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Project Summary

Laboratory and Field Evaluation of the Semi-VOST Method

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An initial laboratory and field evaluation has been completed which assessed the performance of the Semi-Volatile Organic Sampling Train Method (Semi-VOST) for measuring concentrations of principal organic hazardous constituents (POHCs) with boiling points greater than 100°C that are emitted from hazardous waste incinerators. A draft formulation of the methodology was tested through an experimental laboratory program to evaluate method performance characteristics. The program consisted of: (1) determination of minimum compound detection limits; (2) simulation of a flue gas stream to determine the impacts of water vapor, SO_2, NO_x, and HCl on sampling; and (3) determination of precision and bias for the sample preparation and analytical elements of the method. Results of the simulation study are reported for 12 test compounds (POHCs) representing a range of physical and chemical properties which could affect sample train collection and recovery performance. Three of the test compounds (toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane) were selected for further investigation to evaluate method precision and bias under field conditions through the use of four simultaneously-operating Semi-VOST trains. Cylinder gas standards of each compound were blended and dynamically spiked into paired sample trains for determining method bias. Estimates of bias are presented for toluene and 1,1,2,2-tetrachloroethane. Method precision for chlorobenzene is calculated from unspiked sample train results which also included distributive volume experiments to determine sample train breakthrough of POHCs. Project results are presented in Volume I along with recommendations on elements of the method requiring further research. Volume II includes appendices giving detailed descriptions of the method formulation, laboratory and field studies, along with quality assurance data.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in two separate volumes of the same title (see Project Report ordering information at back).

Introduction

The Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act of 1976 (RCRA), re-.quires that the Environmental Protection Agency establish a national regulatory program to ensure that hazardous wastes are managed in a manner which does not endanger human health or the environment. The statute requires EPA to promulgate performance standards for hazardous waste management. Included in the promulgated regulations are provisions for waste disposal by incineration and requirements that hazardous waste incinerators be so operated that the principal organic hazardous constituents (POHCs) are destroyed or removed with a minimum ef-

ficiency of 99.99 percent. To determine destruction and removal efficiency (DRE), EPA has designated the Semi-Volatile Organic Sampling Train Method (Semi-VOST) as the method for measuring concentrations of POHCs with boiling points greater than 100°C that are emitted from hazardous waste incinerators.

The Quality Assurance Division of the Environmental Monitoring Systems Laboratory at Research Triangle Park, North Carolina, has a program to evaluate and standardize EPA source test methods. While participating in this program, Radian Corporation has undertaken an evaluation of the Semi-VOST Method, which is the subject of the full report. The following were the objectives of the program:

- assemble and refine a draft formulation of the Semi-VOST sampling and analysis methodology;
- select a series of Appendix VIII test compounds for method evaluation based on the characteristics of incinerability, water solubility, and adsorption strength on XAD-2® resin;
- design and conduct an experimental laboratory program to evaluate method performance characteristics in terms of minimum compound detection limits, sampling flow rate and volume, and the formation of artifact compounds during the sampling of a simulated flue gas stream containing water vapor, SO_2, NO_x, and HCl;
- determine precision and bias attributable to each of the sample preparation steps and the final GC/MS analysis step;
- design, construct, and evaluate the performance of a dynamic spiking system for determining method bias using experimental field data; and
- carry out a field test study at a hazardous waste incineration facility to evaluate method precision and bias, and the potential of POHC sample train breakthrough.

Procedure

The initial Semi-VOST method formulation contained no analytical protocols but included several sections that were discretionary or that required clarification. Therefore, prior to laboratory experimentation, a refinement in the formulation was developed by surveying members of the technical community who had experience in the use of the Semi-VOST method. Based on the survey responses, a working copy of the method was drafted to encompass both sampling and analysis procedures.

In the application of Semi-VOST, gaseous and particulate components are isokinetically withdrawn from an emission source and collected in a multicomponent sampling train. Key elements of the train include a high-efficiency particulate filter and a packed bed of a porous polymeric adsorbent resin (XAD-2®). The filter is used to separate stack gas particles from gaseous substances, which are then adsorbed on XAD-2®. As a collection sorbent, XAD-2®, a polystyrene-divinylbenzene copolymer, has the advantage of high surface area (300 m^2/g) with an average pore volume of 90 A, which permits collection of semi-volatile compounds. Following sample collection, the train components are extracted with solvent, concentrated, and identified/quantified using high resolution gas chromatography coupled with low resolution mass spectrometry.

After return of the samples to the laboratory, all fractions are spiked with surrogate standards prior to extraction, concentration, and analysis. The use of surrogates provides a measure of the efficiency of the sample preparation procedures. In the sample analyses, an examination of surrogate recovery is used to qualify and possibly correct the analytical results. For example, poor or variable surrogate recovery would suggest difficulties with sample preparation/analysis as opposed to incinerator operation. The spiking compounds should be the stable, isotopically-labeled analogs of the compounds of interest or a compound that would exhibit properties similar to those of the compounds of interest, be easily chromatographed, and not interfere with the analysis. Potential surrogate spiking compounds include deuterated naphthalene, chrysene, phenol, nitrobenzene, chlorobenzene, toluene, and carbon 13-labeled pentachlorophenol.

The condensate knockout trap solution is spiked with the surrogates, transferred to a separatory funnel, acidified, and extracted with methylene chloride. The aqueous phase is made alkaline and re-extracted with methylene chloride. This procedure is used to optimize the recovery of POHCs with different functional groups. The condensate may contain compounds that show great water solubility and low organic solvent solubility. The methylene chloride solutions are combined in a Kuderna-Danish (K-D) evaporator/concentrator and reduced in volume usually to less than 10 ml, and a standard is added for quantitation by gas chromatography coupled with mass spectrometry (GC/MS). Impinger contents are extracted with methylene chloride under both acidic and basic conditions and then concentrated. The methylene chloride/methanol rinses of the probe and filter housing are prepared by spiking with surrogate standards and adding sufficient water to a separatory funnel to force methylene chloride to become immiscible with water and form two phases. The XAD-2® resin is spiked with surrogate standards and transferred with the filter to an all-glass Soxhlet extraction thimble. The module is rinsed with methylene chloride, the solution is added to the Soxhlet, and extraction is conducted for 16 hours.

Analysis is performed by GC/MS using fused silica capillary GC columns. The mass spectrometer is operated in a full (40 to 450 daltons) scanning mode. For most purposes, electron ionization (EI) spectra are collected, since a majority of the potential POHCs give reasonable EI spectra. Also EI spectra are compatible with the NBS Library of Mass Spectra and other reference data that aid in identification.

For quantitation by GC/MS, each sample fraction is spiked with a known amount of an internal standard prior to analysis. The response ratio of the internal standard to each compound of interest in the sample is then compared to a similar ratio established with a calibration curve.

Results and Discussion

Laboratory Evaluation

A laboratory program consisting of three stages was designed and implemented to provide an initial estimate of method precision and bias and to investigate method interferences. The initial portion of the laboratory program involved the selection of compounds to test the limits of the method and for the determination of minimum detection limits (MDL) of the GC/MS. Compound selection was followed by a series of simulated flue gas generation experiments to identify external effects of the sampling environment that would affect the analytical results and to evaluate the overall method precision and bias. Finally, a series of experiments was con-

ducted to determine specifically the precision and bias of the laboratory preparation and analytical portions of the method.

Results from the laboratory studies indicated the following:

- Method precision and bias are compound-specific and cannot be generalized for all classes of chemicals. Laboratory experiments demonstrated that method precision and bias are related to the distribution and recovery of a particular POHC throughout the components of the sampling train. Sample distribution and recovery of a POHC is related to its boiling point, water solubility, and chemical function.
- Compounds adsorbed on XAD-2® resin exhibited better precision and recovery than compounds collected in the condensate and impingers.
- Test compound recoveries were not affected by either simulated flue gas variations in compound concentration by HCl, SO_2, or water vapor, or by variations in sample flow rate and volume.
- Increases in generated flue gas NO_x levels were associated with decreases in the recoveries of 1,4-dioxane, urethane, and phenol.
- For toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane, laboratory experiments showed that the precision of the resin extraction and concentration steps was not significantly different from the precision of the concentration step alone. However, the precision of the separatory funnel extraction and concentration steps was significantly poorer than either the precision of the concentration step alone or the resin extraction and concentration step.
- For chlorobenzene, toluene, and 1,1,2,2-tetrachloroethane, no significant losses were detected when the K-D concentrate was reduced from 5 mL to 2.5 ml using an inert gas for blowdown.

Field Evaluation

Following completion of the laboratory studies, a field test program was conducted to evaluate method performance at an operational hazardous waste incineration facility. A test plan was prepared which included the collection of matrixed sequence of samples for the evaluation of method precision, bias, and POHC sample train breakthrough.

Results from the field evaluation study included the following:

- A preliminary estimate of method bias of -13 percent for toluene was calculated from field test data obtained using the dynamic spiking system.
  - The 87 percent recovery of toluene from the field test data compares favorably with the mean recovery of 91 percent measured from the laboratory baseline performance test of the dynamic spiking apparatus.
  - The identification of toluene in the methylene chloride recovery solvent returned from the field necessitates analysis of additional sample fractions from the test to confirm the toluene bias estimate.
- A preliminary estimate of method bias of -16 percent was calculated for 1,1,2,2-tetrachloroethane.
  - The 84 percent recovery of 1,1,2,2-tetrachloroethane is in agreement with the 85 percent value from the baseline dynamic spiking test.
- The dynamic spiking concept was demonstrated as a viable approach for determining method bias in field evaluation studies.
- A method precision of 19.9 percent for chlorobenzene was calculated from a field test data set consisting of a series of paired, unspiked Semi-VOST trains sampling the emissions from a hazardous waste incinerator.
- No sample train breakthrough of chlorobenzene could be determined from the field test distributive volume experiments. Therefore, the retention volume for chlorobenzene was not exceeded and demonstrates the adequacy of this aspect of the current method formulation.

Recommendations

Based on the results of the method evaluation studies presented in this report, the following recommendations are made for further investigation:

- Method bias and precision have been shown to be compound specific. An investigation should be conducted to determine if Appendix VIII compounds could be aggregated according to properties such as water solubility, chemical similarity, or adsorption strength (retention volume) on XAD-2 to provide estimates of method precision and bias for compound categories.
- Pyridine, pentachlorophenol, and resorcinol exhibited poor recoveries during the flue gas generator experiments. Preliminary studies have indicated that compound losses may be attributed to chromatographic properties, poor solvent extraction, or compound reaction in the aqueous components of the sampling train which become acidified during sample collection. Also, the low recovery of pentachlorophenol may have been due to loss within the flue gas generator. Further laboratory studies are warranted to clarify these observations and to develop simplified screening procedures to demonstrate the applicability of the method's sample preparation (extraction) and analysis (GC/MS conditions) steps to other Appendix VIII compounds or classes of compounds.
- The recovery losses of urethane, phenol, and 1,4-dioxane associated with NO_x flue gas generator levels should be studied using solutions to simulate condensate and impinger contents for evaluating compound reactivity with NO_x. Findings could then be used to plan a second field evaluation of the method which includes POHC artifact formation study objectives.
- The particulate filters from the Semi-Vost samples collected during the field test program were stored and solvent extracted for later analysis. The extracts should be analyzed for semi-volatile compounds in preparation for future studies to evaluate POHC-particulate matter interactions during sample collection.
- The preliminary estimates of method bias for toluene and 1,1,2,2-tetrachloroethane should be finalized by analyzing the remaining sample fractions from the field test. The presence of toluene in the methylene chloride rinse solvent should also be accounted for.
- The dynamic spiking system for determining method bias should be redesigned to improve its reliability in the field. The use of a stable, single gas mixture containing multiple components would simplify op-

eration and delivery of a dynamic spike to two simultaneously-operating Semi-Vost trains. Stable, isotopically-labeled POHCs would be desireable spiking components as it is unlikely that they would be present in the flue gas.

- The existing field study GC/MS analytical data set for unspiked sampling runs should be re-examined to determine if additional flue gas organic compounds could be used to evaluate sample train breakthrough.
- Future field method evaluation studies should include the addition of spiked waste feed materials to permit measurement of method precision and sample train breakthrough for several pre-determined compounds contained in the spiked waste.

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The complete report consists of two volumes, entitled "Laboratory and Field Evaluation of the Semi-VOST Method:"
"Volume I," (Order No. PB 86-123 551/AS; Cost: $11.95)
"Volume II. Appendices," (Order No. PB 86-123 569/AS; Cost: $22.95)
The above reports will be available only from: (cost subject to change)
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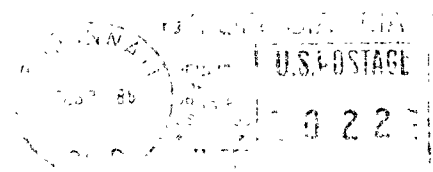*U.S. Environmental Protection Agency*
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