxidic
ES-10 (synth.)	Grand mean	.58	1.87	8.02	10.99
	Repeatability r	.070	.095	.74	.37
	Reproducibility R	.22	.31	2.54	1.17
	Data sets accepted	18	17	20	19
ES-11 (synth.)	Grand mean	1.76	4.57	9.02	15.78
	Repeatability r	.39	.36	.52	1.02
	Reproducibility R	.82	.82	2.72	2.01
	Data sets accepted	19	18	19	19
ES-12 (plant)	Grand mean	1.16	12.55	15.74	72.12
	Repeatability r	.21	1.02	.89	2.77
	Reproducibility R	1.00	2.64	4.22	8.20
	Data sets accepted	18	19	19	18
ES-13 (plant)	Grand mean	2.04	2.25	3.18	27.16
	Repeatability r	.21	.23	.44	1.27
	Reproducibility R	.91	.55	2.07	3.04
	Data sets accepted	19	19	20	19

ES-12 - Fluid bed roaster raffia dust
ES-13 - Nickel alloy plant flue dust

CORRELATION OF MICROPROBE ANALYSIS DATA FOR INDIVIDUAL PARTICLE SPECIATION
- NICKEL COMPOUNDS FROM STATIONARY SOURCES

J.T. Rickman, I.H. Musselman, J.O. Mullis, R.W. Linton
Department of Chemistry
University of North Carolina
Chapel Hill, N.C. 27514

A challenging area of analytical chemistry is the development of new techniques to provide speciation information about elements present in small quantities within complex environmental samples. Microscopic chemical analysis techniques, e.g. laser microprobe mass spectrometry (LAMMS) and scanning electron microscopy coupled to energy dispersive x-ray spectroscopy (SEM/EDS) combine the advantages of high spatial resolution and sensitivity. They are used to investigate chemical species and their physical distribution between or within individual particles. The correlative microscopy studies are part of an EPA-supported project to evaluate methods for nickel speciation in airborne particles produced by stationary sources.

Introduction

As a consequence of the physical and chemical heterogeneity of airborne particles emitted by stationary sources, it is valuable to obtain microscopic analyses of individual particles. For example, the variabilities in elemental concentrations and speciation, both within and between particles, are important factors influencing environmental impact. Of special interest are particles in the respirable size range which also may be less efficiently captured by pollution control devices. Consequently, analytical techniques are desired which provide sub-micrometer spatial resolutions and which are sensitive to chemical components within analytical volumes corresponding to total masses of 10^{-12} grams. Two such techniques utilized in this study are laser microprobe mass spectrometry (LAMMS) and scanning electron microscopy/energy dispersive x-ray microanalysis (SEM/EDS). The LAMMS technique uses high power density pulsed laser beams to ablate and ionize single particles. Mass spectra, including characteristic atomic and cluster ions, provide information on chemical composition. The SEM/EDS provides information on particle morphology (by secondary and backscattered electron imaging) and composition (by analysis of characteristic electron-excited x-ray emissions). Whole particles and particles viewed in cross-section are characterized by SEM/EDS to provide information on inter- and intra-particle compositional variations, respectively. A correlative regimen also is developed permitting SEM/EDS followed by destructive LAMMS measurements on the same individual whole particles. The above techniques are not only complementary, but also may be used to verify information obtained by more conventional bulk analytical techniques (wet chemistry, x-ray powder diffraction). The specialized microprobe techniques serve, therefore, to assist in the evaluation of other analytical methodologies which are more appropriate for applications to routine source or environmental monitoring of toxic elements and compounds. In other instances, sample sizes may be inadequate to permit any analyses other than microprobe studies of individual particles.

To illustrate the combined microprobe techniques, the characterization of micrometer sized particles produced near a fluidized bed roaster (FBR) in a nickel refinery will be discussed. The FBR dust is a useful sample for analytical technique evaluation in that it is known to contain several major classes of nickel-containing compounds (e.g. oxides, sulfides, sulfates) which may have differing environmental impacts. The nickel

subdisulfide (Ni_3S_2) is of particular interest as a result of its possible carcinogenic potency in humans. This project is part of an EPA-supported project to evaluate methods for nickel speciation monitoring in stationary source emissions. More detailed descriptions of the experimental methods and results are available elsewhere (1,2).

Experimental methods

Standard and sample preparation

LAMMS and SEM/EDS correlative study. The particle standards Ni, NiO, NiSO_4 , NiS, and Ni_3S_2 were mounted dry on formvar coated transmission electron microscope (TEM) finder grids. The FBR dust sample was dispersed in freon in an ultrasonic bath. A drop of the sample dispersed in freon was deposited on a coated TEM grid and allowed to dry. All samples and standards were carbon coated to reduce charging in the SEM.

Light microscopy (LM) and SEM/EDS correlative study. Cross-sections of the FBR dust sample and nickel standards were obtained by first embedding the particles in epoxy followed by curing of the epoxy, and final polishing. These particle cross-sections were carbon coated for SEM/EDS. Intra-particle chemical variations were investigated by elemental mapping for Ni and S using characteristic x-ray emissions.

Instrumentation

The SEM/EDS used was an ISI DS-130 SEM with a Tracor Northern TN-5500 energy dispersive spectrometer and digital imaging system. The LAMMS analyses were performed using a Leybold-Heraeus LAMMA-500 instrument.

Correlative procedure

LAMMS and SEM/EDS. Using the SEM/EDS, particles were analyzed at an electron beam energy of 15 keV for 99 seconds live counting time per particle. Particle analysis software generated size and shape information, as well as background-subtracted integral x-ray intensities for specified elements. Grid squares analyzed had an intact formvar coating and contained well-dispersed particles (particles usually greater than 3 micrometers apart). The same particles were then analyzed destructively by LAMMS. The laser and mass spectrometer conditions were selected to allow for complete ablation of each particle and to maximize production of cluster ions characteristic of individual nickel compounds. Details of

SEM/EDS and LAMMS experimental parameters are described elsewhere (2).

LM and SEM/EDS. Particle cross-sections were examined using polarized reflected light, and subsequently mapped for nickel and sulfur distributions using the SEM/EDS.

Results and Discussion

Standards

LAMMS. Fingerprint mass spectra of Ni, NiO, NiSO₄, Ni₃S₂ and NiS were obtained using LAMMS. It was not possible to differentiate between NiS and Ni₃S₂ standards, although all other compounds produced characteristic patterns of positive or negative cluster ions (1,2).

SEM/EDS. A range of +/- sigma values about the average for S/Ni K_α x-ray intensity ratios for NiS (1.9-2.5), Ni₃S₂ (1.2-1.5), and NiSO₄ (1.5-2.6) standards were obtained. Approximately 50 particles were analyzed per standard to obtain these ranges. Variabilities reflect fundamental particle size and shape effects on x-ray emissions as described elsewhere (2). An example of SEM/EDS data is shown in Figure 1 for a particle in the NiS standard. For comparison, a corresponding LAMMS spectrum also is presented.

Nickel refinery sample - Fluidized Bed Roaster (FBR) dust

LAMMS and SEM/EDS. Of 115 FBR particles analyzed by SEM/EDS and LAMMS, LAMMS was used to differentiate 57 into either 1] Ni_xO_y/NiSO₄ or 2] Ni₃S₂/NiS classes. Since only positive ion spectra were used, it was not possible to distinguish Ni_xO_y and NiSO₄ solely from the LAMMS data. The other 58 particles did not produce intense nickel-containing cluster ions owing to lower nickel concentrations and instrumental factors (2). Using the S/Ni x-ray intensity ratios from SEM/EDS the 57 particles were further subdivided into these classes: NiO (17 particles), NiSO₄ (9 particles), NiSO₄ or a mixture including NiSO₄ and Ni_xO_y (17 particles), Ni₃S₂ (6 particles), NiS (4 particles) and a mixture containing NiS and/or Ni₃S₂ (4 particles).

LM and SEM/EDS x-ray mapping. The above results on whole particles

suggested that many contained multiple nickel species, especially oxide and sulfate combinations. This was substantiated by cross-sectional elemental mapping by SEM/EDS. Many particles showed large variations in sulfur distributions, including some with surface enrichments of sulfur. It is likely that such particles contain layers of nickel sulfate deposited on an oxidic nickel core. This was further confirmed by surface analysis using x-ray photoelectron spectroscopy (XPS) showing nickel sulfate as a major surface component. Additional experiments on the particle cross-sections are envisioned using ion microscopy to further characterize intra-particle mixtures of nickel compounds

Acknowledgements

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1. I.H. Musselman, R.W. Linton and D.S. Simons, "The Use of Laser Microprobe Mass Analysis for Nickel Speciation in Individual Particles of Micrometer Size", Microbeam Analysis-1985, 337-341.
2. I.H. Musselman, J.T. Rickman and R.W. Linton, "Fingerprinting of Chemical Species in Microparticles - Correlative Laser and Electron Microprobe Studies", Microbeam Analysis-1987, in press.

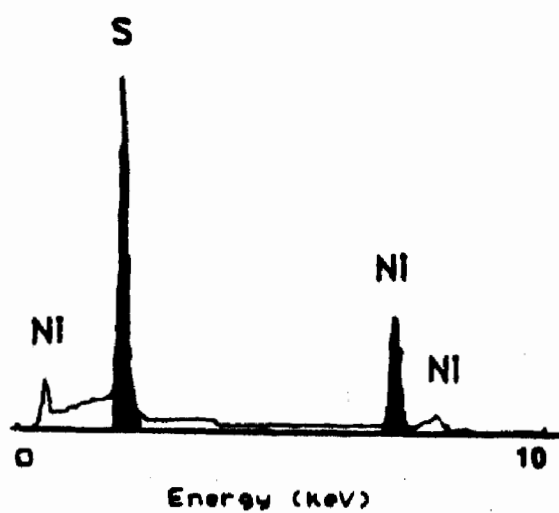
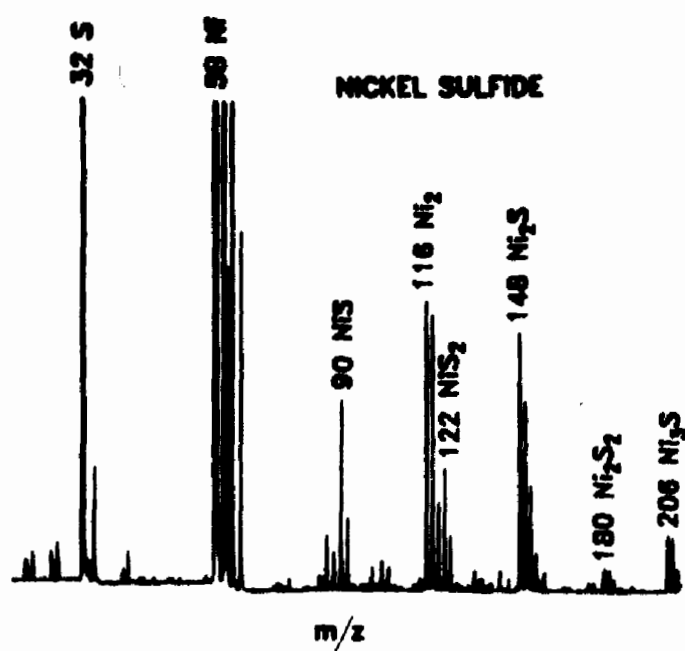


Figure 1. Spectra obtained on NiS standard by LAMMS (top) and SEM/EDS (bottom).

EVALUATION AND OPTIMIZATION OF A WET CHEMICAL METHOD
FOR DETERMINING THE HYDROGEN SULFIDE CONCENTRATION OF
CYLINDER GASES EMPLOYED FOR TRS CEMS QUALITY ASSURANCE

A. K. Jain, M. D. Marks, L. J. Larson,
M. N. Stryker, R. P. Fisher
National Council of the Paper Industry
for Air and Stream Improvement, Inc.
Post Office Box 14483
Gainesville, FL 32604

Existing and developing total reduced sulfur (TRS) continuous emission monitoring system (CEMS) quality assurance programs include, or will include, requirements for the use of hydrogen sulfide (H_2S) calibration gases. NCASI conducted studies to evaluate and optimize a wet chemical method for determining the H_2S content of calibration gases in the 5 to 1500 ppm range. The study showed that sampling time, sample flow rate, holding time after reagent addition, and regulator conditioning were significant parameters. Accurate results were obtained following the proposed procedure upon analyses of 5, 25, 100, 500, and 1500 ppm H_2S in nitrogen cylinder gases.

EVALUATION AND OPTIMIZATION OF A WET CHEMICAL METHOD
FOR DETERMINING THE HYDROGEN SULFIDE CONCENTRATION OF
CYLINDER GASES EMPLOYED FOR TRS CEMS QUALITY ASSURANCE

Introduction

In January, 1985 NCASI published a wet chemical method for determining the H_2S concentration of cylinder gases.¹ This method was developed with a view to assist kraft pulp mills in their total reduced sulfur (TRS) continuous emission monitoring system quality assurance programs by providing them with an independent means of establishing the concentration of H_2S cylinder gases used to calibrate the TRS analyzer; and it was validated for an H_2S concentration range of 5 to 25 parts per million (ppm) in nitrogen. Following the publication of this report it was recognized that there was a need to use this or a similar method for analyzing cylinder gases containing as much as 1500 ppm H_2S . These high concentration cylinder gases are used for calibrating certain TRS continuous emission monitoring systems which contain integral dilution systems and which are widely used in the pulp and paper industry. At present no suitable method is available to establish the H_2S content of these cylinder gases. This paper describes a modified version of the earlier method which has been validated for analyzing the H_2S content of cylinder gases containing 5 to 1500 ppm H_2S in nitrogen.

Method Development Studies

The method for determining the concentration of H_2S in cylinder gas mixtures that was used in this study is based upon trapping H_2S as zinc sulfide in impingers containing solutions of zinc acetate, acidifying the combined trapping solutions in the presence of iodine, and determining unreacted iodine by thiosulfate titration. During this study a number of variables that had an impact on measured H_2S concentrations were examined and optimized. The results of some of those studies are described below. The final method and the required equipment are described in Appendix A. The details of the method have been published elsewhere.²

Regulator Conditioning

Data in Table I present the results of a series of tests employing the method of Appendix A with a cylinder containing approximately 500 ppm H_2S in nitrogen. The data show that at a flow rate of approximately 200 mL/min it took nearly 3 hours to passivate the regulator. The need to passivate the regulator was found to be more pronounced for cylinder gases containing more than 250 ppm H_2S in nitrogen which required lower sample flow rates. Consequently, the regulator passivation step has been included in the procedure.

Holding Time for Samples Prior to Titration

Tests were conducted to examine the effect of storing samples after iodine addition prior to their titration with thiosulfate. The results suggested that a storage time of 30 minutes following iodine addition allowed the iodine reaction to be complete. Table II presents the results of one such test.

Loss of Iodine During Transfer of Impinger Contents

Tests were conducted to determine the loss of iodine when the contents of impingers containing iodine are transferred to a flask for titration. As

an example, the results of one test showed that the thiosulfate titrant requirement decreased from an average of 19.41 mL to 19.24 mL when the contents of impingers containing iodine were transferred to a flask for titration. The method has, consequently, been modified to eliminate the step requiring transfer of impinger contents.

Sample Volume and Sample Flow Rate

Studies showed that highest precision and accuracy were obtained when the H_2S content of the sample was sufficient to consume 35 to 60 percent of added iodine, and sample flow rate was maintained in a specified range. Tables III and IV show the optimum sample volumes and sampling rates for different H_2S concentration ranges.

Method Performance

The performance of the method of Appendix A was evaluated in the H_2S concentration range of 5 to 1500 ppm. The results of precision and accuracy tests are presented below.

Accuracy

The accuracy of the method was established by comparing the results of method analyses of seven different cylinder gases with their known concentrations. For five of the seven cylinder gases the true H_2S concentrations were established by analyzing the cylinder gases with a permeation tube-calibrated gas chromatograph equipped with a flame photometric detector. The details of this gas chromatographic method are described elsewhere.¹ The other two cylinder gases analyzed by NCASI were National Bureau of Standards (NBS) Standard Reference Material H_2S in nitrogen. (Although these NBS reference materials are not yet available commercially, two of these gas standards were made available to NCASI and were used to evaluate the performance of the method under evaluation.)

The results of the accuracy tests are summarized in Table V. These results show that for the H_2S concentration range of 5 ppm to 1500 ppm, the percent difference between the H_2S concentration measured according to the method of Appendix A and the true concentration ranged from -2 to +3 percent. The average for all seven cylinder gases was less than 0.5 percent. These results suggest that the method is accurate and unbiased.

Precision

As shown in Table V, the relative standard deviation of replicate analyses of seven gas mixtures ranged from 0.9 to 2.9 percent. The pooled relative standard deviation of the test method is estimated to be 1.4 percent for tests conducted within a single laboratory.

Literature References

1. "Wet Chemical Method for Determining the H_2S Concentration of Calibration Cylinder Gases," NCASI Technical Bulletin No. 450, NCASI, 260 Madison Avenue, New York, NY 10016 (January 1985).
2. "Modified Wet Chemical Method for Determining the H_2S Concentration of Calibration Cylinder Gases," NCASI Technical Bulletin No. 519, NCASI, 260 Madison Avenue, New York, NY 10016 (March 1987).

APPENDIX A

EQUIPMENT, TEST METHOD, AND CALCULATIONS

Description of Equipment

Figure A-1 shows the sampling train. The stems of the 100 mL impingers (Ace Glass, Type 7541) were lengthened to be approximately 1/2 inch from the bottom in order to increase contact between gas and the trapping solution. The critical orifice may be fabricated from 1/16 inch O.D. stainless steel capillary tubing.

Sampling and Analysis

Prior to sampling, pressurize the stainless steel regulator and expose it to test gases for several hours or overnight to passivate activated sites. Determine the sampling rate, sample volume and sampling time from Tables III and IV. Assemble the sampling train and add 50 mL of 0.091 M zinc acetate solution to each of the first two impingers. Establish a flow rate of gas from the regulator which is 50 to 100 mL in excess of the critical orifice flow rate. Conduct sampling for the desired period. While sampling, titrate 20.0 mL of 0.01 normal iodine solution with 0.01 normal sodium thiosulfate using starch as indicator. At the end of sampling pipette 20.0 mL of 0.01 N iodine solution through the stems of the impingers containing zinc acetate capture solution, dividing it between the two (about 15 mL to the first impinger and the rest to the second). Add 2 mL of 2.8 M hydrochloric acid solution through the stems, dividing it as with the iodine. Cover the stem openings with paraffin film, store for 30 minutes in the dark, then remove the stems with rinsing, and titrate the solution in the impinger bottoms with 0.01 N thiosulfate. The decrease in the amount of thiosulfate titer corresponds to the amount of H_2S captured in the two impingers. Analyze a method blank in a similar manner.

Calculations

Calculate the concentration of H_2S (C_{H_2S}) using the following equation:

$$C_{H_2S}, \text{ ppm} = K N_T (V_{T, \text{ blank}} - V_{T, \text{ sample}}) / V_{m, \text{ std}}$$

where $K = 12,025 \text{ mL (gas)/g eq}$; $N_T = \text{normality of standard thiosulfate solution, g eq/lit}$; $V_{T, \text{ blank}}$ & $V_{T, \text{ sample}} = \text{volume of thiosulfate used in blank and sample titration, mL}$; $V_{m, \text{ std}} = \text{dry standard sample gas volume, L}$.

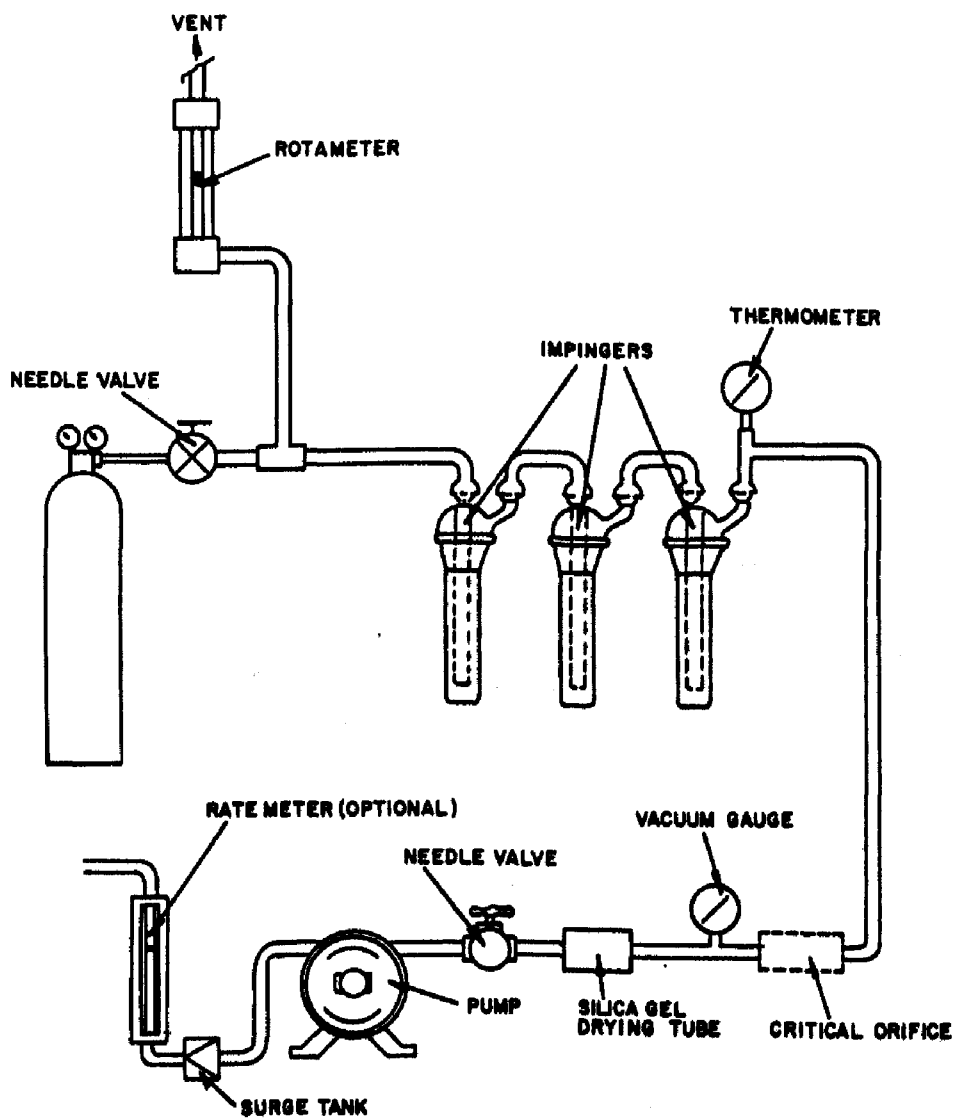


FIGURE A-1. H₂S SAMPLING TRAIN

TABLE I. EFFECT OF REGULATOR CONDITIONING ON
MEASURED H_2S CONCENTRATIONS

No.	Regulator Conditioning Period, minutes	Measured H_2S Concentration, ppm
1	0	508
2	30	507
3	90	518
4	180	526
5	240	521

TABLE II. EFFECT OF HOLDING TIME ON MEASURED H_2S CONCENTRATION

Run No.	Holding Time After Iodine Addition, minutes	Measured H_2S Concentration, ppm
1	15	498
2	20	516
3	30	530
4	40	527
5	60	532

TABLE III. OPTIMUM SAMPLE VOLUMES

Approximate Cylinder Gas H_2S Concentration, ppm	Approximate ppm x Liters Desired
5 to <30	650
30 to <500	800
>500 to 1500	1000

TABLE IV. OPTIMUM SAMPLE FLOW RATES

Cylinder Gas H ₂ S Concentration, ppm	Desired Flow Rates, mL/min
5 to <50	1500 p 500
50 to <250	500 p 250
250 to <1000	200 p 50
>1000	75 p 25

TABLE V. RESULTS OF ANALYSES OF H₂S CYLINDER GASES
BY THE METHOD OF APPENDIX A

No.	Reference Method Test Results		Wet Method Results		Difference, Percent
	H ₂ S Conc., ppm	Test Method	Average H ₂ S Conc., ppm	Relative Standard Deviation, Percent	
1	7.90	GC/FPD	7.84 (6) *	1.6	-1
2	25.4	GC/FPD	25.5 (6)	2.9	0
3	104	GC/FPD	102 (5)	1.0	-2
4	488	GC/FPD	492 (10)	1.2	1
5	1470	GC/FPD	1480 (6)	1.3	1
6	5.15	NBS	5.32 (3)	0.9	3
7	15.4	NBS	15.5 (4)	1.9	1

*Numbers in parenthesis show number of replicate analyses.

EVALUATION OF ETHYLENE OXIDE EMISSIONS:
GAS CHROMATOGRAPHIC ANALYSIS OF
SCRUBBER EFFICIENCY

Jeremy N. Bidwell,
TRC Environmental Consultants, Inc.
East Hartford, CT



As Ethylene Oxide (EtO) is now more recognized as a hazard to man and his environment there is interest in quantifying emissions from a wide variety of processes. As with any testing procedure, an accurate and repeatable method of sampling is needed that is both flexible enough to accommodate a wide variety of sampling conditions and sample concentrations, and is straight-forward enough to be adopted by the analytical community.

Two recent scrubber efficiency tests at hospital supply manufacturers are examined, where EtO was used to sterilize heat sensitive products prior to shipping. Samples were drawn utilizing evacuated stainless steel canisters equipped with low flow regulators to draw 20 minute integrated samples. Sample analysis was performed on a Gas Chromatograph using a Flame Ionization Detector.

This technique has shown itself to be a valuable method of assessing steady state and nonsteady state processes where sample moisture concentrations do not exceed 20%, as is the case with most sterilization processes.

Overview Of Sampling Technique

Many temperature sensitive hospital products must be sterilized prior to shipment by exposure to EtO in a sealed chamber. After a predetermined holding time, the EtO is pumped out of the chamber to the scrubber, often by means of a water seal vacuum pump. At the outlet of the pump (which is also the inlet of the scrubber) as well as at the scrubber outlet, gas stream volumetric flowrates were measured

concurrently with EtO concentrations. A Hastings model GSM-IDSK flow meter was used in conjunction with a strip chart recorder at both sampling locations to continuously monitor flowrates.

Gas samples to be analyzed for EtO concentration were drawn by using a specially fabricated sampling train, as shown in Figure 1. The sampling train consisted of a stainless steel tank of the type used in EPA Method 25 sampling, an on/off toggle valve, a small vacuum gauge, a low flow regulator, and a stainless steel probe. These parts were all fitted together using 1/4 inch stainless steel Swagelok connections and fittings. The tank purge setup (Figure 2) used similar fittings and 1/4 inch Teflon tubing. Each tank was fitted with a quick connect connector to facilitate easy tank replacement, enabling samples to be drawn in quick succession.

Clean sample tanks were stored and transported at a slight positive pressure to prevent contamination. Just prior to sampling, a tank was evacuated; the exact negative pressure (P_i) was read from the manometer on the tank purge setup, and recorded. The tank was then removed from the purge setup and connected to the sampling train with the toggle valve in the "off" position. Sampling began when the toggle valve was switched to the "on" position. After sampling, the valve was switched off and the tank was disconnected from the sampling train and connected to the purge setup. The pressure (P_s) was read and recorded and the tank was then pressurized to approximately one atmosphere with hydrocarbon free air from a compressed gas cylinder connected to the purge setup. This positive tank pressure (P_f) was also read and recorded. The sample dilution which occurs when the tank is pressurized is calculated by:

$$D = \frac{(P_b + P_f)}{(P_s - P_i)} \quad (1)$$

Where P_b = Barometric Pressure

Note that both P_i and P_s are always negative

Pretest Calibrations

Compressed gas cylinders of several concentration ranges of EtO were purchased from Scott Specialty Gases of Plumsteadville, Ohio. Fully Evacuated sampling tanks were filled with these calibration gases and analyzed using the same method used on the samples. Standard gases of other concentration ranges were generated on site by diluting the Scott gases in a sampling tank. This dilution was accomplished by filling a tank to one atm with the gas to be diluted, and fitting the tank with a septum. Another tank was evacuated and left connected to the purge setup. A glass syringe was used to draw out a small volume (V_s) from the first tank and inject it in the second tank through the septum on the purge setup. This second tank was then pressurized to exactly one atm and the dilution factor was calculated using equation 2:

$$D_2 = \frac{V_s}{2(V_t)} \quad (2)$$

Where V_t = Volume of the tank

Dilution factors could be changed by changing the quantity of gas injected (V_s). Example dilution calculations are presented in Table 1.

The low flow regulator on the sampling train is set at a prescribed rate (R) before the testing program by use of a bubble flow meter and a stopwatch. The regulator delivers a constant flowrate until the vacuum side reaches a pressure of 1/2 atm, which occurs when the tank is half filled. After that, the sampling rate drops off toward zero. If the length of the desired sampling period (T) is known, then the optimum sample flowrate (R) would be:

$$R = 0.5 V/T \quad (3)$$

To ensure sample integrity, a blank check was performed on all sample tanks before use by filling each tank with hydrocarbon-free air and then analyzing a sample from each tank on the gas chromatograph. Each sampling train was leak checked prior to sampling by connecting a mercury manometer to the sampling train. With the toggle valve open, the manometer was observed for a loss of vacuum over a ten minute period. Criteria for an acceptable leak rate was based on EPA Method 25, which utilizes a similar apparatus, with less than 2mm Hg vacuum loss over ten minutes.

Sample Analysis

A Hewlett Packard Model 5710 GC was equipped with a six port gas sampling valve and associated equipment as shown in Figure 3. With the needle valve fully closed, the sample tank was attached to the system by means of a quick connect fitting. When the needle valve was opened slightly, the positive pressure inside the sample tank drove gas from the sample tank through the whole system, displacing any existing gases in the sample apparatus with fresh sample gas. This technique used only a fraction of the pressure in the sample tank, allowing several duplicate runs to be made with the same sample. Gas samples of extremely high concentrations were diluted using the same procedure outlined previously for the dilution of standard gasses.

The sample injected into the GC had been diluted in the tank. Therefore, the EtO concentration (C) in the gas stream was found by multiplying the tank concentration (Ct) by the dilution factor (D) as in equation 4:

$$C = (C_t \times D) \quad (4)$$

Efficiency Calculations

For each sample an EtO mass flowrate is calculated using equation 5:

$$H = (Q \times MW \times C \times K) \quad (5)$$

Where H = EtO mass flowrate in lb/hr

Q = Gas Flowrate in standard cubic feet per minute

MW = Molecular Weight of EtO = 44.05 g/mol

C = EtO concentration in parts per million v/v

$$K = \frac{28.3 \text{ L}}{1 \text{ ft}} \times \frac{1 \text{ mol}}{24.04 \text{ L}} \times \frac{60 \text{ min}}{1 \text{ hr}} \times \frac{1 \text{ lb}}{454 \text{ g}} \times \frac{10^{-6} \text{ L}}{\text{L}}$$

$$K = 15.58 \times 10^{-8}$$

For each pair of inlet-outlet EtO mass flowrates, a scrubber efficiency can be calculated using equation 6:

$$E = 100 (H_i - H_o) / H \quad (6)$$

Where E = Percent Efficiency
 H_i = EtO mass flowrate at Inlet
 H_o = EtO mass flowrate at Outlet

TABLE 1
ETHYLENE OXIDE (ETO) SAMPLING DATA

SAMPLE NO.	P_i	P_s	P_f	D
1-I	-645	-414	535	5.10
1-O	-645	-188	520	2.55
2-I	-645	-146	722	2.74
2-O	-645	-78	560	2.13
3-I	-645	-128	618	2.44
3-O	-645	-80	508	2.04

P_i = Tank initial pressure (mm Hg)
 P_s = Tank pressure after sampling (mm Hg)
 P_f = Tank final pressure (mm Hg)

TABLE 2
ETO REMOVAL EFFICIENCY DATA

SAMPLE NO.	Q	C_t	D	C_s	H	E
1-I	120	2869	5.10	14,627	11.9	99.59
1-O	120	24	2.55	60.0	0.049	
2-I	84.0	8930	2.74	21,111	13.8	99.89
2-O	84.0	12	2.13	25.2	0.014	
3-I	60.0	4057	2.44	9397	4.00	97.45
3-O	60.0	124	2.04	248	0.102	

Q = Flowrate (SCFM)
 C_t = EtO concentration in tank (ppm v/v)
D = Dilution factor
 C_s = EtO concentration in stack (ppm v/v)
H = Mass flowrate (lb/hr)
E = Percent efficiency

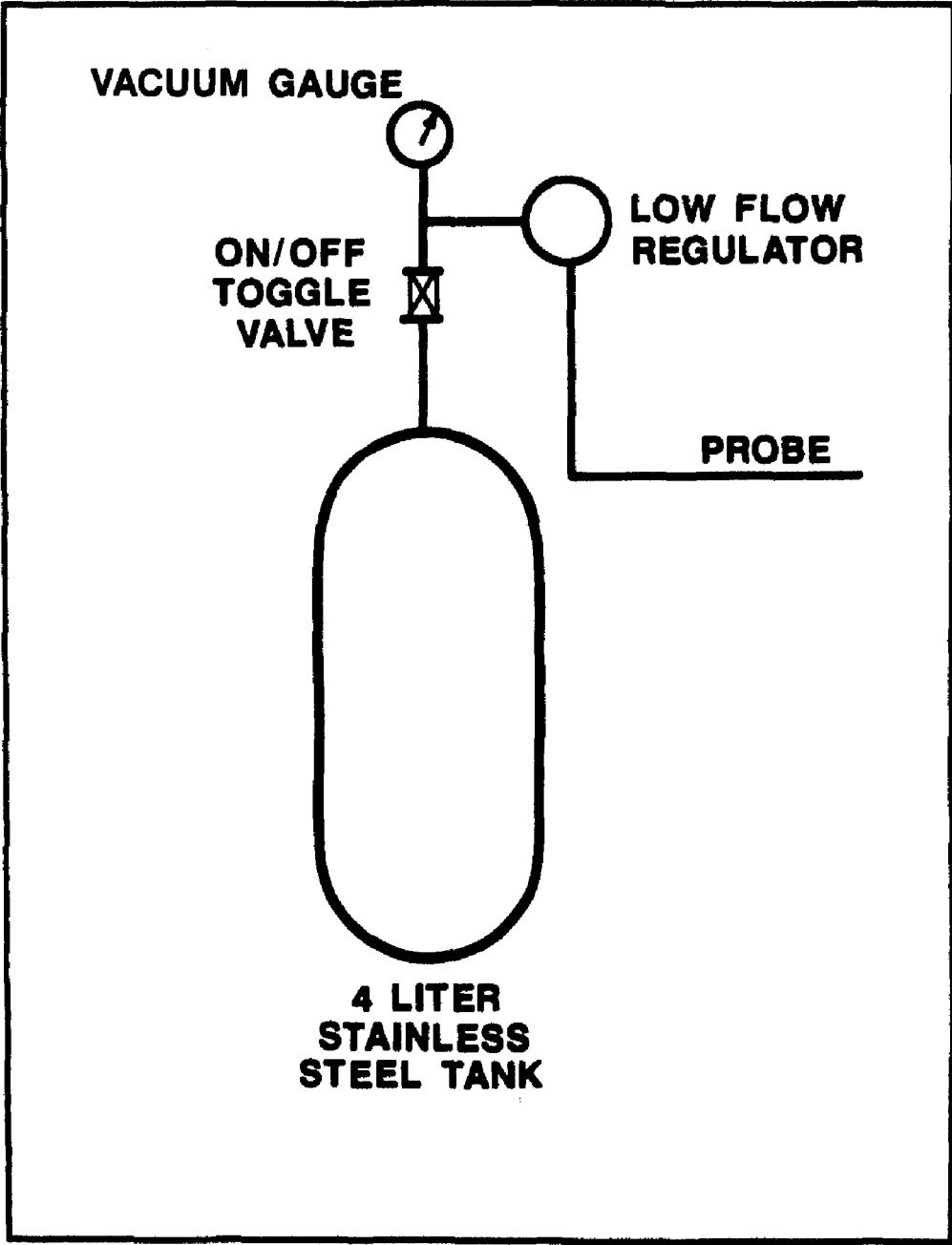


Figure 1. Sampling Train Schematic

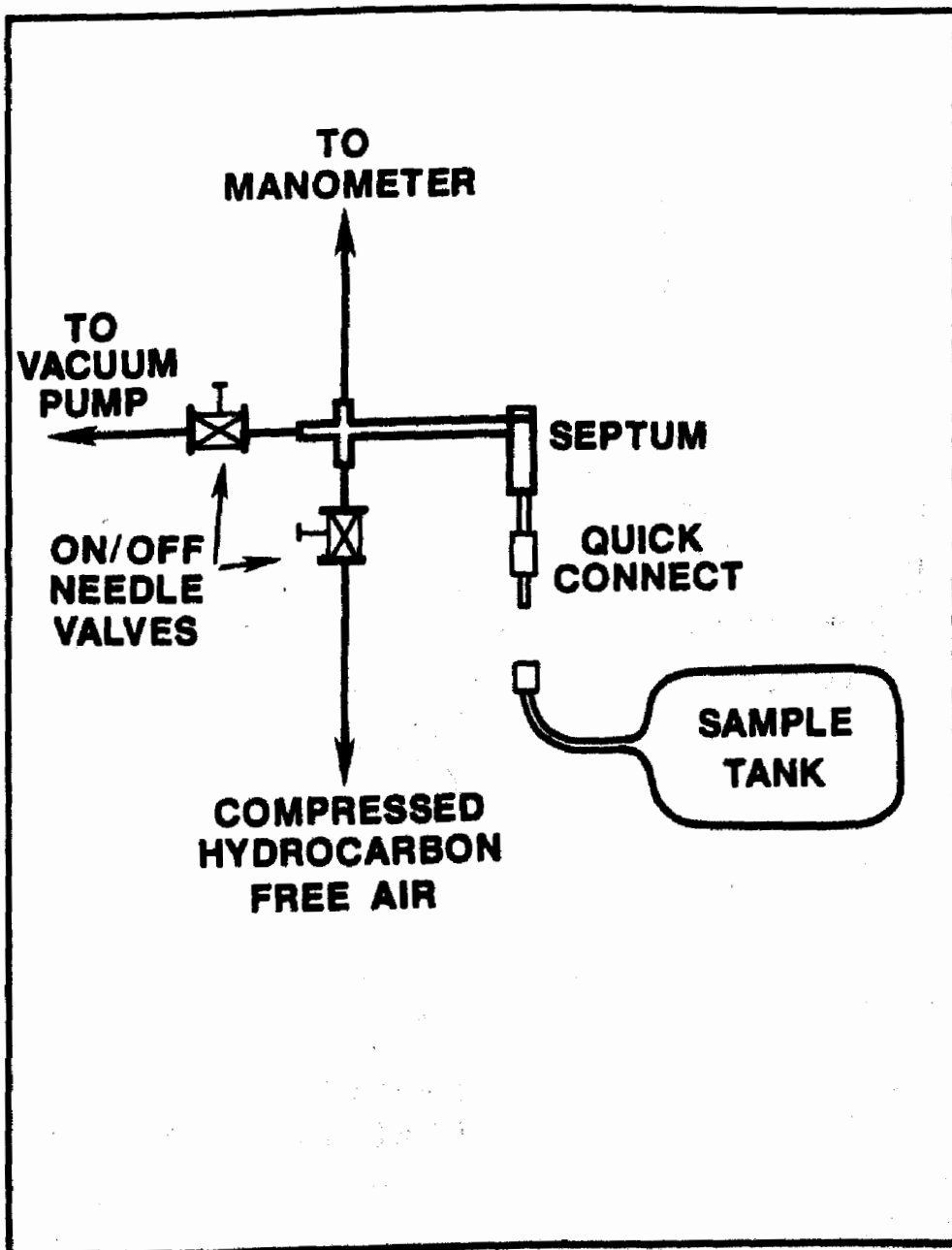


Figure 2. Tank Purge Apparatus Schematic

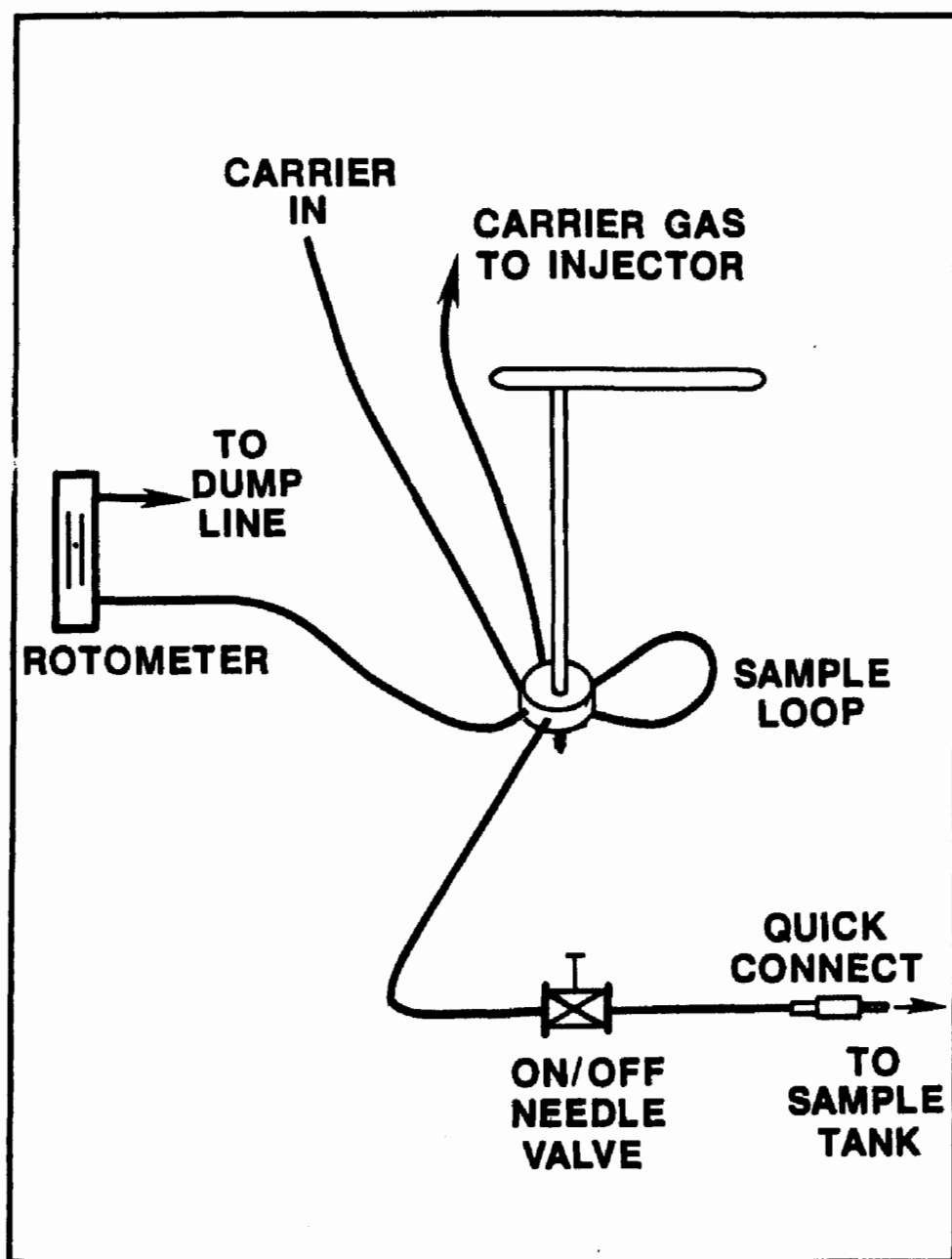


Figure 3. Sample Injection Apparatus

SAMPLING AND ANALYSIS METHOD
FOR DETERMINATION OF CADMIUM IN STATIONARY SOURCE EMISSIONS

by

Thomas E. Ward
Environmental Monitoring Systems Laboratory
Office of Research and Development
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

and

R. F. Moseman, D. B. Bath, J. R. McReynolds,
D. J. Holder and A. L. Sykes
Radian Corporation
Research Triangle Park, North Carolina 27709

ABSTRACT

Field evaluation studies were done to assess the usefulness of a Modified EPA Method 5 sampling train and flame atomic absorption spectrometry for the measurement of cadmium in stationary source stack emissions. These studies were performed at a municipal solid waste incinerator and a sewage sludge incinerator. The methodology developed in these studies is also 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 previously in laboratory evaluations in which the measured overall accuracy and precision were 89.2 percent and 1.7 percent, respectively, for the analytical portion of the methodology. The field sampling validation phase is discussed in this presentation. Collocated, quadruplicate flue gas samples of 30 and 60 dscf in one- and two-hour sampling times 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 detection limit determined in the previous work in this program for the atomic absorption instrument was 0.03 $\mu\text{g/mL}$. The stack sampling 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 $\mu\text{g Cd}$, respectively, per dscf (1.7 to 0.88 $\mu\text{g Cd}$ per dscm). The percent coefficient of variation (precision) of between-train cadmium concentrations averaged 13.5 percent at the municipal incinerator and 3.8 percent at the sewage sludge incinerator. 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. To broaden the scope and applicability of the method beyond that shown in this work, other source categories would have to be tested.

INTRODUCTION

The United States Environmental Protection Agency (EPA) has investigated cadmium emissions from stationary sources as a hazardous air pollutant. Appropriate methods of sampling and analysis must be available to quantify accurately 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, has developed and validated a methodology for sampling and analysis of cadmium emissions. The purpose of this report is to present the results of field studies of cadmium emissions measurement methodology. The objectives of the study were as follows:

- ° Determine the applicability of a Modified EPA Method 5 train and flame atomic absorption spectrometry for the measurement of cadmium emissions from stationary sources.
- ° Assure that the method has a detection limit sufficient to measure expected cadmium in municipal solid waste and sewage sludge incinerator flue gas samples of 30 to 60 dry standard cubic feet.
- ° Combine the results of these determinations to validate the methodologies at stationary sources.

The field studies were conducted at a large municipal solid waste incinerator and a sewage sludge incinerator. At the present time no further source evaluations are planned.

SAMPLING APPROACH METHODOLOGY

The sampling and analytical methods evaluated in these field studies were developed in the associated prior laboratory evaluation phase of the overall program. The methodology uses sample collection by a slightly modified EPA Method 5 (MM5) sampling train, followed by acid digestion of the sample in a Parr bomb and then analysis by flame atomic absorption spectrometry.

The field tests were conducted at a municipal waste incinerator which had been tested previously for cadmium emissions and at a sewage sludge incinerator. Cadmium concentrations reported during the previous testing of the waste incinerator ranged from 23 to 230 $\mu\text{g}/\text{dscm}$. The range of cadmium found in this study was of a similar range from 32 to 115 $\mu\text{g}/\text{dscm}$. The sampling method employed was an MM5 train which used nitric acid in the first two impingers instead of the water used normally in the Method 5¹ train. Separate analyses were performed on the front (probe and filter) and back (impingers) halves of the trains to determine the collection efficiency of each half. The same set-up was used at the sludge incinerator and the range measured there was 836 to 1137 $\mu\text{g}/\text{dscm}$.

In order to assess sampling and sample recovery precision, four "identical" samples were collected simultaneously using a quad-probe which consists of four separate sampling trains operated coincidentally² at a single sampling location. Groups consisting of four simultaneous samples were collected at the rate of one or two groups (quads) each day over a three day period for a total 24 samples at the waste incinerator and 16 at the sludge incinerator. 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 the incinerators could be measured in samples of this size, and 2) this size range of sample volume would not affect adversely the analytical precision and accuracy of cadmium concentration results.

The following procedure was used to recover the cadmium from the sampling train components. For the front half the probe rinses were combined with the glass fiber filter for digestion and then analysis. For the back half the impinger solutions and glassware rinses were combined and then analyzed.

RESULTS

The field testing portion of this study was designed to evaluate the precision of the sampling and sample recovery procedures, the portions of cadmium collected in the front and back halves of the MM5 train, and the effect of the stack sample volume on cadmium measurement.

Table I presents the cadmium concentrations and precision assessments for the quad-train field studies.² The between-train pooled standard deviations were 12.39 and 38 $\mu\text{g/dscm}$ for the waste and sludge incinerators, respectively, and in terms of percent coefficients of variation, the pooled values were 13.54 and 3.8 percent for the waste and sludge incinerators, respectively, which are measures of the precisions of sampling and analysis for the two sources.

Contributions to the variables of standard deviation and percent coefficient of variation shown in Table I 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 major variable which was addressed was the collection efficiency of the sampling train in terms of front and back half portions. No cadmium was detected in the back half, indicating that the front half (probe and filter) was very efficient (>99.99% efficiency) in capturing effectively all the cadmium measured.

A third major variable evaluated in the data set of Table I is the length of the sampling period for each run. About half of the tests were conducted for roughly one hour of sampling time and the other half of the tests for about two 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 two hours at these conditions.

Anomalies in the cadmium concentration data set are described here. The average cadmium concentration level in Test No. 1-M was much lower than for tests 2-M through 6-M. The cadmium concentrations shown for Tests 2-M through 6-M in Table I reflect a reasonably constant average cadmium concentration in the stack gas. However, there is no reason to suspect that the Test No. 1-M 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-M and the other runs is due probably to plant operating conditions. Sample B in Test No. 6-M shows an extremely high value in terms of cadmium per dscm, but since the Dixon outlier test indicates that this value is an outlier it was not included in the statistical analysis.

CONCLUSIONS

Several conclusions and recommendations are made regarding the proposed use of a slightly Modified EPA Method 5 (MM5) sampling train and flame atomic absorption spectrometry for the measurement of stack gas cadmium in stationary sources. Some of these are included from the prior laboratory portion of this program. They are:

1. An MM5 sampling train and flame atomic absorption spectrometry were found to be applicable for the measurement of cadmium in stationary source stack gas samples.
2. The overall accuracy and precision of the analytical steps of the methodology were 89.2 percent and 1.7 percent, respectively. The detection limit of the analytical instrument was 0.03 $\mu\text{g Cd/ml}$ of prepared sample.
3. 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 $\mu\text{g Cd/dscf}$ (1.7 to 0.88 $\mu\text{g Cd/dscm}$).
4. The percent coefficient of variation of between-train cadmium concentrations ranged from 3.4 to 23.1 percent for the six municipal sampling runs conducted and a remarkably close range of 2.8 to 4.7 percent at the four sludge runs. Stack gas samples of approximately 30 and 60 dscf were collected and the cadmium results for the two sample sizes did not differ significantly; therefore, the method bias was not affected by these sample volumes. Greater than 99.9 percent of the cadmium was collected in the front half of the sampling train for each run. This suggests strongly that the HNO_3 in the impingers is not necessary at these sources and that water can be used.
5. 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.
6. 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.
7. To ensure the applicability of the MM5 train for stationary sources with significantly different processes and properties, further field evaluations should be conducted.

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Table I. Cadmium Concentrations and Within-Run Precision Assessments
($\mu\text{g/dscm}$)

Test No.	Sample Train				Average x	Standard ^a Deviation	Percent Coefficient of Variation (% CV)
	A	B	C	D			
<u>Municipal Waste Incinerator</u>							
1-M	32.2	32.8	30.4	32.6	32.0	1.10	3.4
2-M	96.5	85.6	87.2	104.1	93.4	8.63	9.2
3-M	105.5	115.5	73.5	74.9	92.4	21.36	23.1
4-M	76.2	88.0	101.2	76.7	84.8	11.67	13.8
5-M	80.0	111.5	103.3	88.3	95.8	14.24	14.9
6-M	101.4	328.0 ^b	93.8	95.6	96.93	3.97	4.1
pooled						12.39 ^d	13.54 ^d
<u>Sewage Sludge Incinerator</u>							
1-S	886.2	927.8	835.5	886.6	884.0	37.8	4.27
2-S	1,137.1	1,133.4	1,081.9	1,081.4	1,108.5	31.0	2.80
3-S	989.1	1,088.0	993.6	1,057.5	1,032.1	48.7	4.71
4-S	1,097.8	1,041.1	1,030.9	1,081.9	1,062.9	32.0	3.01
pooled						38.0 ^d	3.79 ^d

^aAll sample train results reported in micrograms cadmium per dry standard cubic meter, $\mu\text{g/dscm}$:

$$\frac{\text{probe rinse} + \text{filter} + \text{impingers } (\mu\text{g})}{\text{total volume of stack gas sampled } (\text{m}^3)}$$

^bThis value was excluded from the data analysis because when subjected to a Dixon outlier test^c for Test No. 6-M, it did not meet the acceptance criterion of 126.1 $\mu\text{g/dscm}$, at the 5 percent level of significance (i.e., 95% probability).

^cThe 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 (1957).

^dpooled =

$$\left(\sum_{i=1}^n \frac{s_i^2}{n} \right)^{1/2}$$

A Critique of The Revision to EPA Method 25

Kochy K. Fung, John A. Wood, and Michael L. Porter
ERT, Inc.

INTRODUCTION

G.B. Howe et al.¹ have done some very credible work in solving some of the problems with the original EPA Method 25. The original method was created by the Los Angeles County Air Pollution Control District, now the South Coast Air Quality Management District in 1971. The authors of the proposed new Method 25 have done a good job of using more modern chromatographic column materials and newer catalysts to improve certain aspects of the method. The tests they ran were almost exclusively in lab tests, with a limited amount of field testing.

The authors of this paper wish to share their field experience with Method 25 to predict some problems which will be encountered with the new Method 25. Mr. Wood (who started working for the Los Angeles County APCD in 1970) was one of the originators of Method 25, and has 16 years field experience with the method. Mr. Porter (who joined the Los Angeles County APCD in 1974) has 12 years experience with Method 25, and produced a modification of the method which allows accurate determinations of NMOC on ambient air. Dr. Fung has over 20 years experience in practical analytical chemistry methods development, recently built a Method 25 apparatus to the new specifications and used it in the field. All of the authors are now employees of ERT in Newbury Park, California.

The major problems with the new Method 25 are as follows:

- The method is only suitable for testing emissions of relatively volatile solvents which are not controlled by combustion, yet this limitation is not given in the written method.
- The heated filter box is heated only to 121°C, even though many of the organics encountered in the field will condense at this temperature.
- The heated filter box may be unnecessary.
- The condensate trap will plug with ice much more easily than the original trap.
- The sample tank minimum volume of 4 liters is too small.
- The dry ice should be pelletized, not crushed. Crushed dry ice cakes, and pulls away from the trap.
- The valve on the canisters should be mounted "backwards", so that a leak in the valve packing will not affect the sample during storage.
- The trapped sample gas should not be flushed into the sample tank.
- The condensate trap should not be warmed slowly to ambient temperature.

- The condensate trap must be heated to temperatures several times higher than the recommended 200°C.
- The oxidation catalyst is not necessary and causes significant tailing of the CO₂. The oxidation tube should be packed with 6-8 mesh crushed quartz and operated at 800°C, or at a temperature high enough to burn methane.
- Frequent monitoring of the CO₂ levels by GC while burning the trap is not necessary.
- The flow control valve used to control the pressure in the system while metering sample into the evacuated canister, should be replaced with an upstream pressure regulator.
- The intermediate collection vessel with a volume of at least 6 liters is much too large. A two liter bulb is sufficient and provides better sensitivity.
- The sample tank is pressurized to an excessively high level, causing a decrease in sensitivity.
- Too many replicates are done, increasing the amount of time required for analysis significantly.

There are many other minor problems, but space considerations limit us to discussion of the above problems.

The proposed Method 25 is designed for and has been tested with high volatility solvents such as toluene, isopropyl acetate and hexane. In the field, one encounters a very wide range of substances and conditions. Most printing inks use solvents with a boiling range that goes above 200°C. Also, afterburner systems produce organic compounds with relatively higher boiling points than the laboratory test compounds.

Since the heated filter box is heated only to 121°C, we are certain that in many cases there will be significant losses of moderately volatile organics. There is even some question as to the necessity of the heated filter box. In the original Method 25, the probe was part of the trap, so condensation in the probe was not lost. The removable tip of the probe was an 1/8-inch O.D. stainless steel tube bent 90°. This tip was oriented to point away from the gas stream. The sampling rate was typically around 50 to 100 cc/min, producing a linear flow rate in the tube of about 1.4 ft/sec. The sample gas stream is flowing in the opposite direction at a much higher flow rate. This turned out to be a rather effective particulate filter.

The condensate trap proposed in the new Method 25 was developed by G.B. Howe et al.¹ as a secondary trap to aid in the removal of CO₂ prior to analysis. It was very successful for this purpose. However, they abandoned this approach in their currently proposed method and use the trap as the only trap in the system. This design is similar to designs evaluated and discarded by the Los Angeles County APCD in 1970. These traps had a real problem with plugging when used on afterburner outlets. The traps specified in the original Method 25 were designed to handle a great deal of water without plugging.

The sample collection tank's recommended 4 liter is too small. The optimum based on experience gained from testing over 1,000 sources, is

between 8 and 12 liters. The sample volume doesn't matter much when it comes to measuring source levels of CO_2 , CH_4 or CO ; but it matters a great deal when measuring NMOC especially at relatively low levels. Unpublished data produced by the Los Angeles County APCD in 1970 and 1971 showed that the original Method 25 trap produced good precision when measuring NMOC at ambient levels when a 50 liter sample was taken. A 2 liter sample produced erratic results even with stack samples.

The proposed Method 25 specifies the use of crushed dry ice. This can be used, with care, in an emergency. Pelletized dry ice is far better. Crushed dry ice packs into a hard "snowball" and evaporates away from the surface it is supposed to be cooling. The field technician must constantly breakup the ball with a screwdriver to maintain the proper trap temperature. Pelletized dry ice doesn't pack like this and requires relatively little attention.

While it is not mentioned in the proposed Method 25, if the valves are sealed around the valve stem with a packing should be mounted "backwards". The flow arrow should point away from the tank so that the integrity of the sample in transit doesn't depend on the valve packing.

The sample traps should not be flushed into the original sample tank. This is likely to cause more problems than it is worth. In the original Method 25 system, the loss amounts to less than 1% and the extra handling is likely to compromise the integrity of the sample. Source test engineering calculations usually use the CO_2 concentration. A small leak around the fitting in the trap (which is stored in dry ice) often results in the trap containing nearly pure CO_2 . If this is flushed into the tank, it can cause a considerable error.

The condensate trap should not be warmed slowly to ambient temperature when starting to burn the trap contents. This wastes time and serves no useful purpose. If the oxidizer is working properly, it can handle the trap being dipped directly into a furnace. The long wait suggested in the new Method 25 also requires that more gas be collected, which dilutes the sample and reduces sensitivity.

The condensate trap must be heated to a temperature several times higher than the recommended 200°C . Also the trap must have pure oxygen run through it near the end of the collection cycle. Pyrolysis of the trap contents is likely when heating the trap enough to remove the less volatile compounds which experience shows are collected. Pure oxygen burns out the carbon produced by the pyrolysis.

An oxidation catalyst is not necessary and actually slows the process. We found that alumina retards CO_2 , causing apparent tailing on the combustion process. Crushed quartz, 6 to 8 mesh run at temperatures over 750°C will give complete oxidation of methane, and therefore, most other organics. It doesn't cause tailing and allows the trap to be processed much more rapidly.

Frequent monitoring of the CO_2 levels by extracting sample from the combustion system is not necessary, since the CO_2 monitor is usually set to be sensitive enough for this purpose. The recommended monitor is labor intensive and the extra sample handling increases chances for error.

The proposed Method 25 controls the rate of collection into the intermediate collection vessel with a flow control valve. The flow control valve is just a needle valve which must be adjusted manually

throughout the burn. The Los Angeles County APCD discarded this approach in 1971. The needle valve was replaced by an upstream pressure regulator which is adjusted to maintain atmospheric pressure upstream of the regulator. It does this with variations under 1 Torr throughout the burn no matter what flow rates are used.

The intermediate collection vessel should be as small as possible to attain maximum sensitivity. The suggested 6 liters is much too large for most samples and results in a factor of three loss in sensitivity. We have found that 2 liters is more than adequate for over 90% of the samples. In those rare cases that the 2 liter is not big enough, one can easily switch to another container to finish collecting the sample.

The intermediate collection vessel is also pressurized too much. A final pressure of 860 Torr provides enough gas to run any analyses, while pressurizing to 1060 Torr merely dilutes the sample, decreasing sensitivity.

The proposed Method 25 requires far too many replicate analyses. It requires that each analysis be done in triplicate. If the samples are taken in duplicate, you end up with 12 analytical runs plus the burn progress runs. This totals at least 15 analyses per sample location. The original method required only four analyses, plus occasional replicates for quality assurance. We feel that this is sufficient.

REFERENCES

1. G.B. Howe et al.

THE PYROLYSIS OF ACETYLENE-STYRENE MIXTURES BETWEEN 450 AND 550°C

C. Chanmugathas and Julian Heicklen
Department of Chemistry and
Environmental Resources Research Institute
The Pennsylvania State University
University Park, PA 16802



The pyrolysis of acetylene-styrene mixtures has been studied from 450–550°C in a quartz reaction vessel in the absence and presence of O₂ or NO. The rates of disappearance of reactants and formation of adducts are first-order in each reactant. The major product is polymer with the adducts accounting for about 2.5% and 6.2% of the styrene removed at 450 and 550°C, respectively. The acetylene-to-styrene removal ratio is about 27 independent of temperature. The adducts formed are methyl indene and 1,2-dihydronaphthalene. These are about half-suppressed in the presence of O₂ or NO. The rate coefficients for reactant removal and adduct formation are:

$$\begin{aligned}\log\{k\{\text{C}_2\text{H}_2\}, M^{-1}\text{s}^{-1}\} &= 7.53 \pm 0.10 - (90.6 \pm 1.5)/2.3RT \\ \log\{k\{\text{C}_8\text{H}_8\}, M^{-1}\text{s}^{-1}\} &= 6.63 \pm 0.60 - (98.5 \pm 8.8)/2.3RT \\ \log\{k\{\text{C}_{10}\text{H}_{10}\}, M^{-1}\text{s}^{-1}\} &= 8.27 \pm 0.66 - (143.3 \pm 9.8)/2.3RT\end{aligned}$$

where the activation energies are in kJ/mole and the uncertainties are one standard deviation. As the reaction proceeds, the methyl indene and 1,2-dihydronaphthalene decompose, and indene and naphthalene are formed.

Introduction

Pyrolysis or incomplete combustion of hydrocarbons leads to soot formation. The main route to soot formation at temperatures below 1200°C is the cracking of the hydrocarbons to C_2H_2 which then polymerizes and dehydrogenates. This process involves aromatic compounds as intermediates (1-3). In order to investigate the low-temperature pyrolysis of styrene-acetylene mixture as an avenue for soot or polynuclear aromatic hydrocarbon formation, the present study was undertaken, paying special attention to $C_{10}H_{10}$ formation during the early stages of reaction.

Experimental

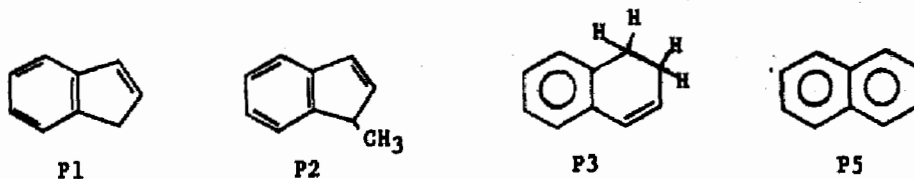
The experimental apparatus and procedure were similar to those described earlier (4-6). Pyrolysis was carried out in a 1090-cm³ spherical quartz vessel surrounded by a cylindrical resistively-heated oven. Kinetic data were obtained by both mass spectrometry and gas chromatography.

The mass spectrometric sampling system consisted of a quartz pinhole (30- μ m diameter) through which the reaction vessel contents continuously bled through a differentially-pumped intermediate region to a modified EAI Quad 160 mass spectrometer. For quantitative analyses, a small measured amount of krypton gas was added to the reaction mixture as an internal standard to minimize the effect of instrumental and sampling fluctuations. The absolute sum of the products with parent masses at m/z 130 (methyl indene and 1,2-dihydronaphthalene) could be measured because they have the same mass spectral sensitivity at m/z 130.

Gas chromatography was used to obtain kinetic data for individual product isomers. The products were analyzed on a flame-ionization gas chromatograph (Varian Series 1200) using a 6-ft, 1/8-in stainless steel column packed with 10% Silar 10C on Chromosorb W/HP. The column was kept at 40°C for 6 min and then temperature programmed to 170° at 4°C/min. The He carrier gas flow rate was 29 ml/min.

Results

When acetylene-styrene mixtures are pyrolysed between 450 and 550°C, there are six heavier products formed in addition to polymer, which accumulates on the wall of the reaction vessel. In order to identify the products, gas-chromatograph-resolved mass spectra were obtained. The mass spectra and gas-chromatographic retention times indicated that P1, P2, P3, and P5 were respectively indene, methyl indene, 1,2-dihydronaphthalene and naphthalene.



The minor products P0 and P4 were respectively, p-methylstyrene and an unidentified isomer of naphthalene (mol. wt. = 128). At 550°C traces of other compounds, including indane (mol. wt. = 188), methyl naphthalene (mol.

wt. = 142), methyl-substituted dihydronaphthalene (mol. wt. = 144), xylenes, toluene, benzene, and a product with mol. wt. = 154 were also seen.

The initial rates of $C_{10}H_{10}$ formation are plotted versus the products of the reactant concentrations in Figure 1. The log-log plots are linear with slope 1.0 indicating a second order reaction. Similar plots are obtained for the initial removal rates of C_2H_2 and C_8H_6 . The intercepts of the plots give the rate coefficients, and they are plotted in Figure 2 in Arrhenius plots. The Arrhenius parameters are listed in Table 1.

Both P2 and P3 formation are partially suppressed by the addition of NO or O_2 . Thus both products are formed in part from a concerted molecular process and in part by a diradical path. Since O_2 and NO have comparable effects, the diradical intermediate is probably a triplet, since O_2 may not scavenge a singlet diradical.

Discussion

The initial products of the reaction are polymer and adducts of acetylene and styrene. By far, the dominant product is polymer with a ratio of acetylene-to-styrene of about 27 independent of temperature. The fraction of styrene consumed which gives $C_{10}H_{10}$ adduct is 2.5% at 450°C and increases to 6.2% at 550°C.

The reactions producing these products are homogeneous second-order reactions. The homogeneity is indicated because the rate coefficients have normal Arrhenius A factors for a second-order addition to produce $C_{10}H_{10}$ or a radical-chain mechanism to produce polymer. Furthermore, the addition of excess inert gases did not effect the reaction. Also, Lundgard and Heicklen (4) have shown that increasing the surface-to-volume ratio by a factor of 59 had no effect on the dimerization of vinylacetylene and only a minimal effect on its polymerization.

The Arrhenius A factors found for both polymer and adduct formation are similar to those found for the corresponding reactions in other systems (4-6), but the activation energies found here for both processes are about 20 kJ/mole higher than for the analogous processes in the other systems.

The secondary products, indene (P1) and naphthalene (P4) come from decomposition of the primary products methylindene (P2) and 1,2-dihydronaphthalene (P3), respectively. The methylindene decomposition presumably proceeds by loss of a methyl group, a conclusion supported by the observation that p-methyl styrene (P0) was found. P3 decomposition probably proceeds by loss of H_2 or 2 H atoms though we have no information on the details of the decomposition.

Polymer formation probably proceeds via a mono-radical chain process. Initiation could proceed either by self-reaction of styrene or acetylene.

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Table I

Arrhenius Parameters for Second-Order Rate Coefficients

<u>Rate coefficients</u>	<u>E_a, kJ/mole</u>	<u>log(A, M⁻¹ sec⁻¹)</u>
k{C ₂ H ₂ }	90.6 ± 1.5	7.53 ± 0.10
k{C ₆ H ₆ }	98.5 ± 8.8	6.63 ± 0.60
k{C ₁₀ H ₁₀ }	143.3 ± 9.8	8.27 ± 0.66

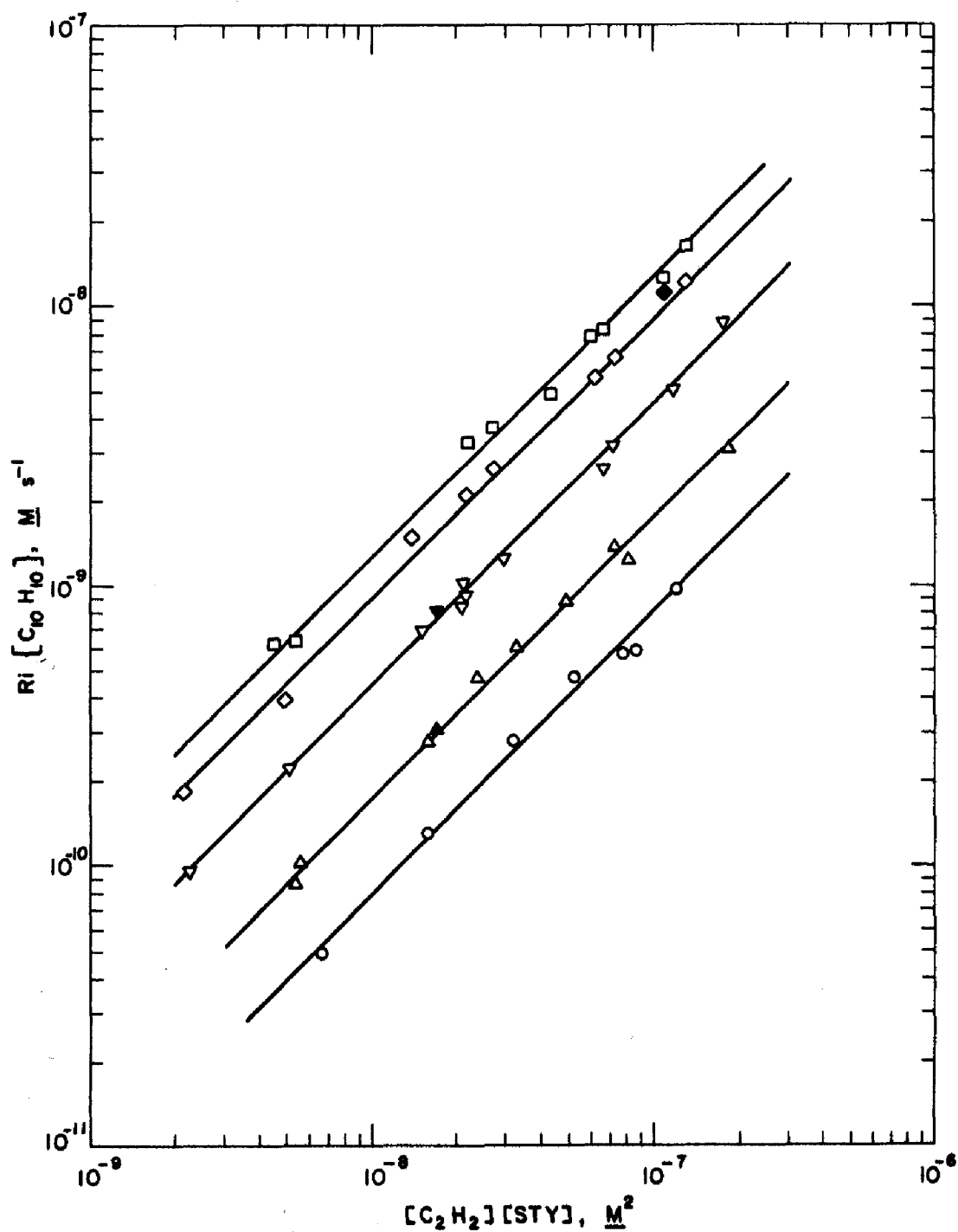


Fig. 1: Log-log plots of initial rates of $C_{10}H_{10}$ formation obtained by mass spectrometry versus $[C_2H_2][C_6H_6]$: O, 450°C; Δ , 475°C; ∇ , 500°C; \diamond , 525°C, \square , 550°C. Filled points are for N_2 present.

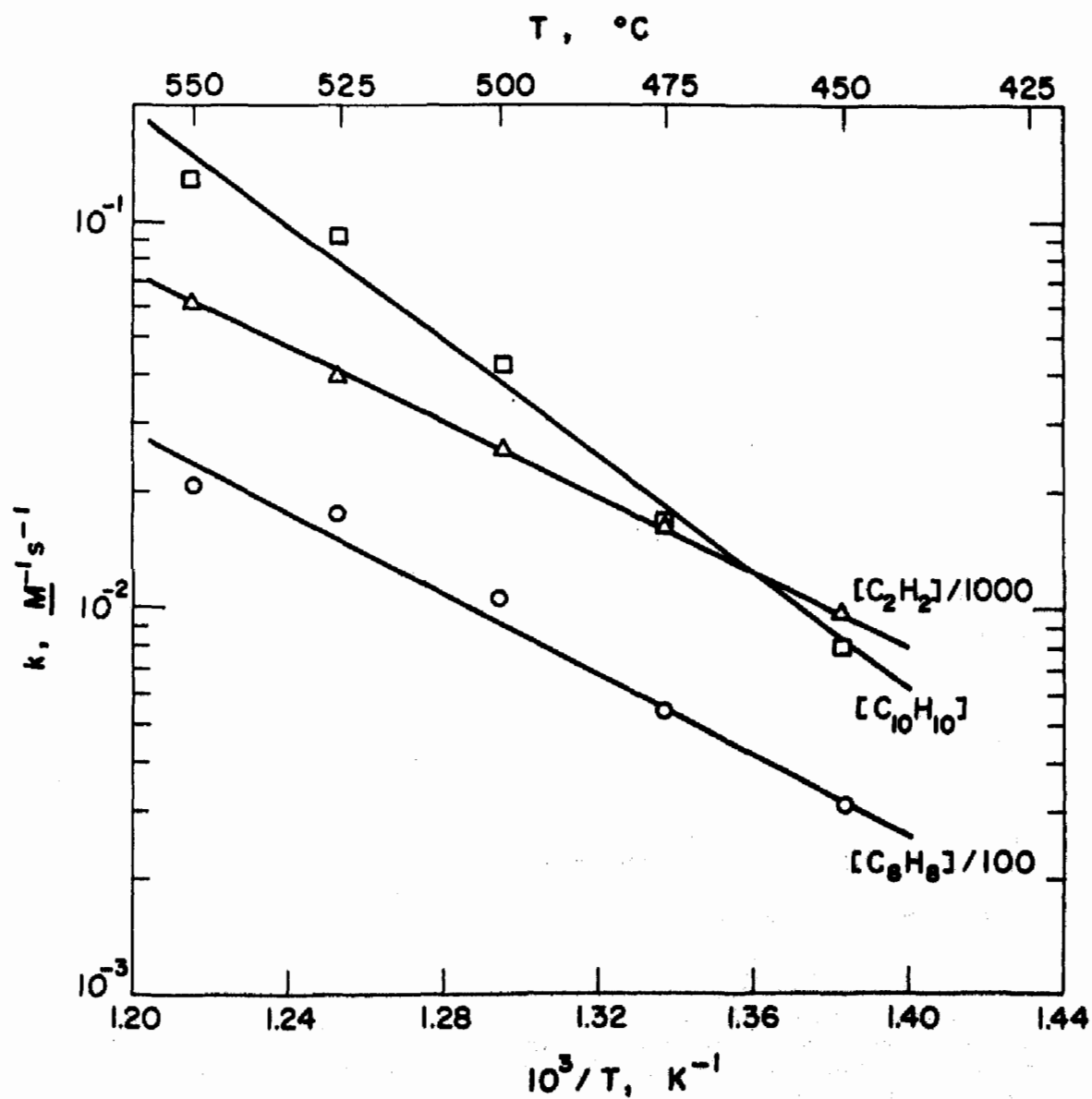


Fig. 2: Arrhenius plots for the rate coefficients: Δ , C_2H_2 removal; \circ , styrene removal; \square , $\text{C}_{10}\text{H}_{10}$ formation.

**ASBESTOS FIBER LOSS FROM AIR SAMPLING CASSETTES:
A STUDY BY TRANSMISSION ELECTRON MICROSCOPY**

William E. Longo & E.J. Jenkins
Micro Analytical Laboratories, Inc.
Gainesville, Florida

The analysis of air samples for asbestos by Transmission Electron Microscopy (TEM) has increasingly become the method of choice for final clearance samples in post-abatement projects. However, the use of both polycarbonate (PC) and mixed cellulose ester (MCE) filter cassettes during air sampling has raised some concerns about possible fiber loss from the filter surface due to both static charge problems and rough handling during sample shipment to the TEM laboratory. Also, it has been suggested, that there may be substantial loss of fibers to the inside of the cowl walls on the cassette during the actual air sampling process.

This investigation found that all of the air samples examined displayed fiber loss to the inside cassette walls. This loss was demonstrated for both the PC and MCE filters. The amount of fiber loss was from 9% up to over 80% and was seen for all types of sampling cassettes including the new black conductive cassettes.

A new washing and re-filtration method was studied that has the potential to overcome the problems of post-fiber loss after sample collection. Briefly, the cassette walls and filter surface are completely washed to remove all of the fibers present and then re-filtered onto a MCE filter (0.22 micron pore size). The direct transfer method is used for TEM sample preparation.

Introduction

Phase contrast microscopy (PCM) is now the most widely used technique for the detection of asbestos on air filter samples. The most common uses for PCM are; (1) general air surveys, (2) air monitoring during abatement projects and (3) final air clearance samples after abatement. However, previous studies have shown that PCM is inadequate for both the general air surveys and final air clearance because it lacks specificity for asbestos and cannot resolve fibers less than 0.25 microns in width.^{1,2} TEM is the only technique that now has the capability of positively identifying all types of asbestos including structures that are less than 0.25 microns wide. However, economics and slow turnaround times has hindered wide spread acceptance of TEM analysis.

Proposed Environmental Protection Agency (EPA) regulations that may go into effect later this year will ban the use of PCM for final air clearance in school abatement projects. The proposed analytical method for final clearance will be TEM. If these EPA regulations become law, the use of TEM for final air clearance will probably become the industry standard and gain a much wider acceptance. Since there are only a few qualified TEM laboratories in the country, most air filter samples will have to be shipped to the laboratory for analysis because in most cases, the logistics of hand carrying sample cassettes across the country will just not be feasible.

There has been a growing concern that the shipment of the sample cassettes to the TEM laboratories may cause fiber loss from the filter surface to the inside of the plastic cowl because of rough handling or static charge problems. If fiber loss was substantial, it would cause erroneous results from the TEM analysis, allowing in the worst case, the re-occupation of a building with unsafe asbestos levels.

We became concerned that the actual fiber loss from the filter surface during sample shipment was probably much higher than was commonly speculated. Since to our knowledge, there have not been any reported studies that actually quantitate fiber loss during shipment using TEM, we decided to investigate this possibility. This paper describes the comparative analysis of both the filter surface and cowl walls for airborne asbestos by TEM. Sample cassettes were examined that were both shipped and hand carried to our facility. Both the clear plastic sampling cassettes and the new black conductive cassettes were studied. Also, since fiber loss would be restricted to the inside of the cassette walls, we studied an alternative sample preparation process that used a washing technique for recovery of all loss fibers.

Experimental Methods

Air cassettes were chosen for this study that had elevated levels of asbestos (greater than 0.02 asbestos structures/cc) when previously analyzed by TEM using current EPA methodology.^{3,4} From these cassettes, the inside filter and support pad was carefully removed and archived. The inside surface of the cassettes was washed with distilled water that contained 0.01% OT aerosol solution. The washing process consisted of filling the cassette with 10-15 ml of the prepared solution, capping the cassette tightly to prevent water leakage, then shaking vigorously for 20-30 seconds. The wash solution is decanted into a 100 ml beaker and saved, this step is

repeated two additional times. The re-filtration procedure for the wash is based on the EPA "Interim Method for Determining Asbestos in Water".⁵ The combined wash solution is then re-filtered onto a 25 mm MCE filter with 0.22 micron pore size and prepared for TEM analysis as described by Burdette and Rood.⁴ Both the (MCE) and the PC filters were examined. The concentration of the asbestos found on the inside of the cowling walls was compared to the results obtained from the filter surface only. Air sample cassettes containing either the MCE or PC filters were run side-by-side during an asbestos abatement project. The filters inside the cassettes were left in place during the washing procedure as described above. The wash solution was then re-filtered onto 25 mm MCE (0.44 micron pore size) filters and prepared for TEM analysis. The washed filters were dried at 50°C for 1.0 hr and also prepared for TEM analysis. Results of the two washed filter surface types were compared.

Results

Shown in Table I is the concentration of the amount of asbestos that was found on the cowling walls for the PC sampling air cassettes. The results for the air cassettes containing the MCE filters are shown in Table II. The amount of asbestos found on the inside of the cowling walls of these samples ranged from 0.033 to 15.150 structures/cc. This represented a total fiber loss from 9% up to 88% that normally would have been missed in the analysis. The MCE filters had an average loss of 54% and for the PC filters, the average loss was 64%. Also, when the cassettes were hand carried to our facility, they demonstrated a fiber loss of almost 50% when the cowling walls were examined.

Tables III & IV show the asbestos removal efficiency of both the MCE and the PC filters that were washed with the 0.01% OT aerosol solution. Throughout this study, we were consistently able to thoroughly wash the MCE filters while the PC filters were always found to contain some residual concentration of asbestos fibers.

Conclusions

All the sample cassettes that we tested at our facility showed extensive fiber loss to the inside cowling walls when examined by TEM. When the amount of fiber loss was compared between the MCE and the PC filters, the differences were minimal. This suggests that for shipping purposes, neither filter type has an advantage.

The amount of loss from sample to sample was variable which limits the use of a standard error factor that can be put into the fiber concentration calculations that are used for these types of analysis.

Since the hand carried cassettes also showed fiber loss it's uncertain at this time whether or not the fiber loss is directly attributed to the shipping or a static charge problem causing the fibers to stick to the cowling walls during the actual sampling. However, when the anti-static cassettes were tested, they also showed a high concentration of fiber loss as shown in Table I. In any case, more experimentation is needed to resolve the question concerning the source of the fiber loss.

Using the proposed washing re-filtration method can overcome both the shipping problems with rough handling and the suspected fiber loss from static charge build up that occurs during the actual air sampling process. This method would allow for the analysis of all the fibers inside of the cassette during the washing process and not just the fibers found on the filter. Future work is needed so that a larger statistical population is examined for a more valid analysis and the question of possible break up of bundles and clumps during the washing process also needs to be addressed.

Acknowledgments

We are indebted to both Dr. Baxter at ENTEK Environmental Services, Inc. for his technical assistance and for initially suggesting the use of the water re-filtration method and Mr. Robert Greene at Law Engineering Testing Co. for providing us with samples for this study. We would also like to thank Mrs. Joanne Ake for her help in preparing this manuscript.

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Table I. Fiber loss on inside of cassette walls; Polycarbonate filters.

Sample no.	Filter size	Structures/cc on filter surface	Structures/cc found on cassette wall	%Fiber loss
1	37mm	1.372	2.484	64
2	37mm	9.121	15.150	63
3	37mm	3.642	8.486	70
4	37mm	6.325	9.616	60

Table II. Fiber loss on inside of cassette wall; Mixed cellulose ester.

Sample no.	Filter size	Structures/cc on filter surface	Structures/cc found on cassette wall	%Fiber loss
1	37mm	3.574	4.689	51
2	37mm	16.005	1.604	9
3	37mm	0.016	0.118	88
4*	25mm	0.038	0.034	47
5*	25mm	0.039	0.033	46
6+	25mm	0.940	3.712	80
7+	25mm	1.304	1.673	56

* Samples hand carried to our facility.

+ Cassettes constructed out of black conductive cowlng.

Table III. Fiber removal efficiency after wash; Polycarbonate filters.

Sample no.	Filter size	Structures/cc on filter before wash	Structures/cc on filter after wash	%Removal
1	37mm	1.372	0.055	97
2	37mm	9.121	0.592	94
3	37mm	12.968	0.683	95

Table IV. Fiber removal efficiency after wash; Methylcellulose ester filters.

Sample no.	Filter size	Structures/cc on filter before wash	Structures/cc on filter after wash	%Removal
1	37mm	3.574	0.00*	100
2	37mm	16.005	0.00	100
3	37mm	0.016	0.00	100

* The concentration of the asbestos present was below detection limit.

A Novel 2.5 μ m Cut Virtual Impactor for
High Volume PM₁₀ Sampling

Robert M. Burton
Environmental Monitoring Systems Laboratory
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

Virgil A. Marple, Ph.D., Benjamin Y.H. Liu, Ph.D.
and Bradley Johnson, Particle Technology Laboratory
University of Minnesota, Minneapolis, MN

A high volume 40 CFM PM₁₀ Virtual Impactor for collecting large amounts of particulate matter separated into two distinct fractions (FINE, 0 to 2.5 μ m; and COARSE, 2.5 to 10 μ m) has been developed for use in the US Environmental Protection Agency's Integrated Air Cancer Project (IACP).¹ Because studies have shown, in general, that the highest levels of carcinogenic/mutagenic potential associated with ambient particulate aerosols are from organic compounds found in the FINE fraction,^{2,3} a requirement for separating and collecting large amounts of particulate matter below 2.5 microns became evident as mutagenicity testing progressed in the program. Particulate emissions from woodstoves, vehicles, and many industrial sources are found in this size range and can be efficiently separated and collected with the virtual impactor.

The IACP is a long-term research program with the goal of identifying carcinogens in ambient air, the sources of these carcinogens, and the associated potential health risk. As the IACP began its initial phase concerned partly with the monitoring of residential woodstove emissions, the low flowrate (16 liter/minute) dichotomous sampler was the only commercially available collector that would provide separation and collection by filtration of both the FINE and COARSE fractions of aerosol.⁴ The IACP required a method for collecting sufficient amounts of the organic rich FINE fraction aerosol to be used in chemical analysis and bioassay testing. Consequently, a 40 CFM virtual impactor was chosen and modified to meet the needs of the IACP. Emphasis was placed on developing a precise, high flow rate sampler that could be utilized cost effectively as an add-on to the existing PM₁₀ Size Selective Inlet high volume samplers.

The sampler has been tested extensively in the laboratory to define its collection characteristics and wall losses. Wall losses overall are 1.7% for liquid particles and 0.8% for solid ones. Although the sampler was designed for a specific application (IACP), it should have wide usage in the sampling of aerosols where large quantities of fractionated fine fraction aerosol is desired.

A Novel 2.5 μm Cut Virtual Impactor for High Volume PM_{10} Sampling

by

R. M. Burton

Environmental Monitoring Systems Laboratory
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

Virgil A. Marple, Ph.D, Benjamin Y.H. Liu, Ph.D.,
and Bradley Johnson, Particle Technology Laboratory
University of Minnesota, Minneapolis, MI

INTRODUCTION

A high volume 40 CFM PM_{10} Virtual Impactor for collecting large amounts of particulate matter separated into two distinct fractions (FINE, 0 to 2.5 μm ; and COARSE, 2.5 to 10 μm) has been developed for use in the US Environmental Protection Agency's Integrated Air Cancer Project (IACP).¹ Because studies have shown, in general, that the highest levels of carcinogenic potential associated with ambient particulate aerosols are from organic compounds found in the FINE fraction,^{2 3} an IACP requirement for separating and collecting large amounts of particulate matter <2.5 microns aerodynamic diameter became evident as mutagenicity testing progressed in the program. Particulate emissions from woodstoves, vehicles, and many industrial sources are found in this size range and can be efficiently separated and collected with the virtual impactor.

The IACP is a long-term research program with the goal of identifying carcinogens in ambient air, the sources of these carcinogens, and the associated potential health risk. As the IACP began its initial phase concerned partly with the monitoring of residential woodstove emissions, the low flowrate (16.7 liter/minute) dichotomous sampler was the only commercially available collector that would provide separation and collection by filtration of both the FINE and COARSE fractions of aerosol.^{4 5} Other available separators required greasing the collection surfaces which could potentially contaminate the collected aerosol. The IACP required a method for collecting sufficient amounts of the organic rich FINE fraction aerosol to be used in chemical analyses and bioassay testing. Consequently, a 40 CFM virtual impactor design was chosen and modified to meet the need of the IACP. Emphasis was placed on developing a precise, high flow rate sampler that could be utilized cost effectively as an add-on to the existing PM_{10} Size Selective Inlet high volume samplers.

EXPERIMENTAL METHOD

The Virtual Impactor Classifier

The principle of operation for the virtual impactor is quite simple. Particle laden air is accelerated through a nozzle impinging into a receiving tube that is slightly larger in diameter than the nozzle. The particles which are larger than the cut size of the virtual impactor have enough inertia to penetrate into the receiving tube and are extracted from the backside with a small amount of flow (minor flow), which is usually 5 to 10% of the flow entering the receiving tube. The remaining portion of the flow containing particles smaller than the cut size (particles with low inertia) reverses direction in the receiving tube and exits at the outer edges of the entrance

to the tube. In this manner, particles both smaller and larger than the cut size of the classifier are kept airborne and can be collected by filtration.

The collection efficiency of a virtual impactor is a function of particle size and is defined as the fraction of particles passing through the nozzle that penetrates through the receiving tube with the large particle sample in the minor flow. Most of the smaller particles that do not have enough inertia to be separated in the receiving tube (those smaller than the cut size) remain with the major air flow. However, a fraction of the small particles equal to the fraction of the minor flow penetrate the receiving tube with the large particles. Therefore, the minimum efficiency of any particle size is the percentage of the total flow passed through the receiving tube. This efficiency can be increased by introducing a clean core of air in the center of the jet providing a small, particle free minor flow. The addition of the clean air jet, however, does complicate the design and operation of the virtual impactor.

To achieve 40 CFM flowrate without creating an unsatisfactory pressure drop across the separator, a 12-nozzle design was used. Half of the virtual impactor stages are located on each side of the unit with the minor flows exiting from the receiving tubes into a central common chamber, the floor of which is the large particle filter. The major flow exits through two cavities (one on each side of the central chamber) and flows downward into a common cavity below the large particle filter chamber and above the small particle filter. The design is shown in Figure 1.

High Volume Virtual Impactor (top view section)

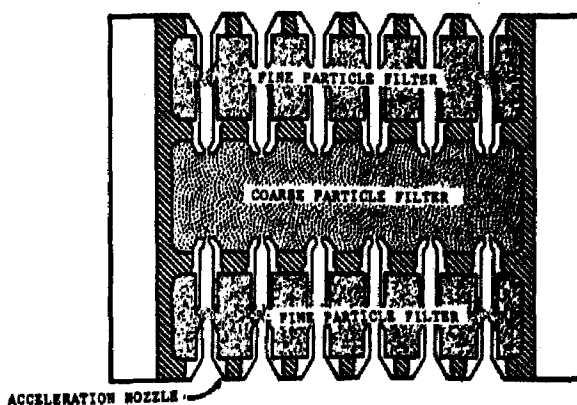


Figure 1

The virtual impactor stages are paired on a common axis so that the minor flows exiting from the receiving tubes impinge on each other, aiding in stopping the large particles before they impact on the opposite wall. In this manner, the losses of the large particles are minimized. Positioning the large particle filter on the floor of the chamber also aids in reducing losses since almost no transport of the minor flow is necessary before the particles are filtered from the airstream. In a similar manner, there is little transport distance between the virtual impactor classifier and the filter for the small particles.

The High Volume Virtual Impactor as an Accessory to the PM₁₀ High Volume Sampler

The impactor (twelve-nozzle unit shown in Figure 2) has two components: a classification head assembly and a filter holder assembly. The classification head assembly contains the twelve virtual impactor stages and cavities leading to the large particle and small particle filters. The filter holder assembly is a casting containing both the small and large particle filters. The filter holder section is designed in such a manner that the filters can be assembled in the laboratory, transported to the field test site, inserted for a run and then returned to the laboratory for disassembly. In normal operation at least two filter holder assemblies would be used with one classification head so that the filters can be changed in the laboratory while the other unit is being used at a field site.

In the high volume sampler the impactor is located between the PM₁₀ inlet and the high volume blower with the flange of the impactor filter holder located between the flanges of the PM₁₀ inlet and the flange of the 8 x 10-inch entrance to the blower (Fig. 2). Because the particles larger than 10 microns have been removed by the PM₁₀ inlet, the particles passing from the PM₁₀ inlet into the cavity surrounding the impactor will not have enough inertia to be impacted on the head of the impactor. With this arrangement, the overall height of the high volume sampler is only increased by about one inch, which is the thickness of the flange and gaskets.

RESULTS

Calibration

The high volume virtual impactors were calibrated using monodispersed oleic acid and ammonium fluoresceine particles generated with a vibrating orifice monodispersed aerosol generator (VOMAG)(Berglund and Liu, 1973). The particles are tagged with a small amount of uranine dye tracer. Particles of a particular size are passed through the high volume virtual impactor and are collected on either the large or small particle filters or lost to one of the surfaces inside the impactor assembly. The quantity of particles being collected on the filters or lost can be determined by washing the respective surfaces with known amounts of water and measuring the dye concentration in the wash water with a fluorometer. By analyzing where the particles are located, the collection efficiency can be determined as well as the losses and exactly where the losses occur. The collection efficiency curve for the impactors is shown in Figure 3.

Also shown in Figure 3 is the collection efficiency for the 16.7 lpm dichotomous sampler. Note that the agreement between the two samplers is very good. Calibration with solid ammonium fluoresceine particles showed the same collection efficiency as with the liquid particles.

Losses, i.e. particles which have been collected at some point other than on either of the two filters as a functional particle size, are shown in Figure 4 for the liquid particles. As expected, the losses are the largest for particles near the cut size (2.5 micron) of the impactor and decrease rapidly for smaller and larger particles. Solid particles have lower losses than liquid particles due to their ability to bounce from a surface and be reentrained into the airstream. Since atmospheric aerosols are generally considered to be solid particles, the loss during ambient sampling will be similar to that determined by the solid calibration particles.

High Volume Virtual Impactor (lateral section view)

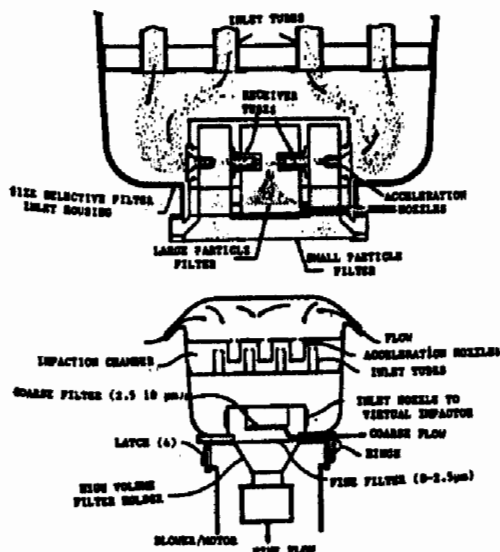


Figure 2

Collection Efficiency Characteristic for
2.5 µm High Volume Virtual Impactor with a
Comparison to Existing 16.7 l/min Dichotomous
Virtual Impactor

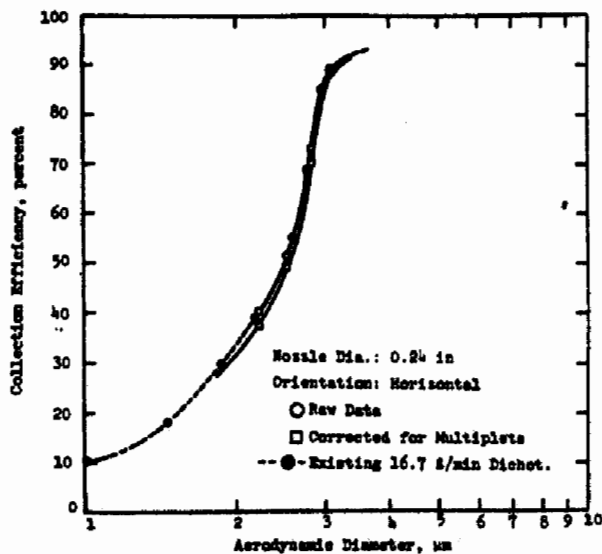


Figure 3

Loss Characteristics for 2.5 Micron Cut High Volume Virtual Impactor

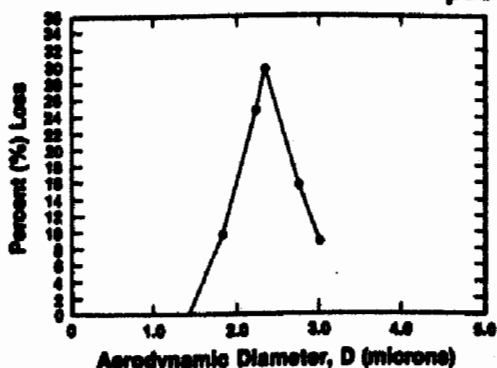


Figure 4

- A. Test Aerosol
for "Worst Case"
Liquid Particles (oleic acid with
uranine dye)
- B. Total (0-10 microns)
Mass Loss

1.7%

Based on integrated loss between
0 and 10 microns for ambient
distribution as shown in Federal
Register, Vol. 49, 40CFR, Part 55,
Page 10481, March 26, 1984.

- C. Location of Losses
Receiver Tubes = 1/2 of Total Losses
Inside Cavity = 1/2 of Total Losses

At first glance, losses as high as 30% (by liquid aerosol) at the cut point appear to be rather large. However, if the losses are considered as a fraction of all particles entering the virtual impactor, i.e. all particles less than 10 µm, the losses are much lower. For example, if the size distribution is that expressed in the Federal Register for the design of the PM₁₀ inlets, the losses for liquid particles would be 1.7% and 0.8% for solid particles. Thus, the losses as a function of the total aerosol mass passing through the virtual impactor are quite low.

In the process of washing the various parts of the impactor to determine where the particles are lost, it was found that approximately half of the particles were in the receiving tube and the other half on the chamber

walls surrounding the two side cavities. If these cavities were larger, the losses would be reduced, possibly by as much as 50%, but then the high volume virtual impactor would not be as compact.

Conclusions

A 2.5 μm diameter cut high volume virtual impactor consisting of twelve parallel virtual impactor stages has been successfully designed for application with a high volume PM_{10} inlet. Use of parallel flow virtual impactor stages and paired opposing receiving tubes has allowed for a design which is very compact with losses not exceeding 1.7% and 0.8% for liquid and solid particles, respectively. Since the sampler classifies particles in size fractions of 0-2.5 μm and 2.5 μm - 10 μm , respectively, the sampler incorporates two filters: one for the small particles (8 x 10-inch) and one for the large particles (2 x 6-inch). These filters are contained in a single filter holder which can be easily transported to and from a laboratory for filter replacement. Although the sampler is capable of passing 40 cfm of air flow, it only increases the height of the high volume sampler by approximately one inch. As an option, the virtual impactor can be operated without a PM_{10} inlet, still providing a 0-2.5 micron fraction plus a fraction > 2.5 microns.

The sampler was designed for a specific application in the Integrated Air Cancer Project; however, it should prove useful in a variety of aerosol sampling situations where large quantities of fractionated FINE fraction aerosol is desired. This sampler is advantageous for collecting large quantities of ambient aerosol (from woodstoves, motor vehicles, etc.) in the 2.5 μm or less particle size range, for both chemical and biological analysis.

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DEVELOPMENT OF EPA'S
AIR TOXICS CONTROL TECHNOLOGY CENTER

Sharon L. Nolen, Gary L. Johnson, and James A. Dorsey
U.S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

and

Lee L. Beck and John D. Crenshaw
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

ABSTRACT

The Air Toxics Control Technology Center (CTC) is a joint effort of the EPA Office of Research and Development (ORD) and Office of Air and Radiation (OAR) to provide technical assistance to State and local air quality regulatory agencies in solving control technology problems related to air toxics. The CTC will support a wide range of State and local mitigation activities, including high-risk point source programs (State initiatives and EPA promoted initiatives), a high-risk urban toxics program, State Implementation Plan (SIP) decisions also affecting air toxics emissions, and Best Available Control Technology (BACT) determinations as they pertain to air toxics control. This program requires the coordination of research and program office expertise in order to respond effectively to State and local requests for assistance. The CTC activity in 1987 is focused on a pilot program to determine and document the achieved effectiveness of the technical assistance program. This effort features implementation of the CTC HOTLINE, a telephone number which can be used by State and local personnel to gain immediate access to EPA expertise in control technology.

The development of the CTC is described in terms of the roles of the participating organizations, how the CTC is operated and requests are handled, and what types of requests are appropriate for the CTC. In addition, experience to date with the CTC operation is discussed and future plans for the Center are outlined. Initial response by the State and local agencies has been encouraging, and both OAR and ORD are optimistic that the CTC will become a very active part of the Agency's air toxics program in the years to come.

INTRODUCTION

The term "hazardous air pollutants," or more recently, "air toxics," encompasses a potentially large number of pollutants. Air toxics may be defined as virtually any substance released into air media which may pose an exposure risk to humans. The sources of air toxics are widely varied and include traditional air pollution sources such as chemical plants, metallurgical processes, and motor vehicles as well as non-traditional sources such as passive tobacco smoke, indoor radon from soil gas, and sewage treatment plants.

While existing control strategies are making a positive impact on reducing ambient air toxics levels, the growth of the national economy and a continued dependence on chemical and petroleum products could worsen the ambient problem and lead to increased public health risks. In addition, much of the current and emerging air toxics risk, for example from home heating and gasoline vapor control, may not be significantly reducible in the near future at costs which society is willing to pay. To address the near-term problem, the Environmental Protection Agency (EPA) announced in June 1985 a strategy, which encompasses both routine and accidental release concerns, for a program to reduce public exposure to toxic air pollutants in the ambient air.

The Air Toxics Strategy now being implemented couples the traditional Federal regulatory programs [e.g., NESHAPs, New Source Performance Standards (NSPS)] with an increasing State and local regulatory responsibility to achieve reduced air toxics risk to the public. Over the next 5-8 years, the strategy calls for the States and local authorities to take the lead regulatory role, with the Agency providing technical and financial assistance to their efforts. EPA's Office of Air and Radiation (OAR) has drafted a 5-year Air Toxics Implementation Plan by which the objectives of the strategy for routine releases would be accomplished, and which could serve as a guide to the EPA's Office of Research and Development in developing a more responsive R&D program in air toxics.

The Implementation Plan for control of routine releases of air toxics defines six components to address the Agency's strategy:

- o Federal Regulatory Program in Air Toxics (NESHAPs, NSPS, etc.)
- o High Risk Point Sources (e.g., non-NESHAP sources with cancer risk exceeding 10^{-4} in local situations)
- o High Risk Urban Toxics (focused on urban ambient environments)
- o Enhancement of State and Local Air Toxics Programs
- o Enforcement and Compliance Programs for Air Toxics
- o Management and Coordination of Air Toxics Programs

As State and local air pollution authorities begin to develop localized air toxics regulations, substantial financial and technical assistance is expected to be required. The enhancement of State and local air toxics programs will provide financial assistance through grants (e.g., Section 105 of the Clean Air Act) and technical assistance through several Agency

offices, including the engineering R&D program. In particular, experience in control technology and source assessment resident in the EPA will provide a prime source of technical expertise for the State and local agencies as they develop their air toxics programs.

Development of Air Toxics Control Technology Center

The shift in emphasis and responsibility from the Federal level to the State and local air toxics programs and the need to transfer expertise from the Federal level to the appropriate level have prompted EPA's Office of Air Quality Planning and Standards (OAQPS) and the Air and Energy Engineering Research Laboratory (AEERL) to develop and implement an innovative technical assistance program. This program is the Air Toxics Control Technology Center (CTC), a collaborative effort among OAQPS, AEERL, and EPA's Center for Environmental Research Information (CERI). It is expected to become a principal element in the enhancement program through the early 1990s. The goals of the Center are to provide:

- o Support to State and local agencies in the implementation of air toxics control programs through technical guidance and support on air pollution control technology questions,
- o Mechanisms to transfer available engineering information of broad interest to State and local authorities,
- o "HOTLINE" telephone access to EPA expertise as an initial quick response to individual problems,
- o In-depth engineering assistance to States on individual problems, and
- o Feedback to EPA on the technical support needs of State and local agencies.

The types of services to be provided by the CTC can be broken into three categories: direct technical support, technical guidance, and requests for assistance. In the area of direct technical support, the CTC will provide available information, data, and engineering analysis on an as-requested basis. Assistance can be provided on a range of topics, including:

- o Evaluation of source emissions
- o Identification of control technology alternatives
- o Development of control costs
- o Assessing impacts of control technology on water, solid waste, or air effluents
- o Solving problems with source testing methods
- o Advice on permit conditions to ensure good operation and maintenance of equipment for air toxics control
- o Providing expert testimony in support of State and local regulatory actions.

In the area of technical guidance, the CTC will focus on topics of national interest that have been identified by the States, including:

- o Publishing control technology documents which discuss
 - Add-on control devices,
 - Process modifications, and
 - Control of area sources
- o Designing and developing microcomputer software to help assess air toxics control problems and evaluate potential alternative solutions
- o Conducting public seminars and workshops on control technology pertaining to air toxics.

The CTC will handle requests for assistance through the CTC "HOTLINE." Through a special telephone number, State and local staffs can contact EPA personnel who are the most knowledgeable about the requested topic. The CTC may not be able to resolve every technical issue that is raised. A primary purpose of the CTC is to provide a quick response based on whatever control technology expertise or information is available within the Agency. Usually, this will involve a series of telephone conversations and result in the compiling of existing information from EPA technical files.

In some cases, it may be appropriate to go beyond the rapid-response level of support and perform additional engineering analyses. Such requests should be made in writing by the requesting agency. Since a more in-depth involvement of Agency staff may be required here, contractor resources may be used to augment EPA in-house support. Decisions on whether or not the CTC can respond to such requests will depend on a number of factors, including public health implications, usefulness to other States, funding limitations, and other CTC priorities.

In its first year, the CTC is being operated as a pilot program. The CTC is a new concept for the air program: no attempt at such broad-based, cooperative technical assistance has been tried before. At this time, we have only a limited indication of the response to this type of support or of the support areas of most demand. The first year will be used to determine the best approach to organize and operate the CTC.

Currently, the CTC is managed by a Steering Committee with representatives from each participating organization. Plans are currently underway to expand the membership of the committee by adding several advisory members, representing Regional, State, and local agencies. In general, the responsibilities of the Steering Committee include:

- o Assessing technical assistance needs of the States
- o Planning activities of the CTC
- o Setting priorities for spending CTC resources
- o Authorizing decisions on allocation of CTC resources

- o Developing outreach activities
- o Coordinating CTC activities with EPA Regional Offices
- o Developing a plan for the permanent operation of the CTC
- o Ensuring appropriate coordination of CTC publications or products.

CTC operation began in the fall of 1986, and the response from the States has been enthusiastic. A number of telephoned requests, received through the "HOTLINE," have been addressed. A standard "HOTLINE" form has been developed to facilitate gathering the pertinent information, and to document the number and nature of incoming requests to track EPA response. Since the purpose of the CTC is to serve a specific client audience, efforts have been made to inform State and local agencies about the Center and its operation. In October 1986, meetings were held with members of the Air Toxics Committee of the State and Territorial Air Pollution Program Administrators (STAPPA) and the Association of Local Air Pollution Control Officials (ALAPCO) to describe the CTC concept and to solicit their response to the program and requests for assistance. Subsequent discussions were held with other STAPPA/ALAPCO members, and helpful comments were received and factored into the CTC program.

EPA is very sensitive about the CTC's ability to respond to State and local needs in a timely and useful way. Both OAQPS and AEERL have committed to establishing a program that can satisfy both issues. While procedures have been developed to expedite the processing of requests, the proof of the concept lies in the progress actually being made. In that regard, responses to four requests received in late 1986 illustrate the success of the program and its diversified nature.

Current Projects

One of the first projects being conducted by the CTC responds to a request by the State of Florida regarding the emissions generated by the air stripping of ground water. Since this problem seems to be of wide concern, the CTC Steering Committee decided to respond to the request by producing a guidance document on control of these emissions. Members of the CTC organizations familiar with ground water stripping have agreed to produce a document pooling the expertise on the subject from each organization. It is expected that the document will be distributed to and used by those with similar concerns.

Another request originated from the Northeast States for Coordinated Air Use Management (NESAUM). The NESAUM States are faced with a deficiency of information on sampling and analytical (S&A) procedures for municipal waste incineration. Although municipal waste incinerators are of increasing concern to the Agency and standards are being considered, interim methods are needed to promote consistency among the States. In this case, the CTC has arranged for the Agency's measurement expert in incineration to assist the group in formulating an interim sampling protocol. EPA will meet with the States to reach a consensus on the S&A procedures to be used. The results of the meetings will be compiled for the States' use.

The State of Colorado asked for help in addressing complaints of eye and lung irritation in an area surrounding a waferboard manufacturing plant. The CTC has contacted similar plants to determine if the plants have had a comparable problem and, if so, how they have addressed it. The CTC will also conduct a site visit in order to assess the situation first-hand. The visiting team will consist of EPA personnel and a knowledgeable contractor representative. The CTC will then provide a report to the State to characterize the emissions and suggest possible control options.

A similar request came from Allegheny County, a local agency in Pennsylvania. They were concerned with five plants in their district which store toluene di-isocyanate in above-ground containers. The principal concern was the ability of the plant to deal with an accidental release of TDI, which could threaten the local population. The CTC was asked for assistance in verifying the effectiveness of the control systems and techniques in place. Again, a team of experienced EPA and contractor personnel was assembled to evaluate the available information, visit two plant sites, and provide a report to the local agency.

Means of Requesting Assistance

Requests for technical assistance are being received, and actions are being taken on them. Our effectiveness will continue to improve as we learn more about the needs of the State and local agencies. Consequently, we are soliciting State and local agency involvement in this endeavor by asking that representatives of these groups contact the CTC with their comments and/or requests for assistance. Formal requests for technical assistance (e.g., plant inspections, cost analysis, expert testimony) should be submitted to:

Air Toxics Control Technology Center
MD-13
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

or the CTC E-mail box: EPA8390. Informal technical assistance can be accessed through the CTC HOTLINE. The HOTLINE number is (919)541-0800 or FTS 629-0800.

Detection and Quantification of Hydroxylated Nitro Polynuclear Aromatic Hydrocarbons and Ketones and Hydroxylated Nitro Aromatic Compounds in an Ambient Air Particulate Extract

M. G. Nishioka and D. A. Contos, Battelle Columbus Division
L. M. Ball, University of North Carolina
J. Lewtas, U.S. EPA

Highest percentages of mutagenic activity for urban air particulate extracts are associated with the polar compound class fractions. Many of the components of these fractions have not been identified, and the mutagenic species, in particular, have not been detected. The identification of hydroxylated nitro polynuclear aromatic hydrocarbons (OH-NO₂-PAH), hydroxylated nitro polynuclear aromatic ketones (OH-NO₂-PAK) and hydroxylated nitro aromatic (OH-NO₂-Ar) compounds is presented here. Bioassay-directed fractionation through four sequential separations led to detection of OH-NO₂-PAH/PAK in a mutagenic and substantially simplified subfraction of an urban air particulate (<1.7 μ m diameter) extract. Identifications have been made from both electron impact (EI) and highly compound selective negative chemical ionization (NCI) HPGC/MS analyses. Quantification of these compounds has been achieved using NCI HPGC/MS.

The presence of OH-NO₂-PAH in particulate matter has been suggested by Lofroth¹, Nielsen², and Schuetzle³ to account for mutagenicity in polar extract fractions. Mechanisms have been proposed^{2,3,4} by which atmospheric hydroxylation of PAH followed by nitration should yield both NO₂-PAH and OH-NO₂-PAH. Similar mechanisms⁵ have been used to explain the formation of OH-NO₂-Ar in smog chamber studies of toluene.

The importance of OH-NO₂-PAH became apparent when OH-NO₂-pyrenes were first identified as mutagenic mammalian metabolites of 1-NO₂-pyrene⁶. The importance of OH-NO₂-Ar became apparent when NO₂-phenols were identified as phytotoxic agents⁷ present in rain⁸. In addition, at least one NO₂-cresol has been identified as a mammalian metabolite of a NO₂-toluene isomer⁹. Increasing evidence suggests that OH-NO₂-PAH are not only important products of metabolism of NO₂-PAH *in vivo* but may also be important genotoxins to which humans may be exposed via urban air particulate matter.

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- (2) Nielsen, T. *et al.* *Envir. Health Perspect.* 1983, **47**, 103-114.
- (3) Schuetzle, D. *Envir. Health Perspect.* 1983, **47**, 65-80.
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- (5) Leone, J. and Seinfeld, J. *Int. J. Chem. Kinetics* 1984, **16**, 159-193.
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ADVANCES IN CONTINUOUS TOXIC GAS

ANALYZERS FOR PROCESS AND ENVIRONMENTAL APPLICATIONS

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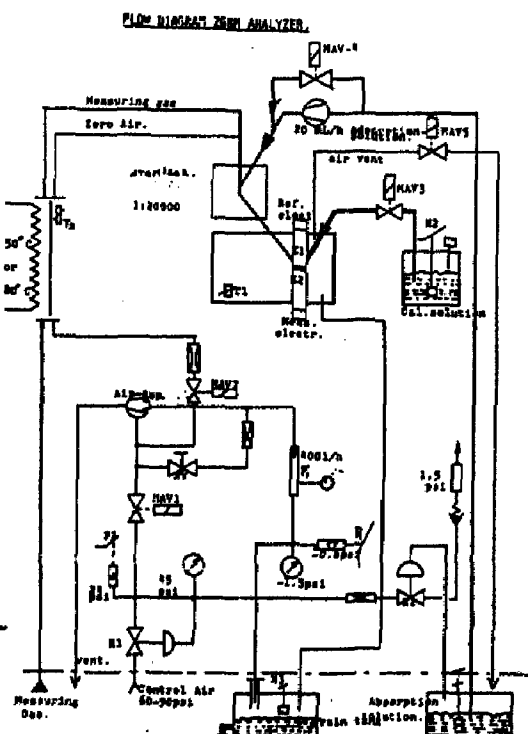
Hermann Schmidtpott, Ph.D.
Compur Monitors, Munich, W.Germany

Hans J. Brouwers
Compur Liaison Office, Mt. Prospect, IL 60056

A continuous microprocessor controlled trace gas analyzer for toxic gases is developed to monitor processes and/or environments with a minimum of human interaction. The ensuing criteria centered around the need to provide a maximum of safety for the employee in the work place. Hence, the analyzer must perform the monitoring task with the greatest amount of accuracy and reliability.

A short response/decay time, wide dynamic range and specificity are considered the prime criteria to obtain reliable and accurate data. This is achieved by selecting optimum detector technology for each toxic gas. The gases for which the analyzer is designed are Hydrogen Fluoride, Fluorine and Hydrogen Chloride. Phosgene can be detected by means of an optional photometric detector system. A sample enrichment system allows detection in the ppb range for most gases.

The basic analyzer system is designed to require no routine maintenance. This is accomplished by reducing the number of moving parts to a minimum. The sample is transported, using an air driven aspirator. All critical analyzer parameters such as sample and reagent flowrates, vacuum, pressure, temperature and reagent levels are continuously surveyed and compared to data stored in the system's nonvolatile memory. An alpha numeric display identifies the cause when one or more parameters do not conform. Automatic calibration and adjustment is performed when the analyzer is started up and at selected time intervals. Hard copy information of calibration data, gas concentrations exceeding present alarm levels and their time of occurrence are available on a built-in printer.



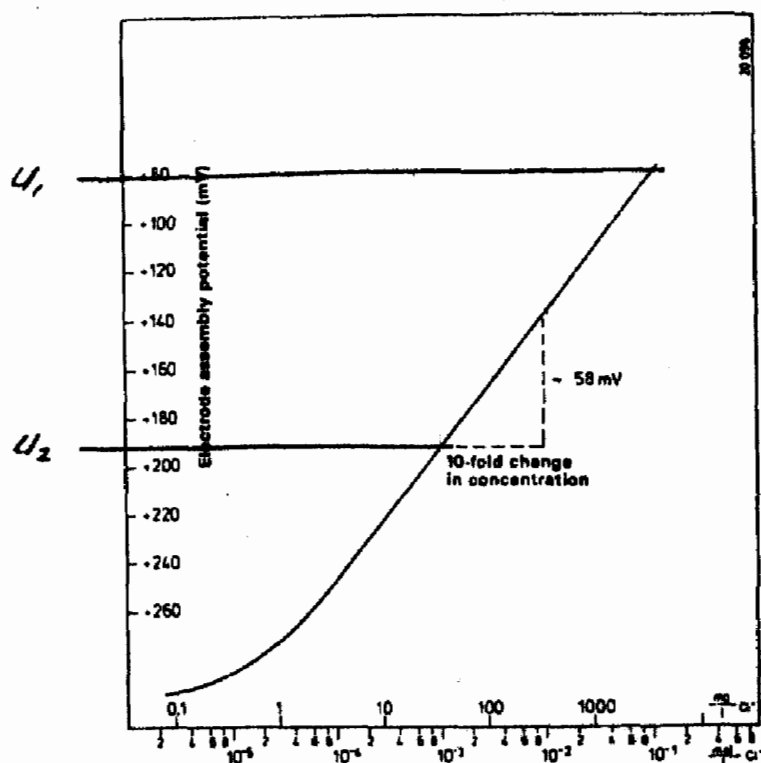
The system has maximum flexibility, as the various parameters of the analyzer can be modified to adapt to the application.

METHOD OF DETECTION

The detection method for HCl, HF and F₂ is the ion specific electrode. Although the principle of detection is similar for all these compounds, the examples in this presentation will concentrate on the method for HCl.

The ion selective electrodes selected for this application are the Ingold chloride specific electrode assembly.

The calibration curve for this assembly can be shown as follows:



The adsorption solution for a measuring range of 0.1 to 1. mg/m³ is as follows:

147.1 g Sodium Citrate-Dihydrate
58.4 g NaCl
160 mL 1.0 m HCl solution
10 mL 0.1 m NaF solution

The above is dissolved in 10 Liters of distilled water. It provides a value of U₁ (mV) at the electrode assembly.

The calibration solution is 70% of the measuring range of the and is made up as follows:

14.7 g Sodium Citrate-Dihydrate
5.8 g NaCl
16 mL 1.0 m HCl solution
70 mL 0.1 m NaF solution

The above is dissolved in 1 liter of distilled water. It provides a potential of U₂ (mV) at the electrode assembly.

Some critical parameters to be aware of are:

- 1 - $E^0 = 105$ mV
- 2 - Ph of both solutions should be 5.8 +/- 0.2
- 3 - Slope of curve should be 56 mV/decade

All measured data are available on the print out, so that individual critical parameters can be verified at all times.

MONITORING OF CEMENT KILN EMISSIONS THROUGH
PLANTS: A CASE STUDY

P.K.Nandi*, Madhoolika Agrawal & D.N.Rao
Centre of Advanced Study in Botany
Banaras Hindu University
Varanasi 221005, INDIA



*
Environmental Planning & Coordination Organization
Prayavaran Parisar, Arera Colony
Bhopal 462 016, INDIA

In certain parts of India, the rapid expansion of cement manufacturing industry has introduced the likelihood of increase in environmental problems arising out of particulate emission from cement kilns. The present study concerns the assessment of dust deposition on leaf surfaces and subsequent plant responses to particulate emission from an 1 million tpa capacity cement plant. The study revealed that the amount of dust deposited on the leaf surfaces of perennial plants like Citrus medica, Mangifera indica and Psidium guyava were negatively correlated with their distances from the emission source. While the magnitude of dust deposition was maximum on C. medica and minimum on P. guyava, the Ca accumulation was found to be maximum in C. medica and minimum in M. indica. A species specific direct relationship between the amounts of dust deposition and foliar Ca accumulation was also observed. Moreover, visible injury symptoms were discernible only on P. guyava and M. indica growing within a radius of 2 km from the emission source. The study thus suggests that the differential responses of plants to particulate kiln emission may serve as a key to use plants for the detection, recognition and monitoring of particulate pollution and its biological effects.

Introduction

In India increasing gap in demand and supply of cement and the presence of vast reserves of cement grade limestone have resulted in rapid expansion of cement manufacturing industries in recent years with subsequent increase in problems arising due to emission of particulates into the atmosphere. Consequently for careful control of particulate pollution in industrial regions, high volume sampler as per specifications of U.S. EPA¹ has been prescribed as a reference method for the monitoring of total SPM¹. Though this method is ideal for measuring quantity and after analysis quality of particulates in the ambient air, it is far away from indicating or help modelling biological effects of such pollutants. On the other hand, leaves of plants may act as efficient dust collectors and show differential responses depending upon the physical and chemical characteristics of particulate matter deposited on them and thus may also act as tools for detection, recognition and monitoring of air pollution effects²⁻⁴. When plants accumulate polluting compounds without changing their chemical nature by metabolism and the pollutants are easily analysed in sample of plant material, they may be used for monitoring of pollution effects also⁴.

In the present study an attempt has been made to use plants for monitoring of particulate emission from cement plants as well as emission induced biological effects.

Site Description and Sources of Atmospheric Emission

The cement plant with an annual production capacity of 1 million ton is located at 21°57' N latitude and 82°20' E longitude on a plain topography and at an elevation of 300 m above mean sea level. The minimum and maximum temperatures of the area range from 13 to 42°C. The predominant wind direction is towards SE and average speed is 6 Km h⁻¹.

The latest dry process technology has been adopted for portland cement manufacture in the plant with inputs of raw materials as cement grade limestone, clay, laterite, breeze coke and gypsum. The principal sources of particulate are the raw mill, rotary kiln and clinker cooler. Emission from cement mill and coal mill are relatively low. Generally, the average particulate emission from the kilns of this type of plants in India amounts to 0.2% or 2 kg Mt⁻¹ of cement produced and when dust arresting devices remain uncharged the total emission may increase to 4%. The fallout dust at the environs of the cement plant thus constitute a heterogeneous mixture with contribution of raw and clinker phase materials predominating.

Experimental Methods

The study was conducted in March 1986. Three to four years old plants of Citrus medica, Mangifera indica and Psidium guajava growing at different directions upto 3 Km from the epicentre of pollution source and upto a distance of 5 Km downwind were selected for measurement of dust load on leaves, foliar calcium level and leaf wash suspension pH (Table I). For the determination of background level of dust a site at 8 km NW was selected.

Plants growing at above mentioned sites were visually examined. Mature leaves were collected, repeatedly washed with deionised distilled water and leafwash suspension was dried to determine the weight of solid matters. Leaf area were measured and then dried in oven at 105° C for 8h. Calcium contents in leaves were determined by flame photometric method after ashing the dried and powdered leaf samples at 480°C with the addition of saturated magnesium acetate. Leaf wash pH were determined with the help of a pH meter. For all measurements at least three replicates were maintained.

Results

The dispersion of particulates from the stacks of cement plant as examined by the measurements of foliar dust load (Table II) and leaf-wash suspension pH (Table I) was found to be quite significant upto 3 Km downwind of the emission source. The magnitude of dust deposition on leaves of plants growing at 1 km NW was found to be comparable to those growing at distances of 3 and 3.5 Km on SW and SE directions, respectively. The levels of leaf surface dust, leaf wash suspension pH and foliar calcium were found to be maximum at the immediate vicinity of the source but these values for plants growing at increasing distances from the source were found to be significantly low. While the magnitude of dust deposition was maximum on C. medica and minimum on P. guyava, the calcium accumulation was found to be maximum in C. medica and minimum in M. indica (Table II). The maximum dust load of 49.2 g m⁻² leaf area of P. guyava was found comparable to a study conducted elsewhere⁵. A species-specific direct relationship between foliar dust load and calcium accumulation was also noted. Chlorotic foliar injury symptoms were only noticed in P. guyava and M. indica growing upto a distance of 2 Km downwind (Table II). On the same site, inspite of thin crust formation on leaves of C. medica no visible injury symptoms were detected in them.

Development of foliar injury symptoms was possibly due to higher dust load and alkalinity of particulate matter on leaf surfaces. Czaja⁶ noted a positive correlation between induction of foliar injury symptoms and the concentrations of calcium silicate in cement kiln dust vis à vis its pH values. It was suggested that on hydration of cement kiln dust, alkaline calcium hydroxide solution is released on leaf surfaces which in turn help saponify the protective cuticle permitting migration of solution through the cuticle to mesophyll tissue⁶. This possibly causes accumulation of calcium in tissue with subsequent changes in plant metabolism and development of injury symptoms, resulting in decreases in photosynthetic potential, energy budget and biomass production of plants^{5,7}.

Conclusions

The measurements of leaf surface dust load, dust-suspension pH and foliar calcium accumulation in plants growing at different locations from the cement plant may help monitoring of particulate emission as well as modelling its dispersion pattern. Plant responses further help recognition, detection and monitoring of biological effects of particulate pollutants.

Acknowledgements

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TABLE I

Leaf-wash pH of plants growing at different locations around a cement plant.

Site No.	Direction	Distance (Km)	Leaf-wash pH
S ₀	-	0	9.2
S ₁	SE	1	9.0
S ₂	NW	1	8.4
S ₃	SE	2	8.8
S ₄	SE	3.5	8.2
S ₅	SW	3	8.2
S ₆	E	3.5	7.8
S ₇	SE	5	7.8
S ₈	NW	8	7.6

TABLE II

Foliar dust load, calcium contents and injury symptoms in plants (P=*P. guyana*, C=*C. medica* and M=*M. indica*) growing at different locations around a cement plant.

Site No.	Plant	Dust load (g m ⁻² leaf area)	Calcium (%)	Injury symptom
S ₀	P	49.2	4.8	Necrosis
	C	-	-	-
	M	-	-	-
S ₁	P	5.8	3.4	Chlorosis
	C	6.5	3.8	-
	M	5.6	3.2	Chlorosis
S ₂	P	3.9	2.05	-
	C	4.2	2.95	-
	M	3.85	1.9	-
S ₃	P	4.2	2.8	Chlorosis
	C	4.56	3.3	-
	M	4.26	2.4	Chlorosis
S ₄	P	3.95	2.1	-
	C	4.3	3.0	-
	M	3.8	1.9	-
S ₅	P	3.8	1.95	-
	C	4.3	2.95	-
	M	3.8	1.9	-
S ₆	P	1.98	1.6	-
	C	2.05	2.5	-
	M	1.95	1.2	-
S ₇	P	2.1	1.62	-
	C	2.2	2.45	-
	M	1.96	1.3	-
S ₈	P	2.05	1.6	-
	C	2.16	2.4	-
	M	1.90	1.25	-

**NON-AQUEOUS ION EXCHANGE CHROMATOGRAPHY AS A
PREPARATIVE FRACTIONATION METHOD FOR SHORT
TERM BIOASSAY ANALYSIS OF WOOD SMOKE EXTRACTS**

Douglas A. Bell
Hani S. Karam
Richard M. Kamens

Department of Environmental Sciences
and Engineering
University of North Carolina
Chapel Hill, NC 27514

Wood smoke contains significant quantities of mutagenic and carcinogenic compounds such as polynuclear aromatic hydrocarbons (PAH). However, PAH account for only 12-25 % of the mutagenicity of wood smoke particles with the remainder appearing in the more polar fractions. These polar fractions have proven to be refractory to chemical characterization and identification of mutagenic species has not been possible.

Two commonly used separation methods for combustion emissions, aqueous phase acid/base/neutral and normal phase HPLC fractionation, have been used on wood smoke but have resulted in low mass recovery or poor separation of polar compounds. In order to address these difficulties, an acid/base/neutral fractionation method was developed using non-aqueous ion exchange chromatography. The two columns utilized were composed of: cation exchange resin, Amberlyst 15, for separating bases; and the anion exchange resin, Amberlyst 26, for separating acids. High recoveries, as determined by GC analysis, were observed for 14 compounds in a standard mixture. Total mass recovery for a wood smoke sample through this scheme was ~100 % with the neutral fraction accounting for 54 % of the mass. Acid, polar acid, neutral and basic fractions were collected and following solvent exchange into DMSO, were tested in the Ames/Salmonella mutagenicity assay. The neutral fraction demonstrated the highest mutagenicity both in the presence and absence of S9 activation.

NON-AQUEOUS ION EXCHANGE CHROMATOGRAPHY AS A PREPARATIVE FRACTIONATION METHOD FOR SHORT TERM BIOASSAY ANALYSIS OF WOOD SMOKE EXTRACTS

INTRODUCTION

The identification of biologically active compounds in complex environmental mixtures is a difficult technical challenge. The polar fractions of wood smoke, which contain 75-90 % of its mutagenic activity, have proven to be particularly refractory to analysis (1). Preparative and semi-preparative methods such as aqueous phase acid/base/neutral separation, open column silica gel chromatography, and normal phase HPLC silica gel fractionation have been successfully used for separation and identification of nonpolar polynuclear aromatic hydrocarbons and partially successful for studying their moderately polar nitrogen and oxygen derivatives (2,3). However, these methods have resulted in low mass recovery and/or poor separation of polar compounds when applied to wood smoke extract(3,5). In order to address these difficulties, an acid/base/neutral fractionation method was developed using non-aqueous ion exchange chromatography.

MATERIALS AND METHODS

Reagents

Chloroform, tetrahydrofuran (THF), and methanol were purchased from Burdick and Jackson, Muskegon, Mi. Ion exchange resins were manufactured by Rohm and Hass and obtained from Alfa, Danvers, MA. Formic acid and isopropyl amine were obtained from Fluka, Ronkonkoma, NY. Source and purity of standard compounds are listed in Table I.

Preparation of Ion Exchange Resins

Preparation was similar to that of Jewell, et al (6). Amberlyst 15, the cation exchange resin, was washed with a methanolic potassium hydroxide solution (5 % by weight) and then rinsed with methanol. It was then converted to the acid state by slowly adding a solution of 5 % volume HCL in methanol and stirring for 30 minutes. The resin was washed with distilled deionized water until the pH of the washing water was neutral. It was then soxhlet extracted for 24 hours each with methanol, dichloromethane, and a chloroform/5 % tetrahydrofuran mixture. The resin was stored in chloroform until used.

The anion exchange resin, Amberlyst 26, was washed with a 5 % HCL solution in methanol and rinsed with methanol. After rinsing, the resin was activated by adding a 5 % methanolic hydroxide solution (described above). The resin was washed, soxhlet extracted (no THF was used) and stored

as described above. Approximately 1 gram of resin per 10 milligrams of sample was slurry packed in chloroform into 25 or 50 ml burettes which were plugged with glass wool and fitted with teflon stopcocks. Columns should not be packed too tightly because the variety of solvents used causes swelling of the resins during the separation.

Preparation of Fractionation Standard

A high concentration standard was prepared by adding approximately 60 mg of each of the compounds listed in Table I to 10 mls of a 10 % THF/Chloroform solution. The compounds were chosen to reflect the expected distribution of acidic, basic and neutral components in wood smoke. Many of these have been identified in wood smoke (see Kamens, et al, these proceedings).

Preparation of Wood Smoke Extract

Smoke from a residential wood stove burning yellow pine was introduced into the UNC Combustion Emission Research Facility chambers and then sampled as described in the literature (1,4) and elsewhere in these proceedings (Kamens, et al). The particulate sample, collected on 13 cm Teflon coated, glass fiber filters (Pallflex T60290), was soxhlet extracted for 16 hours with dichloromethane, concentrated by rotary and nitrogen evaporation and a gravimetric mass was determined for the extract.

Separation Procedure

The general fractionation procedure is outlined in Figure 1 and is similar to Jewell, et al (6) (but without a solvent reflux step). 40-100 mg of standard or sample dissolved in 1ml of 10% THF/chloroform was placed on the Amberlyst 15 column. Acids and neutrals were unretained and were eluted with a 10 % THF/10% methanol/ 80% chloroform mixture. The modification of the chloroform by adding THF increased the recovery of acids from the cation exchange column and the methanol increased elution of the highly polar compounds in wood smoke. The retained bases were removed from the resin with 20 % volume isopropylamine in methanol. The acids/neutrals mixture was concentrated by rotary evaporation to ~1 ml and placed on the anion exchange column. Neutrals were unretained on this column and eluted in 100 % chloroform. Retained acids were then eluted by adding a 1% formic acid/methanol solution. A second, more polar, acidic fraction was collected by eluting with a 20% formic acid/methanol solution. Each elution was carried out at a rate of ~1 ml/minute and the volume of solvent used was 20-50 mls per fraction (~0.5 mls/mg sample). Basic and acidic fractions were rotary evaporated just to dryness to remove any remaining solvent modifier (ie. isopropylamine or formic acid). They were redissolved in fresh solvent

prior to gas chromatography or mass residue analysis. Gravimetric mass measurements of the fractions were accomplished by evaporating the solvent from small aliquots of the sample and weighing the residue.

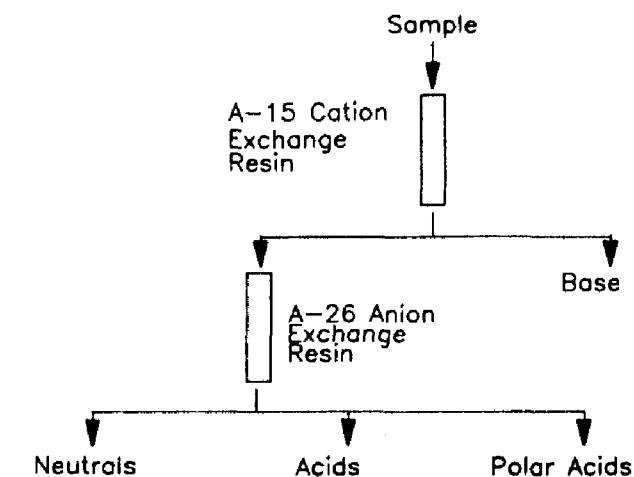


Figure 1 Separation scheme.

Gas Chromatography

Chromatography was performed on a Carlo Erba model 4130, gas chromatograph utilizing a 30m fused silica J & W, DB 1701 capillary column with a flame ionization detector. It was temperature programmed from 130-290°C at 8°C/minute and the injection was splitless with a 20 second hold. A Shimadzu integrator was used and the internal standard method was used for quantitation. Identities of the peaks in the standard mixture were confirmed using the above column and program with a 5992 Hewlet Packard GC/MS system.

Mutagenicity Bioassay

Each wood smoke fraction and the neat sample was tested for mutagenicity in *Salmonella typhimurium* strain TA98 with and without a 10% rat liver homogenate mixture (S9) prepared from Arochlor induced rats as described by Maron and Ames (7). Due to a limitation of mass, each fraction was tested with single plates at four doses which were chosen by estimating the the probable linear dose/response range based on prior testing (data not shown). Mutagenicity slope values were calculated by simple linear regression using all dose levels unless toxicity was observed. Quantitative slope values were calculated for the purpose of comparison and the limited number of data points suggests a qualitative interpretation of mutagenicity results.

RESULTS AND DISCUSSION

Recovery of Fractionation Standard

As is shown in Table I, qualitative separation of the basic standards into the the base fraction was excellent with no neutral or acid overlap. The quantitative recovery of bases was greater than 92%. Five neutral compounds appeared only in the neutral fraction while two compounds, 2,3-dimethyl indole and naphthalic acid anhydride behave partially as weak acids. Phenol and 1-naphthol, relatively weak acids, were split between the neutral fraction (21.5% and 14.4%) and the acidic fractions. The stronger acids, benzoic acid and *p*-nitrophenol, appeared almost entirely in the acidic fractions. Quantitation of 9-phenanthrol was unreliable because of solubility problems. There was no compound which appeared primarily in the polar acid fraction indicating that there is no representative of this class in the mixture. Suitable polar compounds which could be chromatographed and which might appear in this class such as di-acids or di-hydroxylates were not available. The material which did elute in this fraction may have been that which was tightly bound to the anion resin active sites. Total recovery of standards was generally high (>87%).

Mass Distribution of Wood Smoke

The particle extract mass which was fractionated and the mass which appeared in each fraction is displayed in Table II. The slight over recovery of mass may reflect measurement error or may possibly be due to the effect of THF hydrogen bonding with the acids in the sample (8).

Table II. Mass Recovery of Wood Smoke Among Fractions

Sample	Mass Mg	Percent
Whole Extract	51.0	100.0 %
Base	2.4	4.7 %
Neutral	27.6	54.1 %
Acid	20.0	39.2 %
Polar Acid	2.8	5.5 %
Sum	52.8	103.5 %

Measurement error due to balance fluctuation, +/- 5.0 %.		

Mutagenicity

The mutagenic potency in Salmonella strain TA98 was measured by performing a simple least squares linear regression on the dose response data and is expressed as revertants per ug extract as shown in Table III. The total revertants per fraction was calculated by multiplying the slope value of the regression line by the mass appearing in the fraction. Percent mutagenicity distribution is calculated by dividing the revertants per fraction by the revertants in the whole extract.

The unfractionated pine smoke extract was particularly mutagenic when compared with other samples tested in this laboratory (typical values for TA98: -S9 = 0.4 rev/ug; +S9 = 1.2 rev/ug). The neutral fraction was the most potent without adding S9 although not as mutagenic as the whole extract. The acidic fraction makes a significant contribution (16.6%) to the mutagenicity of the sample. The reconstituted sample (reconstituted from the fractions by mass percentage) also had a lower response than the whole sample indicating a possible loss of direct acting mutagens in the fractionation process. This possibility is also suggested by the 68.6 % recovery of percent mutagenicity when the mutagenicity from each fraction was summed. However, given the limited data set, these departures from 100% recovery may simply be due to measurement error.

Indirect acting mutagenicity (+S9) slope values were 2 to 15 fold higher than direct acting values for all of the fractions. The high potency of the base fraction was surprising given that no highly mutagenic basic compounds have previously been identified in wood smoke. However the contribution that the bases make toward the whole sample is small. The neutral fraction, in which polynuclear aromatic hydrocarbons appeared, was the most potent fraction and also contained 93% of the indirect acting mutagenicity of the whole unfractionated extract. The acidic fractions make relatively small contributions to the indirect acting mutagenicity of the sample. Recovery of indirect acting mutagenicity as measured by the reconstituted and summed fractions was 90% and 107% respectively. This suggests there is good recovery of these mutagens through the fractionation scheme.

In assessing the usefulness of this method, the good qualitative separation and the quantitative recovery of standards demonstrates that non-aqueous ion exchange chromatography can be applied to complex mixtures. Further development of the method may result in reducing the overlap of weak acids into several fractions. Manipulation of solvent polarity is critical to solving this problem.

For a separation method to be used in bioassay directed fractionation it requires: 1) high recovery of sample mass through the system in order to make informed decisions about further analysis; and 2) high recovery of 'weighted' mutagenicity. While the bioassay evidence supporting the utility of this fractionation method is limited, the preliminary results presented here indicate that for a non-aqueous sample this method measures up relatively well. This ion exchange separation technique may be especially useful when the investigator wishes to avoid the addition of strong acids and bases (ie H_2SO_4 or NaOH) to the sample as in aqueous phase acid/base/neutral methods.

ACKNOWLEDGEMENTS

The authors would like to thank Drs L. Claxton and J. Lewtas, US EPA for their continued support of this project. We would also like to acknowledge the useful suggestions made by M. Nishioka, Battelle Columbus and the excellent technical support of J. Fulcher and C. Braun, U. of NC.

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Table I. Percent Recovery of Fractionation Standard

COMPOUND	BASE	NEUTRAL	ACID	POLAR ACID	TOTAL RECOVERY	PERCENT STD. DEV. c
Phenol a		21.5%	72.4%	1.8%	101.7%	5.8%
Benzoic acid		3.9%	108.8%	10.9%	123.6%	11.4%
2,6 Diethyl quinoline	98.8%				98.8%	5.2%
Dibenzofuran		106.8%			106.8%	2.6%
2,3 Dimethyl Indol		81.7%	8.9%		90.6%	2.2%
1 Naphthol		14.4%	59.8%	17.5%	91.7%	5.1%
9 Fluorenone		104.1%			104.1%	2.5%
7,8 Benzoquinoline	92.7%				92.7%	6.0%
p nitrophenol			97.9%	0.9%	98.7%	8.5%
Pyrene		99.4%			99.4%	1.9%
Naphthalic acid anhydride		71.7%	9.4%	5.4%	86.5%	7.2%
9 Phenanthrol			29.6%	1.8%	25.4%	14.9%
Pyrene carboxaldehyde b		89.7%			89.7%	0.5%
Benz[a]anthracene 7,12 dione		103.9%			103.9%	1.5%

a All chemicals obtained from Aldrich, Milwaukee, WI, >99% purity unless noted.

b Alfa > 99%

c Peak area deviation among replicate GC runs.

Table III Mutagenic Potency and Distribution

Sample	TA98 -S9			TA98 +S9		
	Revertants Per ug Extract	Revertants Per Fraction	Percent Mutagenicity Distribution	Revertants Per ug Extract	Revertants Per Fraction	Percent Mutagenicity Distribution
Whole Extract	0.82	31365	100.0%	2.48	126595	100.0%
Base	0.19	453	1.4%	3.04	7308	5.8%
Neutral	0.54	14987	47.8%	4.27	117852	93.1%
Acid	0.26	5200	16.6%	0.40	8077	6.4%
Polar Acid	0.31	872	2.8%	0.79	2199	1.7%
Reconstituted	0.44	23352	74.5%	2.16	114174	90.2%
Sum		21512	68.6%		135435	107.0%

Mean (n=3) revertants, controls: -S9 = 23; +S9 = 34;

3 ug 2-nitrofluorene = 272; 3 ug 2-aminoanthracene = 1965.

EFFECTS OF RETROFIT TO REDUCE EMISSIONS FROM EXISTING WOOD STOVES

R.W. Braaten and A.C.S. Hayden
Research Engineer and Research Scientist
Canadian Combustion Research Laboratory (CCRL)
Energy Research Laboratories, CANMET
Department of Energy, Mines & Resources
555 Booth Street, Ottawa, Canada K1A 0G1.

Over the past few years, it has become widely recognized that wood stoves can produce high levels of incomplete combustion products, becoming, in some areas, one of the most serious air pollution sources. Whitehorse, in Canada's Yukon Territory, has one of the highest levels of wood stove-generated air pollution in North America. Most efforts to date, both from the technical and the regulatory side, have concentrated on developing new, cleaner burning appliances. While this approach is commendable, and is resulting in a number of cleaner, more efficient appliances on the market today, the majority of woodstoves installed in homes in North America are of the older, inferior combustion type. That most stoves have been installed in the past eight years or less makes the probability of their replacement in the near term very unlikely. Unless retrofit technologies or use control strategies are applied in an effective manner, the emissions from wood stoves will be with us for a long time to come.

This paper presents some retrofit technologies that offer the potential to reduce the emissions of incomplete combustion products from existing wood stoves, either by forcing a change in the rate in which the wood is actually burned, or by adding on an afterburner-type catalyst to clean up the emissions before they leave the chimney. In particular, laboratory results on the use of a retrofit add-on catalyst fitted to a stove representative of the majority of installations in Whitehorse, are presented. The add-on catalyst makes a major reduction in the amount of particulates emitted, but only when the stove is operated in the updraft position. It is ineffective when the stove is in sidedraft. On the other hand, the add-on is seen to be quite satisfactory in cleaning up carbon monoxide in the exhaust, no matter what the stove operating mode.

Introduction

Over the past few years, it has become widely recognized that wood stoves can produce high levels of incomplete combustion products, becoming, in some areas, one of the most serious air pollution sources. Indeed, Whitehorse, in Canada's Yukon Territory, has one of the highest levels of air pollution due to wood stoves in North America (1).

Most efforts to date, both from the technical and the regulatory side, have concentrated on developing new, cleaner burning appliances. While this approach is commendable, and is resulting in a number of cleaner, more efficient appliances on the market today, the majority of woodstoves installed in homes in North America are of the older, inferior combustion type. That most stoves have been installed in the past eight years or less makes the probability of their replacement in the near term unlikely. Unless retrofit technologies or use control strategies are applied in an effective manner, the emissions from wood stoves will be with us for a long time to come.

Some reduction in emission levels may be possible through consumer education in proper stove operating procedures and fuel conditioning. However, changes to the hardware and/or improved feedback to the operator on the stove's performance offer potentially the most promising means of reducing emissions. In particular, techniques allowing the upgrading of existing equipment at reasonable cost offer the best hope of significant reductions in emission levels through consumer acceptance.

Any emissions reduction technique, to be effective and acceptable to the consumer, should have the following characteristics. The primary requirement is a major reduction in pollutant emissions. At the same time, there should be a significant gain in fuel economy, leading to a reduction in wood consumption, to make adoption of the technique attractive to the user. The technique should have a low capital cost relative to the cost of a new appliance. It should be easy to install (preferably consumer installable), again to minimize cost. It should be uncomplicated to use; coupled to that, a feedback provision should let the user know that the technique is working, increasing satisfaction and ensuring proper operation. There should be no degradation of safety. Preferably, the technique should even offer some safety benefits, such as reduced creosote potential, lessening the chance of a chimney fire.

As mentioned, Whitehorse has a serious air pollution problem due to wood stoves. To attempt to ameliorate the problem, Energy, Mines and Resources Canada, through its Remote Communities Demonstration Program, has been carrying out a field study on improved combustion techniques for wood stoves, over the past heating season (2). The study has focused on three different methods. The first is a replacement of conventional, high polluting stoves with new, clean burning appliances. The second is the replacement of single walled flue pipe with double walled pipe, to reduce the amount of heat supplied to the house by the flue pipe, and force the user to run his appliance at a higher firing rate, hopefully moving the use pattern to the clean side of the critical burning rate of the appliance (3). The third technique was the use of add-on catalytic converters, to ignite and burn off the incomplete the combustion products before they reach the chimney.

Experimental Methods

The specific retrofit technique examined in detail for this paper was the use of a retrofit add-on catalyst to react some of the incomplete combustion products, specifically hydrocarbons and carbon monoxide, which would otherwise condense to form creosote in the flue or be released as undesirable pollutants to the atmosphere.

Test Stove

The specific stove chosen for detailed testing was one constituting nearly one-half the installed wood burning appliances in Whitehorse, so that any successful improvement to this stove would have fairly general applicability. The unit was a large (0.15 cu.m. firebox capacity) stove of the sidedraft design (4), which could also be operated in the updraft mode with the use of a bypass damper.

Retrofit Catalyst

The retrofit catalyst had a ceramic substrate coated with platinum. The catalyst itself was enclosed in a metal container, with provision made to manually bypass the catalyst (for reloading of the stove, etc.) by moving the catalyst so as to open a passage around the catalyst for the flue gases. A certain amount of refractory material was built in to keep the temperatures elevated to ensure catalyst light-off.

Test Procedure

The test results presented in this paper are based on laboratory trials at CCRL using the CSA/ASTM stack loss/dilution tunnel test method. This method generally conforms to the draft US EPA test requirements for wood stove emissions, except for the fuel charge configuration and some minor variations, such as differing dilution tunnel diameter and size of particulate filters. For these tests, the Oregon/EPA fuel charge configuration was used.

Flue gas composition was measured continuously in the following manner: carbon dioxide with an infrared analyzer, oxygen with a paramagnetic analyzer, NO_x by chemiluminescence; carbon monoxide also using an infrared analyzer; hydrocarbons using a cold line flame ionization detector as well as a Byron hydrocarbons 301 analyzer, in order to determine some of the non-straight chain hydrocarbons; . Fuel weight change was determined continuously using a digital scale, and temperatures with chromel-alumel thermocouples. All data were continuously recorded and analyzed on-line with a digital computer/data logging system.

The appliance was operated over firing rates encompassing its normal operating range. No attempt was made to operate at either the minimum burn rate attainable or the maximum burn rate possible when in the non-catalyst mode. The same diameter flue pipe as appliance flue exit diameter was used.

The appliance was operated with a section of straight flue pipe replacing the add-on catalyst for the baseline runs, and using the same light-off procedure for all the catalyst runs, consisting of running at maximum air setting for the first five minutes of the run with the catalyst brought into action after three minutes. After five minutes, the air setting was changed to its final value, if different than maximum, and no further changes made for the rest of the run.

Results

Figures 1a and 1b present performance profiles of the test stove for particulates and carbon monoxide versus firing rate, respectively, with and without the add-on catalyst and with the stove operated in both the updraft and the sidedraft mode.

The emissions of particulates and carbon monoxide for the unmodified stove are seen to be slightly higher in the updraft mode than in sidedraft. At a burning rate of 3 kg/h, total CO emissions are about 1600 grams, being about 25% lower in sidedraft. For total particulates, as determined with the dilution tunnel, comparable levels are 160 and 120 grams, respectively.

The retrofit catalyst does a good job in reducing carbon monoxide levels, in both the updraft and sidedraft modes, to around 500 grams at 3 kg/h, less than 1/3 the normal levels.

The effect of the retrofit catalyst on particulates is not nearly so straightforward.

In the updraft mode, the catalyst is extremely effective, lowering total levels to about 20 grams, about 1/8 the normal levels.

However, in the sidedraft mode, the catalyst appears to be ineffective, probably due to too low temperatures and, perhaps, an inadequate supply of oxygen.

It is also important to notice that the slope of the curves for both particulates and CO, using the add-on catalyst and with the stove operated in the updraft position, is not nearly so steep for decreasing firing rate as for the unaltered stove, indicating even better performance at the lower firing rates typically found in dwellings during the heating season.

While not reported in depth in this paper, preliminary results from the field trial in Whitehorse for the double walled flue pipe indicated a contrary result to what was expected. The double walled pipe used appeared to result in a marked increase in creosote deposition in the flue pipe sections themselves, resulting in complaints from the homeowners using the pipe. On closer examination, it was revealed that the particular double walled pipe chosen had significant slots in the outside wall at the top and bottom of each section, probably to reduce heat build-up. It appears that the slots may have been too successful in this regard, resulting in cold inner surfaces promoting increased creosote. This has led to a more detailed experimental program at CCRL to examine in detail the performance of several double walled pipes, and to formulate an optimized design for wood stove use.

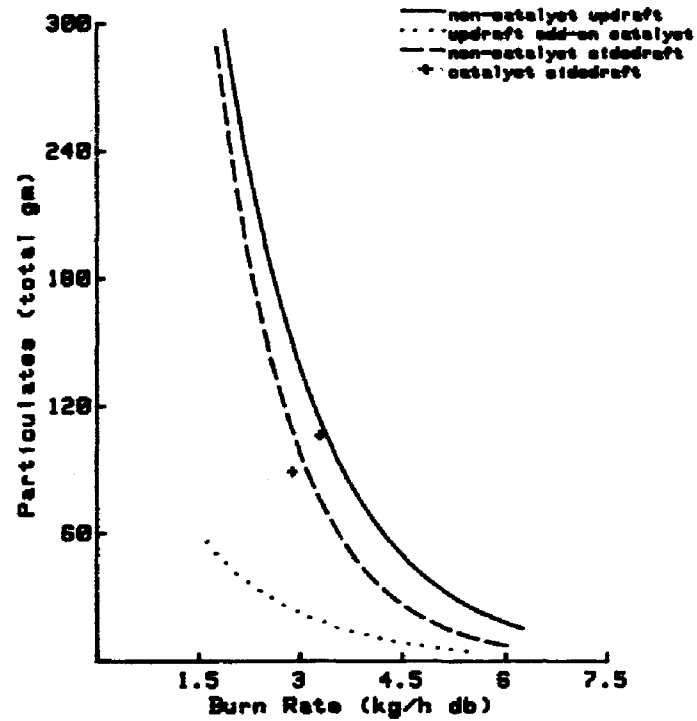
Conclusions

1. Laboratory testing indicates significant emissions reduction potential with the use of the add-on catalyst for the major stove used in Whitehorse. Reductions in total particulate emissions of up to 80% can be expected, but only when operated in the updraft mode.
2. The add-on catalyst resulted in a reduction in total carbon monoxide levels of about 2/3, irregardless of whether the stove was run in the updraft or sidedraft modes.
3. A good add-on catalyst design can be highly effective in reducing wood stove emissions on some stoves. However, the same catalyst may be of little benefit on other stoves, so it is important to be able to identify the stove or conditions under which the catalyst is likely to perform well and use it only on those stoves. Alternatively, add-on catalysts should be designed to function properly on as wide a selection of appliances as possible.
4. Double walled flue pipe may be a means of improving stove performance by promoting higher user firing rates, while lessening creosote potential, but some present pipe designs appear to negate this advantage by too much heat rejection. There is a need for further work to recommend optimum designs to achieve all the desired objectives, including emissions reduction. Further experiments are now being carried out and discussions are being initiated with the approval agency and with Canadian manufacturers to attempt to correct these deficiencies.

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Dilution Tunnel Results



Carbon Monoxide

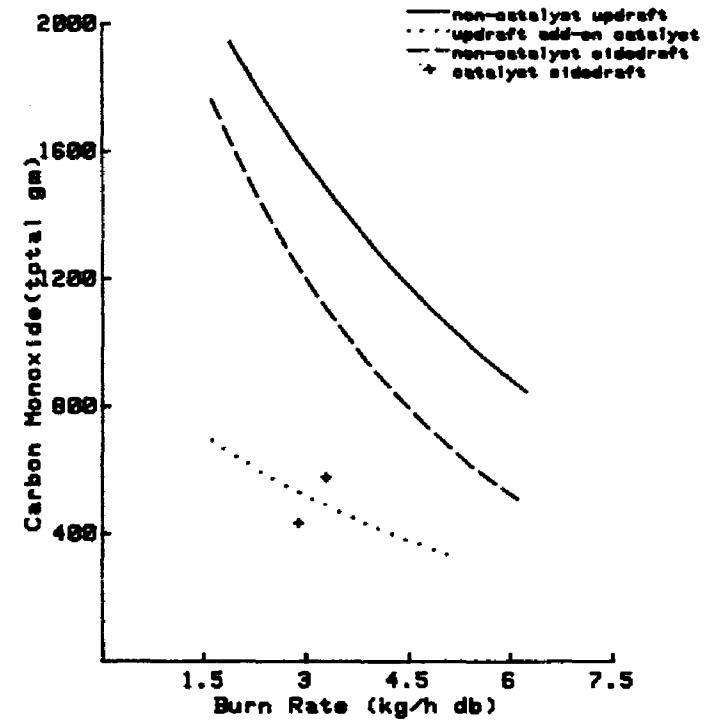


Figure 1. Effect of add-on retrofit catalyst on particulate and carbon monoxide total emissions, when mounted on a sidedraft-design stove, operated in both the updraft and sidedraft modes.

The Contribution of Residential Wood Combustion to Respirable and Inhalable
Particulate Concentrations in Missoula, Montana

James E. Houck
OMNI Environmental Services, Inc.
Beaverton, Oregon

James H. Carlson
Missoula City - County Health Department
Missoula, Montana

Clifton A. Frazier
Desert Research Institute
Reno, Nevada

Robert A. Cary
Sunset Laboratory
Forest Grove, Oregon



Missoula, Montana, has a long history of air pollution due to a large extent to residential wood combustion (RWC), road dust, and winter inversions. Numerous studies have been conducted in the past 10 years examining various aspects of the problem. During the winter of 1986/1987, an extensive ambient and source sampling program was conducted to quantify the ambient levels of particles attributable to specific sources by using chemical mass balance (CMB) receptor modeling. The limiting factor in many CMB studies has been the lack of representativeness in the source profiles used. This is particularly problematic with RWC and road dust sources. The chemical composition of road dust can change dramatically over relatively short distances and the chemical composition of RWC has been shown to be very variable due to the differences in wood fuel, appliance type, and operational parameters.

The source sampling strategy and chemical profiles for several Missoula particulate sources are presented here. Major emphasis was placed on obtaining representative RWC and road dust "fingerprints". Automobile exhaust, diesel truck and train exhaust, and several small wood-products point sources were also sampled and analyzed.

INTRODUCTION

During the period from January, 1984, through July, 1986, there were nine violations of the primary 24-hour particulate standard and 60 violations of the secondary 24-hour standard in Missoula, Montana. All violations except one occurred between December and March. Based on the fact that the ratio of respirable ($<2.5 \mu$) particulate levels to total suspended particulate (TSP) levels ranges from near 1:1 to approximately 1:5, it has become apparent that both residential wood combustion (RWC) and road dust are important sources of ambient particles, with their relative impact depending on meteorological conditions. (RWC emissions are predominantly smaller than 2.5μ in diameter and road dust is predominantly larger than 2.5μ in diameter). Other sources of particles in the Missoula airshed include wood-products industry point sources and vehicular exhaust.

A number of studies have been conducted to assess the sources of airborne particles in Missoula. The results of the studies have concluded that RWC is the major source of respirable particles and road dust is the major source of coarser particles. (See for example reference 1.) However, even previous chemical mass balance (CMB) studies have failed to adequately quantify the relative contributions of particulate sources due to a limited number of samples, non-representative source profiles, or inadequate analytical data.

A key factor in performing CMB source apportionment is representative source profiles containing data for the chemical species that occur at highest concentrations in the sources. The sampling strategy, instrumentation, and analytical techniques used to obtain source data for the Missoula airshed are discussed here. The chemical compositions of a number of sources which have been completed to date are also presented. Selection of ambient samples for detailed analysis is currently in progress.

SOURCE SAMPLING

Several different source sampling techniques were used. Samples for RWC were obtained in the plume, typically one meter from the chimney top to permit organic compounds to condense. A specially-designed sampler with dual inlets was used. One inlet was fitted with a Teflon filter for inorganic analysis and one inlet was fitted with a quartz filter for carbon analysis. No effort was made to size categorize the emissions, as the mean mass distribution of RWC emissions is well less than 2.5μ . Homes in Missoula were selected at random for sampling. Each RWC sample was a composite of three to five wood-burning appliances. Samples from a hog fuel boiler, diesel trucks, and a diesel train were also collected with this sampler.

Road dust samples were collected with a vacuum-cleaner-like device from three paved streets in the vicinity of the ambient monitoring site. One street was classified as residential, one as a collector, and one as a main arterial. Samples before and after application of winter sanding material were collected. The samples were dried at 110°C for 24 hours, sieved to less than 38μ and resuspended onto both Teflon and quartz filters. A dichotomous sampler fitted with a PM_{10} inlet was used for collection of the resuspended dust, which permitted subsequent analysis on two size fractions ($<2.5 \mu$ and $2.5\text{--}10 \mu$). A grab sample of the city sanding material was also dried, sieved, and resuspended in the same fashion.

Vehicular exhaust is being sampled (currently in progress) with a mobile dilution sampler. (For a description of dilution sampling see reference 2.) The vehicular exhaust is being collected onto Teflon and quartz filters after it is mixed (cooled and diluted) with filtered ambient air. The motor vehicles are being selected based on the typical make-up of vehicle types in the Missoula area. Samples are being collected while the vehicles are being driven in a normal fashion through residential and

commercial areas. As with the RWC samples, no attempt has been made to size categorize the emissions, as the predominant mass of vehicular particulate emissions is less than $2.5\ \mu$.

A wood chip (particle board) dryer/sander dust burner was sampled by placing two dichotomous samplers (PM_{10} inlets) into the plume about 1 meter from the exhaust ports. Teflon filters were placed in one sampler, quartz filters in the other. Since this source was a combination of physical and combustion processes, i.e., sander dust burner exhaust is used to remove moisture from wood particles, the size distribution of the emissions could not be assumed to be predominantly in the fine or coarse range, and hence dichotomous, rather than single filter, samplers were required.

ANALYTICAL TECHNIQUES

X-ray fluorescence spectrometric (XRF) analysis was conducted for 27 elements on the Teflon filters with a Kevex Corporation Model 700/8000 X-ray Fluorescence Analyzer. A Cahn 25 electromicrobalance was used to determine particulate mass. Carbon analyses were performed by the thermal/optical technique on the quartz filters. Water soluble metals are being analyzed (in progress) by inductively coupled argon plasma spectroscopy (ICAP) on the Teflon filters after completion of the XRF analysis.

SOURCE PROFILES

The RWC profile (Figure 1) represents the mean values from eight filter sets collected from a total of 35 homes. A variety of woodstoves and fireplaces are included in this composite. The most commonly burned woods were Douglas fir, lodgepole pine, larch, and ponderosa pine. If the homeowner had burned household trash within an hour previous to the sampling visit no sample was taken. The mean ambient temperature was $-6^{\circ}C$ during the sampling. While Figure 1 illustrates the overwhelming importance of quantifying the organic carbon (OC) and elemental carbon (EC) of RWC source samples and of the fine fraction of ambient aerosols in areas where a RWC impact is suspected, the elemental composition of RWC emissions too low to be seen in Figure 1 is important as well for CMB modeling. The key RWC elements in decreasing weight percent in the composite fingerprint are: K (0.35%); Cl (0.18%); S (0.14%); and Ca (0.13%).

The street dust profile is, as mentioned, a composite of three city streets in the vicinity of the ambient monitoring site. The samples were collected prior to the time winter sanding was started. Figure 2 illustrates the chemical composition of the coarse ($2.5-10\ \mu$) fraction. The principal features of both the fine and coarse road dust fingerprints are the presence of organic and elemental carbon and the presence of the geological species of Al, Si, K, Ca, Ti, Fe, and carbonate carbon (CC). In general, the chemical composition of the fine and coarse fractions are relatively similar, except that: (1) There is more than twice as much organic and elemental carbon in the fine fraction; and (2) Measurable carbonate carbon was found in the coarse fraction, while none was found in the fine fraction. The composition of the city sanding material was very similar to the road dust, with the exception that the elemental and organic carbon contents were much lower. This suggests either that much of the road dust originated from the paved streets was derived from the previous year's sanding, or that the chemical composition of the local street dust is similar for a geological reason to that of the sanding. An increased organic and elemental content would be expected, with time, due to vehicular exhaust, tire wear, asphalt, and vegetative fragments. It should be noted that the current source of sanding material is highly-weathered tertiary deposits with a high fine content (12.9 percent less than $75\ \mu$) which is predominantly clay and has a low durability index (34).

Figures 3 and 4 illustrate the chemical profiles of two small wood-products point sources in the Missoula airshed. The chemical composition of emissions from a hog fuel boiler burning pulverized ponderosa pine with a cyclone emission control unit is illustrated in Figure 3. The composite fingerprint is the average composition of three samples. The key features of the fingerprint are the high elemental carbon content and relatively high organic carbon, potassium, and calcium contents. Figure 4 shows the chemical composition of the fine fraction of emissions from a particle board dryer which utilizes the exhaust from a sander dust burner for a heat source. The system is fitted with several cyclones. The composite fingerprint illustrated in Figure 4 is the average of two samples collected from two different cyclone exhaust ports. The key features of its fingerprint are the high chlorine (chloride) content and the relatively high organic carbon, sulfur, potassium, and calcium contents. The chemical composition of both the fine and coarse fractions are quite similar, except the coarse fraction has more than twice as much organic carbon.

Two types of vehicular exhaust fingerprints are being developed. These are for heavy diesel trucks (a diesel train was also sampled) and for gasoline cars and light trucks. A composite fingerprint for diesel trucks has been developed. The three principal chemical species are organic carbon (88%), elemental carbon (8%), and sulfur (0.7%). All other elements were found to be at levels of less than one tenth of one percent. The gasoline car and light truck sampling is currently in progress.

AMBIENT SAMPLING

The ambient monitoring site was Rose Lawn Park, which is in a residential area near a commercial district. Dual dichotomous samplers were operated simultaneously for 24 hours once every 6 days during the winter. Teflon filters were used with one sampler and quartz filters with the other. Based on the particulate mass concentrations determined from these filters and meteorological records, a subset of filters will be selected for detailed chemical analyses. The same chemical species as were measured on the source sample will be measured on the ambient sample to optimize CMB modeling calculations.

CONCLUSIONS

The chemical profiles which are being developed for principal particulate sources in the Missoula, Montana, airshed are distinctively different enough to permit quantitative CMB source apportionment modeling to be conducted. Chemical species were selected for analysis based on their usefulness in distinguishing the impact of major sources characteristic of Missoula. These include 27 elements measured by XRF; carbon species analysis; and analysis of water soluble metals³ (viz. Na and K), which is in progress. Unlike many CMB modeling studies, equal resources were dedicated to measuring the chemical composition of both source and ambient samples in the airshed.

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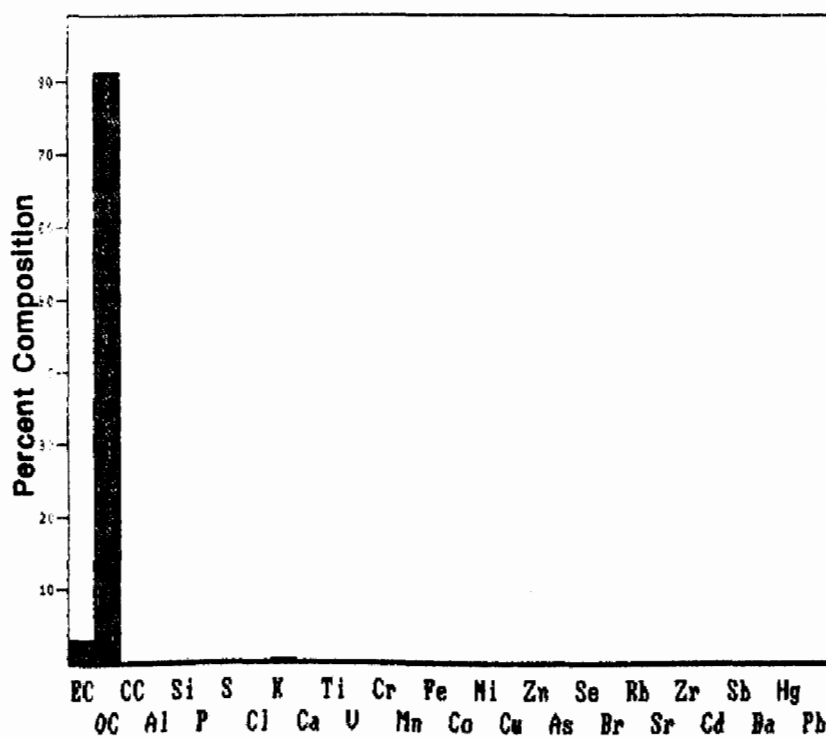


Figure 1. NWC (OT0100001, -2, -3, -8, -10, -11, -13, -14)

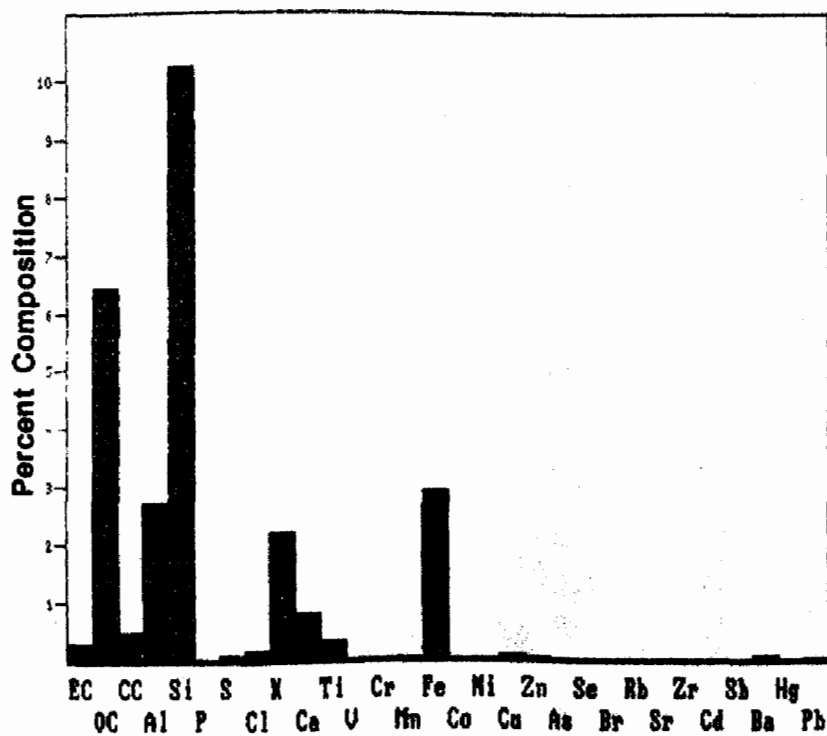


Figure 2. STREET DUST/COARSE (ST0200002, -4, -6)

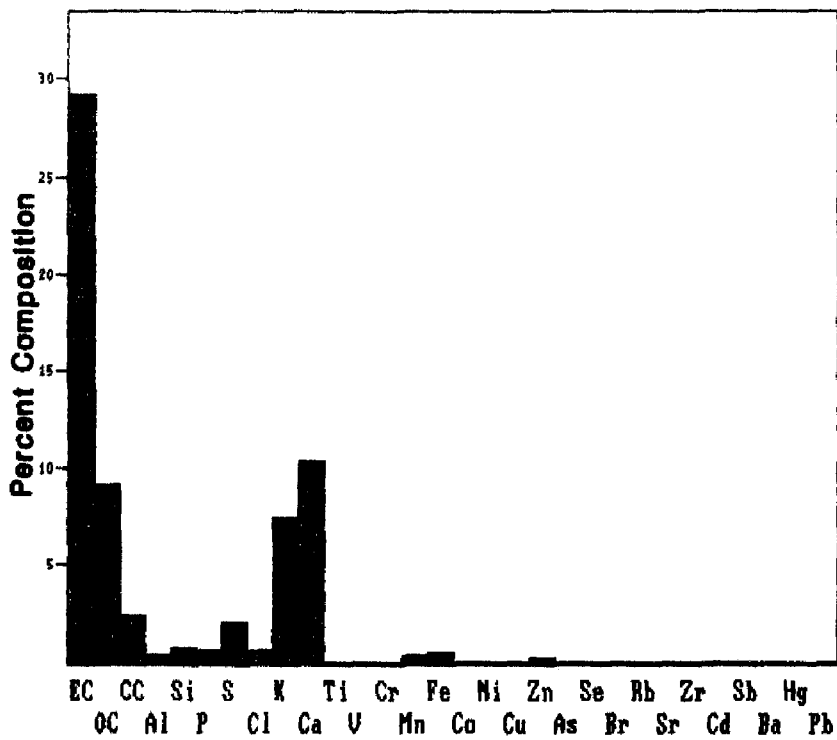


Figure 3. WHITE PINE HOG FUEL BOILER (OT0100005,-6,-7)

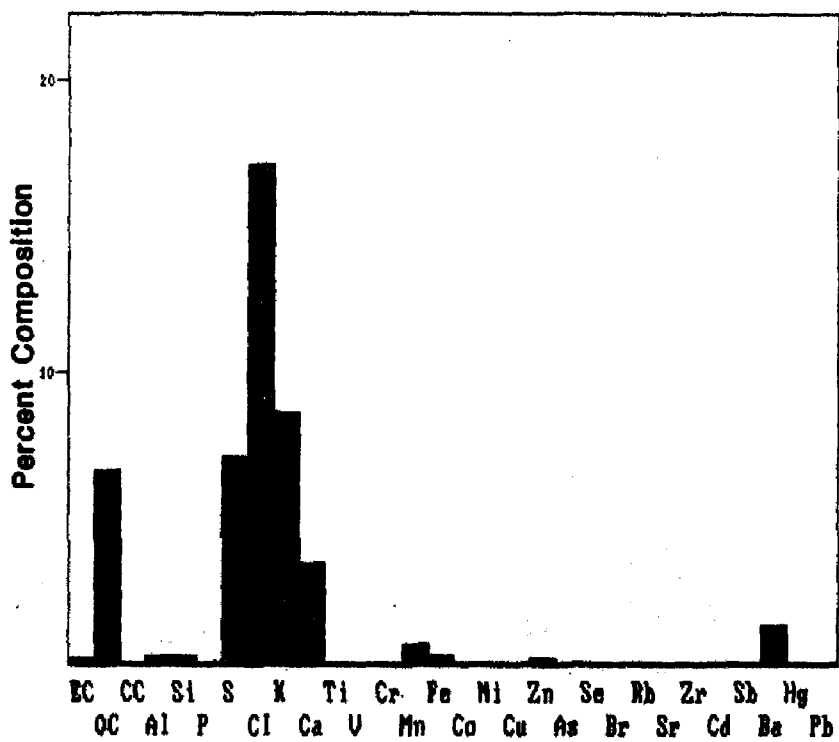


Figure 4. LP CHIP DRYER/FINE (OT0100050,-62)

**FIELD INVESTIGATION OF CATALYTIC AND LOW EMISSIONS
WOODSTOVE PARTICULATE EMISSIONS, EFFICIENCY AND SAFETY**

**Paul Burnet
OMNI Environmental Services
10950 S.W. Fifth Street
Beaverton, Oregon 97005**

**Steve Morgan
Technical Development Corporation
11 Beacon Street, Suite 1100
Boston, MA 02108**

EXECUTIVE SUMMARY

As the Northeast Cooperative Woodstove Study in New York and Vermont nears the conclusion of its second heating season, interim data and findings from the first heating season have been analyzed and reported. The purpose of this paper is to summarize the data and findings from the first heating season and describe methodological changes undertaken in the study during the second heating season, completed in April 1987. The major objective of the Northeast Woodstove Study is to determine the effectiveness of catalytic and low emissions stove technologies in reducing wood use, creosote and particulate emissions. Measurements were taken in 66 homes for gross wood use and creosote accumulation and 32 homes for particulate emissions and directly measured wood use. These data and findings are preliminary and for use in indicating potential directions of, and changes to, the study; the contents of this paper are preliminary and not intended for dissemination.

While catalytic and low emission stove technologies reduce particulate emissions from 75% to 90% compared to conventional stoves in laboratory tests, results from our first year in the field performance are not nearly as impressive. In the first year of the study, particulate emissions in catalytic stoves averaged 24.3 grams per hour, or about 35% lower than conventional stoves. Oregon certified non-catalytic stoves, based on very limited data, averaged emissions levels about 50% lower than conventional stoves. The sample of only three stoves in this group very much reduces the significance of this finding. The performance of add on/retrofit devices revealed no significant difference than that of conventional stoves.

Catalytic and low emission stove technologies appear to reduce creosote accumulation by approximately a factor of 2 in comparison to conventional airtight stoves. Average creosote depositions in chimneys serving catalytic stoves were .51 kg creosote per thousand heating degree days.

Wood use in catalytic stoves averaged about 25% lower than in conventional stoves. This finding is consistent with laboratory efficiency tests for these technology groups. The performance of add-on retrofit stoves in wood use was not significantly better than conventional stoves. Thirty-five catalysts were investigated in the first year study. Of these, 6 physically deteriorated, while another 6 catalytic devices experienced operational and other problems. Laboratory testing of 3 catalysts which failed in the field revealed disparate evidence about the extent to which catalyst combustor, stove technology, and/or operator behavior contributed most to the failures.

I. Background

The Coalition of Northeastern Governors (CONEG) contracted OMNI Environmental Services, Inc. to conduct a two-heating season study of residential woodburning stoves. This study addresses the performance and effectiveness of stoves equipped with catalytic combustors relative to other woodburning appliances. A total of 66 homes were examined in the study; 33 in the Glens Falls area of New York State, and 33 in the Waterbury, Vermont area. Project sponsors include:

- o U.S. Department of Energy;
- o U.S. Environmental Protection Agency (EPA);
- o New York State Energy Research and Development Authority (NYSERDA);
- o Twelve stove and appliance manufacturers;
- o Vermont Agency of Environmental Conservation (VAEC); and
- o New York Department of Environmental Conservation (NYDEC).

A variety of performance parameters were examined in the study:

- o Emissions characteristics of catalytic and non-catalytic stoves;
- o Wood use characteristics of catalytic and non-catalytic stoves;
- o Creosote formation in flues serving catalytic and non-catalytic stoves;

A variety of integrated catalytic stoves, add-on/retrofit devices and low emission non-catalytic stoves were provided by participating manufacturers to the study for installation in the study homes. Study participants were volunteers selected from lists provided by the VAEC and NYDEC. Sixty-six homes participated in the study. A group of 32 homes, divided equally between the two study areas, was designed as Group I. These homes were equipped with computerized data records and emission samplers. Four additional homes in this group were available as backups. A group of 24 homes, designated Group II, was monitored for wood use and maintained user log books. Group III homes, totalling six, had existing catalytic stoves, and were measured for wood use and emissions for a 1-week period. All the study homes had pre-, mid- and post-season woodpile volume, species, and moisture measurements. Creosote weighings were conducted on sweepings from the flues of all study homes.

Most Group I homes had new stoves installed at the beginning of the study, which were to remain in place for the duration of the project. Several existing stoves were left in place to serve as baseline stoves. Most Group II homes will be provided with new stoves for the second heating season of the project, having used their existing conventional stoves for the first season. Group III homes were existing catalytic stoves, and no change of stove technology is to be conducted.

The 1985-86 heating season had the following stove technologies by study group:

	<u>Catalytic</u>	<u>Add-On/Retrofit</u>	<u>Low Emissions</u>	<u>Conventional</u>
Group I	14	12	3	7
Group II	3	0	0	21
Group III	6	0	0	0
Total	<u>23</u>	<u>12</u>	<u>3</u>	<u>28</u>

The stove technology categories were composed of several different stove models, as identified below:

<u>Stove Technology Type</u>	<u>Stove Model Types</u>	<u>Comments</u>
Catalytic	4	Four manufacturers provided new stoves for the study. Group III homes represented three additional models. Catalyst stoves are defined as having the combustor as an integral part of the new stove.
Add-On	3	Add-on devices are defined as units which can be added to virtually any stove at the flue collar.
Retrofit	2	Retrofit devices are designed to fit one stove model or design type, and typically are close-coupled to the stove.
Low Emission	2	Low emission stoves are defined for this study as models which have been certified under the Oregon DEQ program. A third stove was to be included in the study, but manufacturer withdrew unexpectedly in November, 1985, reducing the number of low emission stoves in the study.
Conventional variety		Existing stoves in study homes, representing a range of designs. Generally categorized as typical of conventional woodstove technology.

II. Equipment

Two major objectives of the study involved defining wood use and stove performance under typical home and activity conditions. In addressing these objectives two instruments were developed: the Data LOG'r system and the Automated Woodstove Emission Sampler (AWES).

A. Data LOG'r System

The Data LOG'r is a programmable micro-processor/controller with the capability of receiving, processing, and recording digital and analog signals. As used in this study, it can accommodate over 30 days of data between servicing. The Data LOG'r was programmed to record and store the following information:

- o Starting date, time, and unit (Data LOG'r) serial number;
- o Daily date and time;
- o Flue and catalyst temperatures every 5 to 10 minutes;
- o Room temperature, outdoor temperature, and unit temperatures recorded and stored in 15-minute intervals;
- o Record the alternate home heating system status (on or off);
- o Wood weights and coalbed condition recorded on fueling the stove;
- o Record oxygen measurements when AWES sampling; and
- o Record powerline status every 5 minutes.

The Data LOG'r was also programmed to control the AWES sampler, turning the AWES sampler on and off in the proper sequence.

Wood weights were measured on an electronic scale with an attached woodbasket. Scale readings were recorded by having a study participant use an attached keypad in a prescribed sequence. flue temperature, catalyst temperature (where applicable), ambient room temperature, and auxiliary heating system on/off conditions were recorded at 5-10 minute intervals. Figure 1*shows a diagram of the Data LOG'r and woodbasket scale equipment.

B. AWES Samplers

The AWES Sampler is an automated sampler which allows the determination of total particle and/or semi-volatile emission rates. It consists of a sample probe which is inserted into the stove or chimney, followed by a heated filter, an organic absorbent (XAD-2 resin), silica gel, a flow-regulating orifice, and a pump. Some samplers are equipped with oxygen sensor cells to record oxygen concentration in the flue gas. Figure 2 shows a schematic of the AWES sampler. The samplers used in

*Figure 1 not included in this publication.

this study were designed to operate intermittently without servicing for 1 week, 1 minute on, 29 minutes off. The resulting sample represents an integration of stove emissions during the sampling period. Simultaneous samples were obtained at up to two of four potential locations: before the catalyst, after the catalyst, at the flue collar, and at the chimney exit. Data from samplers at the flue collar and after catalyst locations were compiled for this report for the purpose of comparing stove technologies.

III. Creosote Measurements

A. Methodology

Documentation of creosote accumulation in study home flues was conducted by measuring the net amount of material removed from each chimney by sweeping. Chimneys were swept at the beginning, middle, and end of the 1985-86 study by professional chimney sweeps. Creosote dislodged by the sweeping was collected by the chimney sweeps. The first sweeping was to establish "clean" conditions, while creosote collected in the second and third sweepings was weighed. The mass of creosote collected was then normalized by heating degree days (HDD) occurring during the creosote accumulation period between sweepings. Creosote samples from the mid-season sweeping for all study home chimneys have been sent to the Solar Energy Research Institute (SERI) for chemical analysis.

The heating load, in HDD, during the study period was calculated for each home. Heating degree days were summed for the period between creosote sweepings, yielding the heating load for the specific period for each home. Data were used from the Waterbury and Glens Falls weather recording stations maintained by the Northeast Regional Climate Center. Glens Falls data were used for New York homes and Waterbury data were used for Vermont homes.

B. Results

Creosote measurement data were compiled for individual homes and by stove technology grouping. Results are summarized in Table 1. Data are reported in kilograms of creosote (total mass of material removed from the chimney by sweeping) and are normalized by HDD. Frequency distributions of normalized creosote accumulations are shown by stove technology grouping in Figures 3 through 6.*

Both catalytic and low emission stoves showed similar results. Mean creosote accumulations of 0.51 and 0.55 kg/1000 HDD were obtained from the catalytic and low emission installations, respectively. The catalytic value excludes study homes V05, which was discovered to have an improperly seated combustor, which allowed combustion gases to bypass the combustor. The combustor had apparently been jarred out of

*Figures 3-6 not included in this publication.

position during stove installation. The creosote accumulation value for V05 (with improperly seated combustor) was 2.77 kg/1000 HDD, which is nearly three times higher than the next highest value from a catalytic stove.

Catalytic stove values showed a minimum of 0.19 and a maximum of 0.93 kg/1000 HDD (exclusive of V05 data), with a standard deviation of 0.24. Low emission stove values showed a minimum of 0.16 and a maximum of 1.33 kg/1000 HDD, with a standard deviation of 0.51.

Conventional stoves appear to have lower average rates of creosote accumulation than the add-on/retrofit devices. Mean values of 1.07 and 1.26 kg/1000 HDD were recorded for the conventional and add-on/retrofit groups, with standard deviations of 0.68 and 0.94, respectively. The conventional stove groups had a minimum value of 0.06 and a maximum of 2.91 kg/1000 HDD. The add-on/retrofit group had a minimum value of 0.37 and a maximum of 3.60 kg/1000 HDD.

The high degree of variability in creosote accumulation data (as demonstrated by the high standard of deviation values) is due to a variety of factors, including stove operation practices, burn rates, and flue height, size and construction (inside vs. outside wall, solar exposure, etc.). It should also be noted that creosote is primarily condensed organic material, which may be revolatilized by high flue gas temperatures. Creosote mass in the chimney can therefore vary on a continual basis. These values are intended only to serve as a general indication of creosote accumulation by the various stove technology groups.

IV. Second Year Testing

The second year of testing will provide significantly new and more valuable data for the study. Twenty-four households switched to a different stove technology--conventional to catalytic or low emissions or vice versa. By this switch most of the "noise" created by operator behavior will be eliminated as a variable. Second, the project addressed safety considerations by allowing additional chimney sweeping and making renovations to chimneys which might have been hazardous. Third, the contractor rearranged the sampler locations. Automated Woodstove Emissions Samplers were removed from chimney tops and replaced at the flue collar or above the add-on catalysts, depending upon stove technology. Finally, dual samplers at several locations provided greater confidence in the precision of the AWES data, while still allowing direct comparison in performance to different stove technologies.

CONCLUSION

In August, CONEG will release the final report of the full two-year study. At this printing, CONEG, EPA, and NYSERDA are

considering a third year study. The objective of another year of testing are several in number.

The sponsors wish to investigate further the durability and degradation of catalysts over time. Not only are the sponsors interested in absolute longevity of the catalysts, but also in the reasons for the degradation. To what extent are the combustors themselves, their interaction with stove technologies, and operator behavior responsible for this degradation? The implications for the EPA enforcement actions and consumer behaviors will be significant over the next several years.

The field study will also investigate the impact of operator training on catalytic stove performance, providing an operator manual and face-to-face training. Quality training may have a significant impact on field performance, closing a considerable gap between laboratory and field testing on emissions levels in particular.

For the first time, sponsors are considering an investigation of indoor air emissions. Anecdotal evidence suggesting that low emission non-catalytic and catalytic stoves generate as much or more indoor air particulates and POMs prompt sponsor interest in measuring indoor air emissions. Chimney conditions and their interface with stove technologies may also undergo study in this indoor air investigation. Air changes per hour will also receive attention to enable a study of the impact of house tightness upon indoor air emissions and stove performance.

The study sponsors are also interested in testing the relationship between burn rates and emissions. To do so, multiple AWES could be installed in up to four homes to measure stove emissions under different operating regimes: one AWES collects during high combustor temperature periods; another during low combustor temperatures. A third AWES could record when the bypass lever is open or closed. To improve catalyst efficiency calculations, the sponsors are considering the installation of a second oxygen sensor to an AWES pair, thus permitting calculation of mass concentration, emissions rates and emission factors before and after the combustor.

As EPA moves to implement the New Source Performance Standard, these and related questions will have a major impact on the consumer and stove manufacturers. The research community can make a substantial impact on issues affecting the evolution in stove design and consumer operation of cleaner-burning wood appliances.

Table 1. **Comparison of Performance by Stove Technology Groups**

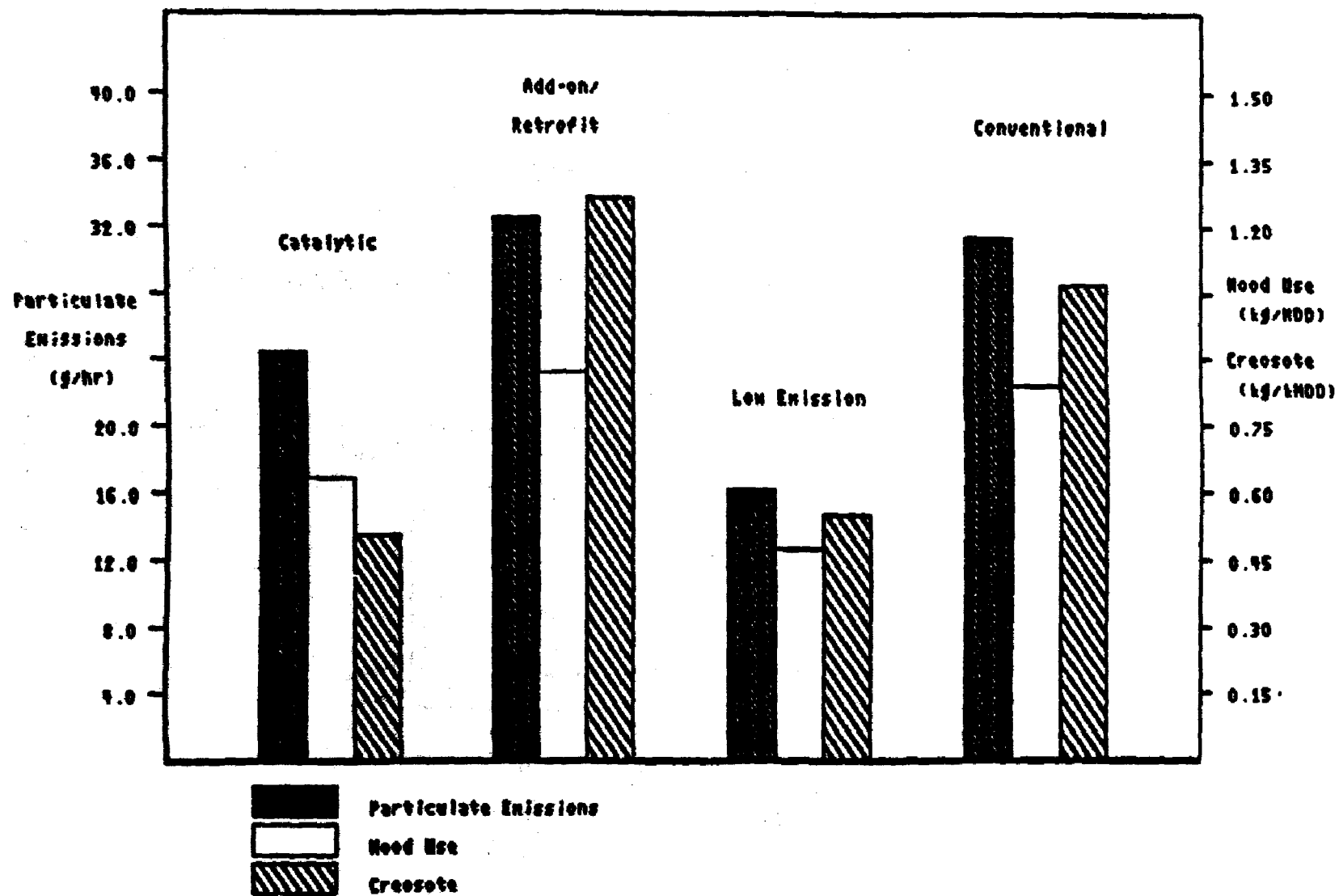
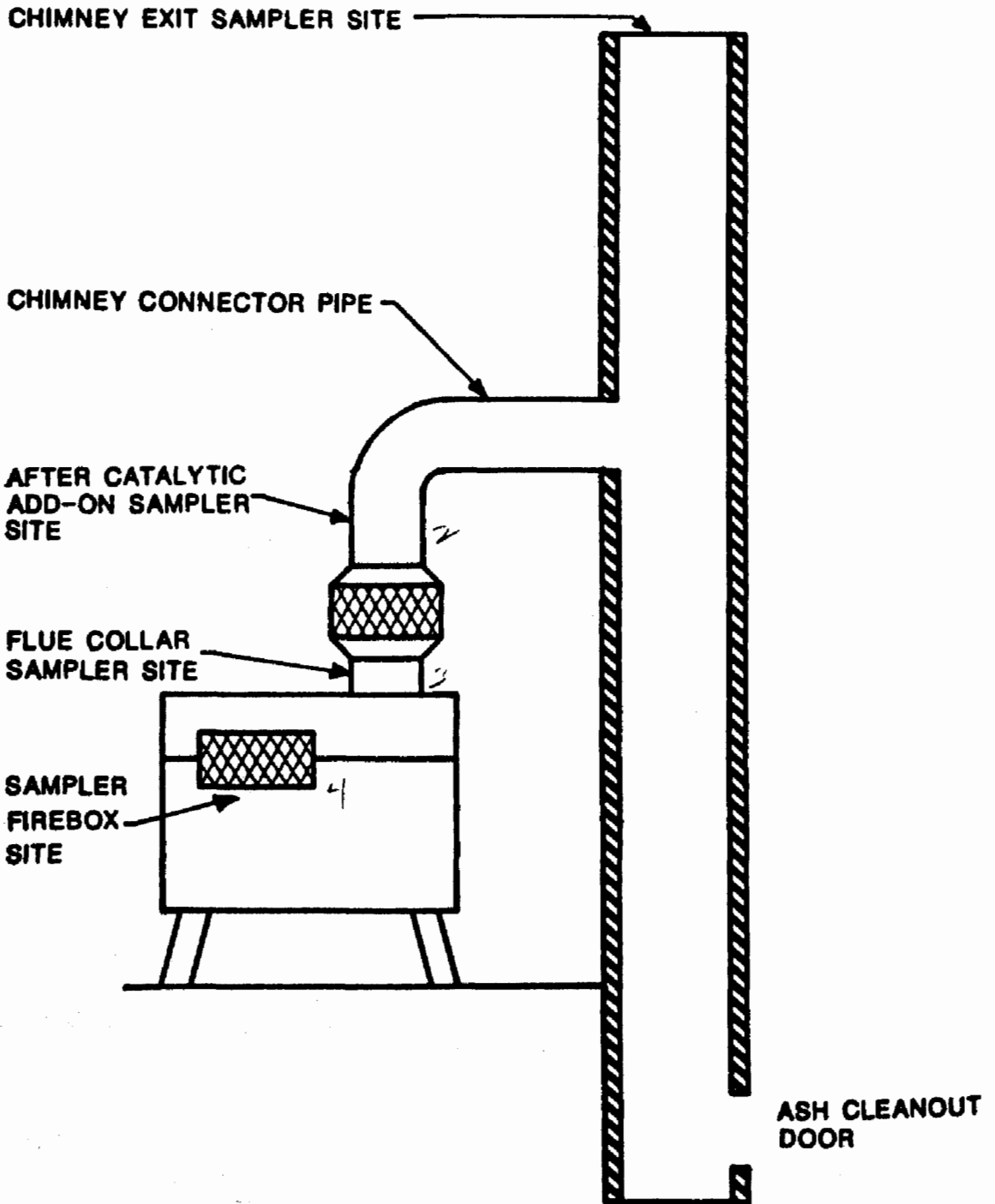


Figure 2



AWES SAMPLER LOCATION SITES

**THE ENVIRONMENTAL PROTECTION AGENCY'S ACCREDITATION
PROGRAM FOR WOOD HEATER TESTING LABORATORIES**

Peter R. Westlin, J.E. McCarley, George W. Walsh
Emission Measurement Branch
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina

In the proposed regulations for certifying new residential wood heaters, the U.S. Environmental Protection Agency (EPA) is planning to accredit emission testing laboratories. The laboratory accreditation involves both the EPA and the National Voluntary Laboratory Accreditation Program (NVLAP), National Bureau of Standards. The NVLAP accreditation requires the laboratory to complete a technical application which describes the testing facility, personnel, and training procedures. An inspection of the laboratory by technical personnel is also required.

The EPA accreditation requires the laboratory to complete a number of administrative items and to complete a demonstration of proficiency using the emission testing procedures defined in the regulation. EPA will review the capabilities of the laboratory personnel to follow the test methods and to prepare an accurate and complete report of the procedures and results.

Laboratory accreditation is a new function for EPA and has resulted in a number of new tasks. These tasks include administering applications, scheduling inspection visits, establishing proficiency demonstration requirements, and reviewing test reports and results for laboratory evaluation purposes. These tasks are designed to provide standardization and consistency between testing laboratories in conducting wood heater certification tests.

INTRODUCTION

On February 18, 1987, the Environmental Protection Agency (EPA) proposed performance standards and rules for new residential wood heaters. According to the rules, wood heaters sold after July 1, 1990, must be certified; that is, prototype wood heaters representing a model line must demonstrate specific emission control capabilities over a range of operations. Only accredited testing laboratories who have demonstrated minimum administrative and technical capabilities may perform the certification emission testing of wood heaters.

The purpose of this paper is to outline EPA's role in the laboratory accreditation program and to discuss the experiences EPA has encountered in implementing the program.

THE REGULATORY REQUIREMENTS

The proposed regulation lists specific requirements for laboratory accreditation. The list includes application to EPA, satisfaction of some administrative qualifications, and demonstration of testing proficiency. The Emission Measurement Branch (EMB) of the Office of Air Quality Planning and Standards is designated to implement the accreditation program and provide the detailed procedures for completion of these requirements.

A testing laboratory seeking accreditation must send a letter of intent to the EMB in Research Triangle Park, North Carolina. Upon receipt of the letter, EMB will issue an outline of the specific administrative and technical steps to be completed by the testing laboratory.

The first step is to be accredited by the National Voluntary Laboratory Accreditation Program (NVLAP), a program sponsored by the National Bureau of Standards, Department of Commerce. The NVLAP accreditation involves completing a detailed application form. The laboratory must describe the testing facility, the qualifications of the personnel, the organization for certification testing, and the quality assurance procedures. A technical expert representing NVLAP will conduct an on-site visit to review the facility and determine its compliance with the requirements of the regulation. The NVLAP usually charges a fee for conducting the accreditation evaluation.

The proposed regulation allows laboratories accredited by the State of Oregon by January 1, 1988 (grandfathered laboratories) to apply for EPA accreditation and forego the NVLAP accreditation.

The second step in the accreditation process is to demonstrate proficiency with the test procedures used in certifying wood heaters. The proficiency test demonstration requirements have been developed by EMB, and these are being distributed to laboratories seeking accreditation. An EMB technical expert will observe the laboratory's techniques during the proficiency demonstration and determine whether the specified procedures are followed.

Step three in the accreditation process is to write a complete report of the proficiency demonstration test and submit this report to EMB for review. The test report format is specified in the test procedures. An EMB technical person will review the test report for completeness and accuracy and will determine whether the specified procedures and calculations have been followed.

An evaluation of proficiency based on a comparison of emission test results with some known results is not part of the proficiency demonstration at this time. However, the emission data contained in the proficiency report are compared, in general, with results from other laboratories in order that dramatic errors can be identified. Requiring a laboratory to retest is a possibility. A more statistically based data review will be explored as more data on the predictability of wood heater performance are developed.

The fourth step in the accreditation process is an EMB review of the results of the on-site evaluation, the report review, and the recommendations of the EMB technical experts involved in the laboratory evaluation. If the laboratory's procedures and report are found to be acceptable, EMB will issue a notice or certificate of accreditation to the laboratory. Accredited laboratories then may conduct certification tests of wood heaters according to the regulations and as long as the procedures and personnel at the laboratory remain the same as during the accreditation evaluation. The accreditation notice includes expiration dates that indicate when the accreditation evaluation shall be repeated.

The proposed regulation includes a requirement for accredited laboratories to participate in an annual demonstration of proficiency. The EMB proficiency test requirements specify when this demonstration must be completed each year and describe other details of the demonstration procedures that may change from year to year.

EPA'S ACCREDITATION PROGRAM EXPERIENCES

NVLAP Accreditation

Accreditation of laboratories measuring the emissions from wood heaters is not an area with which NVLAP has had a great deal of experience; NVLAP has accredited laboratories who determine safety specifications for wood heaters, but has not accredited laboratories who conduct comprehensive emission testing. The EPA has worked with NVLAP in developing criteria for evaluating emission testing capabilities within the usual NVLAP approach.

Administrative complications have developed in combining the tasks of the two accrediting groups, NVLAP and EPA, and in establishing responsibilities for the various functions. In addition, it has become apparent that the best qualified persons available for the evaluation of laboratory capabilities and of the proficiency test results are EPA emission testing personnel within EMB or emission testing contractors familiar with EPA test procedures. Because the budget of neither of the two accrediting groups is sufficient to contract all of the accreditation functions, the burden of the accreditation efforts has fallen upon the EMB emission testing staff. At this time, EMB is conducting the

accreditation program without NVLAP's assistance, and a section of the preamble to the proposed regulation asks for comments on continuing in this fashion.

Test Proficiency Demonstration

The EPA accreditation group has prepared an outline describing the requirements for demonstrating proficiency with the wood heater Test Methods 5G, 5H and 28. Seven elements are identified and defined. These are:

1. Definition of a Testing Laboratory. The testing organization and facilities including the key personnel, the testing shop, the analysis area, and the testing equipment. The testing laboratory may include capacity for more than one wood heater test at a time provided the availability of key personnel and equipment reflects this capability.

2. The Demonstration Test. An emission test of a wood heater selected by EPA and obtained independently by the testing laboratory. There shall be a minimum of eight test runs, two in each of four burn rate categories. The testing laboratory shall follow Method 28 and either Method 5G or 5H (or both) and operate two particulate sampling trains simultaneously. The testing laboratory shall use the same sampling method as will be used for certification testing.

3. Selected Wood Heater. The Catalytic Fir, AK-18, manufactured by Sweet Home Stove Works, Inc. The criteria for selection includes current Oregon certification, relatively small firebox volume (for shorter run times), catalyst equipped, and a burn rate range that spans that specified in the method.

The wood heater selected for the proficiency demonstration may be different in succeeding years. Notification of the selected wood heater and any other changes to the demonstration procedures will be issued by EMB by October 31 of each year, and the annual proficiency demonstration must be completed by April 15 of the following year.

4. Notification and Observations. Notification to EMB at least 30 days prior to the start of the proficiency demonstration. An EPA observer may be present during part or all of the demonstration.

5. Reporting Requirements. A complete test report of the proficiency demonstration as specified in Method 28. Results of the duplicate train values are reported in a separate table. The report should address the criteria for deleting or including test run results as specified in the methods, but no data collected during the proficiency demonstration shall be deleted.

6. Participation and Delivery Dates. Required for all testing laboratories, including the Oregon grandfathered facilities, for the initial proficiency demonstration as described. The report of the initial proficiency demonstration results for the grandfathered testing laboratories is due April 15, 1987. Other testing laboratories shall complete the proficiency demonstration and the reporting before an accreditation certificate is issued by EMB.

7. EPA Response. Review of the test report for compliance with the requirements in the test methods. A written evaluation will be issued by EMB within 30 days of receipt of the report. A certificate of accreditation will be issued upon satisfactory completion of the accreditation requirements.

The four grandfathered testing laboratories and others who have indicated an interest in pursuing the EPA accreditation have received these directions. A number of laboratories have completed the testing portion of the demonstration.

One purpose of the EPA review is to provide guidance to the testing laboratories in achieving consistency and some standardization in the calculation and presentation of test results. The EMB technical personnel use a comprehensive check list in reviewing the reports. This check list covers the completeness of the descriptions of the test facility, the wood heater, the test procedures, and the summary of the results. The reviewer checks the calculations and results in detail using the raw data provided in each report. The reviewer notes discrepancies and brings these to the attention of the testing laboratory. In some severe cases, a testing laboratory may be asked to submit a revised test report.

Another purpose of the test data review is to satisfy a section of the proposed regulation that requires EPA to evaluate the precision of repeatability of wood heater emission test data. By January 1, 1990, EPA is to document the statistical parameters to be used in reviewing both accreditation test data and wood heater certification test data; or, EPA will determine that the data available at that time are insufficient to establish such repeatability values.

Review of Proficiency Test Results

The proficiency test program provides EPA with a unique opportunity to compare results collected with the certification procedures as conducted by different laboratories under conditions simulating actual certification tests. The EMB has only begun collecting the emission test data from the testing laboratories and is not yet prepared to conduct statistical evaluations of the test results. The EMB will likely conduct a rigorous statistical evaluation of duplicate train results as well as comparison of results between laboratories. Establishment of acceptance criteria for laboratory test results will enhance the efforts towards standardization of wood heater certification testing.

SUMMARY

The proposed wood heater regulation has imposed on the EPA a new responsibility of testing laboratory accreditation. The EMB of the EPA has undertaken this task which includes administering applications, scheduling inspection visits, establishing proficiency test demonstration requirements, and reviewing the test reports and results. The EPA will also review the proficiency test data in order to establish acceptance criteria for the results. These tasks are designed to provide standardization and consistency between the testing laboratories in conducting the wood heater certification tests.

IMPORTANCE AND BENEFITS OF DEVELOPING DATA QUALITY OBJECTIVES
FOR AIR TOXICS DATA COLLECTION ACTIVITIES

Gary L. Johnson and Stanley M. Blacker
Quality Assurance Management Staff
U.S. Environmental Protection Agency (RD-680)
Washington, DC 20460

ABSTRACT

Implementation of the EPA Air Toxics Strategy during the next five years will provide several activities which will benefit from the Data Quality Objectives (DQO) process. The DQO process is an approach to designing environmental data collection programs that incorporates consideration of the use of the data in decision-making, the quality of the data needed for the decision, and the available time and resources for the data collection. Accordingly, data collection programs will more likely meet the needs of decision makers in a cost effective manner when the DQO process is used.

The current Air Toxics Strategy calls for an increased State and local role in data collection and in regulation, and an increased Federal role in technical assistance. This paper will describe important elements of the DQO process and will identify several areas of the Air Toxics program where the DQO process may be applied. For one selected area, the paper will address how to apply the DQO process and will discuss the benefits to be derived by following this process.

INTRODUCTION

Environmental data play a critical role in many EPA decisions. In view of the importance to the Agency of such data, the process used to design data collection systems should place heavy emphasis on defining the regulatory (or programmatic) objectives (Why are the data needed?), the decision to be made from the data (How will the data be used?), and the possible consequences of the decision being incorrect (What is the risk of making a mistake?). A design process that fails to explore these issues and focuses only on collecting the "best data possible" can result in potentially serious problems, particularly if those who define the "best data possible" base their definition on the characteristics of the data themselves and do not consider the program decision to be made. The "best data possible" do not always yield the data needed to make the required program decision.

The Quality Assurance Management Staff (QAMS), in response to a requirement established by the Deputy Administrator in May 1984, has proposed an approach to environmental data collection program design based on the development of Data Quality Objectives (DQOs). This process provides a logical, objective, and quantitative framework for finding an appropriate balance between the time and resources available to collect the data and the quality of the data needed to make the decision.

The DQO process is currently being applied to several new Agency data collection programs whose results will impact important regulatory decisions. One of the major environmental issues being addressed by EPA, and one to which the DQO process may be particularly helpful, is the Air Toxics program.

In June 1985, EPA announced a strategy for the control of toxic air pollutant emissions from routine and accidental releases. The routine releases component of the Air Toxics Strategy focuses on the joint efforts of Federal, State, and local programs to deal with air toxics problems. The strategy builds upon existing programs developed under the Clean Air Act, augmented by expanded regulatory decision making by the States and the use of other Federal authorities as appropriate. The nature of the air toxics problem is complex and, as such, the problem has been addressed through several comprehensive programmatic approaches. These programs include:

- * Federal Regulatory Program for Air Toxics
- * High-Risk Point Sources Program
- * High Urban Risk Program
- * Enhancement of State and Local Air Toxics Programs
- * Enforcement and Compliance Programs for Air Toxics

Some approaches will utilize existing data bases to identify air toxics concerns; however, there will be needs for additional, specialized data collection by EPA, the States, and local authorities. As will be discussed later, new environmental data collection programs initiated under the Air Toxics Program will be more cost-effective to

Agency and other decision makers when the programs are designed according to the DQO process.

Overview of DQOs and the DQO Process

Data Quality Objectives are statements of the level of uncertainty that a decision maker is willing to accept in results derived from environmental data, when the results are intended for use in a regulatory or programmatic decision, such as, deciding that a new regulation is needed, setting or revising a standard, or determining compliance. In order to be complete, these quantitative DQOs should be accompanied by clear statements of:

- * the decision to be made;
- * why environmental data are needed and how they will be used;
- * time and resource constraints on the data collection;
- * descriptions of the environmental data to be collected;
- * specifications regarding the domain or universe of the decision; and
- * the calculations or analyses that must be performed on the data to yield information in the form needed for the decision.

These statements suggest that a stepwise process may be defined for each decision and data collection activity that incorporate each of the items above. Moreover, this process integrates logically with other, traditional quality assurance program elements.

Role of DQOs in the QA Program

The development of DQOs should be the first step in initiating any significant environmental data collection program. The DQO process helps to define the purposes for which environmental data will be used and sets guidelines for designing a data collection program that will meet the Agency's programmatic or regulatory objectives. Once DQOs have been developed and the design of the data collection activity has been completed, DQOs are used to define quality assurance (QA) and quality control (QC) programs that are specifically tailored to the data collection program being initiated. From the DQO, a Quality Assurance Project Plan (QAPjP) is prepared which details the QC criteria for the data collection, establishes data custody and analysis procedures, and provides for routine examination of the activity through audits and reviews. Thus, consideration of how the information will be used in the decision-making process is an important element of the QA management system that assures the quality of the data obtained will be sufficient to support the Agency decision. More importantly, perhaps, the DQO and the QAPjP derived from the DQO provide a measure or standard against which progress in the data collection activity may be evaluated.

The DQO Process

The DQO process consists of three stages with several steps in each stage. The first two stages result in proposed DQOs with accompanying specifications and constraints for designing the data collection program. In the third stage, potential designs for the data collection program are evaluated. Stage III results in the selection of a design that is compatible with the constraints of the program and should enable the program to satisfy the goals of the DQO. The process is intended to be iterative among the stages; that is, if the proposed constraints from Stage I, the proposed DQOs from Stage II, and the design alternatives analyzed in Stage III are found to be incompatible, the process may be repeated until the problems have been resolved.

A critical element of the DQO process is the genuine involvement and participation of decision makers. DQOs are developed through a top-down approach. The initial input and perspective of the decision maker is essential to the successful development of DQOs. The role of the decision maker may vary to some degree among programs from providing input or direction throughout the program to reacting to or concurring with options presented by key senior staff. Through their personal involvement, however, decision makers can ensure that the DQO process is used to properly design all significant data collection efforts. The decision maker can best articulate how the data are to be used and define any constraints on the data collection that are imposed by the nature of the decision to be made.

STAGE I: Define the Decision

Stage I is the responsibility of the decision maker. The decision maker states an initial perception of what decision must be made, what information is needed, why and when it is needed, how it will be used, and what the consequences will be if information of adequate quality is not available. Initial estimates of the time and resources that can be reasonably be made available for the data collection activity are also presented.

STAGE II: Clarify the Information Needed

This stage is primarily the responsibility of the senior program staff with guidance and oversight from the decision maker and input from the technical staff. The product of the Stage I process is carefully examined and discussed with the decision maker to ensure that the senior program staff understand as many of the nuances of the program as possible. Next, the senior program staff discusses each aspect of the problem, factoring into the process any necessary considerations of technical or policy issues. With the concurrence of the decision maker, specific guidance for designing the data collection program are generated. The results of Stage II include proposed statements of the type and quality of environmental data required to support the decision, along with other technical constraints on the data collection activity that will help to converge the search for an acceptable design in Stage III. These results are the proposed DQOs.

It is this stage of the DQO process that is generally overlooked.

STAGE III: Design the Data Collection Program

Stage III is primarily the responsibility of the technical staff, but both the senior program staff and the decision maker are involved to ensure that the outputs from Stages I and II are understood by all participants in the process. The objective of Stage III is to develop data collection plans that will meet the criteria and constraints established in Stages I and II. All viable options should be considered and presented to the decision maker for a final selection of the data collection program design. The decision maker must ultimately determine the best balance between the time and resources available to collect the data and the level of uncertainty expected in the final results.

The DQO provides management with an effective tool for improving the credibility and defensibility of regulatory or policy decisions based on environmental data collected. The usefulness of such a management tool can be seen through application of DQOs to one of the Agency's more complex environmental problems, the routine release of toxic air pollutants into the air.

Air Toxics Data Collection Activities

The Air Toxics Strategy proposes a significant change from traditional approaches to air pollution regulations. While the mainstay to date has been the National Emission Standards for Hazardous Air Pollutants (NESHAP) program, the current strategy focuses on a joint regulatory role by the Federal Government, States and local agencies. The State and local roles will be augmented by focused technical guidance and financial assistance from EPA. This approach also depends more on the use of existing and emerging data bases compiled under other authorities, such as New Source Performance Standards (NSPS) and the Superfund Amendment and Reauthorization Act (SARA). The Federal role will include the identification of local situations of sufficiently high cancer risk that State or local regulatory action is warranted. In addition, the problem of toxic air pollutants in urban areas poses several complicated questions. Additional environmental data are needed to help determine the contribution to the "urban soup" of mobile sources versus stationary sources. If risk assessment and other factors indicate that an urban air toxics problem clearly exists, then the decision on what to mitigate will depend on how well the contributing sources to the urban problem can be identified and quantified.

While a number of data collection programs address different aspects of the air toxics problem, all of them may be improved by application of the DQO process. As an example to illustrate how DQOs may be applied to air toxics data collection activities, the Toxics Urban Monitoring Program will be examined according to the steps of the process outlined previously.

DQO Example: The Toxic Urban Monitoring Program

The Toxic Urban Monitoring Program is one of several efforts to compile data on the nature of air toxics in urban areas. Some data are available from earlier monitoring efforts (e.g., SLAMS/NAMS) in which the samples collected for one purpose were analyzed as well for toxic chemicals. In addition, current programs, such as the Toxic Air

Monitoring System (TAMS) network, are helpful, even though the scopes of such programs do not totally address the needs of the urban program. The Toxic Urban Monitoring Program is intended to examine the 30 largest urban areas in the country to provide additional data on the cancer risks associated with the urban environment. In addition, this program will supply additional data on the relative contributions of mobile and stationary sources to the urban mix. Through application of the DQO process to this program, it is possible to define the issues that should be considered so that Agency decision makers may have greater confidence in the results of the monitoring program and the decision to be made.

STAGE I: Define the Decision

For the purposes of this example, it must be recognized that the expertise of the Air Office decision makers will not be duplicated. The discussion that follows is intended ONLY to demonstrate the PROCESS and STRUCTURE of DQOs as they can be applied to the Toxic Urban Monitoring Program. The actual design of the desired monitoring program remains with the Air program office.

In this particular example, a possible decision may be based on the general objectives of the Toxic Urban Monitoring Program. For example, the Federal decision might be stated as whether or not to mitigate the mobile source contribution, depending upon the relative contributions of mobile versus stationary sources. The steps in the DQO process and a few of the issues and questions which may be asked during Stage I based on this possible decision include the following:

- (1) Describe the decision. Are we really concerned about mobile sources? Which mobile sources? What age or engine type should we focus on?
- (2) Describe the information needed. What data are needed? Do we need to monitor source emissions or ambient concentrations? Do we data from street level or building roof level or both? During what time period (i.e., season, time of day, etc.) must data be collected?
- (3) Define the use of the environmental data. How will the monitoring data be used? Do we want the data to use for evaluating changes to current regulatory programs that should be considered. Are there inputs to the decision other than environmental monitoring data? If so, how important are they to the decision vis-a-vis the monitoring data?
- (4) Define the consequences of making an incorrect decision based inadequate environmental data. Under what circumstances could an incorrect decision be made? What are the implications of making an incorrect decision? What happens if we decide to mitigate mobile sources when the environmental data have incorrectly indicated that a problem exists (i.e., a false positive)? What happens if we decide not to mitigate mobile sources when the monitoring data incorrectly indicated that a problem does not exist (i.e., a false negative)?

- (5) Identify the resources and resources available. What resources are available to carry out the monitoring program? Given the available resources, does it make sense to make measurements in all 30 urban areas? If not, which urban areas have the priority?

STAGE II: Clarification of the Information Needed

The information produced by the decision maker should now pass to the senior program staff. The Stage I outputs should, as a minimum, include statements of the decision to be made, the information needed for the decision, why the data are needed, how the data will be used, and the constraints on time and resources. The senior program staff will do a more rigorous analysis of the information provided by the decision maker, even though the decision maker continues to have input to the process. The DQO steps involved and the issues that may be raised are as follows:

- (1) Break down the decision into decision elements. For every decision, there are multiple factors or elements that influence the decision. Which of the elements to mitigate mobile sources depend on what environmental data? Which elements do not?
- (2) Specify the environmental data needed. For each decision element dependent on environmental data, what specific data are needed? Which of the many possible data elements should be measured? What frequency of sampling is required? What lab analyses are required?
- (3) Define the domain of the decision; that is, the portion of the environment, delineated by spatial and temporal boundaries, from which samples will be collected and to which the decision will apply. Should one focus on the industrial sectors of the urban area or focus on where the majority of the population spends most of its day? Should the indoor contributions be estimated? What spatial coverage of the urban area is necessary? What mix of mobile sources and stationary sources is needed to differentiate the ambient contributors? What temporal coverage is needed to distinguish between primary and secondary formation of species?
- (4) Define the result to be derived from the environmental data. Should the results be a weekly average concentration? Should the results demonstrate whether the specific analytes of concern are influenced by meteorology? What statistics are needed to summarize the data?
- (5) Determine the desired performance. How certain of reality does the result have to be for the data to be usable for distinguishing mobile from stationary contributions.
- (6) Determine the need for NEW environmental data. Are there any existing data that have the desired characteristics?
- (7) State the proposed DQOs. What is the level of false positives and false negatives that is acceptable to the data user?

To answer these questions requires an iterative process. This DQO process should enable the decision maker, the senior program staff, and the technical staff to think through the data collection requirements.

STAGE III: Design the Data Collection Program

The proposed DQOs produced by Stage II provide the necessary guidance to the technical staff so they can design the appropriate data collection and analysis schemes. Any of these schemes should provide the needed environmental data in a manner consistent with the acceptable uncertainty in the decision to be made. But, because of possible gaps in the measurement methodology or of resource constraints, the data user may decide not to choose one of the suggested schemes and may have to relax some of the data quality requirements in order to achieve the desired product. These iterations are desired and expected. The DQO process is designed to encourage such necessary iterations.

At the conclusion of Stage III, a final design of the data collection plan for the 30 urban areas in the Toxic Urban Monitoring Program will emerge. The design will identify in quantitative terms such items as the number of sampling locations needed, where the locations need to be sited, the pollutants to measure, the average time for sample collection, the analyses required, the QC parameters associated with sample collection and sample analysis, etc. Through such a design, EPA, the States, and the local agencies should have a comprehensive and effective environmental data base for assessing urban risk. Moreover, the program will provide the necessary quality and level of confidence to support the mitigation decisions that may arise.

Benefits of the DQO Process

Benefits of the DQO process to the staff and to the senior managers may be summarized as follows:

- * For the staff, they have a:
 - clear statement from the data user on what the user needs,
 - clear statement of the time and resource constraints, and
 - clear definition of the data quality needed by the data user.
- * For the manager or decision maker, he has:
 - thought through whether or not he needs new environmental data to support his decision,
 - bought into the effort and is accountable,
 - a clear understanding of what he is likely to get and when, and
 - a clear understanding of the limitations of the data he is likely to get.

Summary

DQOs are statements of the quality of data needed to support a specific decision or action. The DQO process is an interactive process that depends upon the active involvement of the decision maker, associated data users, and the technical design staff. DQOs will provide a useful aid to managers faced with making important policy and regulatory decisions by improving the confidence with which those decisions can be made when they are data dependent.

The current Air Toxics Strategy involves the use of new data collection activities as well as existing data bases to define the nature of the air toxics problem. This example of the application of DQOs to designing the necessary environmental data collection program for the Toxic Urban Monitoring Program provides a framework to assure that the proper data quality can be obtained.

The concept of Data Quality Objectives is a fundamental one. No data should be collected unless there is a rationale for doing so. This should be the first step in any environmental data collection program, and, it is for this reason that DQOs have become a central part of the overall QA program in EPA. Without DQOs, the rest of the Agency's QA program has no logical, quantitative basis.

SOME NEGLECTED ASPECTS OF
ENVIRONMENTAL QUALITY ASSURANCE

Raymond C. Rhodes
Quality Assurance Specialist
Performance Evaluation Branch
Quality Assurance Division
Environmental Monitoring Systems Laboratory
United States Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Progress has been made during the last decade in implementing quality assurance in the Environmental Protection Agency. However, because there are many aspects or elements of a total quality assurance system, it is, perhaps, understandable that some of the elements have in recent years been overemphasized at the expense of equally or more important elements.

Considerable efforts have been expended in improving the quality of chemical analytical operations in the laboratory. However, not enough effort has been put into increasing the quality of the field sampling. When considering that the entire measurement system includes the sampling and sample handling (if any) as well as the chemical analysis, the proportion of variability or uncertainty in the final result that is attributable to the sampling phase of the measurement system is much greater than that for the chemical analysis. More effort needs to be placed on reducing the effects of sampling variables.

Considerable efforts are being expended in establishing goals or objectives for data quality before a project or program begins and in the assessment of data quality during the project or program. More effort should be placed in comparing the actual achieved quality with the goals and in determining the cause of significant differences. Further, simply setting goals and assessing data quality does nothing to improve the quality. Much more effort needs to be spent in determining the major components of variance of the total measurement system and in taking corrective actions to improve data quality.

Progress has been made during the last decade in implementing quality assurance (QA) for environmental measurements. Because there are many aspects or elements of a QA system, it is, perhaps, understandable that some of the elements have in recent years been overemphasized at the expense of other equally or more important elements.

The 23 elements of QA are briefly discussed in the "QA Handbook for Air Pollution Measurement Systems, Volume I, Principles," EPA 600/9-76-005. These elements are also categorized and discussed under four major application areas -- Management, Measurement, Systems, and Statistics -- in the Air Pollution Training Institute course, "QA for Air Pollution Measurement Systems." The neglected aspects of QA are discussed below by considering 15 myths or misconceptions which seem to be prevalent today as they fall under the four major application areas.

Systems

Myth 1. Quality Control (QC) is Achieved by Performing QC Checks. To achieve control of a measurement process, periodic QC checks must be performed. However, the mere performance of the checks will do nothing to control or improve the process, unless the results are evaluated in timely fashion and corrective action taken when indicated.

Myth 2. Performance Audits are QA, QA is Performance Audits. There are those who tend to define QA as primarily the conducting of Performance Audits -- the submittal of carefully prepared and characterized materials traceable as directly as possible to the National Bureau of Standards or other recognized primary standard. Thus, the performance audit is an external check on the accuracy of the measurement system being audited. And if the auditee produces acceptable results, it implies that the routine data from the auditees' measurement system is good.

Certainly the conducting of performance audits is a valuable aspect of QA, and if the results are good, they indicate that the auditee is capable of producing good results. However, such results should not be considered as sufficient to indicate the correctness of routinely obtained data. Knowing the identity of the audit samples, the auditee may take extraordinary care in their analysis.

To assure that the auditee does in fact produce correct routine data requires much more than the performance audit data, e.g., it can require a complete quality system audit, review of procedures and documentation, review of routine QC data, etc. To do QA adequately requires that the personnel involved with the QA responsibilities be thoroughly knowledgeable of the total QC System. In other words, one cannot perform an acceptable function in QA without knowing QC.

Myth 3. Corrective Action is a QA Activity. An important part of a QA system is that of corrective action. This does not mean that the actual conducting of an investigation into the causes of the quality problem and implementing any corrective action is solely QA activities. It is a QA responsibility to assure that a corrective action system is established and is implemented. Certainly, full-time QA persons may identify quality problems, may analyze data to investigate possible causes, and may recommend corrective actions. However, others may also identify quality problems, others may more appropriately investigate quality problems, and more likely than not, others should take the corrective actions.

Myth 4. The Preparation of SOP's is a QA Activity. QA personnel should be concerned that adequate standard operating procedures (SOP's) be prepared for all routine operations of the total measurement system. However, it is not a QA/QC activity to prepare such SOP's. SOP's naturally should be prepared by those who actually perform the operations, or by others thoroughly familiar with all the details of the operations. QA personnel should be concerned that a system for the preparation and control of documented SOP's exists, that the SOP's are clearly written, and adequately reviewed and approved and that there be a defined system for revising and updating the SOP's.

Myth 5. An Observation or Analytical Result That Comes from a Computer Data Base is Known Absolutely and Without Error. All too often data gets into a computer data base without being fully validated, and the data, replete to seven decimal points, are given to a statistician for statistical analysis. It should go without saying that the analysis, and conclusions drawn from the analysis, can be no better than the data. It is possible that invalid conclusions will be drawn and that incorrect actions or decisions will be made.

Statistics

Myth 6. QA is Statistics, Statistics is QA. Some consider statistical QC as synonymous with QA. Statistical QC or statistical process control has recently been given some emphasis by W. Edwards Deming, the American who effectively introduced the concept and principles to the Japanese soon after World War II. Although the application of statistical QC and many other statistical techniques are an important part of a total QA program, there are also many at least equally important but nonstatistical elements of QA.

Myth 7. The Performance of QA Assessment Checks Assures the Attainment of Precision and Accuracy Goals. It is good to have precision and accuracy goals, and it is good to perform assessment checks for precision and accuracy. But the mere performance of the checks does not cause the goals to be achieved. These checks tell you where you are; but they don't necessarily get you where you want to be. To improve the precision or accuracy requires corrective action. Even then you may not achieve the goals because they have been set unrealistically tight considering the inherent capability of the total measurement method. For the project involved, the users of the data must be satisfied with the experienced quality. In the future, either the method must be improved, or more realistic goals must be set.

Myth 8. You Always Sample 10%. QA Project Plans are filled with requirements that 10% of the samples be QC samples. The selection of any such percentage is a cop-out for thinking about what number or percentage of QC samples of various types should be used. In general, the percentages of samples to be used for QC purposes should not be decided on a set percentage basis or even on a statistical sampling basis, but rather upon the operational variables involved. These operational variables might include how frequently the measurement system is calibrated, how many samples are included in an analytical run, the number and type of analytical instruments being used, the number of analytes being analyzed, whether all the samples of a given batch are being analyzed on the same day or different days, etc. In short, the frequency of QC samples should have some basis in what in

QC parlance is called "rational subgroups," i.e., subgroups of samples that have been taken or are being analyzed under very similar, or homogeneous, conditions.

Myth 9. QC Charts are Useful Only for After-the-Fact Data Analysis.

Because of the lengthy time required for some of the more complex and sophisticated chemical analyses, the analyses of real world samples and the corresponding QC samples are not available in a timely manner to effect any real-time QC. Consequently, much QC data are only available long after the samples have been taken. It is true that some worthwhile data analysis can be made long after-the-fact to document quantitatively the QC results of the past. However, except for possible use of the data for long-term control purposes, the real purpose of maintaining control charts to effect real-time control is defeated. Some innovative ideas are needed to control such measurement systems, such as more emphasis in controlling key operational variables of the measurement process, or by making some type of simulation check.

Further, the calculations of control limits for blocks or batches of data, including outliers or out-of-control data, and applying the limits after-the-fact to the same set of data is invalid. The probabilities which normally would be incurred no longer exist. Naturally, if limits are calculated and applied as described above, most of the data points, even those which should really be indicated as out-of-control, will fall within the computed limits.

Measurement

Myth 10. An Equivalent Method is Automatically a Reliable Method.

The ambient equivalency regulations and procedures are excellent mechanisms to assure that a measurement method has been demonstrated to be capable of achieving specified accuracy and precision. However, they do not assure continued operational success in field performance for extended periods of time. Much more evaluation of the reliability of the sampling/analysis operations in field operations needs to be done to determine failure (malfunction) rates, to identify the major component(s) that fail, and to determine the major causes of failure.

Management

Myth 11. QA/QC Applies Only to the Chemical Laboratory. There has been a continuing emphasis on establishing and maintaining an extensive QC system on the laboratory chemical analysis part of the total measurement system. In fact, some feel that the sampling activities are not a part of the measurement system and that QC applies only after the samples reach the laboratory. The chemical laboratory may very well be in excellent control. However, the end result depends as much or more so on variables in the sampling part of the total measurement system.

Myth 12. QA Doesn't Apply to Measurement Method Development. Some have said that QA doesn't apply to methods development, to research, or to sampling/measurement equipment and material procurement efforts.

In reality, basic QA/QC principles can be applied to any identified process having an identifiable product. Basic QA/QC principles are universal in their applications.

Myth 13. Specifying QA Objectives Assures the Attainment of the Objectives. Simply specifying QA objectives for precision, accuracy, and completeness will not make it happen. The objectives must be realistically attainable under the conditions under which the entire measurement system is operating. The entire measurement system may include sample container and equipment preparation, sampling, sample handling and preservation, analysis, computations, and data archival--not just simply the laboratory analysis part of the measurement system. QA objectives cannot be based solely on the laboratory analysis or even on collaborative studies of measurement methods.

Myth 14. Having a QA Project Plan Assures the Execution of QA Activities Outlined Therein. EPA requires the approval of a QA project plan prior to the collection of samples for projects involving the collection of environmental data. This is good, but independent and indepth system audits should be conducted to assure compliance to the requirements of the plan. There has been at least one case where a major EPA contractor as a part of a contract for a project prepared a very adequate QA Project Plan, but did not perform in accordance with the plan. When challenged with this fact, unfortunately after the project was completed, the contractor stated that the contract only required them to prepare the QA Project Plan; it did not specifically state that they were contractually bound to comply with the plan! And so it went.

Myth 15. Having a QA Policy, a QA Organization, and QA Coordinators and Officers Means an Effective QA System Exists. It is good for an organization to have a QA policy, to have working groups and personnel labeled as QA. But the policy, the organization, and the personnel will be ineffective in their QA endeavors unless all management levels from the top down does more than support QA efforts with only lip service. Further, all management levels should have some knowledge and training in QA principles and practices.

All persons working in QA should have completed some formal training in statistical QC and other QA courses such as quality auditing, QA for computer software, systems reliability, process capability studies, acceptance sampling, design of experiments, procurement QA, quality engineering, regression analysis, etc.

Much more planning and implementation of QA training is needed in the environmental organizations. This training should include all of the 23 elements covered briefly in the Principles Volume of the QA Handbook, as well as related administrative areas such as the preparation of QA project plans and SOP's, the development of contractual requirements for quality and monitoring of QA of contracted projects.

Ideally, persons with a QA title and responsibilities should have had many years of active experience in QA/QC work. They should have completed college-level courses in statistical QC and desirably in other related statistics courses as well. Or else they should have completed other readily available courses in QA and statistical QC and furthered their knowledge in all aspects of QA through disciplined self-study and reading. Because of the relative newness of the field of QA or total QC, very few universities have yet developed complete curricula toward the granting of degrees in the field. Persons with assigned QA titles and responsibilities should be aggressive in their efforts to become more knowledgeable in the

field. EPA needs to support much more QA training, particularly for those having QA titles and responsibilities.

Summary and Recommendations

There should be a very concerted effort in environmental monitoring organizations to provide training at all levels for those performing QA and related work. With respect to organization, persons performing QA work should be those who have the most knowledge, experience, and interest in QA.

Further, except in very small organizational units, QA officers and QA coordinators should be dedicated full-time workers in QA without supervisory responsibilities and should report on a staff level as high in the organization as possible. More systems audits should be conducted of internal projects as well as contracted projects. The audit team should be headed by the QA officer or coordinator and assisted by the most QA and technically knowledgeable persons from various parts of the organization. More emphasis needs to be given to the QA requirements of contracts for procurement of sampling and analysis equipment and materials as well as contracts for conducting research and monitoring projects. Quality incentive contracts should be implemented wherever appropriate. Data validation techniques need to be further developed and implemented to assure the validity of data prior to statistical analyses or other uses. Corrective action efforts need to be strengthened to achieve improvement in data quality. Without corrective action, setting of data quality objectives, conducting of performance and systems audits, and assessments of precision and accuracy are only record-keeping efforts which do nothing to improve data quality.

The possible application of statistical analyses for QA is unlimited. More ruggedness tests or other statistically designed studies should be done for measurement methods development, including field operation variables. Components of variation studies of the entire measurement system, including field sampling, should be performed to identify the major sources of variability so that efforts to improve the measurement system may be directed to those areas with greatest possible benefit. Continued application of statistics in areas such as control charts, process capability studies, limits of uncertainty, etc., are needed.

More attention needs to be given to the reliability evaluation of reference and equivalent methods. Evaluations could be made of laboratory-type operations or better from real-world field operations.

The total QA efforts needs to be more progressive or active rather than passive. It should be a challenging program with some healthy "bite". Problem areas should be clearly identified and vigorously attacked. Lastly, a successful QA program requires painstaking devotion and attention to detail by all those who may have an impact on data quality.

Disclaimers

The opinions and judgments of this paper do not necessarily reflect those of EPA management. Except where EPA is specifically mentioned, the observations of this paper relate to Environmental QA in general.

**QUALITY ASSURANCE FOR PRECIPITATION COLLECTION
AND MEASUREMENT: THE EPA STATE-OPERATED NETWORK**

**W. Cary Eaton
Research Triangle Institute
Research Triangle Park, North Carolina**

**Berne I. Bennett
Quality Assurance Division
U. S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina**

Networks that collect and quantify the constituents of precipitation in the United States have increased in number and size in recent years. Several networks have regional or national coverage and sample on a daily or weekly basis. A number of states (presently, 11) participate in the EPA-sponsored State-Operated Precipitation Network that collects weekly samples. As networks have grown, so have the development and application of quality assurance considerations to ensure that accurate, precise, complete, and representative data are obtained.

The need for and benefits of on-site quality assurance audits and technical assistance are discussed. Quality assurance protocols for system and performance audits of wet deposition collection sites are reviewed. The protocols address site characteristics, training, precipitation collection and measurement equipment, sample retrieval and handling, system audits, and the use of simulated precipitation test solutions.

Results from quality assurance studies of the 27-site State-Operated Network are given to illustrate the use of quality assurance protocols.

INTRODUCTION

Wet deposition collection networks in the United States have grown in number and size in the last decade in response to the need for data to determine the extent and nature of acidic precipitation. As the networks have grown, so has the development of protocols and procedures for external quality assurance. Benefits of quality assurance studies of networks are these: provide assurance that established protocols for siting, sample collection, and analysis are being followed; identify non-complying equipment to be fixed and operators who need further training; provide a means of documenting the data base with respect to accuracy, precision, completeness, and representativeness; allow the data quality of several networks to be compared in a systematic way.

The 27-site EPA State-Operated Network, (SON) has been in place since 1982. This paper describes quality assurance procedures established for this network and gives results from visits to the sites in 1985 and 1986. Recommendations for improvement are also given. The procedures are similar to those developed and applied earlier by two other networks - the Utility Acid Precipitation Study Program, (UAPSP), that collect on a daily basis (1) and the National Atmospheric Deposition Program/National Trends Network, (NADP/NTN), that collects weekly samples (2).

QUALITY ASSURANCE PROCEDURES

Siting Criteria Checks

Each site's installation and nearby surroundings are compared to criteria given in urban- or regionally-sited station checklists designed expressly for the State-Operated Network. Important criteria common to either type station are: (a) type and height of nearby groundcover; (b) distance of collector from obstructions; (c) distance of the collector from sources of contamination and pollution; (d) proximity of human or animal activities to the collector; (e) nearby land and water features.

System Audits

During the visit the following system audit topics are reviewed: (a) sample collection equipment and procedures (including plastic bag bucket liners used in the SON network); (b) site laboratory facilities and cleanliness; (c) analysis procedures; (d) communication and recordkeeping; (e) quality control tests and corrective action procedures. Technical assistance is provided whenever an operator is uncertain of procedures or when equipment is in need of maintenance or calibration.

Performance Audits

The accuracy of response of each site's collection and measurement devices are tested during the visit. The audit techniques and tolerances for the SON network are described in Table I.

RESULTS

Siting Criteria Checks

At least one variation from the designated siting criteria was found for most of the SON sites. Many were minor and should have negligible effect on the physical and chemical data base. The most important siting exceptions were these:

Collector/rain gauge obstructions. Several collectors and gauges were near enough to trees, towers, or other equipment such that the object projected onto the collector at greater than a 45 degree angle. Because the sample catch and chemistry may be affected, it was recommended that the samplers be slightly repositioned or that the obstructions be removed.

Proximity to sources. Several sites had sources nearby although the criteria for separation was minimally satisfied. Examples are: asphalt plant; animal stockade; and salt water. It was recommended that data users be made aware of these facts and that the site be moved or the source removed if possible.

Collector/rain gauge positioning. Ideally the collector and rain gauge orifices should be at the same height above ground (~1 m) and be separated by at least 5 but no more than 30 m. Several sites had the collector and gauge positioned within 1 m of each other in the horizontal; others were separated by several meters in the vertical dimension. It was recommended that the rain gauges be repositioned and inoperative gauges be repaired or replaced.

System Audits

System checks were made of the precipitation collector, the rain gauge sample collection procedures, and the field laboratory. Results are noted below.

Precipitation collector. Eleven of 27 collectors were higher above ground than the prescribed 1 meter. This exception was due to placement on

platforms or roofs to avoid snowpack, for security, and to avoid obstructions. The effect is thought to be minimal. Ten collectors were installed with the wet bucket facing N or E rather than the prescribed W. If rainstorms approach predominantly from the S or SW, the collector itself may influence the collection process. Eight collectors lack the event marker capability. Knowing when and for how long the collector is open is an important quality control consideration. All but two sites had properly seating bucket covers. A dry-side bucket was missing at one site; another site had a deteriorated liner. Proper seating is necessary to keep out dust.

Rain gauge. Variations from the desired distance from the collector and height with respect to the collector were noted at about half of the sites. Six sites do not have recording rain gauges; several sites had malfunctioning tipping bucket gauges.

Sample collection procedures. Proper sample collection procedures were followed in virtually all instances. It was noted that not all operators visually check the sample for contamination before returning it to the field laboratory. It was recommended this be done; otherwise contaminants may dissolve and not be noted later.

Field laboratory. The field laboratories had adequate space, were clean, and temperature-controlled. Operators and analysts were trained and familiar with their duties. Variations in measurement technique were noted and discussed. It was recommended that smaller sample aliquots be used, that the network's central laboratory have first priority for samples, and that samples be shipped within three days of collection.

Performance Audits

Performance evaluations were made of: the rain gauge; the precipitation collector; and the pH meter, conductivity cell, and solution balance. Results are given in Table II and discussed briefly below.

Rain gauge. All thirteen weighing-type recording rain gauges agreed within 0.1 inch of the designated audit value over the range 0 to 5 inches. Eight of thirteen gauges were out of tolerance above 5 inches. However, this is a seldom-used range as the gauge bucket is usually emptied before this depth is reached. Most of the gauges were recalibrated to meet specifications.

Precipitation collector. All collectors operated when the sensor was activated. The lid-liner/bucket rim seal was adequate. A number of problems were noted with sensor temperature range and control.

Conductivity meter. Meters at three of twenty field laboratories varied by more than 4 uS/cm from the designated value. Results were quite acceptable otherwise. The quality of deionized water in use at the sites also met specifications.

pH meter. Only two of twenty-one field laboratories had pH results that varied by more than 0.1 pH unit from the designated value. The average absolute variation was 0.054 pH unit.

Mass. Sixteen of the 19 balances checked agree within 1 g of the designated value at a loading of 1646 g. The worst case would be a 10 g variation corresponding to 1.2 percent at an 823 g loading or 0.3 percent at a 3292 g loading.

CONCLUSIONS

The EPA-sponsored State-Operated Network is a weekly precipitation collection network of 27 sites located primarily in the eastern and southeastern United States. State agencies have provided personnel to service the sites and laboratories, to analyze the samples, and submit them to a central laboratory for analysis. The site supervisors, operators, and analysts were found to be familiar with their duties, handled the precipitation samples carefully, analyzed the samples accurately in most cases, and seemed genuinely interested in the network and the data.

A number of the sites should be improved upon in terms of siting and maintenance of sample collection and analysis equipment. Emphasis should be placed on proper placement and operation of precipitation collectors, installation and proper operation of rain gauges, and standardization of field laboratory techniques.

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TABLE I. AUDIT TECHNIQUES AND TOLERANCE LIMITS FOR SON NETWORK COLLECTION AND MEASUREMENT METHODS

<u>Measurement Device and Audit Observable</u>	<u>Audit Technique or Test</u>	<u>Expected Results</u>
1. Recording Rain Gauge - Accuracy of precipitation depth on gauge	- Use calibration weights simulating precipitation.	- Agreement within ± 0.10 inch of audit weight.
2. Precipitation Collector - Lid liner-bucket-rim seal - Sensor activation and heating	- Determine lid drop distance (bucket in - bucket out). - Observe open/close cycle. Determine temperature with thermistor 5 min. after activation.	- Distance >3 mm. - Ambient temperature, prior to activation. Temperature of $50-70^{\circ}$ C attained after activation.
3. Conductivity Meter - Accuracy of response to simulated precipitation samples - Deionized water quality	- Have operator determine conductivity of simulated sample. - Have operator determine.	- Agreement within ± 4 uS/cm. - Conductivity <10 uS/cm.
4. pH Meter - Accuracy of response to simulated precipitation samples	- Have operator determine pH of simulated precipita- tion sample.	- Agreement within ± 0.1 pH unit of established value.
5. Mass by Solution Balance - Accuracy of response to calibrated weights	- Have operator determine mass of weights in the range 800 g to 3300 g.	- Agreement within ± 5 g of stated mass.

TABLE II. PERFORMANCE AUDIT RESULTS: EPA STATE-OPERATED NETWORK, 1985-1986

Measurement Device Audited	Number Audited	Range of Response; Average Response	Comments
1. Rain Gauge - depth	13	All within ± 0.1 inch from 0 to 5 inches.	Out-of-tolerance readings occurred on 8 of 13 but only at 6 inches or greater depth, a seldom-used range.
2. Precipitation Collector - lid liner/bucket rim seal	16	Range 7 to 33 mm; avg. 13.6 mm.	All met 3 mm criterion of acceptability.
- sensor activation and heating	27	All respond and open collector. Range 23 - 100°C; avg. 55°C.	Eight heated at all times. Six did not heat. Twenty- one heat; of these 10 attain temperature $< 50^\circ\text{C}$, three $> 70^\circ\text{C}$.
3. Conductivity Meter - accuracy of response	20	0.3 to 5.80 uS/cm; (a) avg. 1.63 ± 1.76 uS/cm.	EPA performance audit sample; value is 20 or 24 uS/cm.
- deionized water quality	14	0.35 to 3.80 uS/cm; avg. 1.75 uS/cm.	
4. pH Meter - accuracy of response	21	0.01 to 0.18 pH unit; (a) avg. 0.054 ± 0.04 pH unit.	EPA performance audit samples; designated value is 4.28 or 4.39 pH units.
5. Solution Balance Mass - accuracy of response	19	16 of 19 agree within ± 1 g at 1646 g loading.	17 of 19 are accurate within ± 5 g over 823 to 3292 g range. All are within ± 10 g agreement.

(a) Range of differences where difference = | (site value) - (designated value) |.

QUALITY ASSURANCE PROGRAM FOR THE NON-OCCUPATIONAL
PESTICIDE EXPOSURE STUDY (NOPES)

Miriam Lev-On, Joseph C. Delwiche and George Colovos*
Environmental Monitoring & Services, Inc.
Camarillo, California 93010

David E. Camann, J. P. Hsu and Herb Schattenberg
Southwest Research Institute
San Antonio, Texas 78284

Andrew E. Bond and Howard Crist
U.S. EPA, EMSL
Research Triangle Park, North Carolina 27711



A field study of non-occupational exposure to pesticides (NOPES) is being conducted to estimate the exposures of a statistically representative sample of urban population to selected pesticides found in the air, drinking water, and food, as well as through dermal contact. The intended use of the data collected through this study is to obtain the cumulative frequency distribution of exposures to selected pesticides for each of these pathways. The general methodology of the study calls for sampling in predesignated homes, followed by laboratory analysis of the collected samples.

The complexity of this study and the difficulties associated with population surveys, sample collection, chain-of-custody, and analytical speciation of very low level concentrations of 32 target compounds, has required careful planning and the development of a detailed quality assurance plan. This paper presents the QA activities undertaken during the field sampling and analysis phase of the program in the Summer of 1986 in Jacksonville, Florida. The discussion highlights the data validation steps, and results are presented for surrogate and matrix spike recoveries, performance evaluation samples and audits.

*Now with: Roy F. Weston Company, Stockton, California

INTRODUCTION

The general public is subjected daily to non-occupational pesticide exposure via the air, drinking water, food and direct dermal absorption. The U.S. Environmental Protection Agency is systematically investigating the various aspects of non-occupational pesticide exposures by conducting field studies in Jacksonville, Florida for three seasons and in Springfield, Massachusetts for two seasons (1-3). The first phase of the study has been conducted in Jacksonville in the summer (June-August) of 1986.

The main purpose of this study is to estimate the exposures of a statistically representative urban population sample to selected pesticides found in the air, drinking water and food, as well as through dermal contact. Through this study the cumulative frequency distribution of exposures to selected pesticides will be obtained for each of the above mentioned pathways. The data from this study will be used to evaluate seasonal changes, temporal changes and interpersonal usage patterns within any given home which are considered to be the three basic components of the variability of exposure.

The design of an effective QA program that is "built in" to the study design is a key element to the success of a complex multidisciplinary study such as NOPES. The major quality-related elements of this project include the following:

- * Population Survey Design
- * Field Sampling and Analysis
- * Data Processing
- * Data Evaluation and Analysis
- * Estimation of Exposure Through Multiple Pathways.

METHODOLOGY

The methods discussed below pertain only to field sample collection and laboratory extraction and analysis. The statistical methods used for sample selection and household screening are given elsewhere (1).

Sampling Design

The following samples are collected in the participating households in accordance with the sampling matrices provided in the Detailed Work Plan for NOPES (4).

1. "Primary" households: One each indoor, outdoor, and personal exposure 24-hour air sample will be collected at each household.
2. "Duplicate" households: Approximately 11 percent of the "primary households" will be designated as duplicates at which collocated samples will be collected at both indoor and outdoor locations. Collocated personal samples will not be collected due to practical considerations.

3. "Triplicate" households: About 40 percent of the "duplicate" households will be designated as triplicates, and a third concurrent sample will be collected at both the indoor and outdoor locations, for independent extraction and analysis by the Reference Laboratory.
4. "Replicate" households: About 14 percent of the "primary" households will be designated as replicates. A second set of (indoor, outdoor and personal) samples will be collected at least 5 days after the completion of the first monitoring period. Also the replicate sample will be collected on a different day of the week than the primary sample.
5. Dermal exposure households: Personal air sampling will be conducted during periods that include the dermal exposure measurements performed in about 8 percent of the primary households.
6. Drinking water: Household faucet water will be collected at approximately 8 percent of the primary households.

Sampling and Analysis Procedures

A general description of the sampling and analytical procedures used in the NOPES project are given in the NOPES Work Plan and QA Plan (4,5). Data Quality Objectives (DQO) that have been established for NOPES are summarized in Table I. The monitoring effort requires collection and analysis of air (on Poly Urethane Foam Plugs), drinking water, and dermal exposure (on precleaned gloves) samples. These procedures were tested under field conditions during a pesticide exposure pilot study (6).

The PUF plugs, water samples and gloves collected are analyzed by first extracting with distilled-in-glass solvents. The extracts are concentrated and split into two aliquots, one of which is analyzed by GC/ECD for one set of compounds, while the other is analyzed by GC/MS with multiple ion detection (MID) for another set of compounds. Compounds which are determined by GC/ECD are confirmed using a second column with different elution characteristics.

All samples collected are stored in the field under dry-ice and are shipped to the central laboratory within 48 hours. The extraction of all samples and the concentration of their corresponding extracts for GC/ECD and GC/MS/MID analyses are completed no later than 7 days from the sample collection end date, and the analysis of the extracts is completed no later than 30 days from the date of extraction. Table II provides a list of the target pesticides for NOPES together with their Quantitation Limit Goals.

ELEMENTS OF QA PROGRAM

Design of an effective QA program and its implementation has been recognized by EPA since the study's inception as a key element to the success of the study.

The QA program for NOPES consists of the following functions: QA Management, Internal QA/QC Operations, and External QA Evaluations. The program has been organized to meet EPA's QA requirements and to ensure the generation of data of known and documented quality.

QA Management. This function is responsible for coordinating the QA effort through designated QA coordinators of the various organizations participating in the study. A major effort was devoted to developing a detailed Work Plan and QA Project Plan (QAPP) which serve as working documents and are being revised as appropriate (4,5). This category also includes such activities as qualitative systems audits of participating organizations providing summaries of problem areas uncovered, and reviewing data generated in the project. These activities are targeted to provide an assessment of data quality and adherence to the objectives established.

Internal QA/QC. This function pertains primarily to routine activities undertaken by each of the study participants to "control" the data collection and measurement process. Diverse activities such as double entry of all manually entered data, specific procedures for every step in the sampling and analysis effort, and thorough validation, review and flagging of reported data are being used throughout the study. Table III provides a summary of the various QA/QC samples that have been built into the measurement system. The results of these QA/QC samples are used for the routine assessment of measurement system performance and enable immediate corrective action.

External QA. The activities in this function involve independent quantitative assessment of performance. Performance audits include field audits to evaluate samplers' performance and the data collection process, and laboratory performance evaluation, via blind audit spikes provided by EPA and the Reference Laboratory.

RESULTS

Preliminary analytical data in both diskette and hard copy, together with copies of field observations and sample collection documentation, are submitted to the data manager in batches for review and validation.

The data submitted are evaluated as follows:

- * Sample tracking report is generated to identify sampling problems (duration, flow rate) and adherence to extraction and analysis holding times.
- * Initial calibration linearity and continuing calibration drift are evaluated for all runs.
- * Matrix spike recoveries and surrogate recoveries are evaluated, based on summary reports generated from the data base.
- * Quantitation reports are compared to actual data reported on the hard copies for a minimum of two complete samples per extraction batch.
- * Air concentrations obtained for indoor, outdoor and personal exposure are summarized by household and compared for internal consistency.
- * A summary report is generated showing all duplicate and replicate measurements together with the percent differences for all instances and a range of differences observed for each of the target compounds.

Table IV presents a summary of percent matrix spike and surrogate recoveries for the NOPEs Jacksonville Summer 86 sampling phase. Octachloronaphthalene is used as the surrogate compound and added to each of the samples prior to extraction to enable tracking the integrity of the entire analytical system. The results for 255 PUF samples show a mean recovery of 97% with a median of 94% and a coefficient of variation (Std Dev/mean) of 0.15.

For each extraction batch one pre-cleaned PUF is designated as the matrix spike, and matrix spike compounds are added to it prior to extraction. Three of the compounds added are GC/MS target compounds and five are targeted for GC/ECD. The mean recoveries obtained vary from a low of 52% for propoxur (GC/MS) to a high of 108% for gamma-BHC (GC/ECD). Chlorpyrifos is used as a matrix spike compound for both GC/MS and GC/ECD with mean recoveries of 66% and 73%, respectively. It should be noted that the coefficients of variation for all matrix spikes are in the range of 0.15-0.35. These results provide an indication of the complexity of the measurement system, and the variability occurring at the extremely low concentrations encountered.

Table V shows a compilation of the percent difference ranges for duplicate collocated measurements, both indoor and outdoor of sampled households. The results indicate that the overall precision of the measurement system varies among households, with the largest contributor probably being the air concentration levels encountered. This is also evidenced by the sparsity of observed collocated concentrations, above the quantitation limit, for the outdoor samplers. This limited data set provides a semiquantitative measure of precision range and allows the data user to assign some confidence limits to the total exposure assessment.

SUMMARY

Incorporating effective quality assurance measures as an integral part of the NOPEs program ensures the usability of the data generated and the ability to estimate overall errors propagated in the system. It appears that as environmental monitoring studies are becoming more complex in both statistical design and measurement methods used, well planned QA activities and allocation of proper resources are essential to generation of data of known and documented quality.

The phased (seasonal) sampling design for this study enables tracking system performance closely throughout a sampling phase, followed by introducing improvements in procedures for the subsequent phase, whenever problem areas are uncovered. During the upcoming seasons QA would be improved by adding more "real time" internal QA/QC activities, in addition to including a matrix spike duplicate to enable assessment of analytical precision. Also, more audit samples will be available from EPA and the Reference Laboratory to better define analytical accuracy.

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TABLE I. DATA QUALITY OBJECTIVES (DQO)

<u>Descriptor</u>	<u>DQO</u>	<u>Method</u>
Precision	25% Analytical	Matrix Spike Duplicates
	35% Overall	Collocation of Samplers
Accuracy	20% Analytical	PE Samples for Laboratory
	40-50% Overall Laboratory Recovery	Matrix Spike Recovery Surrogate Recovery
	10% Sampler Flow	Mass Flow Controller Audit
Representativeness	Not Quantitative	Validation of Sampling Design
		Statistically Representative Population Sample
		Probe Placement: Indoor, Outdoor, and Personal
Comparability	20%	Split Extracts for Inter-Laboratory Comparison
	Uniformity of Reporting Units	ng/m ³ - air concentration ng/L - drinking water ng/glove - dermal exposure
Completeness	90%	Collection of Targeted Samples
	95%	Valid Extraction of Collected Samples
	95%	Usable Data of Extracted Samples

TABLE II. QUANTITATION LIMIT GOALS FOR TARGET COMPOUNDS

Compound	Quantitation Limit Goals	
	ng on column ^a	ng/m3 ^a
Chlorpyrifos	0.06	11.0
Pentachlorophenol	4.0	730.0
Chlordane	0.8	146.0
Orthophenylphenol	0.2	18.0
Propoxur*	0.2	18.0
Resmethrin	1.0	45.0
Dicofol	1.0	180.0
Captan	0.3	55.0
Carbaryl	0.5	45.0
T-BHC (Lindane)	0.05	9.1
Dichlorvos (DDVP)	2.0	360.0
2,4-D (methyl ester)	1.0	182.0
Malathion*	0.5	45.0
cis-Permethrin	0.4	73.0
trans-Permethrin	0.4	73.0
Heptachlor	0.07	13.0
Aldrin	0.05	9.1
Dieldrin	0.08	15.0
Ronnel	0.07	13.0
Diazinon*	0.6	55.0
Methoxychlor	0.1	18.0
Atrazine*	0.5	45.0
α -BHC	0.04	7.3
Oxychlordane	0.06	11.0
Heptachlor epoxide	0.04	7.3
Bendiocarb*	0.5	91.0
Polpet	0.2	36.0
Chlorothalonil	0.04	7.3
Dacthal	0.05	9.1
Hexachlorobenzene	0.03	5.5
DDT ^c	0.06	11.0
DDE ^c	0.06	11.0
DDD ^c	0.06	11.0

*to be analyzed by GC/MS/MID

^amost quantitation limits above are based on Jacksonville summer study report

^bbased on the assumption that extracts will be concentrated to 10 mL, split to two 5-mL portions, concentrated to 1.0 mL and 0.5 mL for GC and GC/MS, respectively, and that 2 μ L will be injected to either instrument. The total volume of air sampled is assumed to be 5.5 cubic meters.

^cnot analyzed for during Summer 86 phase

TABLE III. SUMMARY OF QA AND QC SAMPLES PER SAMPLING PERIODS

<u>Sample Type</u>	<u>Frequency or Number</u>	<u>Function</u>
Unexposed PUF	2%	Contamination check of PUF batch
Field blanks ^a		
PUF	10	Dynamic blank - account for field contamination
Water	2	
Glove	1	
Laboratory blanks ^b	1 per batch (20-33 samples)	Method blank
Spiked samples	1 per batch (20-33 samples)	Analytical accuracy measure
Duplicate spiked samples	Same as spiked	Analytical precision measure
Collocated samples	11% of households	Overall precision measure
GC/ECD evaluation standards	At the beginning of each 72-hr analysis period	Linearity check
GC/ECD individual standards	At the beginning, middle and end of each 72-hr analysis period	Quantitation
GC/MS initial calibration	Initially and as required	Quantitation/calibration
GC/MS continuing calibration	Every 12-hr analysis period	Monitor response factors
Surrogate	Each sample matrix	Recovery measure
Blind spike sample	Up to 15	External QA evaluation

^ataken to and returned from field.

^bsolvent blanks per sampling period.

TABLE IV. PERCENT MATRIX SPIKE AND SURROGATE RECOVERIES^a
(NOPES Jacksonville Summer 86 Sampling)

<u>Compound</u>	<u>N</u>	<u>Mean</u>	<u>Median</u>	<u>Std. Dev.</u>	<u>Range</u>
A. <u>GC/MS</u>					
Propoxur	8	52	54	20	18-80
Diazinon	8	70	70	19	31-92
Chlorpyrifos	8	66	68	18	31-87
B. <u>GC/ECD</u>					
Chlorpyrifos	8	87	84	15	69-113
Dieldrin	8	89	86	24	46-124
Heptachlor	8	107	114	24	69-133
gamma-BHC (Lindane)	7	108	102	33	73-163
Chlorothalonil	7	62	60	19	39-89
Hexachlorobenzene	3	96	90	13	86-111
OCN ^b	255	97	94	15	36-169

^aAll recoveries reported are for PUF plugs only

^bOCN was used as a surrogate and added to every sample prior to extraction

TABLE V. PERCENT DIFFERENCE RANGES FOR COLLOCATED NOPE SAMPLERS^a
(NOPE Jacksonville Summer 86 Sampling)

<u>Compound</u>	<u>Indoor</u>		<u>Outdoor</u>	
	<u>N</u>	<u>% Diff Range</u>	<u>N</u>	<u>% Diff Range</u>
chlorpyrifos	6	7-68	1	14
diazinon	3	12-73	--	--
propoxur	3	13-21	--	--
dieldrin	2	8-24	--	--
ortho-phenylphenol	2	33-57	--	--
chlordane	1	5	--	--
gamma-BHC (Lindane)	1	10	2	8-18
bendiocarb	1	5	--	--
heptachlor	1	3	--	--

^aOnly concentration values above the QAPP designated quantitation limit have been used in compilation.

DEVELOPMENT OF GASEOUS HYDROGEN CHLORIDE STANDARDS

Robert B. Denyszyn, Ph.D.
David Plessor
Karen Maguire
Scott Specialty Gases
Route 611
Plumsteadville, Pennsylvania

Hydrogen Chloride (HCl) is a very corrosive and reactive gas. Because of the reactivity of HCl, gaseous mixtures are difficult to prepare and stability is questionable.

To develop a stable product at the 100 to 50 ppm level, various technological developments had to occur. A cylinder which could maintain the HCl concentration constant, and an analytical method capable of quantitatively measuring small changes in concentration had to be developed. Previous work at the 1800 to 500 ppm levels had indicated that the use of either molybdenum or manganese steel alloy cylinders could be used for HCl applications. A significant amount of development was necessary to decrease the surface activity of the cylinder. In order to obtain representative samples from the cylinders, several delivery systems were tested and a system constructed of stainless steel 316 was found to perform satisfactorily.

The basic analytical methodology selected to analyze HCl was ion chromatography. To quantitatively analyze the cylinder, triplicate one liter samples were simultaneously collected in water containing a diluted solution of sodium hydroxide. The collected solvents were analysed against multipoint calibration curves to ensure the accuracy of the measurement. Standards were introduced periodically in the analytical scheme, and other measurements were performed to ensure the accuracy and traceability of the gaseous standards.

I. Introduction

Hydrogen chloride (HCl) is one of many pollutants emitted by the incineration of both hazardous waste and trash. Several states have introduced legislation requiring the continuous monitoring of HCl emissions from trash to steam plants. These requirements have prompted the Environmental Protection Agency to evaluate the suitability of various continuous monitors and the calibration of such monitors.

To date, the need for quantitative measurements of HCl in any process has been lacking. Due to this lack of interest for such measurements, little emphasis has been placed on the development of reliable gaseous standards.

In the case of trash to steam incineration, the HCl concentration of interest is 50 ppm and up. The preparation and quantification of HCl at these concentration levels is a real challenge.

In the summer of 1986, Scott Specialty Gases' Research and Development department initiated the development of HCl in inert gaseous matrices. Goals of the mixtures were to:

1. Develop a stable 250, 100, and 50 ppm gaseous standard
2. Develop a suitable delivery system.
3. Develop a cost effective analytical method to quantitatively analyze HCl.
4. Develop gaseous mixtures which have traceability to the national measurement system.

One of the major goals of the project was to develop stable HCl gaseous mixtures. It was determined from the onset of this study that the product would have a stability of $\pm 5\%$ /year, meaning that during the course of a year analytical measurement would not show a change in concentration of more than $\pm 5\%$.

II. Experimental Work

Development of a Suitable Container

HCl is a very corrosive gas which, in the presence of small levels of moisture, will corrode many metal alloys. Specialty gas manufacturers have a variety of cylinder types available to them including: aluminum, steel (manganese and molybdenum/chromium), and stainless steel.

Due to the reactivity of HCl with aluminum, aluminum cylinders were immediately eliminated from the potential list, leaving steel and stainless steel. Steel cylinders have typically been used to store pure HCl, and stainless steel would provide the most corrosion resistant container. Since the requirement is for continuous emission monitors which are typically routinely calibrated, the amount of gas required dictates the need for a container which has a total gaseous volume of 100 - 200 SCF. Even though stainless steel containers are available in this volumetric range, it was felt that steel containers could be made to perform in this application. A major factor was that stainless steel containers are approximately

20 times more expensive than steel containers. Steel containers which are supplied to the specialty gas industry do have their limitations with the major limitation being that the inside is coated with a thick metal oxide which is very reactive.

In order to have any potential success with such a container, the thick oxide surface must be removed and the surface modified to eliminate gas-to-surface interaction. Scott's Aculifetm V process provided such modifications of the surface. Cylinders treated by this process were evaluated with gas mixtures containing 1800 and 500 ppm of HCl respectively with encouraging results (see Table I).

Analytical results seemed to indicate a product which remains stable for at least six months. The data in Table I does not reflect the difficulties incurred while obtaining these measurements. Table II is a summary of some of the values obtained when performing these analyses. The data in Table II shows two problems:

1. The first sample collected and analyzed is almost always low.
2. The analyses performed on 8/18 and 8/19 are significantly lower than what would be expected.

Even though the results were not perfect, it was felt that the Aculife V treated steel cylinders would provide a good starting point for work at 250, 100, and 50 ppm.

Development of Suitable Delivery System

The system used to generate the data in Table II is shown on Figure 1. The system was constructed of stainless steel components. Due to the relatively low results obtained on 8/18/86 and 8/19/86, the delivery system was disassembled. Heavy corrosion was observed at the CGA gland assembly and regulator. It was also noted that the CGA fitting on the cylinder valve had also developed significant corrosion. The corrosion was somewhat surprising in view of the rather low HCl concentration. The corrosion is a sign of HCl lost as well as a sink for further absorption. To eliminate the corrosion, it was decided that all wetted parts prior to the regulator as well as the metering valve would be stainless steel 316 or superior alloys. Other modifications were made to the system resulting in the system shown in Figure 2 which was used for titration work.

The new system had incorporated a nitrogen purge assembly to eliminate moisture in the connection and assembly prior to the withdrawal of the HCl mixture. The regulator was also eliminated. The regulator had provided a lot of surface area for potential adsorption. The system in Figure 2 was satisfactory in as far as HCl mixtures could be delivered to the Greenburgh impingers, but in order to analyze 100 and 50 ppm mixtures, 20 - 30 liters of gas were required to titrate a 0.01 - 0.03M NaOH solution at a flow rate of 1 liter per minute. Triplicate samples from one cylinder took 1 - 1.5 hours. The use of ion chromatography as a quantification of Cl⁻ provided a mechanism to reduce both the volume of solution and gas.

Therefore, a new system was designed and constructed. Schematics of this system are shown in Figure 3. The system, theoretically, was to provide triplicate samples simultaneously at 100 ml per minute with a total of 1 liter of gas mixture per sample.

Unfortunately, at concentrations of 250 ppm, it was found that even with a total flow of 300 ml per minute, the system worked less than ideally. Titrimetric analyses of a 250 ppm HCL in nitrogen cylinder indicated the presence of approximately 250 ppm while the ion chromatographic system showed little or no HCL. The problem was narrowed to the following:

1. The system must be heated and purged with nitrogen prior to and after opening to the atmosphere.
2. A volumetric flow rate through the system of at least 1 - 2 liters per minute must exist when withdrawing product from the cylinder.
3. The use of all metal seals and electropolished stainless steel 316 components provided faster delivery of the gas mixture to the collection system.

In view of the incurred problems, a modified sampling train for ion chromatography was designed (see Figure 4). It incorporated the following features:

1. Delivery system to cylinder valve interface was best if metal seals were used.
2. Delivery from the cylinder was maintained at > 1 liter per minute.
3. The total volume of gas collected was measured using a mass flow totalizer.
4. The system was sealed before and after connection to new cylinders to minimize the effect of moisture intrusion.

Development of a Cost Effective Analytical Method to Quantitate HCL in Nitrogen Mixtures at the 50 PPM Level

A standard titrimetric method was used to initially analyze mixtures of HCL at 500 ppm and higher concentrations. The method consisted of bubbling the HCL gas mixtures through 200 ml of standardized sodium hydroxide solution ranging from 0.01 - 0.03 M. The method was found to be extremely quantitative with a collection efficiency of >99.9% at a flow rate of 1 liter per minute. The end point of the titration was detected using a phenolphthalein indicator. A stock solution of NaOH was stored in polypropylene bottles under N₂ atmosphere to minimize the absorption of atmospheric CO₂. Major drawbacks of this procedure were:

1. The large volume of standardized solution required in order to analyze a few cylinders.
2. In order to titrate HCL mixtures at the 50 ppm level, relatively low concentrations of NaOH solution must be used (millimolar). These relatively low concentrations make the transfer of such solutions difficult without having the influence of atmospheric CO₂.
3. Large volumes of gas mixture must be used (30 - 40 liters) making the analysis time very long.

4. The end point detection is poor, impairing the precision of the method.

Other solutions which can be used to quantitatively collect HCL solutions are: 0.001 M NaOH, 0.001 M NaHCO₃, and 0.001 M Na₂CO₃. For the best results from ion chromatography, a solution of NaHCO₃/Na₂CO₃ is most effective since the eluent used for the separation has the same constituents. The chromatographic system used for the analyses consisted of: a Dionex 2000 ion chromatograph, a Dionex 4270 integrator, and a Dionex autosampler.

Chromatographic conditions were as follows:

Column:	HPIC AS4A
Eluent:	Na ₂ CO ₃ / NaHCO ₃
Flow rate:	2 ml/min
Pressure:	960 psia
Detector Setting:	30 s for less than 100 ppm 100 s for >250 ppm

Precision achieved with 50 ppm equivalent Cl⁻ concentration is shown in Figure 5. The coefficient of variance for triplicate injections showed a value of +0.11%. Response was linear for the equivalent of 10 - 50 ppm. Analysis time ranged from 3 - 8 minutes depending on the analysis performed (manual or automatic).

III. Results To Date

Measurements

A total of 15 cylinders had been prepared for this work; five at each concentration level (250, 100, and 50). Titrimetric analyses were performed on all the 250 ppm HCl mixtures and the results are shown in Table III. Data indicates relatively good agreement from cylinder to cylinder. Further analytical work was performed on A-7778 over a 1.5 month period and our results, as shown in Table IV, show a gas mixture which is not changing very rapidly over a short period of time (<10% per month). There seems to be a bias of 6% between the titrimetric values and the ion chromatographic values. If we take the mean of both methods, the concentration in the cylinder can be quantified to 253 ppm +3%. This value is in good agreement with the gravimetric value which is 250 ppm.

Due to significant sample lost prior to the impingers, fewer analyses have been performed on lower concentration cylinders. Table V summarizes the results obtained to-date on cylinder A-5087 which theoretically contains 100 ppm. The bias between the two methods is larger than at 250 ppm (approximately 14%). The mean concentration of both methods provide us with a cylinder concentration of 95 ppm. In view of the fact that the gas mixture in the cylinder was prepared one month earlier, there is a good probability that this mixture will be found stable.

Results associated with a 50 ppm HCl mixture (cylinder A-10439) are shown on Table VI. The bias between the two analytical methods increased to 38%. Mean concentration after one month was 55 ppm; again in relatively good agreement with the theoretical gravimetric value of 50 ppm +10%. It is doubtful that the concentration would

be higher than 50 ppm since the mass of gas mixture and pure gas is large (30 gm) with a sensitivity of ± 0.2 gm.

Traceability of the Analyses

Traceability to the national measurement system is crucial in analytical work. In this work, this was accomplished via two methods.

1. Titrating the HCl gas in a NaOH standard solution. The NaOH was standardized with potassium hydrogen phthalate, Standard Reference Material 84J (Batch 580508). Flow measurements were made with a wet test meter with an error of 0.5%.
2. In the ion chromatographic method, KCl standard liquid mixtures were prepared using Standard Reference Material 999, (Lot 589910) in 17 megohm-cm water. An internal standard (2 ppm of KBr certified ACS grade) was also used to keep track of any water lost during collection of the gaseous sample. Multipoint calibration curves were generated with both KCl and KBr to quantify both Cl^- and Br^- concentrations. The flow measurement devices and rotometers were calibrated against the same wet test meter used in the titrimetric method.

Propagation of error analysis has not been performed at this time but we feel confident that the overall method should be able to achieve $\pm 1\%$ measurement uncertainty.

IV. Conclusion

At this time, the following can be said:

1. We have evidence that HCl mixtures as low as 50 ppm can be prepared accurately.
2. A purgable, electropolished, heated, stainless steel sampling train is necessary to quantitatively analyze HCl mixtures in the low ppm range.
3. A flow rate of at least 1-2 liters must be used through the delivery system in order to retrieve quantitative samples from the cylinder.
4. Mixtures at the 250, 100, and 50 ppm level are probably stable to better than $\pm 10\%$ per year.

V. Acknowledgment

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TABLE I - Initial Measurements of 1800 and 500 PPM HCL in N2 Mixtures

<u>Cylinder #</u>	<u>Theoretical Conc. (ppmv)</u>	<u>Analytical Results (PPMV)</u>						
		<u>8/5/86</u>	<u>8/7/86</u>	<u>8/13/86</u>	<u>8/18/86</u>	<u>8/21/86</u>	<u>9/30/86*</u>	<u>4/2/87*</u>
A-17241	1800	1812	1734	1736	1563	1687	1668	1584
		<u>8/6/86</u>	<u>8/8/86</u>	<u>8/14/86</u>	<u>8/19/86</u>	<u>8/20/86</u>	<u>9/30/86*</u>	<u>4/2/87*</u>
A-16790	500 ppm	506	492	507	446	475	473	430

*data provided courtesy of Entropy, Research Triangle Park, North Carolina

TABLE II 1800 and 500 PPM Analytical Precision

<u>Cylinder #</u>	<u>Theoretical Concentration</u>	<u>Analytical Results (PPMV)</u>				
		<u>8/5/86</u>	<u>8/7/86</u>	<u>8/13/86</u>	<u>8/18/86</u>	<u>8/21/86</u>
A-17241	1800 ppm	1729	1753	1700	1566	1602
		1824	1720	1770	1516	1627
		1850	1730		1607	1666*
		1882				1696*
		1773				1695*
		1812	1734	1736	1563	1687
		<u>8/6/86</u>	<u>8/8/86</u>	<u>8/14/86</u>	<u>8/19/86</u>	<u>8/20/86</u>
A- 16790	500 ppm	501	469	462	367	471.3
		505	505	513	447*	476.5
		510	494	547	446	476.8
		507	498			
		506	492	50	446	475

*Data used to calculate mean

TABLE III Titrimetric Analyses of 250 PPM HCl Mixtures

<u>Cylinder No.</u>	<u>Date Analyzed</u>	<u>Concentration (ppm)</u>
A-7778	3/13/87	264
A-17442	3/13/87	264
A-17477	3/19/87	262
A-17508	3/19/87	263
A-14512	3/19/87	256

All cylinders were prepared on 3/12/87

TABLE IV Analyses of 250 PPM HCl in Nitrogen (A-7778)

Titrimetric Concentration (ppm)	<u>3/13/87</u> 264	<u>3/26/87</u> 257			<u>4/27/87</u> 260
I.C. Concentration (ppm)	<u>3/20/87</u> 237	<u>3/24/87</u> 247	<u>3/25/87</u> 243	<u>4/15/87</u> 248	<u>4/21/87</u> 250

TABLE V Analyses of 100 PPM HCl Cylinder (A-5087)

Titrimetric Concentration (ppm)	<u>4/10/87</u> 100	<u>4/27/87</u> 102
I.C. Concentration (ppm)	<u>4/23/87</u> 88	<u>4/28/87</u> 90.1

TABLE VI Analyses of 50 PPM HCl in Nitrogen (A-10439)

Titrimetric Concentration (ppm)	<u>3/31/87</u> 64	<u>4/10/87</u> 62	<u>4/27/87</u> 65
I.C. Concentration (ppm)			43 <u>4/28/87</u> 49*

*modified Titrimetric sampling train followed by I.C. analysis

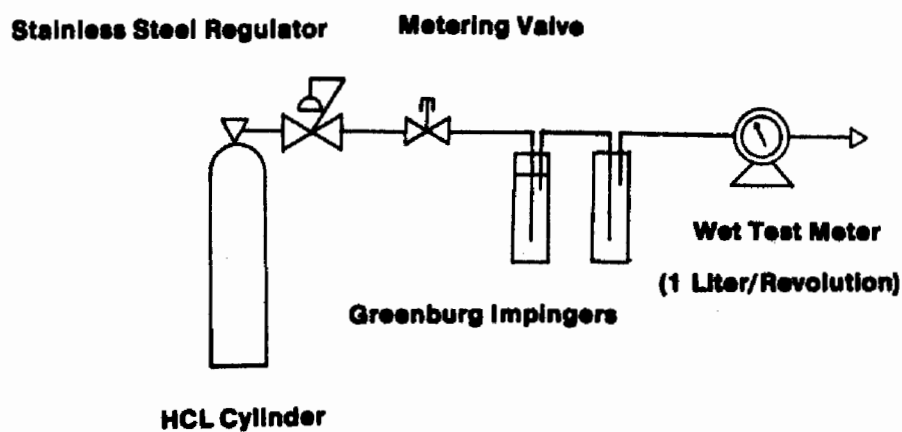


FIGURE 1 - INITIAL SAMPLING TRAIN(Titration)

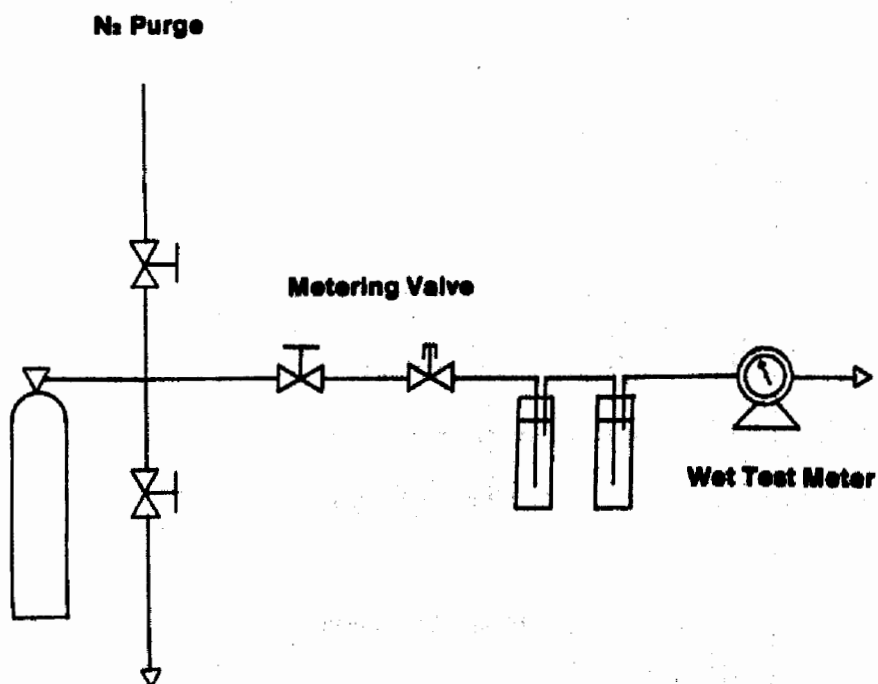


FIGURE 2 - MODIFIED SAMPLING TRAIN (Titration)

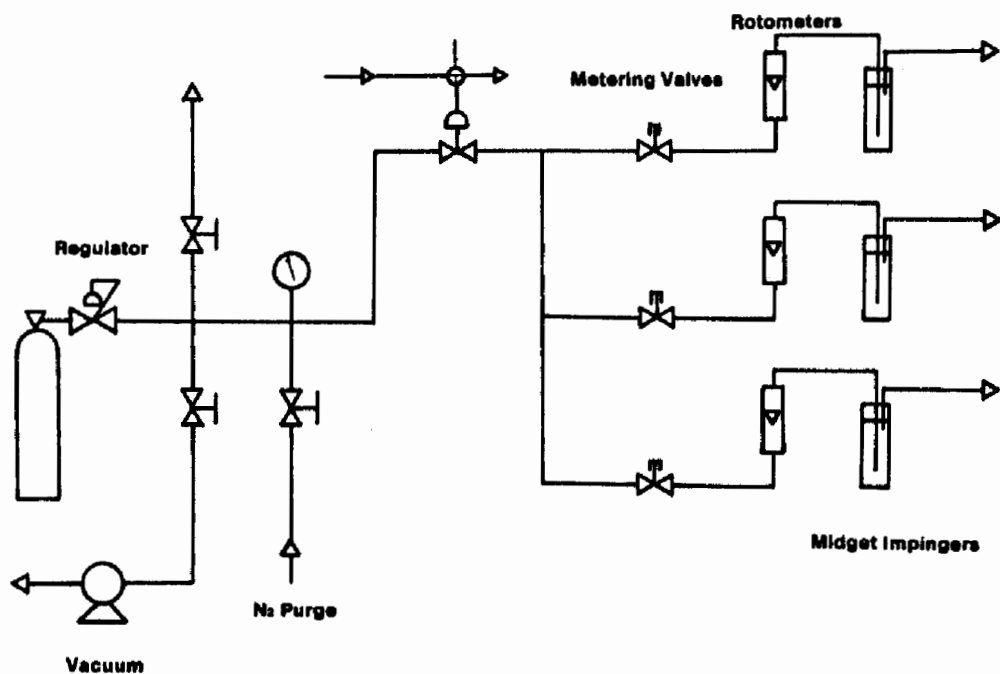


FIGURE 3 - INITIAL SAMPLING TRAIN(I.C.)

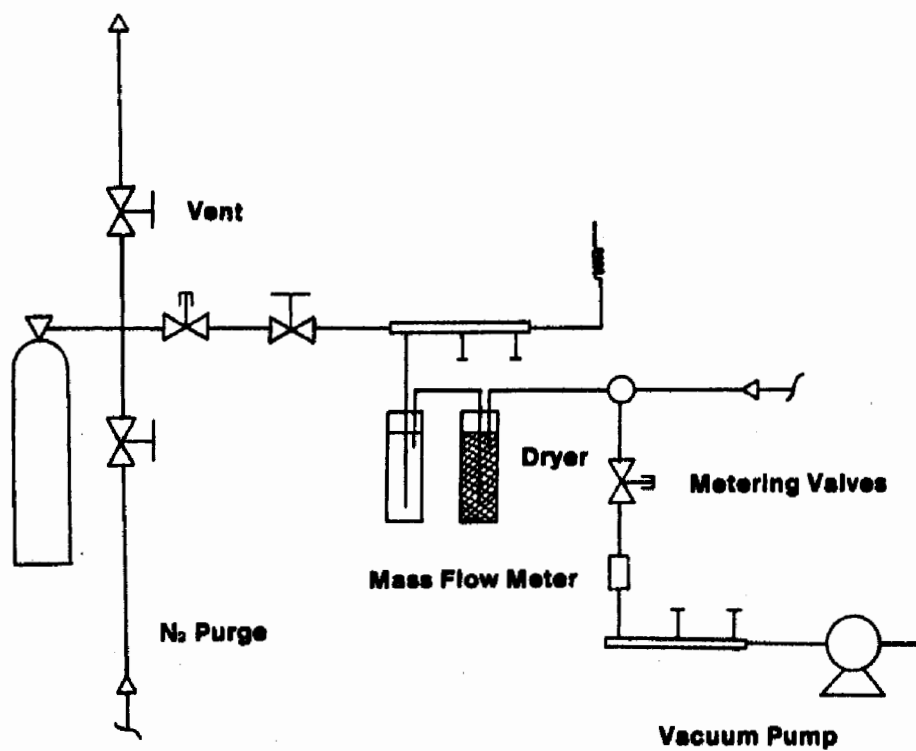


FIGURE 4 - MODIFIED SAMPLING TRAIN(I.C.)

QUALITY ASSURANCE IN THE NONMETHANE
ORGANIC COMPOUND MONITORING PROGRAM

Robert F. Jongleux, Robert A. McAllister,
Dave-Paul Dayton, Denny E. Wagoner
Radian Corporation
Research Triangle Park, NC 27709

Frank F. McElroy, Vinson L. Thompson
Environmental Monitoring Systems Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Harold G. Richter
Office of Air Quality Planning and Standards
Office of Air and Radiation
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711



During the summers of 1984, 1985, and 1986, 4773 measurements of nonmethane organic compound (NMOC) concentrations in ambient air were made with the Cryogenic Preconcentration Direct Flame Ionization Detection (PDFID) method. The development of a quality assurance program for determining the NMOC concentrations with known quality is discussed.

Analytical precision was measured by repeated measurements of site samples. The mean absolute percent difference was 9.8, with a standard deviation of 12.2. The average percent difference was -0.354, with a standard deviation of 15.7. Sampling precision was determined from analyses of duplicate site samples. Absolute percent differences of the duplicate samples for 3 years averaged 11.7, with a standard deviation of 16.4. Accuracy, or bias, was determined from measurements on dry propane standards referenced to National Bureau of Standards (NBS) Standard Reference Material (SRM) 1667b. In three years, average biases for Radian analytical channels ranged from -2.115% to -0.516% relative to EPA-QAD, with a pooled standard deviation of 3.951%.

Data base errors were monitored by a 10% random check of approximately 54 entries for each sample. The error rate in 1986 was 0.015%.

Introduction

A number of dispersion models have been developed to describe quantitatively concentrations of precursor organic compounds and downwind concentrations of ozone in ambient air as a function of time. The Empirical Kinetic Modeling Approach (EKMA) is a model which requires an average total nonmethane organic compound (NMOC) concentration from 6 A.M. to 9 A.M. in parts per million carbon (ppmC), by volume. An important EKMA application is to determine the degree of control of NMOC required in a particular area to achieve compliance with applicable ambient air quality standards for ozone.^{1,2}

Radian Corporation has assisted the U.S. Environmental Protection Agency, participating states, and the District of Columbia in obtaining the NMOC concentration data needed to prepare state implementation plans to meet the National Ambient Air Quality Standards (NAAQS) for ozone. A total of 4773 ambient air NMOC concentrations were measured at 44 sites, representing 22 states and the District of Columbia during the summers of 1984, 1985, and 1986. Because the NMOC data were used for regulatory purposes it was essential that the measurements result in reliable data of known quality.

The Cryogenic Preconcentration and Direct Flame Ionization Detection (PDFID) method was developed by the U.S. Environmental Protection Agency to replace the NMOC gas chromatographic (GC) speciation method.³ The PDFID method was shown^{4,5,6} to have precision and accuracy comparable to the NMOC GC speciation method, and was less costly to perform.

Quality assurance (QA) and quality control (QC) procedures necessary to obtain accurate NMOC data of known quality are the subject of this paper. Data quality parameters considered to be among the more important were accuracy and precision. Details of the Quality Assurance Project Plan (QAPP) unique to the NMOC Monitoring Program are described in the next section. There follows QC results of the program to date, and a description of the ongoing review of the QC procedures and acceptance criteria to improve the definition of data quality.

Quality Assurance Project Plan

Quality Assurance Project Plans (QAPP) were prepared according to EPA Guidelines for each year of the NMOC Monitoring Program. Detailed operating procedures were developed for the field sampling sites. Radian personnel were sent to each site to install and test the sampling equipment, and to train site personnel in the sampling procedure and schedule. The sampling schedule was projected. Integrated 3-hr (6 A.M. to 9 A.M.) ambient air samples were collected daily, Monday through Friday based on a 17-week program (except for July 4 and Labor Day), in electropolished stainless steel canisters. All samples were analyzed by Radian Corporation at the Perimeter Park, NC, laboratory. Canisters were shipped air freight the day of collection and were analyzed within two days of collection, except for Friday's samples, which were analyzed the following Monday.

A duplicate sample was scheduled for each site once every two weeks. For duplicate samples, two canisters were filled simultaneously from the same ambient air intake line. The duplicate-sample schedule was arranged so that the number of duplicate samples taken at each site was equal throughout the sampling period (June 1 through September 30), and so that approximately the same number of duplicate samples was taken each day.

Canisters sent to each site were initially cleaned in the Perimeter Park laboratory and sent under vacuum. A Field Sampling Form was enclosed in the canister shipment case for each canister. The site operator completed the information on the form and returned it with the sample. Upon receipt, the canister was tagged with an identification number and an analysis sheet was prepared which accompanied the sample through analysis. The original field data sheets and analysis sheets became part of the permanent project files.

All calibrations and audit samples used propane standards referenced to National Bureau of Standards (NBS) propane, Standard Reference Material (SRM) No. 1667b., by the U.S. EPA-Quality Assurance Division (QAD) of the Environmental Monitoring Systems Laboratory (EMSL) at Research Triangle Park, NC. All four Radian PDFID channels were calibrated with propane from 0.000 to 9.627 parts per million carbon (ppmC) by volume. "Zero" standard was obtained using air, filtered through fritted stainless steel filters, dried in permeation driers, and cleansed of organic content by passing through a catalytic oxidizer.

Each Radian PDFID channel was calibrated twice daily, once before any sample analysis for the day, and again after completion of the sample analyses. From these data percent calibration drift was calculated.

Four days per week in-house propane quality control samples were prepared by the project QC Monitor, and analyzed by each Radian PDFID instrument. On the fifth day each week, duplicate local ambient air samples were collected by EPA-QAD and analyzed on each Radian PDFID channel, the EPA-QAD PDFID channel, and the EPA-Atmospheric Sciences Research Laboratory (ASRL) GCFID instrument. One of the local ambient air samples was first analyzed by the EPA channels and then by the Radian channels. Then the other local ambient air sample was analyzed first by the Radian channels and then by the EPA channels.

Two site samples were chosen daily at random for an additional analysis on a Radian channel. Each day the QAPP specified the Radian Channels--e.g., A-A, B-D, C-D, D-D, etc.--on which the repeated analyses were to be done, so that over the summer program each channel pair was engaged in the repeated analyses an equal number of times.

In 1986, four sets of three audit propane samples were prepared by EPA-QAD for analysis on all Radian and EPA channels. Concentrations ranged from 0.797 ppmC to 8.980 ppmC. Audit samples were submitted on a random schedule by EPA-QAD from June 30 to September 25, 1986. In 1984 and 1985 two audit samples were used.

Data were transferred daily after review by the project QA Monitor, from data sheets, or log books, to a 20-megabyte magnetic data disk, that contains the NMOC data base. A backup data disk was updated daily. Biweekly meetings with EPA were held to review the data and to investigate any unusual data or data trends. Upon completion of the sampling and analysis for the summer, ten percent of the data was selected randomly for an audit check. For each NMOC datum selected for audit, approximately 54 pieces of data from the original data sheets were checked for correctness and for data transcription errors. A total of 2351 NMOC measurements are in the 1986 data base. Of these, 252 cases were checked for error. Two errors out of 13,608 entries were found and corrected, for an error rate of 0.015%.

Quality Control Results

Calibration factor drift results are given in Table I in terms of percent drift and absolute percent drift. The morning calibration factor was used as the basis for drift because it was the factor used to calculate NMOC concentrations for the entire day. The average calibration factors for 1985 and 1986 are about equal, but are less than in 1984. This result can be explained by the fact that the analytical instrument was housed in a better temperature-controlled environment in 1985 and 1986 than in 1984. Absolute percent differences in 1986 ranged from 0.929 to 1.959% among the Radian Channels.

Precision of the NMOC measurement was determined from repeated analyses of site samples. Table II reports precision in terms of percent differences and absolute percent differences for each year of the program and for three-year pooled values. No trends are evident. The overall average absolute difference is 9.8%, with a standard deviation of 12.2%.

Sampling and analysis precision was determined from duplicate samples. Table III shows the duplicate sample results in terms of percent difference. The first run includes both between-duplicate sample variability and within-duplicate variability, or analytical error. The analytical error was obtained from repeated analysis of site ambient air samples. Note that the standard deviations in terms of percent difference and absolute percent difference are about equal for both between-duplicate and within-duplicate variability.

Accuracy is reported in Table IV in terms of percent bias relative to the EPA-QAD PDFID instrument. The average bias of the Radian channels ranged from +2.76% for 1984 to -1.80% for 1986. No significant differences in bias were noted among the Radian channels. Accuracy was monitored throughout the program using in-house propane QC samples prepared from propane referenced to NBS SRM propane. Table V shows the results for 1984, 1985, and 1986 for Radian Channels A, B, C, and D, and gives pooled values for all four Radian channels. Significant differences are seen again between the absolute percent difference means for 1984 and 1985 (or 1986). The in-house samples were prepared by the project QC Monitor by diluting the certified propane sample with cleaned, dried air by means of flow controllers. The percent difference figures include error caused by the dilution process, and analytical error.

After analysis was completed the canisters were cleaned up before being sent to a site for another sample. The cleanup cycle consisted of first pulling a vacuum of 0.67 kPa on the canister, followed by pressurizing the

canister to 275.8 kPa gauge pressure with cleaned, dried air. This cycle was repeated three times during canister cleanup. During cleanup, six canisters were cleaned simultaneously on a manifold. After the third pressurization, the canisters on the manifold that had the highest NMOC content before cleanup was tested for its NMOC content. If the area counts measured less than 26 (about 0.008 ppmC), the cleanup criterion was met; the canister was reconnected to the manifold and evacuated a fourth time; all the canister valves were closed and the canisters were ready for shipment. The average removal of the NMOC content of the canisters was at least 99.891% in 1986. In 1985, at least 99.898% of the NMOC content was removed. Heating of the canister above room temperature was avoided to protect the passivated electro-polished interior surface of the canister.

Ongoing QA Program

Each year, data quality parameters are reviewed and updated. New acceptance criteria are added as needed. The acceptance criteria for the 1987 NMOC program are given in Table VI and are based on experience gained in the 1985 and 1986 NMOC Programs. For each measurement listed in the first column, a critical acceptance region (CAR) is given in the second column. If the measurement falls in the CAR, no further quality control action is required. If the measurement falls outside the CAR, further action, as listed in the last column, is given. In addition, an ongoing list of measurements not falling within the CAR is maintained to expedite QA review and reporting.

In data validation, the measurement taken is the percent error in the data base. For each NMOC concentration measurement, there is an average of 54 items recorded on original data sheets that need to be checked on the magnetic disk data base for accuracy of calculation and data transfer. Any errors that are found are corrected. The data base is validated after all NMOC measurements have been taken for the summer and data transfers to the magnetic data disks have been completed. If an error rate equal to or greater than 0.03% is found in the first 10% of the randomly selected NMOC concentration measurements, a validation of an additional 10% of the data base is required. If the error rate is still 0.03% or higher when the additional 10% of the data is validated, an additional 10% will need to be validated.

Tables I through VI are available upon request by contacting Dr. Robert A. McAllister, Radian Corporation, P.O. Box 13000, Research Triangle Park, NC 27709. (919) 541-9100.

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MONITORING A WIDE RANGE OF
AIRBORNE ORGANIC CONTAMINANTS



William R. Betz,
G.D. Wachob, M.C. Firth,
Supelco, Inc., Supelco Park,
Bellefonte, PA 16823-0048

Airborne organic contaminants at toxic waste sites and indoor air pollution sites typically range from highly volatile to nonvolatile compounds. These compounds are also typically present at low levels. Thus, they must be concentrated for effective qualitative and quantitative characterization of these atmospheres. Two or more adsorbent tubes, with dissimilar adsorption and desorption characteristics, must often be used.

A new multi-bed adsorbent tube containing three Class I, nonspecific adsorbents effectively adsorbs airborne organic compounds ranging from volatile (e.g., vinyl chloride) to nonvolatile (e.g., PCBs) in a size-exclusion mode. Carbotrap C (a graphitized carbon black, surface area $\approx 10 \text{ m}^2/\text{g}$) adsorbs nonvolatile compounds, Carbotrap (a graphitized carbon black, $\approx 100 \text{ m}^2/\text{g}$) adsorbs semivolatile compounds, and Carbosieve S-III (a carbon molecular sieve, $\approx 800 \text{ m}^2/\text{g}$) adsorbs volatile compounds. Characteristics of these adsorbents will be discussed.

A highly efficient thermal desorber is used to ballistically heat the tube and desorb the trapped compounds. They are transferred, via gas flow reversal, to a packed or capillary GC column in a discrete injection slug. This allows the column to refocus the sample and eliminates the need for a cryotrap. Desorption efficiencies for a wide range of organic contaminants will be described. Column choice, oven temperatures, and other key considerations for the chromatographic analyses will also be discussed.

Characterization of both ambient air and indoor air atmospheres has become the focus of concern for many air sampling analysts. Evaluation of these atmospheres typically entails qualitative and quantitative analyses of a wide range of organic contaminants present at "extremely low" concentrations. Multi-bed adsorbent tubes, used in thermal desorption modes, are very useful for these analyses. Because the airborne contaminants exist in many molecular sizes and shapes, and may possess one or more functional groups, choosing the appropriate adsorbents becomes difficult. By using Class I, nonspecific adsorbents (no ions or active groups), an analyst need not be concerned over which functional group(s) an adsorbate possesses.

By definition, a Class I adsorbent is without ions or active groups. Only a Class I adsorbent interacts nonspecifically with all four types of adsorbate molecules (Table I). Therefore, a multi-bed adsorbent tube containing Class I adsorbents adsorbs and subsequently releases a wide range of organic compounds possessing different functional groups. Furthermore, an appropriately designed multi-bed tube will differentiate between molecules of various sizes by size-exclusion. When a molecule enters an adsorbent tube containing Class I adsorbents of progressively larger surface area (Figure 1), the tube functions as a small gas chromatographic packed column in which the migration rate of each adsorbate is inversely proportional to its molecular size.

Carbotrap[™] and Carbotrap C graphitized carbon blacks and Carbosieve[™] S-III carbon molecular sieve are classified as Class I adsorbents (1). For these adsorbents, surface area ranges from 10 to 800 m²/gram (Table II). Because these adsorbents interact nonspecifically with adsorbates, the entire surface of each material is available for adsorbate/adsorbent interaction. Adsorption is a function of the surface-surface interactions, or dispersion forces, between the adsorbate and adsorbent surfaces. Adsorbates having small molecular size, such as vinyl chloride, migrate quickly through the graphitized carbon blacks and are adsorbed on the microporous surface of the carbon molecular sieve. Larger adsorbates, possessing larger surface areas, interact more strongly with available surfaces. Consequently, larger adsorbates adsorb to the surfaces of the graphitized carbon blacks. After they are collected from the air sample, all adsorbed compounds can be thermally desorbed by using flow-reversal techniques.

Another key advantage to using a multi-bed adsorbent tube containing nonspecific adsorbents is that water adsorption also is a function of size-exclusion. Larger adsorbate molecules compete more readily for the available adsorbent surface. Specific retention volumes (breakthrough volumes) were determined for water and vinyl chloride, using Carbosieve S-III adsorbent and for water and chlorobenzene, using Carbotrap. In each case, the specific retention volume of the organic compound is a magnitude of 1000 greater than that of water (Table III). The surfaces of these adsorbents (and that of Carbotrap C as well) are therefore considered to be hydrophobic.

Specific retention volume data are excellent tools with which to characterize the adsorptive properties of adsorbents. In this work, characterization evaluations were performed by following procedures outlined in EPA Document # 600/7-78-054 (2). These evaluations focused on adsorbate/adsorbent interactions occurring in the low coverage (or Henry's Law) region, using established specific retention volumes, adsorption coefficients, and equilibrium sorption capacities. Specific retention volumes (Table IV) were determined at elevated temperatures. The resulting straight line equation was extrapolated, via linear regression analysis, to obtain the specific retention volume at ambient temperature (V_g^t 20°C). This value is expressed in milliliters of gas per gram of adsorbent, and therefore is useful for determining adsorbent bed weights.

To establish working ranges for the three Class I adsorbents, the specific retention volumes of several key compounds, possessing different sizes and functional groups, were determined. Because the functional range for Carbotrap overlaps those for Tenax® GC and Amberlite® XAD-2 adsorbents, comparative evaluations were performed for these adsorbents (Table V). Note that adsorbent density, as well as unit surface area, plays an important role in determining the total available surface area per tube volume (Table V, line 6). Specific retention volumes, summarized in Table VI, indicate that of the three adsorbates evaluated, Carbotrap adsorbent possesses the greatest affinity for most of the adsorbates used. Tenax GC possesses a greater affinity for n-pentanoic acid because of dipole-dipole interactions between the acid functional group on the adsorbate molecule and phenylene oxide groups on the adsorbent's surface.

The working range for Carbotrap C adsorbent was established by using the same eight adsorbates, plus adsorbates having larger surface areas. Specific retention volumes for Carbotrap C adsorbent (Table VII) are smaller than those for Carbotrap (Table VI), reflecting the smaller surface available for interactions with adsorbates. In the multi-bed tube, Carbotrap and Carbotrap C adsorbents will retain these large molecules. Therefore, only smaller adsorbates were used to characterize the Carbosieve S-III carbon molecular sieve (Table VIII). The large specific retention volume for vinyl chloride, 1.26×10^6 ml/gram, illustrates the adsorbing capacity of this material.

The excellent trapping performance of the adsorbents in the multi-bed tube was complemented by using thermal desorption to rapidly transfer the adsorbates to the gas chromatographic column. The thermal desorption unit used is capable of heating the adsorbent tube to the appropriate temperature in approximately 20 seconds. This rapid transfer eliminates the need for cryofocusing. For example, the rapid removal of the C2 hydrocarbons at 330°C, versus the commonly used 200°C desorption temperature, provides more effective transfer and improved resolution of these adsorbates (Figure 2).

The GC column is also a key factor in the thermal desorption/gas chromatography analysis. The column must refocus, as well as separate, the desorbed analytes. A 6 ft. x 1/8" stainless steel column packed with 60/80 mesh Carbopack™ B packing, at a temperature of 35°C, provided the best results for the C2 analysis in Figure 2.

Both packed and wide-bore capillary columns were chosen to provide effective refocusing and separation of the adsorbates cited in Methods TO-1, TO-2, and TO-3 in EPA Document # 600/4-84-041 (3). Two packed columns were chosen to evaluate the 24 adsorbates cited in these three methods. A 0.1% SPTM-1000 phase coated on 80/100 Carbowax C was used to analyze the nonchlorinated and chlorinated hydrocarbons cited in Method TO-1 (Figure 3). Airborne concentrations of these collected adsorbates ranged from 50 to 100 parts per trillion in a 10 liter air sample. A desorption chamber temperature of 330°C and an initial column temperature of 35°C provided effective chromatography. A 1% SP-1000 phase coated on 60/80 mesh Carbowax B was used to evaluate the adsorbates in Methods TO-2 and TO-3 (Figure 3). This column also was effective for evaluating the TO-1 adsorbates.

A 60 meter x 0.75 mm ID SUPELCOWAXTM 10 bonded phase capillary column (1.0 µm phase film thickness) was effective for evaluating the TO-1, TO-2, and TO-3 adsorbates (Figure 4). A desorption chamber temperature of 330°C and an initial column temperature of 35°C, the same temperatures as used with the packed column, were chosen. The adsorbates cited in all three methods were analyzed effectively under the same analytical parameters.

Desorption efficiency for these 24 adsorbates was determined by vapor-spiking the adsorbent tube with known quantities of each adsorbate. The adsorbates were injected directly through the thermal desorber/gas chromatographic system to establish the control (100%) value. Desorption efficiency was determined by comparing peak areas for desorbed and directly injected samples. Desorption efficiency was determined for both the nonchlorinated and chlorinated adsorbates cited in the EPA methodology (Table IX). Recovery data also were determined for bromoform and acrylonitrile.

In conclusion, a multi-bed adsorbent tube containing three Class I, non-specific adsorbents adsorbs a wide range of airborne organic contaminants in a size-exclusion mode. When this tube is interfaced with a thermal desorber capable of rapidly transferring adsorbates to a GC column, accurate quantitative and qualitative data are obtained for the adsorbates of interest.

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*British Pat. No. 1310422
German Pat. No. 1935500

Table I
Classification of Molecules and Adsorbents by Capacity
for Nonspecific and Specific Interaction (1)

Molecule Type	Adsorbent Class		
	Class I (no ions or active groups)	Class II (localized positive charges)	Class III (localized negative charges)
Group A (e.g., n-alkanes) spherically symmetrical shells or σ -bonds		nonspecific interactions governed mainly by dispersion forces	
Group B (e.g., aromatic hydrocarbons) electron density locally concentrated on bonds or links, π -bonds	nonspecific interactions		nonspecific and specific interactions
Group C (e.g., organometallics) positive charge localized on peripheral links			
Group D (e.g., acids and bases) functional groups with locally concentrated electron density and positive charge on adjacent links			

Table II
Physical Properties of the Class I, Nonspecific Adsorbents
Used in the Multi-bed Tube

Adsorbent	Surface Area (m ² /gram)	Density (grams/ml)
Carbotrap C	10	0.72
Carbotrap	100	0.38
Carbosieve S-III	800	0.61

Table III
Specific Retention Volumes Show Class I Adsorbents
Have Hydrophobic Properties

Adsorbent	Adsorbate	Specific Retention Volume (ml/gram)
Carbosieve S-III	water	2.3×10^3
	vinyl chloride	1.26×10^6
Carbotrap	water	8.0×10^2
	chlorobenzene	1.58×10^6

Table IV
Equation for Calculating Specific Retention Volume (2)

Breakthrough Volume (V_g^t) =

$$\begin{aligned}
 & \frac{\text{ml of gas}}{\text{grams of adsorbent}} = \frac{\text{calculated volume of gas passing through the system}}{\text{weight of adsorbent (grams)}} \\
 & = j F_c \frac{(t_r - t_a)}{W_a}
 \end{aligned}$$

Table V
Physical Properties of Adsorbents

Property	Carbotrap	Adsorbent Tenax GC	Amberlite XAD-2
Surface Area (m^2/g)	100.0	23.5	364.0
Particle Size (mesh)	20/40	35/60	20/40
Density (g/ml)	0.38	0.14	0.38
Pore Volume (cc/g)	---	0.053	0.854
Bed Weight (g)	0.4637	0.1650	0.3966
Total Surface Area (m^2)	46.37	3.878	144.4

Table VI
Specific Retention Volumes for Adsorbents

Adsorbate	Carbotrap	V_g^t 20°C (ml/g) Tenax GC	Amberlite 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 VII
Specific Retention Volumes for Adsorbates on Carbotrap C

Adsorbate	V_g^t 20°C (ml/g)
n-Decane	2.97×10^5
Benzylamine	5.38×10^4
Chlorobenzene	5.48×10^3
p-Xylene	3.75×10^4
p-Cresol	1.27×10^5
n-Pentanoic Acid	1.71×10^5
Cyclohexanone	8.28×10^3
2-Methyl-2-Propanol	3.17×10^3

Table VIII
Specific Retention Volumes for Adsorbates on Carbosieve S-III

Adsorbate	V_g^t 20°C (ml/g)
Chloromethane	1.83×10^4
Vinyl Chloride	1.26×10^6

Table IX
Desorption Efficiency of the Multi-bed Trap
for Adsorbates Cited in EPA Methodology

Adsorbate	Desorption Efficiency (%)
Benzene	100
1-Heptene	99
n-Heptane	99
Toluene	99
Ethylbenzene	100
m-Xylene	100
p-Xylene	99
o-Xylene	99
Isopropylbenzene (Cumene)	99
1,1-Dichloroethylene	101
3-Chloropropene	100
Chloroform	94
1,2-Dichloroethane	102
1,1,1-Trichloroethane	100
Carbon Tetrachloride	99
1,2-Dichloropropane	101
Vinyl Chloride	101
Dichloromethane	98
Chlorobenzene	100
Tetrachloroethylene	99
Trichloroethylene	101
Bromoform	100
Acrylonitrile	100

Figure 1
Multi-bed Adsorbent Tube

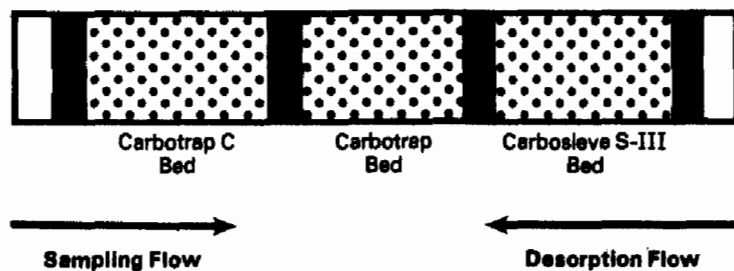


Figure 2
Comparison of Desorption Temperatures

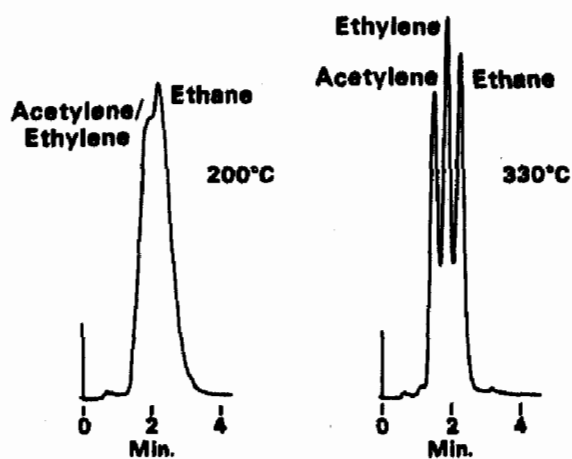


Figure 3
Thermal Desorption Analyses on a Packed Column

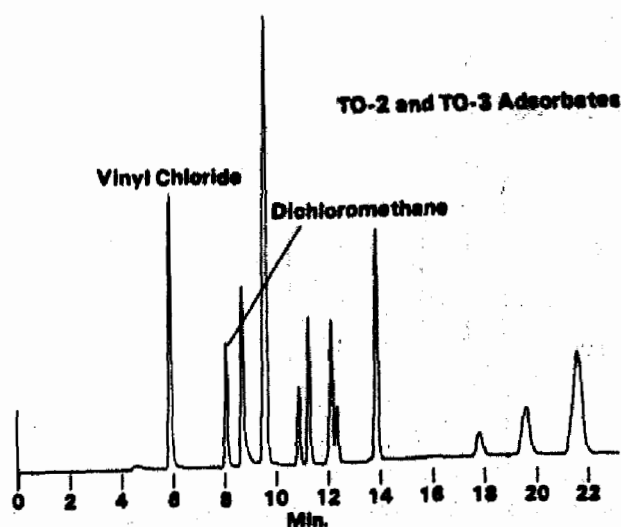
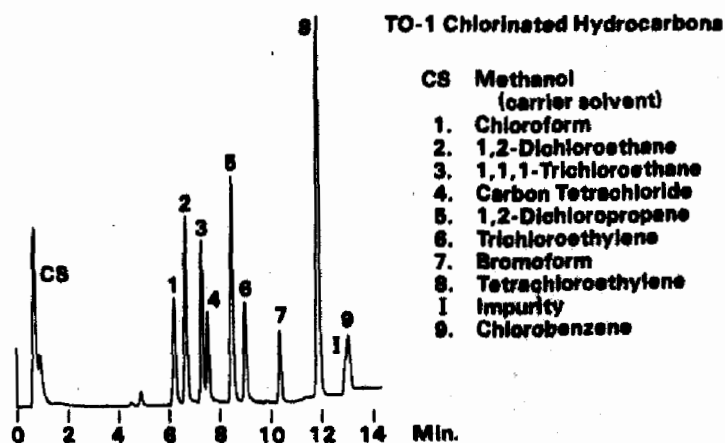
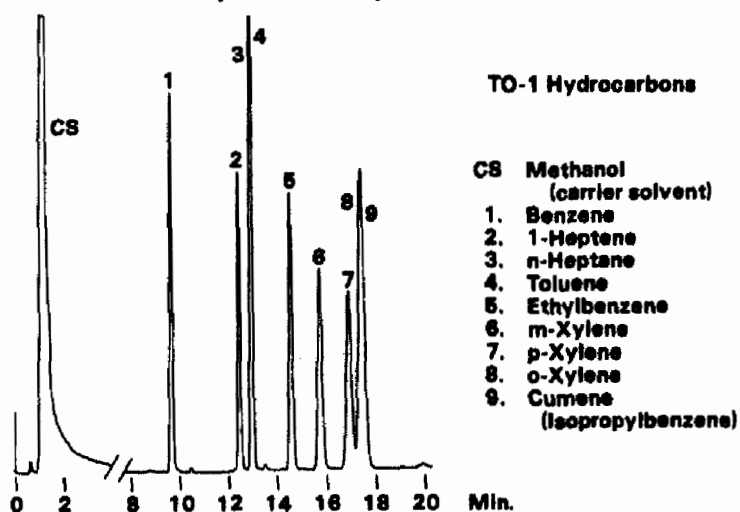
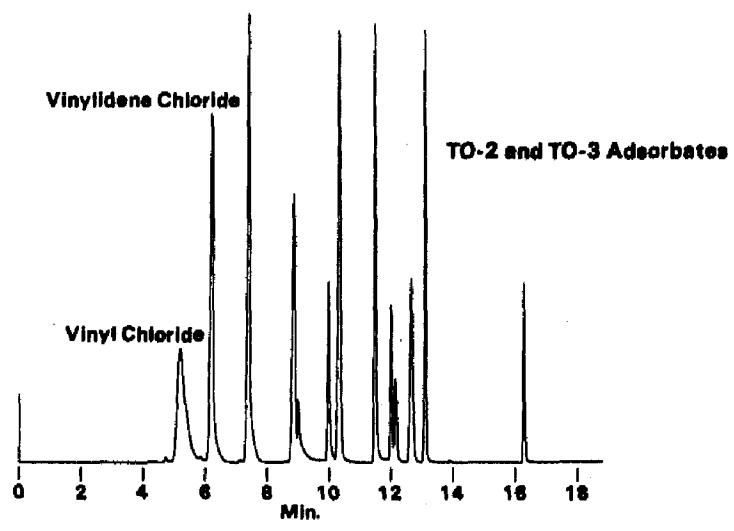
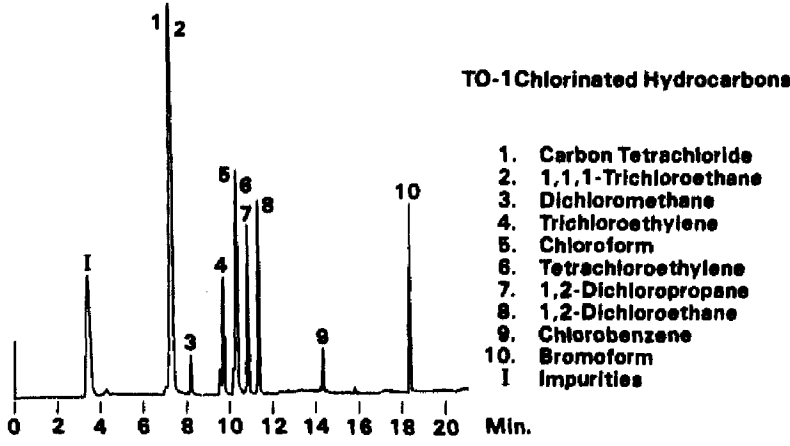
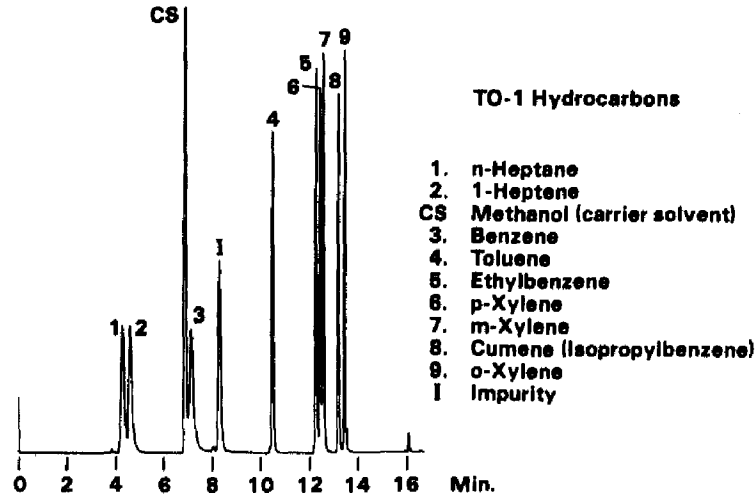


Figure 4
Thermal Desorption Analyses on a Wide Bore Capillary Column



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