THE TOXICITY CHARACTERISTIC LEACHING PROCEDURE (EPA METHOD 1311) AND THE SYNTHETIC PRECIPITATION LEACHING PROCEDURE (EPA METHOD 1312)

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1. SCOPE AND APPLICATION

1.1 The toxicity characteristic leaching procedure (TCLP) is designed to determine the mobility of both organic and inorganic analytes in liquid, solid, and multiphasic wastes, soils, and sediments under conditions that simulate those found in a landfill. This SOP applies to TCLP extractions using EPA Method 1311 for both inorganic and organic analytes.

1.2 The synthetic precipitation leaching procedure (SPLP) is designed to determine the mobility of both organic and inorganic analytes in liquid, solid, and multiphasic wastes, soils, and sediments under conditions that simulate rainwater percolating through a sample. This SOP applies to SPLP extractions using EPA Method 1312 for both inorganic and organic analytes.

1.3 Aqueous sample extracts scheduled for metals analysis are digested according to DEP SOP MT-024 and non-aqueous sample extracts are digested according to DEP SOP MT-060. Sample extracts scheduled for metals are then analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or

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inductively coupled plasma mass spectrometry (ICPMS). Applicable tests are TCLP-ICP, TCLP-ICPMS, SPLP-ICP, and SPLP-ICPMS.

1.4 Aqueous sample extracts scheduled for mercury analysis are digested according to DEP SOP HG-018 and non-aqueous sample extracts are digested according to DEP SOP HG-020. Sample extracts are then analyzed by cold vapor atomic absorption spectroscopy (CVAAS, for mercury analysis) or cold vapor atomic fluorescence spectroscopy (CVAFS, for low level mercury analysis). Applicable tests are TCLP-HG-H, SPLP-HG-AF, and SPLP-HG-H.

1.5 Sample extracts that are scheduled for organic analysis are extracted in preparation for gas chromatography mass spectrometry (GC/MS), gas chromatography with nitrogen-phosphorus detection (GC/NPD), or gas chromatography with electron capture detection (GC/ECD). Applicable tests are TCLP-AH-AA, TCLP-BNA, TCLP-PS-CL, SPLP-AH-AA, SPLP-BNA, SPLP-PAH, SPLP-PS-CL, and SPLP-PS-NP.

2. SUMMARY OF THE METHOD

2.1 The sample undergoes a preliminary evaluation, which may include determination of percent solids, percent dry solids, and/or particle size reduction.

2.2 For samples with $< 0.5\%$ dry solids, the sample filtrate is defined as the extract. For samples with $\geq 0.5\%$ dry solids, the solid and liquid phases are separated and the solid phase is extracted with the appropriate extraction fluid. Any filtrate obtained is combined with the extract and this is determined to be the total extract.

2.3 In TCLP extractions the type of extraction fluid used is determined by the sample pH.

2.4 In SPLP extractions the extraction fluid used is determined by the sampling location, sample type, and analysis required.

2.5 The volume (mL) of extraction fluid used in either leaching procedure is calculated by multiplying the mass of solid sample (g) by 20.

2.6 After the sample has been extracted in the appropriate fluid, the solid and liquid phases are separated by filtration. The liquid extract is combined with any filtrate collected prior to extraction.

2.7 The liquid portion of the sample is then prepared appropriately for each test.

3. APPARATUS AND EQUIPMENT

3.1 Agitation apparatus (agitator).

3.2 Accumet AB15 pH meter.

3.3 Millipore pressure filtration device.

3.4 Top-loading balance.

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3.5 Fisherbrand borosilicate glass TCLP filter, 142 mm OR Whatman Glass borosilicate glass microfiber filters, TCLP, acid treated, low metal, 142 mm.

3.6 Thermolyne heating/stirring plate.

3.7 250 mL beakers.

3.8 2 L beakers.

3.9 Jack stand.

3.10 Compressed nitrogen or air connection for the filtration device.

3.11 Vented oven.

3.12 9.5 mm (0.375 inch) standard sieve, preferably Teflon coated.

3.13 Watch glass large enough to cover a 250 mL beaker.

3.14 Polypropylene extraction vessels.

3.15 Teflon extraction vessels.

3.16 Aluminum foil.

3.17 Constant temperature water bath.

3.18 1 L polypropylene bottles for storing extracted samples.

3.19 Disposable stir bars.

3.20 6” wide Teflon tape.

3.21 Separatory funnel.

3.22 Narrow range pH paper, 0 - 5.0 pH units.

3.23 2 mL class A volumetric flask.

3.24 1 L, 50 mL, and 10 mL class A graduated cylinders.

3.25 1.0 mm standard sieve.

3.26 Laboratory spatulas.

4. REAGENTS AND CHEMICALS

Note: See DEP SOP MT-069 for further instruction on reagent documentation. All containers of reagents and standards (purchased and prepared) in the laboratory are required to have laboratory information management system (LIMS) labels which includes a serial number. This includes the purchased acetic acid, the purchased sulfuric acid, the purchased nitric acid, the prepared 1.0 N sodium hydroxide, the prepared 60:40 sulfuric acid/nitric acid mix, and the prepared TCLP or SPLP extraction fluid.

4.1 Deionized (DI) Water.

4.2 1.0 N Trace Metal Grade Hydrochloric Acid (HCl) - Dilute 8.3 mL of concentrated HCl to 100 mL with DI water. Expiration date is provided by the manufacturer of the concentrated HCl.

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4.3 Reagent Grade A.C.S. Glacial Acetic Acid, commercially available. Expiration date provided by the manufacturer.

4.4 Trace metal grade sulfuric acid (H_2SO_4), commercially available. Expiration date provided by the manufacturer.

4.5 Trace metal grade nitric acid (HNO_3), commercially available. Expiration date provided by the manufacturer.

4.6 Universal sediment spike solution. Expiration date provided by the manufacturer of the single-element standards used to prepare the spike.

4.7 1.0 N Sodium Hydroxide (NaOH) - Dilute 40 g solid NaOH to 1 L with DI water. This solution is used in the preparation of TCLP extraction fluid #1 (section 4.9.1). Expiration date is 1 year from preparation.

4.8 60/40 w/w mixture of H_2SO_4/HNO_3 - This solution is made by volume measurements using the densities of H_2SO_4 and HNO_3. The density of H_2SO_4 is 1.84 g/mL (Merck Index) and the density of HNO_3 is 1.51 g/mL (Merck Index). Slowly add 32.8 mL of H_2SO_4 to 26.5 mL of HNO_3. This solution can be diluted to 50 % of its normal strength by carefully adding an additional 59.3 mL of DI water. The diluted solution will make it easier to adjust the pH of the extraction fluid. Expiration date is provided by the manufacturer of the concentrated acids.

4.9 TCLP Extraction Fluids:

4.9.1 Extraction Fluid #1 - Add 11.4 mL of glacial acetic acid to 1 L of DI water. To this solution add 128.6 mL of the 1.0 N NaOH solution (see 4.7). Dilute this solution to 2 L with DI water. The pH must be 4.93 pH units ± 0.05 pH units (4.88 - 4.98 pH units). Add more acid or base to adjust the pH if necessary.

4.9.2 Extraction Fluid #2 - Add 11.4 mL of glacial acetic acid to 1 L of DI water**.** Dilute this solution to 2 L. The pH must be 2.88 pH units ± 0.05 pH units (2.83 - 2.93 pH units). Add more acid to adjust the pH if necessary.

4.10 SPLP Extraction Fluids:

4.10.1 Extraction Fluid #1 - Determine the total amount of extraction fluid required. Add DI water to the SPLP carboy. The exact volume is not critical because this solution does not have a defined acid concentration and is not buffered, but prepare at least a liter more than the calculated required volume.

Slowly add diluted 60/40 H_2SO_4/HNO_3 solution (see 4.8) a couple of drops at a time until the pH reaches the desired level. If too much of the acid solution is added and the pH falls below the level needed add more DI water until a pH of 4.20 ± 0.05 pH units (4.15 - 4.25 pH units) is obtained.

4.10.2 Extraction Fluid #2 is made in the same manner as extraction fluid #1, except the final pH must be between 4.95 and 5.05.

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Note: Extraction fluids will be considered expired one week after preparation. Fresh extraction fluid should be prepared for each extraction.

Note: Be sure to label the extraction fluid carboy with the LIMS label which includes the serial number and expiration date of the solution.

5. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1 Samples are stored in the metals room or refrigerator, located in the Receiving/Custody Room of the laboratory. If samples are also to be analyzed for organics they will be stored in a refrigerator. Allow the chilled samples to come to room temperature before determining pH or beginning an extraction.

5.2 All glassware should be cleaned thoroughly according to DEP SOP MT-007. The filtration unit should be cleaned by disassembling the apparatus (especially by removing the O-rings), soaking in soapy water, scrubbing gently with a brush (be careful not to harm the Teflon coating), and thoroughly rinsing with DI water. If the filtration unit was previously used with a sample containing high concentrations of trace metals, briefly soaking in a 10 % HNO_3 bath may be required. HCl must **NOT** be used to clean the stainless steel filtration units.

Note: If the filtration unit cannot be cleaned because of an organic residue, use an organic solvent (hexanes, acetone, methanol, or methylene chloride) to dissolve the residue. Repeat these steps as necessary. Be sure to discard the organic waste in the appropriate waste container.

5.3 Samples are not preserved prior to extraction.

5.4 Sample Maximum Holding Times (Days) for TCLP and SPLP

	From: Field Collection To: TCLP extraction	From: TCLP extraction To: Preparative extraction	From: Preparative extraction To: Determinative analysis	Total elapsed time
Mercury	28	NA	28	56
Metals	180	NA	180	360
Semi-volatiles	14	7	40	61

If sample holding times are exceeded, values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a sample does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the sample exceeds the regulatory level.

6. SAMPLE PREPARATION PROCEDURE

Note: Before beginning sample preparation ensure that all support equipment has been properly calibrated. This includes thermometer, balance, and pH meter calibration checks.

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Document the identity of the thermometer, balance, and pH meter/probe on the MT-TCLP-SPLP-EXT form. Be sure to check to make sure the most up-to-date form is used by checking the form version on the DEAR intranet.

A copy of the MT-TCLP-SPLP-EXTextraction form is located in both the TCLP and SPLP Prep folders on \\FLDEP1\DEAR\LABS\LAB5\Chemistry\InorganicPrep\METALS. Save the working copy with the test name and extraction number (e.g., Extraction logbook TCLP-#679.xlsx).

The preparation staff is responsible for completing the electronic version of the MT-TCLP-SPLP-EXT extraction form. Any handwritten notes shall be sent to the analysis lab so that the analysis staff can include a copy with their laboratory reports. The electronic MT-TCLP-SPLP-EXT form as well as handwritten notes will be crosschecked with the analysis data. At this point the electronic version will be printed and included with the final data write-up package. This is the official preparation record. To eliminate handwritten notes, a DEP laptop should be used.

Note: Bolded text indicates data that is entered into the MT-TCLP-SPLP-EXT extraction form.

6.1 Preliminary Evaluations:

6.1.1 Perform an initial inspection of the original sample. Note on the MT-TCLP-SPLP-EXT extraction form the number of sample phases, whether the sample is homogeneous or heterogeneous, whether the sample is 100 % solid and describe the appearance of the sample. It may be necessary to centrifuge the sample prior to filtration – see Appendix C.

Note: It may be advantageous to perform the particle size reduction step (6.1.4 – 6.1.6) prior to the determination of the percent solid. If the percent solid test yields greater than 25 g of solid material and the solid was not placed in the oven it can be used for the extraction (assuming it will yield enough extract to support all needed analytical measurements).

6.1.2 Determination of Preliminary Percent Solids:

6.1.2.1 For TCLP and SPLP, percent solids are defined as that fraction of a waste sample from which no liquid may be forced out by an applied pressure. If the sample is sand or soil and obviously contains no liquid, the sample may be assumed to be 100 % solids and there is no need to determine the percent solids. Proceed to section 6.1.4.1. If it is uncertain whether the sample is 100 % solid, then percent solids must be determined.

6.1.2.2 **Mass of Clean Filter -** Weigh a clean (if necessary, see 6.1.2.3 for cleaning procedure), dry, acid rinsed filter that will be used in sample filtration along with a piece of aluminum foil and record as the mass. Write the sample ID # on the aluminum foil for identification purposes.

6.1.2.3 If a pre-washed filter is not used, clean the filter by rinsing it with 1 N HNO_3 followed by three consecutive rinses of DI water and let dry.

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6.1.2.4 **Mass of Clean Receiving Vessel** - Weigh the beaker that will receive the filtrate. Set up the filtration device using the pre-weighed filter. Place the filtrate-receiving beaker beneath the filtration device outlet. Use a jack, if necessary, to raise the receiving beaker so that the beaker mouth is at the same level as the outlet. This will ensure that the receiving beaker catches all of the filtrate.

6.1.2.5 **Mass of Beaker + Waste** - Weigh approximately 103 g homogenized sample into the transfer beaker and record the weight. The additional 3 g is to account for the sample that may stick to the transfer beaker.

6.1.2.6 Transfer the sample into the filtration device. If the sample contains a liquid and solid phase, decant the liquid into the filtration device first to prevent clogging the filter.

6.1.2.7 Tighten the fixtures holding the top on the filtration device. Place the sealing white O-ring on the top and attach the gas line. Gradually apply a pressure of 1 - 10 psi. (Applying instantaneous pressure can prematurely plug the filter.) If no filtrate comes out or the filtrate flow slows to less than 1 drip per 2 minutes, slowly increase pressure in 10 psi increments to a maximum of 50 psi. It is important that pressure be increased slowly so that the filter does not prematurely plug. When pressurizing gas passes through the filter or when the filtrate flow is less than 1 drip per 2 minutes, stop filtration. Stop the gas flow, vent the excess pressure and remove the gas line from the filtration device. If there is a significant solid phase remaining in the beaker, proceed to 6.1.2.8. If not, proceed to 6.1.2.9.

Note: Some wastes, such as paint wastes and some oily wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material may not filter. If this is the case, the material within the filtration device is defined as the solid.

Note: Do not replace the original filter with a fresh filter under any circumstances. Use only one filter when determining the preliminary percent solid.

6.1.2.8 If necessary, open the filtration device and transfer as much of the solids as possible to the filtration device. You may add some of the filtered liquids back to the solids to loosen them. DO NOT RINSE THE SOLID WITH DI WATER!!! This will dilute the sample and it will not be useable. Reassemble the filtration device and return the receiving vessel back under the filtration device. Apply pressure again (see section 6.1.2.7) and proceed with determining percent solids.

6.1.2.9 **Mass of Dirty Beaker** - Weigh the dirty transfer beaker.

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6.1.2.10 **Mass of Subsample** - Automatically calculated in worksheet (Mass of Beaker + Waste – Mass of Dirty Beaker).

6.1.2.11 **Mass of Vessel + Filtrate** - Weigh the receiving beaker and filtrate and record weight. This filtrate may have both an aqueous and non-aqueous phase.

6.1.2.12 **Mass of Filtrate** - Automatically calculated by worksheet. (Mass of Vessel + filtrate – Mass of Clean Receiving Vessel)

6.1.2.13 **Mass of Solid** - Automatically calculated by worksheet. (Mass of Subsample- Mass of Filtrate)

6.1.2.14 **Preliminary % Solid** - Automatically calculated by worksheet. (Mass of Solid/Mass of Subsample * 100)

6.1.2.15 If the preliminary percent solids are < 0.5 %, then proceed to the sample filtration step (6.3.6.3). In this case, the sample will be filtered with a filtration device and the resulting filtrate will be defined as the TCLP or SPLP extract. If the percent solid test yielded enough filtrate to support all analytical tests, this filtrate can be used as the TCLP extract.

Note: If the 100 g preliminary percent solids sample portion yielded greater than 25 g of solid, then this solid can be used for extraction (although particle size reduction may be required). 25 g of solid is extracted with 500 mL extraction fluid, which should yield sufficient fluid for the digestion procedure. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample, whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics and pesticides are both analytes of concern.

6.1.3 Determination of Percent Dry Solids - The determination of percent dry solids is necessary to determine whether or not the sample is greater than or less than 0.5 % dry solid. If the sample is greater than or equal to 0.5 % dry solid, the solid and liquid phases are separated and the solid phase is extracted with the appropriate extraction fluid. If the sample is less than 0.5 % dry solid, the filtrate is defined as the TCLP or SPLP extract.

6.1.3.1 Percent dry solids do not need to be determined if the preliminary percent solid is over 20 %, but see Note below. Proceed to section 6.1.4.1. If the preliminary percent solids are < 20 %, the percent dry solids will need to be determined.

Note: Some wastes, such as oily wastes and some paint wastes may not pass through the filter and will contribute to the percent solid. Percent dry solids should still be determined for these types of samples even though the percent solid is over 20 % because some oil or paint may evaporate in the oven at 100 °C ± 20 °C. Consult supervisor if the solid portion of the TCLP sample is not a routine sediment.

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6.1.3.2 The % dry solids may be determined by weighing the used filter and corresponding foil (from the filtration device in the preliminary percent solid determination). Place in an oven set at 100 °C ± 20 °C and dry until two successive weights differ by less than 1 %. Record both weights as **Filter Paper + Dry Solids #1** and **Filter Paper + Dry Solids #2**.

6.1.3.3 **% Dry Solids** - Automatically calculated by worksheet. ((Filter Paper + Dry Solids #2 – Mass of Clean Filter)/Mass of Subsample * 100)

6.1.3.4 If the percent DRY solids are < 0.5 %, go to the sample filtration step (6.3.). The sample will be filtered through a Millipore, or equivalent, pressure filtration device; the resulting filtrate is defined as the TCLP or SPLP extract.

6.1.4 If the percent DRY solids are $\geq$ 0.5 % proceed to the particle size reduction step.

6.1.4.1 Particle size reduction is necessary if:

a) The solid portion of sample does not pass through a 9.5 mm (0.375 in) standard sieve.

OR

b) The surface area per gram of material is not equal to or greater than 3.1 cm^2.

6.1.5 Surface area criteria apply only to filamentous waste materials such as paper or cloth (see Method 1311, section 7.1.3 for a more detailed description). The method states that there is no method for particle size reduction for materials that do not obviously meet this criteria.

6.1.6 To reduce particle size of the subsample, crush, cut, or grind until particles are small enough. If particle size of the sample is reduced, note on extraction sheet in the sample notes section that particle size reduction was performed. If particles can't be reduced to < 9.5 mm with available equipment, contact supervisor.

6.2 Determination of which extraction fluid is to be used:

6.2.1 SPLP:

6.2.1.1 Extraction Fluid #1 should be used if the samples are soil from a site east of the Mississippi River or if they are waste or wastewater samples. Proceed to sample extraction, section 6.3.

6.2.1.2 Extraction Fluid #2 should be used if the samples are soil from a site west of Mississippi. Proceed to sample extraction, section 6.3.

6.2.2 TCLP:

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6.2.2.1 **Mass of Subsample -** Place a 250 mL beaker on the balance and tare. Weigh 4.9 to 5.1 g of the solid phase of the sample into the beaker.

Note: If the percent dry solid is > 0.5 % but a 4.9 to 5.1 g subsample of the solid phase cannot be obtained, weigh 4.9 to 5.1 g of the total sample.

6.2.2.2 Pour the subsample into a 1 mm sieve. Any sample that does not pass through sieve, break-up until the entire sample passes through. If it is obvious the sample will pass through the sieve without size reduction it is not necessary to pass through the sieve.

6.2.2.3 **Volume of DI water -** Add 96.5 mL of DI water. Cover with a watch glass or parafilm, and stir vigorously on a stir plate for 5 minutes using a magnetic stirrer.

6.2.2.4 **Initial pH** - Measure and record the pH with a calibrated pH meter. A solid state pH probe is preferred due to the interference from TCLP samples with standard pH electrodes.

6.2.2.4.1 If the pH of the sample is less than 5.0 pH units, extraction fluid #1 is used for the sample extraction. Record 'no' in the 3.5 mL HCl added box.

6.2.2.4.2 HCl addition - If the pH is greater than 5.0 pH units, add 3.5 mL 1.0 N HCl and record yes in the **3.5 mL HCl added** box. Swirl the sample and heat at 50 °C for 10 minutes in a water bath. Let the solution cool to room temperature, and measure/record the pH as the **pH after HCl + Heat**.

Note: Record the LIMS serial number of the 1.0 N HCl on the MT-TCLP-SPLP-EXT extraction form.

6.2.2.4.3 If the pH is less than 5.0, use extraction fluid #1.

6.2.2.4.4 If the pH is greater than 5.0, use extraction fluid #2. Ensure that the correct **Extraction Fluid to be Used** is listed on the MT-TCLP-SPLP-EXT extraction form.

6.3 Sample Extraction:

Note: If the sample requires analysis for organics, tumble the sample in a glass or PTFE extraction vessel.

Note: Each time a reusable extraction vessel is used, its identification number must be recorded on the MT-TCLP-SPLP-EXT extraction form. Following twenty (20) extractions in a particular vessel, that vessel must be used for a blank extraction in order to assess carryover contamination. To properly clean a glass or PTFE extraction vessel, first rinse with dilute HCl (20-50 %). Then after rinsing with DI water three times, wash glassware with an organic solvent, such as methanol (CH_3OH), followed by rinsing with DI water three times.

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6.3.1 A minimum sample size of 100 g (solid and liquid phases), is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample, whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics and pesticides are both analytes of concern. If a different amount of sample is used, please explain in the notes section of the MT-TCLP-SPLP-EXT extraction form.

6.3.2 If the sample is 100 % solid, as determined by the preliminary percent solid measurement, no filtration is required. Proceed to section 6.3.6.2.

6.3.3 If sample is liquid or multiphasic, liquid/solid separation is necessary. Filter the sample through a filtration device. The liquid filtrate is collected and stored for later processing (see section 6.5). The solid remaining on the filter paper is extracted.

6.3.4 Preparing samples for Extraction - If filtration is needed, assemble the filtration device using a purchased, pre-washed filter or a clean filter that has been rinsed with 1 N HNO_3 followed by three consecutive rinses of DI water.

6.3.5 **Mass of Clean Receiving Vessel** - Weigh the filtrate receiving vessel and record the weight. Place the filtrate receiving beaker beneath the filtration device outlet. Use a stand, if necessary, to raise the receiving beaker so that the beaker mouth is at the same level as the outlet. This ensures the receiving beaker catches all of the filtrate.

6.3.6 **Mass of Subsample + Beaker -** Weigh an appropriate amount of sample and record the weight.

6.3.6.1 If the sample is $\geq$ 0.5 % dry solids, divide 100 g by the percent solids (in decimal form) to determine the amount of sample needed to filter to get 100 g of solid phase. This calculation is automatically completed in the worksheet.

6.3.6.2 If the sample is 100 % solid, weigh out approximately 103 g. The extra sample takes into account the sample loss occurring from the adherence of sample to the walls of the transfer vessel.

6.3.6.3 If the sample is < 0.5 % dry solids, the filtrate is defined as the extract. Be sure to filter enough sample to get at least 500 mL of extract if possible -- this will be enough for metals and mercury digestions. Skip to the filtrate finalization step (section 6.5).

Note: If the sample has a low percent solid, a large sample volume will be needed to produce the recommended amount of 'solid' sample. Enough solids should be generated for extraction so that the volume of the extract is sufficient to support all necessary analyses. If the amount of extract generated by a single extraction is not sufficient to perform all analyses, more than one extraction may be performed and the extracts from each combined.

6.3.7 **Mass of Dirty Beaker -** Transfer the sample into the filtration device from the transfer beaker. Weigh the dirty transfer beaker and record the mass.

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6.3.8 Re-tighten the fixtures holding the top on the filtration device. Place the sealing white O-ring on the top and attach the gas line. Gradually apply a pressure of 1 - 10 psi. (Applying instantaneous pressure can prematurely plug the filter!) If no filtrate comes out or the filtrate flow slows to less than one drip per 2 minutes, slowly increase pressure in 10 psi increments to a maximum of 50 psi. It is important that pressure be increased slowly so that the filter does not prematurely plug. When pressurizing gas passes through the filter or when filtrate flow is less than one drip per 2 minutes, stop filtration. Stop gas flow and remove the gas line from the filtration device.

6.3.9 **Mass of Subsample -** Automatically calculated by the worksheet. (Mass of waste + beaker – Mass of dirty beaker)

6.3.10 **Mass of Receiving Vessel + Filtrate -** Weigh the receiving vessel and filtrate and record the mass.

6.3.10.1 Transfer the filtrate into a clean sampling container, the size of which will depend on the amount of filtrate collected. If doing several extractions for one sample, use a larger container to begin with and store all filtrate from all extractions in that container.

6.3.10.2 Carefully transfer the dirty filter from the filtration device to the extraction vessel using a clean spatula if necessary. Also, if the solid is thick and/or viscous, place a clean filter atop the dirty one to soak up the solid. This allows for cleaner transfer of the solid from the filtration device to the extraction vessel.

6.3.11 **Mass of Filtrate -** Automatically calculated by the worksheet (Mass of vessel + filtrate – Mass of clean receiving vessel).

6.3.12 **Mass of Solid** - Automatically calculated by the worksheet (Mass of subsample – Mass of Filtrate).

6.3.13 **Volume of Extraction Fluid Needed** - Automatically calculated by the worksheet (Mass of Solid (g) * 20 = Volume needed (mL)).

6.3.14 **Extraction Fluid Used** - Choose which extraction fluid will be used from the pull down menu.

6.3.15 **pH of Extraction Fluid** - Automatically populates from the extraction fluid preparation section. Confirm that the pH is correct.

6.3.16 An Extraction Blank must be prepared for each set of TCLP samples that are extracted together. The Extraction Blank is prepared in the same manner as the samples. If both types of extraction fluid are used, prepare two blanks - one for each type of extraction fluid.

6.3.17 **Volume of Extraction Fluid Used** - Slowly add the appropriate amount of extraction fluid to the solid in the extraction vessel. Record the volume of extraction fluid added.

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6.3.18 Tighten the extraction vessel lid and stretch Teflon tape around the vessel lid to provide additional protection from leaks. Place extraction vessel inside of a large ziplock bag to help contain any leaks that occur during tumbling. Secure the extraction vessel into the rotator/tumbler. Check carefully for correct attachment. It may appear secure but can fall out of the agitator when touched. Make sure that the samples are evenly balanced and secure.

6.3.19 Sample Tumbling - Turn on the tumbler and let the samples turn over a few times. Turn off the tumbler and check around the vessel lips for any leaks or bulging. Try to squeeze the vessel. If any leaks are noticed, remove the vessel and replace the Teflon tape as necessary. If bulging is observed or the vessel cannot be squeezed, unscrew the vessel and vent into a hood. Securely replace the vessel in the tumbler. Repeat the above steps while checking and fixing any leaks. If no leaks are observed, the extraction may proceed. The samples must rotate for 18 hours ± 2 hours**. Record the temperature of room, the revolutions per minute of the agitator, time & date extraction started and time & date extraction complete. The temperature** of the laboratory where the samples are tumbled must be in the range of 21 °C – 25 °C, if not, contact supervisor. The tumbler must be rotating at 30 ± 2 rpm, if not, contact supervisor.

6.4 Extract Filtration and Finalizing the Extract:

6.4.1 After the 18 ± 2 hour rotation period, the material in the vessel must be separated into liquid and solid phases by filtering through a clean filtration device with a clean, acid rinsed filter. Clean the filter (if not prewashed by the manufacturer) by rinsing it with 1 N HNO_3 followed by three portions of DI water. Pour the non-filtered extract into the filtration device through the top intake. Place the sealing white O-ring on the top and attach the gas line. If necessary, gradually apply pressure of 1 - 10 psi, (filtrate should come out of the filtration device).

Note: If the extract contains mostly aqueous liquids with fine particulate solids, it MAY be necessary to centrifuge the extract PRIOR to filtration to prevent the sample from clogging the filter – see Appendix C.

Note: Applying instantaneous pressure can prematurely plug the filter! If no filtrate comes out or the filtrate flow slows to less than one drip per 2 minutes, slowly increase pressure in 10 psi increments to a maximum of 50 psi. It is important that pressure be increased slowly so that the filter does not prematurely plug. When pressurizing gas passes through the filter or when filtrate flow is less than one drip per 2 minutes, stop filtration. Stop gas flow and remove the gas line from the filtration device.

Note: If the filter plugs and there is still un-filtered liquid in the filtration vessel, replace the vessel containing the filtered extract with the dirty extraction vessel. Scratch a hole in the bottom of the filter paper with a clean spatula to allow fluid and solid to drain back into the dirty extraction vessel. Replace with a new cleaned filter and repeat the filtration process.

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6.4.2 Determine if the extract is multiphasic. Determine which of the phases is non-aqueous by removing a small aliquot (~2 mL) with a disposable pipette and attempting to mix the aliquot in an equal volume of DI water. Non-aqueous waste will not be miscible and form beads of solution that will not dissolve in water.

Note: NOTIFY YOUR SUPERVISOR AND THE ANALYSIS GROUP SUPERVISOR IMMEDIATELY IF THERE ARE BOTH AQUEOUS AND NONAQUEOUS PHASES.

6.4.3 If only one phase is present and it is aqueous, record the **Recovered Aqueous Extraction Fluid Volume** and if there was a liquid phase separated from the original sample (see section 6.3.3) skip to section 6.5, if not skip to section 6.7.

6.4.4 If more than one phase is present, separate the two phases using a separatory funnel. Record the **Mass of Clean Vessel for the non-aqueous phase.** Transfer each phase into a separate clean bottle and label with the LIMS sample ID and then indicate which phase is in the bottle after determination in the following steps.

6.4.5 Record the **Volume of the Aqueous Phase** using a class A graduated cylinder.

6.4.6 Record the **Mass of Vessel + Non-aqueous phase** using a calibrated balance.

6.4.7 The **Mass of Non-Aqueous Phase** is calculated by the MT-TCLP-SPLP-EXT extraction form.

6.4.8 Density Determination of the Non-Aqueous Phase of extract:

6.4.8.1 Record the **Mass of the clean Receiving Vessel.** Use a class A 2 mL volumetric flask as the clean receiving vessel.

6.4.8.2 Carefully measure exactly 2 mL into the 2 mL class A volumetric flask. Record **Volume of Subsample.**

6.4.8.3 Record the **Mass of Vessel + Non-Aqueous Phase.**

6.4.8.4 The **Mass of Subsample, Density of Non-Aqueous Phase,** and **Volume of Non-Aqueous Phase** is automatically calculated by the MT-TCLP-SPLP-EXT extraction form.

Note: If the extract is needed for organic analysis it must be transferred to a clean amber glass bottle.

6.5 Filtrate Finalization:

If there was a liquid filtrate obtained in section 6.3.3 determine if it is multiphasic. If so, determine which of the phases is non-aqueous by removing a small aliquot (~2 mL) with a disposable pipette and attempting to mix the aliquot in an equal volume of DI water. Non-aqueous waste will not be miscible and form beads of solution that will not dissolve in water.

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6.5.1 If the filtrate is aqueous and not multiphasic, record the **Recovered Aqueous Filtrate Volume** and skip to section 6.6 if there is an extract or 6.7 if there is no extract.

6.5.1.1 If filtrate is completely non-aqueous and there is an extract (percent solid > 0.5 %), skip to 6.5.6.

6.5.1.2 If the filtrate is completely non-aqueous and there is no extract (percent solid < 0.5 %), the **Density** and **Volume of Non-Aqueous Phase** do not need to be recorded. Skip to 6.7.

6.5.2 If more than one phase is present, separate the two phases using a separatory funnel. Record the **Mass of Dirty Vessel** (the beaker or container that held the filtrate prior to transferring to the separatory funnel).

6.5.3 Record the **Mass of Clean Receiving Vessel for Non-Aq Phase**.

6.5.4 Record the **Volume of Aqueous Phase** using a class A graduated cylinder**.**

6.5.5 Record the **Mass of Vessel + Non-Aqueous Phase.**

6.5.6 Density Determination of the Non-Aqueous Phase of Filtrate:

6.5.6.1 Record the **Mass of the clean Receiving Vessel.** Use a class A 2 mL volumetric flask as the clean receiving vessel.

6.5.6.2 Carefully measure exactly 2 mL into the 2 mL class A volumetric flask. Record **Volume of Subsample.**

6.5.6.3 Record the **Mass of Vessel + Non-Aqueous Phase.**

6.5.6.4 The **Mass of Subsample, Density of Non-Aqueous Phase,** and **Volume of Non-Aqueous Phase** is automatically calculated by the MT-TCLP-SPLP-EXT extraction form.

6.6 Combining the Extract and Filtrate:

The aqueous phase of the extract and the aqueous phase of the filtrate are combined into one bottle and the non-aqueous phase of the extract and non-aqueous phase of the filtrate are combined into one bottle.

6.6.1 The **Combined Aqueous Volume (filtrate + extract)** and **Combined Non-Aqueous Volume (filtrate + extract)** are automatically calculated by the MT-TCLP-SPLP-EXT extraction form.

6.6.2 Divide the aqueous phase (extract + filtrate) into two portions of equal size.

Note: If organic analyses are required, separate approximately 3/4 of the sample for organic analysis (about 1600 mL) and store in an amber glass bottle. Mark the organic sample number on the side of the bottle and give it to the organic prep group. Approximately 300-400 mL should be kept for metals preparation.

Note: Non-aqueous final extracts and any portion of an extract intended for organic analysis are not preserved. Samples can be digested for metals prior to preservation if they are digested immediately after extraction and filtration. After removal of sample for digestion, a portion of the remaining extract must be preserved for

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possible future use. If the sample is not digested immediately after extraction and filtration, then a portion of it must be preserved prior to digestion.

6.6.3 Check for precipitation by adding HNO_3 to a small sub-sample (~2 mL). If no precipitation occurs acidify one portion of the extract's **aqueous phase** by adding HNO_3 until the liquid phase's pH is < 2. Record the results of the precipitation test and if the sample was preserved on the MT-TCLP-SPLP-EXT extraction form. Mark the acidified extract's bottle as 'preserved'.

WARNING - DO NOT ACIDIFY ANY NON-AQUEOUS PORTION OF THE SAMPLE. Nitric acid should not be mixed with organic compounds because of the possibility of a dangerous reaction.

6.7 Filtrate/Extract Digestion for Metals Determination:

6.7.1 Aqueous TCLP extract should be digested in the same manner as water samples for total recoverable metals analysis (DEP SOP MT-024) except that they need to be diluted 10-fold (1:10) prior to digestion.

6.7.2 The aqueous SPLP extract should be digested undiluted in the same manner as water samples for total recoverable metals analysis (DEP SOP MT-024).

6.7.3 Non-aqueous phases for either TCLP or SPLP should be digested according to DEP SOP MT-060 except that 5 mL of the non-aqueous TCLP extract is digested instead of 0.5 g.

6.7.4 Be sure to include an extraction fluid blank in the digestion.

6.7.5 Batch like samples together. For example, do not batch paint samples with soil samples. Create as many batches as necessary to ensure an accurate representation of the matrices present.

6.7.6 Batch each type of extraction fluid separately.

6.7.7 The batch QC should contain a set of matrix spikes, an LFB, and a digestion blank. UNIVERSAL SEDIMENT spiking solution should be used with a spike factor of 2 for the LFB and matrix spikes.

6.7.8 For either type of digestion the preparation staff is responsible for completing the electronic MT-TCLP-SPLP-EXT extraction form digestion form (MT-TCLPSPLP-DIG). Any handwritten notes shall be given to the analysis lab so that copies may be included with the data write-up. The MT-TCLP-SPLP-EXT extraction form will be crosschecked with the analysis data and a finalized copy will be printed and included with the data package.

6.7.9 The preparation date entered in LIMS for the TCLP samples is the agitation start time (when the samples started tumbling).

7. QUALITY CONTROL

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7.1 A minimum of one extraction fluid blank per batch of 20 samples or less is extracted using the required extraction fluid. If both extraction fluids are used, include two extraction blanks one for each extraction fluid type.

7.2 Metals digestion only - The QC required by the preparation DEP SOPs, MT-024 and MT-060, must be included as appropriate.

7.3 The method of standard additions must be employed for a metallic contaminant if: (1) Recovery of the contaminant from the TCLP or SPLP extract is not at least 50 % and the concentration does not exceed the regulatory level (assess matrix spike recovery), **AND** (2) The concentration of the contaminant measured in the extract is within 20 % of the appropriate regulatory level.

8. SAFETY/HAZARDOUS WASTE MANAGEMENT

8.1 Review the Laboratory Health and Safety Plan located on the DEAR intranet.

8.2 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, hood shield, etc. Safety glasses must be worn all the time in the Lab.

8.3 All the non-hazardous wastewater can be dumped into sink if its pH range is 10 - 5. If it is not, the wastewater has to be neutralized before dumping.

8.4 Store any wastes that cannot be disposed of down the sink in a 2 L bottle (properly labeled with **Hazardous Wastes** labels) in the hood next to the instrument. Make sure the bottle stays capped after use and place the bottle in the cabinet below the hood in the metals lab when it is NO MORE THAN 90 % FULL. When two bottles reach 90 % full, notify supervisor. Approved personnel will dump them into the Hazardous Waste drum located in Bldg C.

9. REFERENCES

9.1 EPA Method 1311, revision 0, November 1992.

9.2 EPA Method 1312, revision 0, September 1994.

9.3 DEP SOP MT-007, Procedure for Cleaning Metals Labware.

9.4 DEP SOP MT-024, Preparation of Water Samples for Metals Analysis by ICP-AES and ICP-MS.

9.5 DEP SOP MT-060, Hot Block Digestion of Soil, Sediment, Waste, and Tissue Samples for Total Recoverable Metals

9.6 Quality Manual, Bureau of Laboratories, FDEP.

9.7 Laboratory Health and Safety Plan.

9.8 DEP SOP MT-069, Metals Standard and Reagent Preparation Procedure.

9.9 The Merck Index, Twelfth Edition. New Jersey: Merck and Co., Inc., 1996

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9.10 DEP SOP HG-018, Digestion of Water Samples for Total Mercury Analysis (EPA Method 245.1 Modified).

9.11 DEP SOP HG-020, Digestion of Sediment and Waste Samples for Total Mercury Analysis (EPA Method 245.5 Modified).

Appendix A

Maximum Concentrations of Contaminates For Toxicity Characteristics

Contaminant	Regulatory Level (mg/L)
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Selenium	1.0
Silver	5.0
Mercury	0.2
Benzene	0.5
Carbon Tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
o-Cresol	200.0
m-cresol	200.0
p-cresol	200.0
Cresol	200.0
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
1,1-Dichloroethylene	0.7
2,4-Dinitrotoluene	0.13
Endrin	0.02
Heptachlor (and its hydroxide)	0.008

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Contaminant	Regulatory Level (mg/L)
Hexachlorobenzene	0.13
Hexachloro-1,3-butadiene	0.5
Hexachloroethane	3.0
Lindane	0.4
Methoxychlor	10.0
Methyl Ethyl Ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5
Trichloroethylene	0.7
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1.0
Vinyl Chloride	0.2

Appendix B

Totals Threshold for Possible TCLP Violations

NOTE: Only applicable to samples which are 100 % solid.

Contaminant	Threshold (mg/kg)
Arsenic	100
Barium	2000
Cadmium	20
Chromium	100
Lead	100
Mercury	4
Selenium	20
Silver	100

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Appendix C

Procedure for Centrifuging

1) If the sample contains mostly aqueous liquids with fine particulate solids, it MAY be necessary to centrifuge the sample PRIOR to filtration to prevent the sample from clogging the filter.
2) The centrifuge must be operated with great care. The minimum number of centrifuge containers that may be used is two. Each centrifuge container must be balanced with a twin centrifuge container. Place opposing containers side by side on a countertop after filling each with the amount of sample needed and use a disposable transfer pipette to balance the liquid level between opposing containers.
3) Cover each centrifuge container with a small piece of aluminum foil to prevent spills. Wipe up any excess fluid on the exterior of each container. The centrifuge should be kept dry.
4) Wrap one paper towel around each container to ensure a snug fit into the rotor and place the containers in the centrifuge making sure that samples that were balanced with one another are opposite each other in the centrifuge rotor.
5) Close and secure the centrifuge lid. Turn the knob to 10 to start the rotor turning. After a few seconds turn the speed knob to 30. Allow the rotor to accelerate for about 30 seconds and observe the centrifuge for any excessive shaking. If the centrifuge remains fairly steady turn the knob to 60 on the dial. Stay with the centrifuge until it stops accelerating, about 1 to 2 minutes. DO NOT LEAVE THE CENTRIFUGE UNATTENDED WHILE IT IS ACCELERATING.
6) Allow the centrifuge to run for at least 30 minutes. Samples that are very cloudy may need a centrifugation time of 60 to 120 minutes to be effective. When the determined time has passed stop the rotor by turning the control knob until it points to zero. The rotor will take several minutes to come to a stop.
7) After centrifuging the sample, determine the preliminary percent solid starting from 6.1.2.

Appendix D

Appendix of Significant Changes

04/12/2011	"Class A" added to description of glassware in section 3; Extraction Fluid expiration date added. Instructions added to prepare extraction fluid fresh for each extraction.
04/10/2013	Changed how prep dates for TCLP are documented in LIMS. (See 6.7.9.)
04/18/2014	Entire SOP revised for clarification.
04/07/2016	The form MT-TCLP-SPLP-EXT replaces the TCLP/SPLP extraction logbook.

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