



## Project Summary

# Laboratory Validation of VOST and SemiVOST for Halogenated Hydrocarbons from the Clean Air Act Amendments List

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The Clean Air Act Amendments of 1990, Title III, present a need for stationary source sampling and analytical methods for the list of 189 compounds. EPA has used Volatile Organic Sampling Train (VOST) and Semivolatile Organic Sampling Train (SemiVOST) sampling and analytical methods for this type of sampling of organic compounds in the past, but these methodologies have been completely validated for only a few of the organic compounds. In this study, the applicability of VOST and SemiVOST techniques to Clean Air Act halogenated compounds has been evaluated under laboratory conditions. The methods were evaluated first to determine whether the compounds could be analyzed successfully. For SemiVOST and VOST compounds, the analytes were analyzed by gas chromatography/mass spectrometry (GC/MS) techniques. Retention times for the analytes were determined, and reference mass spectra were generated so that primary and secondary quantitation ions could be selected. Recovery of the compounds from the sorbents was evaluated, and analytical detection limits were determined from spiked sorbents. Quadruple sampling trains were used to collect replicate samples for statistical evaluation of the dynamic spiking techniques for liquids (SemiVOST). This report presents the results of the laboratory experiments.

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*that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

The Clean Air Act Amendments of 1990, Title III (CAAA), present a need for stationary source sampling and analytical methods for the list of 189 analytes. The U.S. Environmental Protection Agency (EPA) has used VOST (SW-846 Methods 0030 and 5040 or 5041) and SemiVOST (SW-846 Methods 0010 and 8270) sampling and analytical methods for sampling and analysis of a wide variety of organic compounds in the past, but these methodologies have been completely validated for only a few of the compounds to which they have been applied. Validation of the methodology establishes how well the methodology will perform for a given compound under a defined set of conditions, i.e., the bias and precision when the method is applied to a given compound at a particular stationary source.

In this study, the applicability of VOST and SemiVOST techniques to the CAAA halogenated organic compounds has been evaluated under laboratory conditions. Analytical methods were evaluated first to determine whether the compounds could be analyzed successfully. For SemiVOST compounds, a methylene chloride solution of the analytes was analyzed by gas chromatography/mass spectrometry (GC/MS) techniques. Retention times for the analytes were determined, and reference spectra were generated so that primary and secondary quantitation ions could be selected. Compounds were also assigned



to the closest-eluting Internal Standard for quantitative calculations. For the VOST technique, a methanol solution of the analytes was spiked into water and the analytes were purged from the water in order to determine retention times, generate reference mass spectra, assign quantitation standards, and select appropriate quantitation ions. Compounds which did not survive the application of the analytical methodology were dropped from further evaluation in the VOST and SemiVOST methods. In the SemiVOST method, chloroacetic acid could not be chromatographed successfully. In the VOST method, bis(chloromethyl) ether, chloromethyl methyl ether, and epichlorohydrin could not be analyzed. However, bis(chloromethyl) ether and epichlorohydrin were also tested by the SemiVOST methodology. Modification of the existing methodology or development of new methods will be required for the compounds which could not be analyzed successfully. Recovery of the compounds from the sorbents was evaluated, and analytical detection limits were determined from spiked sorbents.

Quadruple sampling trains were used for simultaneous collection of replicate samples for statistical evaluation of the dynamic spiking techniques for gases (VOST) and liquids (SemiVOST). With successful execution and statistical evaluation of the dynamic spiking techniques, the VOST and SemiVOST methodology, with dynamic spiking, will be subjected to complete validation in the field. This report presents the results of the laboratory experiments.

### Experimental Procedures

The halogenated compounds listed under CAAA, Title III, that were evaluated under this set of experiments are listed in Table 1. Neither 2,3,7,8-tetrachlorodibenzodioxin, dibenzofurans, nor the PCBs were evaluated in this experiment since EPA has specialized methods for these compounds in stationary source sampling and analysis. Some compounds are listed for both VOST and SemiVOST evaluation since there is potential overlap in the range that each method collects. (VOST is used for compounds boiling between 30 and 100°C with some allowance to 130°C and some extension below 30°C with appropriate precautions, whereas SemiVOST is used to collect compounds boiling above 100°C.) The overlap occurs in the boiling range between 100°C and 130°C, where compounds might be appropriately assigned to either method.

### VOST Method

The GC/MS retention times, characteristic ions and reference mass spectra were developed for each of the compounds of

**Table 1. Clean Air Act Amendments Halogen Compounds Investigated**

| Compound                    | Boiling Point °C | VOST | SemiVOST |
|-----------------------------|------------------|------|----------|
| Allyl chloride              | 44 - 46          | X    |          |
| bis(Chloromethyl) ether     | 106              | X    | X        |
| Carbon tetrachloride        | 77               | X    |          |
| Chlorobenzene               | 132              | X    | X        |
| Chloroform                  | 60.5 - 61.5      | X    |          |
| Chloromethyl methyl ether   | 55 - 57          | X    |          |
| Chloroprene                 | 59.4             | X    |          |
| 1,3-Dichloropropylene       | 105 - 107/730 mm | X    | X        |
| Epichlorohydrin             | 115 - 117        | X    | X        |
| Ethyl chloride              | 12*              | X    |          |
| Ethylene dibromide          | 131 - 132        | X    | X        |
| Ethylene dichloride         | 83               | X    |          |
| Ethylidene dichloride       | 57               | X    |          |
| Methyl bromide              | 4*               | X    |          |
| Methyl chloride             | -24.2*           | X    |          |
| Methyl chloroform           | 74 - 76          | X    |          |
| Methylene chloride          | 39.8 - 40        | X    |          |
| Methyl iodide               | 41 - 43          | X    |          |
| Propylene dichloride        | 95 - 96          | X    |          |
| Tetrachloroethylene         | 121              | X    | X        |
| 1,1,2-Trichloroethane       | 110 - 115        | X    | X        |
| Trichloroethylene           | 86.9             | X    |          |
| Vinyl bromide               | 16/750 mm*       | X    |          |
| Vinyl chloride              | -13.4*           | X    |          |
| Vinylidene chloride         | 30 - 32          | X    |          |
| Benzotrichloride            | 219 - 223        |      | X        |
| Benzyl chloride             | 177 - 181        |      | X        |
| Bromoform                   | 150 - 151        |      | X        |
| Chloroacetic acid           | 189              |      | X        |
| 2-Chloroacetophenone        | 244 - 245        |      | X        |
| Chlorobenzilate             | 147              |      | X        |
| 1,2-Dibromo-3-chloropropane | 196              |      | X        |
| 1,4-Dichlorobenzene         | 173              |      | X        |
| 3,3'-Dichlorobenzidine      | mp = 165         |      | X        |
| Dichloroethyl ether         | 65 - 67/15 mm    |      | X        |
| Hexachlorobenzene           | 323 - 326        |      | X        |
| Hexachlorobutadiene         | 210 - 220        |      | X        |
| Hexachlorocyclopentadiene   | 239              |      | X        |
| Hexachloroethane            | 186              |      | X        |
| Pentachloronitrobenzene     | 328              |      | X        |
| Pentachlorophenol           | 309.5            |      | X        |
| 1,1,2,2-Tetrachloroethane   | 147              |      | X        |
| 1,2,4-Trichlorobenzene      | 214              |      | X        |
| 2,4,5-Trichlorophenol       | 248/740 mm       |      | X        |
| 2,4,6-Trichlorophenol       | 246              |      | X        |

\*Below the recommended lower boiling point limit of 30°C for VOST.

interest for the VOST method. The analytical method was EPA Method 5041. The GC column used was DB-624, 0.53 ID, 3 µ film thickness, on a Finnigan-MAT 4500 GC/MS system. Reference mass spectra, primary and secondary quantitation ions for the compounds, and relative retention times are available in the complete EPA report.

To determine the recovery of the compounds from VOST tubes, clean VOST tubes were spiked with a methanol solution containing approximately 50 ng of

each compound using the flash evaporation technique. The quantitation standards were spiked into the water purge flask and spiked tubes were desorbed as a pair through the purge trap employing standard VOST methodology. A pair of unspiked tubes was analyzed as a blank. The recoveries were based on the comparison of the amount calculated to the amount spiked. The analytical system was calibrated by spiking the purge water with methanolic solutions of the compounds of interest at appropriate concentrations. Dif-

ferences in observed concentrations between direct desorption from the purge water and desorption from spiked VOST tubes at a given level was attributed to the efficiency of desorption of the compounds from the VOST tubes. Five replications were performed to provide data for statistical analysis (Table 2).

Detection limits were determined by Federal Register procedure. The detection limit for a range of compounds on VOST tubes was estimated to be 10-20 ng, based on previous determinations of VOST method detection limits for similar compounds. Ten pairs of VOST sorbent tubes were spiked at two times the estimated method detection limit (20 ng). The analytical system was calibrated using spiked VOST tubes, according to the procedure specified in Method 5041. The standard deviations of the determinations and the actual detection limits were calculated using the Federal Register procedure (Table 3).

The entire sampling (Method 0030) and analytical (Draft Method 5041) procedure was evaluated using quadruple sampling trains set up in the laboratory. The quadruple trains as originally configured in the laboratory consisted of four complete trains with a gaseous dynamic spiking system using a certified cylinder of a gaseous mixture of the compounds of interest to provide the spike immediately prior to the entry of the stack sample to the VOST sampling train. The spike was a gas mixture in a pressurized cylinder with certified concentration. The gas was metered into each VOST sampling train through a mass flow controller to control the flow precisely and Teflon® lines to minimize interaction of the halogenated compounds with reactive surfaces such as stainless steel. Laboratory experiments demonstrated that the trains as configured did not obtain proportional response to changes in the apparent flow rate of the pressurized gas. The metering system was changed to needle valves with the flow rate verified by measurement with bubble flowmeters before and after each sampling run. Teflon® lines were also heat-traced to 130°C all of the way from the regulator of the gas cylinder to the entry point into the sampling train. The exact point of spiking was changed to ensure that the standard gaseous mixture was being spiked directly into the flowing gas stream. Accurate spiking of an accurately known quantity of the compounds of interest allows a complete evaluation of the sampling and analysis methodology of the VOST. A quad train or a dual train is required during stack evaluation under Method 301 (Protocol for the Field Validation of Emission Concentrations from Sta-

tionary Sources). Preliminary laboratory experiments demonstrated that the modifications to the gaseous dynamic spiking system on the quadruple VOST trains could be used to obtain accurate and reproducible spiking with target analytes.

A Latin Square experimental design was used to evaluate dynamic spiking of the quadruple VOST trains in their original configuration. The Latin Square is a statistical experimental design that was used to test run, train, and concentration as variables to determine if a variable has a significant effect. The evaluation of the results of the Latin Square experiment for the VOST trains demonstrated that a proportionate response to apparent changes in gas flow rate was not being obtained and catalyzed the reconfiguration of the quadruple VOST trains to provide accurate and reproducible spiking.

### **SemiVOST Method**

The GC/MS retention times, characteristic ions and reference mass spectra were developed for each of the compounds of interest for the SemiVOST method. The GC column used was DB-5, 0.32 mm ID, 30 m, 1.0 µ film thickness, on a Finnigan-MAT 4500 GC/MS system. Reference mass spectra, primary and secondary quantitation ions, and retention times are found in the complete EPA report describing this work.

To determine the recoveries of the compounds from the XAD-2® sampling medium, XAD-2® sampling cartridges were spiked with a methylene chloride solution containing approximately 250 µg of each halogenated organic compound. Surrogate standards were also spiked into XAD-2® cartridges to monitor the performance of the sample preparation methodology. The spiked cartridges were extracted and concentrated employing standard SemiVOST methodology. An unspiked cartridge was analyzed as a method blank. The final volume for analysis was 5 mL, the normal final extract volume for the SemiVOST procedure. All recoveries were based on the amount added. Five replications were performed to allow calculation of the mean and standard deviation, with statistical evaluation of the outliers. The GC/MS system was calibrated with methylene chloride solutions of the compounds of interest, according to the standard SemiVOST procedure (Table 4).

Method detection limits were determined by Federal Register procedure. Ten cleaned XAD-2® sampling cartridges were spiked at two times the method detection limit that was estimated from the results of the recovery study. The actual method

detection limits and standard deviations were calculated using the *Federal Register* procedure (Table 5).

The entire SemiVOST sampling (Method 0010) and analysis method (SemiVOST; analytical procedure the same as Method 8270 with modified sample preparation procedures) was evaluated using quadruple trains set up in the laboratory. The quad train consists of four complete trains with a dynamic spiking system to provide the spike into a heated line just after the probe. The liquid dynamic spiking system consisted of a constant flow syringe pump with Teflon® lines to a glass-lined stainless steel needle introduced into the sampling lines just behind the probe. The syringe pump flow was set to provide about 10 mL of solution over a 2-hour sampling period with a gas flow rate of 0.5 cfm through the probe. The dynamic spiking system temperatures were regulated to provide a drop of spiking solution at the beveled tip of a glass-lined stainless steel needle. The drop was not allowed to evaporate nor to drop to the heated glass surface of the sampling line. Use of a dynamic spiking system allows a complete check of the SemiVOST sampling and analysis methodology. Either a dual or a quad train is required during stationary stack emissions evaluation under EPA Method 301. In order to statistically evaluate the train and allow for run and train differences and spiking levels, a Latin Square design was used. In the Latin Square there were four replications, four spiking levels and four trains. The spiking levels were 100, 300, 500 and 700 µg of each compound. In the laboratory, the sampling trains were operated at stack temperature conditions with nitrogen gas as the diluting gas to make up the total volume required for SemiVOST sampling (Table 6).

### **Results**

GC retention times, reference mass spectra, and primary and secondary ions used for the quantitative calculations developed for each compound are available in the full report and are not presented here.

**VOST.** All of the candidate VOST target compounds except bis(chloromethyl) ether, chloromethyl methyl ether, and epichlorohydrin were chromatographable and could be identified using the VOST GC/MS analytical procedure.

The results of the spiking studies of the VOST sorbents are presented in Table 2. The recoveries range from 90.4% for vinyl chloride to 127.2% for allyl chloride. All of the compounds that were observed

**Table 2.** Recoveries of Compounds from VOST Sorbents (Tenax GC®- Tenax GC®/Petroleum-Based Charcoal)

| Compound                  | Mean*<br>(Percent) | Standard<br>Deviation<br>(Percent) | Percent<br>Coefficient<br>of<br>Variation |
|---------------------------|--------------------|------------------------------------|---|
| Ethyl chloride            | 95.8               | 10.73                              | 11.20                                     |
| Ethylene dichloride       | 123.0              | 5.61                               | 4.56                                      |
| Methyl iodide             | 127.2              | 6.91                               | 5.43                                      |
| Allyl chloride            | 101.6              | 2.88                               | 2.84                                      |
| Methylene chloride        | 42.10              | 8.62                               | 24.32                                     |
| Ethylidene dichloride     | 31.90              | 6.31                               | 17.81                                     |
| Chloroprene               | 29.80              | 7.48                               | 21.10                                     |
| Methyl chloride           | 92.64              | 20.30                              | 46.30                                     |
| Chloroform                | 36.40              | 5.48                               | 15.46                                     |
| Carbon tetrachloride      | 30.30              | 5.46                               | 15.40                                     |
| 1,2-Dichloroethane        | 33.30              | 7.07                               | 19.96                                     |
| Vinyl chloride            | 31.90              | 7.68                               | 21.67                                     |
| Trichloroethylene         | 28.20              | 4.54                               | 12.81                                     |
| Propylene dichloride      | 30.60              | 5.58                               | 15.75                                     |
| cis-1,3-Dichloropropene   | 31.60              | 5.56                               | 15.69                                     |
| trans-1,3-Dichloropropene | 31.10              | 5.68                               | 16.04                                     |
| 1,1,2-Trichloroethane     | 106.4              | 14.58                              | 13.71                                     |
| Tetrachloroethylene       | 111.6              | 7.50                               | 6.72                                      |
| Ethylene dibromide        | 97.0               | 14.42                              | 14.86                                     |
| Methyl bromide            | 97.4               | 9.53                               | 9.78                                      |
| Chlorobenzene             | 94.2               | 9.53                               | 9.78                                      |
| Vinyl bromide             | 110.8              | 10.30                              | 9.30                                      |
| Methyl chloroform         | 103.4              | 12.70                              | 12.28                                     |

\*Average of 5 values.

**Table 3.** VOST Method Detection Limits

| Compound                  | Mean*<br>(ng) | Standard<br>Deviation<br>(ng) | Method<br>Detection<br>Limit<br>(ng) |
|---------------------------|---------------|-------------------------------|--------------------------------------|
| Ethyl chloride            | 34.20         | 8.72                          | 24.59                                |
| Ethylene dichloride       | 24.90         | 6.12                          | 17.26                                |
| Methyl iodide             | 30.50         | 7.11                          | 20.05                                |
| Allyl chloride            | 29.80         | 5.14                          | 14.49                                |
| Methylene chloride        | 42.10         | 8.62                          | 24.32                                |
| Ethylidene dichloride     | 31.90         | 6.31                          | 17.81                                |
| Chloroprene               | 29.80         | 7.48                          | 21.10                                |
| Methyl chloride           | 92.64         | 20.30                         | 46.30                                |
| Chloroform                | 36.40         | 5.48                          | 15.46                                |
| Carbon tetrachloride      | 30.30         | 5.46                          | 15.40                                |
| 1,2-Dichloroethane        | 33.30         | 7.07                          | 19.96                                |
| Vinyl chloride            | 31.90         | 7.68                          | 21.67                                |
| Trichloroethylene         | 28.20         | 4.54                          | 12.81                                |
| Propylene dichloride      | 30.60         | 5.58                          | 15.75                                |
| cis-1,3-Dichloropropene   | 31.60         | 5.56                          | 15.69                                |
| trans-1,3-Dichloropropene | 31.10         | 5.68                          | 16.04                                |
| 1,1,2-Trichloroethane     | 32.80         | 5.92                          | 16.71                                |
| Tetrachloroethylene       | 29.30         | 5.42                          | 15.28                                |
| Ethylene dibromide        | 29.80         | 5.75                          | 16.22                                |
| Methyl bromide            | 43.70         | 10.19                         | 28.74                                |
| Chlorobenzene             | 29.80         | 4.64                          | 13.08                                |
| Vinyl bromide             | 30.60         | 6.40                          | 18.05                                |
| Methyl chloroform         | 43.80         | 7.86                          | 22.16                                |

\*Average of 10.

showed recoveries that were acceptable for further study. Recovery from sorbent is essential for analytical determination using Method 5041.

Method Detection Limits for the candidate VOST analytes are reported in Table 3. The highest value is 46 ng/sample with most between 10 and 20 ng/sample. A full VOST sample of 20 L of stack emissions would then have a range of 0.5 - 2.3 ng/L of gas sampled. This range of Method Detection Limits is acceptable.

The laboratory experiment with the quadruple train set up for evaluation of VOST gaseous dynamic spiking was performed. The Latin Square experimental design required four spiking levels, provided from a pressurized cylinder by means of mass flow controllers, with four runs on four trains. The results of the Latin Square experiment showed that only one effective level of spiking had been achieved in spite of apparent changes in flow rate. The mass flow controllers functioned erratically, most of the time in a fully open position. A reconfiguration of the quadruple VOST train system to use heated needle valves to regulate the gas flow, bubble flow meters to measure actual flow before and after sampling, and heated Teflon® lines throughout the dynamic spiking system to ensure that compound condensation does not occur was developed. Preliminary results obtained in the laboratory indicate that the modified spiking system provides a constant flow. However, the reconfigured spiking system has not yet been evaluated completely. Preliminary results demonstrate that the delivery of compounds is consistent at a given level.

**SemiVOST.** Chloroacetic acid was the only SemiVOST candidate target compound that could not be chromatographed successfully using the standard conditions for SemiVOST. Erratic results during calibration suggested possible problems with stability in solution for bis(chloromethyl) ether, epichlorohydrin, and 3,3'-dichlorobenzidine.

The recoveries from the spiked XAD-2® resin sampling cartridges are shown in Table 4. The recoveries ranged from 38% for pentachloronitrobenzene to 275% for 3,3'-dichlorobenzidine. The method states that a range of 50 to 150% is acceptable. Using the criteria from the SemiVOST method five compounds would not achieve an acceptable recovery from the XAD-2® sorbent. The compounds with low recoveries were hexachlorobutadiene, hexachlorobenzene, pentachloronitrobenzene, chlorobenzilate and 3,3'-dichlorobenzidine. Even though these five recoveries were out of range the compounds were retained as candidate targets for the SemiVOST method for the rest of the study.

**Table 4. Recoveries of Compounds from SemiVOST Sorbents (XAD-2<sup>®</sup> Resin)**

| Compound                    | Mean*<br>(Percent) | Standard<br>Deviation<br>(Percent) | Percent<br>Coefficient<br>of<br>Variation |
|-----------------------------|--------------------|------------------------------------|---|
| bis(Chloromethyl) ether     | 59.3               | 8.10                               | 13.67                                     |
| Epichlorohydrin             | 75.2               | 11.10                              | 14.76                                     |
| cis-1,3-Dichloropropene     | 71.0               | 10.46                              | 14.74                                     |
| trans-1,3-Dichloropropene   | 79.4               | 12.01                              | 15.13                                     |
| 1,1,2-Trichloroethane       | 78.8               | 9.98                               | 12.67                                     |
| Ethylene dibromide          | 89.2               | 12.56                              | 14.08                                     |
| Tetrachloroethylene         | 61.1               | 7.66                               | 12.20                                     |
| Chlorobenzene               | 96.6               | 12.10                              | 12.52                                     |
| Bromoform                   | 80.8               | 11.30                              | 13.99                                     |
| 1,1,2,2-Tetrachloroethane   | 102.0              | 14.05                              | 13.78                                     |
| Dichloroethyl ether         | 104.4              | 11.80                              | 11.30                                     |
| 1,4-Dichlorobenzene         | 95.0               | 12.43                              | 13.08                                     |
| Benzyl chloride             | 103.2              | 13.08                              | 12.68                                     |
| Hexachloroethane            | 87.4               | 12.46                              | 14.26                                     |
| 1,2-Dibromo-3-chloropropane | 92.0               | 13.27                              | 14.42                                     |
| 1,2,4-Trichlorobenzene      | 90.6               | 13.35                              | 14.74                                     |
| Hexachlorobutadiene         | 47.8               | 6.42                               | 13.43                                     |
| Benzotrichloride            | 76.8               | 11.80                              | 15.36                                     |
| Chloroacetophenone          | 141.6              | 21.43                              | 15.14                                     |
| Hexachlorocyclopentadiene   | 53.0               | 9.51                               | 17.95                                     |
| 2,4,6-Trichlorophenol       | 93.8               | 15.16                              | 16.16                                     |
| 2,4,5-Trichlorophenol       | 108.2              | 15.24                              | 14.08                                     |
| Hexachlorobenzene           | 4.8                | 5.63                               | 12.29                                     |
| Pentachlorophenol           | 69.8               | 10.55                              | 15.11                                     |
| Pentachloronitrobenzene     | 38.0               | 4.58                               | 12.06                                     |
| Chlorobenzilate             | 47.6               | 6.88                               | 14.45                                     |
| 3,3'-Dichlorobenzidine      | 275.0              | 5.83                               | 20.31                                     |

\* Average of 5 values.

**Table 5. SemiVOST Method Detection Limits**

| Compound                    | Detection Limit |             |
|-----------------------------|-----------------|-------------|
|                             | µg/mL           | Total<br>µg |
| bis(Chloromethyl) ether     | 11.4            | 57.0        |
| Epichlorohydrin             | 9.8             | 49.0        |
| cis-1,3-Dichloropropene     | 5.8             | 29.0        |
| trans-1,3-Dichloropropene   | 6.5             | 32.5        |
| 1,1,2-Trichloroethane       | 9.0             | 45.0        |
| Ethylene dibromide          | 10.7            | 53.5        |
| Tetrachloroethylene         | 13.4            | 67.0        |
| Chlorobenzene               | 9.5             | 47.5        |
| Bromoform                   | 10.6            | 53.0        |
| 1,1,2,2-Tetrachloroethane   | 8.2             | 41.0        |
| Dichloroethyl ether         | 11.0            | 55.0        |
| 1,4-Dichlorobenzene         | 12.9            | 64.5        |
| Benzyl chloride             | 12.0            | 60.0        |
| Hexachloroethane            | 10.9            | 54.5        |
| 1,2-Dibromo-3-chloropropane | 12.6            | 63.0        |
| 1,2,4-Trichlorobenzene      | 13.1            | 65.5        |
| Hexachlorobutadiene         | 15.7            | 78.5        |
| Benzotrichloride            | 12.7            | 63.5        |
| Chloroacetophenone          | 13.9            | 69.5        |
| Hexachlorocyclopentadiene   | 14.5            | 72.5        |
| 2,4,6-Trichlorophenol       | 11.6            | 58.0        |
| 2,4,5-Trichlorophenol       | 16.5            | 58.0        |
| Hexachlorobenzene           | 13.4            | 67.0        |
| Pentachlorophenol           | 30.7            | 153.5       |
| Pentachloronitrobenzene     | 13.0            | 65.0        |
| Chlorobenzilate             | 15.6            | 78.0        |
| 3,3'-Dichlorobenzidine      | 19.3            | 96.5        |

Method detection limits (Table 5) for candidate SemiVost compounds ranged from 29.0 to 153.5 µg/sample based on a final concentration volume of 5 mL. Assuming a sampling rate of 0.5 cfm and a two-hour sampling period, the limits would range from 0.5 to 2.5 µg/cf of emission gas sampled. The majority of the compounds tested would be near 1 µg/cf.

A full SemiVOST Latin Square quadruple train spiking experiment was performed. The average recoveries ranged from 8.9% for pentachlorophenol to 513% for hexachlorocyclopentadiene. Eighteen of the twenty-seven targeted compounds had an average recovery between 50 and 150 percent. Difficulties with recovery of pentachlorophenol are illustrative of the erratic behavior exhibited by this compound under test conditions; pentachlorophenol is outstandingly sensitive to chromatographic conditions such as cleanliness of the injector port and condition of the chromatographic column. Problems with the recovery of hexachlorocyclopentadiene are attributed to difficulties in calibration, possibly due to stability problems with this compound in the calibration solution.

## Conclusions

Gas chromatographic retention times, mass spectra and primary secondary quantitation ions were determined for most of the halogenated compounds listed under Title III, CAAA. Of the targeted 45 compounds, only four could not be chromatographed successfully: chloroacetic acid, bis(chloromethyl) ether, chloromethyl methyl ether, and epichlorohydrin. The full set of Latin Square SemiVOST quad train experiments and tests performed to evaluate run-to-run reproducibility indicate that 70% of the candidate target compounds should be evaluated on actual stationary sources. Although the complete Latin Square VOST experiment was not successful, consistent results obtained with the modified dynamic spiking system indicate that the VOST may be useful on most of the targeted VOST compounds. Since standard solutions of both volatile and semivolatile compounds containing all of the compounds of interest that could be chromatographed successfully are available, no compounds will be removed from the set for field testing of the trains.

**Table 6.** Recoveries of Compounds from SemiVost Latin Square Experimental Runs

| Compound                    | Mean*<br>(Percent) | Standard<br>Deviation<br>(Percent) |
|-----------------------------|--------------------|------------------------------------|
| bis(Chloromethyl) ether     | 18.28              | 9.22                               |
| Epichlorohydrin             | 75.20              | 24.11                              |
| cis-1,3-Dichloropropene     | 21.90              | 6.55                               |
| trans-1,3-Dichloropropene   | 20.34              | 5.80                               |
| 1,1,2-Trichloroethane       | 53.13              | 14.82                              |
| Ethylene dibromide          | 66.31              | 14.56                              |
| Tetrachloroethylene         | 49.68              | 14.48                              |
| Chlorobenzene               | 75.96              | 13.46                              |
| Bromoform                   | 99.27              | 22.25                              |
| 1,1,2,2-Tetrachloroethane   | 81.05              | 12.77                              |
| Dichloroethyl ether         | 75.78              | 11.99                              |
| 1,4-Dichlorobenzene         | 68.16              | 10.90                              |
| Benzyl chloride             | 78.72              | 20.43                              |
| Hexachloroethane            | 85.43              | 35.1                               |
| 1,2-Dibromo-3-chloropropane | 66.24              | 6.91                               |
| 1,2,4-Trichlorobenzene      | 58.20              | 10.94                              |
| Hexachlorobutadiene         | 58.34              | 10.69                              |
| Benzotrichloride            | 67.02              | 16.58                              |
| Chloroacetophenone          | 79.64              | 18.03                              |
| Hexachlorocyclopentadiene   | 513.04             | 254.26                             |
| 2,4,6-Trichlorophenol       | 4.61               | 16.30                              |
| 2,4,5-Trichlorophenol       | 52.69              | 39.78                              |
| Hexachlorobenzene           | 32.85              | 18.35                              |
| Pen'achlorophenol           | 8.93               | 10.50                              |
| Pentachloronitrobenzene     | 38.24              | 20.66                              |
| Chlorobenzilate             | 43.63              | 35.49                              |
| 3,3'-Dichlorobenzidine      | 86.42              | 165.82                             |

\*Four quadruple runs were performed (total of 16 samples); two sets of results were rejected as outliers, leaving 14 samples.



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The complete report, entitled "Laboratory Validation of VOST and SemiVOST for Halogenated Hydrocarbons from the Clean Air Act Amendments List" consists of two volumes:

Volume 1: (Order No. PB93-227 163/AS; Cost: \$36.50, subject to change) and

Volume 2 (Order No. PB93-227 171/AS; Cost: 36.50, subject to change).

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