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# Project Summary

# Field Test of a Generic Method for Halogenated Hydrocarbons: SemiVOST Test at an Agricultural Chemical Manufacturing Facility

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**A field evaluation study was conducted for the halogenated semivolatile organic compounds (SVOCs) listed in Title III of the Clean Air Act Amendments (CAAA) of 1990 that may be sampled and analyzed by the SemiVOST method. The performance of the halogenated SVOCs in the test methodology had been evaluated in the laboratory and in two previous field studies. Dynamic spiking techniques were applied in the field, using a sampling strategy statistically designed to meet the requirements of EPA Method 301 for method evaluation. The second field test provided insufficient valid SemiVOST data to allow thorough statistical evaluation of the results because of problems encountered in the preparation of the samples for analysis. A protocol to address SemiVOST sample preparation was written (Draft Method 3542), and this new sample preparation protocol was applied to this field evaluation to improve compound recovery and precision. Using the criteria for acceptable method performance in the EPA *Handbook for Hazardous Waste Incineration*, 25 of 28 analytes tested show acceptable performance in the SemiVOST method. Using the criteria of EPA Method 301 for acceptable performance, 18 of 28 analytes show acceptable performance in the SemiVOST method.**

***This Project Summary was developed by EPA's National Exposure Research 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 evaluation of a stationary source test method for a particular analyte or group of analytes requires that the precision and bias of the method be established experimentally. The SemiVOST (Semivolatile Organic Sampling Train, SW-846 Method 0010 for sampling and Method 8270 for analysis), applicable to all organic compounds with boiling points above 100°C, was used to evaluate the halogenated SVOCs listed in the CAAA. The U.S. Environmental Protection Agency (EPA), under the authority of Title III of the CAAA of 1990, has evaluated selected halogenated SVOCs in the laboratory[1] and in field tests at two different source catagories.[2,3] The second field test, at a high moisture source, did not produce sufficient data to perform a Method 301 statistical test.

Lack of clarity in the existing sample preparation procedure was identified as the cause of the loss of SemiVOST data in the second field test. To clarify the existing sample preparation procedure, SW-846 Draft Method 3542 was written to address sample preparation. As a test of the new procedure and to provide method evaluation data for a second source category, a third method evaluation field test was conducted. To challenge the sample preparation methodology, a test site was selected at which moisture levels were high (approximately 55%). At this test site, a field evaluation of the SemiVOST sam-

pling procedure was performed with dynamic spiking of halogenated SVOCs. Quadruple collocated probes with four similar sampling trains (two spiked trains, two unspiked trains) were used. EPA Method 301 provided statistical guidelines for design of the sampling strategy.

## Procedure

The field evaluation was conducted at a chemical manufacturing facility that operates a multipurpose incinerator to burn aqueous waste, with small amounts of chloroacetic acid, trichloroethylene, and toluene. During a presurvey visit to the test site, grab samples for SemiVOST were taken and analyzed in order to characterize the test matrix and evaluate any potential interferents. No significant levels of any of the compounds of interest were present in the background emissions matrix.

Sampling was performed by withdrawing stack gas from a single port in the stack, through a quad probe, into four similar sampling trains. Two of the trains for each quad sampling run were dynamically spiked and two were unspiked. Sampling methodology followed SW-846 Method 0010, except that

- a quad probe was used instead of the regular single probe;
- a heated glass elbow equipped with a dynamic spiking injection port connected the probe to the heated filter;
- because of the high moisture levels, a single condenser was not sufficient to cool the stack gas entering the XAD-2® module to the temperature of 20°C (68°F) required by Method 0010. A second condenser with its own recirculating pump was added to cool the stack gas sufficiently.

For dynamic spiking, halogenated SVOCs were introduced into the sampling system in methylene chloride solution by syringe injection through the heated glass elbow. Liquid feed rates of the spiking solution were metered by motor-driven syringe pumps.

Reagent and field blanks were collected, with one field blank for every three Quad sampling runs.

Train components were prepared for analysis using the Draft Method 3542 protocol, "Preparation of Modified Method 5 (SW-846 Method 0010) Train Components for Analysis by SW-846 Method 8270." The parts of the SemiVOST train yield three extracts to be analyzed according to the procedures of Method 8270: (1) the particulate matter/filter extract, combined with the extract of the front half rinse, (2) the condensate rinse and condenser rinse fractions, and (3) the combination of the XAD-2® extract with the rinse of the back half of the filter holder and the rinse of tubing connecting the filter holder to the condenser. A critical step in the preparation of SemiVOST train samples, especially with high levels of moisture present during sampling, is the correct transfer of the wet XAD-2® from the sampling module to the Soxhlet extractor, a procedure specifically addressed by Draft Method 3542.

Analyses were performed according to the protocol of Method 8270, with the following exceptions:

- Each final extract volume was 5 mL, rather than 1 mL as specified in Method 8270 for the extraction of water or soil;
- Filters, XAD-2®, and condensate were extracted separately to generate three extracts for analysis;
- Impinger contents were archived.

## Results and Discussion

Overall recoveries for spiked surrogate compounds (spiked in the laboratory immediately prior to preparation of samples) were 92.3%, so no correction for surrogate recoveries was made in the statistical treatment of the data. As anticipated, the most and highest recoveries for the dynamically spiked compounds are obtained from the XAD-2®. Only the least volatile compounds are recovered from the filter and front half rinse, including hexachlorobenzene, pentachlorophenol, pentachloronitrobenzene, chlorobenzilate, and 3,3'-dichlorobenzidine. Possibly because of the high level of moisture in the source, relatively high (≥ 10% of the 500-600 μg spiked) recoveries are obtained from the condensate for epichlorohydrin, dichloroethyl ether, and hexachlorobenzene. Other compounds frequently observed in the condensate extracts include pentachloronitrobenzene, chlorobenzilate, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, hexachlorobenzene, and 2-chloroacetophenone.

The "Protocol for the Field Validation of Emission Concentrations from Stationary Sources" (EPA Method 301) was used to calculate both bias and precision of emission concentration data. Semivolatile halogenated organic compounds that have bias correction factors in the 0.70 to 1.30 window show acceptable performance in the sampling and analytical method. Precision estimates equal to or less than 50% are considered acceptable. According to the criteria of EPA Method 301, the following compounds demonstrated a correction factor and precision within the acceptable range: *trans*-1,2-dichloropropene, 1,1,2-trichloroethane, ethylene dibromide, bromoform, 1,1,2,2-tetrachloroethane, dichloroethyl ether, benzyl chloride, 1,4-dichlorobenzene, 1,2-dibromo-3-chloropropane, hexachloroethane, 1,2,4-trichlorobenzene, hexachlorobutadiene, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, hexachlorobenzene, pentachloronitrobenzene, and chlorobenzilate. The following compounds failed to meet the acceptance criteria of EPA Method 301: epichlorohydrin, bis(chloromethyl) ether, *cis*-1,3-dichloropropene, tetrachloroethylene, chlorobenzene, benzotrichloride, 2-chloroacetophenone, hexachlorocyclopentadiene, pentachlorophenol, and 3,3'-dichlorobenzidine. Chloroacetic acid was not recovered.

Statistical calculations for the SemiVOST compound recoveries were also performed using the methods presented in the EPA *Handbook for QA/QC Procedures for Hazardous Waste Incineration*.[5] To meet the acceptance criteria for the EPA Handbook, the compound recovery must be in the range of 50% to 150%, with a precision of 50% or less. The following compounds met the acceptance criteria of the EPA Handbook: epichlorohydrin, *cis*-1,3-dichloropropene, *trans*-1,3-dichloropropene, 1,1,2-trichloroethane, ethylene dibromide, tetrachloroethylene, chlorobenzene, bromoform, 1,1,2,2-tetrachloroethane, dichloroethyl ether, benzyl chloride, 1,4-dichlorobenzene, 1,2-dibromo-3-chloropropane, hexachloroethane, 1,2,4-trichlorobenzene, hexachlorobutadiene, benzotrichloride, 2-chloroacetophenone, 2,4,6-trichlorophenol, hexachlorocyclopentadiene, 2,4,5-trichlorophenol, hexachlorobenzene, pentachlorophenol, pentachloronitrobenzene, and chlorobenzilate. Bis(chloromethyl) ether and 3,3'-dichlorobenzidine failed to meet acceptance criteria, and chloroacetic acid was not recovered at all. The compound recoveries in this third field test are all higher than the compound recoveries in the first field evaluation study.[2] The difference in recoveries is consistent and is usually in the range of 10% to 20% higher in the second data set from the third field test. However, the most noticeable difference in the two field data sets is the precision: most of the values for the first data set are in the acceptable range (< 50% relative standard deviation), whereas most values for the second field test are 20% relative standard deviation or less. Careful and conscientious application of the procedures

of Draft Method 3542 raised the recoveries and improved the precision of the final data set.

## Conclusions

Based on the field evaluation of the SemiVOST method for halogenated SVOCs listed in Title III of the CAAA, the following conclusions may be drawn:

- Most of the semivolatile halogenated organic compounds selected for testing show successful performance in the SemiVOST methodology: 18 of 28 compounds meet EPA Method 301 test criteria, and 25 of 28 compounds meet EPA Handbook test criteria for successful performance of the SemiVOST methodology.
- The only semivolatile halogenated organic compounds tested that do not meet any criteria for acceptable performance of the test methodology are bis(chloromethyl) ether and 3,3'-dichlorobenzidine.
- Modified sample preparation procedures described in Draft Method 3542 were tested under severe field conditions at a stationary source with a moisture level of 55%. When the procedures of Draft Method 3542 are followed, acceptable SemiVOST method performance can be obtained for the majority of the analytes.
- In a comparison of the results for recovery and precision from a test at a coal-fired power plant (the first SemiVOST field evaluation test) and this test at an agricultural chemical facility, the application of the procedures described in Draft Method 3542 elevated recoveries for most of the analytes by 10% to 20% and improved precision by a factor of four.
- For compounds that show consistent but low recovery, the SemiVOST method could be used as a screening method to establish the presence or absence of these compounds at a test site.

## References


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2. *Field Test of a Generic Method for Halogenated Hydrocarbons.* U.S. Environmental Protection Agency. EPA/600/R-93/101. NTIS PB93-212181.

3. *Field Test of a Generic Method for Halogenated Hydrocarbons: SemiVOST Test at a Chemical Manufacturing Facility.* U.S. Environmental Protection Agency. In Press. 1996.

4. *Protocol for the Field Validation of Emission Concentrations from Stationary Sources,* U.S. Environmental Protection Agency, EPA/450/4-90-015. April 1991. *Federal Register*, Vol. 57, No. 250. Appendix A to Part 63. December 1992.

5. Handbook. *Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration.* EPA/625/6-89/023. January 1990.

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*The complete report, entitled "Field Test of a Generic Method for Halogenated Hydrocarbons: SemiVOST Test at an Agricultural Chemical Manufacturing Facility," (Order No. PB97-162499; Cost: $44.00, subject to change) will be available only from:*

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