

## Liquid-Solid Partitioning as a Function of Leachate pH - Prescriptive

<b>Parameter</b>	Leaching potential of soil samples as a function of extract pH
<b>Analytical Method</b>	Parallel extractions of as-received solid material in dilute acid or base and de-ionized water
<b>Introduction</b>	<p>This method is intended to be used as part of an environmental leaching assessment for the evaluation of disposal, beneficial use, treatment effectiveness, and site remediation options.</p> <p>This method is a leaching characterization method that is used to provide values for intrinsic material parameters that control leaching of inorganic species under equilibrium conditions. This test method is intended as a means for obtaining a series of extracts of a solid material (i.e., the eluates), which may be used to estimate the liquid-solid partitioning (e.g., solubility and release) of constituents as a function of pH under the laboratory conditions described.</p> <p>This method is not for use under the Hazardous Waste Regulation for the classification of hazardous wastes (see TCLP) or for determining suitability for disposal in a secure landfill (see MLEP).</p>
<b>Method Summary</b>	<p>This method consists of three and potentially four parallel extractions of a soil in dilute acid or base and deionized water at a 20:1 fluid to soil (dry weight) ratio. A schedule of acid and base additions is formulated from a pre-test titration curve or prior knowledge indicating the required equivalents / gram acid or base to be added to the series of extraction vessels so as to yield a series of three eluates having pH values of 5, 7, and 9, plus a fourth at the natural soil eluate pH if it is outside 4.5 to 9.5. In addition to the three (or four) test extractions, two method blanks (low and high pH) without solid samples are carried through the procedure in order to verify that analyte interferences are not introduced as a consequence of reagent impurities or equipment contamination, plus a Lab Control Sample (lowest pH only). The bottles are tumbled in an end-over-end fashion for 48 hours. At the end of the specified contact interval, the liquid and solid phases are roughly separated via settling or centrifugation. Extract pH, conductivity (i.e., specific conductance), and oxidation-reduction potential (ORP) measurements are then made on an aliquot of the liquid phase and the remaining bulk of the eluate is clarified by either pressure or vacuum filtration. Analytical samples of the filtered eluate are collected and preserved as appropriate for the desired chemical analyses. The eluate concentrations of constituents of potential concern (COPCs) are determined and reported. In addition, COPC concentrations may be plotted as a function of eluate pH and compared to QC and assessment limits for the interpretation of method results.</p> <p>This method is prescriptive. It must be followed exactly as described. Where minor deviations are permitted, these are indicated in the text.</p> <p>Instrumental analysis for parameters of interest may be conducted using any BC MOE approved instrumental technique. MDLs vary substantially by technique employed. For lowest detection limits, ICPMS is recommended for analysis of most metals, and CVAAS or CVAFS is recommended for analysis of mercury.</p>

**MDL(s) and EMS Analyte Code(s)**

Analyte	CAS No.	Approx. MDL mg/L	EMS Analyte Code
Arsenic	7440-38-2	As per instrumental procedure	
Barium	7440-39-3		
Beryllium	7440-41-7		
Cadmium	7440-43-9		
Chromium	7440-47-3		
Cobalt	7440-48-4		
Copper	7440-50-8		
Lead	7439-92-1		

Manganese	7439-96-5		
Molybdenum	7439-98-7		
Nickel	7440-02-0		
Selenium	7782-49-2		
Thallium	7440-28-0		
Uranium	7440-61-1		
Vanadium	7440-62-2		
Zinc	7440-66-6		
<b>Additional Analytes:</b>	<b>CAS No.</b>	<b>Approx. MDL mg/L</b>	<b>EMS Analyte Code</b>
Chloride	16887-00-6		
Diisopropanolamine (DIPA)	110-97-4		
Ethylene Glycol	107-21-1		
Methanol	67-56-1		
Nonylphenol	84852-15-3		
Nonylphenol Ethoxylates: Nonylphenol Monoethoxylate (NP1EO)	104-35-8		
Nonylphenol Diethoxylate (NP2EO)	20427-84-3		
Octylphenol (OP)	140-66-9		
Octylphenol Ethoxylates: Octylphenol Monoethoxylate (OP1EO)	2315-67-5		
Octylphenol Diethoxylate (OP2EO)	2315-61-9		
Pentachlorophenol (PCP)	87-86-5		
Perfluorooctanesulfonic acid (PFOS)	1763-23-1		
Perfluorooctanoic acid (PFOA)	335-67-1		
Phenol	108-95-2		
Sodium	7440-23-5		
Sulfolane	126-33-0		

Note: Of the above, only metals and PCP require leaching at all three (or four) pH levels. The others require only one leach usually pH 7.

Leachability of other COPCs may also be assessed by this procedure if permitted under Protocol 2 or by other Ministry guidance.

**EMS Method  
Code**

\*\*\*Refer to [EMS Parameter Dictionary](#) on the ministry website for all current EMS codes.

**Matrix**

Soil

**Interferences  
and Precautions**

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents may be necessary. Refer to each analytical method to be used for specific guidance on instrumental QC procedures. This method is not applicable for characterizing the leachability of volatile organic substances. For determining leachability of volatile organic substances (e.g., benzene, toluene, xylenes, trichloroethylene, perchloroethylene, naphthalene), the Zero Headspace Extractor (ZHE) portion of EPA Method 1311 should be used (without particle size reduction).

**Sample Handling and Preservation**

**Containers:** Glass or Plastic. 2 x 500 mL soil jars recommended. A minimum of 500 grams dry weight equivalent sample is required for the test.

**Sample Collection:** Samples should be collected in such a way as to exclude particle sizes >9.5 mm, where possible. Sampling should be representative and reproducible.

**Preservation:**

**Soil Samples:** None.

**Leachates:** For metals, preserve with HNO<sub>3</sub> (pH < 2). Preserve only after filtration has been completed.

Analyte(s)	Leaching Container	Filter*	Comments
Metals, Sodium	Glass, Plastic	0.45 µm or Glass Fibre	-
Chloride	Glass, Plastic	0.45 µm	-
Methanol, SVOC Analytes	Glass	Glass Fibre	-
PFOS	Glass, Polypropylene	Glass Fibre	No Teflon™ surfaces of any kind may be used.
VOC (EPA 1311 ZHE)	Glass	Glass Fibre	-

\*Filters should be tested for compatibility (no adsorption or leaching of the analytes of interest).

**Stability**

**Holding Time:**

**Soil Samples:** 180 days for metals.

**Leachates:** 180 days for metals and chloride, 7 days for SVOC analytes, 14 days VOC analytes. 1 hour maximum for pH and oxidation/reduction potential after completion of tumbling time.

**Storage:**

**Soil Samples:** Soils may be stored refrigerated at ≤6°C or at ambient temperature.

**Leachates:** Leachates may be stored refrigerated (≤6°C) or at ambient temperature (metals and chloride only).

Analyte(s)	Soil Hold Time (days)	Extract Hold Time (days)	Preservative
Metals, Sodium	180	180	HNO <sub>3</sub> to pH <2
Chloride	unlimited	28	None
Methanol, SVOC Analytes	14	14	NaHSO <sub>4</sub> to pH <2
VOC (EPA 1311 ZHE)	48 hours 14 days frozen	14	NaHSO <sub>4</sub> or HCl to pH <2

**Procedure**

**1. Reagents:**

Deionized Water (interference-free)

2.0 N Nitric Acid (HNO<sub>3</sub>): Trace Metals grade or better. Alternative solution normalities may be used as necessary. In such cases, the amounts of HNO<sub>3</sub> solution added to samples should be adjusted based on the equivalents required in the schedule of acid/base additions.

1.0 N Potassium Hydroxide (KOH): ACS Grade or better. Alternative solution normalities may be used as necessary. In such cases, the amounts of KOH solution added to samples should be adjusted based on the equivalents required in the schedule of acid/base additions.

## 2. Homogenization:

Analysts are advised to take reasonable measures to ensure that the sample as received is homogenized to the extent practical, prior to employment of this method. If the heterogeneity of the sample is suspected as the cause of unacceptable precision in replicate test results or is considered significant based on professional judgment, the sample mass used in the test procedure may be increased to a greater minimum dry mass than 50 g with the amount of extractant increased proportionately to maintain the designated liquid/solid ratio (L/S).

## 3. Moisture Content:

Dry approximately 10 g of homogenized sample to a constant weight at  $105 \pm 5^\circ\text{C}$  as per the BC Environmental Laboratory Manual "Moisture Content" method.

3.1 Calculate the solids content as follows:

$$\text{SC} = \frac{M_{\text{dry}}}{M_{\text{test}}}$$

Where: SC = solids content of "as-tested" material (g-dry/g)

$M_{\text{dry}}$  = mass of dry material specified in the method (g-dry)

$M_{\text{test}}$  = mass of "as-tested" solid equivalent to the dry-material mass (g)

3.2 Calculate the moisture content (wet basis) as follows:

$$\text{MC}_{\text{wet}} = \frac{M_{\text{test}} - M_{\text{dry}}}{M_{\text{test}}}$$

Where:  $\text{MC}_{\text{wet}}$  = moisture content on a wet basis ( $\text{g}_{\text{H}_2\text{O}}/\text{g}$ )

(Multiply x100 to convert units to percent moisture.)

$M_{\text{dry}}$  = mass of dry material specified in the method (g-dry)

$M_{\text{test}}$  = mass of "as-tested" solid equivalent to the dry-material mass (g)

## 4. Particle Size Reduction:

This method is intended for the characterization of soils (as opposed to waste). Particle size reduction is not required or recommended. As-received samples are mixed as well as possible and subsamples are taken, avoiding particles > 9.5 mm.

## 5. Pre-test Titration (if required)

In order to conduct the parallel batch test in Section 7, a schedule of acid and base additions should be formulated from either a pre-test titration or based on prior knowledge of the acid/base titration curve of the sample. This section describes the procedure for obtaining a titration curve of the test material, when sufficient prior knowledge is unavailable. If the schedule of acid and base additions will be generated from prior knowledge, proceed to Section 6 (note that test results are also required for pH, ORP, and conductivity for a soil eluate with no added acid or base, taken from either a pre-test sample or from a full-scale sample extraction).

Conduct a 5 point parallel extraction test using 10 g dry weight equivalent samples. Prepare 5 bottles each containing as-received soil (10 g dry weight) plus 20 meq base, 10 meq base, 20 meq acid, 10 meq acid, and zero acid or base. Add sufficient water to achieve a 20:1 liquid:soil ratio, taking into account the moisture content of the sample. For example,

Sample has 20% moisture = 80% solids content (SC)

To prepare the test sample containing 20 meq base:

Weigh  $10/0.8 = 12.5$  g sample as received.

Add 50 mL DI water.

Add 20 mL 1.0 N KOH

(1.0 N KOH = 1000 meq/L. 20 meq =  $20/1000 = 0.020$  L = 20 mL 1.0 N KOH.)

Add  $200 - 50 - 20 = 130$  mL DI water to achieve a 20:1 ratio.

Tumble the samples as per Section 7. Measure the pH, ORP, and conductivity within 1 hour from completion of tumbling. The pH from the test sample with no acid or base added represents the natural soil eluate pH (for section 7.1).

**5.1** Plot pH vs. meq of acid and base added and interpolate to estimate the meq of acid and base required to achieve the target pH values of 5, 7, and 9.

**5.2** Additional pH tests using smaller additions of acid and base may be required if the initial curve does not provide sufficient definition to accurately estimate the required additions.

## 6. Formulation of Acid and Base Additions Schedule

A schedule of acid and base additions is used in the main extraction procedure (Section 7) to set up three (or four) extractions of the test material plus two method blanks and an LCS. Based on either prior knowledge of the acid/base titration curve of the sample or the results of the pre-test titration procedure in Section 5, formulate a schedule of test extractions using the following steps.

**6.1** Calculate and record the amount of "as-tested" material equivalent to the dry-material mass of 50 g as follows:

$$M_{\text{test}} = \frac{M_{\text{dry}}}{\text{SC}}$$

Where:  $M_{\text{test}}$  = mass of "as-tested" solid equivalent to the dry-material mass (g)

$M_{\text{dry}}$  = mass of dry material specified in the method (g-dry)

SC = solids content of "as-tested" material (g-dry/g)

**6.2** Determine the acid volumes and base volumes required to achieve the target pH of 5, 7, 9 as follows:

$$V_{\text{a/b}} = \frac{\text{Eq}_{\text{a/b}} \times F}{N_{\text{a/b}}}$$

Where:  $V_{\text{a/b}}$  = volume of acid or base to be used (mL)

$\text{Eq}_{\text{a/b}}$  = equivalents of acid or base selected for the target pH as determined from the pre-test titration curve (meq/g) remembering that 10g was used for the pretest and routinely 50 g is used for the test

F = scale up factor, mass used in test (g) / mass used in pretest (g) routinely 5

$N_{\text{a/b}}$  = normality of the acid or base solution (meq/mL)

**6.3** Calculate the volume of moisture contained in the "as tested" sample as follows:

$$V_{\text{W, sample}} = M_{\text{test}} \times (1-\text{SC})$$

Where:  $V_{\text{W, sample}}$  = volume of water in the "as tested" sample (mL)

$M_{\text{test}}$  = mass of "as-tested" solid equivalent to the dry-material mass (g) SC = solids content of "as-tested" material (g-dry/g)

**6.4** Calculate the volume of deionized water required to bring each extraction to a L/S of 20 mL/g-dry solid as follows:

$$V_{\text{RW}} = M_{\text{dry}} \times \text{L/S} - V_{\text{W, sample}} - V_{\text{a/b}}$$

Where:  $V_{\text{RW}}$  = volume of deionized water required to complete L/S (mL)

$M_{\text{dry}}$  = mass of dry material specified in the method (g-dry)

L/S = liquid-to-dry-solid ratio (20 mL/g)

$V_{\text{W, sample}}$  = volume of water in "as tested" sample (mL)  $V_{\text{a/b}}$  = volume of acid or base for the extraction recipe (mL)

### 6.5 Method Blanks and LCS

In the schedule table, include two additional extractions for processing Method Blanks.

Method Blank extractions are performed using the same equipment, reagents, and extraction process as the test samples, but without solid sample.

The Method Blanks and LCS should include:

- a) MB<sub>acid</sub>: deionized water + maximum volume of acid used
- b) MB<sub>base</sub>: deionized water + maximum volume of base in the schedule
- c) LCS: deionized water + maximum volume of acid used + a spike of all the analytes of interest

## 7. Extraction Procedure:

Use the schedule of acid and base additions (Section 6) as a guide to set up the tests as follows:

**7.1** Place the dry equivalent mass ( $50 \pm 0.5$  g) of the "as tested" sample, calculated above, into each of the three test position extraction vessels, or into each of four test position extraction vessels if the natural pH of the sample eluate (from Section 5) was outside the range of pH 4.5 – 9.5.

NOTE: Do NOT put any solid material (e.g., synthetic or clean soil matrix) in the method blank or LCS extraction vessels.

**7.2** Add  $200 \pm 5$  mL of deionized water to both the test sample and Method Blank and LCS vessels.

**7.3** Add and record the appropriate volume of acid or base ( $\pm 2\%$  of target value) to each vessel to achieve the target pH.

**7.4** Taking into account the moisture content contributed by the sample, the 200 mL already added and the volume of acid or base, add the appropriate volume of deionized water ( $\pm 5\%$  of target value) to the test samples and Method Blank and LCS samples, to achieve the required 20:1 liquid:solid ratio.

**7.5** Tighten the leak-proof lid on each bottle and tumble all extractions (i.e., test samples, Method Blanks and LCS's) in an end-over-end fashion at a speed of  $30 \pm 2$  rpm at  $23 \pm 2^\circ\text{C}$  for  $48 \pm 4$  hours. Remove the extraction vessels from the rotary tumbler.

**7.6** For each extraction vessel, decant a small portion of unpreserved, unfiltered eluate into a secondary container for pH and ORP measurement. Measure and record the pH and ORP of the extracts within 1 hour of the completion of tumbling to avoid neutralization of the solution due to exposure to carbon dioxide, especially when alkaline materials are tested.

NOTE: ORP measurement is required for potential evaluation of whether oxidation is likely to change the liquid-solid partitioning (LSP) of COPCs.

NOTE: If the final pH is  $> \pm 0.5$  units from the target, this must be flagged on the Certificate of Analysis. A test repeat is not required unless laboratory error is suspected.

**7.7** Clarify the eluates (prior to filtration) by allowing the bottles to stand, or centrifuge the extraction vessels if required to achieve a clear extract that can be filtered (e.g., 3000 - 4000 rpm for 10 – 30 minutes using a standard benchtop centrifuge).

**7.8** Separate the solid from the remaining liquid in each extraction vessel by pressure or vacuum filtration through a clean  $0.45 \mu\text{m}$  pore-size membrane. The filtration apparatus may be exchanged for a clean apparatus as often as necessary until sufficient liquid has been recovered to conduct the required tests.

**7.9** Immediately preserve and store the volume(s) of eluate required for chemical analysis. Preserve all analytical samples in a manner that is consistent with the determinative chemical analyses to be performed. Since samples for metals are filtered and preserved, digestion is not necessary prior to analysis unless turbidity is observed in the filtrate (i.e., due to precipitation after filtration and/or preservation). Filtration and preservation must be completed within no more than 4 hours of the completion of tumbling time.

**Quality Control**

Summary of QC Requirements		
QC Component	Minimum Frequency	Minimum Data Quality Objectives
Method Blank (MB)	One at each pH level tested per batch (minimum 2 per 20 samples; at high and low pH levels)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples; at low pH level)	80% - 120%
Lab Duplicates (DUP)	One per batch (max 20 samples)	<50% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS); spiked post-extraction	Optional	None

If DQOs are not met, repeat testing or report qualified test results.  
 Typical precision is tabulated below (taken from US EPA Method 1313).

**MEDIAN METHOD PRECISION ACROSS STUDY MATERIALS**

Analyte	Symbol	Repeatability		Reproducibility	
		Median %RSD <sub>r</sub>	IQR %RSD <sub>r</sub>	Median %RSD <sub>R</sub>	IQR %RSD <sub>R</sub>
Antimony	Sb	16%	12-25%	33%	24-45%
Arsenic	As	19%	13-24%	47%	37-61%
Barium	Ba	10%	7-15%	22%	18-36%
Boron	B	7%	5-9%	12%	8-21%
Calcium	Ca	5%	4-11%	9%	6-28%
Molybdenum	Mo	15%	6-23%	30%	18-46%
Selenium	Se	9%	6-13%	21%	18-31%
Vanadium	V	10%	6-12%	27%	23-41%

**Reporting:** Minimum reporting requirements are as follows:

- Moisture (as %).
- Conductivity, pH, and ORP of the eluate for the untreated sample, measured from the pre-test sample (with zero addition of acid or base), or, if the natural soil eluate pH was outside 4.5 – 9.5, then report these parameters from the natural pH test position.
- Target pH and Final pH of all test samples, plus conductivity and ORP.
- Analytical test results in units of mg/L.
- QC sample test results.
- Any deviations from the protocol as written (e.g. temperature exceptions).

**References**

1. US EPA Method 1313, Liquid-Solid Partitioning as a Function of Extract pH using a Parallel Batch Extraction Procedure, Revision 0, October 2012.
2. BC MOE Sample Preservation & Holding Time Requirements, Version: 06-Nov-2015 (refer to most recent version for updates).

**Revision History**

Feb. 28, 2017 First version. Method was designed by the CSAP Leachate Testing Procedure Working Group, with translation into a working method by BCELTAC.