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Reaching
Beyond
the Standard

STANDARD OPERATING PROCEDURE

**TCLP EXTRACTION - EPA SW 846
1311**

**SPLP EXTRACTION – EPA SW846
1312**

WET_08-9

**OUTREACH LABORATORY
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REVISION 9**

APPROVAL:

	
LABORATORY DIRECTOR	DATE

TCLP EXTRACTION – EPA SW 846 1311
SPLP EXTRACTION - EPA SW 846 1312

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TCLP EXTRACTION - EPA SW 846 1311

SPLP EXTRACTION - EPA SW 846 1312

1.0 PURPOSE

The purpose of this procedure is to simulate the leaching which might occur in a landfill containing the particular waste (sample(s)).

2.0 SCOPE & APPLICATION

The TCLP (Toxicity Characteristic Leaching Procedure) and the SPLP (Synthetic Precipitation Leaching Procedure) are designed to simulate the leaching that might occur in a sanitary landfill containing the particular waste. The TCLP and SPLP are suitable for determining the mobility of both organic and inorganic compounds present in liquid, solid, and multiphase wastes.

3.0 SUMMARY

- 3.1 For liquid samples (i.e., those containing less than 0.5% dry solid material), the waste after filtration through a 0.6 to 0.8 μ m glass fiber filter, is defined as the TCLP extract or the SPLP extract.
- 3.2 For wastes containing than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an acidic fluid equal to 20 times the weight of the solid phase. The extraction fluid chosen for a particular waste is a function of the alkalinity of that waste. A special extractor vessel is used when testing for volatile analytes. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μ m glass fiber filter.
- 3.3 If compatible, (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

4.0 DEFINITIONS

- 4.1 Accuracy – The closeness of agreement between an observed value and an accepted value.

- 4.2 Batch – A group of samples that behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, the number of samples analyzed as a group is 20 samples or less.
- 4.3 Bias – the deviation due to matrix effects of the measured value from a known spiked amount.
- 4.4 CCB – Continuing Calibration Blank – A blank ran during or at the end of analysis.
- 4.5 CCV – Continuing Calibration Verification standard – A standard ran during or at the end analysis.
- 4.6 ICB – Initial Calibration Blank – A blank ran right after making a calibration curve.
- 4.7 ICS – Initial Calibration Standard – A standard ran right after making a calibration curve.
- 4.8 LCS – Laboratory control Sample – A known matrix spiked with representative of the target analyte. This is used to document laboratory performance.
- 4.9 Matrix – The component or substrate which contains the analyte of interest, i.e.: surface water, drinking water, soil, etc.
- 4.10 MD or DU - Matrix Duplicate – An intralaboratory split sample which is used to document the precision of a method in a given sample matrix.
- 4.11 MS - Matrix Spike – Aliquot of sample spiked with a known concentration of target analyte. The spiking occurs prior to preparation of analysis. A matrix spike is used to document the bias of a method in a given matrix.
- 4.12 MSD - Matrix Spike Duplicate – A second matrix spike used to document precision in a give matrix.
- 4.13 MB – Method Blank – An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is ran through the complete sample preparation procedures and analytical process. The method blank is used to document contamination resulting from analytical process.
- 4.14 Precision – The agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate/replicate analyses.

- 4.15 Solid portion of waste – the portion of the sample not passing through a 0.6 to 0.8 um glass fiber filter.

5.0 INTERFERENCES

Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

6.0 SAFETY PRECAUTIONS

6.1 Hazardous Chemicals/Equipment

All work shall be performed under a fume hood when working with the hazardous chemicals.

6.2 Radiological Hazards

When radioactive materials are capable of being volatilized or airborne, perform all work under a fume hood.

6.3 General Laboratory Safety

Refer to the Laboratory Chemical Hygiene Plan, SOP#GEN_22 for general laboratory safety.

7.0 EQUIPMENT & SUPPLIES

- 7.1 Rotary Extractor - Capable of rotating extraction vessels in and end-over-end fashion at 30 ± 2 rpm.
- 7.2 Extraction Vessel - 2 liter borosilicate glass having Teflon lined lid.
- 7.3 Extraction Vessel – 2 liter plastic container with a plastic lid.
- 7.4 Zero-Headspace Extraction Vessel (ZHE) - made of 316 stainless steel, viton o-rings, and having a minimum volume of 500 ml.
- 7.5 Filter Holder - Buchner funnel capable of holding a 110 mm diameter filter and with a minimum volume of 300 ml. (Alternatively, a pressure filter holder may be used).
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- 7.6 Vacuum Flask - 1200 ml, glass; Fleaker Pyrex 5900 or equivalent
- 7.7 Vacuum Pump - Precision Model PV35, or equivalent.
- 7.8 Top-loader Balance - Capable 0.01 g, mettler PC 4400 or equivalent.
- 7.9 pH Meter; Cole-Parmer 835 or equivalent.
- 7.10 Combination pH electrode, Orion 915600 or equivalent.
- 7.11 Magnetic stirrer – Corning PC-351 or equivalent
- 7.12 Magnetic stir bar
- 7.13 VOA Vials - 40 ml with Teflon-lined lids.
- 7.14 Amber Glass Bottles - 1000 ml, narrow mouth with Teflon-lined lids.
- 7.15 Aluminum Weigh Boats - For % moisture determination.
- 7.16 Water Bath - Set to 50°C.
- 7.17 Glass Fiber Filters - 90 to 110 mm diameter and 0.6 - 0.8 um pore size.
- 7.18 200 ml glass beakers and watch glasses - for initial pH determination.
- 7.19 Plastic sample containers of various sizes.
- 7.20 1 liter volumetric flask, class A.

8.0 REAGENTS

All reagents are ACS grade or better.

- 8.1 DI Water - ASTM Type II; <10 umho/cm.
- 8.2 Glacial acetic acid, $\text{CH}_3\text{CH}_2\text{OOH}$
- 8.3 Hydrochloric acid, concentrated, HCl
- 8.4 Nitric Acid, concentrated, HNO_3



- 8.5 Sulfuric Acid, concentrated, H_2SO_4
- 8.6 Sodium Hydroxide, pellets, NaOH
- 8.7 Hydrochloric Acid - 1N: Dilute 83 ml of concentrated hydrochloric acid with DI water to 1 liter in a volumetric flask.
- 8.8 Nitric Acid - 1N: Dilute 28 ml of concentrated nitric acid with DI water to 1 liter in a volumetric flask
- 8.9 Sulfuric acid/nitric acid (60/40 weight percent mixture) $\text{H}_2\text{SO}_4/\text{HNO}_3$. Cautiously mix 60 g of concentrated sulfuric acid with 40 g of nitric acid. If preferred, a more dilute $\text{H}_2\text{SO}_4/\text{HNO}_3$ acid mixture may be prepared making it easier to adjust the pH of SPLP extraction fluids #1 and #2.
- 8.10 Sodium Hydroxide - 1N: Dissolve 40 g of sodium hydroxide pellets in DI water and dilute to 1 liter with DI water in a 1 liter volumetric flask.
- 8.11 Sodium Hydroxide – 10 N: Dissolve 400 g of sodium hydroxide pellets in DI water. When cooled to room temperature, dilute with DI water to 1 liter in a volumetric flask.
- 8.12 Compressed Nitrogen; Air Gas UN1066 or equivalent.
- 8.13 TCLP Extraction Fluid #1 - Add 5.7 ml of glacial acetic acid to each 500 ml increment of DI water. Add 64.3 ml 1N sodium hydroxide per each increment, and dilute to 1000 ml with DI water per increment. Adjust the pH to 4.93 ± 0.05 with glacial acetic acid or sodium hydroxide. Check pH on the day of use. A twenty-liter batch of Extraction Fluid #1 is made by diluting 114ml of glacial acetic acid, and 129 ml of 10N sodium hydroxide to 20 liters with DI water. Each batch is identified by fluid type and date prepared.
- 8.14 TCLP Extraction Fluid #2 - Add 5.7 ml of glacial acetic acid to each 994.3 ml increment of DI water. Adjust the pH to 2.88 ± 0.5 with glacial acetic acid. Check pH on day of use. A twenty-liter batch of Extraction Fluid #2 is made by diluting 114 ml of glacial acetic acid to 20 liters with DI water. Each batch is identified by fluid type and date prepared. Check pH on the day of use.
- 8.15 SPLP Extraction Fluid #1 – Add 60/40 weight percent mixture of sulfuric and nitric acids (or a suitable dilution) to DI until the pH is 4.20 ± 0.05 . The fluid is used for samples from a site that is from a site east of the Mississippi River.

NOTE: SPLP Extraction Fluids #1 and #2 are unbuffered and the exact pH may not be attained.

- 8.16 SPLP Extraction Fluid #2 – Add 60/40 weight percent mixture of sulfuric and nitric acids (or a suitable dilution) to DI until the pH is 5.00 ± 0.05 . The fluid is used for samples from a site that is from a site west of the Mississippi River.
- 8.17 SPLP Extraction Fluid #3 - DI water that has also been passed through a carbon filter bed.
- 8.18 Analytical standard shall be prepared according to the appropriate analytical method.

9.0 SAMPLE HANDLING & PRESERVATION

- 9.1 Soil samples should be collected and stored in airtight glass containers with Teflon-lined lids. Containers should have minimal or no headspace after filling with the sample. A minimum of 100 grams of sample should be collected. The samples should be kept at 4°C or lower except during preparation. Soil samples should be extracted within three days of receipt or within holding times for each test method. Refer to CFR 55 #61 for maximum holding times to extraction.
- 9.2 Aqueous samples should be collected in airtight glass containers with Teflon-lined lids. Containers should have no headspace after filling with the sample. A minimum of one liter of sample should be collected. The samples should be kept between 35 and 40°F except during sample preparation. Samples should be extracted within 3 days of receipt.
- 9.3 Samples are shipped refrigerated where applicable and with great care given to prevent loss of sample. Where radiological samples are shipped, specific regulations must be adhered to as well as safety precautions as to the packing and shipping of the samples.

10.0 QUALITY CONTROL

- 10.1 A minimum of one blank (using same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction batch. (A blank is to be performed on each new batch of extraction fluid).

11.0 PROCEDURE



11.1 Preliminary Investigations

Determination of solid/liquid content.

11.1.1 If the waste obviously contains no liquid portion, proceed with the extraction without further solids determination.

11.1.2 Weigh a minimum 100 gram well-mixed portion into a pressure filter container or vacuum filter which has a preweighed (to 0.1 mg) glass fiber filter in place.

11.1.3 Gradually apply vacuum until air moves through the filter, or no additional liquid passes through the filter for 2 minutes.

11.1.4 Weigh the filter and residue.

11.1.5 Determine the percent solids by subtracting the filter's tare weight from the gross weight.

11.1.5.1 If the solid portion is $\geq 0.5\%$ or 0.5g of the total weight, extraction must be performed on the solid phase. Particle size reduction will be required if the solid particles are greater than 1 cm in their narrowest dimensions. If particle size is required, crush, cut, or grind the waste until the size requirements are met. The solids must then be extracted and the extract must be combined with any liquid filtrate generated in the previous step. The method of extraction will depend on the type of analysis required. The remainder of this section will address the different types of extractions separately.

11.1.5.2 If the solid portion is $< 0.5\%$ of the total, the filtered liquid is considered to be the TCLP extract and no further action is taken with the solids portion. Filter sufficient volume of the sample to provide the laboratory with enough liquid to perform the final analysis. The volume needed will depend on the analyses required.

11.2 TCLP Extraction for semi volatile, pesticides, herbicides, and metals analyses

11.2.1 After particle size reduction if required, weigh 5 grams of the solid into a 125 ml container. Add 96.5 ml of DI water, and mix for 5 minutes.



Measure the pH and record mixing time and pH in TCLP Extraction logbook.

11.2.2 If pH is <5, proceed to the extraction step using extraction fluid #1.

11.2.3 If pH is >5, add 3.5 ml 1N HCl, slurry briefly, cover and heat at 50° C for 10 minutes. Allow the solution to cool and measure the pH.

11.2.3.1 If pH is <5, proceed to the extraction step using extraction fluid #1.

11.2.3.2 If pH is >5, proceed to the extraction step using extraction fluid #2.

11.2.4 The extraction step should provide enough extract such that, when combined with any initial liquid filtrate (if compatible), there will be sufficient volume for all analytical fractions. The following are the desired volumes for the various fractions: semi volatile - 1000 ml, pesticides/herbicides - 1000 ml, metals - 250 ml. The ratio of extraction fluid to solids in the extraction step is 20:1.

11.2.4.1 Weigh into a 2 liter glass jar (a plastic 2 liter jar may be used if TCLP metals only are to be analyzed) enough of the solid portion of the waste to meet the requirements above. If the waste is 100% solids, use 90 grams and add 1800 milliliters extraction fluid as determined above. If the sample is less than 100% solids calculate the sample volume required by the following equation.

$$\frac{100}{S} = EW$$

S -% solids of the sample

EW-sample weight required to obtain 100 g solids.

Alternitively if insufficient sample volume remains the extraction fluid volume can be adjusted from 2000 ml to the correct volume by multiplying the amount of solids by 20.

NOTE: Remember the liquid portion of sample has to be added to the final extract.

- 11.2.4.2 Cap the jar tightly and tape the lid shut. Place in the rotary extractor and rotate for 18 ± 2 hours.
- 11.2.4.3 Following extraction, filter the extract through a 110 mm glass fiber filter by use of Buchner funnel with vacuum filtration. Alternatively pressure filtration may be used if the solids are likely to plug the filter rapidly.
- 11.2.4.4 Measure the pH of the filtered extract and record.
- 11.2.4.5 If compatible, combine this filtered extract with the initial filtrate and split into the various fractions. If initial filtrate and extract are not compatible (not miscible) they must be kept separate and analyzed separately with the results being combined mathematically. The semi volatile portion is collected in a 1 liter amber glass jar with Teflon-lined lid. A 500 ml amber glass jar with Teflon-lined lid is used for pesticides/herbicides. The portion for metals analysis is collected in a 250 ml plastic container. To the metals portion, add concentrated nitric acid to a pH of <2 . Store at 4°C until analysis.

11.3 TCLP Extraction for Volatiles

The extraction step should provide enough extract such that, when combined with any initial liquid filtrate (if compatible), there will be sufficient volume for the volatiles analysis. Approximately 80 ml (two VOA vials) is normally provided. The extraction fluid to solids ratio is 20:1. A maximum of 25 grams of solids may be used in this extraction since the extractor has an internal volume of 500 ml.

- 11.3.1 Assemble the ZHE extraction vessel but do not put the top on. Extraction fluid #1 may be used to wet the Viton o-rings. Make certain the 90 mm glass fiber filter and screens are in place in the vessel top. Weigh into the assembled bottom portion enough sample such that there will be maximum of 25 grams of the solids portion of the waste. As quickly as possible, attach the top of the vessel and secure each fastener. Exposure of the sample or extract to the atmosphere should be kept at the minimum possible. Use cold sample if, at all possible, to minimize loss of volatiles. If the sample contains a liquid portion, filter the sample as discussed in section 11.2 under preliminary investigations using the ZHE apparatus as the pressure filter. Retain the filtrate for combination with the extract (if compatible). Determine the weight of sample remaining in the ZHE extractor and



introduce the appropriate amount of extraction fluid #1 into the closed system containing the solids. Fluid introduction may be accomplished by using a pump or other method capable of overcoming the pressure required to retract the piston.

11.3.2 After filling with extraction fluid and the ZHE device in the vertical position, gently apply gas pressure beneath the piston to force all headspace out of the ZHE device. At the first appearance of liquid from the device, discontinue pressure and close the outlet valve. Repressurize the ZHE with 5 - 10 psi and check all fittings for tightness. Rotate for 18 +/- 2 hours.

11.3.3 After the 18 hour agitation period, ascertain that the pressure has been maintained. The extraction fluid is then filtered and collected in the appropriate container. Filtration should be accomplished as quickly as possible to limit any exposure to the atmosphere, but should not be so rapid as to produce "fizzing" of the liquid which may result in loss of volatiles. Extract may be collected in a gas-tight syringe and transferred to 40 ml VOA vial. If the initial liquid filtrate was produce, the extraction fluid should be transferred directly into this filtrate, if compatible. A separate container must be used if the liquids are not compatible. Store the extracts/filtrates at 4°C until analysis.

11.4 SPLP Extraction for semi volatile, pesticides, herbicides, and metals analyses

NOTE: Determination of appropriate extraction fluid:

For soils: sample is from a site east of the Mississippi River, extraction fluid #1 is used; sample is from a site west of the Mississippi River, extraction fluid #2 is used.

For wastes and wastewater: extractionfluid # 1 is used.

For cyanide-containing wastes and/or soils: extraction fluid #3 is used.

11.4.1 The extraction step should provide enough extract such that, when combined with any initial liquid filtrate (if compatible), there will be sufficient volume for all analytical fractions. The following are the desired volumes for the various fractions: semi volatile - 1000 ml, pesticides/herbicides - 1000 ml, metals - 250 ml. The ratio of extraction fluid to solids in the extraction step is 20:1.



- 11.4.1.1 Weigh into a 2 liter glass jar (a plastic 2 liter jar may be used if TCLP metals only are to be analyzed) enough of the solid portion of the waste to meet the requirements above. If the waste is 100% solids, use 90 grams and add 1800 milliliters of the appropriate SPLP extraction fluid. If the sample is less than 100% solids calculate the sample volume required by the following equation.

$$\frac{100}{S} = EW$$

S - % solids of the sample

EW-sample weight required to obtain 100 g solids.

Alternitively if insufficient sample volume remains the extraction fluid volume can be adjusted from 2000 ml to the correct volume by multiplying the amount of solids by 20.

NOTE: Remember the liquid portion of sample has to be added to the final extract.

- 11.4.1.2 Cap the jar tightly and tape the lid shut. Place in the rotary extractor and rotate for 18 ± 2 hours.
- 11.4.1.3 Following extraction, filter the extract through a 110 mm glass fiber filter by use of Buchner funnel with vacuum filtration. Alternatively pressure filtration may be used if the solids are likely to plug the filter rapidly.
- 11.4.1.4 Measure the pH of the filtered extract and record.
- 11.4.1.5 If compatible, combine this filtered extract with the initial filtrate and split into the various fractions. If initial filtrate and extract are not compatible (not miscible) they must be kept separate and analyzed separately with the results being combined mathematically. The semi volatile portion is collected in a 1 liter amber glass jar with Teflon-lined lid. A 500 ml amber glass jar with Teflon-lined lid is used for pesticides/herbicides. The portion for metals analysis is collected in a 250 ml plastic container. To the metals portion, add concentrated nitric acid to a pH of <2 . Store at 4°C until analysis.
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11.5 SPLP Extraction for Volatiles

The extraction step should provide enough extract such that, when combined with any initial liquid filtrate (if compatible), there will be sufficient volume for the volatiles analysis. Approximately 80 ml (two VOA vials) is normally provided. The extraction fluid to solids ratio is 20:1. A maximum of 25 grams of solids may be used in this extraction since the extractor has an internal volume of 500 ml.

11.5.1 Assemble the ZHE extraction vessel but do not put the top on. Extraction fluid #3 may be used to wet the Viton o-rings. Make certain the 90 mm glass fiber filter and screens are in place in the vessel top. Weigh into the assembled bottom portion enough sample such that there will be maximum of 25 grams of the solids portion of the waste. As quickly as possible, attach the top of the vessel and secure each fastener. Exposure of the sample or extract to the atmosphere should be kept at the minimum possible. Use cold sample if, at all possible, to minimize loss of volatiles. If the sample contains a liquid portion, filter the sample as discussed in section 11.2 under preliminary investigations using the ZHE apparatus as the pressure filter. Retain the filtrate for combination with the extract (if compatible). Determine the weight of sample remaining in the ZHE extractor and introduce the appropriate amount of extraction fluid #1 into the closed system containing the solids. Fluid introduction may be accomplished by using a pump or other method capable of overcoming the pressure required to retract the piston.

11.5.2 After filling with SPLP extraction fluid #3 and the ZHE device in the vertical position, gently apply gas pressure beneath the piston to force all headspace out of the ZHE device. At the first appearance of liquid from the device, discontinue pressure and close the outlet valve. Repressurize the ZHE with 5 - 10 psi and check all fittings for tightness. Rotate for 18 +/- 2 hours.

11.5.3 After the 18 hour agitation period, ascertain that the pressure has been maintained. The extraction fluid is then filtered and collected in the appropriate container. Filtration should be accomplished as quickly as possible to limit any exposure to the atmosphere, but should not be so rapid as to produce "fizzing" of the liquid which may result in loss of volatiles. Extract may be collected in a gas-tight syringe and transferred to 40 ml VOA vial. If the initial liquid filtrate was produce, the extraction fluid should be transferred directly into this filtrate, if compatible. A separate container

must be used if the liquids are not compatible. Store the extracts/filtrates at 4°C until analysis.

12.0 CALCULATIONS

$$\text{Percent solids (\%)} = \frac{(A - B) * 100\%}{C}$$

Where:

A = weight of dried glass fiber filter after filtering sample (g)

B = tarred weight of glass fiber filter (g)

C = Sample volume (ml)

13.0 METHOD PERFORMANCE

This method has been validated by EPA.

14.0 POLLUTION PREVENTION

Refer to Laboratory Chemical Hygiene Plan, SOP # GEN_22 for laboratory pollution control.

15.0 WASTE MANAGEMENT

Refer to SOP #GEN-19 (Hazardous Material Management) and SOP # GEN_20 (Waste Disposal) for laboratory waste management.

16.0 REFERENCES

16.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 1311, SEPA.

16.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 1312

16.3 CFR 55 #61,

17.0 MISCELLANEOUS / ATTACHMENTS

17.1 Sample Maximum Hold Times (days)

Volatiles:

From Field collection to TCLP extraction – 14
From TCLP extraction to Prep extraction – N/A
From Prep extraction to Analysis – 14

Semi-volatiles:

From Field collection to TCLP extraction – 14
From TCLP extraction to Prep extraction – 7
From Prep extraction to Analysis – 40

Mercury:

From Field collection to TCLP extraction – 28
From TCLP extraction to Prep extraction – N/A
From Prep extraction to Analysis – 28

Metals, except mercury:

From Field collection to TCLP extraction – 180
From TCLP extraction to Prep extraction – N/A
From Prep extraction to Analysis – 180

17.2 Attachments follow:

17.2.1 Volatile Analytes (EPA SW 846 – Table I)

17.2.2 EPA SW 846 - Figure 2. Zero-Headspace Extractor (ZHE)

17.2.3 TCLP diagram (EPA SW 846)