



## Project Summary

# Comparison of Solid Adsorbent Sampling Techniques for Volatile Organic Compounds in Ambient Air

R. M. Riggin and R. A. Markle

The objective of this study was to compare the performance of three solid adsorbents (Tenax<sup>®</sup>, an experimental polyimide resin, and Sphero carb<sup>®</sup>) as well as whole air collection in canisters followed by cryogenic trapping/gas chromatography for sampling and analysis of a target list of volatile organic compounds in ambient air.

A series of 14 experimental sampling runs, wherein parallel samples were collected using each of the techniques, were conducted over a one-month period. Several of the runs used audit or other reference standards as a check on method performance for known analyte concentrations.

Compared to the three adsorbent methods, whole air collection in canisters followed by cryogenic trapping/gas chromatography offered better precision and accuracy for the compounds of interest, especially when a mass selective detection system was employed. None of the three adsorbents gave optimal performance for the entire list of compounds, although in general Tenax<sup>®</sup> gave the best results. Sphero carb<sup>®</sup> was the best adsorbent for chloroethene (vinyl chloride), dichloromethane, and 1,1,2-trichloro-1,2,2-trifluoroethane.

The polyimide material suffered from a number of operational problems which weigh heavily against its use in ambient air sampling.

*This Project Summary was developed by EPA's Environmental Monitoring Systems 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

The Methods Development and Analysis Division of the Environmental Monitoring Systems Laboratory (EMSL) of the U.S. Environmental Protection Agency (EPA) develops and evaluates state-of-the-art and emerging analytical techniques for determining organic compounds in ambient air. Recently a priority listing of volatile organics has been established, and EMSL is focusing on further development of analytical methodology for the determination of these compounds.

In general one of two approaches, cryogenic trapping or gas/solid adsorption, is used to preconcentrate volatile organics in ambient air. Each approach has advantages and limitations. Cryogenic trapping has been demonstrated to provide excellent recovery and precision for a number of volatile organic compounds but is somewhat inconvenient when used in the field because of the complexity and size of the apparatus. Solid adsorbents can be conveniently transported to the field for sam-

pling and returned to the laboratory for analysis. Unfortunately none of the existing solid adsorbents show recoveries comparable to cryogenic trapping techniques for a wide range of components.

By far the most widely employed adsorbent for volatile organic compounds is Tenax® GC. Tenax® has the advantage of good thermal stability which allows for efficient desorption of higher boiling compounds (e.g., C-12 hydrocarbons) during the analysis step. A primary limitation of Tenax® is the low retention volume of highly volatile compounds (e.g., vinyl chloride, 1,2-dichloroethane, etc.). In order to extend the applicability of solid adsorbent collection to more volatile compounds, EMSL has conducted development and evaluation studies for various adsorbents which could be used in place of or in combination with Tenax®. The two most promising materials for this program are a polyimide material formed from pyromellitic anhydride and 4,4'-diaminodiphenylsulfone, and carbon molecular sieves (CMS) sold under the tradenames Spherocarb®, and Carbosieve®, or Carbosphere®.

The objective of the work described in the full report was to compare the performance of the three adsorbents (Tenax®, polyimide, and Spherocarb®) as well as whole air collection in canisters followed by cryogenic trapping for sampling and analysis of representative volatile organic compounds at realistic concentrations in ambient air. The target compounds of concern are listed in Table 1.

### Procedure

Three adsorbents—Tenax®, polyimide, and Spherocarb®—as well as cryogenic trapping/gas chromatography were operated in parallel to sample ambient air, using the sampling manifold shown in Figure 1. The air stream was spiked with 1-10 ng/liter levels of each target compound in order to ensure the presence of a detectable concentration.

Cryogenic sampling was accomplished by collecting integrated samples, over the entire two-hour sampling period, using specially treated stainless steel canisters. The canister samples were then analyzed by cryogenic trapping/gas chromatography using flame ionization (FID), electron capture, and mass selective detectors.

Duplicate ten-liter samples were collected using each of the three adsor-

bents. In addition five and twenty-liter samples were collected for analysis by EPA.

All adsorbent samples were analyzed by gas chromatography/mass spectrometry. The analytes were thermally desorbed from the cartridges onto a liquid nitrogen-cooled trap and subsequently transferred onto a wide-bore SE-30 capillary column. The individual compounds were eluted using a temperature program of -70°C to 150°C at 8°/minute. Components were quantified by comparing the integrated ion intensity for a characteristic ion of each compound to that of standard injected on the same day.

### Results and Discussion

A series of experimental runs, listed in Table 2, were conducted during July and August of 1984. As indicated in Table 2, Runs 4 and 11 were clean air experiments using an audit cylinder supplied by EPA and Run 5 was a similar experiment using the Battelle calibration cylinder.

In order to compare the performance of the various methods for ambient air, the apparent recovery of the adsorbent samples for each run, relative to the cryogenic trapping value, was calculated. Use of the cryogenic trapping value was considered to be most appropriate, since this technique generally agreed best with the expected concentration, and gave better precision than did any of the adsorbent techniques. Most of the values used for the cryogenic trapping were obtained using the mass selective detector, because this detection system was less subject to po-

tential interferences. However, the toluene and 1,2-dimethylbenzene values were obtained using FID due to limitations on the number of ions which could be monitored using the mass selective detector.

Comparative data for the adsorbents is summarized in Table 3. For poorly retained compounds the low volume Tenax® sample (nominally 5 liters) was used, whereas for better retained compounds the duplicate 10 liter Tenax® samples were used for these calculations.

As expected, none of the adsorbents performed best for all of the target compounds. Tenax® performed best for 3-chloropropene (allyl chloride), trichloromethane (chloroform), 1,2-dichloroethane, 1,1,1-trichloroethane, benzene, tetrachloromethane (carbon tetrachloride), trichloroethene, tetrachloroethene (perchloroethylene), and 1,2-dimethylbenzene (o-xylene). Tenax® and polyimide gave essentially identical results for toluene. As expected, on the basis of breakthrough volume data, Tenax® gave essentially no recovery for chloroethene (vinyl chloride) and 1,1-dichloroethene (vinylidene chloride).

Polyimide performed better than both Spherocarb® and Tenax® only for 1,1-dichloroethene, although only 55 percent recovery and 28 percent standard deviation were obtained. Polyimide gave essentially no recovery for chloroethene, despite the good recovery obtained for this compound in high purity air sampling. Polyimide also gave disappointingly low and variable recovery for 1,1,2-trichloro-1,2,2-trifluoroethane

Table 1. List of Target Compounds

Compound	Concentration in Calibration Cylinder, µg/L <sup>a</sup>
Chloroethene (Vinyl chloride)	2.58
Acrylonitrile	1.30
1,1-Dichloroethene (Vinylidene chloride)	1.70
Dichloromethane (Methylene chloride)	1.33
3-Chloropropene (Allyl chloride)	1.94
Trichlorotrifluoroethane (Freon 113)	3.41
Trichloromethane (Chloroform)	2.67
1,2-Dichloroethane	2.42
1,1,1-Trichloroethane (Methyl chloroform)	2.97
Benzene	1.47
Tetrachloromethane (Carbon tetrachloride)	3.62
Trichloroethene	2.69
Toluene	1.77
Tetrachloroethene (Perchloroethylene)	3.39
Chlorobenzene	2.20
1,2-Dimethylbenzene (o-xylene)	2.04

<sup>a</sup>At 25°C and 1 atmosphere.

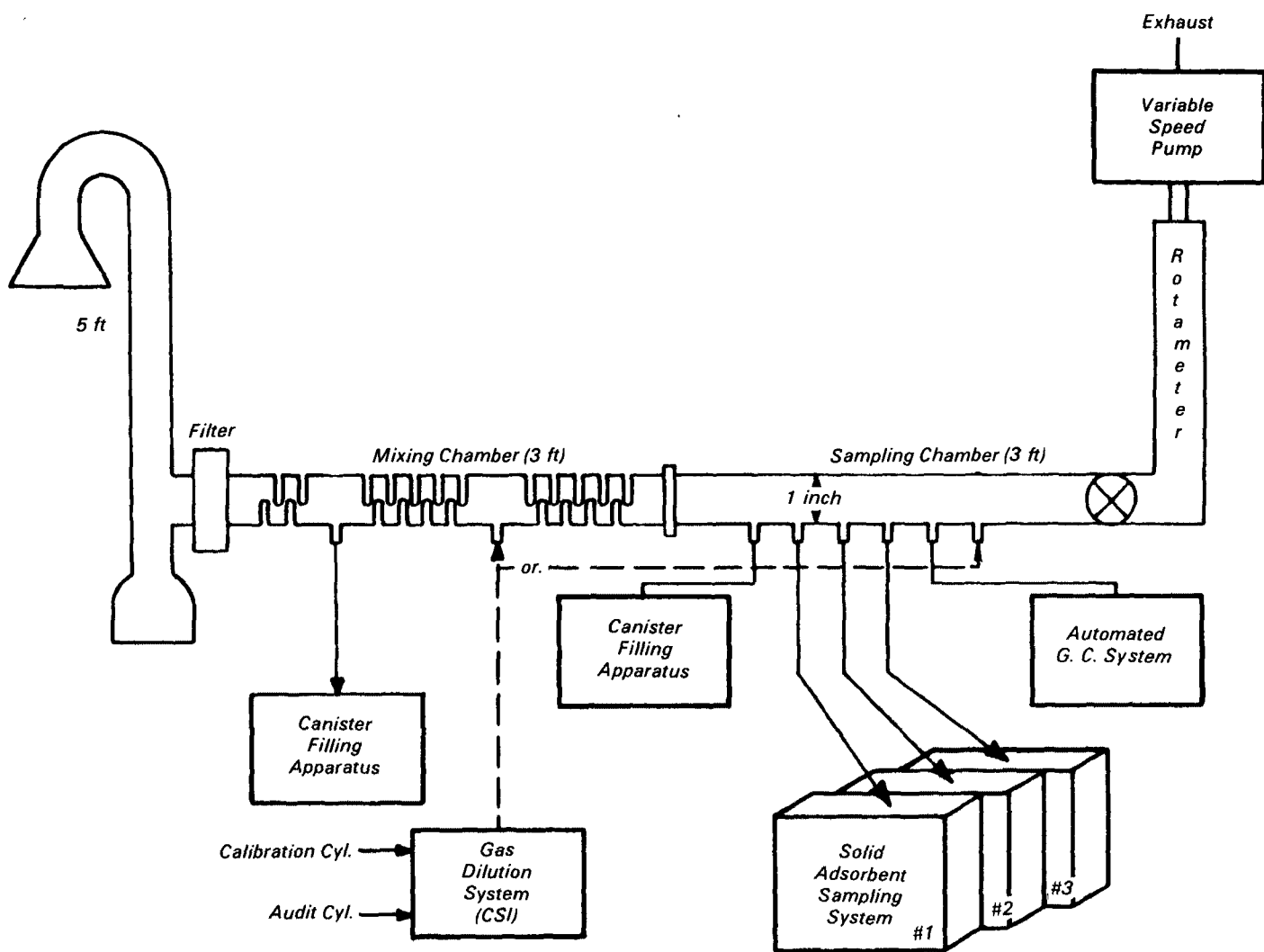


Figure 1. Sampling manifold.

(Freon 113), 1,1,1-trichloroethane, and tetrachloromethane. An operational problem that weighs heavily against the use of this material for ambient air sampling is the adsorption of a significant amount of moisture onto the adsorbent. The presence of water in the matrix led to the chromatographic column plugging during virtually all of the ambient air sampling runs (plugging of the column was not observed for any dry air runs using the audit or calibration cylinders). A similar phenomenon is observed for Spherocarb®. However, in that case the cartridge is prepurged with dry air, at room temperature, prior to analysis to remove adsorbed moisture. A similar approach was not successful in eliminating the problem for the polyimide material, indicating that the adsorbed moisture is difficult to desorb

due to kinetic or thermodynamic factors.

Spherocarb® gave the best results of the three resins only for chloroethene, dichloromethane, and 1,1,2-trichloro-1,2,2-trifluoroethane and extremely poor results for 1,1-dichloroethene, 3-chloropropene, 1,2-dimethylbenzene, and tetrachloromethane. In the case of 1,1-dichloroethene artifactually high recovery, possibly due to dehydrohalogenation of 1,1,1-trichloroethane, was a major problem. Although low recoveries were anticipated for the other three compounds, on the basis of earlier work, the low recovery of 1,1-dichloroethene was not observed previously.

Despite the problems discussed above, the data set provides important information for ambient air sampling.

Inspection of the raw data reveals that, except for the major problem areas discussed above, the individual values generally agree with the values obtained by cryogenic trapping within a factor of two or better (i.e., 50 to 150% relative recovery). In view of the large temporal and spatial variability of organic pollutant concentrations observed in ambient air, this extent of agreement between methods is quite good. Furthermore, the health effects information and mathematical models used to assess the significance of the data are subject to much greater uncertainties.

Another encouraging aspect of the data set is the very low blank levels observed. Our previous work with the open-style Tenax® tubes commonly employed in other laboratories resulted

**Table 2.** List of Sampling Runs

Run #	Sampling Date	Description
1	07/12/84	Trial Run, Ambient Air
2	07/17/84	Ambient Air
3	07/19/84	Ambient Air
4	07/20/84	Audit Cylinder
5	07/24/84	Calibration Cylinder
6	07/26/84	Ambient Air
7	07/27/84	Ambient Air
8	07/30/84	Ambient Air
9	07/31/84	Ambient Air
10	08/02/84	Ambient Air
11	08/03/84	Audit Cylinder
12	08/06/84	Ambient Air
13	08/07/84	Ambient Air
14	08/09/84	Ambient Air

**Table 3.** Performance Data for Solid Adsorbents Relative to Cryogenic Trapping

Compound	Tenax Breakthrough Volume <sup>a</sup> , Liters/Cartridge	Average Recovery Relative To Cryogenic Trapping, %		
		Tenax	Polyimide	Spherocarb
Chloroethene	0.8	--- <sup>b</sup>	--- <sup>b</sup>	73(23) <sup>d</sup>
1,1-Dichloroethene	Not Given	--- <sup>b</sup>	52(28)	410(260)
Dichloromethane	4	83(21)	86(31)	85(12)
3-Chloropropene <sup>c</sup>	6	87(35)	140(68)	29(14)
1,1,2-Trichloro-1,2,2-Trifluoroethane	Not Given	39(25)	17(14)	69(30)
Trichloromethane <sup>c</sup>	13	100(36)	75(25)	65(17)
1,2-Dichloroethane <sup>c</sup>	18	100(15)	65(15)	75(14)
1,1,1-Trichloroethane <sup>c</sup>	9	130(42)	51(14)	46(10)
Benzene	27	100(18)	130(34)	140(63)
Tetrachloromethane <sup>c</sup>	13	110(37)	53(19)	29(9)
Trichloroethene	28	112(26)	100(33)	90(33)
Toluene	122	70(19)	70(17)	43(8)
Tetrachloroethene	106	88(27)	78(30)	72(30)
Chlorobenzene	249	78(35)	57(21)	53(19)
1,2-Dimethylbenzene	334 <sup>e</sup>	55(21)	40(15)	20(7.9)

<sup>a</sup>Data from Reference 2 at 90°F.<sup>b</sup>No meaningful data obtained.<sup>c</sup>Low volume (nominally 5 liters) Tenax valued used for these compounds. Medium volume (nominally 10 liters) Tenax value used for all other compounds.<sup>d</sup>Value in parentheses is standard deviation for all sampling runs, except for audit and calibration cylinder sampling.<sup>e</sup>Value for ethylbenzene.

in much larger blank levels being obtained. In our hands the VOST-style traps, which are positively sealed during storage and analysis (desorption), provide much lower blank levels.

One must recognize that the composition of the atmosphere being sampled may have a significant impact on the performance of any of the adsorbents, due to chemical and physical effects which are not fully understood. Therefore, the results obtained in this study may not be observed in all ambient air sampling situations. Ideally one should check the method performance using the air sample of interest spiked with known quantities of the compounds to be determined. Since such experiments

are expensive to conduct, it is usually not possible to obtain such data. For this reason any ambient air sampling data should be viewed as qualitative, or at least semiquantitative, unless such data are provided. The use of directly spiked cartridges or spiked clean air studies cannot substitute for such data.

### Conclusions and Recommendations

The significant conclusions to be drawn from this study are presented below:

- 1) Compared to the three adsorbent methods tested, canister sampling followed by cryogenic trapping/gas chromatography offers better

precision and accuracy for the compounds of interest in this study, especially when a mass selective detection system is employed to overcome most potential interferences.

- 2) None of the three adsorbents evaluated gave the best performance for all of the target compounds. Tenax<sup>®</sup> gave the best performance for 3-chloropropene, trichloromethane (chloroform), 1,2-dichloroethane, 1,1,1-trichloroethane, benzene, tetrachloromethane (carbon tetrachloride), trichloroethene, tetrachloroethene, and 1,2-dimethylbenzene. Polyimide performed best only for 1,1-dichloroethene (vinylidene chloride). Spherocarb<sup>®</sup> performed best only for chloroethene (vinyl chloride), dichloromethane, and 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113). Toluene gave comparable results when Tenax<sup>®</sup> and polyimide were used, but lower recoveries on Spherocarb<sup>®</sup>.
- 3) The polyimide adsorbent has several operational difficulties which diminish its usefulness in ambient air sampling. A major artifact peak, acetonitrile, is generated when clean cartridges are stored longer than 24-48 hours before analysis. In addition, a significant amount of water is adsorbed during sampling, which leads to plugging of the chromatographic column during analysis.
- 4) Spherocarb<sup>®</sup> should be used only if highly volatile compounds such as chloroethene (vinyl chloride) or dichloromethane are of interest, since several of the target compounds appear to be degraded in the sampling and analysis process for this adsorbent. High levels (artifacts) of 1,1-dichloroethene (vinylidene chloride) are formed on Spherocarb<sup>®</sup> in many instances.
- 5) With a few exceptions, the recovery relative to cryogenic trapping/GC and precision obtained for the target compounds on solid adsorbents is considered to be acceptable for most ambient air studies. Generally, individual data points for the solid adsorbents agreed within a factor of two with the cryogenic sampling data.

6) The Volatile Organic Sampling Train (VOST) style cartridges gave low blank levels and are suggested as an alternative to the open style cartridge.

On the basis of the results obtained in this study, further evaluation of the polyimide material for ambient air sampling appears to be unwarranted, since a number of operational difficulties were encountered for which no obvious solution exists. Furthermore, no significant advantages in terms of recovery of highly volatile compounds were observed, in comparison to Tenax<sup>®</sup>, when sampling ambient air.

The results of this study indicate that the use of the VOST style cartridge offers substantially better blank levels for Tenax<sup>®</sup> than the conventional open-style cartridges. If this finding is independently verified, all further studies should use the VOST style cartridge.

*Ralph M. Riggin and Richard A. Markle are with Battelle's Columbus Laboratories, Columbus, OH 43201.*

*James D. Mulik is the EPA Project Officer (see below).*

*The complete report, entitled "Comparison of Solid Adsorbent Sampling Techniques for Volatile Organic Compounds in Ambient Air," (Order No. PB 86-127 651/AS; Cost: \$11.95, subject to change) will be available only from:*

*National Technical Information Service*

*5285 Port Royal Road*

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*The EPA Project Officer can be contacted at:*

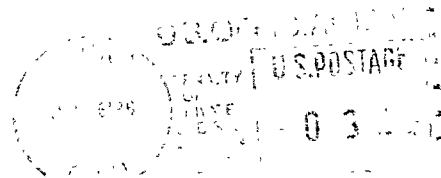
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