



Project Summary

Comparison of Ambient Air Sampling Techniques for Volatile Organic Compounds

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The objective of this study was to carry out a comparison of ambient air sampling techniques. A series of fourteen experimental sampling runs were carried out at a field site adjacent to Battelle's chemistry laboratory. Ambient air was drawn through a sampling manifold and was continuously spiked with a mixture of fifteen volatile organic compounds (VOCs) to give concentrations 1 to 3 ng/l above background air. These compounds were chloroethene, 1,1-dichloroethene, dichloromethane, 3-chloropropene, 1,1,2-trichloro-1,2,2-trifluoroethane, trichloromethane, 1,2-dichloroethane, 1,1,1-trichloroethane, benzene, tetrachloromethane, trichloroethene, toluene, tetrachloroethene, chlorobenzene, and 1,2-dimethylbenzene.

During the sampling period passivated stainless steel canisters were utilized to collect whole air integrated samples upstream and downstream of the spiking region. An automated gas chromatographic system was employed to analyze the contents of the sample canisters using capillary column separation and multiple detectors for sample analysis (electron capture, flame ionization and mass selective detectors). Tenax GC adsorbent samples were also collected downstream of the spiking region in parallel with the integrated canister samples. These samples were analyzed by standard gas chromatographic/mass spectrometric techniques.

In comparing analytical results, whole air collection via canisters gave better precision for the compounds of interest in this study. An estimate of

precision (% standard deviation) for the canister sampling method ranged from 4 to 10 percent (using the mass selective detector). For Tenax, precision values ranged from 8 to 16 percent. When comparing measured recoveries with expected concentrations, the canister sampling approach yielded values from 89 to 120 percent. Recoveries, using Tenax adsorbent, ranged from 8 to 104 percent.

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 Branch of the Environmental Monitoring Systems Laboratory (EMSL) 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 priority listing of volatile organics has been established and the EMSL is focusing on further development of analytical methodology associated with the detection of these compounds. Primary emphasis has been placed on developing field-compatible analytical systems.

During the past two years a joint effort by Battelle's Columbus Laboratories and EPA has resulted in the development and evaluation of a prototype system for the analyses of sixteen volatile organic compounds (VOCs).

The system consists of a reduced-temperature trap for condensing organics from ambient air, and a capillary column gas chromatograph (GC) with flame ionization (FID) and electron capture detectors (ECD) to quantitatively monitor the VOCs. Software development using the basic programming capability of the GC system permits automatic sampling and analysis to be achieved with minimal operator interfacing. The prototype system has been tested with respect to sample drying procedures (selective removal of water vapor), co-collection of reactive ambient air species, and collection and release efficiency. The prototype design has also been evaluated by comparing two nominally identical systems using calibration mixtures and ambient air. Excellent results were obtained during these laboratory tests and the following recommendations were made:

- The automated GC system should be field tested. During the field tests the reduced temperature trapping system should be compared with other preconcentration techniques such as solid adsorbents and passive dosimeters.
- Many of the target compounds tested in the laboratory also co-elute with other ambient air species. Although the combination of capillary column and flame ionization and electron capture detectors alleviate some of the identification and quantitation concerns, other more selective detectors are needed. Integrating a mass selective detector (MSD) into the automated gas chromatographic system is recommended. The greater specificity of this detector over other detection systems will allow better differentiation of co-eluting GC peaks and thus improve quantitative capability.

The full report focuses on the comparison of two ambient air sampling techniques. Specifically, whole air collection into specially treated canisters was compared with Tenax GC adsorbent sampling techniques. Analysis of the canisters' contents was accomplished with the automated GC system, while Tenax adsorbed samples were analyzed by standard gas chromatographic mass spectrometric techniques. The comparison study was carried out at a site adjacent to Battelle's chemistry laboratory. To assure detectable concentrations, the sampling manifold was spiked with a mixture of fifteen VOCs

and the comparison focused on these compounds.

Procedure

Tenax and whole air sampling (using passivated stainless steel canisters) were operated in parallel employing the sampling manifold and apparatus shown in Figure 1. Fourteen test runs were carried out at the field site. Eleven sampling runs were made with spiked ambient air while the remaining three runs involved the injection of calibration mixtures. Each test run lasted two hours.

Canister samples were analyzed with an automated capillary column gas chromatograph equipped with electron capture, flame ionization and mass selective detectors. This instrument was also programmed to collect and analyze "real time" integrated samples directly from the manifold.

Five, ten (duplicate), and twenty liter samples were collected using Tenax adsorbent sampling techniques. These samples were analyzed by gas chromatography/mass spectrometry.

Results and Discussion

Overview

The comparison study was carried out at a field site adjacent to Battelle's chemistry laboratory. The evaluation study consisted of fourteen sampling runs as listed in Table 1. Runs 4 and 11 were clean air experiments using dilution mixtures from an audit cylinder supplied by EPA, while run 5 was a similar run using Battelle's calibration cylinder. The remaining sampling runs were made with spiked ambient air. The analytical precision of the three detectors from the automated GC system was obtained by replicate analysis of canisters collected from the sampling manifold during the tests. A comparison was also made of concentrations of the six target compounds that were detected by both the electron capture and mass selective detector. Whole air canister concentrations determined by the cryogenic GC system (using the mass selective detector response) were also compared with those values obtained from Tenax GC adsorbent devices.

Analytical Precision of MSD, ECD, and FID Detectors

An estimate of the analytical precision of the cryogenic GC system was determined from triplicate analyses of spiked and background canisters col-

lected during each sample period. For these analyses, twelve compounds were detected with the FID; six compounds were detected with the ECD. Due to the limitation in software only six compounds were monitored with the MSD.

A summary of the analytical precision of all three detectors is shown in Table 2. In viewing the spiked canister data set, an average analytical precision of ± 7.3 percent was found for the six compounds analyzed with the MSD. Tetrachloroethene had the lowest value ($\pm 4.0\%$) while (Freon-113) displayed the highest relative standard deviation (RSD) value ($\pm 10.1\%$). A significantly lower average RSD value of ± 3.7 percent was obtained for the same six compounds analyzed with the ECD. The RSD values ranged from ± 1.3 percent (tetrachloromethane) to ± 10.1 percent (Freon-113). With the FID detector an average RSD value ($\pm 7.7\%$) similar to the MSD was found. However when the six additional compounds that were also detected by the FID were included in the calculations, the average RSD value was lowered to ± 5.8 percent. Toluene exhibited the lowest RSD value ($\pm 1.8\%$) while tetrachloromethane produced the highest RSD value ($\pm 14.4\%$).

The background canister data, also shown in Table 2, follow the same trend as the spiked canister data. An average RSD value of ± 7.2 percent was found for the six compounds analyzed with the MSD, while an average RSD value of ± 3.6 percent was obtained with the ECD. With the FID detector, the average RSD value was ± 8.5 percent. When the five additional FID detected compounds were included in the FID calculations, the average RSD value was lowered to ± 7.0 percent (chloroethene was not found in background air i.e. <0.1 ng/l).

Comparison of ECD and MSD Responses

The six compounds that were detected by both the electron capture and mass selective detectors were 1,1,2-trichloro-1,2,2-trifluoroethane, trichloromethane, 1,1,1-trichloroethane, tetrachloromethane, trichloroethene and tetrachloroethene. A comparison of concentrations was carried out by determining average percent relative difference values between the two detectors i.e., $[100 (\text{ECD response} - \text{MSD response}) / \text{average response}]$. Three data sets were examined and include the spiked canisters, the background

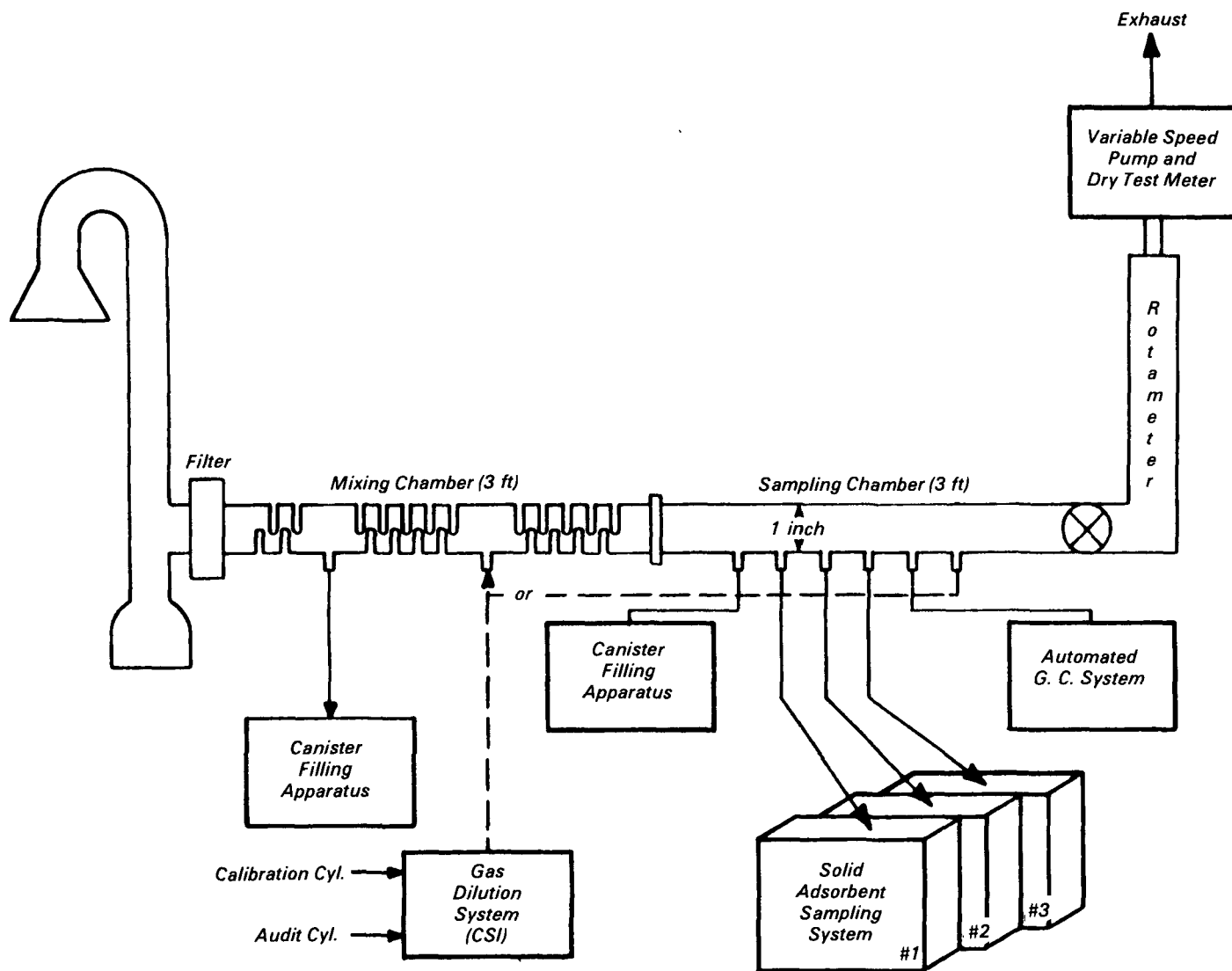


Figure 1. Diagram of sampling manifold and instrumentation employed during field program.

Table 1. List of Sampling Runs

| Run No. | Sampling date | Description |
|---------|---------------|-------------------------|
| 1 | 7/12/84 | Ambient air (trial run) |
| 2 | 7/17/84 | Ambient air |
| 3 | 7/19/84 | Ambient air |
| 4 | 7/20/84 | Audit cylinder |
| 5 | 7/24/84 | Calibration cylinder |
| 6 | 7/26/84 | Ambient air |
| 7 | 7/27/84 | Ambient air |
| 8 | 7/30/84 | Ambient air |
| 9 | 7/31/84 | Ambient air |
| 10 | 8/02/84 | Ambient air |
| 11 | 8/03/84 | Audit cylinder |
| 12 | 8/06/84 | Ambient air |
| 13 | 8/07/84 | Ambient air |
| 14 | 8/09/84 | Ambient air |

canisters, and samples collected in real time.

A summary of the average percent relative difference values from the three data sets is shown in Table 3. For 1,1,2-trichloro-1,2,2-trifluoroethane, negative average percent relative difference values were observed for all three data sets and indicated that the MSD recorded concentrations were in general higher than the corresponding ECD values. On the other hand, trichloromethane, tetrachloromethane and trichloroethene gave positive average percent relative difference values for all three data sets. The positive values denoted higher rela-

Table 2. Analytical Precision Data From Replicate Analyses of Spiked and Background Canisters

| Compound | Spiked canisters detector precision ($\pm\%$) ^(a) | | | Background canisters detector precision ($\pm\%$) | | |
|---------------------------------------|---|------|------|--|-----|------|
| | MSD | ECD | FID | MSD | ECD | FID |
| Chloroethene | NM ^(b) | NM | 7.4 | NM | NM | NM |
| 1,1,2-Trichloro-1,2,2-trifluoroethane | 10.1 | 10.1 | 10.0 | 10.4 | 3.9 | 18.7 |
| Trichloromethane | 7.3 | 4.3 | 3.3 | 12.4 | 9.2 | 1.6 |
| 1,2-Dichloroethane | NM | NM | 3.6 | NM | NM | 1.1 |
| 1,1,1-Trichloroethane | 8.7 | 2.0 | 3.6 | 4.5 | 2.0 | 2.9 |
| Benzene | NM | NM | 1.6 | NM | NM | 3.6 |
| Tetrachloromethane | 6.4 | 1.3 | 14.4 | 4.9 | 1.7 | 15.1 |
| Trichloroethene | 7.3 | 2.8 | 11.9 | 8.6 | 2.7 | 7.2 |
| Toluene | NM | NM | 1.8 | NM | NM | 1.7 |
| Tetrachloroethene | 4.0 | 1.7 | 2.7 | 2.3 | 1.8 | 5.2 |
| Chlorobenzene | NM | NM | 2.9 | NM | NM | 15.2 |
| 1,2-Dimethylbenzene | NM | NM | 6.7 | NM | NM | 4.9 |

^(a)Detector precision is defined as the percent relative standard deviation.

^(b)NM - not detected.

Table 3. Average Percent Relative Difference Values Obtained By Comparing Electron Capture and Mass Selective Detector Responses During the Field Study^(a)

| Compound | Average relative difference values (%) | | |
|---------------------------------------|--|-------------------------|----------------------|
| | spiked canisters | background canisters | real time samples |
| 1,1,2-Trichloro-1,2,2-trifluoroethane | -11.8 | -8.8 | -12.4 |
| Trichloromethane | 9.2 | 15.0 | 2.2 |
| 1,1,1-Trichloroethane | 3.2 | -6.0 | -1.9 |
| Tetrachloromethane | 23.2 | 0.5 | 23.4 |
| Trichloroethene | 19.6 | 36.9 | 24.1 |
| Tetrachloroethene | -3.6 | 5.7 | -5.1 |

^(a)Percent relative difference values = $\left(\frac{\text{ECD response} - \text{MSD response}}{\text{average response}} \right) \times 100$.

tive ECD responses for these three compounds. Tetrachloroethene and 1,1,1-trichloroethane showed no consistent bias. The spiked canister and real time sampling data showed very similar percent relative difference values as one would expect since both types of sampling were carried out downstream of the sample spiking port. Although the same general trend is also observed with the background canister data, the somewhat larger variation resulted because these samples were collected upstream of the spiking port and therefore generally contained much lower concentrations of the six target compounds.

Tenax GC Adsorbent Versus Whole Air Collection/Cryogenic Preconcentration Comparison Study for Ambient Air

In order to compare the data from the two collection methods, the appropriate Tenax GS concentration values were ratioed to the corresponding concentrations found by cryogenic trapping/GC analysis of canister samples. The ratios provided a direct measure of the rela-

tive recovery of the Tenax GC adsorbent for each compound. The comparison was done on this basis because the canister/cryogenic trapping concentrations generally agreed better with the diluted concentration generated in the manifold (see full report). Likewise literature data has shown that several of the fifteen target compounds have low breakthrough volumes on Tenax GC and are therefore not efficiently collected.

In Table 4 a summary of the performance data for Tenax GC relative to canister/cryogenic trapping is given. Each compound is listed along with its breakthrough volume and the average Tenax GC recovery relative to canister/cryogenic trapping obtained over the ten sampling runs. As indicated in the table for those compounds in which breakthrough volumes were very low, the nominally 5 liter Tenax GC adsorbent sample was used in the comparisons; the remaining concentration values were taken from the 10 liter samples. The values used for the canister samples were obtained using the mass selective detector, because this detection system was less subject to potential 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.

For the compounds, chloroethene and 1,1-dichloroethene, no meaningful data was obtained with the Tenax GC adsorbent. With the exception of the anomalous behavior of 1,1,2-trichloro-1,2,2-trifluoroethane, the compounds dichloromethane through trichloroethene gave very reasonable relative recoveries ranging from 83 to 130 percent. However a dramatic fall off in recovery is observed for the less volatile compounds, toluene, tetrachloroethene, chlorobenzene and 1,2-dimethylbenzene. The reason for the relatively low recoveries for these higher boiling compounds is unclear.

Conclusions

The significant findings from this study are presented below:

- (1) Replicate analysis of canisters collected upstream and downstream of the spiking region with the automated GC system provided precision data for each detector. For concentrations varying from 1 to 70 ng/l an average RSD of ± 3.7 percent was found for the six compounds detected by the electron capture detector (1,1,2-trichloro-1,2,2-trifluoroethane, trichloromethane, 1,1,1-trichloroethane, tetrachloromethane, trichloroethene, and tetrachloroethene). An RSD of ± 7.3 percent was obtained for the same six compounds analyzed with the mass selective detector. A similar value of ± 7.7 per-

Table 4. Performance Data for Tenax Relative to Cryogenic Trapping/GC Analysis of Canister Samples

| Compound | Tenax GC breakthrough volume ^(a) , liters/cartridge | Average Tenax GC recovery relative to cryogenic trapping, % |
|---------------------------------------|--|---|
| Chloroethene | 0.8 | (b) |
| 1,1-Dichloroethene | Not Given | (b) |
| Dichloromethane | 4 | 83 (21) ^(d) |
| 3-Chloropropene ^(c) | 6 | 87 (35) |
| 1,1,2-Trichloro-1,2,2-trifluoroethane | Not Given | 39 (25) |
| Trichloromethane ^(c) | 13 | 100 (36) |
| 1,2-Dichloroethane ^(c) | 18 | 100 (15) |
| 1,1,1-Trichloroethane ^(c) | 9 | 130 (42) |
| Benzene | 27 | 100 (18) |
| Tetrachloromethane ^(c) | 13 | 110 (37) |
| Trichloroethene | 28 | 112 (26) |
| Toluene | 122 | 70 (19) |
| Tetrachloroethene | 106 | 88 (27) |
| Chlorobenzene | 249 | 78 (35) |
| 1,2-Dimethylbenzene | 334 | 55 (21) |

^(a)Data from reference 5 in the full report at 90°F.

^(b)No meaningful data obtained.

^(c)Low volume (nominally 5 liters) Tenax GC value used for these compounds. Medium volume (nominally 10 liters) Tenax GC value used for all other compounds.

^(d)Value in parentheses is standard deviation for all sampling runs (excluding audit and calibration cylinder sampling runs).

cent was found with the flame ionization detector.

- (2) The six compounds that were detected by both the electron capture detector and mass selective detector were compared using percent relative difference values [100 (ECD response-MSD response)/average response]. Relative difference values ranged from -11.8 percent (1,1,2-trichloro-1,2,2-trifluoroethane) to 36.9 percent (trichloroethene).
- (3) Tenax GC adsorbent samples also were collected in parallel with the integrated canister samples and then were analyzed by standard gas chromatographic mass spectrometric techniques. Analysis of duplicate Tenax samples (10 L) resulted in RSD values that ranged from 8 to 16 percent. Recovery relative to canister sampling was as follows: chloroethene and 1,1-dichloroethene (no meaningful data), dichloromethane (83%), 3-chloropropene (87%), 1,1,2-trichloro-1,2,2-trifluoroethane (39%), trichloromethane (100%), 1,2-dichloroethane (100%), 1,1,1-trichloroethane (130%), benzene (110%), tetrachloromethane (110%), trichloroethene (112%), toluene (70%), tetrachloroethene (88%), chlorobenzene (78%) and 1,2-dimethylbenzene (55%).

Recommendations

Additional studies should be undertaken under controlled conditions with analytical uncertainties minimized as much as possible by employing the same analysis procedure for all collected samples. Techniques to be compared should include distributive air volume sampling with Tenax adsorbent, passive sampling using personal exposure devices, and whole air collection in canisters.

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W. M. McClenny is the EPA Project Officer (see below).

The complete report, entitled "Comparison of Ambient Air Sampling Techniques for Volatile Organic Compounds," (Order No. PB 86-120 953/AS; Cost: \$11.95, subject to change) will be available only from:

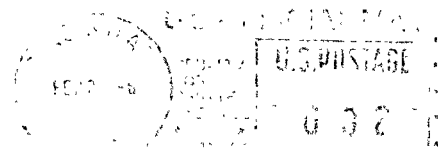
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