Toxicity Characteristic Leaching Procedure and Synthetic Precipitation Leaching Procedure Using Zero-Headspace Extraction

FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION

CHEMISTRY PROGRAM

2600 BLAIR STONE ROAD

TALLAHASSEE, FLORIDA 32399

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Toxicity Characteristic Leaching (TCLP) Procedure and Synthetic Precipitation Leaching Procedure (SPLP) Using Zero-Headspace Extraction (ZHE)

TABLE OF CONTENTS

1. SCOPE AND APPLICATION……..…….... 3

2. SUMMARY OF METHOD……...……... 4

3. APPARATUS AND EQUIPMENT DESCRIPTION…….. 5

4. REAGENTS AND CHEMICALS…… 6

5. SAMPLE COLLECTION, PRESERVATION AND STORAGE PROCEDURES……..8

6. CLEANING AND TESTING THE ZHE APPARATUS……..…… 9

7. SAMPLE PREPARATION PROCEDURE ……...……. 10

8. SAMPLE ANALYSIS PROCEDURE……... 13

9. INTERFERENCES……15

10. QUALITY ASSURANCE…… 15

11. SAFETY, HAZARDOUS WASTE MANAGEMENT AND POLLUTION PREVENTION….15

12. REFERENCES…….. 16

APPENDIX OF SIGNIFICANT CHANGES…… 16

APPENDIX: TCLP AND SPLP SAMPLE PREPARATION FORM ….……17

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1. SCOPE AND APPLICATION

1.1. The TCLP and SPLP methods are sample preparation techniques used to determine the mobility of volatile organic analytes present in soils, wastes, and wastewater and are based on EPA Method 1311 (TCLP) and Method 1312 (SPLP).[1,2] The TCLP and SPLP procedures only differ in the extraction fluid used. The resulting sample extract must be analyzed by an appropriate analysis method once the sample is prepared. The analysis method used for volatiles analysis is EPA Method 8260D described in SOPs VO-002 and VO-003.[3]

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:

Maximum Concentration of TCLP Volatile Analytes

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

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1.3. FDEP Laboratory Test IDs and Equivalent EPA Methods covered by this SOP

TCLP-VOC - EPA Method 1311 Toxicity Characteristic Leaching Procedure
SPLP-VOC - EPA Method 1312 Synthetic Precipitation Leaching Procedure

1.4. Refer to the following Standard Operating Procedures (SOPs) for additional procedural information:

These supporting SOPs contain critical details not fully described within this method SOP. The analyst must be completely familiar with all of these SOPs.

1.4.1. *Safety and Waste Management Practices in the Organic Analysis Groups* (SOP **OG-001**).

1.4.2. *Glassware and Equipment Cleaning Procedures* (SOP **VO-007**).

1.4.3. *Data Review/Authorization Procedures for the Volatile Organic Laboratory* (SOP **VO-010**).

1.4.4. *Quality Assurance/Quality Control Measurements in the Volatile Organics (VOC) Laboratory* (SOP **VO-001**).

1.4.5. *Measurement of VOCs in Water by GC/MS,* (SOP **VO-002**).

1.4.6. *Measurement of VOCs in Sediments and Waster by GC/MS,* (SOP **VO-003**).

1.4.7. *Non-Conformance Reporting System* (SOP **LB-002**).

1.4.8. *Standard Operating Procedure for Reporting Qualified Data* (SOP **CM-008**)

1.4.9. *Standard Operating Procedure for Records Storage and Retention* (SOP **LB-006**)

1.5. The TCLP or SPLP analysis is not normally recommended if a total analysis of the sample indicates that the concentration of the regulated compounds are at levels below the regulatory limits. However, there may be instances where the TCLP analysis is warranted regardless of the total result, such as when the leach amount is of research interest instead of regulatory interest. The 20X dilution factor that is part of the TCLP and SPLP procedures 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 device called the Zero Headspace Extractor. A percent solids determination using the ZHE is not needed for samples that are dry solids.

2.2. The ZHE filtrate is defined as a TCLP or SPLP extract for samples containing < 0.50 percent solids as determined by the TCLP procedures. The TCLP or SPLP extract may

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then be analyzed by any approved waste or water analytical method. For our application EPA Method 8260D is used for analysis.

2.3. The liquid and solid phases are separated in samples containing ≥ 0.50 percent solids, and the liquid phase is set aside temporarily. The solid phase is subjected to the Zero Headspace Extraction procedure using the appropriate extraction fluid for TCLP or SPLP and the resulting leachate is added to the initial liquid phase (if miscible). The combined liquid portions are defined as the TCLP (or SPLP) 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-weighted average concentration.

3. APPARATUS AND EQUIPMENT

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

3.1. Syringes and Core Samplers:

3.1.1. Hamilton Microliter/Gastight Syringes (Class A): 5 µL, 10 µL, 50 µL, and 50 mL. The Hamilton syringes are delicate and must be handled with care. Many of the syringes are equipped with Chaney adapters to improve the reproducibility of the injections and to minimize the bending of the plunger. The syringes are cleaned by 10 to 15 rinses with methanol. The Hamilton syringes must never be heated in an oven or damage may result. Damaged or corroded syringes must be cleaned and discarded into the sharps container. The average life expectancy for a syringe that is used daily is typically no more than a few months to a year. Regardless of use, the microliter syringes should be inspected and the calibration verified quaterly.

3.1.2. Encore Sampler: 25 g capacity.

3.2. Volumetric Flasks (Class A) and Graduated Cylinders: 10 mL, 25 mL, 50 mL, 100 mL, 200 mL and 500 mL.

3.2.1. The volumetrics are equipped with a Teflon (PTFE) or pennyhead ground glass stopper.

3.2.2. The volumetric flasks and graduated cylinders are cleaned by rinsing with methanol and laboratory reagent water. The volumetrics are dried in a low temperature oven at less than 120 °C. Never use a brush or strong alkali solution to clean the volumetrics.

3.3. Glass and Metal Sample Containers:

3.3.1. 42 mL VOA vials with a Teflon®/silicone septa and polypropylene open-top cap.

3.3.2. 4 L Glass Bottle with Teflon® lined cap.

3.3.3. Glass Jar with silicon/Teflon lined septum, 250 mL and 500 mL.

3.3.3. Metal Can with lid, 1 quart. The metal can must be baked at 170 °C for 24 hours prior to use.

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3.4. Thermo Magapure MP-3 Glass Distillation Unit or Solution 2000 Water Purifier System.

3.5. Thermo Heratherm OMH400 Mechanical Convection Oven.

3.6. Mettler Toledo XS6002S Top-loading Balance, capable of weighing 0.01 g.

3.7. Mettler Toledo A-250XPR205 Analytical Balance, capable of weighing 0.00001g

3.8. Hach pH Meter HQ1110, with a 3-in-1 Combination Electrode and pHydrion pH Paper.

3.9. Flammable-Rated Refrigerator, Fisher Scientific Isotemp, Model 426-2.

3.10. Flammable-Rated Freezer, Kelvinator Scientific, Model BT30CWFMS-2.

3.11. Flammable-Rated Freezer, Fisher Scientific Isotemp.

3.12. Stainless steel spatulas.

3.13. Millipore Zero Headspace Extractor (ZHE), Part Number YY30-090-HW

3.14. Millipore 5-Liter Pressure Vessel.

3.15. Tedlar® Sample Bags.

3.16. 90 mm diameter 7 µm Glass Fiber Filters.

3.17. Air or Nitrogen Gas Cylinder.

3.18. 3 Mil Sealable Polyethylene Bags, Quart Size

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 **references 12.1 through 12.4** before attempting to prepare solutions for analysis.

Sources of the reagents and chemicals are given, but may change based on availability, quality and cost. The use of a different source is acceptable without modification of the procedures provided the products are equivalent.

4.1. Organic Solvents:

4.1.1. Methanol (Purge & Trap grade): CH_3OH - Purge & Trap grade methanol is purchased in 500 mL amber bottles from Fisher Scientific. The Purge & Trap grade is used for any application where the methanol comes in direct contact with a sample.

4.1.2. Methanol (HPLC grade): CH_3OH - HPLC grade methanol is purchased in 4 L amber bottles from Fisher Scientific. The HPLC grade methanol is used for general cleaning applications where the methanol does not come in contact with samples or the item is baked prior to coming in contact with samples.

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4.2. Acids and Bases:

4.2.1. Hydrochloric Acid, HCl - Fisher Certified ACS Plus Grade.

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

4.2.2. Glacial Acetic Acid, CH_3CO_2H - Fisher Reagent ACS Grade.

4.2.3. Sodium Hydroxide, NaOH - Fisher Certified, 1.0 N.

4.3. Laboratory Reagent Water:

Type 1 laboratory reagent water is prepared in the laboratory from the municipal water supply The criteria for laboratory reagent water is that it must not contain any analytes of interest at a concentration greater than 20% of the reporting limit. Other non-target compounds may be detected in the laboratory reagent water, but must not interfere with the analysis of the target compounds. Examples of a non-target compounds commonly observed are methanol (used in glassware cleaning and standard preparation) and siloxanes (from surfactants, pump oils and column bleed).

4.3.1. Type 1 Laboratory Reagent Water: Municipal water is purified with a Solution 2000 Water Purification System that uses activated carbon cartridges and ion-exchange cartridges to remove impurities. The laboratory reagent water is evaluated every day, when sample data is collected, as a method blank sample.

4.4. Laboratory Reagent Sand:

The laboratory reagent sand may require removal of trace VOCs prior to use. If so, the sand may be cleaned by first rinsing with HPLC methanol and laboratory water three times each. The rinsed sand is poured as a thin layer into a large stainless-steel pan and baked at 105 °C or higher overnight. The sand may be stored in a beaker in the VOC laboratory oven at 105 °C.

4.5. Preparation of TCLP Extraction Fluid # 1:

4.5.1. Add 2 L of laboratory reagent water into a clean 4.0 L glass bottle.

4.5.2. Add 50 mL of laboratory reagent water to a 100 mL volumetric flask. Weigh 10.29 g of NaOH into the 100 mL volumetric flask. Stir until fully dissolved, then transfer the NaOH solution to the 4L bottle. (Alternatively, 257 mL of 1N NaOH may be used)

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

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

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

4.5.6. The extraction fluid must be used within 30 days.

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4.6. Preparation of SPLP Extraction Fluid: Laboratory reagent water is used to perform the SPLP extraction procedure.

5. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

The collection, preservation and storage of samples begins with the preparation of the sampling kit used to contain the sample. The kits are provided by the laboratory and are prepared based on the sample requests recieved on a weekly basis.

5.1. Sample Kit Assembly:

5.1.1. Add two 25 g Encore samplers (if collecting for total soil analysis)

5.1.2. Add two 500 mL bulk glass jar containers

5.2. Sample Collection:

5.2.1. Remove the Encore samplers from the foil pouch and fill each with a plug of soil as directed in the manufacture instructions. Do not use the Encore to collect liquid or pure product samples. When possible, product samples may be delivered in their original container.

5.2.2. Label the Encore samplers and return them to the foil pouch.

5.2.3. Fill the bulk sample jar and leave minimal head space. Wipe the lip of the jar with a VOC-free tissue and seal the jar tight with the Teflon/silicon septa lid. The bulk jar can be used to collect liquid waste samples, however extreme care should exercised to assure the jar seals well. Double bagging of liquid waste samples in sealable polyethylene bags is strongly recommended.

5.2.4. The outside of the bagging and glass bulk jar must be labeled with a field identification. Chain-of-custody labels may be placed across the container lids to give added security to the integrity of the sample. Fill out all applicable chain-of custody forms.

5.3. Sample Preservation and Storage:

5.3.1. Encore samplers may be stored in a flammable-rated refrigerator at 4.0 ± 2 °C for up to 48 hours after sampling. The soil Encore samplers must be analyzed or extracted within 48 hours of sampling to avoid sample expiration. The contents of the Encore samplers must be transferred as soon as possible to a hermetically sealed soil vial or into a methanol extract and stored at < -7.0 °C. The extracted or transferred samples must be analyzed within 14 days of sample collection. The Encores are typically used for screening the samples prior to TCLP preparation to determine if TCLP preparation is warranted

5.3.2. The bulk sample jars must be store in a flammable-rated refrigerator at 4.0 ± 2 ° C and have a holding time of 14 days. Waste samples should be stored in a separate refrigerator from the water or soil samples and placed in individual 3 mil polyethylene bags to minimize potential cross-contamination.

5.3.3. The refrigerator units may be monitored with a refrigerator blank on a weekly basis. The refrigerator blanks should stay in the refrigerator for a minimum of seven days and then be analyzed as a sample. The criteria for the refrigerator

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blank is the same as the laboratory reagent water blank. It should be assumed that samples may have been compromised if the refrigerator blank is contaminated. Appropriate elevation of MDLs, sample qualifiers, and comments may be added to potentially affected samples.

5.3.4. Following the extraction procedure, the sample extracts must be preserved as required by the applicable analytical method.

6. CLEANING AND TESTING THE ZHE APPARATUS

The Zero Headspace Extractor (ZHE) can be difficult to clean and can pose a high risk for contaminating future TCLP/SPLP 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 ensure the apparatus is functioning properly.

(Note: a ZHE Demo video can be found at https://www.biocompare.com/Life-Science-Videos/566684-MilliporeSigma-Zero-Head-Space-TCLP-Demo-Video/)

6.1. If the ZHE has been previously used, then make sure all solids from the unit have been properly disposed. Always dispose of waste in accordance with the safety and hazardous waste disposal **SOP, OG-001**. The ZHE units must be cleaned thoroughly after every use.

6.2. Disassemble the ZHE with care so that the individual parts are not nicked or otherwise damaged. The inlet/outlet valve in each ZHE lid 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.

6.3. 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.

6.3.1. 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 since 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 bottle washing room since methylene chloride is a target compound.**

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

6.5. Badly stained metal parts can be acid rinsed for 2-10 seconds with 3 M HCL to remove most corrosion or stains. Clean again with soapy water and rinse well with water.

6.6. Bake the cleaned metal parts, except for the ZHE base, in the oven at 160^{o}C overnight. The Viton® O-rings and ZHE base must be baked at ≤ 120^{o}C for a short period of about 20 minutes.

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6.7. Reassemble the ZHEs. All of the primary ZHE components are marked with an identification number, so make sure the correct parts are used for each ZHE.

6.8. ZHE Clean Check: Add 250 mL of laboratory reagent water to each ZHE, pressurize the unit and tumble the units for about 1 hour. Check to make sure the unit is pressure tight. Collect the laboratory reagent water just as for a sample and analyze by GC/MS. Use the Clean Check results to determine if any ZHE needs to be cleaned again. Any ZHE that was cleaned with methylene chloride or was used previously for a highly contaminated sample must be tested individually. A composite or batch blank test will suffice for all other ZHEs. A ZHE must be re-cleaned if the Clean Check sample contains more than the MDL of any analyte, including ketones and petroleum compounds. Record the results in the ZHE logbook.

6.9. ZHE Storage: After a ZHE has been properly cleaned and checked, disassemble it, empty the water out, and allow it to air dry. This will eliminate the possibility of corrosion or mold growth. After air drying the ZHE, tag and store the ZHE components in the ZHE cabinet in the VOC laboratory. The components may be covered with aluminum foil.

6.10. Since the ZHE cleaning procedures require a long processing time, it is suggested that cleaning be started as early as possible.

7. SAMPLE PREPARATION PROCEDURE

NOTE: Disassemble the necessary number of ZHE's several days before they will be needed and bake them overnight. Use only properly cleaned ZHE's for the TCLP/SPLP sample extractions and always choose a ZHE at random for the TCLP/SPLP extraction blank. A pressure test and batch clean test must be performed prior to using the ZHEs.

7.1 All glassware must be cleaned according to the glassware cleaning **SOP VO-007**.

7.2 Samples must be extracted within a holding period of 14 days following collection.

7.3. Print out a backlog and determine which samples will be prepared. Samples may be assigned by the section administrator or senior chemists. The assigned samples must be ckecked out from the locked refrigerators.

7.4. Fill out the header information in the TCLP and SPLP Sample Preparation Logbook found in Appendix A.

7.5. Each sample must be visually inspected for broken containers, sample headspace, loose lids, upside down septa and chain-of-custody seals (if applicable). Any problems are noted in the TCLP/SPLP logbook.

7.6 Preliminary Percent Solids Determination:

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 it may be impossible to determine the percent solids by this technique. Samples that promptly plug the filter may be treated as 100 percent solid.

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7.6.1. Assemble the ZHE devices and place a pre-weighed 0.7-µm glass fiber filter between the filter screens of each ZHE device. Record the filter weight in the TCLP/SPLP logbook.

7.6.2. Inspect the sample for appearance, odor 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 volatile loss. Record the sample description and particle reduction in the TCLP/SPLP logbook.

7.6.3. Weigh and transfer approximately 100 g of each sample into a designated ZHE unit. Special care must be exercised to ensure that the subsamples are representative of the samples, particularly if there are multiple phases. Also, always use clean utensils for each sample to prevent cross contamination. Do not handle the sample more than is absolutely necessary to minimize volatile loss. Finish the assembly of the ZHE devices in a ventilated area according to the manufacturer's instructions. Record the sample weight and ZHE number in the TCLP/SPLP logbook.

7.6.4. Connect a pressure-regulated source of clean air or nitrogen to the fitting at the bottom of the ZHE and attach a pre-weighed Tedlar® bag to the liquid inlet/outlet valve at the top of the ZHE (A 50 mL gastight syringe may be used in place of the Tedlar® bag). Starting at 20 psi pressure, gradually increase the air 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.

7.6.5. 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 pressure of 50 psi is reached.

7.6.6. Weigh the collected filtrate in the Tedlar® bag 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 the percent wet solids as follows:

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

7.6.7. If the percent wet solids is < 0.5 percent, then the collected filtrate is defined as the TCLP/SPLP extract.

7.6.8. If the percent wet solids value is ≥ 0.5 percent, then TCLP or SPLP extraction of the solid fraction is required using the appropriate extraction solution. Take precaution to avoid losses of the extracted liquid (including entrained liquid in the ZHE device). Measurement of the percent dry solids is used to determine if TCLP/SPLP extraction is necessary in samples with entrained liquid or wet solids with weights close to the 0.5% level.

7.7. Percent Dry Solids Determination and Calculation:

7.7.1. Remove the solid phase and filter from the ZHE.

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7.7.2. Dry the filter with the solid phase on it at 105 ± 5 °C overnight. **Warning: Do not heat samples that may present a fire hazard.**

7.7.3. Determine the percent dry solids as follows:

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

7.7.4. TCLP extraction with fluid #1 or SPLP extraction with laboratory reagent water is required if the percent dry solids is ≥ 0.5 percent. The filtrate previously collected is defined as the TCLP/SPLP extract if the percent dry solids are < 0.5 percent.

7.8. Procedure for Samples with > 0.5 Percent Dry Solids:

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 (i.e. 20 x 25 = 500).

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

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

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

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

7.10. Label and weigh the Tedlar® bags, recording the weight in the TCLP/SPLP logbook.

7.11. Charge the sample into a clean ZHE. Place a fresh glass fiber filter between the screens and assemble 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 (if any) quickly close the valve and connect a pre-weighed 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. Ensure that all of the liquid phase is in the Tedlar® bag and the **piston is up to the top of the cylinder** leaving no headspace 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 in the notebook.

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

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

7.13. Pre-rinse the TCLP or SPLP extraction fluid chamber using 500 mL of extraction fluid and then refill with 150 mL of fresh extraction fluid. Set the chamber up in a hood and connect to gas cylinder according to the manufacturer's instructions.

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7.14. Pressurize the chamber to approximately 15-20 psi and slowly open the liquid outlet valve to let the extraction fluid fill the tubing and the dead volume in the bottom of the chamber. When you start seeing bubbles emerging from the outlet valve, immediately close the valve.

7.15. Use the extraction fluid chamber to deliver extraction fluid into the ZHE. Pour the calculated volume of extraction fluid (up to 500 mL) into the fluid chamber. Make sure there are no air bubbles in the transparent tubing before pumping the extraction fluid into the ZHE. To prevent air from entering the ZHE, add an additional 50 mL of extraction fluid to the chamber before pumping the extraction fluid into the ZHE.

7.16. After pumping the extraction fluid into the ZHE, quickly close the top valve of the ZHE and the outlet valve of the chamber. Discontinue pressure, vent the chamber and disconnect the gas supply hose.

7.17. Gently rotate the ZHE several times and then force out the headspace by pressurizing the ZHE to 20 psi and slowly opening the top valve; close the valve when you see liquid without air bubbles coming out of the ZHE. This usually happens abruptly, so exercise caution.

7.18. Inspect the ZHE rotary instrument for damage or contamination. Verify that the tumbler operates at 30 RPM. Record the rotation speed in the TCLP/SPLP logbook.

7.19. Verify all valves on the ZHEs are closed and the pressure is ≅ 20 psi. Record the pressures in the TCLP/SPLP logbook. Place the ZHE on the rotary agitator and tumble for 18 ± 2 hours.

7.20. Use a min/max thermometer to verify that the room temperature is maintained at 23 ± 2 ºC during the extraction period. If the room temperature is not properly maintained the preparation must be repeated.

7.21. At the end of the tumbling period, check the pressure for each ZHE. The sample must be re-extracted if the pressure has dropped below 15 psi.

7.22. If the primary filtrate from the sample collected previously is miscible with the leachate, then 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.

7.23. 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. Do not pressurize the ZHE above 50 psi during the extraction procedure. An in-line glass fiber filter may be used if it is suspected that the glass fiber filter in the ZHE has ruptured.

7.24. An extraction blank must be prepared with each batch of up to 20 TCLP/SPLP samples. The blank is prepared by adding a 25 g aliquot of laboratory reagent sand into a randomly selected ZHE. The extraction blank is carried through the entire extraction process just as a sample.

7.25. A sample extraction duplicate must be prepared for every sample batch of up to 20 samples.

8. SAMPLE ANALYSIS PROCEDURE

8.1. The sample extracts must be analyzed within the holding times of the applicable analytical method.

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8.2. The TCLP/SPLP filtrates and extracts with only one aqueous phase are analyzed as regular water sample. Refer to the VOC Water Analysis by GC/MS SOP **VO-002**.

8.3. TCLP/SPLP filtrates with a non-aqueous phase(s) are analyzed as a waste sample. Refer to the VOC Sediment/Waste Analysis by GC/MS SOP **VO-003**.

8.4. Multi-phasic filtrates and extracts are a little more complicated since each phase must be analyzed separately and the results mathematically combined. Instructions for handling multiphasic samples is found in the DEP laboratory SOP CM-027. Before the analysis, however, the volume of each phase must be determined either directly or by measuring the weight and density of each phase. The volume of the phase is needed in the mathematical recombination and may be calculated by dividing the weight by the density. Each phase must then be analyzed separately, as water (aqueous) or waste (non-aqueous). The TCLP/SPLP results are reported in units of µg/L. The following information must be determined in order to carry out the needed calculations:

V_1 = Phase 1 volume (L)
V_2 = Phase 2 volume (L)
C_1 = Concentration of compound in the first phase (µg/L)
C_2 = Concentration of compound in the second phase (µg/L)

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

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

Example: An example of calculation is given below:

Sample # 12345: The TCLP/SPLP extract is biphasic.

Reported concentration of ETB in aqueous phase is 3.80 µg/L
Aqueous phase DF = 1000
Aqueous phase volume = 483 mL
Reported concentration of ETB in oil phase is 4.19 µg/L
Oil phase DF = 1E6
Oil phase volume = 10.3 mL
Weight of oil phase sample for extraction = 2.092 g
Weight of methanol for extraction = 2.207 g
Density of oil phase = 0.83 g/mL
Analysis MDL = 0.50 ug/L

In the oil phase:

$$[\text{ETB}] = \frac{4.19\ \text{µg/L} \times 2.207\ \text{g} \times 1\text{E}6 \times 0.83\ \text{g/mL}}{0.79\ \text{g/mL} \times 2.092\ \text{g}}$$

[ETB] = 4.6E6 µg/L

In the aqueous phase:

[ETB] = 3.80 µg/L × 1000 = 3800 µg/L

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For the sample as a whole:

$$[ETB] = \frac{(3800\ \mu g/L \times 483\ mL) + (4.6E6\ \mu g/L \times 10.3\ mL)}{(483\ mL + 10.3\ mL)}$$

$$[ETB] = 1.0E5\ \mu g/L$$

8.6. MDL Calculation for Multi-phasic samples

$$MDL\ (\mu g/L) = \frac{(MDL_1 \times V_1) + (MDL_2 \times V_2)}{V_1 + V_2}$$

Example:

The MDL calculation is:

MDL for aqueous phase = 0.5 µg/L x 1000 (DF) = 500 µg/L

$$MDL\ for\ oil\ phase = \frac{0.50\ \mu g/L \times 2.207\ g \times 1E6 \times 0.83\ g/mL}{0.79\ g/mL \times 2.092\ g}$$

MDL for oil phase = 5.5E5 µg/L

$$The\ combined\ MDL = \frac{(500\ \mu g/L \times 483\ mL) + (5.5E5 \times 10.3\ mL)}{(483\ mL + 10.3\ mL)}$$

The combined MDL = 1.2E4 µg/L

9. INTERFERENCES

9.1. Significant losses of volatile organic compounds may occur due to improper handling, transport or storage. Samples for TCLP analysis must be collected as prescribed by the soil and waste sampling procedures in SOP **VO-003**. Sample handling during transfer to the extraction vessel and during the extraction process are equally critical to minimize losses or avoid cross-contaminations

9.2. Heavy oils, paint, and adhesive samples appear to be liquid in nature, but frequently due not filter well. This interference can be minimized by filtering slowly and filtering the easiest phase first (for multiphase samples). The phase filtered first can be selected by the orientation of the ZHE devise during the extraction process.

9.3. Description of interferences specific to the analytical methods may be found in the analytical SOPs.

10. QUALITY ASSURANCE

10.1 A matrix spike and duplicate matrix spike must be prepared and analyzed for each sample batch.

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10.1.1. The matrix spike compounds are added after the filtration of the sample.

10.2. At least one blank must be included in each batch of TCLP/SPLP samples and analyzed with the TCLP/SPLP extracts and filtrates. The ZHE clean check data must also be included in the batch QC folder.

10.3. For more specific information regarding QA/QC measures, review the quality control measures for the analytical method.

11. SAFETY/HAZARDOUS WASTE MANAGEMENT AND POLLUTION PREVENTION

11.1. Review the Laboratory Safety SOP Manual and the Contingency Plans and Emergency Procedures for a Hazardous Waste Generator. See Safety **SOP, OG-001**.

11.2. Safety equipment must be used when appropriate and must be maintained in good operating condition. Safety glasses, long pants, and closed-end shoes must be worn in the laboratory at all times.

11.3. Always use a safety shield 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.

11.4. Use **CAUTION** with strong irritants such as acids and bases. Avoid breathing the fumes of these irritants by using them in a hood when possible and keeping the face away from open containers of these chemicals. Avoid contact of these irritants with skin and clothing by appropriate use of gloves, apron, face mask and hood shield.

11.5. Store any wastes that cannot be disposed of down the sink (see Laboratory Safety SOP Manual) in 4 L bottles and properly labeled with **Hazardous Wastes** labels. These wastes must be disposed in the appropriate waste storage container found in the Hazardous Waste storage room in Bldg. C. Waste from the VOC lab includes chemical standards, used pump oil, methanol extract waste, hazardous sample and oily sample waste.

11.6. All the non-hazardous waste water can be disposed into the sink if its pH range is 5 - 10. If it is not, then the waste water has to be neutralized before being disposed.

12. REFERENCES

12.1. T*est Methods for Evaluating Solid Wastes, Third Edition, SW-846,* Method 1311, Revision 0, July 1992.

12.2 T*est Methods for Evaluating Solid Wastes, Third Edition, SW-846,* Method 1312, Revision 0, September 1994.

12.3. *Test Methods for Evaluating Solid Wastes, Fourth Edition, SW-846,* Method 8260D, Revision 4, June 2018.

12.4. *Test Methods for Evaluating Solid Wastes, Fourth Edition, SW-846,* Method 8000D, Revision 5, March 2018.

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12.5. Millipore Zero Headspace Extractor (ZHE) Operations and Maintenance Manual, Catalogue Number YT30090HW, Revision A, February 1991.

12.6. Florida Department of Environmental Protection, Quality Manual, Bureau of Laboratories.

12.7. Florida Department of Environmental Protection Laboratory Safety Manual, **OG-001**.

12.8. Florida Department of Environmental Protection, Standard Operating Procedure **CM-027** Result Calculations for Multiphasic Samples.

13. SOP UPDATE REVISION SUMMARY

The following revisions were made to this SOP from the prior version

- Incremented revision number and date.
- Corrected minor typos.
- Updated Section 3 Equipment.
- Updated Section 5 Sample Collection, Preservation and Storage.
- Updated Section 7 Sample Preparation Procedure.
- Updates Section 12 References.

APPENDIX OF SIGNIFICANT CHANGES

2/15/2023	Updated Section 3 Equipment, Section 5 Sample Collection, Preservation and Storage, Section 7 Sample Preparation Procedure, and Section 12 References.
01/25/2024	Updated SOP format.
01/27/2025	Clarified TCLP extraction fluid recipe. Added demo link for ZHE device.

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Appendix: TCLP and SPLP Sample Preparation Form

STATE OF FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION BUREAU OF LABORATORIES	**Volatiles Laboratory** **TCLP and SPLP Sample Preparation Form** **By EPA Methods 1311 or 1312** **INSTRUCTIONS**	

Use and Purpose of Log book:

This log book is to be used at the lab bench to record information and data while preparing samples for TCLP or SPLP analysis. The TCLP and SPLP Sample Preparation Log was designed to be self-explanatory to anyone familiar with the EPA Method 1311 (TCLP), EPA Method 1312 (SPLP), and our Laboratory SOP VO-005. If you are not familiar with these documents, then please review them before using this log book.

Description of Form Header Information:

The top portion of each Sample Preparation Form contains general information that can be filled in prior to starting the filtering and extraction procedures. Please fill in all of the requested information or check the appropriate box(s). If the information requested is not applicable, then mark the box(s) with N/A.

Description of Form Table Information:

The table in the Sample Preparation Form contains information specific to each sample in a preparation batch:

- The Sample ID should come from the LIMs ID assigned to the sample.
- The Zero Headspace Extractor number (ZHE#) comes from the number stamped into the extractor device.
- The Sample Weight to be extracted is given in grams.
- The Extraction Fluid volume should be determined based on the sample size according to the SOP.
- The pre- and post-weight of the 0.70 micron TCLP filter. The post-weight includes all collected solids.
- The Solids Dry Weight is the weight of the dry collected solids after subtracting the pre-filter weight.
- The % Solids = (Solids Dry Weight/ Original Sample Weight)x100.
- The Tedlar Bag weights before and after filtration are used to determine the weight of filtrate collected.

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STATE OF FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION BUREAU OF LABORATORIES	**Volatiles Laboratory** **TCLP and SPLP Sample Preparation Form** **By EPA Methods 1311 or 1312**	**PAGE 1**

Analyst's Initials:	**ALL ITEMS MUST BE COMPLETED BY ANALYST**
Date (MM/DD/YY): / /	**Room Temperature 23 ± 2 ºC?** ☐ Yes ☐ No
EPA Method 1311 TCLP by SOP VO-005-3 ☐ (check one) **EPA Method 1312 SCLP by SOP VO-005-3** ☐	**ZHEs Passed Pressure and Leak Test to 50 PSI?** ☐ Yes ☐ No **(Do not use failed ZHEs until repaired and retested)**
Extraction Fluid Type Used: **EPA Method 1311 Fluid # 1** ☐ (check one) **EPA Method 1312 Fluid # 3** ☐	**Extraction Fluid LIMs Preparation Label:**
Tumbler Rotation Speed 30 ± 2 rpm? ☐ Yes ☐ No	
Tumbling Start Date and Time: / / : **(Tumble Time must be 18 ± 2 hours)**	**Tumbling End Date and Time:** / / :

Sample #	ZHE#	Sample Wt (g)	Extract Fluid Vol (mL)	Filter Pre Wt. (g)	Filter Post Wt. (g)	Solids Dry Wt. (g)	% Solids	Tedlar Bag Wt. (g) [Before/After]
Sand Blank								
DUP								
DUP								

Density Calculations (if required):

PLACE A COPY OF THIS DOCUMENT IN THE JOB FOLDER

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