



## Project Summary

# Performance Testing of Method 1312-QA Support for RCRA Testing

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The question of how to access the risks associated with ground water contamination from soils containing toxic substances or wastes disposed of in a monofill environment is a critical issue for the U.S. Environmental Protection Agency (EPA). A major limitation of using Methods 1310 and 1311 for this purpose is the fact that the sanitary landfill co-disposal scenario does not apply to contaminated soils or wastes disposed of in a monofill environment. If these methods are used to assess sites for cleanup purposes, the acetic acid leaching fluid could selectively solubilize toxicants (specifically lead) and incorrectly classify the soil or waste as hazardous when, in fact, no mobilization (leaching) would be expected to occur in the environment. The EPA is considering the use of a newly-created synthetic acid precipitation leach test for soils and wastes (Method 1312) to provide information about the mobility (leachability) of both organic and inorganic contaminants present in these materials. This new test method is similar to the TCLP (Method 1311) except that the acetic acid buffer extraction fluid has been replaced by a dilute nitric acid/sulfuric acid mixture. This acid mixture simulates the nature of the precipitation occurring in the region where the soil sample originated. A pH 4.2 acid precipitation solution is used for extraction of wastes.

The purpose of the full report is to present results obtained from a precision evaluation of and ruggedness test for Method 1312 for soils only.

Several different soils were fortified with semi-volatile organics, metal salts and volatile organics, and then leached in replicates of 3 or 6 to determine method precision. A ruggedness evaluation was performed by making minor changes in specified method values to identify procedural variations requiring careful control.

*This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, 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 full report summarizes the quality assurance support provided to the Office of Solid Waste in FY-88 and FY-89 by the Quality Assurance and Methods Development Division, Environmental Monitoring Systems Laboratory-Las Vegas, Office of Research and Development, under D109 QO1, "QA Support for RCRA." The major activity conducted by the EMSL-LV under D109 QO1 was the evaluation of EPA Method 1312, a proposed synthetic acid precipitation leach test for soils and wastes.

The question of how to assess the risks associated with ground water contamination from soils containing toxic substances or wastes disposed of in a monofill environment is a critical issue for the EPA. The large number of samples needing analysis under legislative mandate requires that a leaching procedure be rapid, accurate, reproducible, rugged,

and suitable for a variety of matrices. A major limitation of using Methods 1310 and 1311 for this purpose is the fact that the sanitary landfill co-disposal scenario does not apply to contaminated soils or wastes disposed of in a monofill environment. If these methods are used to assess sites for cleanup purposes, the acetic acid leaching fluid could selectively solubilize toxicants (specifically lead) and incorrectly classify the soil or waste as hazardous when, in fact, no mobilization (leaching) would be expected to occur in the environment. The EPA is considering the use of a newly created synthetic acid precipitation leach test for soils and wastes (Method 1312) to provide information about the mobility (leachability) of both organic and inorganic contaminants present in these materials. This new test method is similar to the TCLP (Method 1311) except that the acetic acid buffer extraction fluid has been replaced by a dilute nitric acid/sulfuric acid mixture. This acid mixture is either pH 4.2 or 5.0, which simulates the nature of the precipitation occurring where the soil sample originated. A pH 4.2 acid precipitation solution is used for extraction of wastes.

The full report summarizes results obtained from a precision evaluation of and ruggedness test for Method 1312 for soils only. Several different soils were fortified with semi-volatile organic compounds, metal salts and volatile organic compounds, and then leached in replicates of 3 or 6 analyses to determine method precision. Minor changes were made in specified method values, and a ruggedness evaluation was performed to identify procedural variations requiring careful control.

## Experimental Design

### Extractable Compounds Procedure

Two different types of soil were used in the single laboratory (EMSL-LV, LESC) precision and ruggedness evaluation of the Method 1312 protocol: an eastern soil with high organic content and a western soil with low organic content (sandy type). These soils were first screened for background level and then fortified with selected TCLP target compounds at levels suitable for regulatory purposes. Refer to Table 2 for the amount of each extractable compound typically spiked into 100 grams of soil.

The spiked soil samples were leached according to the procedure described in Method 1312. Triplicate aliquots of the

eastern soil were leached using four different extraction fluids (pH 3.2, 4.0, 5.0, 6.1) to determine if the pH of the leaching fluid has a significant effect on either method precision or recovery. Triplicate aliquots of the western soil were spiked at two different analyte concentration levels, leached, and analyzed to obtain data on the matrix sensitivity of the method as well as its dynamic range.

A ruggedness evaluation was designed to determine the sensitivity of Method 1312 to modest departures from the leaching protocol which can be expected during routine application of the protocol. The ruggedness evaluation of Method 1312 for both volatile and non-volatile species was performed by following the test procedure of Youden and Steiner (Statistical Manual of the AOAC, 1975) which is designed to determine the level of significance for  $n$  variables using just  $n+1$  different measurements (in this case seven variables were chosen with eight experiments). For the semi-volatile compounds and the metals, the western soil was used for the ruggedness evaluation.

### Volatile Compounds Procedure

The single laboratory precision and ruggedness evaluation of Method 1312 for volatile organic compounds was performed by Acurex and Midwest Research Institute (MRI) as a single parallel laboratory study. Two contaminated soils originating in the western (Soil 1) and eastern (Soil 2) U.S. from Superfund sites and two soils prepared by combining a clean soil from Hayward, California with two different municipal sludges in the laboratory (identified as California Urban Soils 3 and 4) were used for the precision evaluation of Method 1312. These soil samples were analyzed to measure organic and inorganic contaminants in order to establish appropriate spiking levels for the fortification mixture containing 27 Method 1312 volatile target analytes. The fortified soils were leached in the ZHE and analyzed according to the procedure in Method 1312.

The California Model Urban Soils (Soils 3 and 4) were prepared by separately mixing clean Hayward, California soil (dried overnight at 120°C) with two municipal sludges from San Francisco Bay area sites. They were prepared to simulate a worst case soil that might be tested by Method 1312. Aliquots of 25 grams of Soils 3 and 4 were placed into a ZHE, then spiked directly with the ZHE piston up using 240  $\mu$ L of fortification solution containing 200  $\mu$ g/mL of 27 volatile analytes (Table 3). The ZHE was

assembled as quickly as possible and then was placed in a refrigerator at 4°C for 1 hour prior to the addition of leaching fluid. Following this equilibration period the sample was leached. The soil leachate was transferred to an evacuated Tedlar bag. Each bag was used to fill several VOA vials. These vials were capped and then immediately stored at 4°C until they were analyzed. The leachate was analyzed for volatile compounds by GC/MS (Method 8260). Soils 3 and 4 were leached in replicates of 6 analyses to obtain additional data to evaluate precision. For the Method 1312 ruggedness test for volatile compounds using the ZHE, the clean Hayward, California soil was used. Refer to Tables 6 and 7 for the variables and fortification levels.

## Results and Discussion

### Extractable Compounds Precision

The precision of Method 1312 was evaluated by measuring the repeatability of recovery of 14 semi-volatile organic compounds, lead and cadmium. Table 1 presents the data for an eastern soil, and Table 2 that for a western soil. The recovery determinations were made by fortifying soil samples prior to using the leaching procedure. The reported variability is a combination of that from the leaching test (Method 1312) and that from the analytical methods (Method 3250/8270 for organics and Method 6010 for inorganics). The variability of the organic analytical methods can be estimated from the RSDs (relative standard deviations) of the organic surrogate data; they are reported with the sample data. The organic surrogates added to the eastern soil leachate had recoveries greater than 60 percent and RSDs less than 9 percent while the recoveries for the semi-volatile analytes varied from 0 to 75 percent and the RSDs for analytes with reasonable recoveries ranged from 10 to 12 percent. The RSDs of the recoveries of most compounds reported in Table 1 are less than 10 percent. The precision of the Method 1312 recoveries for most compounds at all four pH values is similar to those of the GC/MS surrogate and is better than the precision obtained using Method 1311. Large (greater than 15 percent) RSDs were observed for 10 compounds. Three of these, 1,1-dichlorobenzene, 2,4-dimethylphenol, and 2,4-dinitrophenol, present analytical difficulties due to their volatility or reactivity. The fourth compound, hexachlorobenzene, had very low recovery and its ve

**Table 1. Method 1312 Precision Results from Eastern Soil<sup>a</sup>**

	Extraction Fluid pH									
	3.2		4.0		5.0		6.0		Method 1311	
	Avg. % Rec.	% RSD	Avg. % Rec.	% RSD	Avg. % Rec.	% RSD	Avg. % Rec.	% RSD	Avg. % Rec.	% RSD
<b>FORTIFIED ANALYTES</b>										
<i>bis(2-chloroethyl)-ether</i>	75.6	9.5	80.2	12.5	69.4	5.7	71.1	6.0	56.6	14.7
<i>2-Chlorophenol</i>	61.4	8.8	62.5	6.8	52.1	9.1	57.2	9.5	42.5	15.5
<i>1-4-Dichlorobenzene</i>	15.8	5.3	17.2	12.3	16.0	10.1	15.3	12.3	7.9	11.7
<i>1-2-Dichlorobenzene</i>	11.5	20.2	11.3	8.0	9.9	12.1	11.0	21.5	8.2	5.8
<i>2-Methylphenol</i>	47.6	9.9	47.3	7.7	40.4	7.6	43.5	12.6	40.8	14.4
<i>Nitrobenzene</i>	72.9	2.3	80.4	10.0	66.9	4.3	65.5	4.3	45.2	12.8
<i>2,4-Dimethylphenol</i>	12.3	9.1	13.7	18.4	8.4 <sup>b</sup>	0.4	7.8	3.8	3.8	27.5
<i>Hexachlorobutadiene</i>	1.2	3.5	1.5	12.9	1.2	5.8	1.2	13.4	0.3	22.4
<i>Acenaphthene</i>	4.9	1.0	5.7	8.1	5.2	6.6	4.7	10.5	1.7	10.9
<i>2,4-Dinitrophenol</i>	60.4	16.3	68.9 <sup>b</sup>	6.1	56.7	10.4	46.8	13.1	20.8	70.9
<i>2,4-Dinitrotoluene</i>	57.5	3.9	60.4	5.4	52.7	5.6	49.8	3.3	27.7	10.8
<i>Hexachlorobenzene</i>	0.1	42.5	0.2	12.0	0.1	43.3	0.1	0.0	0.0	
<i>γ-BHC</i>	3.4 <sup>b</sup>	9.4	3.1	16.3	3.6	17.7	2.8 <sup>b</sup>	12.1	5.0	22.3
<i>β-BHC</i>	5.3	8.5	5.4	13.3	5.5	2.9	4.8	2.4	4.0	18.2
<b>METALS</b>										
<i>Lead</i>	3.2 <sup>b</sup>	3.6	1.4	4.3	1.3	31.4	1.5	16.1	6.3 <sup>b</sup>	0.0
<i>Cadmium</i>	55.7	1.5	38.7	2.3	33.5	18.8	30.3	16.8	37.4	7.5
<b>SURROGATES (in Leachate)</b>										
<i>2-Fluorophenol</i>	62.0	5.3	65.8	6.5	58.2	2.5	59.3	4.1		
<i>d<sub>5</sub>-Phenol</i>	77.0	6.2	83.3	5.4	71.7	1.5	70.1	2.9		
<i>d<sub>5</sub>-Nitrobenzene</i>	64.5	3.2	71.8	8.3	65.5	4.4	62.5	1.5		
<i>2-Fluorobiphenyl</i>	62.0	3.7	70.1	8.4	59.1	4.0	60.5	6.9		
<i>2,4,5-Tribromophenol</i>	68.8	7.6	71.6	5.1	58.1	6.6	56.4	3.2		
<i>d<sub>14</sub>-D-Terphenyl</i>	89.3	8.6	97.9	6.7	80.5	2.8	77.1	6.8		

<sup>a</sup>Triplicate analyses.

<sup>b</sup>Duplicate analyses: one value was rejected as an outlier at the 90% confidence level using the Dixon Q test.

large RSD, in part, is the result of measurements made near the quantitation limit of Method 8270.

In general, semi-volatile analyte recoveries were lower and the RSDs were higher for the western soil than for the eastern soil. This appears to be related to the extraction and measurements steps since the RSDs of the organic surrogates added to the soil leachate were also higher for the western soil. The eastern (high organic content clay) and western (low organic content sand) soils are considerably different and thus the matrix sensitivity suggested is reasonable and is consistent with previous TCLP work. In Table 2, the surrogate RSDs vary from 7 to 63 percent and the semi-volatile analyte RSDs range from 6 to 55 percent for the western soil. Thus, the analytical variability of Methods 3520/8270 is comparable to the total variability of the leaching procedure. The precision data reported for the western soil is in general agreement with that of a prior precision valuation of the TCLP (Method 1311) for extractable components. In the TCLP

precision study, RSDs for replicate leachings were usually less than 30 percent. The precision results for the eastern soil are much better than those of the previous TCLP study.

The recovery of lead from both the eastern and the western soils was very low and the precision was poor. The large RSDs are, in part, the result of the fact that analytical measurements were made near the quantitation limit of Method 6020 (ICP/MS). Cadmium had reasonable recovery (30 to 56 percent) from the eastern soil and its replicate leaching had recovery RSDs less than 20 percent. Cadmium recovery was only 4 to 9 percent from the western soil. The precision (variability) of the triplicate leachings of cadmium was much greater for the western soil (63 percent RSD versus 2.3 percent RSD at pH 4.0). Thus, cadmium showed a greater sensitivity to soil type in these experiments than did lead.

Both cadmium and lead recoveries are sensitive to the pH of the leaching fluid. Lead recovery is significantly greater when the pH 3.0 leaching fluid is used,

although all of the lead recovery values are low (1.3 to 3.2 percent). Cadmium recovery is also greater when low pH leaching fluid is used, but it varies over a greater range than lead (30 to 56 percent). The method precision for both metals is worst when the recoveries are lowest. Interestingly, lead recovery was low and only moderately higher when Method 1311 was used to leach the fortified eastern soil; this is in contrast to the results obtained in a recent inter-laboratory study that showed dramatically higher lead recoveries with Method 1311. The reason for this difference is not known, but points out the need for further study on the sensitivity of leaching methods to soil type as well as to the metal species presented in the sample.

In contrast to results for the metals, the pH of the leaching fluid has little effect on either the recovery or the precision (variability) of replicate leachings for semi-volatile organic compounds. Periodic monitoring of the pH of the fluid during the leaching showed that the pH of the fluid changed negligibly after the first

**Table 2. Method 1312 Precision Results from Western Soil**

	Amount Spiked (µg)	pH = 4.2 High Spiking Level		pH = 5.0 Low Spiking Level <sup>c</sup>	
		Avg. % Rec. <sup>a</sup>	% RSD	Avg. % Rec. <sup>a</sup>	% RSD
<b>FORTIFIED ANALYTES</b>					
bis(2-chloroethyl)-ether	1040	45.1	13.7	59.2	14.2
2-Chlorophenol	1620	58.9	28.6	32.4	54.9
1,4-Dichlorobenzene	2000	12.8	11.8	13.6	34.6
1,2-Dichlorobenzene	8920	15.0	6.0	17.0	28.4
2-Methylphenol	3940	40.5	12.2	28.6	32.6
Nitrobenzene	1010	36.1	14.6	45.2	21.3
2,4-Dimethylphenol	1460	3.6	23.3	1.2	87.6
Hexachlorobutadiene	6300	2.5	17.0	4.5	22.8
Acenaphthene	3640	22.2	20.6	8.4 <sup>b</sup>	7.7
2,4-Dinitrophenol	1300	20.5	-	1.8 <sup>b</sup>	15.7
2,4-Dinitrotoluene	1900	61.6	30.1	30.8	54.4
Hexachlorobenzene	1840	0.2	41.8	0.8	173.2
γ-BHC	7440	21.2	23.8 <sup>b</sup>	16.6	55.2
β-BHC	640	13.2	33.7	10.2	51.7
<b>METALS</b>					
Lead	5000	0.3	27.0	0.2	51.7
Cadmium	1000	4.4	63.0	9.1	71.3
<b>SURROGATES (In Leachate)</b>					
2-Fluorophenol	200	65.1	7.5	34.4	60.6
d <sub>5</sub> -Phenol	200	93.5	10.4	51.7	62.7
d <sub>5</sub> -Nitrobenzene	100	41.4	52.4	46.4	10.6
2-Fluorobiphenyl	100	44.0	42.1	36.8	15.6
2,4,5-Tribromophenol	200	68.0	10.3	50.7	57.1
d <sub>14</sub> -D-Terphenyl	100	100.1	8.1	87.7	13.6

<sup>a</sup>Triplicate analyses.

<sup>b</sup>Duplicate analyses; one value was rejected as an outlier at the 90% confidence level using the Dixon Q test.

<sup>c</sup>The low spiking level was 0.20 times the high spiking level.

hour of the 18-hour leaching period. The final leachate pH of all the eastern soil samples was nearly the same (pH 4.57 to pH 4.64) for the pH 4, 5 and 6 fluids and was thus unaffected by the initial pH of the leaching fluid. The final leachate pH was low (pH 4.14) when pH 3.2 fluid was used. This might be partly responsible for the higher recovery observed for the metals with low pH leaching fluid.

### Volatile Compounds Precision

The precision of Method 1312 was evaluated by measuring the repeatability of recovery of 27 volatile organic compounds using four different types of soil. A summary of the precision data for these compounds is presented in Table 3. Soil 1 was collected at a Superfund site west of the Mississippi River and Soil 2 came from a Superfund site in the eastern United States. Excluding isobutanol, a polar water soluble compound with known purging difficulties, the average recoveries for the target analytes ranged from 10 percent to 85 percent for

Soil 1 and ranged from 7 percent to 89 percent for Soil 2. Twenty-two of the 26 (85 percent) analytes for Soil 1 and 17 of 26 (65 percent) analytes for Soil 2 had RSDs less than 20 percent. Only four analytes had RSDs greater than 50 percent; these analytes present significant analytical difficulties during the purge-and-trap GC/MS analysis (Method 8260). Vinyl chloride and the Freons are extremely volatile and are not trapped efficiently; acrylonitrile is water soluble and does not purge well. In general, recoveries were lower and RSDs were higher from the eastern soil than from the western soil. This matrix sensitivity appears most pronounced for carbon tetrachloride, ethylbenzene, tetrachloroethene, Freon 13 (trichlorofluoromethane) and Freon 113 (1,1,2-trichloro-trifluoroethane).

In general, replicate leachings of the sludge-contaminated soils (Soils 3 and 4 in Table 3) exhibited greater variability (larger RSD) than those of the Superfund soils (Soils 1 and 2). For Soil 3, 20 of the 27 volatile analytes had RSD values between 28 percent and 42 percent and 5

of the target analytes had RSDs greater than 50 percent. Ethyl acetate display highly variable recoveries ranging from to 50 percent, its lack of precision probably reflects the known difficulties associated with purging polar compounds from water. The sludge sample used to prepare Soil 3 contained acetone (120 ppm) which resulted in an apparent high recovery (116 percent) for acetone. For Soil 4, 19 of 27 volatile analytes had RSDs between 24 and 41 percent for only two compounds, both polar, ethyl acetate and acetone, had RSD values greater than 50 percent.

Three volatile surrogate compounds were spiked into the leachates of Soils 4 just prior to analysis by Method 8260. Surrogate recoveries were consistently high (greater than 90 percent with RSD less than 6 percent) and indicated that the purge-and-trap and GC/MS system used in the volatile analyses were performing satisfactorily. The Method 1312 precision data reported for Soils 1 and 2 is in general agreement with that reported in a previous precision evaluation of the TCLP (Method 1311). The RSDs reported in the TCLP study generally ranged from 3 percent to 20 percent for three different types of waste; volatile compound recoveries were found to be matrix and compound dependent.

### Ruggedness

The minor procedural variations used in the AOAC type ruggedness evaluation of Method 1312 for semi-volatile compounds and metals are listed in Table 4. Two levels of each experimental condition are assigned capital and lower case letters and are varied in the manner shown in the matrix given in Table 4. The group differences calculated from the recovery results are shown in Table 5. Columns V<sub>a</sub>, V<sub>c</sub>, and V<sub>d</sub>, nearly all group difference values have the same significance generally this indicates possible significance of the column variable. Usually a difference which is more than twice the standard deviation of the analytical methods is significant and should be further studied. Most values in Column V<sub>a</sub> are negative, which implies that the extractable compounds had greater recovery with pH 5.0 leaching fluid than with pH 4.2 fluid. However, since all the differences in Column V<sub>a</sub> of Table 6 are less than twice the analyte standard deviations calculated from the RSDs and recoveries given for the western soil in Table 2, the V<sub>a</sub> group differences are insignificant and careful control of leaching fluid pH does not appear to

**Table 3. Method 1312 Precision Results on Volatile Compounds**

Compound Name	Soil No. 1		Soil No. 2		Soil No. 3		Soil No. 4	
	Avg. % Rec. <sup>a</sup>	% RSD	Avg. % Rec. <sup>a</sup>	% RSD	Avg. % Rec. <sup>b</sup>	% RSD	Avg. % Rec. <sup>c</sup>	% RSD
Acetone	44.0	12.4	43.8	2.25	116.0	11.5	21.3	71.4
Acrylonitrile	52.5	68.4	50.5	70.0	49.3	44.9	51.8	4.6
Benzene	47.8	8.29	34.8	16.3	49.8	36.7	33.4	41.1
n-Butyl alcohol (1-Butanol)	55.5	2.91	49.2	14.6	65.5	37.2	73.0	13.9
Carbon disulfide	21.4	16.4	12.9	49.5	36.5	51.5	21.3	31.5
Carbon tetrachloride	40.6	18.6	22.3	29.1	36.2	41.4	24.0	34.0
Chlorobenzene	64.4	6.76	41.5	13.1	44.2	32.0	33.0	24.9
Chloroform	61.3	8.04	54.8	16.4	61.8	29.1	45.8	38.6
1,2-Dichloroethane	73.4	4.59	68.7	11.3	58.3	33.3	41.2	37.8
1,1-Dichloroethene	31.4	14.5	22.9	39.3	32.0	54.4	16.8	26.4
Ethyl acetate	76.4	9.65	75.4	4.02	23.0	119.8	11.0	115.5
Ethylbenzene	56.2	9.22	23.2	11.5	37.5	36.1	27.2	28.6
Ethyl ether	48.0	16.4	55.1	9.72	37.3	31.2	42.0	17.6
Isobutanol (4-Methyl-1-propanol)	0.0	NA	0.0	NA	61.8	37.7	76.0	12.2
Methylene chloride	47.5	30.3	42.2	42.9	52.0	37.4	37.3	16.6
Methyl ethyl ketone (2-Butanone)	56.7	5.94	61.9	3.94	73.7	31.3	40.6	39.0
Methyl isobutyl ketone	81.1	10.3	68.9	2.99	58.3	32.6	39.8	40.3
1,1,1,2-Tetrachloroethane	69.0	6.73	41.1	11.3	50.8	31.5	36.8	23.8
1,1,2,2-Tetrachloroethane	85.3	7.04	58.9	4.15	64.0	25.7	53.6	15.8
Tetrachloroethene	45.1	12.7	15.2	17.4	26.2	44.0	18.6	24.2
Toluene	59.2	8.06	49.3	10.5	45.7	35.2	31.4	37.2
1,1,1-Trichloroethane	47.2	16.0	33.8	22.8	40.7	40.6	26.2	38.8
1,1,2-Trichloroethane	76.2	5.72	67.3	8.43	61.7	28.0	46.4	25.4
Trichloroethene	54.5	11.1	39.4	19.5	38.8	40.9	25.6	34.1
Trichlorofluoromethane	20.7	24.5	12.6	60.1	28.5	34.0	19.8	33.9
1,1,2-Trichlorotrifluoroethane	18.1	26.7	6.95	58.0	21.5	67.8	15.3	24.8
Vinyl chloride	10.1	20.3	7.17	72.8	25.0	61.0	11.8	25.4

<sup>a</sup>Triplicate analyses.

<sup>b</sup>Six replicate analyses.

<sup>c</sup>Five replicate analyses.

**Table 4. Variables Selected for Method 1312 Ruggedness Test on Semi-Volatile Compounds**

Parameter	Type	Rug 1	Rug 2	Rug 3	Rug 4	Rug 5	Rug 6	Rug 7	Rug 8
pH	A, a	A	A	A	A	a	a	a	a
Extraction time	B, b	B	B	b	b	B	B	b	b
Particle size	C, c	C	c	C	c	C	c	C	c
Extractor	D, d	D	D	d	d	d	d	D	D
Liquid/Solid Ratio	E, e	E	e	E	e	e	E	e	E
Temperature	F, f	F	f	f	F	F	f	f	F
Filter	G, g	G	g	g	G	G	G	G	g

A = 4.2 pH

a = 5.0 pH

B = 18 hr

b = 16 hr

C = not reduced

c = reduced (grinded)

D = standard vessel

d = bottle

E = ratio = 20 (2000 mL H<sub>2</sub>O/100g)

e = ratio = 16 (1600 mL H<sub>2</sub>O/100g)

F = Ambient approx. 77°F (25°C)

f = 60 - 65°F (16-18°C)

G = one filter

g = two filters

**Table 5. Ruggedness Test Results - Group Differences for Semi-Volatile Test Compounds**

Fortified Analytes	V <sub>a</sub>	V <sub>b</sub>	V <sub>c</sub>	V <sub>d</sub>	V <sub>e</sub>	V <sub>f</sub>	V <sub>g</sub>
bis (2-Chloroethyl)ether	-2.70	1.75	-2.20	6.40	-0.35	2.90	-1.55
2-Chlorophenol	-10.92	-4.77	-8.08	0.23	-5.88	-3.93	2.27
1,4-Dichlorobenzene	-2.52	1.77	-1.07	4.88	-0.67	-1.08	-2.77
1,2-Dichlorobenzene	-4.40	1.90	-2.70	4.80	-0.30	-1.50	-4.90
2-Methylphenol	-4.20	-0.05	-7.90	2.40	2.05	0.40	0.15
Nitrobenzene	-1.72	2.87	-3.03	4.22	1.03	1.23	-0.82
2,4-Dimethylphenol	1.00	0.25	-3.55	0.95	0.15	1.30	0.30
Hexachlorobutadiene	-2.25	-0.60	0.70	1.00	0.50	2.25	-0.45
Acenaphthene	-3.70	2.30	-2.05	7.05	-2.10	5.50	-2.25
2,4-Dinitrophenol	-22.35	-6.15	-24.70	5.90	-21.95	-0.15	5.00
2,4-Dinitrotoluene	-4.90	0.40	-2.75	1.65	2.10	4.00	-4.75
Hexachlorobenzene	0.00	0.05	0.10	-0.05	-0.00	0.15	0.05
γ-BHC	-4.68	-1.88	-0.97	2.68	3.47	3.97	-0.97
β-BHC	-2.15	-6.35	6.30	-5.60	8.55	4.05	1.20
Lead	0.20	-0.20	0.0	-0.55	-0.10	0.10	-0.10
Cadmium	-3.6	-0.80	7.7	-1.85	-5.42	-2.08	-3.30

a critical parameter for Method 1312. A similar comparison of analyte method precision with the mostly small differences given in Columns V<sub>c</sub> and V<sub>d</sub> leads to the same conclusion for the experimental parameters, particle size reduction and extractor vessel type. The other four variables, extraction time, liquid solid ratio, extraction temperature, and number of filters used, do not appear to affect the performance of Method 1312. Since none of the seven variables tested is a critical parameter, Method 1312 appears rugged for the leaching of semi-volatile compounds and metals. These results concur with a previous ruggedness evaluation that demonstrated the TCLP to be "fairly rugged" for the semi-volatile organic analytes which were unaffected by variables B, D, and E in Table 4 in addition to the parameters: (a) headspace amount, (b) medium acidity, (c) acid washing of filter, and (d) filter type. It is interesting to note that the EPA had previously intended to investigate extraction temperature but was unable to do so due to a lack of the laboratory equipment necessary to vary the temperature. This study addressed this issue and determined that extraction temperature is not a critical method parameter for the leaching of semi-volatile organic compounds and metals.

The variables chosen for evaluation in the ruggedness test of Method 1312 for volatile organics are listed in Tables 6 and 7. Variables C and G are not method parameters, per se; they were chosen to determine the effect of analyte concen-

tration upon compound recovery and to determine the effect of buffering the leaching fluid. The group differences calculated from the recovery results are given in Table 8. Since the differences in columns V<sub>a</sub>, V<sub>d</sub>, and V<sub>e</sub> are generally small (absolute value less than 5) and of random sign, the variables leaching fluid pH, leaching fluid liquid/solid ratio, and extraction time, do not exhibit an observable effect on analyte recoveries and, thus, are not critical parameters for Method 1312. Due to the large magnitude of many values and the general uniformity of value sign, the variables associated with Columns V<sub>b</sub>, V<sub>c</sub>, and V<sub>g</sub> may be significant. Particle size reduction (Column V<sub>f</sub>) generally resulted in increased recoveries for the more highly volatile compounds. Smaller soil particle size probably decreases compound volatility loss during the soil spiking step by facilitating adsorption of the fortified compounds by increasing the surface area of the soil particles. As grinding a soil sample would increase the loss of environmentally incorporated analytes, particle size reduction should not be considered a critical method parameter in the leaching of real soil samples. Addition of 0.1M acetate buffer (Column V<sub>g</sub>) adversely affected recoveries of virtually all the volatile compounds studied. This effect is probably the result, in large part, of chromatographic analysis difficulties caused by the loading of acetic acid onto the capillary GC column and/or into the purge and trap system used in Method 8260. Fortifying the soil at lower

concentration (i.e., 1 ppm versus 4 ppr yielded better overall recoveries (Column V<sub>c</sub>) for the more highly volatile compounds. This higher recovery may be related to limited analyte solubility in the purge vessel and/or could result from less compound loss during the soil spiking step. Interestingly, the only experimental parameter of importance appears to be the type of ZHE used. The Millipore ZHE gave higher recovery than the Associated Design ZHE for nearly all the organic compounds. This result is surprising given our experience with leakage difficulties associated with use of the Millipore ZHE and is in contrast with the results of a previous ruggedness evaluation of the TCLP for volatile compounds. In that study, the only critical parameter identified was the type of ZHE; the Millipore ZHE produced lower analyte recoveries than the Associated Design ZHE and had notable leakage problems. The reason for this major discrepancy is not known but it may be related to operator experience with the different ZHE devices in the different laboratories.

## Recommendations

Method 1312 is suitable for the characterization of soil samples. However, additional information on the performance of the method as a model for the mobility of toxicants in the environment is required. It is recommended that studies be conducted to: measure the mobility of different lead- and mercury containing compounds in the soil; compare the mobility of toxicants in soil columns with Method 1312 mobility; and develop specific performance data for SW-846 methods (i.e., Method 8150 and Method 8081) when they are used to analyze Method 1312 leachates.

## Conclusions

Method 1312 is a reasonably rugged and precise method that can be used to address the mobility of pollutants in soil samples. The performance of Method 1312 for leaching organic compounds was very similar to that of Method 1311 (TCLP). Method 1312 was less efficient at leaching cadmium and lead than was Method 1311.

**Table 6. Variables Selected for Method 1312 Ruggedness Testing for Volatile Compounds**

Variable	Upper case (A)	Lower case (a)	Experiment Number							
			1	2	3	4	5	6	7	8
Extraction fluid pH	4.1	4.3	A	A	A	A	a	a	a	a
ZHE apparatus	MP	AD	B	B	b	b	B	B	b	b
Analyte soil conc.*	0.8 ppm	4 ppm	C	c	C	c	C	c	C	c
Extraction time	20 hrs	16 hrs	D	D	d	d	d	d	D	D
Liquid/solid ratio	22:1	18:1	E	e	E	e	e	E	e	E
Particle size reduction	with	without	F	f	f	F	f	f	F	F
Buffer addition	with	without	G	g	g	G	g	G	G	g
% Recovery of analytes			s	t	u	v	w	x	y	z

\*Fortified soil nominal concentration level. Refer to Table 7 for experiment dependent fortification levels.

Abbreviations: MP: Millipore AD: Associated Design ppm: mg/kg

**Table 7. Soil Fortification Levels for Ruggedness Experiments**

Variable Combination	Solid/Liquid Ratio	Sample grams	Leachate mL	Spike Level mg/kg	Max. Leachate Conc. µg/kg
C E	1:22	22	484	0.88	40
c E	1:22	22	484	4.40	200
C e	1:18	22	396	0.72	40
c e	1:18	22	396	3.60	200

**Table 8. Ruggedness Test Results for Method 1312 Group Differences for Volatile Test Compounds**

Compound Name	Conditions						
	V <sub>a</sub>	V <sub>b</sub>	V <sub>c</sub>	V <sub>d</sub>	V <sub>e</sub>	V <sub>f</sub>	V <sub>g</sub>
Chloromethane	-6	13	16	0	0	12	-18
Bromoethane	1	11	20	2	6	8	-12
Vinyl chloride	-9	11	14	0	-3	11	-11
Chloroethane	-7	24	23	-8	-1	18	-38
Methylene chloride	-2	34	69	-7	8	26	-45
Acetone	7	76	119	40	30	87	37
Carbon disulfide	-5	12	19	5	3	10	-15
1,1-Dichloroethane	-6	11	13	4	1	13	-14
1,1-Dichloroethane	0	15	19	6	6	8	-20
trans-1,2-Dichloroethane	-5	13	18	7	4	8	-15
Chloroform	1	17	29	4	6	6	9
1,2-Dichloroethane	5	3	8	0	1	3	-2
2-Butanone	8	-3	11	9	6	-1	20
1,1,1-Trichloroethane	1	5	7	-1	0	14	-6
Carbon Tetrachloride	-1	4	6	-1	1	13	-6
Bromodichloromethane	7	3	9	3	3	6	-1
1,1,2,2-Tetrachloroethane	3	3	5	-2	4	-1	-2
1,2-Dichloropropane	8	7	5	2	-1	5	-10
cis-1,3-Dichloropropene	8	3	6	3	5	5	1
Trichloroethene	1	3	4	1	2	6	-3
Dibromochloromethane	1	2	7	1	4	2	2
1,1,2-Trichloroethane	3	1	7	0	4	5	-1
Benzene	3	6	9	1	3	6	-1
trans-1,3-Dichloropropene	8	4	4	1	4	6	-3
Bromoform	-1	2	3	-2	5	-2	-1
4-Methyl-2-pentanone	31	38	-27	-20	40	28	58
Tetrachloroethene	1	2	2	2	2	3	-1
Toluene	4	4	9	1	3	5	-3
Chlorobenzene	2	1	7	2	4	0	-1
Ethylbenzene	4	3	6	4	3	4	-5
Styrene	-1	-1	6	3	2	-6	-4

Table 8. (continued)

Compound Name	Conditions						
	V <sub>a</sub>	V <sub>b</sub>	V <sub>c</sub>	V <sub>d</sub>	V <sub>e</sub>	V <sub>f</sub>	V <sub>g</sub>
p-Xylene	1	2	5	5	1	-1	-2
o-Xylene	0	2	9	2	3	-1	-2
1,4-Dichlorobenzene	-1	-1	4	4	1	-6	2
Trichlorofluoromethane	-7	10	9	2	-1	17	-13
Acrylonitrile	10	13	4	2	17	1	-8
n-Butanol	0	0	0	0	0	0	0
Ethyl acetate	11	-5	8	-12	16	-20	29
Ethyl ether	7	5	-2	-2	5	7	0
Isobutanol	0	0	0	0	0	0	0
1,1,2-Trichlorotrifluoroethane (Freon-113)	-7	10	9	1	-3	15	-12
1,1,1,2-Tetrachloroethane	2	4	6	-1	4	3	-4

NOTE: n-Butanol and isobutanol were not recovered in any of the ruggedness experiments.

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The complete report, entitled "Performance Testing of Method 1312-QA Support for RCRA Testing," (Order No. PB 89-224 901/AS; Cost: \$21.95, subject to change) will be available only from:

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