



Project Summary

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

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A series of laboratory and field tests have been conducted to evaluate EPA SW-846 Method 0010 for the measurement of Clean Air Act identified halogenated semivolatile organic compounds (SVOCs) commonly found in stationary source emissions. This evaluation involved the application of EPA's Method 301 guidelines with four Method 0010 sampling trains being run simultaneously. The sampling method in Method 0010 was conducted as written with the exception that known concentrations of selected target compounds being dynamically spiked into two of the sampling trains during source sampling. Sample analysis was performed according to SW-846 Method 8270.

Laboratory tests were initially performed to evaluate the sampling and analytical methods. Dynamic spiking procedures for the Method 0010 sampling train were also developed and evaluated for field application during the laboratory phase.

The first field tests were performed at a stationary source site with low levels of moisture and minimal organic background in the source emissions.¹ No problems were encountered with either the field or laboratory portions of the first field test. Many of the compounds under evaluation in the method were recovered with acceptable precision and accuracy.²

A second series of field tests were conducted at a chemical manufacturing facility where chemical wastes and wet sludge were burned in a coal-fired boiler. The results, as reported herein, reveal that significant analytical difficulties and poor recoveries of dynami-

cally spiked analytes were encountered. After reviewing the field and laboratory notebooks and after a visual inspection of the sample extracts, the poor recoveries were attributed to four factors:

- Water saturated sorbent from the Method 0010 sampling train,
- Use of methanol in the field and laboratory to effect complete recovery of wet sorbent from the sampling module for subsequent analysis,
- Use of extraction techniques that did not effect a complete separation of methylene chloride from methanol; and
- Loss of targeted compounds during evaporation of the methanol solution.

A list of recommended modifications to the sample protocol are presented to help prevent the reoccurrence of these problems in future field tests.

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 validation of a source emissions method for any group of analytes requires that the precision and bias of the sampling and analytical methodologies be es-

established experimentally in the laboratory and demonstrated through various field tests at the appropriate source category. An examination of the readily available stationary source validation methods data (Stationary Source Sampling and Analysis Directory, Version 2, etc.), reveals that the required precision and bias data are not available for many of the halogenated SVOCs listed in Title III of the Clean Air Act Amendments of 1990 (CAAA). Often the validation information is available for the analytical methodology but not for the corresponding sampling methodology. Validated laboratory and field data can be found for only a small percentage of the Clean Air Act analytes at any source category.

The U.S. Environmental Protection Agency, under the authority of Title III, CAAA, is charged with providing sampling and analytical methods for selected halogenated SVOCs (Table 1). Method 0010 (*Modified Method 5 Sampling Train*), applicable to compounds with boiling points above 100°C, was selected as the appropriate sampling method while Method 8270 (*Gas Chromatography/Mass Spectrometry for Semivolatile Organics: Capillary Column Technique*) was selected as the analytical method. An appendix to Method 0010 provides a brief sample preparation procedure for the components of the Method 0010 sampling train.

The results of a laboratory evaluation³ using dynamic spiking of selected analytes from a liquid solution into a Method 0010 sampling train are shown in Table 1. Several of the halogenated SVOCs showed erratic or unacceptable performance relative to the precision and bias reported for the earlier laboratory analysis.³ These poor recoveries were anticipated based on a working knowledge of the SVOCs chemical properties, practical experiences with XAD-2® recoveries, and experiences with gas chromatography/mass spectrometry (GC/MS). Where possible, laboratory recovery and precision data were collected for all the Table 1 compounds. The field studies data demonstrate that the method is not applicable for the poor performers. The level of difficulty for these compounds was quantified and the applicability of the sampling and analytical methodology as a screening method for these analytes was evaluated.

A first field method evaluation study was conducted at a coal burning electric power plant.⁴ Acceptable recoveries (100% ± 50%) were obtained for trans-1,3-dichloropropene (52%), 1,1,2-trichloroethane (56.4%), ethylene dibromide (58.9%), chlorobenzene (62.3%), bromoform (99.3%), 1,1,2,2-tetra-

chloroethane (64.0%), dichloroethyl ether (60.9%), 1,4-dichlorobenzene (56.2%), benzyl chloride (78.7%), hexachloroethane (74.0%), 1,2,4-trichlorobenzene (59.5%), hexachlorobutadiene (65.4%), benzotrifluoride (60.1%), 2-chloroacetophenone (56.0%), and 2,4,5-trichlorophenol (62.7%).

A second field test was conducted at a chemical manufacturing facility where waste chemicals were incinerated in a coal-fired boiler. The host facility scheduled the delivery so that chemical waste was continually fed into the boiler during the testing period. Grab SVOC samples (sampling Method 0010) were collected during a site pre-survey and returned to the laboratory for analysis to characterize the background matrix. No target analytes were detected at a value above the analytical Method Detection Limit (MDL). Other SVOCs present in the source background included low levels of aliphatic and aromatic hydrocarbons.

This report contains the results of a second series of field tests to evaluate EPA SW-846 Method 0010 and its associated analytical procedure Method 8270 for halogenated SVOCs. The results of the earlier laboratory evaluations and a first field test^{3,4} indicated that this method was applicable to a wide range of halogenated SVOCs. The second field test, conducted at a combustion source that contained a complex matrix of organic compounds and significant quantities of water, was intended to demonstrate the method's ruggedness.

Procedures

SW-846 Method 0010, with the following modifications, was used to simultaneously collect quadruplicate halogenated SVOCs source samples:

- A quad probe (four heated borosilicate glass liners mounted in one probe assembly) was used instead of the standard single probe (Figure 1); and
- A heated glass elbow equipped with a spiking injection port (Figure 2) was used to connect the probe to the heated filter.

Flue gas temperatures and velocity measurements of the gaseous stationary source emissions were monitored and the samples were collected as closely to isokinetically as possible.

EPA Method 301¹ requires dynamic spiking to be performed in the field, with two sampling trains spiked and two trains unspiked in each sampling run. Six complete and valid quadruple sampling runs are required to meet the Method 301 sta-

tistical criteria. A total of 8 sampling runs using quadruple sampling trains were performed in the second field study resulting in 16 spiked trains and 16 unspiked trains being collected. The spiked SVOCs (Table 1) were introduced to the sampling system as a methylene chloride solution by syringe injection through a heated glass elbow (Figure 2) mounted at the outlet of the probe. A volume of 20-30 mL of spiking solution was introduced continuously during a 1-hr sampling run. The Teflon® line from the motor-driven syringe pump was connected to a piece of glass-lined stainless steel tubing with a beveled tip. The actual volume of liquid spiked was measured gravimetrically by recording pre- and post-test weights for the syringe and all connecting tubing.

Prior to field deployment, standard Method 0010 preparation procedures were followed: all glassware was pre-cleaned, resin and filters were cleaned and blanked, and all train components were calibrated and leak-checked. Sampling train components were assembled in the onsite laboratory following standard Method 0010 procedures. After the sampling trains were moved to the sampling location, final assembly of the trains occurred, the trains were leak-checked, and all heaters were turned on in preparation for sampling. When all temperatures reached the set points and stabilized, meter boxes were turned on and the sampling flow rate was adjusted to approximately 0.014 m³/min (0.50 ft³/min). The dynamic spiking syringe pump flow (0.3-0.5 mL/min) was started immediately after gas flow had been established. Dynamic spiking was performed continuously for the duration of the 1-hr sampling run.

Upon completion of sampling, the trains were disassembled into four sections: the probe; the spiking glassware/filter holder; the XAD-2® sampling module; and the impinger train. The individual probes inserted into the stack for each sampling run were not recovered after every sampling run, since the analytes were spiked into the train after the probe and before the filter. Methanol and methylene chloride (50:50, as specified in Method 0010) were used as the sampling train rinses and recovery solvents. Reagent blanks and field blanks were also collected.

The components of the sampling trains were prepared for laboratory analysis according to the Method 0010 sample preparation protocol, using Method 8270 GC/MS procedures, with the following exceptions:

- Extracts (three per sampling train) were generated from methylene chloro-

Table 1. Halogenated Compounds, Title III of the Clean Air Act Amendments, for Which Laboratory Testing Has Evaluated the Applicability of the SemiVOST Method

Compound	Boiling Point	Comments
Benzotrichloride	219-223°C	Acceptable performance in laboratory.
Benzyl Chloride	177-181°C	Acceptable performance in laboratory.
bis(Chloromethyl) Ether ^a	106°C	Unacceptably low recovery in laboratory.
Bromoform	150-151°C	Acceptable performance in laboratory.
Chloroacetic Acid	189°C	Cannot be analyzed by SemiVOST method.
Chlorobenzene ^a	132°C	Acceptable performance in laboratory.
2-Chloroacetophenone	244-245°C	Acceptable performance in laboratory.
Chlorobenzilate	147°C	Unacceptably low recovery in laboratory.
1,2-Dibromo-3-Chloropropane	196°C	Acceptable performance in laboratory.
1,4-Dichlorobenzene	173°C	Acceptable performance in laboratory.
3,3'-Dichlorobenzidine	MP = 165°C	Erratic performance in laboratory.
Dichloroethyl Ether	65-67°C ^b	Acceptable performance in laboratory.
1,3-Dichloropropene	105-106°C ^c	Unacceptably low recovery in laboratory.
Epichlorohydrin ^a	115-117°C	Acceptable performance in laboratory.
Ethylene Dibromide ^a	131-132°C	Acceptable performance in laboratory.
Hexachlorobutadiene	210-220°C	Acceptable performance in laboratory.
Hexachlorocyclopentadiene	239°C	Erratic performance in laboratory.
Hexachloroethane	186°C	Acceptable performance in laboratory.
Pentachloronitrobenzene	328°C	Unacceptably low recovery in laboratory.
Pentachlorophenol	309.5°C	Unacceptably low recovery in laboratory.
1,1,2,2-Tetrachloroethane	147°C	Acceptable performance in laboratory.
Tetrachloroethylene ^a	121°C	Unacceptably low recovery in laboratory.
1,1,2-Trichloroethane ^a	110-115°C	Acceptable performance in laboratory.
2,4,5-Trichlorophenol	248°C ^d	Erratic performance in laboratory.
2,4,6-Trichlorophenol	246°C	Unacceptably low recovery in laboratory.

^a Also tested in VOST methodology.

^b Boiling temperature at 15 mm Hg.

^c Boiling temperature at 730 mm Hg.

^d Boiling temperature at 740 mm Hg.

ride extraction of XAD-2® sorbent, filter, condensate, and rinses used in the Method 0010 sampling train;

- The final volume of the extracts was 5 mL (as specified in the SemiVOST method), rather than 1 mL as Method 8270 requires for the extraction of water or soil;
- Filters, XAD-2®, and condensate were extracted separately; and
- Impinger contents were archived.

Analytical Results

Table 2 summarizes the analytical results for all eight quadruplicate field sampling runs. Analytical Method 8270 requires that six surrogate compounds be spiked into the samples immediately before ex-

traction with their recoveries demonstrating the extraction efficiency. The Table 2 results *are not* corrected for Method 8270 surrogate compound recoveries.

The targeted analytes were recovered in the XAD-2® modules of both spiked sampling trains for Runs 1, 2, 3, and 6 only. Several sampling train components showed no or only partial recovery of expected analytes. For many samples, no recovery or poor recovery of the surrogate compounds was observed. If none of the surrogate compounds are recovered in any one of the sampling train components, then that sampling run (all of the quadruplicate sampling trains) cannot be considered complete and the data cannot be used in performing Method 301 statistical calculations. The Table 2 results indicate

that the SemiVOST method cannot be validated from this field test based on the limited analytical data.

Recoveries of each analyte for sampling Runs 1, 2, 3, and 6, corrected for Method 8270 surrogate compounds, are shown in Table 3. Dynamically spiked compounds were observed in the XAD-2® extracts (where the most retention of SVOCs is expected) for only the four complete sets of paired spiked sampling trains.

Discussion

The mean halogenated SVOC recoveries from the laboratory study, the first field test, and the four complete second field test runs are shown in Table 4. Where the compounds were recovered as expected, the second field test results are similar to

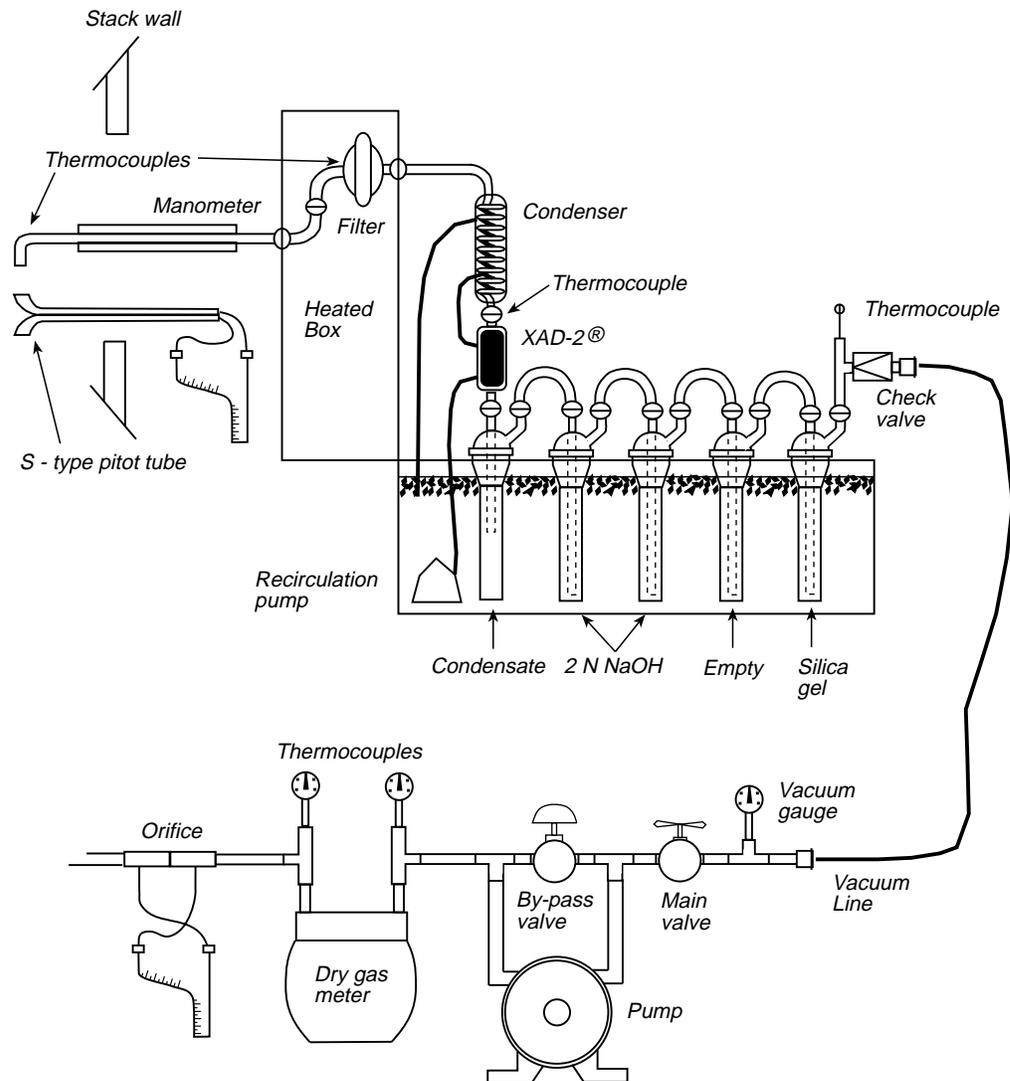


Figure 1. Method 0010 sampling train.

previous studies results.⁴ The sparseness of data do not support a rigorous statistical comparison of these study results. However, an examination of all the second field study analytical results shows that:

- Method 8270 surrogate compound recoveries from XAD-2® are generally low.
- Chemically analogous compounds spiked in the laboratory exhibited poor recovery. Therefore, the recovery problem is most likely not due to the field spiking process. Although Method 8270 surrogate compounds are not

halogenated, isotopically labeled compounds exhibit the same chemical behavior and can be distinguished from the unlabeled compounds by mass spectrometry. Several isotopically labeled analogs of the Table 1 compounds were used as surrogates in addition to the Method 8270 compounds. Both were spiked immediately before sample extraction. Several of these isotopically labeled compounds were not recovered at all (for example, five of six isotopically labeled compounds were not observed in Run 4A).

- The majority of the analytes that were dynamically spiked in the field are not recovered.
- Recoveries for the analytes that are observed range from 4% to 63% versus the required 100% ± 50%.

Since most of these compounds are retained in XAD-2® of the Method 0010 train, analyte recovery from the XAD-2® is the most important consideration in the laboratory analysis. In the second field test, only four of the eight paired spiked sampling trains showed acceptable recoveries¹ of laboratory and field spike surrogate compounds. The variance between the second field test results and the ear-

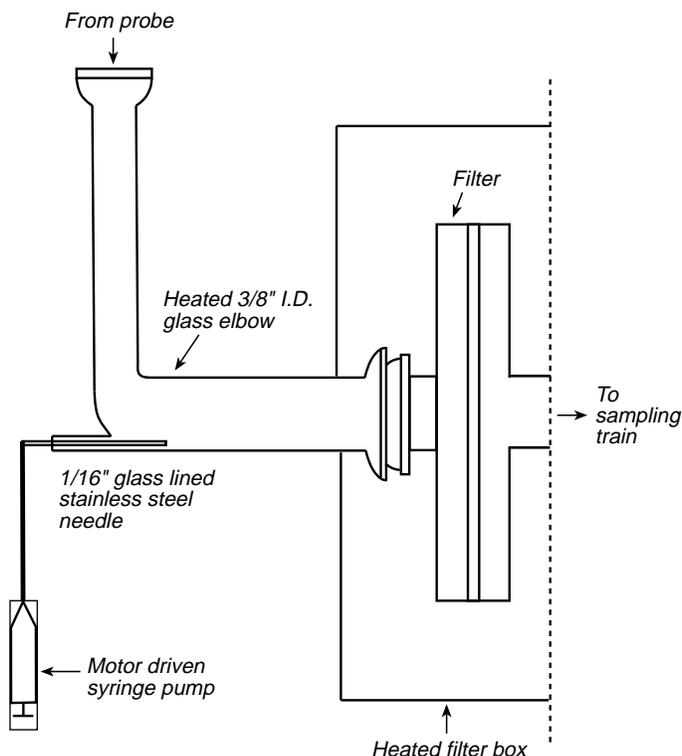


Figure 2. Dynamic spiking apparatus for a liquid solution of semivolatile organic compounds.

lier laboratory and first field test results warranted further investigation to determine the potential cause(s) for these low recoveries.

A review of the Method Blank (clean XAD-2® or unused methylene chloride:methanol solution, spiked only with the surrogate compounds and the isotopically labeled surrogate compounds) and Method Spike (clean sampling train media spiked in the laboratory with surrogate compounds, isotopically labeled compounds, and halogenated SVOCs) data suggest that the laboratory spiking, sample preparation, and analysis procedures were in control. The Method Blank and Method Spike samples were processed with the field samples. The Method Blanks, prepared and analyzed with the sampling train components, showed acceptable-to-high surrogate and isotopically labeled compound recoveries. The Method Spike recoveries were excellent for most of the isotopically labeled compounds and halogenated SVOCs. The erratic and low recoveries from the second field test samples encompassed all the sampling train components.

The archived extracts from the sampling train components, Methods Blanks, and Methods Spikes were examined to

determine if any differences were apparent. Several key observations were noted:

- Method Blank and Method Spike extracts were consistently light yellow and looked like several mL of organic solvent (methylene chloride);
- Field sample extracts ranged in color from clear to nearly brown;
- Some field sample extracts included two distinct phases, an aqueous layer and an organic layer;
- Some field sample extracts were totally aqueous, with no organic solvent present or only a small pool of organic liquid floating on the top of a large aqueous layer; and
- Some of the field samples unexpectedly had no or little odor of methylene chloride.

A review of step-by-step laboratory procedures with the laboratory staff revealed that many of the field samples had required longer than the usual amount of time to concentrate to 5 mL by Kuderna-Danish procedures (3-4 hr rather than 30-40 min).

The major difference between the laboratory and field Method Blanks and Method Spikes is most likely associated with the amount of moisture in the samples. While the laboratory samples were dry, any added moisture in the field samples could have caused a problem with the transfer of XAD-2® from the sampling module to the extraction vessel.

The physical transfer of wet XAD-2® from the glass field sampling module to the Soxhlet extractor is relatively difficult. Dry XAD-2® pours readily from the sampling module; wet XAD-2® sticks to the glass walls of the sampling module. Since water and methylene chloride are immiscible, any wet XAD-2® is not readily removed from the walls of the sampling module with pure methylene chloride rinses. Wet XAD-2® can be readily removed from the sampling module with methanol rinses. The investigation revealed that the laboratory staff had used a small amount of pure methanol (10-20 mL of methanol added to 300-400 mL of methylene chloride) to complete the transfer of the wet XAD-2®.

The high moisture levels in the stationary source emissions resulted in wet sampling train sorbent and a large volume of aqueous condensate (100-200 mL). When wet sorbent is extracted with methylene chloride, the extract contains water. If there is sufficient water to form a distinct aqueous phase, the analyst is aware that a large amount of water is present and documented procedures are followed to appropriately dry the XAD-2® extract. If a distinct aqueous phase does not form during extraction, the analyst may not be aware that large amounts of water are present and may not dry the extract thoroughly.

Complicating this potential excess water problem is the introduction of additional methanol (miscible with the water) when transferring the XAD-2® to the extraction vessel. Three experiments were conducted to examine these potential effects:

1. To evaluate the effect of moisture on compound recovery, dry XAD-2® in the thimble of a Soxhlet extractor was moistened by pouring 200 mL of reagent water through the sorbent (approximately 50 mL of water was retained by the sorbent). The wet XAD-2® was first spiked with surrogate compounds and halogenated SVOCs and then Soxhlet extracted with methylene chloride. No distinct water layer was observed after extraction. Recoveries were 10-15% lower than the analyte recoveries from dry sorbent.

Table 2. Summary of Results for All Eight Runs and All Sampling Trains, Using Surrogate-Corrected Data

Run	Train A			Train B			Train C			Train D		
	X	C	F	X	C	F	X	C	F	X	C	F
1	y	y	y	y	y	y	y	y	y	y	y	y
2	y	y	y	y	y	y	y	y	y	n	y	y
3	y	y	y	y	y	y	y	y	y	y	y	y
4	n	y	n	n	y	n	y	y	n	y	y	y
5	p	y	y	p	y	n	y	y	y	y	y	y
6	y	y	n	y	n	n	p	y	y	p	y	y
7	n	n	n	y	y	y	p	y	p	y	y	p
8	n	y	p	y	y	y	p	y	y	y	y	p
Total	4			6			5			6		

Total indicates sets of recoveries of analytes and/or surrogate compounds from XAD-2®

Note: For each sampling run Trains A and B were spiked trains, Trains C and D were unspiked. Recoveries for C and D Trains refer to recoveries of surrogate compounds and isotopically labeled analogs. A run is considered complete when all analytes and/or surrogate compounds are recovered from XAD-2®, for all four trains (indicated by y). No more than *four* runs can be considered complete.

- X = XAD-2® module.
- C = Condensate fraction.
- F = Filter fraction.
- p = Partial success; some but not all analytes detected.
- y = All analytes detected.
- n = No analytes detected.

Reproducibility was also somewhat lower but still acceptable.

2. According to the Method 0010 sample preparation protocol, all of the methylene chloride extracts of sampling train components are dried by pouring each extract through a bed of sodium sulfate, a drying agent. When the drying procedure was modified by the addition of sodium sulfate to the round bottom flask during Soxhlet extraction of the wet XAD-2® spiked in the laboratory, recoveries improved slightly (5-10% higher, not statistically different) and reproducibility returned to the levels observed with dry sorbent.
3. A solution of 50:50 methanol:methylene chloride (the composition of the field rinse) was spiked with surrogate compounds and halogenated SVOCs and 15 mL of water was added. This amount of water was not sufficient to effect phase separation. An aliquot of this solution was poured through a bed of sodium sulfate to dry the extract. The sodium sulfate solidified and prevented the drying of the remaining solution. The remaining, undried solution continues to channel down between the solidified drying agent and the walls of the funnel. In this experiment, the solidification of the sodium sulfate was observed and the

solidified sodium sulfate was not replaced with new, dry sodium sulfate. (The solidification of sodium sulfate bed is not normally obvious and will go unnoticed unless a specific check is made.) For these solutions that were imperfectly dried, an extensive amount of time (5 hr rather than 30-40 min) was required to achieve a final volume of 5 mL. The final composition of the solution was methanol/water. Methylene chloride, which is more volatile than methanol and water, is preferentially vaporized under Kuderna-Danish concentration. The analysis of these methanol/water extracts yielded poor recoveries and reproducibility of spiked compounds.

However, if sufficient water was then added to a second aliquot of the methylene chloride/methanol/water solution to effect phase separation, the aqueous phase could then be discarded. Normal drying procedures then produced dry extracts that showed compound recoveries and analytical reproducibility parallel to the recoveries and reproducibility obtained from wet XAD-2®.

Experiment 1 shows that wet XAD-2® can still produce good recovery of the compounds spiked before extraction. The water retained during sampling and ex-

traction does not cause recovery and precision problems. Experiment 2 shows that addition of a drying agent to the extraction flask during extraction has no significant effect. Experiment 3 shows that, if no extraordinary steps are taken, the presence of *both* water and methanol in the extracts will severely depress analyte recoveries and lower reproducibility.

It is possible to overcome the effects of wet XAD-2® and the presence of methanol and water in the sampling train rinses. If the amount of methanol and water present in the methylene chloride extract is low, some depression of recoveries may occur but acceptable results can still be obtained. Larger amounts of water and methanol severely depress the spiked compounds recoveries and reproducibility. For this second field method evaluation study, the presence of water and methanol in the sample extracts resulted in insufficient analytical data being obtained and subsequently, an unsuccessful method evaluation study.

Conclusions and Recommendations

The following conclusions may be drawn from the laboratory and field tests results of this project:

- Laboratory and field experience are consistent with the expectations based on the selected compounds' chemical and physical properties. Com-

Table 3. Percent Recoveries of Spiked Semivolatile Halogenated CAAA Compounds in Four Replicate Runs Corrected for Surrogate Recoveries^a

Compound	Run 1		Run 2		Run 3		Run 6		Mean (%)	Standard Deviation	Coefficient Variation
	Train A	Train B									
<i>epichlorohydrin</i>	15	18	21	21	6	10	13	20	15.5	5.17	33.37
<i>cis-1,3-dichloropropene</i>	61	14	61	66	56	65	64	70	57.1	16.75	29.32
<i>trans-1,3-dichloropropene</i>	73	40	83	86	170	76	79	92	87.4	34.50	39.48
<i>1,1,2-trichloroethane</i>	70	52	70	78	65	73	72	76	69.5	7.58	10.91
<i>1,2-dibromoethane</i>	69	47	72	83	68	76	75	81	71.4	10.45	14.64
<i>tetrachloroethene</i>	65	2	62	67	53	63	66	71	56.1	21.03	37.46
<i>chlorobenzene</i>	75	48	77	85	71	80	77	85	74.8	11.05	14.79
<i>bromoform</i>	70	82	75	87	69	82	84	87	79.5	6.76	8.51
<i>1,1,2,2-tetrachloroethane</i>	78	94	81	92	75	87	84	91	85.3	6.48	7.60
<i>bis(chloroethyl)ether</i>	85	98	83	92	74	96	92	95	89.4	7.58	8.48
<i>1,4-dichlorobenzene</i>	80	88	78	87	73	89	88	96	84.9	6.86	8.09
<i>benzyl chloride</i>	82	91	77	85	74	93	92	92	85.8	6.96	8.12
<i>hexachloroethane</i>	74	85	76	86	70	83	88	91	81.6	6.95	8.51
<i>1,2-dibromo-3-chloropropane</i>	81	87	78	85	72	90	96	95	85.5	7.76	9.08
<i>1,2,4-trichlorobenzene</i>	91	94	78	88	73	95	97	97	89.1	8.45	9.48
<i>hexachlorobutadiene</i>	89	80	78	90	74	91	86	93	85.1	6.49	7.62
<i>benzotrichloride</i>	82	52	74	86	75	84	90	92	79.4	11.95	15.05
<i>2-chloroacetophenone</i>	92	87	84	87	78	94	93	90	88.1	4.99	5.66
<i>hexachlorocyclopentadiene</i>	54	62	62	61	61	68	60	83	63.9	8.05	12.61
<i>2,4,6-trichlorophenol</i>	81	74	80	78	71	86	95	97	82.8	8.74	10.57
<i>2,4,5-trichlorophenol</i>	83	77	83	79	75	85	97	97	84.5	7.86	9.30
<i>hexachlorobenzene</i>	64	0	65	76	75	69	117	83	68.6	30.38	44.28
<i>pentachlorophenol</i>	63	76	57	58	53	59	85	69	65.0	10.21	15.71
<i>pentachloronitrobenzene</i>	48	63	56	63	56	73	88	65	64.0	11.42	17.85
<i>chlorobenzilate</i>	60	79	80	56	45	59	78	85	67.8	13.56	20.02
<i>3,3'-dichlorobenzidine</i>	0	0	35	0	5	0	0	0	5.0	11.46	229.13

^a Surrogate recoveries shown in Appendix A.

pounds expected to perform well did so. The performance of compounds yielding poor chromatographic performance or high reactivity has been quantified.

- Laboratory and field results have been consistent through the series of studies, with the best recoveries and reproducibility obtained under laboratory conditions.
- Laboratory studies demonstrated that the low recoveries of analytes and surrogate compounds from XAD-2® could most likely be attributed to wet XAD-2® and the use of methanol in the laboratory to effect complete transfer of the wet XAD-2® without properly removing the methanol.

- Spiking of isotopically labeled compounds (although not specifically required by the sample preparation methodology) at the time of extraction provides extremely valuable information on the methods' performance because of their comparable chemical behavior to the compounds of interest.
- Low recoveries of analytes and surrogate compounds from extracts that incorporated a field rinse of 50:50 methylene chloride:methanol were attributed to the use of inadequate amounts of water extraction to effect a complete separation of methylene chloride from the water and the methanol.

Recommendations based on these laboratory and field method evaluation studies include:

- A protocol specifically to address the preparation of the components of the Method 0010 sampling train should be written to clearly describe the exact procedures that should be used to ensure that water and methanol are separated from the methylene chloride extracts and to specifically prohibit the use of methanol in transfer of wet sorbent.
- With a clearly written sample preparation protocol, a field method evaluation study using dynamically spiked

Table 4. Comparison of Percent Recoveries of Semivolatile Halogenated Organic Compounds in Laboratory and Field Studies (Uncorrected for Surrogate Recoveries)

Compound	Mean Recoveries		
	Laboratory ^a	Field 1 ^b	Field 2 ^c
bis(chloromethyl)ether	18.3	0.0	0.0
epichlorohydrin	75.2	6.0	13.4
cis-1,3-dichloropropene	21.9	49.1	50.3
trans-1,3-dichloropropene	20.4	52.0	79.8
1,1,2-trichloroethane	53.1	56.4	60.3
1,2-dibromoethane	66.3	58.9	62.5
tetrachloroethene	49.7	53.2	49.4
chlorobenzene	76.0	62.3	65.1
bromoform	99.3	59.8	69.3
1,1,1,2-tetrachloroethane	81.1	64.0	73.9
dichloroethyl ether	75.8	60.9	77.0
1,4-dichlorobenzene	68.2	56.2	73.5
benzyl chloride	78.7	67.4	73.9
hexachloroethane	85.4	74.0	70.9
1,2-dibromo-3-chloropropane	66.2	44.8	73.8
1,2,4-trichlorobenzene	58.2	59.5	76.1
hexachlorobutadiene	58.3	65.4	77.1
benzotrichloride	67.0	60.1	72.4
2-chloroacetophenone	79.7	56.0	79.5
hexachlorocyclopentadiene	513.0	42.3	59.6
2,4,6-trichlorophenol	45.6	59.8	75.4
2,4,5-trichlorophenol	52.7	62.7	76.6
hexachlorobenzene	32.9	44.6	56.4

^aLaboratory study; mean of 16 replicates.

^bFirst field study; mean of 12 replicates (six pairs of spiked sampling trains).

^cSecond field study; mean of 8 replicates (four pairs of spiked sampling trains).

analytes at a wet source should be performed to test the procedures.

- Modification of the sample preparation method to use procedures for removing analytes from the XAD-2® without removing the resin from the sampling module should be explored (elution, supercritical fluid extraction, etc.).
- Solid phase extraction techniques should be evaluated to minimize the solvent volume used in the extraction of filter/front half rinse samples and condensate/condensate rinse samples.

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The complete report, entitled "Field Test of a Generic Method for Halogenated Hydrocarbons: SemiVOST Test at a Chemical Manufacturing Facility," (Order No. PB97-115349; Cost: \$28.00, subject to change) will be available only from:

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