



Empore™

Extraction Disks

January 1996

Method Summary

SW-846 Method 3535 Solid Phase Extraction Test Methods for TCLP Leachates

A solid-phase extraction disk method (Method 3535) has been validated for extraction of the semivolatile organic analytes from Method 1311 Toxicity Characteristic leachates. The validation data have been reviewed and accepted by the EPA SW-846 Workgroup and are scheduled for inclusion in the proposed 4th Update to SW-846 (anticipated early 1996). Copies of the draft method are available from the Methods Section Office at (202) 260-4761, until the time they are proposed officially by an announcement in the Federal Register.

Once accepted by the workgroup, draft methods may be used in most RCRA applications – the only exceptions being those analyses for which the use of SW-846 methods is mandatory. Applications considered “mandatory” are: hazardous waste characterizations, delisting programs, characterization of free liquids, emissions monitoring from trial burns, and determining air emissions from process equipment. This method pertains to the first two of these applications in which the solids are subjected to acidic buffers to “leach” potentially toxic materials which are then quantified. The leachate preparation must follow Method 1311; the sample preparation of that leachate for the semi-volatiles analyses can be done by any reliable method (including the proposed method 3535, which is detailed herein) according to EPA sources. Technical questions regarding specific RCRA applications and methods can be directed to the EPA Methods Information Communication Exchange (MICE) at (703) 821-4690.

This method summary is an extension of the Method 3535 application note. As additional analyte groups or matrices are validated by this method, specific conditions will be outlined in a similar document.

Method Summary

TCLP leachates are prepared according to the procedure outlined in EPA Method 1311. The leachates are filtered with 0.6-0.8 micron glass fiber filters as directed in the method, and specific aliquots are prepared for each of the semivolatile organic analyte groups: organochlorine pesticides, herbicides, base/neutral and acid extractables. For each analyte group, a measured volume of sample is extracted using a 3M Empore™ Extraction Disk with SDB-XC (47mm). With the exception of the acid herbicides (extracted at pH 1.0), all other analytes were extracted without modifying the buffer pH. The analytes are eluted with acetone/ethyl acetate (acid herbicides with acetonitrile), dried with sodium sulfate, and concentrated or diluted to the desired final volume for analysis by the determinative method.

TCLP Validation Study

The validation data summarized herein were generated in a single laboratory by a single operator. Multiple operator data and two additional laboratories’ data sets were submitted to the EPA in the validation data package.

Buffer solutions were prepared according to EPA Method 1311. With the exception of the acid herbicides fraction, all samples were extracted without pH modification. The buffers (Buffer #1 pH = 2.88, Buffer #2 pH = 4.93) were spiked as is at low and high levels, and recoveries were determined for evaluation of the extraction efficiency. Soils were then leached with each buffer as per Method 1311, and the leachates

fortified at both low and high levels to assess matrix effect on extraction efficiency. A third data set was generated using soils containing ethylene glycol at 1% and 10% levels. The leachates from these soils were spiked with the analytes of concern at action levels to determine the efficacy of extraction in the presence of other organic matter. (See *Fortification Levels* below.)

Fortification Levels:

	Low mg/L	Action mg/L	High mg/L		Low mg/L	Action mg/L	High mg/L
<u>Organochlorine Pesticides</u>				<u>Base/Neutral Extractables</u>			
Toxaphene	0.25	0.5	1.0	1,4-Dichlorobenzene	3.75	7.5	15.0
Chlordane	0.015	0.03	0.06	2,4-Dinitrotoluene	0.065	0.13	0.26
Endrin	0.01	0.02	0.04	Hexachlorobenzene	0.065	0.13	0.26
Heptachlor ¹	0.004	0.008	0.16	Hexachlorobutadiene	0.25	0.5	1.0
Lindane	0.2	0.4	0.8	Hexachloroethane	1.5	3.0	6.0
Methoxychlor	5.0	10.0	20.0	Pyridine	2.5	5.0	10.0
				<u>Acid Extractables</u>			
<u>Acid Herbicides</u>				Cresol ¹ (o,m,p-)	100	200	400
2,4-D	5.0	10.0	20.0	2,4,5-trichlorophenol	200	400	800
2,4,5-TP	0.5	1.0	2.0	2,4,6-trichlorophenol	1.0	2.0	4.0
				Pentachlorophenol	50	100	200

¹Heptachlor/Heptachlor Epoxide and the cresols were spiked in the combined totals indicated.

Methods

Organochlorine Pesticides

- 1. Prepare Sample.** Measure a **250 mL** aliquot of the leachate and set aside. The validation data were generated without modifying pH of the leachates.
- Using a 6-place stainless steel manifold, place a 47mm SDB-XC disk on the glassware base. Wet the disk with acetone (about 1 ml) to preswell this polymer material. Place the reservoir atop the base and clamp in place. The vacuum source should be capable of pulling about 20-25 inches Hg.
- 3. Prewash.** Add about 5 mL acetone to the reservoir, rinsing down the sides in the process. This should be done with a receiving vial in the reservoir to capture the waste solvent. Turn on the vacuum momentarily until a few drops of solvent are seen coming through the disk, then release the vacuum and allow the solvent to soak for one minute. Resume the vacuum to draw all of the solvent through the disk, and allow to air-dry with vacuum on. Repeat the prewash with 5 mL ethyl acetate. Remove the receiving vial and dispose of the solvent as appropriate.
- 4. Condition.** Add 5 mL methanol to the reservoir. Apply vacuum until a few drops appear below the disk, then release the vacuum. Allow the disk to soak for about 1 minute. From this point until the extraction is completed, it is critical to leave a layer of liquid atop the disk to keep the sorbent from drying and returning to a hydrophobic state. Apply vacuum and draw the methanol level down until 1-2 mm remain atop the disk.
5. Add about 15 mL reagent water to the remaining methanol in the reservoir. Apply vacuum and again draw through most of the water – leaving about 2-3mm of water above the disk.

6. **Extraction.** Add the 250 mL leachate sample to the remaining water in the reservoir and turn on the vacuum. Allow the entire sample to filter. Allow the disk to air-dry with the vacuum on after the sample extraction has been completed.
7. Add 4 mL of acetone to the sample bottle that contained the spiked leachate. Swirl thoroughly to dissolve any residue which might be adsorbed to the container. Set aside.
8. **Elution.** With a receiving vial in place, transfer the acetone from the sample bottle to the reservoir, rinsing down the sides in the process. Add an additional 2 mL acetone, rinsing down the sides of the reservoir. Allow to soak for 1 minute. Apply vacuum momentarily until a drop appears on the drip tube, then release the vacuum. Allow to soak for one minute, then turn on full vacuum and draw all of the acetone through and into the receiving vial.
9. Repeat the bottle rinse and elution in the above step using 5 mLs ethyl acetate.
10. Add a second 5 mL aliquot of ethyl acetate directly to the reservoir, rinsing down the sides. Collect all the aliquots in the same receiving vial.
11. Remove the elution-receiving vial from the manifold. Dry the solvent with anhydrous granular sodium sulfate. Transfer solvent to glassware suitable for the concentration step. Rinse the sodium sulfate twice with additional ethyl acetate and add the solvent to the concentrator tube.
12. Proceed to concentration step followed by analysis as per Method 8081 or equivalent.

Base/Neutral and Acid Extractables

Base/Neutral Fraction:

1. **Prepare sample.** Measure a 250 mL aliquot of leachate and set aside. The pH was not adjusted for the validation studies.

The extraction procedure is identical to that of the OCP's detailed above. The buffers were extracted as is, with no pH adjustment or other modifiers.

Acid Fraction:

1. **Prepare sample.** Measure a 25 mL aliquot of leachate and set aside. These should be extracted without pH adjustment.

The extraction for this fraction is, again, the same as the OCP method.

Eluants may be combined from both fractions for GC/MS analysis.

Acid Herbicides

NOTE: The validation study incorporates a modification to EPA Method 8321 (HPLC/UV for the determinative method). Method 8321 uses a diethyl ether liquid/liquid extraction of the chlorinated phenoxyacid compounds, then solvent-exchanges to acetonitrile. This method uses acetonitrile as the elution solvent and eliminates diethyl ether altogether.

As part of the interlaboratory validation, one laboratory used the HPLC method; the other used GC/ECD for the determinative method (EPA Method 8150). Sample preparation directions for both determinative methods are outlined herein.

1. **Prepare sample** – Measure a 250 mL aliquot of leachate. Adjust the pH to 1.0 with sulfuric acid (1:1) and set aside.
2. Using a 6-place stainless steel manifold, place a 47mm SDB-XC disk on the glassware base. Wet the disk with acetone (about 1 mL) to preswell the polymer material. Place the reservoir atop the base and clamp in place.

3. **Pre-wash** the glassware and disk by adding about 5 mL of acetonitrile to the reservoir, rinsing down the sides in the process. This should be done with a receiving vial in the reservoir to capture the waste solvent. Turn on the vacuum momentarily until a few drops of solvent are seen coming through the disk, then release the vacuum and allow the solvent to soak for two minutes. Resume the vacuum to draw all of the solvent through the disk, and allow to air-dry with vacuum on. Remove the receiving vial and dispose of the solvent as appropriate.
4. **Condition** the SPE disk. Add 5 mL methanol to the reservoir. Apply vacuum until a few drops appear below the disk, then release the vacuum. Allow the disk to soak for about 1 minute. From this point until the extraction is completed, it is critical to leave a layer of liquid atop the disk to keep the sorbent from drying and returning to hydrophobic state. Apply vacuum and draw the methanol level down until 1-2 mm remain atop the disk.
5. Add about 15 mL reagent water to the remaining methanol in the reservoir. Apply vacuum and again draw through most – leaving about 2-3mm of water above the disk.
6. **Extraction** – Add the 250 mL leachate sample to the remaining water in the reservoir and turn on the vacuum. Allow the entire sample to filter. Allow the disk to air-dry with the vacuum on after the sample extraction is completed.
7. Place 5 mL of acetonitrile in the sample container that contained the spiked sample. Rinse the container and set aside.
8. **Elution** – Place a receiving vial in the manifold to capture the elution solvent. Using a pipette, transfer the acetonitrile from the container rinse to the reservoir, rinsing down the sides. Apply vacuum until a few drops appear on the drip tip, then release the vacuum. Let soak one minute, then draw through into the receiving vial.
9. Repeat this step with a second 5 mL aliquot of acetonitrile.
10. Elute with a third 5 mL aliquot of acetonitrile dispensed directly into the reservoir.
11. **Concentration:**

HPLC (EPA Method 8321) – Place the elution vial in a warm water bath and using a gentle stream of nitrogen, decrease the volume to less than 10 mLs. Transfer the solvent to a 10 mL volumetric flask and adjust to a 10 mL final volume with acetonitrile.

GC/ECD (EPA Method 8150) – Follow the above directions through step 10. Add approximately 3 grams granular anhydrous sodium sulfate to the vial and allow to sit for about 15 minutes. Transfer the solvent to an appropriate vial and add 2 mL diazomethane solution. Allow the derivitization to proceed for 30 minutes. Concentrate to less than 10 mLs as detailed above, and adjust to a 10 mL final volume.
12. Analyze by HPLC/UV (Method 8321) or GC/ECD (EPA Method 8150).

RECOVERY STUDIES

	Average Percent Recovery								
	BLH n=28	SB1L n=7	SB1H n=7	SB2L n=7	SB2H n=7	1% Organic SB1A SB2A n=4 n=4		10% Organic SB1A SB2A n=4 n=4	
Organochlorine Pesticides									
Chlordane	102	80	97	91	97	86	96	90	98
Endrin	89	106	106	124	81	97	103	97	100
Heptachlor	95	88	104	71	70	93	97	95	85
Heptachlor Epoxide	96	92	110	118	91	98	90	96	88
Lindane	107	104	126	74	92	99	101	101	99
Methoxychlor	95	107	109	73	87	92	96	94	93
Toxaphene	89	75	82	87	97	74	79	83	89
Base/Neutral Extractables									
1,4-Dichlorobenzene	66	51	56	50	65	65	62	66	53
2,4-Dinitrotoluene	97	89	90	86	92	87	89	93	76
Hexachlorobenzene	93	84	88	86	94	76	79	85	70
Hexachlorobutadiene	68	53	43	57	50	71	64	65	57
Hexachloroethane	58	50	65	51	66	71	69	72	57
Nitrobenzene	86	80	94	80	105	84	81	81	71
Pyridine*									
Acid Extractables									
o-Cresol	88	86	90	97	103	94	81	88	88
m- & p-Cresol	87	77	83	83	96	95	88	82	96
2,4,5-Trichlorophenol	90	93	99	94	96	94	86	96	87
2,4,6-Trichlorophenol	94	106	115	104	101	96	110	99	108
Pentachlorophenol	79	79	110	81	80	80	111	94	97
Acid Herbicides									
2,4-D	92	93	90	101	98	89	78	95	94
2,4,5-TP(Silvex)	92	98	91	75	112	79	99	78	91

B1 = pH 2.886; B2 = pH 4.937

BLH = Average %R for buffers 1 and 2 spiked at low and high levels

SB1 = Soil leach with buffer #1

Organic Effect: 1% & 10% Ethylene glycol:

SB2 = Soil leach with buffer #2

SB1A = Soil leach, buffer 1, action (A)level

low (L) and high (H) level spikes

SB2A = Soil leach, buffer 2, action (A)level

* Pyridine recoveries using the SDB sorbent membrane are low. The EPA workgroup stated this was not considered to be a problem since pyridine recoveries by the standard method are extremely variable.

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