

GUIDE TO THE TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP)

PRELIMINARY EVALUATIONS

Perform preliminary evaluations on a minimum 100 gram aliquot of sample. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include:

- Determination of **percent solids**.
- Determination of whether the sample contains insignificant solids and is therefore, its own extract after filtration.
- Determination of whether the solid portion of the sample requires **Particle size reduction**.
- Extraction fluid **determination** for the nonvolatile TCLP extraction of the waste.

- Percent solids**
- Percent solids is defined as that fraction of a waste sample from which no liquid may be forced out by an applied pressure, as described below.
 - If the waste will obviously yield no liquid when subject to pressure filtration (i.e. is 100% solids). Proceed to **Particle size reduction**.
 - If the sample contains one or more liquid phase(s).
 - Determine and record the volume of each phase of the sample.
 - Determine the percent solids by using the filtration device.
 - Note:** Some wastes, such as oily wastes, obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, this material may not filter. If this is the case, the material inside the filtration device is defined as a solid. Do not replace the filter during the percent solids determination.

If sample contains one or more liquid phase(s),

- Preweigh the filter, sample container, and the filtrate container.
- Assemble the filtration device with the filter in place.
- Weigh out an aliquot of the sample (100 gram minimum) and record the weight.
- Quantitatively transfer the sample to the filtration device and attach the gas hose to the filtration device. Place the filtration container underneath the filtration device.
- If sample residue has adhered to the sample container, reweigh the sample container and recalculate the amount of sample transferred to the filtration device.

Follow Instructions for Filtering samples.

Instructions for Filtering samples

- Apply between 1 and 10 psi of pressure to the filtration device until the pressurized gas moves through the filter (ripples from the gas will form on the surface of the filtrate or hissing from the gas moving through the filter will be heard).
- If there is no pressurized gas moving through the filter under 10 psi, and if no additional liquid has passed through the filter in any two minute increment, increase the pressure in 10 psi increments to a maximum of 50 psi.
- Proceed to the next 10 psi incremental increase if no additional liquid or gas passes through the filter.
- When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi, stop the filtration.

Calculate the weight of the liquid phase (filtrate): $Wt. of filtrate = (wt. of filtrate container + filtrate) - (wt. of filtrate container)$

Calculate **Percent solids**: $\% \text{ solids} = \frac{((\text{Sample wt.}) - (wt. of filtrate))}{(\text{sample wt.})} \times 100$

Percent Dry Solids

- If the **percent solids** is $\geq 0.5\%$ and a small amount of liquid is entrapped in the filter, determine Percent dry solids.
- Remove the solid phase and the filter from the filtration device.
- Dry the filter and solid phase at $100 \pm 20 \text{ }^\circ\text{C}$ until two successive weightings of the filter are within $\pm 1\%$. Record the final weight.
- $100 - \left[\left(\frac{\text{Final wt. of dried filter}}{\text{Initial wt. of dried filter}} \right) \times 100 \right] \leq 1\%$
- Note:** Caution should be used to ensure that the solid phase will not flash (ignite) upon heating and it is recommended that the drying oven is vented to a chemical fume hood.
- Calculate Percent dry solids: $\left[\frac{(\text{wt. of dry waste} + \text{filter}) - (\text{tare wt. of filter})}{(\text{sample wt.})} \right] \times 100$.
- If Percent dry solids is $\geq 0.5\%$, separate the liquid phase from the solid phase on a fresh aliquot of the sample and perform particle size reduction if necessary and determine the appropriate extraction fluid.

If the **Percent solids or Percent Dry solids** is $< 0.5\%$, go to **Nonvolatile TCLP extraction or Volatile TCLP extraction.**

Particle size reduction

- If the **Percent solids or Percent Dry solids** is $\geq 0.5\%$, then determine if the solid phase requires particle size reduction.
- Particle size reduction is required if the solid phase is incapable of passing through a 9.5 mm sieve or if the surface area per gram is less than $3.1 \text{ cm}^2/\text{g}$.
- Note:** Surface area per gram criteria are meant for filamentous (paper, cloth, and similar) waste materials. Measure the surface area of a portion of the sample with a ruler. Weigh the measured portion of the sample. Divide the area by the weight to calculate surface area per gram and to determine if the reduction of the particle size for the sample is required.
- If particle size reduction is required, prepare the solid phase of the sample for extraction by grinding, crushing or cutting the solids to meet the particle size requirements.
- Note:** If solids require the **Volatile TCLP extraction**, minimize the exposure of the solid phase to the atmosphere and do not generate heat during the particle size reduction step.

Extraction fluid determination

- If the **Percent solids or Percent dry solids** is $\geq 0.5\%$, determine the appropriate extraction fluid for **Nonvolatile TCLP extraction.**
- Note:** Only extraction fluid #1 is used for the **Volatile TCLP extraction.**
- Reduce the solid phase (if necessary) to a particle size of approximately 1 mm in diameter and transfer 5 grams to a beaker.
- Add 96.5 ml of water, cover with a watchglass and stir for 5 minutes. Measure and record the pH.
- If the pH of the slurry is ≤ 5.0 , use extraction fluid #1 for the nonvolatile TCLP extraction.
- If the pH of the slurry is > 5.0 .
 - Add 3.5 ml of HCl, and stir briefly.
 - Cover the beaker with a watchglass and place on a hotplate.
 - Heat to $50 \text{ }^\circ\text{C}$ and hold at $50 \text{ }^\circ\text{C}$ for 10 minutes.
 - Let the slurry cool to room temperature and record the pH.
 - If the pH is ≤ 5.0 , use extraction fluid #1, otherwise use extraction fluid #2 for the nonvolatile TCLP extraction.

Go to either the **Nonvolatile TCLP extraction or the Volatile TCLP extraction.**

NONVOLATILE TCLP EXTRACTION

- Perform **Preliminary evaluations** on the sample.
- A minimum of 100 grams of sample (solid and liquid phases) is required for this procedure.
- Enough solids should be generated for extraction such that the volume of the TCLP extract will be sufficient to support all of the analyses required.
- The required TCLP extract volume = sample volume for each test + volume for matrix spikes.

If the **Percent solids**, as determined in the **Preliminary Evaluations**, is $< 0.5\%$ then,

- Generate the required volume for analysis by filtering the sample through the filtration device using the procedure as described in **Instructions for Filtering samples**. The filtrate is the TCLP extract. If two phases are present after filtration, process each phase separately and combine the results mathematically.
- Record the pH of the extract. Aliquot and preserve the extract for sample extraction and analysis. Store extract at $4 \text{ }^\circ\text{C}$.

If the **Percent solids**, as determined in the **Preliminary Evaluations**, is $\geq 0.5\%$ then,

- Calculate the amount of sample to generate the required TCLP extract volume.
 - Amount of sample required for extraction = $\left[\frac{\text{Required TCLP extract volume}}{(1+19 \times \text{Percent solids})} \right]$
 - Weigh out the appropriate amount of sample.
- If the **Percent solids** is 100% then,

Proceed to **Particle size reduction** if necessary to reduce the particle size of the sample.

If the **Percent solids**, as determined in the **Preliminary Evaluations**, is $\geq 0.5\%$ and $< 100\%$ then

- Transfer the sample to the filtration device and separate the liquid phase from the solid phase as described in **Instructions for Filtering samples**. Save the filtrate for recombination with the sample extract or for independent analysis.

Proceed to **Particle size reduction** if necessary to reduce the particle size of the solid phase of the sample.

- After the particle size of the sample or solid phase has been reduced to meet method requirements, transfer the material (including the filter used to separate the phases) to the extraction vessel.
- Note:** A plastic extraction vessel can be used for extracting inorganic analytes. A glass extraction vessel must be used for extracting the organic compounds.

1. Refer to **Extraction fluid determination** for the appropriate extraction fluid.

- Two methods can be used to calculate the weight of extraction fluid:
 - $20 \times (\text{Percent solids}) \times (\text{sample wt.})$ if **Percent solids** is 100%.
 - $20 \times (\text{sample wt.} - \text{wt. of filtrate})$ if **Percent solids** is $\geq 0.5\%$ and $< 100\%$.
- Note:** Because subsampling errors can occur between the original determination of the **Percent solids** and the selection of the weight of the multiphase sample for filtration and extraction, calculate the actual weight of filtered solids at the time the material is separated for extraction.
- Prepare the appropriate extraction fluid as follows:
 - Extraction fluid #1: Add 5.7 ml of acetic acid for every liter of extraction fluid required to 500 ml of laboratory grade water, add 64.3 ml of 1 N NaOH for every liter of extraction fluid required and dilute to the final volume. Use a pH meter to adjust if necessary, the pH of the solution to 4.93 ± 0.05 with acetic acid or 1 N NaOH.
 - Extraction fluid #2: Add 5.7 ml of acetic acid for every liter of extraction fluid required to 500 ml of laboratory grade water and dilute to the final volume. Use a pH meter to adjust if necessary, the pH of the solution to 2.88 ± 0.05 with acetic acid or 1 N NaOH.
- Add the extraction fluid to the extraction vessel.
- Wrap Teflon tape around the threads of the extraction vessel.
- Close the extraction vessel.
- Place the extraction vessel in the TCLP rotation device, secure the vessel, and rotate the vessel at 30 rpm for 18 ± 2 hrs.
- Ambient temperature in the extraction room shall be maintained at $23 \pm 2 \text{ }^\circ\text{C}$ during agitation.
- Note:** As agitation continues, pressure may build up within the vessel for some types of solids. To relieve excess pressure, the extractor vessel may be periodically opened inside a fume hood.
- Filter the sample as described in **Instructions for Filtering samples**. The filter may be changed, if necessary to facilitate filtration.
- Save filtrate and discard solids.

If the **Percent solids** = 100%,

- Record the pH of the TCLP extract and aliquot and preserve the extract for sample extraction and analysis. Store extract at $4 \text{ }^\circ\text{C}$.

If original sample contained one or more liquid phase(s) and the extract is *miscible* with the filtrate,

- Combine the extract with filtrate, this becomes the TCLP extract.
- Record the pH of the TCLP extract and aliquot and preserve the extract for sample extraction and analysis. Store extract at $4 \text{ }^\circ\text{C}$.

If original sample contained one or more liquid phase(s) and the extract is *not miscible* with the filtrate,

- Record the pH of the filtrate.
- Record the pH of the extract.
- Aliquot and preserve the extract and filtrate separately for sample extraction and analysis. Store extract and filtrate at $4 \text{ }^\circ\text{C}$.
- Combine results from the analyses for the extract and filtrate mathematically according to the volume ratio of the original phases.
 - Final analyte concentration = $\frac{[(V_1) \times (C_1) + (V_2) \times (C_2)]}{(V_1 + V_2)}$
 - V_1 = the volume of the first phase (L).
 - C_1 = the concentration of the analyte of concern in the first phase (mg/L).
 - V_2 = the volume of the second phase (L).
 - C_2 = the concentration of the analyte of concern in the second phase (mg/L).

Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations.

WHAT IS TCLP?

The Resource Conservation and Recovery Act (RCRA) governs the proper management of hazardous waste. RCRA enforces a "cradle to grave" system regulating the handling of hazardous wastes from creation to final disposal.

The TCLP determination is part of the Toxicity Characteristic (TC) rule. Toxicity is one of four characteristics used to determine if a solid waste, excluding listed hazardous wastes, is classified as a hazardous waste. The other three characteristics are Ignitability, Corrosivity, and Reactivity. The toxicity characteristic leaching procedure is located in: *Test Methods for Evaluating Solid Wastes*, SW-846 Method 1311, July 1992.

The TCLP model assesses risks to ground water when potentially hazardous TC waste is co-disposed with garbage into sanitary landfills. The leachate is analyzed for appropriate analytes.

TCLP is comprised of four fundamental procedures:

- sample preparation for leaching
- sample leaching
- preparation of leachate for analysis
- leachate analysis

The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphase samples. For liquid samples (e.g. those containing less than 0.5% dry solid material), the liquid phase after filtration through a 0.7 micron glass fiber filter is defined as the TCLP extract. For samples containing solids greater than or equal to 0.5%, the liquid phase, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed for the extraction of nonvolatile analytes is a function of the alkalinity of the solid phase of the waste. A special extractor is used when testing for volatile analytes.

Following extraction, the liquid extract is separated from the solid phase by filtering through a 0.7 micron filter. If compatible (e.g. multiple phases will not form on recombination), the initial liquid filtrate of the sample is added to the liquid extract, and the combined liquids (TCLP extract) are processed together. If incompatible, the liquids are processed separately and the results are mathematically combined to yield a volume-weighted average concentration.

WHEN IS THE USE OF TCLP APPLICABLE?

The Toxicity Characteristic (TC) is utilized to determine whether a solid waste is classified as a hazardous waste because it exhibits the characteristic of toxicity. The TC of a waste material is established by determining the levels of 8 metals and 31 organic chemicals in the controlled conditions. The regulatory levels of TC constituents in the TCLP leachate are listed in the adjacent tables.

The most common reasons for performing the TCLP are:

- Determining if an unknown waste is hazardous according to 40 CFR 261.24.
- Determining what type of disposal (hazardous waste or solid waste) is appropriate. Solid wastes are **not necessarily** hazardous.
- Demonstrating the effectiveness of treatment processes to comply with Land Disposal Restrictions (LDR) or "Land Ban" requirements.
- Fulfilling shipping or transportation requirements.

WHEN IS THE USE OF TCLP INAPPROPRIATE?

Unnecessary hazardous waste determinations:

- Generator's knowledge of waste (e.g. chocolate ice cream).
- Exempt waste (e.g. household garbage).
- Material is not a solid waste (e.g. clean sand, laundry detergent).
- Generator's testing of waste (total constituent analysis).
- The solid waste is a listed hazardous waste.

Unnecessary Land Ban determinations:

- Some LDRs are for total constituents, not for TCLP extract concentrations.
- Generator's testing of waste (total constituent analysis).
- Pure liquid waste samples (waste is TCLP extract; waste would fail paint filter test).

If a pure liquid waste sample fails the paint filter test (SW-846 Method 9095, Sept. 1986), the waste is banned from land disposal.

The TCLP test cannot predict the potential for toxic chemicals to leach from oily waste, through soil, to contaminate ground water.

MAXIMUM CONCENTRATION OF CONTAMINANTS FOR TCLP AND ZHE			
Contaminant	Regulatory Level (mg/L)	Contaminant	Regulatory Level (mg/L)
Metals:			
Arsenic	5	Volatiles, continued:	
Barium	100	1,1-Dichloroethylene	0.7
Cadmium	1	Methyl ethyl ketone	200
Chromium 5	5	Tetrachloroethylene	0.7
Chromium 6	1	Trichloroethylene	0.5
Lead	5	Vinyl chloride	0.2
Mercury	0.2	Herbicides & Pesticides:	
Selenium	1	Chlordane	0.03
Silver	5	2,4-D	10
Volatiles:			
Benzene	0.5	Endrin	0.02
Carbon tetrachloride	0.5	Heptachlor (and its epoxide)	0.008
Chlorobenzene	100	Lindane	0.4
Chloroform	6	Methoxychlor	10
1,2-Dichloroethane	0.5	Toxaphene	0.5
		2,4,5-TP (Silvex)	1
Contaminant			
Regulatory Level (mg/L)			
Semivolatiles:			
p-Cresol	200	1,4-Dichlorobenzene	7.5
m-Cresol	200	2,4-Dinitrotoluene	0.1
Cresol	200	Hexachlorobenzene	0.1
Hexachlorobenzene	0.1	Hexachlorobutadiene	0.5
Hexachloroethane	3	Hexachloroethane	3
Nitrobenzene	2	Nitrobenzene	2
Pentachlorophenol	100	Pentachlorophenol	100
Pyridine	5	Pyridine	5
2,4,5-Trichlorophenol	400	2,4,5-Trichlorophenol	400
2,4,6-Trichlorophenol	2	2,4,6-Trichlorophenol	2

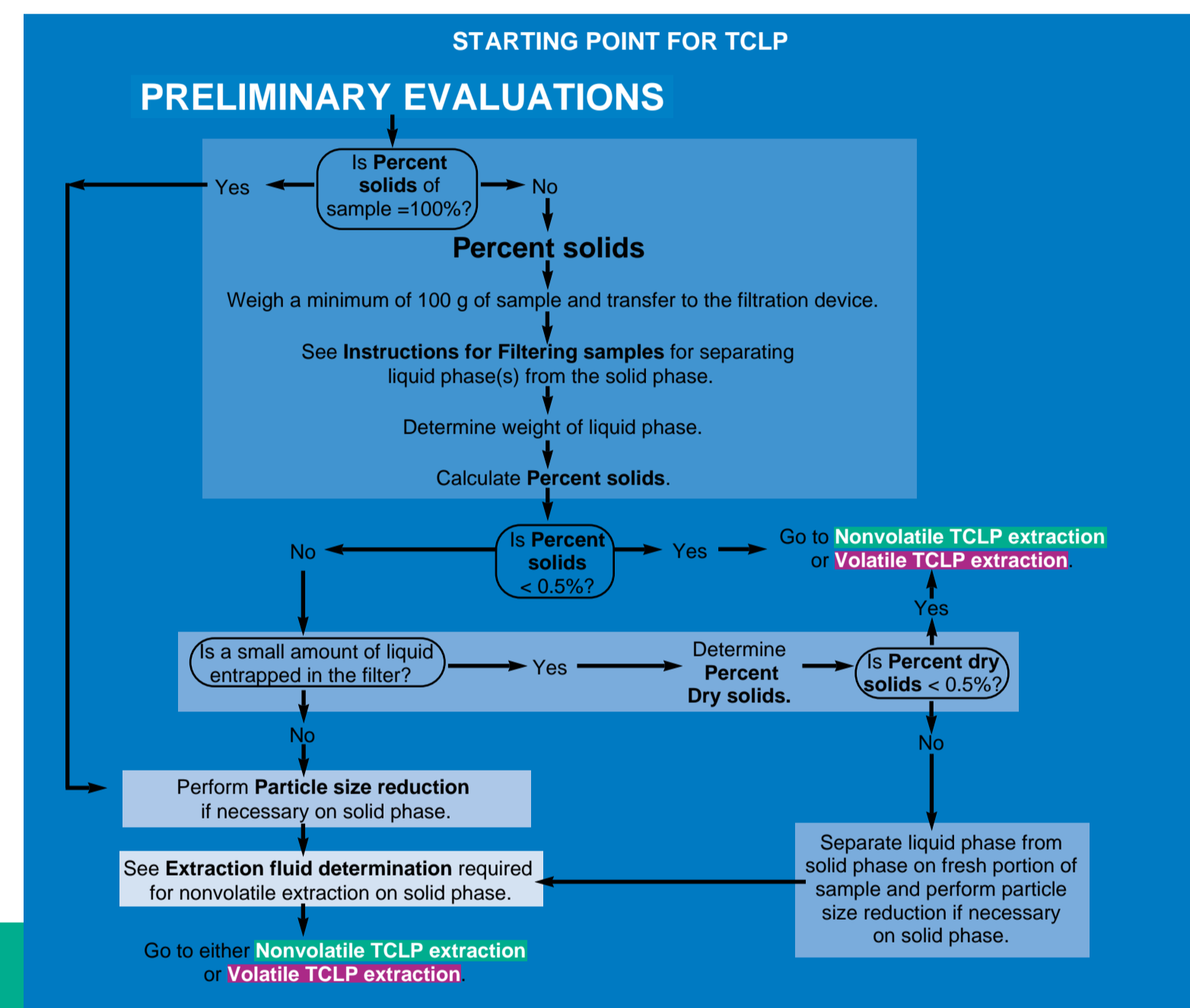
SAMPLE MAXIMUM HOLDING TIMES (DAYS)				
Analytes	From Field collection to TCLP extraction	From TCLP to Preparative extraction	From Preparative extraction to Determinative analysis	Total elapsed time
Volatiles	14	NA	14	28
Herbicides & Pesticides	14	7	40	61
Semivolatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

THE TCLP PROCESS



Hazardous Waste Filtration Units

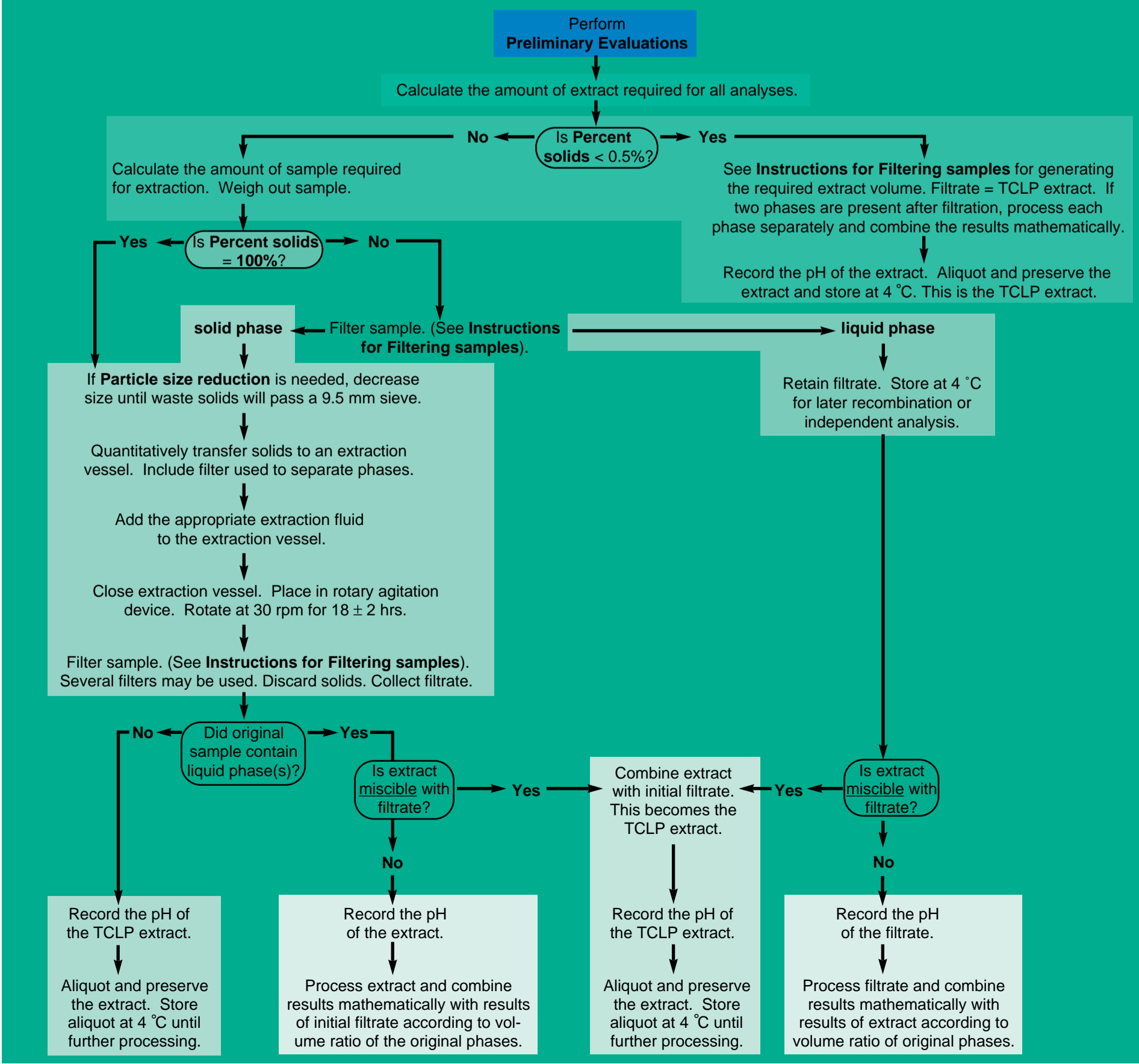
Pressure filtration units used for the initial solid/liquid phase separation of samples as well as the filtration of leachate. The units also can be used to perform the preliminary percent solids determination on all TCLP and SPLP samples prior to extraction.



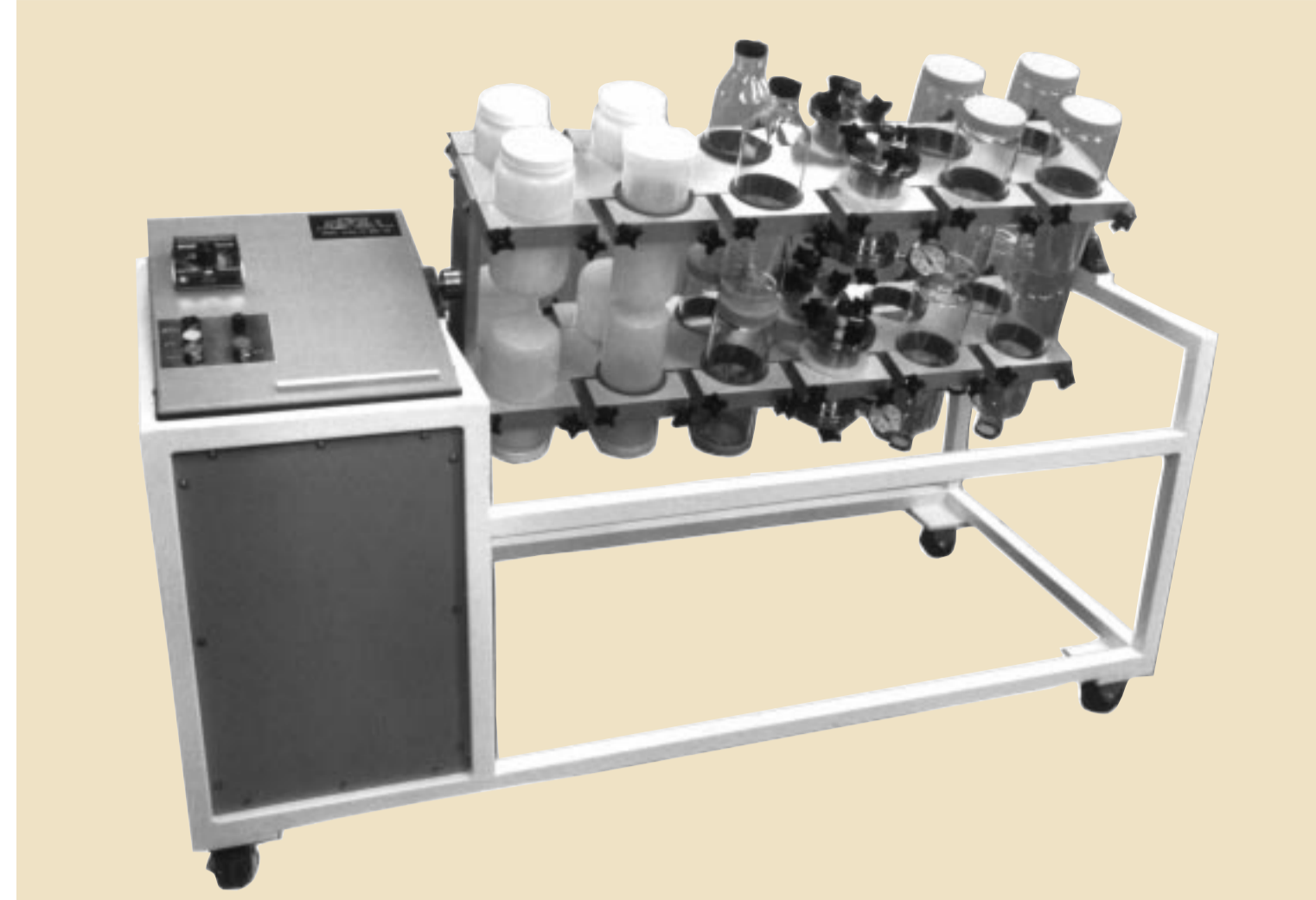
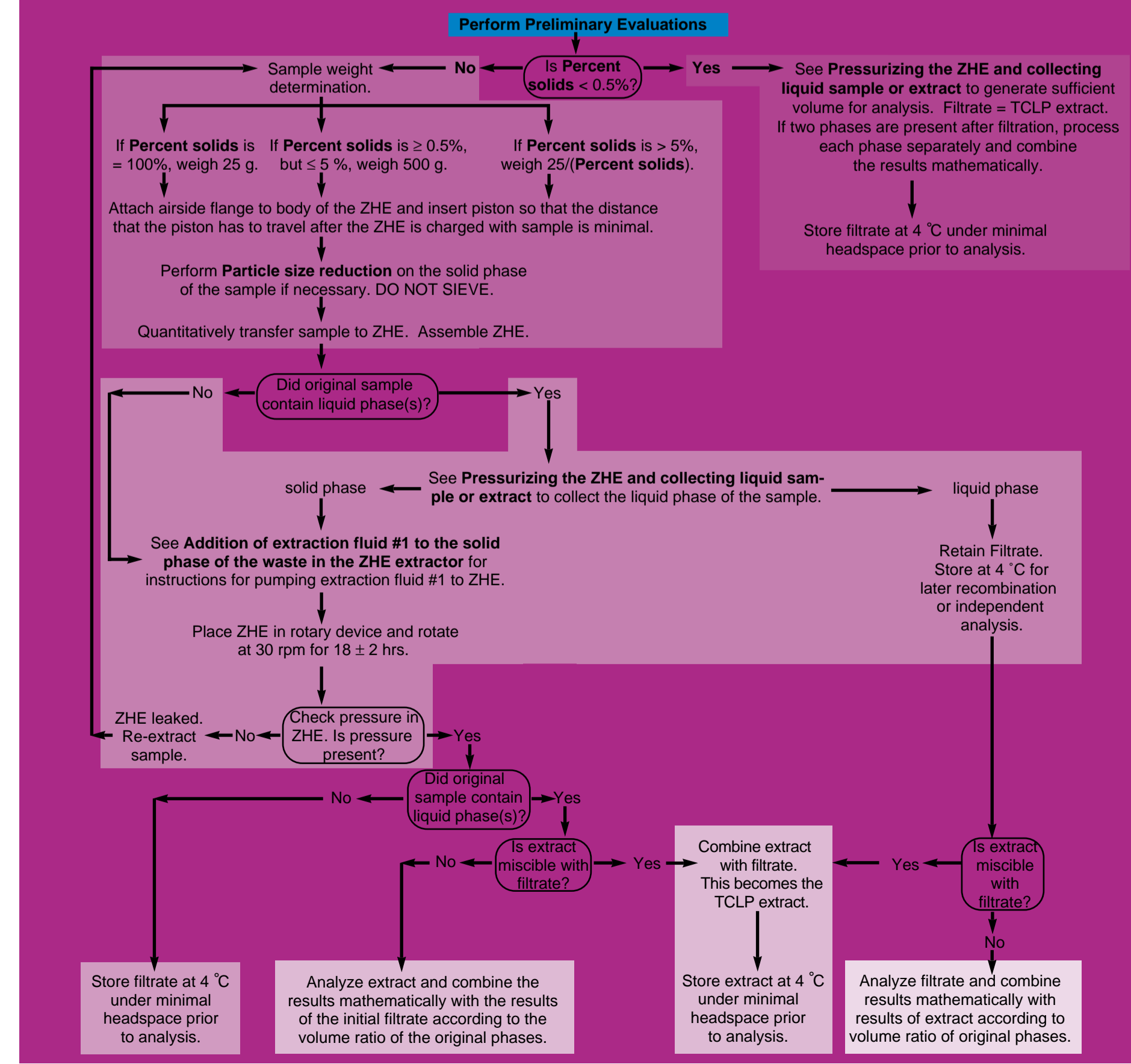
Zero-Headspace Extraction Vessel

Extractor used for separating solid samples and their volatile extracts during the TCLP and the SPLP. Permits the sealed extraction and pressure filtration of volatile pollutants without losses due to evaporation.

NONVOLATILE TCLP EXTRACTION



VOLATILE TCLP EXTRACTION



Rotary Agitator

Device used for the rotary agitation of solid waste samples to stimulate leaching effects in the environment for the analysis of inorganic and organic hazardous contaminants.

VOLATILE TCLP EXTRACTION

- Perform **Preliminary evaluations** on the sample.
- Use the ZHE to obtain the TCLP extract for the analysis of volatile compounds only.
- The **Percent solids** from **Preliminary evaluations** is used to determine amount of sample to charge the ZHE extractor.
- Perform **Particle size reduction** on the solid phase if necessary before placing the sample in the ZHE extractor.
- Do not allow the sample, the initial liquid phase or the extract to be exposed to the atmosphere longer than necessary.

If the **Percent solids** is $< 0.5\%$,

- Assemble the ZHE except for the filter pack and waste side flange.
- Quickly transfer the required amount of sample to the ZHE.
- Place the filter pack on the ZHE body and attach the waste side flange.
- Close the quick-exhaust/relief and the liquid inlet/outlet valves.
- See instruction for **Pressurizing the ZHE and collecting liquid sample of extract.**

Pressurizing the ZHE and collecting liquid sample of extract.

- Pressurize the ZHE to 10 psi.
- Slowly open the liquid inlet/outlet valve.
- At the first sign of liquid, immediately close the valve.
- Attach the sample collection device, open the liquid inlet/outlet valve and collect the TCLP extract.
- If no additional liquid has passed through the filter in any two minute interval,
- Slowly increase the pressure in 10 psi increments to 50 psi.
- After each incremental increase of 10 psi,
 - If no additional liquid has passed through the filter in any two minute interval, proceed to the next 10 psi increment.
- When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in the flow of liquid within a two minute period, stop the filtration.
- Close the liquid inlet/outlet valve.
- Disconnect the sample collection device.
- Store filtrate at $4 \text{ }^\circ\text{C}$ under minimal headspace prior to analysis. This ends the TCLP extraction for volatile analytes.
- If two phases are present after filtration, process each phase separately and combine the results mathematically.

Sample weight determination (for samples where the **Percent solids** $\geq 0.5\%$.)

- If the **Percent solids** is $\geq 0.5\%$ and,
 - $\leq 5\%$, weigh out 500 grams of sample, else
 - $> 5\%$, weigh out $25/(\text{Percent solids})$.
- Assemble the ZHE.
- Original sample contained one or more liquid phase(s) (the **Percent solids** is $\geq 0.5\%$ and $< 100\%$),
 - See instructions for **Pressurizing the ZHE and collecting liquid sample or extract** to collect the liquid phase.
 - Store the initial liquid phase at $4 \text{ }^\circ\text{C}$ under minimal headspace prior to recombination or analysis.

Addition of extraction fluid #1 to the solid phase of the waste in the ZHE extractor

- Two methods can be used to calculate the weight of extraction fluid:
 - $20 \times (\text{Percent solids}) \times (\text{sample wt.})$ if **Percent solids** is $\geq 0.5\%$ and $< 100\%$.
 - $20 \times (\text{sample wt.} - \text{wt. of filtrate})$ if **Percent solids** is $\geq 0.5\%$ and $< 100\%$.
- Note:** Because subsampling errors can occur between the original determination of the **Percent solids** and the selection of the weight of the multiphase sample for filtration and extraction, calculate the actual weight of filtered solids at the time the material is separated for extraction.
- Prepare the extraction fluid #1 as follows:
 - Extraction fluid #1: Add 5.7 ml of acetic acid for every liter of extraction fluid required to 500 ml of laboratory grade water, add 64.3 ml of 1 N NaOH for every liter of extraction fluid required and dilute to the final volume. Use a pH meter to adjust if necessary the pH of the solution to 4.93 ± 0.05 with acetic acid or 1 N NaOH.
 - Attach the extraction fluid device to the liquid inlet/outlet valve.
 - Open the quick release inlet/outlet valves and pump the extraction fluid into the ZHE.
 - Close the valve, and rotate the ZHE 2 or 3 times.
 - Place the ZHE in its support chair with the liquid inlet/outlet valve facing upward.
 - Pressurize the ZHE to 10 psi.
 - Slowly open the liquid inlet/outlet valve.
 - At the first sign of liquid, immediately close the valve.
 - Repressurize the ZHE to 10 psi.
 - Place the ZHE vessel in the TCLP rotation device, secure the vessel, and rotate the vessel at 30 rpm for 18 ± 2 hrs.
 - Ambient temperature in the extraction room shall be maintained at $23 \pm 2 \text{ }^\circ\text{C}$ during agitation.
 - After the agitation period is completed, check the pressure in the ZHE by quickly opening and closing the quick release/exhaust valve.
 - If all the pressurizing gas has leaked from the ZHE, perform the extraction again with a fresh portion of sample.

If original sample did not contain a liquid phase (**Percent solids** = 100%) then,

- Connect the sample collection device to the ZHE and collect the extract according to the instructions in **Pressurizing the ZHE and collecting liquid sample or extract**. This is the TCLP extract for volatile compounds.

If original sample contained one or more liquid phase(s) and the extract is *miscible* with the filtrate,

- Connect the sample collection device containing the liquid phase of the sample to the ZHE and collect the extract of the solid phase according to the instructions in **Pressurizing the ZHE and collecting liquid sample or extract**. This is the TCLP extract for volatile compounds.

If original sample contained one or more liquid phase(s) and the extract is *not miscible* with the filtrate,

- Connect the sample collection device (different than the one used to collect the initial liquid phase of the sample) to the ZHE and collect the extract according to the instructions in **Pressurizing the ZHE and collecting liquid sample or extract**.
- Combine the results of the analyses for the extract and initial liquid mathematically according to the volume ratio of the original phases.
 - Final analyte concentration = $\frac{[(V_1) \times (C_1) + (V_2) \times (C_2)]}{(V_1 + V_2)}$
 - V_1 = the volume of the first phase (L).
 - C_1 = the concentration of the analyte of concern in the first phase (mg/L).
 - V_2 = the volume of the second phase (L).
 - C_2 = the concentration of the analyte of concern in the second phase (mg/L).

Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations.

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