



## Project Summary

# Evaluation of Sampling Methods for Gaseous Atmospheric Samples

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Laboratory tests of air sampling methods were conducted with FEP Teflon bags, Tedlar bags, five-layered polyethylene-aluminized bags, Pyrex glass bulbs, stainless steel canisters electropolished by the Summa process and by a Research Triangle Institute process, Tenax-GC cartridges, charcoal tubes, and nickel cryogenic traps. The sampling methods were evaluated for collection and recovery efficiency; interferences from ozone, nitrogen oxides, sulfur dioxide, and water vapor; sample stability in storage; analytical accuracy, reproducibility, and limits of detection; simplicity; and convenience. Tests were conducted with mixtures of 27 organic compounds comprising a range of chemical and physical properties. Mixtures of the model compounds were prepared in a specially designed permeation/dilution system. Mixtures were prepared in clean ("zero") air at parts per billion and parts per trillion concentration levels.

For the storage/stability studies, mixtures of the test compounds stored in the various containers were sampled and analyzed after storage for zero, three, and seven days. Dynamically flowing mixtures of the inorganic gases and vapors and test compounds were prepared for the interference studies. Tests were conducted at two concentration levels of the interference mixture. A quality assurance program was employed for all measured and analyzed data.

An automatic air monitoring sampler was designed and fabricated to collect organic gases and vapors on sorbent cartridges. The prototype sampler was

designed to collect duplicate samples and up to 12 series samples for various selectable sampling periods. A printer automatically recorded sample identification and sample volume.

*This Project Summary was developed by EPA's Environmental Sciences Research 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

Because *in situ* measurement of organic vapors in the atmosphere is not always feasible, samples are often collected in the field and returned to the laboratory for analysis. The quality of the analyses of the various organic substances in the atmosphere directly depends on the validity of the sample collection, storage, and transfer methods employed. Various methods have been used to collect gaseous atmospheric samples. These include collection in liquids, on solid adsorbents, in plastic and rigid containers, and in cryogenic traps. Serious limitations have been reported for all methods, including adsorption of analyte species on container walls, permeation of vapors through the walls of plastic bags, interference from water vapor, production of artifact contamination, sample loss through chemical reaction with the container walls or other chemical species in the sample, and inefficient collection and transfer of analyte species.

This study was undertaken to test and evaluate various methods of collecting

and transferring gaseous atmospheric samples for analysis of a variety of toxic organic pollutants by gas chromatography. In addition, in response to a need for an automatic organic vapor sampler in ambient air monitoring, a sampler to collect sequential and replicate samples on sorbent cartridges was designed and fabricated.

The following types of sample containers were employed in the study:

1. Polymeric bags
2. Glass bottles
3. Stainless steel canisters
4. Tenax-GC sorbent cartridges
5. Charcoal sorbent cartridges
6. Cryogenic tubular traps

Sampling methods were tested with synthetic mixtures of 27 organic compounds comprising a range of chemical and physical properties (see Table 1).

**Table 1.** Organic Compounds Tested

Chemical Group	Compound	Boiling Point (°C)
Chloroalkanes	Methyl chloride	-24.2
	1,2-Dichloropropane	96.4
	Chloroform	61.7
	1,1,2,2-Tetrachloroethane	146.2
	1,1,1-Trichloroethane	74.1
Chloroalkenes	Vinyl chloride	-13
	Tetrachloroethylene	121
	2-Chloro-1,3-butadiene	59.4
	1,1-Dichloroethylene	37
	Allyl chloride	45
Chlorinated aromatics	Chlorobenzene	132
	m-Dichlorobenzene	173
	Benzyl chloride	215
Aromatics	Benzene	80.1
	Toluene	110.6
	1,2,3-Trimethylbenzene	176.1
	Ethylbenzene	136.2
	o-Xylene	139.1
Alkanes	n-Decane	174.1
Nitro compounds	Nitrobenzene	210.8
Phenols	o-Cresol	190.9
Acrylo compounds	Acrylonitrile	77
Ethers	Furan	31.4
	Bis-(2-chloroethyl)ether	178
	Propylene oxide	34.3
	α-Epichlorohydrin	116.5
Sulfur compound	Methyl mercaptan	6.2

The evaluation of the sample collection and transfer methods included the following considerations:

1. Limits of applicability
2. Collection efficiency
3. Recovery (transfer) efficiency for gas chromatographic analysis
4. Analytical accuracy and detection limits
5. Effect of potential interferences, including ozone, NO<sub>x</sub>, SO<sub>2</sub>, and water vapor
6. Sample stability in storage
7. Quality of gas chromatograms
8. Simplicity and convenience

Synthetic mixtures of the model compounds were prepared in a permeation/dilution system designed to deliver the compounds in the concentration range of 10 ppt to 100 ppb in clean ("zero") air.

In the study of potential interferences, mixtures of ozone (O<sub>3</sub>), nitrogen oxides (NO<sub>x</sub>), sulfur dioxide (SO<sub>2</sub>), and water vapor were prepared in air and mixed with the model compounds in a mixing bulb within the permeation/dilution system oven. Samples collected from the permeation/dilution system were analyzed with gas chromatography by using capillary columns and either flame ionization or electron capture detectors.

Two experimental designs were developed. In one design the sampling volume (≈30 L), sampling time, sampling rate, and relative humidity (30%) were held constant. No O<sub>3</sub>, NO<sub>x</sub>, or SO<sub>2</sub> was added. Model compound concentration and storage time were variable parameters. Tests were conducted at three concentration levels: zero, low (> 10 ppt < 1 ppb), and high (> 1 ppb < 100 ppb). Samples were analyzed after being stored less than one day, after three days, and after seven days.

In the other experimental design, the test mixture concentration (ppb level), sample volume (30 L), sampling time, and sampling rate were held constant. Concentrations of O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub>, and water vapor were variable parameters. Tests were conducted at two levels: low (O<sub>3</sub> ≈ 75 ppb, NO<sub>x</sub> ≈ 100 ppb, SO<sub>2</sub> ≈ 100 ppb, relative humidity ≈ 30%) and high (O<sub>3</sub> ≈ 500 ppb, NO<sub>x</sub> ≈ 500 ppb, SO<sub>2</sub> ≈ 200 ppb, and relative humidity ≈ 90%). Triplicate samples were collected with each type of sampling device.

### Procedures

Polymeric bags (FEP Teflon and Tedlar) were cleaned before testing by flushing them with clean air and exposing them to ozone and direct sunlight irradiation. Five-layered aluminized bags could not be made reasonably clean and were dropped from the study. Glass bulbs were prepared from 2-L round-bottom Pyrex glass flasks fitted with Teflon high-vacuum stopcocks. They were filled with clean air and evacuated at 150 °C. Two types of steel canisters were tested. One was fabricated in the laboratory of electro-polished stainless steel and had a 2-L capacity. The other was a 6-L stainless steel container manufactured and sold by D&S Instruments, Ltd. polished by the Summa process. Both types of canisters were cleaned by filling them with clean air and evacuating them at 150°C. Virgin Tenax-GC was extracted with methanol, dried in a vacuum oven at 100°C, and sieved through 30/60 mesh. Charcoal tubes (from the National Institute of Occupational Safety and Health) were

purchased commercially and used as they were received. Cryogenic traps were made of coiled nickel tubing (0.25 in. o.d. x 24 in. long) and were washed with methanol and pentane, thermally conditioned at 160°C with a helium gas purge, and filled with clean glass beads.

Sampling was accomplished by connecting the sampling devices to the glass sampling manifold of the permeation/dilution system used to generate the test gas mixtures. Bags, Tenax-GC cartridges, charcoal tubes, and nickel cryogenic traps were connected directly to the manifold. The steel canisters and glass bulbs were connected to the manifold through a metal bellows pump. Bags were filled with 10 or 20 L of sample. Glass bulbs and steel canisters were filled to about 15 psig. A 30-L sample volume was used with the Tenax-GC cartridges, charcoal tubes, and cryogenic traps.

Samples in bags, glass bulbs, and steel canisters were transferred to a gas chromatograph by a gas sampling valve equipped with a stainless steel sampling loop. Typically, 200 mL of sample was passed through the sampling loop while it was immersed in liquid oxygen. Bulbs and canisters were placed in a heated box (50° to 90°C) during sample transfer to minimize loss of test compounds to the container walls. Tenax-GC cartridge samples were transferred by a thermal desorption chamber equipped with a nickel capillary cryogenic trap. Cryogenic trap samples were first transferred to Tenax-GC cartridges by a thermal purge with helium gas and then transferred to a gas chromatograph via the thermal desorption chamber. Charcoal trap samples were placed in a flask and desorbed with a carbon disulfide/methanol solution. Aliquots were injected into a gas chromatograph equipped with an electron capture detector

## Results

### Storage Stability Studies

Storage/stability studies of polymeric bags, glass bulbs, and steel canisters were not conducted at the low (ppt) concentration level of test compounds. In low-level tests of Tenax-GC cartridges, charcoal tubes, and cryogenic traps, most test compounds could not be detected or could not be measured because of interferences in the gas chromatogram. Results for the high-level studies are reported below.

Teflon and Tedlar bags developed high levels of background contamination when stored in lab air. Consequently, storage tests were conducted with the bags stored in sealed steel boxes which had been flushed with clean dry air. In tests conducted with 15 of the 27 model compounds, Teflon bags showed large losses after seven days of storage. In Tedlar bags, the long-term losses (comparisons of Day 0 analyses with Day 7 analyses) were generally low. Recoveries of test compounds on Day 0 were generally  $\geq 70\%$ . However, propylene oxide, *a*-epichlorohydrin, and *o*-cresol could not be detected.

Long-term losses in the glass bulbs were generally low. Recoveries of test compounds were generally  $\geq 75\%$  for compounds with boiling points below that of ethylbenzene. Recovery of compounds with higher boiling points was generally lower. Propylene oxide, *a*-epichlorohydrin, and *o*-cresol could not be detected.

Long-term losses were generally low in the steel containers electropolished by a Research Triangle Institute process and in the Summa-polished containers. Recoveries of test compounds with boiling points below that of ethylbenzene were generally slightly higher for the Summa-polished canisters, and the recoveries of compounds with higher boiling points were even higher. Recoveries for the Summa-polished canisters generally were  $\geq 72\%$ . Propylene oxide, *a*-epichlorohydrin, and *o*-cresol could not be detected.

No long-term losses of test compounds were apparent in the results obtained with Tenax-GC cartridges. For compounds with breakthrough volumes greater than the sampling volume, recoveries generally were  $> 85\%$ . Recovery was highly variable for those compounds with smaller breakthrough volumes, even after applying corrections for breakthrough. These compounds had breakthrough volumes ranging from 1 to 18 L. All test compounds could be detected with the Tenax-GC cartridges.

Most test compounds could not be detected in samples collected in charcoal tubes. High recoveries were obtained only for 1,2-dichloropropane and bis-(2-chloroethyl)ether. Long-term losses of these compounds were 14% and 23%, respectively.

For tests of a mixture of 14 test compounds at the high concentration level, unpacked cryogenic traps gave poor recoveries, except for bis(2-chloroethyl)ether. Traps packed with glass beads and cooled with dry ice were used

for tests at the low concentration level. However, most compounds either were not detected or were obscured by interferences in the gas chromatogram.

### Interference Studies

Teflon bags were not included in the interference studies. Recoveries from Tedlar bags were generally lower with the high-level interference mixture of  $O_3/NO_x/SO_2$ /water vapor than with the low-level mixture. Recoveries of compounds with low boiling points in the presence of the low-level mixture were generally lower than recoveries obtained in the storage/stability study. Recoveries with the low-level mixture generally were  $\geq 71\%$ . Methyl mercaptan and the three test compounds reported in the storage studies were not detected.

Increasing the level of interference produced mixed results from the glass bulbs; the most prevalent effect was a decrease in the recovery of test compounds. For compounds with boiling points  $\geq 74^\circ C$ , recoveries with the low-level mixture generally were greater than those obtained in the storage studies. Recoveries of all compounds generally were  $\geq 72\%$ . The four test compounds which were undetected in the polymeric bags were also undetected in the glass bulbs.

Increasing the level of interference in the Summa-polished canisters resulted in a decrease in recovery for the majority of detectable test compounds. In comparison with the results obtained in the storage studies, recoveries at the low level of interference were either decreased or unchanged for compounds with boiling points  $\leq 37^\circ C$  and either increased or unchanged for those with boiling points  $\geq 74^\circ C$  (except for bis-2(chloroethyl)ether and the four undetected compounds). Recoveries of all compounds generally were  $\geq 74\%$  with the low-level mixture.

Generally, increasing the level of interference in Tenax-GC cartridges did not produce a significant change in recoveries of those test compounds with breakthrough volumes greater than the sampling volume. When a glass fiber filter impregnated with sodium thiosulfate was placed in the sampling line ahead of the Tenax-GC cartridge, recoveries at both interference levels were generally improved. The filter, however, did not remedy the problem of chromatographic interferences that occurred for several compounds. Recoveries of the majority of compounds that could be measured and

had breakthrough volumes greater than the sampling volume were lower than those obtained in the storage studies.

The interference studies with charcoal tubes were generally unproductive. Tetrachloroethylene and 1,1,2,2-tetrachloroethane were the only compounds observed with the electron capture detector.

Because of poor results obtained in the storage/stability study, liquid oxygen was used to cool the packed nickel cryogenic traps. Excessive water, which collected in the traps and was subsequently transferred to the Tenax-GC cartridges along with the test compounds, was removed by storing the cartridges in a culture tube that contained a quantity of calcium sulfate. The presence of the low-level interference mixture generally resulted in lower recoveries of the test compounds. However, even with the liquid oxygen coolant, recoveries in the absence of the interference mixtures were generally poor. Comparison of high-level results with low-level results was precluded by the high variability in observed recoveries.

### ***Design and Construction of an Automatic Air Sampler***

A prototype sampler was designed and constructed to collect ambient air samples automatically in Tenax-GC cartridges over a period of 72 h. The sampler operates at 120 volts AC and consists of a control unit connected to two independent sampling heads by flexible gas flow lines, heater supply lines, and thermocouple wires. Each sampling head is housed in a heated sample cover and accommodates six sampling cartridges plus one blank. The control unit incorporates a vacuum pump, a flow meter, a flow integrator, and a printer. Two sampling heads allow for duplicate sampling and the collection of up to 12 series samples. Cartridges are transported in the sampling head block, which is disconnected from the sampling lines and sealed with cap plates on both ends. Sampling rates can be set from 7 mL/min to 1.5 L/min. Sampling periods are available between 15 min and 12 h. The printer prints time of day, date, and sample volume, and it identifies the sample lines being used.

Short-term laboratory tests indicated that the sampler operated properly. The level of contamination developed in clean cartridges stored in sealed sample heads for seven days was approximately 2 times the level developed in cartridges sealed in culture tubes.

## **Conclusions**

Teflon and Tedlar bags are subject to leakage, permeation of gases through the bag wall, and release of contaminants from the wall by the interference mixture employed in this study. Safe storage of samples is limited to 24 h or less unless bags are protected from dirty environments.

Glass bulbs break easily, which may seriously limit the amount of sample available for analysis. Although low recoveries were obtained in the storage studies of compounds with high boiling points, results from the interference studies suggest that low levels of inorganic gases and vapors present in ambient air may improve recoveries of these compounds.

Ruggedness and ease of cleaning are two particular advantages of passivated stainless steel canisters for field sampling. However, even when pressured to two atmospheres, the small volume of these containers may seriously limit the amount of sample available for analysis. Overall, recoveries of test compounds at the low level of interferences was comparable to results obtained with Tedlar bags and glass bulbs. These containers, as well as the bags and bulbs, may not be suitable for some compounds (e.g., methyl mercaptan, propylene oxide, *a*-epichlorohydrin, and *o*-cresol).

For compounds with sufficiently high breakthrough volumes, a relatively large sample (all of which is available for analysis) can be collected in a Tenax-GC cartridge. The sampling cartridges are light, small, and do not retain significant amounts of carbon dioxide and water. Low breakthrough volume is a problem with some compounds. Also, great care is required to avoid contamination of cartridges by contact with ambient air before and after sampling. Low levels of inorganic gases and vapors present in ambient air may result in poor recoveries of some compounds and analytical interferences that preclude analyses for certain other compounds. Improved recoveries may be obtained by using glass fiber filters impregnated with sodium thiosulfate. The filter also can be expected to produce improvements in the recoveries of compounds collected in the other types of containers.

Results obtained with charcoal tubes and nickel cryogenic traps were generally poor. Neither sampling method, as employed in this study, showed sufficient promise for use in ambient air sampling.

## **Recommendations**

The three most promising types of sampling devices (Pyrex glass bulbs, Summa-polished stainless steel canisters, and Tenax-GC cartridges) should be further evaluated under field conditions. The study should focus on gaseous organic priority pollutants with the objective of establishing a generalized standard sampling protocol for priority pollutants. Field testing should include the following:

1. Indoor and outdoor sampling
2. Comparison of performances under a variety of ambient conditions
3. Test compounds representative of all types of gaseous organic priority pollutants
4. Spiking samples quantitatively with test compounds and labeled surrogate compounds
5. Evaluation of sodium thiosulfate-impregnated filters with all sampling devices
6. *In situ* comparisons with other sampling methods being used in other field studies

The automatic sampler requires further testing before it can be judged acceptable for ambient air monitoring. The reliability, accuracy, and reproducibility of the sampler need to be evaluated in the laboratory and in the field under a variety of ambient conditions. The sampler should be modified so that information on power interruptions during sampling will be recorded.

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*The complete report, entitled "Evaluation of Sampling Methods for Gaseous Atmospheric Samples," (Order No. PB 84-190 735; Cost: \$23.50, subject to change) will be available only from:*

*National Technical Information Service  
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