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LABORATORY SOP FOR EPA METHOD 1311 (TCLP) VOLATILE ORGANICS BY ZERO HEADSPACE EXTRACTION

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1. Scope and Application

1.1. The TCLP method is a sample preparation technique used to determine the mobility of volatile analytes present in soils, wastes and wastewater and is based on EPA Method 1311. After extraction, the extract must be analyzed by the appropriate analysis method, i.e. 8260C.

1.2. The analytical results for the sample extracts are used in determining the hazardous nature of a sample. The sample is considered hazardous if any of the TCLP analyte concentrations are equal to or greater than the current regulatory limits (see Table below). The following compounds may be determined by this method:

Analyte	Concentration Level (mg/L)
Acetone	---
Benzene	0.50
Bromoform	---
2-Butanone (MEK)	200
Carbon disulfide	---
Carbon tetrachloride	0.50
Chlorobenzene	100
Chloroform	6.0
Dibromochloromethane	---
1,2-Dichlorobenzene	---
1,3-Dichlorobenzene	---
1,4-Dichlorobenzene	7.5
1,1-Dichloroethane	---
1,2-Dichloroethane	0.50
1,1-Dichloroethene	0.70
1,2-Dichloropropane	---
Ethyl Benzene	---
Methylene Chloride	---
Methyl isobutyl ketone	---

1,1,2,2-Tetrachloroethane	---
1,1,-Trichloroethane	---
Tetrachloroethene	0.70
Toluene	---
Trichloroethene	0.50
Trichlorofluoromethane	---
Vinyl chloride	0.20
Xylene (total)	---

1.3. A TCLP analysis is not normally required if a total analysis of the sample indicates that the concentration of the regulated compounds are at levels below the regulatory limits. The 20X dilution factor that is part of the TCLP procedure for solid samples should be taken into consideration when making this determination.

2. Summary of the Method

2.1 A percent solids determination is performed on samples containing a liquid fraction using a Zero Headspace Extractor (ZHE). A percent solids determination using the ZHE is not needed for samples that are 100 % dry solids.

2.2 The ZHE filtrate is defined as a TCLP extract for samples containing <0.5 percent dry solids. The TCLP extract may then be analyzed according to the routine waste or water analytical method.

2.3 The liquid and solid phases are separated in samples containing ≥0.5 percent solids, and the liquid phase is set aside temporarily. The solid phase is subjected to the ZHE procedure and the resulting leachate is added to the initial liquid phase (if miscible). The combined liquid portions are defined as the TCLP extract and are analyzed as a routine water or waste sample. If the sample contains more than one phase, then each phase is analyzed separately and the analytical results are mathematically combined to yield a volume – weight average concentration.

3. Apparatus and Equipment

The operation, cleaning and scheduled maintenance procedures prescribed by the equipment manufacturers are followed as provided in the Operator's Manuals.

3.1. Associated Design and Manufacturing, Co. Zero Headspace Extractor (ZHE)
3.2. Associated Design and Manufacturing, Co. Pressure Vessel.
3.3. Tedlar® Sample Bags.
3.4. Associated Design and Manufacturing, Co. Sample collection syringes, 500 ml and 1000 ml.
3.5. Mettler Toledo electronic balance ≤0.1g

4. Reagents and Chemicals

Working with volatile compounds presents a number of challenges not normally confronted in the handling of most other chemicals. Volatile compounds are easily lost from prepared solutions or, when present in the laboratory environment, can cross-contaminate other reagents or samples. Review the

techniques for handling volatile compounds found in the analytical methods before attempting to prepare solutions for analysis.

4.1 Organic Solvents

4.1.1. Methanol (Purge & Trap grade): For use where the methanol comes in direct contact with a sample.

4.1.2. Methanol (HPLC grade). For use in general cleaning applications where methanol does not come in contact with samples.

4.2 Acids and Base

4.2.1 Hydrochloric Acid, Certified ACS Grade

4.2.1.1 A 6 M HCl solution used for sample preservation is prepared by making a 1:1 dilution of the HCl into laboratory reagent water.

4.2.2 Glacial Acetic Acid, Reagent ACS Grade

4.2.3 Sodium Hydroxide, 1.0N

4.3 Laboratory Reagent Water

4.3.1 Reagent water is provided using a de-ionization system provided and maintained by U.S. Filter. The water is monitored by daily analysis of method blanks.

4.4 TCLP Extraction Fluid #1:

4.4.1 Add 3.5 L of laboratory reagent water into a clean 4.0 L glass bottle.

4.4.2 Measure 257 ml of 1N NaOH with a graduated cylinder and add the NaOH solution to the 4.0 L bottle.

4.4.3 Measure 22.8 ml of glacial acetic acid with a graduated cylinder and add the acid to the 4.0 L bottle.

4.4.4 Fill the bottle to the 4.0 L mark with laboratory reagent water and cap the bottle.

4.4.5 Mix the bottle well and test the pH of the extraction fluid. The pH must be between 4.88 and 4.98. Record the pH in the ZHE/TCLP logbook.

4.5 Alternatively, the extraction fluid can be purchased prepared and certified from chemical suppliers. The pH should be confirmed prior to use.

5. Sample Collection, Preservation and Storage

5.1 Sample kits contain glass jars with Teflon lined lids for the collection of samples.

5.1.1. The jars are completely filled with no head space to minimize the loss of volatile analytes.

5.1.2. Several jars are collected to allow the determination of percent solids andparticle size without compromising the entire sample.

5.1.3. Samples that have headspace, insufficient amounts or that have been collected in alternative containers are noted on the COC.

5.1.4. The samples must be stored in a refrigerator at 4.0° C ± 2° C and opened only immediately prior to extraction.

5.1.5 Extractions must be performed within 14 days of collection and the determinative analysis performed within 14 days of extraction preparation.

6. Cleaning and Testing the ZHE Apparatus

6.1. The ZHE can be difficult to clean and can pose a high risk for contaminating future TCLP samples if the following cleaning procedures are not used. In addition to cleaning, there are several testing procedures that need to be

performed before proceeding with the extraction to insure the apparatus is functioning properly.

6.2. If the ZHE has been previously used, make sure all solids from the unit have been properly disposed. Always dispose of waste in accordance with safety and hazardous waste disposal guidelines. The ZHE must be cleaned thoroughly after every use.

6.3. Disassemble the ZHE with care so that the individual parts are not damaged. The inlet/outlet valve in each ZHE must also be disassembled, but do not remove the valve o-rings unless they show wear or damage. The inlet/outlet valve is a frequent source of contamination if not disassembled and cleaned.

6.4. Wipe all of the ZHE parts with paper towels to remove excess waste and dispose of these towels with the sample waste. Use laboratory grade detergent to clean all of the ZHE parts followed by methanol and water rinses. Repeat this step until there is no visible contamination when the surface and crevices of the ZHE are wiped with a clean white towel.

6.4.1 In cases where the ZHEs are contaminated with oily waste, it may be necessary to first wipe or rinse all parts with methylene chloride, followed by methanol and water. Do not soak the o-rings or other polymer/plastic parts in the methylene chloride as this may result in damage. Following the methanol rinse, clean each part again thoroughly with detergent. Repeat these steps until there is nothing physically stuck or coated on the ZHEs and o-rings. **Do this away from VOC operations in the extraction lab since methylene chloride is a target compound.**

6.5. Soak the small stainless steel (screens, fittings, etc.) and o-rings in a beaker with methanol and sonicate for 30 minutes.

6.6. Bake the cleaned metal parts, except for the ZHE base, in the oven at 170°C overnight. The Viton® o-rings and ZHE base must be baked at ≤120°C for about 20 minutes.

6.7. Reassemble the ZHE. All of the primary components are marked with an identification number. This ID number is also placed in a ziploc bag where the small parts, (screens, o-rings, etc.) are placed. Make sure the correct parts are used for each ZHE.

6.8. The ZHE must be checked for ease of piston movement after each use.

6.8.1 Assemble the ZHE with all components but the inlet flange. Apply 15 psi to the base and observe the cylinder for movement of the piston.

6.8.2 If it takes more than 15 psi, the o-rings in the device needs to be replaced. record the results on the ZHE extraction worksheets.

6.9. The ZHE must be checked for leaks after each use.

6.9.1 Pressurize the device to 50 psi, allow it to stand for 1 hour, and recheck the pressure.

6.9.2 If pressure is lost, check all fittings and inspect and replace o-rings, if necessary. Retest the device and record results on the ZHE worksheets.

7. Sample Preparation Procedure

7.1 Percent Solids (Percent Solid Determination Form)

7.1.1 A percent solids determination is required for all samples containing visible liquid content. Samples that will not yield a filterable liquid fraction when subjected to pressure filtration can be excluded from the percent solids

determination. The percent solids determination can be misleading if the sample plugs the filter, such as with grease, oil or paint samples. In the most severe cases in may be impossible to determine percent solids by this method. Samples that promptly plug the filter may be treated as 100 percent solid.

7.1.2 Assemble the ZHE devices and place a pre-weighed 0.7 um glass fiber filter between the filter screens of each ZHE device. Record the filter weight on the ZHE worksheets.

7.1.3 Inspect the sample for appearance and particle size. The sample particle size must be reduced by crushing or cutting if it is more than 1 cm in the narrowest dimension. Handle the sample as little as possible to avoid volatiles loss. Record the sample description and particle reduction on the ZHE worksheets.

7.1.4 Carry the following procedures out in a well ventilated area.

7.1.5 Weigh and transfer approximately 100 g of sample into the ZHE unit. Ensure that the subsamples are representative of the samples. Always use clean utensils for each sample to prevent cross contamination. Assemble the ZHE device according to the manufacturer's instructions and record the sample weight and ZHE number on the ZHE worksheets with the corresponding sample ID.

7.1.6 Connect a pressure-regulated source of clean air or nitrogen to the fitting at the bottom of the ZHE device and attach a pre-weighed Tedlar bag or gastight syringe to the liquid inlet/outlet valve at the top of the ZHE. Starting at 20 psi, gradually increase the pressure in the ZHE unit until the piston begins to move. The initial movement of the piston may occur abruptly, so make sure that the inlet/outlet valve at the top is closed and the ZHE unit is held secure until the piston has moved.

7.1.7 Slowly open the inlet/outlet valve to collect any liquid fractions of the sample. Allow the pressure to remain at this level until no more filtrate emerges from the ZHE for 2 minutes. Increase the pressure by 10 psi increments to collect more filtrate until a maximum of 50 psi is reached.

7.1.8 Weigh the collected filtrate in the Tedlar bag or syringe and calculate the weight of the liquid phase. Determine the weight of the wet solid phase by subtracting the weight of the liquid phase from the weight of the total sample. Record the weight of the filtrate and wet solid phase. Calculate percent wet solids as follows:

$$\text{percent wet solids} = \frac{\text{wt of wet solid phase}}{\text{Total wt. of sample charged into ZHE}} \times 100$$

7.1.9 If wet solids are <0.5%, obtain a seperate aliquot of the sample and carry it through this extraction procedure, collecting the filtrates in a Tedlar bag or syringe for analysis (Form A).

7.1.10 If the percent wet solids is ≥ 0.5 %, then the TCLP extraction with extraction fluid #1 is required unless the entrained liquid in the solid phase can be accounted for. Measurement of the percent dry solids is used to determine if TCLP extraction is necessary in the sample with entrained liquid or wet solids with weights close to the 0.5% level.

7.2 Percent Dry Solids Determination and Calculation:

7.2.1 Remove the solid phase and filter from the ZHE.

7.2.2 Dry the filter with the solid phase on it at 100 ± 20° C overnight. **Warning: do not heat samples that may present a fire hazard.**

7.2.3 Determine the percent dry solids as follows:

$$\frac{\text{(wt. of dry sample + filter) – wt. of filter}}{\text{Total wt. of sample charged in the ZHE}} \times 100 = \text{percent dry solids}$$

7.2.4 TCLP extraction is require if the percent dry solids is ≥ 0.5 percent. The filtrate previously collected is defined as the TCLP extract if the percent dry solids is <0.5 percent.

7.3 Procedure for samples with >0.5 percent dry solids (Form B or C).
The total capacity of the ZHE is approximately 500 mL. Since the method requires the addition of extraction fluid equal to 20 times the sample weight, the ZHE can only accommodate a maximum of 25 g of solid material.

7.3.1 For samples with percent dry solids < 0.5 percent, the previously collected filtrate may be used as the TCLP filtrate. If additional filtrate is needed, weigh out up to 500 g subsample of waste and record the weight.

7.3.2 If the sample contains > 0.5 percent solids, the amount of waste to charge into the ZHE is determined as follows:

$$\frac{25}{\text{Percent dry solids}} \times 100 = \text{wt of waste to charge into the ZHE}$$

Weigh out the appropriate subsample of waste and record the weight.

7.3.3 Label and weigh the Tedlar bag, recording the weight on the ZHE worksheet.

7.3.4 Charge the sample into a clean ZHE. Place a fresh glass fiber filter between the screens and assemble the ZHE in the hood. Pressurize the unit to approximately 15-20 psi and slowly open the top liquid inlet/outlet valve to force all headspace out of the ZHE. When the first drop of liquid appears, close the valve and connect the preweighed Tedlar bag. With the Tedlar bag attached, reopen the liquid inlet/outlet valve to collect the liquid portion of the waste. Increase the pressure in 10 psi increments up to 50 psi. Insure that all of the liquid phase is in the Tedlar bag and the piston is up to the top of the cylinder leaving no head space in the ZHE unit. Close the liquid inlet/outlet valve, discontinue pressure to the unit and vent the ZHE before removing the gas supply hose. Disconnect and weigh the Tedlar bag, recording the weight on the worksheet.

7.3.5 Determine the volume of extraction fluid to add to the ZHE as follows:

$$\frac{20 \times \text{percent solids} \times \text{wt. of waste charged into ZHE}}{100} = \text{Volume of fluid}$$

7.3.6 With the ZHE in the vertical position, attach the syringe containing the proper amount of extraction fluid to the inlet/outlet valve. Open the inlet/outlet valve and begin transferring the extraction fluid while applying vacuum to the bottom of the unit.

7.3.7 After the extraction fluid has been added, check that all valves are in their closed positions. Manually rotate the unit in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet

valve on top. Pressurize the ZHE to 5-10 psi and slowly open the valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. Perform this action quickly and stop at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all valves to ensure they are closed.

7.3.8 Place the ZHE in the rotary agitation apparatus and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature of the extraction room should be maintained at 23 ± 2 ° C during the agitation.

7.3.9 At the end of the tumbling period, check the pressure of the ZHE by quickly opening and closing the inlet/outlet valve and noting the escape of gas. If no gas escapes, the unit is leaking and the sample must be re-extracted.

7.3.10 If the primary filtrate from the sample is miscible with the leachate, the two solutions may be collected in the same Tedlar bag. Immiscible phases must be kept separate and stored in individual Tedlar bags or sample vials.

7.3.11 The extraction procedures must be performed in a hood and all of the leachate from each ZHE must be collected into the appropriate Tedlar bag. An in-line glass fiber filter may be used if it is suspected that the glass filter in the ZHE has ruptured.

7.3.12 Analyze the extracts by the appropriate water methods within 14 days of extraction. Follow the QA/QC prescribed in the methods. The matrix spike compounds are added after the filtration of the sample.

8.0 Sample Analysis Procedure

8.1 Immiscible multiphase filtrates and extracts must be analyzed separately and the results mathematically combined. Before the analysis, the volume of each phase must be determined by weighing the filtrate and extract (assuming the density of each to be 1.0).

8.2 The analytical results for the individual phases of a biphasic sample are mathematically combined as follows:

$$\text{Reported value (ug/L)} = \frac{C_1V_1 + C_2V_2}{V_1 + V_2}$$

Where:

V_1= Phase 1 volume (L)

V_2= Phase 2 volume (L)

C_1= Concentration of compound in Phase 1 (u/L)

C_2= Concentration of compound in Phase 2 (u/L)

9.0 Safety/Hazardous Waste Management

9.1 Refer to Laboratory Chemical Hygiene Plan, Revision 1 February 28, 1999

9.2 Safety equipment must be used when appropriate and must be maintained in good operating condition. Safety glasses, lab coat and closed end shoes must be worn in the laboratory at all times.

9.3 Always use fume hoods when handling pressurized ZHEs. The sash must be positioned as low as possible when working in the hood. Check the valve positions and gas line connections before pressurizing the ZHEs. Use the lowest pressure possible to perform the extraction procedure. Do not exceed a pressure of 50 psi when using the ZHEs.

10 References

10.1 *Test Methods for Evaluating Solid Wastes, Third Edition, SW-846,* Method 1311. July 1992

10.2 GA EPD Quality Assurance Plan.

Georgia Department of Natural Resources/EPD

Toxicity Characteristic Leaching Procedure (TCLP)(Method EPA SW846-1311)

Percent Solid Determination Form

Analyst_____ **Date**_____ **Drying Oven temp**_____**(100°C ± 20°C)**

I. Sample Description						
1. Sample ID						
2. ZHE ID#						
3. Physical State						
4. Number of Phases						
II. Percent Solids						
a. Weight of sample (gms)						
b. Sample left in container (gms)						
c. Weight of subsample in ZHE (**a - b**) (gms)						
d. Initial weight of dry filter (gms)						
e. Weight of container to collect filtrate (gms)						
f. Filtrate+container after filtration (gms)						
g. Total filtrate collected (**f - e**) (gms) **(See note 3 below)**						
h. %Wet Solids: **[(c-g)/c x 100%]** **(See note 1 & 2 below)**						
III. Percent dry solid calculation for 100% Liquid						
i. Filter + residue after filtration (gms)						
j. Residue left on filter (**i-d**) (gms)						
k. Next to last weighing of dried filter +residue (gms) (two successive weighing yield the same value within ±1%) **(See note 4 below)**	1st- 2nd-					
L. Last dried filter+residue weighing (overnight in oven)						
m. **(k) x (0.99) > L < (k) x (1.01)**						
n. % Dry solids = **[(k –d)/ c] x100%**						

Note: *1. If percent wet solids (j) or dry solids (o) is < 0.5%, then the filtrate is defined as the TCLP extract, proceed with a new TCLP sample and extract it through the ZHE device thru **Form A***
*2. If percent wet solids >0.5% or sample is 100% solid then proceed TCLP procedure thru **Form B***
*3. If sample is multiphase then proceed TCLP procedure thru **Form C***
*4. Percent dry solid calculation is used only if **ALL** these are true: (1) No solid sample is visibly left on filter; (2) Filter appears to be only wet; (3) % wet solids calculation is very close to 0.5 %*

Georgia Department of Natural Resources
Environment Protection Division
Toxicity Characteristic Leaching Procedure (TCLP)(Method EPA SW846-1311) Form A (100% Liquid)

I. Sample Preparation							
1. **Sample ID**							
2. ZHE ID#							
3. Particle size reduction?	Yes/No	Yes/No	Yes/No	Yes/No	Yes/No	Yes/No	
4. Filtrate miscible with extraction fluid?	Yes/No	Yes/No	Yes/No	Yes/No	Yes/No	Yes/No	
II. Record of Extraction (gms)							
a. Target sample weight in volume = **100g**							
b. Weight of sample (gms)							
c. Sample residue left in container (gms)							
d. Amount of sample in the ZHE = (**b - c**) (gms)							
e. ZHE pressure at start of extraction (psi)							
f. ZHE pressure at end of extraction (psi)							
g. Weight of empty Tedlar bag							
h. Weight of Tedlar bag + Extraction Fluid							
i. Total extraction fluid collected in Tedlar bag = (**h – g**)							

Extraction Fluid Manufacturer & Lot Number_____

TCLP Rotator ID: 0099481 Lab ID: 07 RPM verification: _____RPM (30 ± 2) Temp. begin tumbling_____(23°C ± 2) Temp. end tumbling_____(23° C ± 2)

Extraction start time & Date_____ **Extraction stop time & Date**_____ **Analyst** _____

Georgia Department of Natural Resources
Environment Protection Division
Toxicity Characteristic Leaching Procedure (TCLP)(Method EPA SW846-1311) Form B (100% Solid)

I. Sample Preparation						
1. **Sample ID**						
2. ZHE ID#						
3. Particle size reduction?	Yes/No	Yes/No	Yes/No	Yes/No	Yes/No	Yes/No
4.Filtrate miscible with extraction fluid?	Yes/No	Yes/No	Yes/No	Yes/No	Yes/No	Yes/No
II. Record of Extraction (gms)						
a. Target sample weight = **[(25g x 100%]** **%Wet Solid**						
b. Weight of sample (gms)						
c. Sample residue left in container (gms)						
d. Amount of sample in the ZHE = (**b - c**) (gms)						
e. Weight of Extraction Fluid to charge in the ZHE = **(20) x (d) x (% Wet Solid)** (gms)						
f. ZHE pressure at start of extraction (psi)						
g. ZHE pressure at end of extraction (psi)						
h. Weight of empty Tedlar bag						
i. Weight of Tedlar bag + Extraction Fluid						
j. Total extraction fluid collected in Tedlar bag = (**i – h**)						

Extraction Fluid Manufacturer & Lot Number_____

TCLP Rotator ID: 0099481 Lab ID: 07 RPM verification: _____RPM (30 ± 2) Temp. begin tumbling_____(23°C ± 2) Temp. end tumbling_____(23° C ± 2)

Extraction start time & Date_____ **Extraction stop time & Date**_____ **Analyst** _____

Georgia Department of Natural Resources
Environment Protection Division

Toxicity Characteristic Leaching Procedure (TCLP)(Method EPA SW846-1311) Form C (Solid/Liquid phase)

I. Sample Preparation						
1. **Sample ID**						
2. ZHE ID#						
3. Particle size reduction?	Yes/No	Yes/No	Yes/No	Yes/No	Yes/No	Yes/No
4.Filtrate miscible with extraction fluid?	Yes/No	Yes/No	Yes/No	Yes/No	Yes/No	Yes/No
II. Record of Extraction (gms)						
a. Target sample weight = **[(25g x 100%]** **%Wet Solid**						
b. Weight of sample (gms)						
c. Sample residue left in container (gms)						
d. Amount of sample in the ZHE = (**b - c**) (gms)						
e. Weight of empty Tedlar bag for collecting filtrate						
f. Weight of Tedlar bag + Initial filtrate						
g. Weight of filtrate in the Tedlar bag = (**f - e**)						
h. Weight of Extraction Fluid to charge in the ZHE = **(20) x (d) x (% Wet Solid)** (gms) **100%**						
i. ZHE pressure at start of extraction (psi)						
j. ZHE pressure at end of extraction (psi)						

I. Sample Preparation						
1. **Sample ID**						
k. Total weight of Tedlar bag (**f**) + Extraction fluid **(if filtrate from the sample is miscible with the leachate)**						
l. Total fluid collected in Tedlar bag = (**k – e**)						
m. Weight of Second empty Tedlar bag **(if initial filtrate not miscible with extraction fluid)**						
n. Weight of Second Tedlar bag plus Extraction fluid						
o. Total extraction fluid collected in Second Tedlar bag (**n – m**)						

Extraction Fluid Manufacturer & Lot Number_____

TCLP Rotator ID: 0099481 Lab ID: 07 RPM verification: _____RPM (30 ± 2) Temp. begin tumbling_____(23°C ± 2) Temp. end tumbling_____(23° C ± 2)

Extraction start time & Date_____ **Extraction stop time & Date**_____ **Analyst** _____