TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP)

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1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the method for performing the extraction portion of the Toxicity Characteristic Leaching Procedure (TCLP). The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multi-phase wastes. The intent of this leachate procedure is to simulate the conditions that may be present in a landfill where water may pass through the land- filled waste and travel into the groundwater carrying the soluble materials with it. This procedure does not apply to volatile organic analytes.

This SOP is based on Environmental Protection Agency (EPA) Methods SW846/1311and those requirements set forth in the latest approved version of the National Environmental Laboratory Accreditation Committee (NELAC) Quality Systems section. .

2.0 METHOD SUMMARY

For liquid wastes (i.e. those containing less than [<] 0.5 percent [%} dry solid material), the waste, after filtration through a 0.6 to 0.8 micron *(*μm) glass fiber filter, is defined as the TCLP extract.

For wastes containing greater 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 is then reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter.

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.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

Soil samples should be collected in wide-mouth glass containers with Teflon-lined caps. From the time of sample collection until after analysis, samples must be refrigerated at 4 ± 2 degrees Celsius (^{o}C) for periods specified by the Scientific, Engineering, Response and Analytical Services (SERAS) Task Leader or the EPA/Environmental Response Team (ERT) Work Assignment Manager (WAM).

The TCLP extract will be submitted to the proper laboratory section for the required testing within one day of the extraction being completed. All TCLP extracts will be stored at 4 ± 2 ^{o}C and handled per SERAS SOP #2003, *Sample Storage, Preservation and Handling*. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH <2, unless precipitation occurs. In the event of precipitation, the extract will not be acidified to pH <2.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Potential interferences that may be encountered are inherent to the analytical methods analyzed on the extracts.

5.0 EQUIPMENT/APPARATUS

The following are standard materials and equipment required for soil pH determination:

- Agitation Apparatus - The agitation apparatus will be capable of rotating the extraction vessels in an end over end fashion at 30 ± 2 rpm.
- Extraction Vessels
  - Inorganic Analytes - Borosilicate glass bottles or polyethylene bottles shall be used for either organic or inorganic analytes.
  - Organic Analytes - Borosilicate glass bottles shall be used for organic analytes.
- Filtration Device, a 316 stainless steel or polytetrafluoroethylene (PTFE) lined pressure filtration device (filter holder) will be used to filter all samples and extracts. This device will be capable of holding an internal pressure of 100 psi.
- Vacuum/Pressure Pump, a dedicated vacuum/pressure pump for each filtration device. The pressure pump will be used to provide 60 ± 5 psi to the filtration device for pressure filtering of all samples and extracts.
- Filters, 0.7 μm borosilicate glass. When evaluating the mobility of metals, each filter shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1 L per rinse). Glass fiber filters are fragile and should be handled with care.
- pH Meter, accurate to ± 0.05 units at 25 ^{o}C
- Laboratory balance, accurate to within ± 0.01 grams
- Beakerlenmeyer flask, glass, 500 mL
- Watch glasses, appropriate diameter to cover beaker or Erlenmeyer flask.
- Magnetic Stirrer
- Extraction Fluid Containers, 20-Liter, glass construction for inorganic or organic analysis. Polyethylene containers may only be used for inorganic analytes.

6.0 REAGENTS

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all chemicals will conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

- Deionized (DI) water, prepared using an appropriate filtration purification system, capable of producing American Society of Testing and Materials (ASTM) Type II water or equivalent
- Hydrochloric acid (1N) HCl, made from ACS reagent grade
- Nitric acid (1N) HNO_3, made from ACS reagent grade
- Sodium Hydroxide (1N), NaOH, made from ACS reagent grade
- Glacial acetic acid, CH_3CH_2OOH, ACS reagent grade
- Extraction Fluid, prepared in 1-L batches or it may be made in larger batches as required by the total number of extractions required. For larger batches, the following procedures should be scaled by the total number of required extractions.
  - Extraction Fluid #1 - Add 5.7 mL of glacial CH_3CH_2OOH to 500 mL of reagent water. Add 64.3 ml of 1N NaOH, and dilute to a volume of 1L. When correctly prepared, the pH of this fluid will be 4.93 ± 0.05.
  - Extraction Fluid #2 - Dilute 5.7 mL of glacial CH_3CH_2OOH with reagent water to a volume of 1 L. When correctly prepared, the pH of this fluid will be 2.88 ± 0.05.

7.0 PROCEDURES

7.1 Preliminary Evaluations

Preliminary evaluations shall be performed on a minimum 100 gram aliquot of waste. This aliquot may not actually undergo extraction. These preliminary evaluations include: (1) determination of the percent solids (Section 7.1.1.); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Section 7.1.2); (3) determination of whether the solid portion of the waste requires particle size reduction (Section 7.1.3); and (4) determination of which of the two extraction fluids are to be used for the TCLP extraction of the waste (Section 7.1.4).

1. Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.
   - If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids proceed to section 7.1.3.
   - If the sample is liquid or multi-phase, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Section 5.3 and outlined in Sections 7.1.1.3 through 7.1.1.9.
   - Pre-weigh the filter and the container that will receive the filtrate.

- Assemble the filter holder and filter following the manufacturers' directions. Place the filter on the support screen and secure.

- Weigh out a sub-sample of the waste (100 gram minimum) and record the weight.

- Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

- Transfer the waste sample to the filter holder (liquid and solid phases). Spread the sample evenly over the surface of the filter. If filtration of the waste at 4 ^{o}C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm to room temperature in the device before filtering.

  Gradually apply gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not passed through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

  NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

- The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

  NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, as outlined in Section 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

- Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Section 7.1.1.3) from the total weight of the filtrate filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the total waste sample, as determined in 7.1.1.5.

  Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent Solids} = \frac{\text{Weight of Solid}}{\text{Total Weight of Waste}} \times 100$$

2. If the percent solids determined in Section 7.1.1.9 is equal to or greater than 0.5%, then proceed to Section 7.1.3 to determine whether the solid material requires particle size reduction. If the percent solids determined in Section 7.1.1.9 is less than 0.5% then proceed to Section 7.2.9 to perform the TCLP.

3. Determination of whether the waste requires particle size reduction - Any material which does not pass through a 9.5mm (0.375 inch) standard sieve requires size reduction. The material should be prepared for extraction by crushing, cutting or grinding the waste to a particle size as described above.

4. Determination of appropriate extraction fluid - If the solid content of the waste is greater than or equal to 0.5%, determine the extraction fluid as follows:

   - Weigh out a small sub-sample of the solid phase of the waste, reduce the solid to a particle size of approximately 1mm or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask.

   - Add 96.5 mL of reagent water to the beaker, cover with a watch glass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. Proceed to Section 7.2.

   - If the pH is >5.0, add 3.5 mL 1N HCl, slurry briefly, cover with a watch glass, heat to 50 ^{o}C, and hold at 50 ^{o}C for 10 minutes.

   - Let the solution cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2. Proceed to Section 7.2.

5. If the aliquot of waste used for the preliminary evaluation (Sections 7.1.1 - 7.1.4) was determined to be 100% solid at Section 7.1.1.1, then it can be used for the Section 7.2 extraction (assuming at least 100 grams remain).

7.2 Procedure When Volatiles are Not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample may be appropriate, depending on the solids content of the waste sample (percent solids, see Section 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semi-volatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single TCLP will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

1. If the waste is 100% solids, weigh out a sub-sample of the waste (100 gram minimum)

and proceed to Section 7.2.9.

2. If the waste is liquid or multi-phase, liquid/solid separation is required. This involves the filtration device described in Section 5.3.2 and is outlined in Sections 7.2.3 to 7.2.8

3. Pre-weigh the container that will receive the filtrate.

4. Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Section 5.4).

5. Weigh out a sub-sample of the waste (100 gram minimum) and record the weight.

   If the waste contains <0.5% dry solids (Section 7.1.2), the liquid portion of the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the TCLP extract.

   For wastes containing >0.5% dry solids, use the percent solids information obtained in Section 7.1.1 to determine the amount of sample to be filtered to produce 100 grams of solids per required TCLP extraction.

6. Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solids portion of the waste through the same filtration system.

7. Transfer the waste sample to the filter holder (liquid and solid phases). Spread the sample evenly over the surface of the filter. If filtration of the waste at 4 ^{o}C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm to room temperature in the device before filtering.

   Gradually apply gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not passed through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

   NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

8. The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either

analyzed (See section 7.2.12) or stored at 4 °C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, as outlined in Section 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

9. If the waste contains <0.5% dry solids (See section 7.1.2), proceed to Section 7.2.13. If the waste contains >0.5% dry solids (see Section 7.1.1 or 7.1.2), and if particle size reduction of the solid was needed in Section 7.1.3, proceed to Section 7.2.10. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to 7.2.11.

10. Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a particle size as described in Section 7.1.3. When the particle size has been appropriately altered, transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

11. Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of Extraction Fluid} = \frac{20 \times \%\text{Solids} \times \text{Veight of Waste Filtered}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Section 7.1.4) to the extractor vessel. Apply Teflon tape to the threads of the bottle, and close tightly. Secure in the rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature of the room shall be maintained at 23 ± 2 °C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

12. Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Section 7.2.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid washed (see Section 4.4) if evaluating the mobility of metals.

13. Prepare the TCLP extract as follows:

- If the waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.2.12 is defined as the TCLP extract. Proceed to Section 7.2.14.

- If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Section 7.2.12 with the initial liquid phase of the waste obtained in Section 7.2.7. This combined liquid is defined as the TCLP extract. Proceed to Section 7.2.14.

- If the initial liquid phase of the waste, as obtained from Section 7.2.7, is not or may not be compatible with the filtered liquid resulting from Section 7.2.12, do not combine these liquids. Submit these two liquids separately, and notify the laboratory that they are both considered the TCLP extract for that sample.

- Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH <2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4 ^{o}C) until analyzed.

8.0 CALCULATIONS

This section is not applicable to this SOP.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

The following general QA procedures apply:

- All data must be documented on TCLP Extraction Log/TCLP Extraction Fluid Preparation Log data sheets (Appendices A and B, respectively) or in site or laboratory notebooks.

- All instrumentation must be operated in accordance with the manufacturer's instructions. Equipment check-out procedures and calibration activities must be performed prior to commencing this procedure.

- A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in the extraction vessel.

- Duplicate samples should be processed with the frequency of one in twenty samples. Duplicate samples will be used to determine precision.

- Samples must undergo TCLP extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES (DAYS)

	From: Field collection To: TCLP Extraction	From: TCLP Extraction To: Preparative Extraction	From: Preparative Extraction To: Determinative Analysis	Total Elapsed Time
Semi-volatiles	14	NA	40	61
Mercury	28	NA	28	56
Metals (except mercury)	180	NA	180	360

10.0 DATA VALIDATION

For the pH meter, ± 0.1 pH unit represents the limit of accuracy under normal conditions, especially for measurement of water and poorly buffered solutions[(1)].

Results will be reviewed by the Engineering Evaluation Unit (EEU) Task Leader prior to release. This information will be utilized to qualify the environmental sample results accordingly with the project's data quality objectives.

11.0 HEALTH AND SAFETY

General laboratory and field safety practices should be followed. Waste samples should be handled with care due to the uncertainty of the properties and contents involved. Refer to the specific material safety data sheet (MSDS) for the hazardous properties of any chemical or reagent utilized in this analysis. All excess samples, used samples, and waste material generated during analysis must be disposed in accordance with SERAS SOP #1501, *Hazardous Waste Management.*

When working with potentially hazardous materials, follow EPA, Occupational Safety and Health Association (OSHA), and Corporate health and safety procedures. More specifically, refer to SERAS SOP #3013, *Laboratory Safety Program.*

12.0 REFERENCES

[(1)] American Society of Testing and Materials (ASTM). 1995. *Annual Book of ASTM Standards*, Designation D4972 - 95a: Standard Test Method for pH of Soils.

NELAC. *Quality Systems*, current approved version.

United States Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1996. *Test Methods for Evaluating Solid Waste,* SW-846, 3rd ed.. Method 1311.

12.0 APPENDICES

A. TCLP Extraction Log
B. TCLP Extraction Fluid Preparation Log

APPENDIX A
TCLP Extraction Log
SOP #1831
November 2005

APPENDIX B
TCLP Extraction Fluid Preparation Log
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