



# Project Summary

## Field Test of a Generic Method for Halogenated Hydrocarbons: A VOST Test at a Chemical Manufacturing Facility Using a Modified VOST Sampling Method

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Because of the lack of commercial availability of SKC Lot 104 petroleum-based charcoal, the lot of charcoal specified for use in the Volatile Organic Sampling Train (VOST, SW-846 Method 0030), a laboratory study was performed to select an appropriate substitute. On the basis of performance, availability, and cost, Anasorb 747®\* was selected as the substitute for SKC Lot 104, and a draft sampling protocol for the modified VOST train was written. In the modified VOST sampling train, the second tube containing sequential beds of Tenax® and charcoal was replaced by a tube containing only Anasorb®. This replacement necessitated the use of two Tenax® front tubes in the train, for a total of three sorbent tubes. A field evaluation study, using dynamic spiking and quadruple sampling trains, was conducted to provide a statistical comparison of the performance of the VOST and the modified VOST methodologies for the volatile halogenated organic compounds listed in Title III of the Clean Air Act Amendments of 1990.

\* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

*This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

Validation of a method for a particular analyte or group of analytes means that the performance of the methodology for these analytes has been established and demonstrated through field tests at the type of source category of interest: that is, the precision and bias of the method have been established experimentally. Field validation may be performed by performing spiking operations in the field so that the precision and bias of the method can be demonstrated from sample collection through analysis, using either static or dynamic spiking procedures as specified in EPA Method 301, the Validation Protocol. Another procedure for validation of a method is a side-by-side comparison of a candidate method to a validated method to establish comparable performance for the same analytes in the same matrix (same source category).

Under Title III of the Clean Air Act Amendments of 1990, identification and/or validation of sampling and analytical methods are required for the volatile halogenated organic compounds which are listed (Table 1). The candidate test method is the Volatile Organic Sampling Train (VOST), which consists of SW-846 Sampling Method 0030 and SW-846 Analytical Method 5040 or 5041. Method 0030, the sampling protocol, requires the use of Tenax® and a specific petroleum-based charcoal (SKC Lot 104) or its equivalent. Since SKC Lot 104 charcoal is no longer commercially available and Method 0030 contains no performance specifications for the charcoal, a laboratory study was performed to identify an acceptable equiva-

lent. Several candidate sorbents were studied in the laboratory, and Anasorb 747® was selected as a candidate sorbent for a field test because of its performance, availability, and cost. In the course of the laboratory studies, the decision was made to use only Anasorb® in the back tube rather than the sequential beds of Tenax® and charcoal which had been used previously. Use of a back tube consisting of only Anasorb® necessitated the use of two Tenax® front tubes in a modified VOST train. A new sampling protocol was written to incorporate the use of the modified sorbent tube structure. The analytical procedures of Method 5041 were also modified to include individual analysis of each of the three sorbent tubes to examine

compound distribution. In routine application, the analysis would be performed with paired Tenax® tubes.

A presurvey conducted at a chemical manufacturing facility established that no compounds of interest were present above a level of 5 times the Method Detection Limit. Evaluation of the modified VOST method was accomplished by performing sampling and analysis following Draft Method 0031 and Method 5041, using Method 0030 as the reference method required by EPA Method 301. The bias of the method can be evaluated by comparing the results obtained by one candidate method to the results obtained by a validated method. To determine the precision of the test method, multiple or collocated

**Table 1.** Volatile Halogenated Organic Compounds, Title III of the Clean Air Act Amendments, for Which Laboratory Testing has Determined the Applicability of the VOST Method

| Compound                                     | Boiling point (°C)   | Comments   |
|--|----------------------|--|
| allyl chloride (3-chloropropene)             | 44-46                | Acceptable performance in laboratory                 |
| bis(chloromethyl) ether                      | 106 <sup>1</sup>     | Decomposes in water; cannot be analyzed              |
| carbon tetrachloride                         | 77                   | Recovery too high in laboratory study                |
| chlorobenzene                                | 132 <sup>1</sup>     | Acceptable performance in laboratory                 |
| chloroform                                   | 60.5-61.5            | Acceptable performance in laboratory                 |
| chloromethyl methyl ether                    | 55-57                | Decomposes in water; cannot be analyzed              |
| chloroprene                                  | 59.4                 | Acceptable performance in laboratory                 |
| 1,3-dichloropropylene                        | 105-106 <sup>2</sup> | Acceptable performance in laboratory                 |
| epichlorohydrin                              | 115-117 <sup>1</sup> | Soluble in water; cannot be analyzed                 |
| ethyl chloride (chloroethane)                | 12 <sup>3</sup>      | Acceptable performance in laboratory                 |
| ethylene dibromide (1,2-dibromoethane)       | 131-132 <sup>1</sup> | Acceptable performance in laboratory                 |
| ethylene dichloride (1,2-dichloroethane)     | 83                   | Acceptable performance in laboratory                 |
| ethylidene dichloride (1,1-dichloroethylene) | 57                   | Acceptable performance in laboratory                 |
| methyl bromide (bromomethane)                | 4 <sup>3</sup>       | Recovery unacceptably high in laboratory             |
| methyl chloride (chloromethane)              | -24.2 <sup>3</sup>   | Erratic and unacceptably high recovery in laboratory |
| methyl chloroform (1,1,1-trichloroethane)    | 74-76                | Recovery too high in laboratory study                |
| methylene chloride                           | 39.8-40              | Recovery too high in laboratory study                |
| methyl iodide (iodomethane)                  | 41-43                | Acceptable performance in laboratory                 |
| propylene dichloride (1,2-dichloropropane)   | 95-96                | Acceptable performance in laboratory                 |
| tetrachloroethylene                          | 121 <sup>1</sup>     | Acceptable performance in laboratory                 |
| 1,1,2-trichloroethane                        | 110-115 <sup>1</sup> | Acceptable performance in laboratory                 |
| trichloroethylene                            | 86.9                 | Acceptable performance in laboratory                 |
| vinyl chloride                               | -13.4 <sup>3</sup>   | Acceptable performance in laboratory                 |
| vinyl bromide (1,1-dichloroethene)           | 16 <sup>4</sup>      | Acceptable performance in laboratory                 |
| vinylidene chloride                          | 30-32                | Acceptable performance in laboratory                 |

<sup>1</sup> Above the maximum VOST boiling point of 100°C; included in the testing because compounds in the range of 100-132°C are frequently tested by the VOST method.

<sup>2</sup> Boiling temperature at 730 mm Hg.

<sup>3</sup> Below the common lower temperature limit of 30°C usually used for VOST.

<sup>4</sup> Boiling temperature at 750 mm Hg.

simultaneous samples are taken and analyzed. In this field test, known concentrations of volatile halogenated analytes were introduced into the VOST trains and into the modified VOST trains, using the same certified cylinder as a source of the compounds. Using the same dynamic spiking procedures, multiple collocated simultaneous samples were taken using both methods at the same source.

Bias is any systematic positive or negative difference between the measured values and the true value of a sample. Bias may result from analytical interferences, errors in calibration, or inefficiencies in the collection of the analyte. When the bias of the method is determined for a given analyte, a correction for the bias may be made. The EPA Method 301 allows for this correction within a range of 90-110% when a candidate method is being compared to a reference method. Bias values outside this range may be grounds for rejecting the candidate method.

Precision is the variability in the data from the entire measurement system (both

sampling and analysis) as determined from multiple or collocated sampling trains. Following the EPA Method 301 procedures, two paired sampling trains are used to determine the precision of the entire system. Use of quadruple (Quad) trains with four collocated sampling probes allows operation of two spiked trains and two unspiked trains. The EPA Method 301 requires that the precision of the candidate method not be significantly different from the reference method in order for the candidate method to be considered acceptable. To determine bias and precision in the field, a total of at least 16 samples using quadruple collocated sampling trains was collected using both VOST and modified VOST.

Statistical analysis of the results from the field studies with dynamic spiking show that the two methods are at least equivalent, with the modified VOST methodology frequently being somewhat superior in compound recovery and precision.

## Procedure

Sampling was performed by withdrawing stack gas from a single port in the stack through a Quad probe, then directing the sampled gas simultaneously to four similar VOST or modified VOST sampling trains. The Quad probe contains four similar heated probes that can be inserted into the stack as one unit. The front end of the Quad probe was positioned in the center of the stack and remained in that location during each day of testing; no traverse of the stack was performed with the Quad probe. The true concentration of the components of the stack gas was of no interest to this program as long as any quantities of the compounds of interest were equal for each train, so traversing was not required. For modified VOST sampling, two of the trains of each Quad run were dynamically spiked (Trains A and B) and two were unspiked (Trains C and D). The configuration of the modified VOST sampling train is shown in Figure 1.

Dynamic spiking of candidate VOST compounds into the modified VOST train

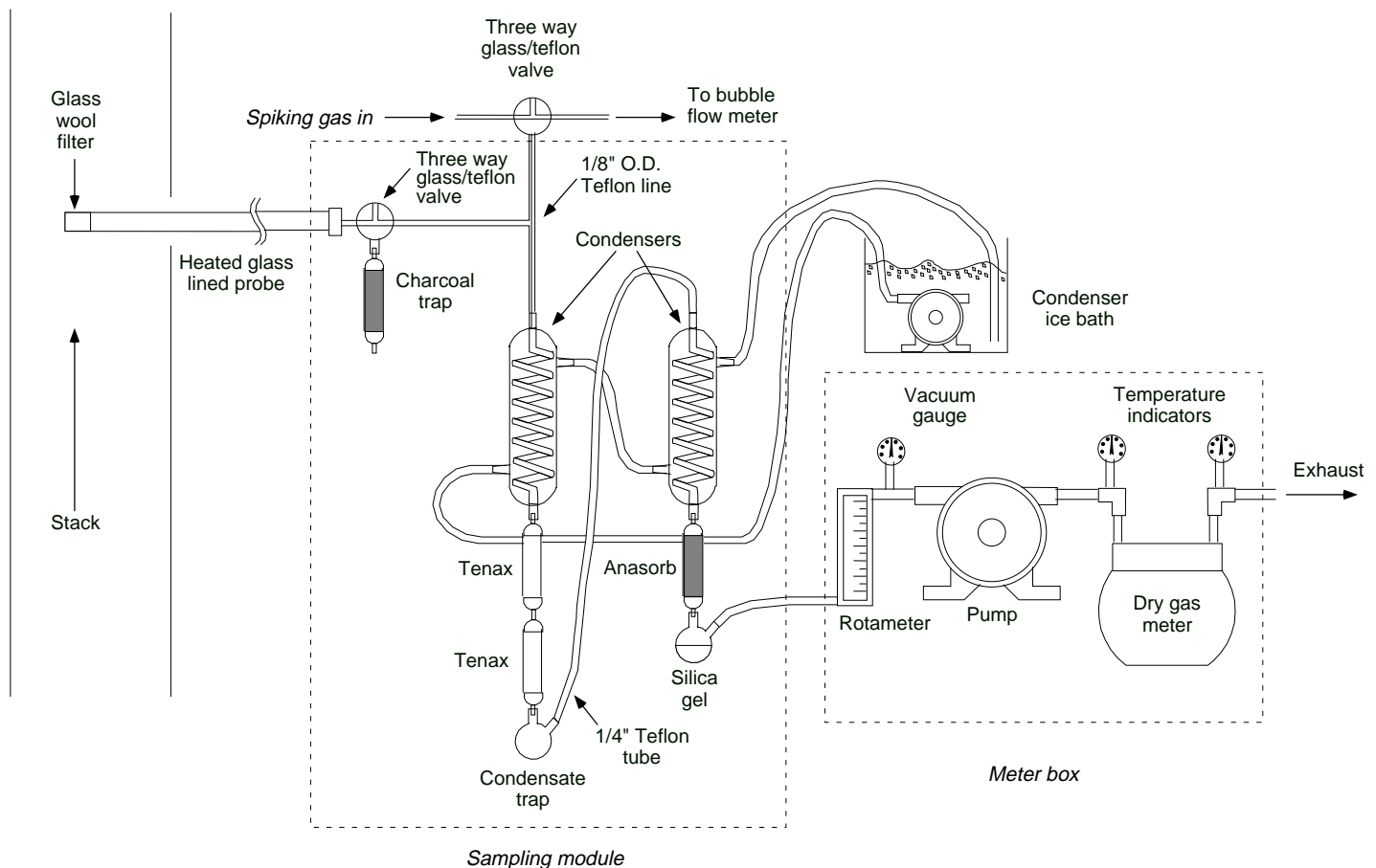


Figure 1. Modified VOST sampling train.

was performed using a compressed gas cylinder containing the volatile halogenated organic compounds. The same cylinder was used for spiking both the VOST train and the modified VOST train, with the composition and concentration of the volatile halogenated organic compounds in the cylinder established by independent laboratory tests. The boiling point of 100°C cited in Method 0030 was extended to approximately 135°C to allow the inclusion of chlorobenzene, a compound frequently determined by the VOST methodology. The Modified VOST spiking apparatus shown in Figure 2, was used for dynamic spiking. In the field, the spiking gas was allowed to flow through the spiking apparatus for two hours before directing the flow to the sampling trains to minimize any adsorptive losses during actual Quad sampling runs. A total of ten (10) Quad sampling runs for both VOST and modified VOST was performed in the field to provide adequate samples for statistical comparison of the two methods and to allow backup samples in the event that

any samples became invalid due to breakage or loss of data during analysis.

Analysis of field samples was performed according to SW-846 Method 5041 (VOST), analyzing each tube individually to establish distribution of compounds. The three tubes associated with each modified VOST sample set were analyzed in the following order: Anasorb®, Tenax® #2, Tenax® #1. No condensate was observed in the collection of samples.

## Results and Discussion

Mean recoveries of the volatile halogenated organic compounds using the modified VOST sampling method are shown in Table 2. No background corrections were made because background levels of the analytes were less than 5 times the Method Detection Limit. Methyl chloride exhibited erratic recoveries, far above 100% in most analyses. This erratic behavior upon analysis had been observed in laboratory studies, in the first field test of the VOST method, and in this field test of both the VOST and modified VOST methods. The

compound is apparently being formed during sampling and analysis.

Surrogate compound recoveries from the Tenax® tubes were uniformly high, so correction for surrogate recoveries was not made. The same surrogate compounds were used to spike the Anasorb® tubes prior to analysis, and recovery of the less volatile surrogate compounds from Anasorb® is poor; correction of Anasorb® results for surrogate recovery would distort the analytical results.

Examination of the observed distribution of analytes among the three sorbent tubes of the modified VOST sampling train demonstrates the necessity of a second Tenax® tube in the sampling train. Methyl chloride, vinyl chloride, and ethyl chloride are found primarily on the back (Anasorb®) tube. The following compounds are found primarily (>90%) on the front Tenax® tube: ethylidene dichloride, chlorobenzene, chloroform, propylene dichloride, methyl chloroform, carbon tetrachloride, ethylene dichloride, trichloroethene, cis-1,3-dichloropropene, trans-1,3-dichloropropene, 1,1,2-trichloro-

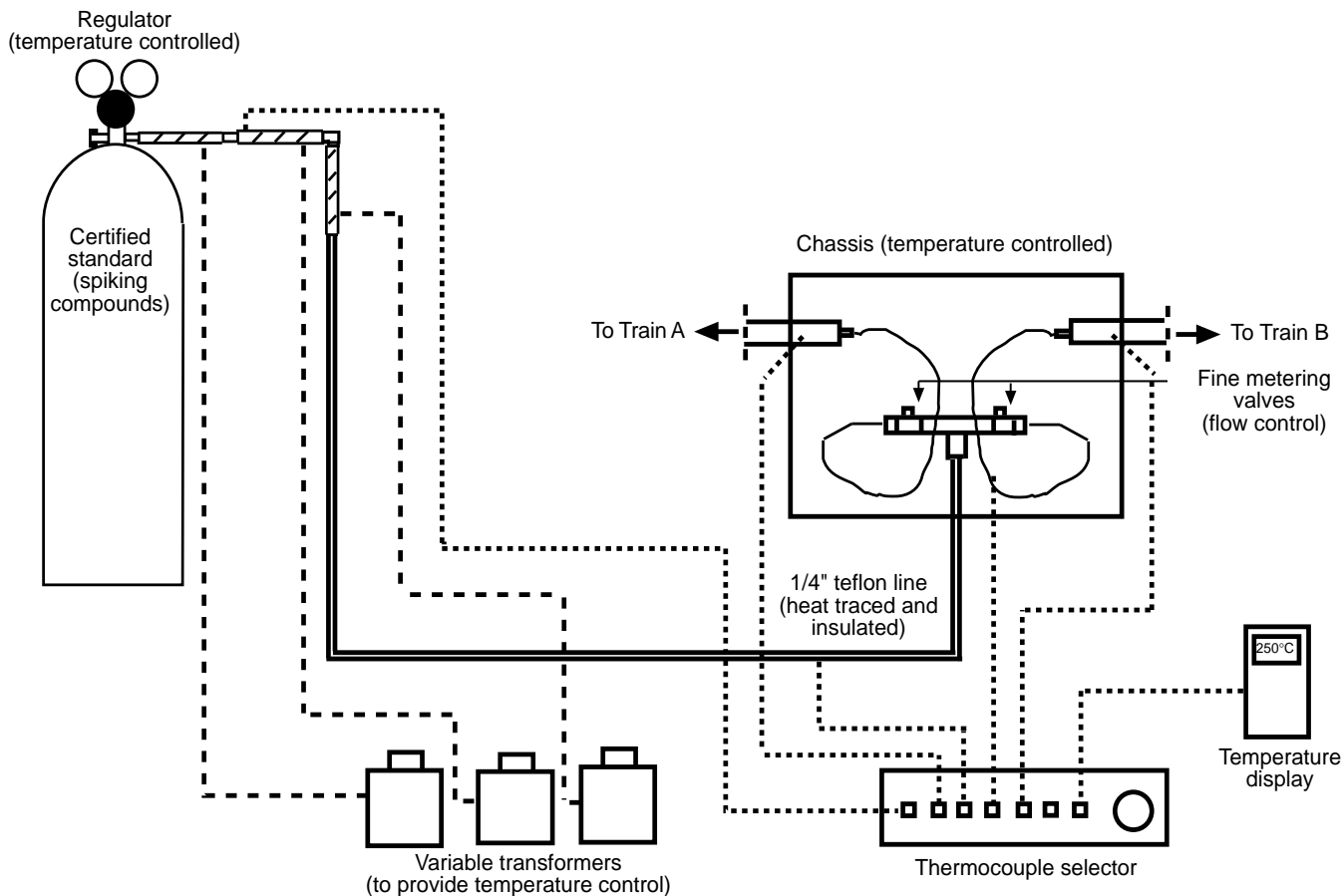


Figure 2. Modified VOST spiking apparatus.

**Table 2.** Mean Recoveries of Volatile Halogenated Organic Compounds, Using the Modified VOST Method

| Compound                                  | Mean Recovery (Percent) <sup>1</sup> | Percent Relative Standard Deviation |
|---|--------------------------------------|-------------------------------------|
| methyl chloride (chloromethane)           | 167.5                                | 56.4                                |
| 1,2-dichloropropane (propylene chloride)  | 149.4                                | 14.0                                |
| trichloroethene                           | 148.7                                | 3.4                                 |
| methylene chloride                        | 120.7                                | 10.9                                |
| cis-1,3-dichloropropene                   | 118.4                                | 21.0                                |
| 1,1,2-trichloroethane                     | 117.3                                | 20.5                                |
| ethylene dibromide (1,2-dibromoethane)    | 108.5                                | 23.2                                |
| chloroform                                | 98.4                                 | 20.4                                |
| vinylidene chloride (1,1-dichloroethene)  | 96.8                                 | 17.2                                |
| ethylidene chloride (1,1-dichloroethane)  | 96.2                                 | 12.6                                |
| chlorobenzene                             | 91.6                                 | 13.0                                |
| carbon tetrachloride                      | 89.3                                 | 12.5                                |
| methyl iodide (iodomethane)               | 89.0                                 | 11.9                                |
| methyl chloroform (1,1,1-trichloroethane) | 87.1                                 | 12.1                                |
| chloroprene                               | 85.8                                 | 15.3                                |
| ethylene dichloride (1,2-dichloroethane)  | 83.2                                 | 25.1                                |
| trans-1,3-dichloropropene                 | 75.2                                 | 32.6                                |
| tetrachloroethene                         | 61.8                                 | 8.9                                 |
| methyl bromide (bromomethane)             | 45.7                                 | 46.7                                |
| ethyl chloride (chloroethane)             | 45.3                                 | 30.0                                |
| vinyl chloride                            | 44.2                                 | 24.2                                |
| vinyl bromide                             | 38.0                                 | 22.5                                |
| allyl chloride (3-chloropropene)          | 26.0                                 | 21.1                                |

<sup>1</sup> The shaded area indicates recoveries from 50 to 150 percent with percent relative standard deviation of 50 or less.

ethane, tetrachloroethene, methyl iodide, allyl chloride, ethylene dibromide, and chloroprene. Other analytes were distributed among the three tubes.

Comparative results for the VOST and modified VOST are shown in Table 3. In most instances, recovery for modified VOST is equivalent to or better than recovery for VOST, and precision for modified VOST is equivalent to or better than precision for VOST.

## Conclusions and Recommendations

Based on the field evaluation of the modified VOST method as compared to the VOST method, the following conclusions may be drawn:

- On the basis of a compound-by-compound comparison of recovery and precision, the two methods are com-

parable and, where they differ, the modified VOST usually shows better performance with respect to both recovery and precision.

- The only compound which showed acceptable performance in the VOST but not in the modified VOST is methyl bromide. However, the range in both the recovery and precision is sufficiently large that the differences between the results for the VOST and the modified VOST cannot be considered statistically significant.
- Methyl chloride (chloromethane) has shown erratic performance, with extremely high recoveries and poor precision in several laboratory studies, in two field tests using VOST, and in the field test using the modified VOST methodology. Methyl chloride is not an appropriate analyte for any form

of the VOST method because quantitative calculations are unreliable for this analyte. Even qualitative information (i.e., presence or absence) is suspect because methyl chloride may be formed on the sorbent tubes from decomposition of other halogenated compounds.

- The following compounds were not sampled and analyzed successfully in this field evaluation using either VOST or modified VOST: methyl chloride (chloromethane), vinyl chloride, ethyl chloride (chloroethane), allyl chloride (3-chloropropene), and vinyl bromide. Other than methyl chloride, all of the analytes which show poor performance contain a double bond. Application of VOST or modified VOST methodology for accurate quantitative determination of analytes containing

**Table 3.** Results of VOST and Modified VOST: Recovery and Precision

| Compound                                   | Modified VOST                      |                                     | VOST                               |                                     |
|--|------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|
|  | Mean Percent Recovery <sup>1</sup> | Percent Relative Standard Deviation | Mean Percent Recovery <sup>1</sup> | Percent Relative Standard Deviation |
| methyl chloride (chloromethane)            | 167.5                              | 56.4                                | 255.3                              | 58.1                                |
| ethylidene dichloride (1,1-dichloroethane) | 96.2 <sup>2</sup>                  | 12.6                                | 86.0 <sup>2</sup>                  | 13.2                                |
| chlorobenzene                              | 91.6 <sup>2</sup>                  | 13.0                                | 84.8 <sup>2</sup>                  | 27.9                                |
| vinyl chloride                             | 44.2                               | 24.2                                | 37.3                               | 39.5                                |
| vinylidene chloride (1,1-dichloroethene)   | 96.8 <sup>2</sup>                  | 17.2                                | 77.8 <sup>2</sup>                  | 25.1                                |
| chloroform                                 | 98.4 <sup>2</sup>                  | 20.4                                | 95.3 <sup>2</sup>                  | 14.3                                |
| propylene dichloride (1,2-dichloropropane) | 149.4 <sup>2</sup>                 | 14.0                                | 117.7 <sup>2</sup>                 | 30.0                                |
| methyl bromide (bromomethane)              | 45.7                               | 46.7                                | 52.8 <sup>2</sup>                  | 27.8                                |
| ethyl chloride (chloroethane)              | 45.3                               | 30.0                                | 31.4                               | 37.6                                |
| methylene chloride                         | 120.7 <sup>2</sup>                 | 10.9                                | 90.8 <sup>2</sup>                  | 11.7                                |
| methyl chloroform (1,1,1-trichloroethane)  | 87.1 <sup>2</sup>                  | 12.1                                | 96.8 <sup>2</sup>                  | 19.4                                |
| carbon tetrachloride                       | 89.3 <sup>2</sup>                  | 12.5                                | 85.7 <sup>2</sup>                  | 13.8                                |
| ethylene dichloride (1,2-dichloroethane)   | 83.2 <sup>2</sup>                  | 25.1                                | 78.6 <sup>2</sup>                  | 27.7                                |
| trichloroethene                            | 148.7 <sup>2</sup>                 | 3.4                                 | 124.0 <sup>2</sup>                 | 16.8                                |
| cis-1,3-dichloropropene                    | 118.4 <sup>2</sup>                 | 21.0                                | 83.5 <sup>2</sup>                  | 16.1                                |
| trans-1,3-dichloropropene                  | 75.2 <sup>2</sup>                  | 32.6                                | 47.9                               | 35.0                                |
| 1,1,2-trichloroethane                      | 117.3 <sup>2</sup>                 | 20.5                                | 81.4 <sup>2</sup>                  | 14.4                                |
| tetrachloroethene                          | 61.8 <sup>2</sup>                  | 8.0                                 | 57.5 <sup>2</sup>                  | 12.5                                |
| methyl iodide (iodomethane)                | 89.0 <sup>2</sup>                  | 11.9                                | 77.8 <sup>2</sup>                  | 20.4                                |
| allyl chloride (3-chloropropene)           | 26.0                               | 21.1                                | 36.4                               | 29.6                                |
| ethylene dibromide (1,2-dibromoethane)     | 108.5 <sup>2</sup>                 | 23.2                                | 81.6 <sup>2</sup>                  | 31.0                                |
| chloroprene                                | 85.8 <sup>2</sup>                  | 15.3                                | 76.4 <sup>2</sup>                  | 12.3                                |
| vinyl bromide                              | 38.0                               | 22.5                                | 28.4                               | 30.9                                |

<sup>1</sup> Mean of 6 runs (12 sets of dynamically spiked tubes).

<sup>2</sup> Indicates acceptable performance, using the criteria of recovery from 50 to 150 percent, with percent relative standard deviation of 50 or less.

a double bond is questionable. Because recoveries of these analytes tend to be low, there tends to be a low bias in the quantitative determination.

On the basis of the laboratory and field efforts conducted for the volatile halogenated organic compounds from Title III of the Clean Air Act Amendments, the following recommendations are made:

- Careful consideration of the chemical and physical properties of candidate VOST or modified VOST analytes can predict when successful performance

of the sampling or analytical methodology is unlikely. For example, analysis of water-soluble compounds will either be completely unsuccessful or show a low bias, because water-soluble compounds cannot be quantitatively purged from water in the course of the analysis.

- Neither the VOST nor the Modified VOST is recommended as a sampling or analytical method for methyl chloride (chloromethane). Even the accuracy of VOST or modified VOST

as a screening method to establish the presence of methyl chloride in an emissions matrix is questionable.

- Modification or replacement of the VOST methodology should be investigated to provide a sampling and analytical method feasible for application to volatile, polar, water-soluble analytes.
- If surrogate compound recoveries are 90% or above, no corrections for surrogate recoveries should be made in either VOST or modified VOST.

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**Merrill D. Jackson** is the EPA Project Officer (see below).

*The complete report, entitled "Field Test of a Generic Method for Halogenated Hydrocarbons: A VOST Test at a Chemical Manufacturing Facility Using a Modified VOST Sampling Method," (Order No. PB95-142055; Cost: \$27.00; subject to change) will be available only from*

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