

# Method Evaluation Study: The Application of SemiVOST to the Nonhalogenated Semivolatile Organic Compounds from the Clean Air Act Amendments

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A laboratory study and three field studies were performed to evaluate the application of the SemiVOST (EPA sampling Method 0010, EPA sample preparation Draft Method 3542, and EPA analytical Method 8270) to the semivolatile halogenated organic compounds (approximately 80 compounds) listed in the Clean Air Act Amendments (CAAA) of 1990. In these initial studies, PCBs, dioxins, and pesticides were excluded. Subsequently, a laboratory study was performed to assess the feasibility of the application of the SemiVOST methodology to the semivolatile nonhalogenated organic compounds listed in the CAAA (approximately 70 compounds). Several of the semivolatile organic compounds were eliminated from consideration as SemiVOST analytes because they could not be analyzed successfully by gas chromatography/mass spectrometry (GC/MS), reacted with other compounds in solution, or were insoluble in methylene chloride at the levels required to perform dynamic spiking in the field. The remaining CAAA semivolatile organic analytes were grouped as acid/neutrals and base/neutrals and evaluated in the field using the guidance of EPA Method 301 for experimental design and statistical evaluation of the data. Quadruple SemiVOST trains were run in the field, with dynamic spiking of the semivolatile analytes from a methylene chloride solution of either acid/neutral or base/neutral compounds into two of the sampling trains. The bias and precision of the overall SemiVOST methodology (sampling, sample preparation, and analysis) applied to each of the semivolatile organic analytes were evaluated.

## INTRODUCTION

A wide range of semivolatile organic analytes is encompassed in the SemiVOST sampling and analytical methodology, which consists of the following components:

- Sampling Method: SW-846 Method 0010<sup>1</sup>;
- Sample Preparation Method: SW-846 Proposed Method 3542<sup>2</sup>; and
- Analytical Method: SW-846 Method 8270<sup>1</sup> (since the analytical procedure rather than the analyte list will be used from Method 8270, the exact designation (i.e., 8270, 8270A, or 8270B) is irrelevant).

The SemiVOST is broadest in scope and applicability to semivolatile organic compounds, but the performance of the methodology for a specific analyte is not known until the performance is established experimentally. The parameters of concern are bias (accuracy) and precision (variability), since most criteria for acceptable performance of a method are based on the bias and precision demonstrated for the entire method (sampling through analysis) under field conditions.

Method evaluation studies for the halogenated semivolatile organic CAAA analytes have been performed at three field sites in two source categories.<sup>3,4</sup> The comparable studies have been initiated for the nonhalogenated CAAA analytes. A preliminary laboratory study<sup>5</sup> was performed to evaluate the ability of the nonhalogenated

semivolatile organic compounds to be analyzed successfully, their stability and compatibility in methylene chloride solution, and their ability to survive dynamic spiking into a SemiVOST train.

Because the following compounds exhibited reactivities, insolubility in methylene chloride, and chemical interactions, they were excluded from further study in this program: hydroquinone, 1,4-phenylenediamine, captan, 1,3-propane sultone, ethylene thiourea, hexamethylene-1,6-diisocyanate, catechol, 2,4-toluenediamine, and maleic anhydride. The laboratory study indicated that the optimum grouping of analytes in order to avoid chemical interactions in the spiking solutions was acid and neutral compounds in one solution, and basic and neutral compounds in a second solution. The selection of acid, base and neutral groupings was somewhat subjective. The phenols, cresols and phthalates were placed in the acidic group. The nitrogen-containing (excluding nitro-compounds and quinone (mistaken for quinoline) made up the basic group. The neutral group included hydrocarbons, oxygenated compounds, the chlorinated pesticides and quinoline.

## **EXPERIMENTAL APPROACH**

The field test site selected was a coal-fired power plant owned and operated by a public utility. A presurvey showed that none of the designated semivolatile organic analytes was present in the gaseous emissions at a level above the method detection limits. A dynamic spiking level of 500  $\mu\text{g}$  was therefore planned. With 500  $\mu\text{g}$  spiked into the train, virtually complete retention of the analyte on XAD-2<sup>®</sup>, and quantitative recovery should be observed. This value is at approximately the middle of a standard Method 8270 calibration curve, and should be readily analyzed even if only 50% recovery is obtained.

The Method 0010 sampling train was modified to allow simultaneous collection of samples in quadruplicate as per EPA Method 301<sup>6</sup>, with liquid dynamic spiking of a solution of semivolatile organic compounds occurring in the sampling train between the probe and heated filter. A quad probe, consisting of four heated borosilicate glass probe liners mounted in one probe assembly, was used with four similar SemiVOST trains. Each of the probe liners and spiking injection ports was individually heated and the temperatures were maintained at  $130 \pm 15^\circ\text{C}$ . Flue gas temperatures and velocity measurements were monitored and the sample was collected as closely to isokinetic conditions as possible. Because accurate determination of the background levels of organic compounds in the gaseous emissions was of no interest to this program, the stack was not traversed.

A heated glass elbow equipped with a spiking injection port was used to connect the probes of the spiked trains to the heated filter. The mass of solution delivered was used in the calculation of theoretical amount spiked for the purpose of determining recovery. The liquid spike was maintained as a droplet at the tip of the glass-lined stainless steel tubing so that the liquid spike could volatilize as it entered the gas stream and become a gaseous spike at that point. The spiking liquid was never allowed to drip into the sampling line.

Clean sampling train components were assembled in the on-site mobile laboratory, with final assembly of the trains after they were moved to the actual sampling location. Once they were assembled, the sampling trains were leak-checked. Upon completion of the pre-test leak checks, heaters for spiking glassware, filter holders, and probes were turned on. Sampling at a rate of approximately 0.50  $\text{ft}^3/\text{min}$  was initiated, and the syringe pump for dynamic spiking was started after the gas flow had been established. At the end of the one-hour sampling period, the syringe pumps were turned off and then the meter boxes were turned off. The sampling trains were then leak-checked in the same manner used to perform the pre-test leak checks. Sampling trains were disassembled into three sections: the spiking glassware/filter holder, XAD-2<sup>®</sup> module, and the impinger train. Since the spiking point was after the probe, the probes could remain in place for the next quad sampling run.

## **RESULTS AND DISCUSSION**

Two sets of ten dynamic spiking SemiVOST sampling runs were performed in the field, using an Acid/Neutral spiking solution to generate one set of samples and a Base/Neutral spiking solution for the second set. Results for the nonhalogenated semivolatile compounds are shown in Table 1, using Method 301 statistical calculations

and EPA QA/QC Handbook<sup>7</sup> statistical calculations. The two modes of statistical calculations generally produce comparable results when acceptance criteria are considered for a given analyte. Although there are more factors to be considered in the overall Method 301 statistical calculation, in general analytes with a recovery of 70-130% and precision  $\leq 50\%$  relative standard deviation will meet Method 301 acceptance criteria. Method 301 also requires a calculation of a correction factor, this factor must be between 0.70 and 1.30. The EPA QA/QC Handbook acceptance criteria are slightly broader, with recovery of 50-150% and precision  $\leq 50\%$  relative standard deviation required to meet acceptance criteria.

For all analytes and both methods tested, Table 1 summarizes the experimental results for the field testing at a coal-fired power plant. Of the 55 semivolatile organic compounds tested by the SemiVOST method, 36 met Method 301 acceptance criteria and 45 met EPA QA/QC Handbook acceptance criteria. Analyte distribution through the SemiVOST train generally follows a predicted path, with the most polar and water-soluble analytes showing a significant component in the condensate and the least volatile compounds showing a significant component on the filter. The major quantity of most of the analytes is collected on the XAD-2®.

The effect of an emissions matrix is not straightforward to predict, but for most semivolatile compounds, laboratory performance is a reasonably reliable guide to field performance.

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**Table 1. Statistical Evaluation of Field Data Obtained from Ten Valid Quadruple SemiVOST Sampling Runs with Dynamic Spiking of Title III Clean Air Act Analytes (Ten Acid/Neutral Sampling Runs, Ten Base/Neutral Sampling Runs)**

Semivolatile Organic Compound	Mean Recovery	Meets Method 301 Acceptance Criteria? <sup>3</sup>	Meets EPA QA/QC Handbook Acceptance Criteria? <sup>4</sup>
<b>Acids<sup>1</sup></b>			
di-n-butyl phthalate	46 ± 54%	No	No
bis(2-ethylhexyl) phthalate	48 ± 23%	No	No
m-/p-cresol <sup>7</sup>	69 ± 14%	No	Yes
dimethyl phthalate	82 ± 17%	No	Yes
phenol	89 ± 9%	Yes	Yes
o-cresol	90 ± 15%	Yes	Yes
2,4-dinitrophenol	111 ± 31%	Yes	Yes
4-nitrophenol	114 ± 31%	Yes	Yes
4,6-dinitro-o-cresol	122 ± 14%	Yes	Yes
<b>Bases<sup>1</sup></b>			
quinone <sup>6</sup>	2 ± 438%	No	No
hexamethylphosphoramide	14 ± 118%	No	No
trifluralin	27 ± 41%	No	No
dimethylaminoazobenzene	31 ± 51%	No	No
3,3'-dimethoxybenzidine	37 ± 38%	No	No
o-anisidine	39 ± 39%	No	No
o-toluidine	56 ± 30%	No	Yes
benzidine	65 ± 119%	No	No
N,N,-dimethylaniline	67 ± 24%	No	Yes
aniline	70 ± 24%	No	Yes
4,4'-methylene bis(2-chloroaniline)	89 ± 36%	Yes	Yes
3,3'-dimethylbenzidine	92 ± 44%	Yes	Yes

Table 1. Continued

Semivolatile Organic Compound	Mean Recovery	Meets Method 301 Acceptance Criteria? <sup>3</sup>	Meets EPA QA/QC Handbook Acceptance Criteria? <sup>4</sup>
N,N,diethylaniline	95 ± 19%	Yes	Yes
carbaryl	99 ± 19%	Yes	Yes
ethyl carbamate	103 ± 14%	Yes	Yes
caprolactam	114 ± 12%	Yes	Yes
N-nitrosomorpholine	116 ± 12%	Yes	Yes
N-nitrosodimethylamine	117 ± 13%	Yes	Yes
propoxur	123 ± 12%	Yes	Yes
2-acetylaminofluorene	147 ± 23%	No	Yes
<b>Neutrals<sup>2</sup></b>			
styrene oxide	0.5 ± 1481%	No	No
phthalic anhydride	5.3 ± 144%	No	No
methoxychlor	73 ± 19%	No <sup>7</sup>	Yes
toluene	76 ± 11%	No <sup>7</sup>	Yes
m-/p-xylene <sup>6</sup>	79 ± 12%	Yes	Yes
quinoline <sup>5</sup>	80 ± 19%	Yes	Yes
styrene	84 ± 10%	Yes	Yes
o-xylene	85 ± 11%	Yes	Yes
1,4-dioxane	87 ± 11%	Yes	Yes
cumene	88 ± 11%	Yes	Yes
ethylbenzene	89 ± 12%	Yes	Yes
parathion	89 ± 28%	Yes	Yes
isophorone	93 ± 12%	Yes	Yes
acetophenone	96 ± 12%	Yes	Yes
naphthalene	96 ± 11%	Yes	Yes
dibenzofuran	100 ± 12%	Yes	Yes
dichlorvos	101 ± 18%	Yes	Yes
DDE	102 ± 15%	Yes	Yes

**Table 1. Continued**

Semivolatile Organic Compound	Mean Recovery	Meets Method 301 Acceptance Criteria? <sup>3</sup>	Meets EPA QA/QC Handbook Acceptance Criteria? <sup>4</sup>
4-nitrobiphenyl	102 ± 14%	Yes	Yes
heptachlor	103 ± 12%	Yes	Yes
biphenyl	103 ± 12%	Yes	Yes
lindane	104 ± 12%	Yes	Yes
nitrobenzene	109 ± 12%	Yes	Yes
2,4-dinitrotoluene	109 ± 12%	Yes	Yes
methyl isobutyl ketone	112 ± 11%	Yes	Yes
chlordanes	142 ± 16%	Yes <sup>7</sup>	Yes

<sup>1</sup>Values represent the mean from ten complete quad sampling runs with dynamic spiking, two spiked trains and two unspiked trains.

<sup>2</sup>Values represent the mean from twenty complete quad sampling runs with dynamic spiking, two spiked trains and two unspiked trains. Neutral compounds were spiked with both the Acid and the Bases, and all neutral data are included in the composite values.

<sup>3</sup>EPA Method 301 acceptance criteria include recovery of 70 - 130%, with a precision ≤ 50 % relative standard deviation and a correction factor between 0.70 and 1.30.

<sup>4</sup>EPA QA/QC Handbook acceptance criteria include recovery of 50 - 150%, with a precision ≤ 50 % relative standard deviation.

<sup>5</sup>Quinoline was placed in Neutral solution rather than Basic solution because of confusion of name with quinone.

<sup>6</sup>Listed together in the table because of chromatographic coelution.

<sup>7</sup>The correction factors (CF) for toluene and methoxychlor were 1.31 and 1.40; the CF for chlorodane was 0.71, however this was due to high variability of the unspiked trains.

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