



Project Summary

Audit Materials for Semivolatile Organic Measurements During Hazardous Waste Trial Burns

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Two audit materials have been developed to assess the accuracy and precision of semivolatile organic measurements using EPA Method 0010 SW 846. The first audit material is prepared by spiking known quantities of organic compounds onto XAD-2 resin in glass cartridges. It is used to evaluate the analytical portion of the method. The second audit material is prepared by spiking known quantities of organic compounds onto Carbotrap™ in stainless steel cartridges. It is used to evaluate the sampling and analytical portions of the method. Recovery efficiencies were found to be between 88 and 98 percent for XAD-2 audit cartridges and between 91 and 108 percent for Carbotrap™ audit cartridges. In general, test compounds were found to be stable on XAD-2 audit cartridges under refrigeration over an 8-month period and on Carbotrap audit cartridges at room temperature over a 2-month period. An interlaboratory study was used to assess the accuracy and precision of the audit materials for six test compounds: pyridine, toluene, o-xylene, chlorobenzene, 1,1,2,2-tetrachloroethane, and nitrobenzene. The study involving five cooperating laboratories revealed an overall mean bias percentage of -29 percent. The mean within-laboratory variability was 22 percent. These variabilities generally agree with corresponding values obtained in an interlaboratory comparison study of methods for volatile and semivolatile compounds on solid waste samples.

This Project Summary was developed by EPA's Atmospheric

Research and Exposure Assessment 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

Operators of hazardous waste incinerators are currently using Method 0010 to monitor stack emissions during hazardous waste trial burns. The sampling train consists of a series of traps and impingers that collect particulates and gaseous semivolatile organics. An adsorbent material, XAD-2 resin, is used to absorb organic vapors with boiling points greater than 100°C. The overall accuracy of the process of trapping, desorbing, and analyzing these organic vapors by Method 0010 can be assessed by Agency personnel using audit materials.

Research Triangle Institute (RTI) has investigated two audit materials for delivery of test compounds that could be used in performance audits during hazardous waste trial burns. The first audit material is XAD-2 resin contained in glass cartridges that has been spiked with known amounts of several semivolatile organic compounds. This audit material is sent to the laboratory involved in the trial burn. The laboratory recovers these compounds by Soxhlet extraction, concentrates the extract by Kuderna-Danish evaporation, and analyzes the extract by gas chromatography/mass spectroscopic (GC/MS) detection. This audit material is intended to assess only the analytical portion of Method 0010. The second audit material is an adsorbent, Carbotrap,

contained in stainless steel cartridges that have been spiked with known amounts of semivolatile organic compounds and delivered to the trial burn sites. Once at the site, the compounds are thermally desorbed from the audit cartridge onto an operating Method 0010 sampling train, which collects them on XAD-2 resin for subsequent recovery and analysis. This audit material is intended to assess the combined sampling and analytical portions of Method 0010.

Measurement errors can occur in either the sampling or the analytical portions of Method 0010. The use of two different, but identically loaded, audit materials allows one to begin to locate the source of an observed measurement error. If the measurement error were in the sampling portion, one would expect to see accuracy or precision problems for the Carbotrap audit cartridges, but not for the XAD-2 audit cartridges. If the measurement error were in the analytical portion, one would expect to see accuracy or precision problems in both sets of audit cartridges. Statistical tests should be used to verify that any apparent accuracy or precision problems are significant. These audit materials cannot detect measurement errors arising from other sources such as the volumetric sampling rate.

Experimental Procedures

RTI performed initial recovery and stability studies for several test compounds on the two audit materials. A batch of identical audit cartridges was prepared by injecting the same known quantities of the test compounds onto the sorbent material. These audit cartridges were then analyzed by RTI or, in some cases, by a cooperating laboratory. In the recovery studies, the injected and measured loadings for multiple cartridges were compared to yield the means and relative standard deviations of the recovery efficiencies. In the stability studies, the measured loadings for multiple dates were compared to yield data on the stability of the batch.

The XAD-2 audit cartridges were loaded by volatilizing a solution of the test compounds in methylene chloride with a flash evaporation unit. Once volatilized, the test compounds were carried from the unit by a nitrogen flow, were diluted with room air, and were sorbed on the XAD-2 resin with a Nutech Model 201 sample pump. The audit cartridges were immediately sealed after loading and then were stored under refrigeration.

The XAD-2 audit cartridges to be analyzed at RTI were Soxhlet extracted for 16 hours with methylene chloride. Internal standards having different boiling points from those of the test compounds were added to the extracts. The extracts were concentrated by Kuderna-Danish evaporation. The concentrated extracts were analyzed by gas chromatography with flame ionization detection (GC/FID). The same analytical techniques were followed by the cooperating laboratory with the exception that analysis was by GC/MS detection. Deuterated versions of the test compounds were added as internal standards to the cooperating laboratory XAD-2 resin.

The Carbotrap audit cartridges were loaded by volatilizing a solution of the test compounds in methylene chloride with a flash evaporation unit. Once volatilized, the test compounds were carried from the unit by a helium flow and were sorbed onto the Carbotrap. The audit cartridges were immediately sealed and then were stored at room temperature.

The Carbotrap audit cartridges to be analyzed at RTI were desorbed by two different methods: direct thermal desorption into a gas chromatograph and thermal desorption onto XAD-2 resin. For direct thermal desorption, the cartridges were connected to the sample inlet of a gas chromatograph and were heated to 475°C. A helium flow carried the volatilized test compounds from the Carbotrap to the gas chromatograph's column. For thermal desorption onto XAD-2 resin, the cartridges were heated and the volatilized test compounds were carried from the cartridges by a helium flow. The compounds were diluted with room air and were sorbed onto the XAD-2 resin with a Nutech Model 201 sample pump. The subsequent extraction, concentration, and analysis were as described above.

The Carbotrap audit cartridges to be analyzed by the cooperating laboratories during the interlaboratory study were thermally desorbed onto XAD-2 resin. The cartridges were heated to 400°C and were purged with a nitrogen flow. The volatilized test compounds were diluted with filtered ambient air and were sorbed onto the XAD-2 resin with a Method 0010 sampling train.

The accuracy and precision of Method 0010 were measured by conducting an interlaboratory study involving cooperating laboratories. Audit samples were prepared and delivered to laboratory personnel who were experienced in Method 0010. The

accuracy of the method was estimated by comparing the theoretical amount of test compounds loaded onto the audit cartridges to the amount measured by the cooperating laboratories. The average bias percentage between the theoretical loading and the multiple measured loadings for each laboratory's measurements of a compound was used as an index of the accuracy of the method. The between-laboratory variability was estimated by comparing the results of measurements at several different laboratories. The relative standard deviation of the average measured loadings for multiple laboratories' measurement of a compound was used as an index of the between-laboratory variability of the method. The within-laboratory variability was measured by providing several cartridges loaded at, or near, the same level. The relative standard deviation of the multiple measured loadings for each laboratory's measurements of a test compound was used as an index of the within-laboratory variability of the method.

Five laboratories agreed to participate in the interlaboratory study. Each laboratory received an audit kit containing seven Carbotrap audit cartridges, seven XAD-2 audit cartridges, and necessary supplies for thermal desorption of test compounds. The following test compounds were spiked onto both types of audit material: pyridine, toluene, o-xylene, chlorobenzene, 1,1,2,2-tetrachloroethane, and nitrobenzene. Of the seven Carbotrap audit cartridges supplied, three identical cartridges were loaded at approximately 200 micrograms (μg) of each compound per cartridge, three identical cartridges were loaded at approximately 2,000 μg of each compound per cartridge, and one cartridge was a blank. The same loading scheme was also used for the seven XAD-2 audit cartridges.

The level at which each test compound was loaded onto the audit material was verified at RTI before the materials were shipped to the cooperating laboratories. Test compound names and a broad loading range (i.e., 50 to 5,000 μg) were provided to the laboratories, but the exact level at which the compounds were loaded was not disclosed.

Results

The XAD-2 recovery study demonstrated that test compounds could be loaded onto and quantitatively recovered from XAD-2 audit cartridges. For RTI's analyses, the uncorrected mean recovery percentages ranged from

73 to 103 percent, and the corrected mean recovery percentages ranged from 79 to 140 percent. The uncorrected data indicate generally good recoveries for the test compounds. The corrected data were obtained by dividing the uncorrected mean recovery percentages for the test compounds by the mean recovery percentages of the internal standards. In general, the corrected percentages improved the recovery percentages, but in some cases the recovery percentages declined after correction. The corrected data suggest that it is difficult to correct for evaporative losses in test compounds with low boiling points. This difficulty is due to the use of internal standards with boiling points and recovery percentages that are different from those of the test compounds.

For the analyses by the cooperating laboratory, the corrected mean recovery percentages of the XAD-2 audit cartridges ranged from 88 to 98 percent. The improvement relative to RTI's corrected values is probably due to the cooperating laboratory's use of internal standards that are deuterated versions of the test compounds.

The Carbotrap recovery study demonstrated that test compounds could be loaded onto and quantitatively recovered from Carbotrap audit cartridges. For these cartridges that were desorbed onto XAD-2 resin, the mean recovery percentages ranged from 80 to 108 percent.

The XAD-2 stability study demonstrated that test compounds were stable on XAD-2 audit cartridges under refrigeration for periods of at least 269 days. The mean recovery percentages ranged from 98 to 106 percent after 4 days, from 99 to 106 percent after 151 days, and from 97 to 109 percent after 269 days. The greatest change in the measured loadings during the 269-day period was -6 percent. RTI did not use internal standards for these analyses. The excellent recovery percentages during the XAD-2 stability study are due to improvements that were made in the Kuderna-Danish evaporator after the completion of the XAD-2 recovery study.

The Carbotrap stability study demonstrated that most of the test compounds were stable on Carbotrap audit cartridges at room temperature for periods of at least 60 days. The nitrobenzene loading on the cartridges declined by 23 percent during this period. For the remaining test compounds, the mean recovery percentages ranged from 91 to 99 percent after 1 day, from 90 to 100

percent after 30 days, and from 95 to 95 percent after 60 days. The greatest change in the measured loadings (excluding nitrobenzene) during the 60-day period was -6 percent. RTI directly desorbed the test compounds from these Carbotrap audit cartridges into a gas chromatograph.

After the recovery and stability studies had been completed, XAD-2 and Carbotrap audit cartridges were prepared for the interlaboratory study. A portion of each batch of cartridges was analyzed by RTI. The mean recovery percentages for the low-loading (i.e., ~200 µg of each compound) Carbotrap audit cartridges ranged from 97 to 105 percent. The mean recovery for the high-loading (i.e., ~2,000 µg of each test compound) Carbotrap audit cartridges ranged from 101 to 102 percent. The mean recovery percentages for the low-loading XAD-2 audit cartridges ranged from 104 to 110 percent. The mean recovery percentages for the high-loading XAD-2 audit cartridges ranged from 94 to 100 percent. The relative standard deviations of the recovery percentages ranged from 1 to 23 percent with a mean value of 6 percent. These results indicate that RTI had accurately and reproducibly loaded the XAD-2 and Carbotrap audit cartridges.

The results of the interlaboratory study are summarized in Tables 1 and 2. Table 1 gives the test compounds loaded onto the audit cartridges, the expected loadings of each compound on the audit cartridges, and the average bias percentages for audit cartridges that were loaded by RTI and analyzed by the cooperating laboratories. The latter values are the averages for measurements of three identical cartridges that were given to the cooperating laboratories. They compare the cooperating laboratories' measured loadings with RTI's expected loadings.

The overall average bias percentage for both audit materials in the interlaboratory study is -27 percent. The unusually high value for the Laboratory E/pyridine/XAD-2/low-loading combination was found to be an outlier at the 99-percent confidence level, relative to the other measured pyridine loadings. If this value is discarded, the overall bias percentage is -29 percent. The overall average bias percentage for the Carbotrap audit cartridges alone is approximately equal to the corresponding value for the XAD-2 audit cartridges alone (i.e., -28 and -32 percent, respectively, and excluding the anomalous Laboratory E value).

The overall average bias percentage for the low-loading audit cartridges (excluding the outlier) is -23 percent. This value is less than the corresponding value of -35 percent for the high-loading audit cartridges.

The overall average bias percentages for each laboratory are given below:

Laboratory	Overall mean bias percentage
A	-60
B	-39
C	-5
D	-39
E	-11 ^a

^aExcluding the outlier.

The results from the interlaboratory study show large variations in bias percentages between laboratories and within individual laboratories. For example, the average bias percentage for the six test compounds at the two loadings for both types of audit material for Laboratory A is -60 percent (range of -88 to -27 percent) compared to Laboratory C's average bias percentage of -5 percent (range of -33 to +21 percent).

The large range in the average bias percentages for test compounds within a particular laboratory may be attributed to the group of test compounds selected for the interlaboratory study. The individual compounds were selected with more emphasis placed on the class of compounds that they represent rather than the boiling point of the particular compound. Many cooperating laboratories indicated the need to modify their existing Method 0010 analytical procedures to accommodate low-boiling test compounds such as toluene (B.P. = 110°C), chlorobenzene (B.P. = 132°C), and tetrachloroethane (B.P. = 146°C).

The average measured loadings that were reported by the cooperating laboratories were used to calculate the between-laboratory variability. This value is defined as the relative standard deviation of the average measured loading among the five cooperating laboratories for each test compound/audit material/loading combination. The between-laboratory variabilities for the interlaboratory study are given in Table 2.

These values range from 10 to 68 percent (excluding the outlier) with an overall average value of 42 percent. In general, the between-laboratories variabilities are consistent across the various audit material/loading

Table 1. Mean Bias Percentage for Measured Loadings Interlaboratory Study

Carbotrap audit cartridge

Expected loading ($\mu\text{g}/\text{cartridge}$)		Cooperating laboratories and average bias percentage										
		A		B		C		D		E		
Compound	Low	High	Low	High	Low	High	Low	High	Low ^a	High	Low ^b	High
Pyridine	197	1,970	-64	-68	-19	-31	+5	+12	-63	-42	-4	-34
Toluene	174	1,740	-48	-88	-27	-56	+7	+13	+76	-59	-22	-29
o-Xylene	176	1,760	-58	-70	-19	-39	+1	+21	-45	-42	-23	-32
1,1,2,2-Tetra- chloroethane	319	3,190	-49	-69	-30	-43	+1	-4	-56	-27	-28	-46
Chlorobenzene	221	2,210	-76	-82	-13	-59	+7	+10	-51	-56	+13	-29
Nitrobenzene	241	2,410	-27	-46	-17	-27	-17	+4	-14	+32	-34	+7

XAD-2 resin audit cartridge

Expected loading ($\mu\text{g}/\text{cartridge}$)		Cooperating laboratories and average bias percentage										
		A		B		C		D		E		
Compound	Low	High	Low	High	Low	High	Low	High	Low	High	Low ^c	High
Pyridine	197	1,970	-52	-60	-20	-39	+20	+7	-42	-64	+306 ^d	+8
Toluene	174	1,740	-57	-83	-51	-66	-16	-27	-53	-71	+15	-23
o-Xylene	176	1,760	-53	-61	-30	-46	-13	-24	-44	-56	+19	-24
1,1,2,2-Tetra- chloroethane	319	3,190	-52	-63	-33	-46	-30	-33	-27	-48	+13	-33
Chlorobenzene	221	2,210	-71	-73	-53	-67	-15	-25	-52	-57	+36	-2
Nitrobenzene	241	2,410	-37	-44	-18	-35	-6	-20	-10	-2	+20	-25

^aOne of the three Kuderna-Danish evaporators went dry; data for this sample are not included in the calculations.

^bOne of three loaded cartridges was reported as "non detected"; data for this sample are not included in the calculations.

^cTwo of three loaded cartridges were reported as "sample lost"; the average percent bias is for a single sample.

^dFound to be an outlier at the 99-percent confidence level.

Table 2. Relative Standard Deviations for the Average Measured Loadings Between the Cooperating Laboratories in the Interlaboratory Study

Compound	Carbotrap audit cartridge		XAD-2 resin audit cartridge	
	Low	High	Low	High
Pyridine	47	42	43 ^a	49
Toluene	49	68	36	59
o-Xylene	33	48	38	30
1,1,2,2-Tetrachloroethane	32	40	33	22
Chlorobenzene	51	61	63	56
Nitrobenzene	10	32	23	21

^aThe single measured loading from Laboratory E is excluded as an outlier.

combinations and across the various test compounds. The mean relative standard deviations across the various audit material/loading combinations are given below:

<i>Audit material/loading combination</i>	<i>Mean RSD (%)</i>
Carbotrap/low loading	37
Carbotrap/high loading	48
XAD-2/low loading	41 ^a
XAD-2/high loading	40

^aExcluding the outlier.

The mean relative standard deviations across the various test compounds are given below:

<i>Test Compound</i>	<i>Mean RSD (%)</i>
Pyridine	45 ^a
Toluene	56
o-Xylene	37
1,1,2,2-Tetrachloroethane	32
Chlorobenzene	58
Nitrobenzene	22

^aExcluding the outlier.

The relative standard deviations for the three measured loadings within each laboratory are given in Table 3. These values are used to calculate the within-laboratory variabilities, which are defined as the mean relative standard deviation for each laboratory. These values ranged from 0 to 94 percent with an overall mean value of 22 percent. The minimum, maximum, and mean relative standard deviations for each laboratory are given below:

<i>Lab.</i>	<i>Relative standard deviation (%)</i>		
	<i>Min.</i>	<i>Max.</i>	<i>Mean</i>
A	9	94	49
B	2	20	8
C	0	31	11
D	7	54	23
E	0	82	19

In general, the relative standard deviations are consistent within each laboratory, but tend to differ between laboratories. Also, note that within-laboratory variabilities are less than the between-laboratories variability. The mean within-laboratory (i.e., 22 percent) is approximately one-half of the mean between-laboratories variability (i.e., 42 percent).

In 1984, EPA-Las Vegas published the results of an interlaboratory comparison study of methods for volatile and semivolatile compounds.(1) Nine laboratories participated in the study. Semivolatile compounds with boiling points up to 500°C were spiked onto five different waste samples. Each laboratory was requested to analyze three replicates of each waste sample. The semivolatiles were extracted from the waste samples with methylene chloride by sonification under neutral anhydrous conditions. They were analyzed by a GCMS with a fused silica capillary column. The high and low spike levels corresponded to those levels that would give approximately 50 and 10 nanograms (ng) of the semivolatile compounds on the gas chromatography column during analysis if 100-percent extraction recovery were achieved.

The relative standard deviation for the within-laboratory component was less than 30 percent, and the between-laboratories variability was about twice the value. The ranges of both components were 5 to 300 percent. It appears that the within-laboratory and between-laboratories variabilities from the current study generally agree with the corresponding values from the EPA-Las Vegas study.

Conclusions and Recommendations

The XAD-2 and Carbotrap audit materials have been studied with sufficient detail to conclude that they are ready to be used as routine quality assurance audit materials. In general, test compounds can be loaded onto and recovered quantitatively from these audit materials. Additional work will be needed to study the stability of specific test compounds and to study the use of these audit materials for test compounds with higher boiling points than those of this study.

The results of the interlaboratory study indicate that these audit materials can successfully determine the precision and accuracy of Method 0010. The general agreement between the results of this study and the EPA-Las Vegas study support this conclusion. The precision and accuracy of the method can be better defined if the interlaboratory study would be extended to additional laboratories and to additional test compounds.

It is recommended that EPA consider establishing precision and accuracy specifications for Method 0010 and consider using these audit materials on a

routine basis. Information derived by using these audit materials is an important component in assessing the performance of the emission test method, but should not be the sole criterion for acceptance of the emission test data.

Reference

1. Gurka, D. F. Project Summary. Inter-laboratory Comparison Study: Methods for Volatile and Semivolatile Compounds. Publication No. EPA/600/S4-84-027. U.S. Environmental Protection Agency, Las Vegas, Nevada. 1984. 7 pp.

Table 3. Relative Standard Deviations for Measured Loadings Within Each Cooperating Laboratory in the Interlaboratory Study

Carbotrap audit cartridge

Cooperating laboratories and percent relative standard deviations

Compound	A		B		C		D		E	
	Low	High	Low	High	Low	High	Low ^a	High	Low ^b	High
Pyridine	49	36	11	11	31	16	38	7	82	13
Toluene	62	47	12	11	20	8	36	25	37	5
o-Xylene	73	46	8	20	21	3	26	14	37	0
1,1,2,2-Tetra- chloroethane	31	32	9	3	24	7	25	29	18	17
Chlorobenzene	66	28	13	10	20	6	29	27	28	21
Nitrobenzene	24	19	9	9	9	0	8	15	0	13

XAD-2 resin audit cartridge

Cooperating laboratories and percent relative standard deviations

Compound	A		B		C		D		E	
	Low	High	Low	High	Low	High	Low	High	Low ^c	High
Pyridine	92	22	4	8	6	8	7	14	--	11
Toluene	73	9	2	9	10	5	16	30	--	17
o-Xylene	94	17	5	8	8	9	16	24	--	17
1,1,2,2-Tetra- chloroethane	89	17	5	3	7	10	28	13	--	11
Chlorobenzene	69	21	6	6	8	9	13	54	--	13
Nitrobenzene	68	13	8	4	11	11	38	21	--	6

^aOne of the three Kuderna-Danish evaporators went dry; data for this sample are not included in the calculations.

^bOne of the three loaded cartridges was reported as "none detected"; data for this sample are not included in the calculations.

^cTwo of three loaded cartridges were reported as "sample lost"; no relative standard deviation can be calculated.

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The complete report, entitled "Audit Materials for Semivolatile Organic Measurements During Hazardous Waste Trial Burns," (Order No. PB 90-239 971/AS; Cost: \$15.00, subject to change) will be available only from:

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