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 TCLP and SPLP sample extracts scheduled for mercury analysis are analyzed according to DEP SOP HG-023 (test TCLP-TDA). Non-aqueous TCLP sample extracts are analyzed according to DEP SOP HG-022. Aqueous low-concentration SPLP extracts are digested and analyzed according to DEP SOP HG-001 (test SPLP-HG-AF).

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 ≥ 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 Thermo Orion Star A211 pH meter with ATC probe.

3.2.1 The ATC probe is a temperature measuring device and must be calibrated annually. Calibrate the ATC probe at room temperature and 50 ° using the procedure from DEP SOP LB-035. Label the ATC probe with the calibration date, due date for the next calibration and the serial number.

3.2.2 Record the temperature on the digital display after each pH measurement.

3.3 Millipore pressure filtration device.

3.4 Top-loading balance.

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

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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 Amber glass extraction vessels (disposable).

3.17 Aluminum foil.

3.18 Constant temperature water bath.

3.19 1 L polypropylene bottles for storing extracted samples.

3.20 Disposable stir bars.

3.21 6" wide Teflon tape.

3.22 Separatory funnel.

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

3.24 2 mL class A volumetric flask.

3.25 1 L, 50 mL, and 10 mL class A graduated cylinders.

3.26 1.0 mm standard sieve.

3.27 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. Reagents and standards are stored at room temperature in B411.

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 SED SPK 4 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 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) one drop 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.

4.11 pH Buffers

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4.11.1 pH 2 buffer: Purchased standard from Fisher Scientific. The expiration date is provided by the manufacturer. This buffer is not maintained by the stockroom and must be ordered directly from Fisher Scientific. Used as a calibration standard for the Thermo Orion Star A211 pH meter.

4.11.2 pH 4 buffer: Purchased standard from Fisher Scientific and can be ordered from the laboratory stockroom. The expiration date is provided by the manufacturer. Used as a calibration standard for the Thermo Orion Star A211 pH meter.

4.11.3 pH 7 buffer: Purchased from Fisher Scientific and can be ordered from the laboratory stockroom. The expiration date is provided by the manufacturer. Used as a calibration standard for the Thermo Orion Star A211 pH meter.

4.11.4 pH 5 buffer: Purchased from SPEX Certiprep. The expiration date is provided by the manufacturer. This buffer is not maintained by the stockroom and must be ordered directly form Fisher Scientific or SPEX Certiprep. Used as a second source standard to verify the pH meter calibration.

4.12 PQL standards

4.12.1 PQLMSTCLP1 and PQLMSTCLP2: Standard prepared at the PQL level for the ICP-MS test, TCLP-ICPMS. The standard is digested with each batch of samples scheduled for TCLP-ICPMS. See DEP SOP MT-074 for preparation.

4.12.2 DVPQLTCLP1: Standard prepared at the PQL level for the atomic emission test, TCLP-ICP. The standard is digested with each batch of samples scheduled for TCLP-ICP. See DEP SOP MT-061 for preparation.

4.12.3 PQLMSSPLP1: Standard prepared at the PQL level for the ICP-MS test, SPLP-ICPMS. The standard is digested with each batch of samples scheduled for SPLP-ICPMS. See DEP SOP MT-074 for preparation.

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

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

A copy of the MT-TCLP-SPLP-EXT extraction form is located in both the TCLP and SPLP Prep folders on \\floridadep\data\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 are responsible for completing the electronic version of the MT-TCLP-SPLP-EXT extraction form. Any handwritten notes shall be sent to the analysis lab for the analysis staff to include a copy with the laboratory reports. The electronic MT-TCLP-SPLP-EXT form along with any handwritten notes will be cross-checked with the analysis data. Then the electronic version will be printed and included with the final data report. This is the official preparation record. To eliminate handwritten notes, a DEP laptop should be used to record all information at the TCLP lab bench.

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

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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 the 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.

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. The lid of the filtration unit can be removed to transfer the sample.

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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 the 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.

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

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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). A 25 g portion of the solid extracted with 500 mL extraction fluid 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.

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 %. Wait one hour between weight measurements. 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 extraction 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 ≥ 0.5 %, proceed to the particle size reduction step (6.1.6).

6.1.4.1 Particle size reduction is necessary if:

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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 criterion.

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:

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. Break up any sample that does not pass through the sieve until the entire sample passes through. If it is obvious that the sample will pass through the sieve without size reduction, it is not necessary to pass it 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. See the Thermo Orion Star A211 User Manual, located in the drawer below the pH meter, for operation. Use the pH Meter Calibration Logbook to document

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the calibration check of the pH meter using the pH 2, 4, 7, and 5 pH buffers.

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 an amber glass (disposable) 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 with DI water three times. Next, rinse glassware with an organic solvent, such as methanol (CH_3OH), followed by DI water three times.

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

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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. If possible, filter enough sample to get at least 500 mL of extract, as 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.

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.

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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 (see section 6.2).

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 or SPLP 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. The Extraction Blank is used as the method blank.

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.

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**

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temperature of room using two significant figures, 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. A min/max thermometer must be used to document the temperature range throughout the tumbling process. Record the min/max temperatures on the worksheets. 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 rinses of DI water. Pour the non-filtered extract into the filtration device through the top intake. Centrifugation may be necessary prior to filtering the sample (see Appendix C). Place the sealing white O-ring on the top and attach the gas line. If necessary, gradually apply pressure of 1 - 10 psi for the filtrate to pour out of the filtration device into a clean, disposable amber glass sample bottle.

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.

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

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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 Receiving Vessel** for the non-aqueous phase. Transfer each phase into separate clean bottles, label each with the LIMS sample ID, and indicate which phase is in each bottle.

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** are 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.

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 section 6.5.6.

6.5.1.2 If the filtrate is completely non-aqueous and there is no extract (percent solid < 0.5 %), skip to section 6.5.6.

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).

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6.5.3 Record the **Mass of Clean Receiving Vessel** for the non-aqueous 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 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** are 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.

Note: If organic analyses are required, separate approximately 3/4 of the aqueous sample from Portion 1 for organic analysis (about 750 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 250 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 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.

6.6.1 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 combined aqueous phase (extract + filtrate) into two portions of equal size: Portion 1 and Portion 2.

6.6.2.1 Prepare matrix spikes prior to preservation: From Portion 1, pour some of the aqueous phase into two 50 mL digestion vessels up to the 5 mL graduation mark. Spike the 5 mL portion with 2 mL of SED SPK 4 (spike factor = 2). Fill to the 50 mL graduation mark with DI water (dilution of 10). Then, preserve the matrix spike with 100 µL of concentrated nitric acid.

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6.6.2.2 Check for precipitation by adding HNO_3 to a small sub-sample (~2 mL) of Portion 1. If no precipitation occurs, acidify Portion 2 of the extract's **aqueous phase** by adding HNO_3 until the 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' to be sent for digestion for metals determination.

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:

NOTE: Use the MT-TCLP-SPLP-DIG form to record all digestion information including the serial numbers of the standards and reagents used.

6.7.1 The aqueous TCLP extract shall be diluted 10-fold prior to digestion, but otherwise digested in the same manner as water samples for total recoverable metals analysis (DEP SOP MT-024).

6.7.2 The aqueous SPLP extract shall 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.

6.7.4 Be sure to include an extraction fluid blank in the digestion. The extraction blank serves as the method blank for the batch.

6.7.5 Batch samples with similar matrices 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 shall contain a set of matrix spikes, an LFB, a PQL, and the TCLP or SPLP extraction blank. The SED SPK 4 spiking solution should be used with a spike factor of 2 for the LFB and matrix spikes.

Note: The matrix spikes are to be prepared after filtration of the TCLP extract and before preservation (See section 6.6.2.1).

6.7.8 For either type of digestion, the preparation staff is responsible for completing the electronic MT-TCLP-SPLP-EXT extraction form and MT-TCLP-SPLP-DIG digestion form. Any handwritten notes shall be given to the analysis lab so that copies may be included with the data report. The MT-TCLP-SPLP-EXT extraction form will be cross-checked with the analysis data and a finalized copy will be printed and included with the final data report. To eliminate handwritten notes, a DEP laptop should be used to record all information at the TCLP lab bench.

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

7. QUALITY CONTROL

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 with these irritants on skin and clothing by appropriate use of gloves, apron, face mask, hood shield, etc. Safety glasses must be worn at all times in the lab.

8.3 All the non-hazardous wastewater can be dumped into sink if its pH range is –5 - 10, flushing with lots of water. If it is not, the wastewater must be neutralized before dumping.

8.4 Store any waste that cannot be disposed of down the sink in a 2 L bottle (properly labeled as **Hazardous Waste**) in the hood next to the instrument. Be sure to recap the bottle 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 properly dispose of the waste 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.

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

9.6 Laboratory Quality Manual.

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

9.10 DEP SOP HG-018, Digestion of Water Samples for Total Mercury Analysis.

9.11 DEP SOP HG-009, Analysis of Total Mercury in Water and Aqueous Wastes by Cold Vapor Atomic Absorption (CVAA) Spectroscopy.

9.12 DEP SOP HG-022, Analysis of Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry.

9.13 DEP SOP HG-001, Trace-level Total Mercury in Water by Purge and Trap (Dual Gold Traps) and Cold Vapor Atomic Fluorescence Detection (CVAFD).

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

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Contaminant	Regulatory Level (mg/L)
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
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

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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

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 and place the twin sample containers opposite each other in the centrifuge rotor to ensure the centrifuge stays balanced.
5) Close and secure the centrifuge lid. Turn the speed dial to 10 to start the rotor turning. After a few seconds, turn the speed dial to 30. Allow the rotor to accelerate for about 30 seconds and observe the centrifuge for any excessive shaking. If the centrifuge remains steady, turn the dial to 60. Observe the centrifuge until it stops accelerating, for about 1 to 2 minutes. DO NOT LEAVE THE CENTRIFUGE UNATTENDED WHILE IT IS ACCELERATING.

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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 speed dial until it points to zero. The rotor will take several minutes to come to a stop. DO NOT OPEN THE CENTRIFUGE LID UNTIL IT HAS COME TO A COMPLETE STOP.

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 to prepare extraction fluid fresh for each extraction added.
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.
05/16/2022	A min/max thermometer must be used to document the min/max temperatures during the temperature range throughout the tumbling process. The min/max temperatures must be documented on the worksheets. (See 6.3.19)
04/30/2024	Added section 3.2.2 which requires prep chemist to record ATC temperature readout of each pH measurement. Changed PQL name for TCLP 1 and 2 for ICPMS in section 4.12.1. Added section 4.12.3 to include the name of the SPLP PQL. Updated new network location in section 6, where TCLP and SPLP folders are stored.

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