



Project Summary

Annular Denuder Sampler for Phase-Distributed Semivolatile Organic Chemicals

R. W. Coutant, P. J. Callahan, and J. C. Chuang

The objectives of this study were (1) to design and construct a high-efficiency, high-volume denuder sampler to separately collect and maintain the integrities of the vapor and particle-associated fractions of organic chemicals that may be phase distributed in the atmosphere; and (2) to use this apparatus in a series of field measurements to determine the phase distribution of selected polynuclear aromatic hydrocarbons.

The design approach involved consideration of diffusive mass transport and the physical limitations of the standard General Metal Works PS-1 high-volume sampler. The goal was to achieve a compact denuder, with a removal efficiency for volatile PAH of at least 90 percent at flow rates of up to 200 L/min, which could readily be coupled to the PS-1 sampler. The result is a 20.3 cm x 8.25 cm compound annular denuder consisting of a solid aluminum core plus 12 concentric cylindrical aluminum shells, with annuli thicknesses of 1.6 mm. The shells are coated with approximately 30 μ m-thick layers of silicone grease that serves as the vapor phase collector. Laboratory tests of this denuder show no detectable (<10 percent) removal of ambient particulate matter larger than 0.1 μ m mean diameter at flow rates of 100-200 L/min. The vapor collection efficiency, as measured with naphthalene, is better than 95 percent, and it has the capacity for removal of approximately 180 μ g of naphthalene with better than 90 percent efficiency.

The field experiments consisted of three series: (1) outdoors during the winter; (2) indoors within a laboratory; and (3) outdoors during the summer. In these experiments, a denuder difference approach was followed to monitor the phase distributions of 18 PAH: naphthalene, quinoline, acenaphthylene, anthracene, phenanthrene, pyrene, fluoranthene, cyclopenta(c,d)pyrene, benz(a)anthracene, chrysene, retene, benzo(a)pyrene, benzo(e)pyrene, benzo-fluoranthene, perylene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene, and coronene. The 2-, 3-, and 4-ring PAH all showed considerable potential for volatilization, but no evidence (<0.02 ng/m³) was seen for the heavier PAH in the vapor phase. The results in general are consistent with previous work and extend the overall body of information on the phase distributions of PAH and their tendencies for artifact formation as a result of volatilization during sampling.

This report is being submitted in fulfillment of Contract No. 68-02-4127 (WA-41 and WA-46) by Battelle Columbus Division under the sponsorship of the U.S. Environmental Protection Agency. It covers a period of March 1, 1987, to September 30, 1988, and work was completed as of September 30, 1988.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a

separate report of the same title (see Project Report ordering information at back).

Introduction

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

From the viewpoints of atmospheric fate and transport and, more importantly, human health risk assessment, it may be necessary to distinguish between the vapor and particle-bound PAH. Traditional sampling methods have used only filtration to collect ambient aerosol. More recently, the use of backup traps containing polyurethane foam (PUF) or other vapor sorbents such as XAD-2 to collect vapor passing through or stripped from the filter has become more widespread. While this approach may permit total collection of PAH, it does not take into account the possibility of artifact formation as a result of either condensation or vaporization during the sampling process. Furthermore, there is the possibility that the integrity of collected sample may be altered by reaction of PAH with reactive species such as ozone during sampling. Other researchers have used vapor denuder systems to examine the questions of carbonaceous particle integrity and sampling of chlorinated organic compounds.

In two previous work assignments conducted under this contract, a research level denuder sampler was used to evaluate the phase distributions of selected PAH during ambient air sampling. Results of that work were published recently. The denuder used in that study was an open tubular design that necessitated limitation of the sampling rate to only 15 L/min, a rate well below the 200 L/min normally used for ambient air sampling with the PS-1 sampler. Many PAH and other semivolatile organic compounds (SVOC) are present in ambient air at levels that are so low as to require the use of the larger sampling

rate to provide enough sample for analytical and bioassay purposes. A practical denuder sampler for PAH and other SVOC therefore requires the use of a more efficient denuder system that will permit sampling at rates of the order of 100-200 L/min.

A paper describing the design, construction and preliminary laboratory evaluation of a high volume annular denuder sampler that satisfies these needs has been prepared for publication in the open literature, and is attached for easy reference as Appendix A of this report.

Objective

The objectives of WA-41 were to design and construct a high-efficiency, high-volume denuder sampler that would separately collect and maintain the integrities of the vapor and particle-associated fractions of organic chemicals that are phase distributed in the atmosphere. The specific goal was to construct compact denuder that could be readily integrated within the normal PS-1 sampler structure, while achieving at least 90 percent removal efficiency for SVOC vapors at a sampling rates up to 200 L/min. Additionally, this device should not interfere with normal filtration sampling of ambient particulate matter.

The objective of WA-46 was to utilize this high efficiency denuder sampler in a series of denuder difference type experiments to determine the phase distribution of selected polynuclear aromatic hydrocarbons in the ambient air. These field experiments were to include measurements made during both winter and summer months to attempt to encompass the normal range of ambient PAH sampling conditions.

Procedure

The denuder difference method was used in a series of ambient PAH sampling experiments conducted during both winter and summer months in Columbus, Ohio. The denuder was a high volume compound annular denuder (HVCAD) that was designed for easy interface with a standard PS-1 sampler for sampling at flow rates of 100 to 200 L/min. A finite-element model based on laminar flow with finite wall reaction kinetics was developed and used for design of the annular denuder. Analyses of PUF and filter samples for 18 PAH were performed by GC/MS.

Results and Discussion

Results of the experiments were analyzed in terms of (1) the artifact re-

sulting from volatilization of PAH during the sampling process, and (2) the vapor/condensed phase distribution of volatile PAH. Data analysis included previously reported data from sampling runs made during 1985-1986 and the current set of data. A summary of the vapor and artifact levels is shown in Table 1. In general, the tendency for artifact formation correlates well with the equilibrium vapor pressures of the pure compounds, and appreciable artifact formation was seen with the 2-, 3-, and 4-ring PAH, but not with the heavier PAH such as BaP.

The vapor/adsorbed phase distribution of the volatile PAH were analyzed in terms of the Dubinin-Radushkevich isotherm. Use of this isotherm allowed generalization of the observed vapor concentrations with specific correlation with the vapor pressures and polarizabilities of the PAH. The data were used to derive a general set of Dubinin-Radushkevich parameters which are recommended for consideration of other PAH and sampling conditions.

Conclusions and Recommendations

A denuder sampler capable of operating at a minimum of 95 percent vapor removal efficiency at flow rates up to 200 L/min was designed and constructed. This denuder is compact and couples readily to the PS-1 sampler. The holder serves as an interface to the PS-1 sampler and as a transport container. Laboratory tests of this denuder show a detectable (<10 percent) removal of ambient particulate matter larger than 0.5 μm at flow rates of 100-200 L/min. The vapor collection efficiency, as measured with naphthalene, is better than 95 percent, and it has the capacity for removal of approximately 180 μg of naphthalene with better than 90 percent efficiency.

Use of the sampler in a series of outdoor and indoor denuder difference sampling experiments yielded phase distribution data that are consistent with previous work. The results show that 2-, 3-, and 4-ring PAH are sufficiently volatile that measurable quantities of these compounds are found in the vapor phase. Also, these same compounds show considerable tendencies for volatilization as a consequence of changes in ambient conditions during the sampling process. This sampling artifact is shown to be correlated with the vapor pressures of the PAH. The dependence of PAH distribution between vapor and adsorbed state

Table 1. Summary of PAH Vapor and Artifact Levels Determined with both OTD and HVCAD Samplers(a)

Compound	Vapor		Artifact	
	Range	Median	Range	Median
Naphthalene(b,c)	9.1-47.3	22.4	47.1-89.8	75.5
Quinoline(c)	45.4-81	62.3	7.7-43.8	9.5
Acenaphthylene(c)	22.3-99.5	66.8	16.9-80.3	57.9
Anthracene	14.0-92.3	56.6	12.7-92.2	31.9
Phenanthrene	25.0-86.5	50.6	12.7-80.3	44.7
Pyrene	21.0-91.1	60.9	0.7-99.5	16.3
Fluoranthene	26.6-90	60.4	4.5-61.7	16.5
Cyclopenta(c,d)pyrene	(compound not consistently detected)			
Benz(a)anthracene	7.5-67.2	32.5	8.3-53.0	30.5
Chrysene	15.0-64.8	40.3	5.7-50.2	17.5
Retene(c)	30.7-92.3	78.1	3.3-21.1	7.4
Benzo(a)pyrene	ND(d)	ND	ND	ND
Benzo(e)pyrene	ND	ND	ND	ND
Benzofluoranthene	ND	ND	ND	ND
Perylene	ND	ND	ND	ND
Benzo(g,h,i)pyrene	ND	ND	ND	ND
Indeno(1,2,3-c,d)pyrene	ND	ND	ND	ND
Coronene	ND	ND	ND	ND

(a) Expressed as percentage of total amount of each compound

(b) Some PUF data for naphthalene suspect because of possible breakthrough

(c) Compounds determined only in current series of experiments

(d) Not detected consistently in PUF samples

is shown to be well-represented by the Dubinin-Radushkevich isotherm. As a rule-of-thumb, ambient PAH vapor concentrations are approximately 1/10,000th of the equilibrium vapor concentrations of the pure compounds. Limited data on quinoline obtained in this study suggest lower vapor concentrations for this polar PAH. While the normalized concentrations (using phenanthrene as a reference) of volatile PAH in ambient air appear to vary some with the seasons, the normalized concentrations of the same compounds in the adsorbed phase appear to be relatively constant. Seasonal variations

in the relative amounts of some of the volatile PAH such as acenaphthylene and pyrene may be due to the reactivity of these compounds.

The denuder design and performance model developed on this program provides a sophisticated, but easy to use, mechanism for extending the current annular denuder design to other sampling needs and applications. For example, the design of a compact compound annular denuder for use with low-volume indoor samplers would be quite straight-forward.

It is recommended that consideration be given to the phase distributions of

other types of SVOC than the PAH included in this study. Such compounds as the polar PAH and pesticides would be expected to be more strongly adsorbed than the compounds studied here. While, in principle, the Dubinin-Radushkevich isotherm should apply to such compounds, with appropriate corrections for their polarizability, other generalizations derived from the current work, such as the relationship between artifact and vapor pressure, may not apply.

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Robert G. Lewis is the EPA Project Officer (see below).

The complete report, entitled "Annular Denuder Sampler for Phase-Distributed Semivolatile Organic Chemicals," (Order No. PB 89-169 858/AS; Cost: \$21.95, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
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Telephone: 703-487-4650

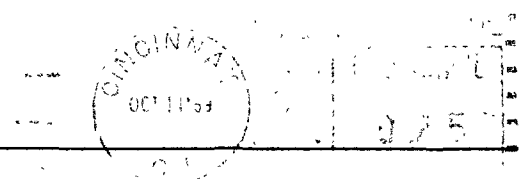
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