



Project Summary

Field Evaluation at an Agricultural Chemical Manufacturing Facility of VOST and SemiVOST Methods for Selected CAAA Organic Compounds

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Laboratory testing and one field evaluation study had previously been performed to assess the performance of nonhalogenated volatile and semivolatile organic analytes from Title III of the Clean Air Act Amendments (CAAA) of 1990 in the Volatile Organic Sampling Train (VOST) and Semivolatile Organic Sampling Train (SemiVOST) methods. For this work assignment, a second field evaluation study was performed at a different source to demonstrate that the methodology is not source-specific. At an agricultural chemical manufacturing facility, an incinerator that burned chemical waste was selected for the second field method evaluation test site. The field test was designed according to the guidelines of the Environmental Protection Agency (EPA) Method 301, using gaseous and liquid dynamic spiking with three spiking schemes. Volatile organic compounds were spiked into two of four quadruple VOST trains as a gaseous spike; semivolatile organic compounds were spiked as a liquid spike into two of four quadruple SemiVOST trains either as a solution of Acid/Neutral compounds or Base/Neutral compounds. These two solutions were spiked in separate sampling runs to avoid compound losses due to known acid/base chemical reactions. A minimum of ten quadruple sampling runs each were performed for VOST, Acid/Neutral SemiVOST and Base/Neu-

tral SemiVOST. Each quadruple run used four collocated sampling probes into four similar sampling trains, with two spiked trains and two unspiked trains. Statistical analysis of the results was performed according to the guidelines of EPA Method 301, as well as EPA's Handbook of Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration. Bias and precision were good for the Neutrals, poor for the Acidic and Basic compounds. The field test and statistical analysis of the results are discussed in this report.

Using the EPA Method 301 criteria for acceptable performance (correction factor between 0.70 and 1.30, with relative standard deviation of 50% or less), the VOST methodology showed acceptable performance in a chemical waste incinerator emissions matrix for the following compounds: benzene, *n*-hexane, 2,2,4-trimethylpentane, and toluene. These VOST results are consistent with the first field test, where the carbon disulfide correction factor was also unacceptable. Using the EPA Method 301 criteria for acceptable performance (correction factor between 0.70 and 1.30, with relative standard deviation of 50% or less), the SemiVOST methodology showed acceptable performance in a chemical waste incinerator for the following compounds: Acids: di-*n*-butyl phthalate, dimethyl phthalate; Bases: carbaryl, N-nitrosodimethylamine, N-

nitrosomorpholine; Neutrals: 1,4-dioxane, 2,4-dinitrotoluene, 4-nitrobiphenyl, acetophenone, biphenyl, chlordane, cumene, DDE, dibenzofuran, ethylbenzene, isophorone, lindane, *m/p*-xylene, methyl isobutyl ketone, naphthalene, nitrobenzene, *o*-xylene, and toluene. In the first field test, the following compounds showed acceptable performance: Acids: 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-*o*-cresol, *o*-cresol, phenol; Bases: 3,3'-dimethylbenzidine, 4,4'-methylene bis (*o*-chloroaniline), 4,4'-methylenedianiline, caprolactam, carbaryl, ethyl carbamate, N,N-diethylaniline, N-nitrosodimethylamine, N-nitrosomorpholine, propoxur, quinoline; Neutrals: 1,4-dioxane, 2,4-dinitrotoluene, 4-nitro-biphenyl, acetophenone, biphenyl, chlordane, cumene, DDE, dibenzofuran, dichlorvos, ethylbenzene, heptachlor, isophorone, lindane, *m/p*-xylene, methyl isobutyl ketone, naphthalene, nitrobenzene, *o*-xylene, parathion, and styrene. In general, far fewer of the polar semivolatile compounds (Acids and Bases) showed acceptable correction factor and precision in the second field test than in the first field test because of the challenging source conditions. Chemical interactions of polar compounds with a high moisture and chemically reactive background source matrix would be expected to be significant.

The methodology is therefore not source-specific. If the methodology were source-specific, no compounds would have met acceptance criteria at the second source. However, some Acids, some Bases, and most Neutrals met acceptance criteria at the second source, so the methodology is not source-specific. However, the performance of individual compounds is influenced by conditions at a particular source.

This Project Summary was developed by National Exposure Research Laboratory's Air Measurements Research Division, 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

A field method evaluation test at an incinerator burning chemical wastes was performed for the VOST and the SemiVOST. The EPA methods were applied exactly as written, with no deviation from the written methodology allowed. The objective of the field test was to establish the bias and precision of the VOST and

SemiVOST specific analytes using Method 301¹ criteria. Method 301, a method validation protocol, served as the basis for the design and execution of this method validation study. The specific analytes were pesticides and nonhalogenated organic compounds listed in Title III of the CAAA of 1990, which had previously been tested at a coal-fired power plant. The chemical waste incinerator test site was chosen to demonstrate that the test methodology is not source-specific.

The VOST methodology (sampling and analytical) consists of a combination of the following EPA methods:

- For sampling, SW-846 Method 0030²
Volatile Organic Sampling Train
- For analysis, SW-846 Method 5041³
Protocol for Analysis of Sorbent Cartridges from Volatile Organic Sampling Train: Wide-bore Capillary Column Technique.

Method 0030 describes the collection of volatile principal organic hazardous constituents (POHCs) from the stack gas effluents of hazardous waste incinerators. The method defines volatile POHCs as having boiling points less than 100°C (212°F). Method 0030 states that many compounds that boil above 100°C (212°F) may also be efficiently collected and analyzed.

The SemiVOST methodology consists of a combination of the following EPA methods:

- For sampling, SW-846 Method 0010⁴:
Modified Method 5 Sampling Train
- For sample preparation, SW-846 Proposed Method 3542⁵:
Extraction of Semivolatile Analytes Collected Using Modified Method 5 (Method 0010) Sampling Train
- For analysis, SW-846 Method 8270⁶:
Gas Chromatography/Mass Spectrometry for Semivolatile Organics: Capillary Column Technique

The SemiVOST methodology defines semivolatile organic compounds as compounds with boiling points above 100°C (212°F).

To be a candidate for the SemiVOST or VOST methodologies, an analyte must be able to be analyzed by gas chromatography/mass spectrometry (GC/MS). Laboratory studies⁷ identified volatile and semivolatile organic compounds and pesticides listed in Title III of the CAAA of 1990 that could be analyzed by GC/MS. The candidate analytes identified for the VOST methodology were benzene, carbon disulfide, *n*-hexane, 2,2,4-trimethylpen-

tane, and toluene. Since the boiling point of toluene is 111°C, toluene was also tested using SemiVOST. After laboratory confirmation of the composition and concentration of certified cylinders, the cylinders were used to perform dynamic spiking in the field method evaluation study. The candidate analytes identified for the SemiVOST methodology included 10 Acids, 20 Bases, and 24 Neutral semivolatile organic compounds from Title III of the CAAA. These analytes were dynamically spiked in the field as an Acid/Neutral solution or as a Base/Neutral solution.

EPA Method 301 guidelines were followed for experimental design, number of samples collected, and statistical evaluation. A methodology (sampling and analytical) is determined to be valid when it meets the acceptance criteria for bias and precision outlined in Method 301. Method 301 provides guidance on the experimental design, the number of samples to be collected, and the calculations to determine bias and precision. The bias and precision of an analyte must fall within a specified range (correction factor between 0.70 and 1.30, with relative standard deviation of 50% or less). Method 301 requires either testing the candidate method side-by-side with a validated method, or introducing a known amount of the target analyte(s) into the sampling train without interrupting normal sampling procedures. For this field evaluation, the analytes were dynamically spiked in the field because comparable validated reference methods do not exist. Dynamic spiking is the accepted means of introducing a known analyte. During dynamic spiking, analytes are introduced into the sampling train, as close as possible to the end of the probe, for the duration of the sampling run.

EPA Method 301 provides guidelines for design of the sampling scheme to ensure that a sufficient number of valid samples are collected to statistically evaluate precision and bias. For dynamic spiking in the field, four similar sampling trains are operated from four collocated probes. Two of the trains are dynamically spiked; two trains are unspiked. Method 301 requires at least six complete sampling runs (twelve paired spiked trains, twelve paired unspiked trains) in order to statistically assess the data. For this field test, eleven complete quad VOST sampling runs were made; eight complete Acid/Neutral sampling runs were made; and eleven complete Base/Neutral sampling runs were made. Data collected for each sampling run were statistically analyzed according to Method 301 and the QA/QC Handbook for Hazardous Waste Incineration.⁸

Experimental Approach

A chemical waste incinerator was selected as the test site for this field method evaluation study. A site presurvey established that no high levels of the compounds of interest were present in the background, and that the moisture level of source was high (approximately 55%). The dynamic spiking level projected for the VOST methodology was 250 ng per analyte; for the SemiVOST methodology, 500 µg per analyte.

To collect samples, stack gas was drawn from a single port in the stack through a quad probe. The stack gas was then directed to four similar VOST sampling trains or to four similar SemiVOST sampling trains. The quad probe contains four similar heated sampling 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. The true concentration of the components of the stack gas was of no interest to this program, so traversing the stack was not required. For both VOST and SemiVOST methodologies, two of the quadruple sampling trains were spiked and two were unspiked, according to the guidelines of EPA Method 301.

VOST dynamic spiking was performed by introduction of the compounds of interest from a certified gas cylinder at a flow rate of approximately 3 mL/min for the duration of the 20-min VOST sampling run. Method 0030 sampling procedures were followed. SemiVOST dynamic spiking was performed by introduction of the compounds of interest from a methylene chloride solution (either Acid/Neutrals or Base/Neutrals) through a heated glass elbow equipped with a spiking injection port positioned between the end of the probe and prior to the heated filter. Approximately 20 mL of the solution was introduced into the spiking injection port using a syringe pump, which operated at a rate appropriate for maintaining a hanging drop of the spiking solution throughout the one-hour sampling run. Method 0010 sampling procedures were followed.

VOST field samples were analyzed according to the analytical procedures described in Method 5041. The VOST tubes were analyzed individually, with the back tube first, in order to determine the distribution of the analytes on the VOST tubes and to demonstrate that breakthrough had not occurred. SemiVOST field samples were prepared according to the procedures of Proposed Method 3542 and analyzed according to the procedures of EPA Method 8270. Three samples were analyzed for each SemiVOST train: the filter/

front half rinse, the XAD-2® and condenser rinse, and the condensate/condensate rinse. For both VOST and SemiVOST, field blanks, reagent blanks, method blanks, and method spikes were prepared and analyzed.

Results and Discussion

The SemiVOST method is most effective for the Neutral compounds at the source tested. Because of the high moisture levels of the source, the polar and water-soluble Acidic and Basic compounds were washed through the sorbent into the condensate of the sampling train, where the pH-adjusted extraction required by the SemiVOST method did not result in quantitative recoveries.

The results of the statistical calculations are summarized below:

- Four of five VOST analytes met EPA Method 301 acceptance criteria for bias and precision;
- Nineteen of 24 Neutral compounds met EPA Method 301 acceptance criteria for bias and precision;
- Two of 10 Acidic compounds met EPA Method 301 acceptance criteria for bias and precision;
- Three of 20 Basic compounds met EPA Method 301 acceptance criteria for bias and precision.

Comparable results are obtained when the statistical calculations are performed according to the guidelines of the EPA QA/QC Handbook.

During the dynamic spiking experiments for the SemiVOST in the field, the Base/Neutral spiking solution changed color from yellow to a dark green approximately one-half hour after the solution was poured into the syringe for spiking. Three aliquots of the spiking solution were analyzed in the laboratory: an aliquot of the solution that was not sent to the field, an aliquot of unused solution that had been taken to the field but not opened, and remaining spiking solution from an aliquot of the solution that had changed color. The color change was due to photochemical reaction of benzidine, 4,4'-methylene-dianiline, 3,3'-dimethylbenzidine, and 3,3'-dimethoxybenzidine, photoreactive dyes. The natural ultraviolet light in the field was sufficient to cause the photoreactive compounds to react and change the color of the solution. The aliquot of the solution remaining in the laboratory did not change color under the artificial ultraviolet light in the laboratory.

Upon analysis of both VOST and SemiVOST, the presence of molecular iodine (I₂) in the background matrix was established by a major I₂ chromatographic

peak. The reactivity of the I₂ was demonstrated by the disappearance of acenaphthene-d₁₀ (a Method 8270 internal standard added immediately before analysis) from several of the XAD-2® extracts and by the appearance of iodinated compounds in the chromatograms. The XAD-2® extracts were quantified by using an alternative internal standard (Method 8270 uses six internal standards so an alternative is available). However, the chemical reactivity of the background source matrix did affect compound recoveries, especially for the Acids and Bases. Reaction could occur in the sampling train, on the sorbent or in the condensate, during the extraction/concentration process, or in the heated injection port of the gas chromatograph.

When the analyte distribution of the VOST samples was determined, all of the VOST analytes showed >90% recovery of spiked analyte from the front (Tenax®) tube. When the analyte distribution of the SemiVOST samples was determined, the Neutral compounds, as expected, showed primary recovery from the XAD-2® sorbent. The major exception was 1,4-dioxane, a polar water-soluble Neutral compound recovered mostly from the condensate. Polar water-soluble compounds washed through the sorbent. The Acid and Basic analytes showed primary recovery from the condensate, with the least volatile analytes recovered from the filter. Low recoveries for the Acidic and Basic compounds can be attributed to the high moisture level of the source: the compounds washed through the XAD-2® and into the condensate, where they were extracted with poor recoveries. Laboratory experience has demonstrated that polar water-soluble analytes present in an aqueous solution (the condensate) are recovered poorly (30-60% recovery) using the pH-adjusted extraction technique specified by the SemiVOST method.

Three factors in this field method evaluation study acted to reduce the recoveries of polar semivolatile analytes from the SemiVOST train:

- A high level of moisture in the source washed the polar (Acidic and Basic) analytes through the SemiVOST train to be retained in the condensate. Recovery of polar water-soluble semivolatile organic analytes from aqueous media tends to be poor under standard conditions of pH-adjusted extraction.
- The high level of molecular I₂ present in the source reacted more readily with functionalized molecules (Acids and Bases) than with Neutral com-

pounds. Chemical reaction with the background stationary source matrix reduced recoveries of Acidic and Basic compounds.

- Photochemical reactivity reduced the recovery of photochemically active compounds such as dyes or dye intermediates.

Conclusions and Recommendations

The following conclusions may be drawn from the results of the second VOST and SemiVOST method evaluation field test for selected Clean Air Act analytes:

- The method is not source-specific. If the method were source-specific, the methodology would succeed or fail completely, depending upon the source. There would be only one source or only one type of source where any compounds meet acceptance criteria. At all other sources or source types, the methods would fail completely and no compounds would meet acceptance criteria. Since both VOST/SemiVOST field tests demonstrate some compounds that perform acceptably at both source types, the method is not specific to the source. However, factors characteristic of a specific source affect the performance of specific compounds, and an overall evaluation of the performance of the methodology at the two sources says that both the VOST and SemiVOST methods perform better and more consistently with Neutral (i.e., non-polar) compounds.
- Using the EPA Method 301 criteria for acceptable performance (correction factor between 0.70 and 1.30, with relative standard deviation of 50% or less), the VOST methodology showed acceptable performance in a chemical waste incinerator emissions matrix for the following compounds: benzene, *n*-hexane, 2,2,4-trimethylpentane, and toluene.
- Using the EPA Method 301 criteria for acceptable performance (correction factor between 0.70 and 1.30, with relative standard deviation of 50% or less), the SemiVOST methodology showed acceptable performance in a chemical waste incinerator for the following compounds. Acids: di-*n*-butyl phthalate, dimethyl phthalate; Bases: carbaryl, N-nitrosodimethylamine, N-nitrosomorpholine; Neutrals: 1,4-dioxane, 2,4-dinitrotoluene, 4-nitrobiphenyl, acetophenone, biphenyl, chlordane, cumene, DDE, dibenzofuran, ethylbenzene, isophorone, lindane, *m/p*-xylene,

methyl isobutyl ketone, naphthalene, nitrobenzene, *o*-xylene, and toluene.

- The following compounds did not meet Method 301 acceptance criteria: Acids: 2,4-dinitrophenol, 4-nitrophenol, bis(2-ethylhexyl) phthalate, 4,6-dinitro-*o*-cresol, *m/p*-cresol, *o*-cresol, phenol; Bases: 2-acetylaminofluorene, 3,3'-dimethoxybenzidine, 3,3'-dimethylbenzidine, 4,4'-methylene bis (*o*-chloroaniline), 4,4'-methylene dianiline, 4-aminobiphenyl, aniline, benzidine, caprolactam, dimethylaminoazobenzene, ethyl carbamate, N,N-diethylaniline, N,N-dimethylaniline, *o*-anisidine, *o*-toluidine, propoxur; Neutrals: dichlorvos, heptachlor, methoxychlor, parathion, styrene.
- The chemical composition of the background source matrix is a significant factor in the success or failure of the sampling and analytical methodology.
- In a reactive background emissions matrix, reactive organic compounds (such as acids and bases) show the effects of interaction with the background matrix far more strongly than less reactive compounds such as hydrocarbons.
- Interaction of the spiking solution with natural ultraviolet light can be a significant factor in determining the recoveries of spiked compounds. The Base/Neutral spiking solution contained photoreactive dyes (members of the benzidine family), which reacted with the natural ultraviolet radiation at the test site as the Base/Neutral solution was being poured into the syringe for spiking.
- Application of the SemiVOST to polar reactive semivolatile compounds produces widely variable results at different sources, depending upon the reactivity of the background matrix. Laboratory tests will demonstrate that the methodology can in general be applied to a particular analyte and can predict certain failure of the methodology under field conditions. That is, if an analyte cannot be quantitatively extracted from the XAD-2® and analyzed reproducibly, failure under field conditions is highly probable. However, successful performance under laboratory conditions does not guarantee that field testing at a given source will be successful. The characteristics of the particular source must be considered.
- When a source such as the chemical waste incinerator has a high moisture

content, it is essential to monitor the desorption temperature of the VOST tubes to ensure that the tubes become sufficiently hot for quantitative desorption of the collected analytes. The high level of moisture collected on the tubes during sampling (up to several mL of collected water) slowed the heating of the tubes being desorbed for analysis. If the temperature does not reach the desorption temperature specified by Method 5041 for the period of time required by the method, analyte recoveries will not be quantitative.

On the basis of the results of this field method evaluation study, the following recommendations can be made:

- When polar water-soluble semivolatile organic compounds are sampled by the SemiVOST at a source with high moisture, the polar compounds tend to wash through the sampling train to be collected in the condensate. When polar water-soluble semivolatile compounds are dissolved in the condensate, these compounds are recovered poorly by the pH-adjusted extraction techniques required by the SemiVOST. Two possible solutions to this problem should be explored:
 - Investigate the use of sorbents which retain polar water-soluble semivolatile organic compounds better than XAD-2® does to prevent the compounds from washing through the SemiVOST train to the condensate.
 - Because the semivolatile organic compounds dissolved in the condensate are typically present at low concentrations in a large volume of condensate, direct analysis of the condensate (direct aqueous injection into GC/MS or High Performance Liquid Chromatograph [HPLC]) will probably not be sensitive enough. Some technique such as solid phase extraction for concentrating the organic compounds for analysis will be needed in order to perform successful analysis within the detection limits of the instrumentation.
- Faced with a candidate analyte for either VOST or SemiVOST for which no method validation information is available, laboratory experimentation can aid in establishing the validity of assigning the analyte to a particular methodology:
 - Determine whether the compound can be analyzed by either liquid in-

jection (GC/MS) or purge and trap GC/MS. This information is frequently available from the literature. If the compound cannot be analyzed by GC/MS, neither VOST nor SemiVOST can be applied.

- Determine whether the compound can be recovered quantitatively from the sorbent. If the compound cannot survive thermal desorption or extraction/concentration, neither VOST nor SemiVOST can be applied. If the compound is recovered poorly or erratically, an informed decision regarding the applicability of the methods as screening methods can be made.
- Determine whether the compound can be recovered quantitatively from a dynamically-spiked sampling train. If the compound cannot be recovered after passage through a heated sampling train, the sampling methodology will not collect the compound quantitatively and is not appropriate. Use of some basic laboratory experimentation can prevent the erroneous assumption that because an analyte was not observed when VOST or SemiVOST was applied in the field, the analyte is not present at the test site. If neither method is appropriate for the analyte, the organic compound could not possibly be observed, even if present.

Careful consideration of the chemical properties of candidate analytes is essential in predicting success or failure in the application of VOST or SemiVOST sampling and analytical methodology.

For compounds with marginal or unacceptable performance in the VOST or SemiVOST methods, a detailed study of the chemical properties of these compounds may provide guidance for the modification of existing methods to optimize the methodology for these compounds.

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The complete report, entitled "Field Evaluation at an Agricultural Chemical Manufacturing Facility of VOST and SemiVOST Methods for Selected CAAA Organic Compounds," (Order No. PB97-174585; Cost : \$85.00, subject to change) will be available only from:

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