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Project Summary

Field Test of Generic Method for Halogenated Hydrocarbons

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Validation of a method for a particular analyte or group of analytes means that the performance of the sampling and analytical 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. In examination of the available method validation data for organic compounds listed in Title III of the Clean Air Act Amendments (CAAA) of 1990, the lack of overall method validation data is readily apparent. In some cases, analytical methods have been validated for a number of analytes, but there is no validation information for the sampling methodology. Full validation for sampling and analytical methods, for both field and laboratory operations, is available for fewer than 10 % of the analytes listed in Title III of the CAAA at any source category. Field validation may be performed by 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). Another procedure for validation of a method is to perform spiking operations in the field so that the precision and bias of the method can be demonstrated from sample collection through analysis. Both dynamic and static procedures for the validation of a method are permitted in EPA's Validation Protocol in Method 301.

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

The United States Environmental Protection Agency (EPA), under the authority of Title III of the Clean Air Act Amendments (CAAA) of 1990, requires the identification and/or validation of sampling and analytical methods for the halogenated volatile and semivolatile organic compounds which are listed (Table 1 and Table 2). The candidate methods for testing the volatile organic compounds are VOST (SW-846 Sampling Method 0030 and SW-846 Analytical Methods 5040 or 5041), and for testing the semivolatile organic compounds, SemiVOST (SW-846 Sampling Method 0010 and SW-846 Analytical Method 8270) is used. The VOST and SemiVOST methods were first evaluated in a laboratory environment, and dynamic spiking procedures were also developed and evaluated. The results of the laboratory study were reported in an earlier document.

After the laboratory evaluation, the next step was to attempt to validate the two candidate test methods at a coal-fired power plant that does not routinely emit high levels of these hazardous air pollutants (HAPs). The absence of high levels of the HAPs was determined by analyzing samples collected during a pretest survey. A field test was planned to further verify the analyte spiking methodology in a non-laboratory environment and to assess the added effect of sampling a com-

bustion matrix (stack gas). Minimizing the source contribution of the HAPs in the sample matrix simplified the evaluation of the results for the effectiveness of the spiking procedures. A source with significant levels of all the HAPs shown in Tables 1 and 2 could not be located.

Results and Discussion

Validation of VOST and SemiVOST was accomplished by performing sampling and analysis following the EPA methods except for the use of a quadruple (QUAD) probe system required by EPA Method 301. Validation procedures for a method include protocols for determining and documenting the quality of data generated by that method. The bias (systematic error) and precision (reproducibility of measurement) are determined in a statistically valid manner. The procedures for validating a method for a given analyte or set of analytes require introducing known concentrations of the analyte(s) into the sampling train or comparing the candidate method against a validated test method. The bias of the method can be evaluated by determining the recovery of the known quantity of analyte which has been spiked into the sampling train or by comparison of the results obtained by the candidate method to the results obtained by the validated method. In order to determine the precision of the test method, multiple or collocated simultaneous samples are taken and analyzed. If dynamic spiking techniques are used, it is essential that the analyte be introduced into the sampling train as near to the end of the probe as possible, and that the analyte be introduced continuously for the duration of the sampling operation.

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 70 to 130%. Bias values outside this range may require the rejection of the candidate method.

Precision is the variability in the data that is obtained from the entire measurement system (both sampling and analysis) as determined from the multiple or collocated sampling trains. Following the EPA Method 301 procedures, two paired sampling trains were used to determine the precision of the entire system. Use of QUAD trains with four collocated sampling probes allows operation of two spiked trains and two unspiked trains. EPA Method 301 requires that the precision not be greater than 50 % relative standard deviation for the method to be valid. To determine bias and precision in the field, a total of 24 samples using quadruple collocated sampling trains was collected. For quadruple trains, six complete sampling runs constitute the minimum Method 301 requirement.

The halogenated compounds listed in the CAAA of 1990 for which method validation is required and for which laboratory testing has been performed are shown in Tables 1 and 2. Pesticides, polychlorinated biphenyls, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, and dibenzofurans were excluded from this study, since specialized methods are available for these analytes. Not all of the candidate analytes for the VOST and SemiVOST performed successfully in those methods. Four compounds could not be analyzed by the VOST of SemiVOST methods either in the laboratory or in the field:

- Bis(chloromethyl) ether, chloromethyl methyl ether, and epichlorohydrin could not be analyzed by the VOST analytical method. Since these compounds are water-soluble and react with water, the failure of the VOST analytical methodology was anticipated.
- Chloroacetic acid could not be analyzed in the SemiVOST analytical method because of its unstable and reactive nature.

The laboratory evaluation included the following components:

- Determination of chromatographic retention times for both volatile and semivolatile compounds using gas chromatography/mass spectrometry (GC/MS);
- Determination of recoveries from sorbents for both volatile and semivolatile compounds;
- Determination of analytical method detection limits for both volatile and semivolatile halogenated organic compounds; and
- Design, construction, and evaluation of dynamic spiking equipment and techniques for use in the field spiking of volatile and semivolatile halogenated organic compounds.

The field validation of the VOST and SemiVOST was accomplished by dynamically spiking the trains with the specific halogenated organic compounds while simultaneously sampling emissions from a combustion source. During each QUAD sampling run, only two of the four sampling trains were dynamically spiked; the other two unspiked trains were used to establish the background level of any target compounds in the stack gas. A sampling scheme to meet the requirements of method validation was designed statistically to ensure the collection of appropriate numbers of samples for each method. Samples were analyzed according to SW-846 Method 5041 and SW-846 Method 8270, with statistical evaluation of data. Results are summarized in Tables 3 and 4.

Based on the work performed in the laboratory and the field evaluation of the VOST and SemiVOST methods, the following conclusions may be drawn from the results shown in Tables 3 and 4:

- Using the criteria for acceptable performance of recovery between 50 and 150 %, with a percent standard deviation of 50 or less, the VOST methodology performed successfully in a coal-fired boiler emission matrix at a nominal concentration of 12 ng/liter for the following compounds: cis-1,3-dichloropropene, trans-1,3-dichloropropene, trichloroethene, methyl chloroform (1,1,1-trichloroethane), carbon tetrachloride, vinyl chloride, 1,1,2-trichloroethane, tetrachloroethene, chlorobenzene, vinylidene chloride (1,1-dichloroethene), chloroform, methylene chloride, ethylene dichloride (1,2-dichloroethane), ethylidene dichloride (1,1-dichloroethane), methyl iodide (iodomethane), propylene dichloride (1,2-dichloropropane), vinyl bromide, methyl bromide (bromomethane), and ethyl chloride (chloroethane).
- Using the criteria for acceptable performance of recovery between 50 and 150 %, with a percent relative standard deviation of 50 or less, the SemiVOST methodology performed successfully in a coal-fired boiler emissions matrix at a nominal concentration of 6 $\mu g/ft^3$ for the following compounds: hexachloroethane, benzyl chloride, hexachlorobutadiene, 1,1,2-trichloroethane, 2,4,5-trichlorophenol, chlorobenzene, dichloroethyl ether, benzotrichloride, bromoform, 1,2,4-trichlorobenzene, ethylene dibromide (1,2-dibromoethane), 1,1,2,2-tetrachloroethane, 1,4-dichlorobenzene, 2-chloroacetophenone, tetrachloroethene, and trans-1,3-dichloropropene.

- The VOST methodology did not perform acceptably under the field conditions for methyl chloride (chloromethane), chloroprene, ethylene dibromide (1,2-dibromoethane), and allyl chloride (3-chloropropene).
- The SemiVOST methodology did not perform acceptably under the field conditions for 2,4,6-trichlorophenol, cis-1,3-dichloropropene, 1,2-dibromo-3-chloropropane, hexachlorobenzene, pentachloronitrobenzene, pentachlorophenol, hexachlorocyclopentadiene, chlorobenzilate, epichlorohydrin, 3,3'-dichlorobenzidine, and bis(chloromethyl) ether.
- Some compounds were tested in both methodologies because they exhibited volatility (boiling points) appropriate for inclusion in either method. The following compounds performed acceptably in both VOST and SemiVOST: tetrachloroethene, trans-1,3-dichloropropene, 1,1,2-trichloroethane, and chlorobenzene. Ethylene dibromide (1,2-dibromoethane) performed acceptably in the SemiVOST methodology, but did not meet recovery criteria for the VOST methodology. cis-1,3-Dichloropropene performed acceptably using the VOST methodology but did not meet the criteria for successful performance in the SemiVOST methodology.

Table 1. *Halogenated Compounds for Which Laboratory Testing Has Determined the Applicability of the VOST Method.*

Compound	*Boiling point (°C)*	*Comments*
Allyl chloride	*44-46*	*Acceptable performance in laboratory*
bis(chloromethyl) ether	*106* [1]	*Decomposes in water; cannot be analyzed*
Carbon tetrachloride	*77*	*Recovery too high in laboratory study*
Chlorobenzene	*132* [1]	*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* [2]	*Acceptable performance in laboratory*
Epichlorohydrin	*115-177* [1]	*Decomposes in water; cannot be analyzed*
Ethyl chloride	*12* [3]	*Acceptable performance in laboratory*
Ethylene dibromide	*131-132* [1]	*Acceptable performance in laboratory*
Ethylene dichloride	*83*	*Acceptable performance in laboratory*
Ethylidene dichloride	*57*	*Acceptable performance in laboratory*
Methyl bromide	*4* [3]	*Recovery unacceptable high in laboratory*
Methyl chloride	*-24.2* [3]	*Erratic and unacceptable n laboratory*
Methyl chloroform	*74-76*	*Recovery too high in laboratory study*
Methylene chloride	*39.8-40*	*Recovery too high in laboratory study*
Methyl iodide	*41-43*	*Acceptable performance in laboratory*
Propylene dichloride	*95-96*	*Acceptable performance in laboratory*
Tetrachloroethylene	*121* [1]	*Acceptable performance in laboratory*
1,1,2-Trichloroethane	*110-115* [1]	*Acceptable performance in laboratory*
Trichloroethylene	*86.9*	*Acceptable performance in laboratory*
Vinyl chloride	*-13.4* [3]	*Acceptable performance in laboratory*
Vinyl bromide	*16* [4]	*Acceptable performance in laboratory*
Vinylidene chloride	*30-32*	*Acceptable performance in laboratory*

[1] 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.
[2] Boiling temperature at 730 mm Hg.
[3] Below the common lower temperature limit of 30°C usually used for VOST.
[4] Boiling temperature at 750 mm Hg.

Table 2. *Halogenated Compounds for which Laboratory Testing has Determined the Applicability of the SemiVOST Method.*

Compound	*Boiling point (°C)*	*Comments*
Benzotrichloride	*219-223*	*Acceptable performance in laboratory*
Benzyl chloride	*177-181*	*Acceptable performance in laboratory*
bis(Chloromethyl) ether [4]	*106*	*Unacceptably low recovery in laboratory*
Bromoform	*150-151*	*Acceptable performance in laboratory*
Chloroacetic acid	*189*	*Cannot be analyzed by SemiVOST method*
Chlorobenzene [4]	*132*	*Acceptable performance in laboratory*
2-Chloroacetophenone	*244-245*	*Acceptable performance in laboratory*
Chlorobenzilate	*147*	*Unacceptably low recovery in laboratory*
1,2-Dibromo-3-chloropropane	*196*	*Acceptable performance in laboratory*

Table 2. *Halogenated Compounds for which Laboratory Testing has Determined the Applicability of the SemiVOST Method (continued).*

Compound	Boiling point (°C)	Comments
1,4-Dichlorobenzene	173	Acceptable performance in laboratory
3,3'-Dichlorobenzidine	MP=165	Erratic performance in laboratory
Dichloroethyl ether	65-67 [4]	Acceptable performance in laboratory
1,3-Dichloropropene	105-106 [3]	Unacceptably low recovery in laboratory
Epichlorohydrin [1]	115-117	Acceptable performance in laboratory
Ethylene dibromide [1]	131-132	Acceptable performance in laboratory
Hexachlorobenzene	323-326	Unacceptably low recovery in laboratory
Hexachlorobutadiene	210-220	Acceptable performance in laboratory
Hexachlorocyclopentadiene	239	Erratic performance in laboratory
Hexachloroethane	186	Acceptable performance in laboratory
Pentachloronitrobenzene	328	Unacceptably low recovery in laboratory
Pentachlorophenol	309 5	Unacceptably low recovery in laboratory
1,1,2,2-Tetrachloroethane	147	Acceptable performance in laboratory
Tetrachloroethylene [1]	121	Unacceptably low recovery in laboratory
1,2,4-Trichlorobenzene	214	Acceptable performance in laboratory
1,1,2-Trichloroethane [1]	110-115	Acceptable performance in laboratory
2,4,5-Trichlorophenol	248 [2]	Erratic performance in laboratory
2,4,6-Trichlorophenol	246	Unacceptably low recovery in laboratory

[1] Also tested in VOST methodology.
[2] Boiling temperature at 740 mm Hg.
[3] Boiling temperature at 730 mm Hg.
[4] Boiling temperature at 15 mm Hg.

Table 3. *Results of VOST Field Validation* [1]

Compound	Percent recovery	Percent RSD
Methyl chloride (chloromethane)	937.0	53.8
Ethylidene dichloride (1,1-dichloroethane)	75.7	13.7[2]
Chlorobenzene	88.2	22.0[2]
Vinyl chloride	110.4	27.3[2]
Vinylidene chloride (1,1-dichloroethylene)	88.0	31.3[2]
Chloroform	81.8	14.8[2]
Propylene dichloride (1,2-dichloropropane)	67.2	9.6[2]
Methyl bromide (bromomethane)	53.7	20.2[2]
Ethyl chloride (chloroethane)	50.3	28.7[2]
Methylene chloride	77.7	27.1[2]
Methyl chloroform (1,1,1-trichloroethane)	109.6	43.5[2]
Carbon tetrachloride	106.7	47.2[2]
Ethylene dichloride (1,2-dichloroethane)	76.6	33.0[2]
Trichloroethylene	125.5	15.6[2]
cis-1,3-Dichloropropene	136.8	26.0[2]
trans-1,3-Dichloropropene	134.9	38.1[2]
1,1,2-Trichloroethane	98.0	22.1[2]
Tetrachloroethene	97.7	21.9[2]
Methyl iodide (iodomethane)	72.8	37.6
Allyl chloride (3-chloropropene)	29.9	19.5
Ethylene dichloride (1,2-dibromoethane)	34.9	31.6
Chloroprene	40.1	22.4
Vinyl bromide	60.7	34.3[2]

[1] Chloromethyl methyl ether, bis(chloromethyl) ether, and epichlorohydrin could not be analyzed by the VOST methodology.
[2] Acceptable performance by the analyte in the VOST method, using acceptability criteria of 50-150% recovery, with Percent Relative Standard Deviation of 50 or less.

Table 4. *Results of SemiVOST Field Validation* [1]

Compound	Percent recovery	Percent RSD
bis(Chloromethyl) ether	0.0	–
Epichlorohydrin	6.0	128.1
cis-1,3-Dichloropropene	49.1	37.5
trans-1,3-Dichloropropene	52.0	35.2[2]
1,1,2-Trichloroethane	56.4	37.7[2]
1,2-Dibromoethane	58.9	36.9[2]
Tetrachloroethene	53.2	37.2[2]
Chlorobenzene	63.3	35.1[2]
Bromoform	59.8	37.6[2]
1,1,2,2-Tetrachloroethane	64.1	35.3[2]
Dichloroethyl ether	60.9	34.7[2]
1,4-dichlorobenzene	56.1	35.2[2]
Benzyl chloride	60.1	36.5[2]
Hexachloroethane	74.0	36.9[2]
1,2-Dibromo-3-chloropropane	44.8	36.0
1,2,4-Trichlorobenzene	59.5	35.7[2]
Hexachlorobutadiene	65.4	43.1[2]
Benzotrichloride	60.1	36.5[2]
2-Chloroacetophenone	56.0	40.7[2]
Hexachlorocyclopentadiene	42.3	61.8
2,4,6-Trichlorophenol	49.8	47.0
2,4,5-Trichlorophenol	62.7	43.2[2]
Hexachlorobenzene	44.6	33.9
Pentachlorophenol	42.4	41.5
Pentachloronitrobenzene	43.4	37.9
Chlorobenzilate	40.7	50.6
3,3'-Dichlorobenzidine	4.4	164.9

[1] Chloroacetic acid could not be analyzed by the SemiVOST methodology.
[2] Acceptable performance by the analyte in the SemiVOST method, using acceptability criteria of 50-150% recovery, with Percent Relative Standard Deviation of 50 or less.

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The complete report, entitled "Field Test of a Generic Method for Halogenated Hydrocarbons," (Order No. PB93-212181AS; Cost: $36.50, subject to change) will be available only from:
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