

Strong Acid Leachable Metals (SALM) in Soil - Prescriptive

Parameter Metals in Soil and Sediment.

Analytical Method Nitric – Hydrochloric acid digestion, Instrumental analysis.

Introduction This revised method was prepared for BC MOE by the BCELTA to provide improved consistency of results for metals in soil, in support of the Waste Management Act, Contaminated Sites Regulation (CSR). All definitive elements of the method have been prescribed to minimize inter-laboratory variability, particularly for incompletely recovered elements like barium.

The BC CSR includes Water and Soil as matrix types, but Soil is only broadly defined (CSR, section 1). Carter's definition of Soil (Reference: Carter) as being "less than 2 mm" material is used for this method.

This method may also be used for marine and freshwater sediment applications, where sediment is defined as being "less than 63 µm" material. However, by default, laboratories are instructed to apply the method on the "less than 2 mm" fraction, except by special request.

This method uses a mixture of nitric acid, hydrochloric acid, and de-ionized water, with a standardized digestion time and temperature. Laboratories are allowed some flexibility regarding apparatus and heating methods, but variations in acid mixture composition, digestion time, or digestion temperature are not permitted.

Method Summary Samples are dried at ≤ 60°C, sieved, and digested with a mixture of nitric acid, hydrochloric acid, and de-ionized water. Instrumental analysis of sample extracts can be performed by a variety of analytical methods.

This method provides the sample preparation procedure for the analysis of Total Metals, as referenced within the BC CSR. Total Metals does not imply a complete dissolution of silicate materials, as would occur with digestions using perchloric and hydrofluoric acids. The strong acid leach prescribed by this method is intended to dissolve those metals that may be environmentally available. The method achieves near complete recoveries of some important metals, but many others are only partially recovered (see Table 1 for examples). Metals not dissolved with this method are unlikely to be of environmental consequence.

This method is prescriptive. It must be followed exactly as described. Where minor deviations are permitted, this is indicated in the text. All results must be reported on a dry weight basis.

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

This method is applicable to the following parameters:

Parameter	CAS Number	EMS Code	Parameter	CAS Number	EMS Code
Aluminum	7429-90-5	AL-T	Molybdenum	7439-98-7	MO-T
Antimony	7440-36-0	SB-T	Nickel	7440-02-0	NI-T
Arsenic	7440-38-2	AS-T	Phosphorus	7723-14-0	P-T
Barium	7440-39-3	BA-T	Potassium	7440-09-7	K-T
Beryllium	7440-41-7	BE-T	Selenium	7782-49-2	SE-T
Boron	7440-42-8	B-T	Silver	7440-22-4	AG-T
Cadmium	7440-43-9	CD-T	Sodium	7440-23-5	NA-T
Calcium	7440-70-2	CA-T	Strontium	7440-24-6	SR-T
Chromium	7440-47-3	CR-T	Sulfur	7704-34-9	S-T
Cobalt	7440-48-4	CO-T	Thallium	7440-28-0	TL-T
Copper	7440-50-8	CU-T	Thorium	7440-29-1	TH-T
Iron	7439-89-6	FE-T	Tin	7440-31-5	SN-T
Lead	7439-92-1	PB-T	Titanium	7440-32-6	TI-T

Lithium	7439-93-2	LI-T	Tungsten	7440-33-7	W-T
Magnesium	7439-95-4	MG-T	Uranium	7440-61.1	U-T
Manganese	7439-96-5	MN-T	Vanadium	7440-62-2	V-T
Mercury	7439-97-6	HG-T	Zinc	7440-66-6	ZN-T

Other metals may be analyzed by this method if acceptable performance is demonstrated and validated. This method is not suitable for the determination of silica or silicon.

EMS Method Code*

FS82

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

Method Limitations

This method does not dissolve all silicate materials and may result in a partial extraction, depending on the sample matrix, for some metals, including, but not limited to aluminum, barium, beryllium, chromium, strontium, titanium, thallium, tungsten, and vanadium.

Unpublished studies by some BC laboratories have shown that dissolved antimony and tin may re-sorb to undigested solids over time after the sample extract has been diluted. Once the solids have been removed from the sample extract, antimony and tin are more stable.

This method is suitable for the digestion of samples with silver concentrations of up to 0.5 mg/L in the extract after dilution to final volume, which is equivalent to 50 mg/kg in soils, based on a 1 g sample size and 100 mL final volume (Reference: US EPA 200.2).

This method is suitable for digesting samples with tin concentrations of up to 100 mg/L in the sample extract after dilution to final volume, which is equivalent to 1% in soils, using a 1 g sample size and 100 mL final volume (Reference: US EPA 200.2).

The solubility and stability of barium is limited in the presence of free sulfate using this method (Reference: US EPA 200.2).

This method does not adequately recover elemental sulfur, and is not appropriate for the assessment of BC CSR standards for elemental sulfur in soil.

Matrix

Soil and sediment

Interferences and Precautions

The interferences encountered will differ depending on the instrumental method used to analyze the sample extracts. These interferences should be clearly outlined and controlled in the analysis procedure. High concentrations of acids may cause physical interferences with some instrumental techniques.

Sample Handling and Preservation

Sampling should be done by qualified personnel. Samples must be collected and stored such that degradation or alteration of the sample is minimized. Collect the sample in a clean polyethylene or glass container, and tightly cap immediately after sampling.

Preservation: None

Stability

Holding Time:

Metals (except Mercury): 180 days

Mercury: 28 days

When tin and antimony analyses are required, the sample extracts must be separated from the undigested solids within 4 hours of diluting to final volume. The decanted or filtered sample extract must be analyzed within 7 days.

Results reported for samples digested beyond holding times must be qualified.

Storage: For mercury, store at $\leq 6^{\circ}\text{C}$ unless dried (freezing is permitted, but is not recommended due to the potential for container breakage). For all other metals, there is no requirement for storage temperature (ambient storage temperature conditions are suitable).

The potential for loss of mercury by storage at ambient temperature is due to conversion of Hg(II) to volatile Hg(0) by microbial activity. Dried soils are stable at ambient temperature for at least 28 days (refer to References, Bull Environ Contam Toxicol (2015) 94:570–576).

Equipment and Supplies

1. Heating source (e.g. block digester, hotplate, water bath) capable of maintaining a sample extract temperature of $95 \pm 5^\circ\text{C}$.
2. Balance, minimum 3 place.
3. Drying oven (not required).
4. Sieve, 2 mm (ASTM-E11 Sieve No. 10, US Sieve No. 10, Tyler 9 Mesh) or Sieve, 63 μm (ASTM-E11 Sieve No. 230, US Sieve No. 230, Tyler 250 Mesh). It is recommended that a stainless steel screen/sieve with all tin solder be used. Sieves must not be constructed of brass or contain lead solder. Polypropylene or nylon sieves may also be used.
5. Acid dispensers.
6. Vapor refluxing cover to fit digestion vessel (e.g. reflux cover, watch glass etc.).
7. Digestion vessels (e.g. block digester tube, beaker, flask, etc.).
8. Gloves.
9. Spatula.

Reagents

1. Nitric acid (HNO_3) conc. (67 - 70%), reagent grade minimum.
2. Nitric acid (1+1) – add 500 mL concentrated HNO_3 to 400 mL de-ionized water and dilute to 1 L.
3. Hydrochloric acid (HCl) conc. (34 - 37%), reagent grade minimum.
4. Hydrochloric acid (1+1) – add 500 mL concentrated HCl to 400 mL de-ionized water and dilute to 1 L.
5. Water, de-ionized (ASTM Type I or equivalent recommended).

Safety

Nitric and hydrochloric acid must not be premixed; they should be added individually to each sample vessel. Mixtures of nitric and hydrochloric acid must not be stored in closed containers.

Wear appropriate PPE (Personal Protective Equipment) including lab coat, gloves, and safety glasses. Add acids to samples and perform digestions under a fume hood.

Procedure

Samples are prepared and digested using the following procedures:

Sample Homogenization and Sub-Sampling

1. Inspect the sample and record any unusual or significant characteristics (e.g. lead shot pellets, metal turnings, nails, shells, etc.).
2. Remove any obviously foreign material such as vegetation.
3. If the sample has separated into visually discrete layers (e.g. aqueous, organic, and sediment phases), the entire sample must be homogenized prior to sub-sampling. The aqueous phase must not be decanted.

Note: Special project requirements may involve alternative procedures such as decanting of the aqueous fraction. Indicate any departures or deviations from the prescribed method with a qualifying statement in the laboratory report.

4. Homogenize the entire sample by vigorous stirring using a spatula. If it is not possible to homogenize the sample in the container it was received in, the sample can be transferred to a larger container prior to homogenization. Clean the spatula and mixing container between samples.
5. Where moisture determination is required, a separate sub-sample must be taken prior to drying and sieving.

Sample Preparation – Drying

1. Dry the sample to a constant weight at a temperature of $\leq 60^\circ\text{C}$. Freeze drying is acceptable.

Note: Sample drying temperature must not exceed 60°C to minimize volatilization of analytes such as mercury (Reference: US EPA 200.2).

2. Alternatively, moist or wet samples may be wet-sieved. If a sample is sieved when moist, a moisture determination must be done on the sieved portion (not on the “as received” sample) in order to convert results to dry weight.

Sample Preparation – Sieving

1. Sieve each sample through a 2 mm sieve. By special request, some sediment applications may require the use of a 63 μm sieve. If a 63 μm sieve is used, this must be indicated on the laboratory report. DO NOT pulverize samples to pass through either sieve type. Easily friable materials (dried clay clods, disintegrating rock, etc.) should be disaggregated prior to screening. Where necessary, non-pulverizing disaggregating tools like rolling mills, mortar and pestle, or flail grinders may be used.
2. Where available, it is recommended that a minimum of 25 grams of sample is sieved to ensure representative sub-sampling for the digestion stage.
3. Discard the portion of sample that did not pass through the sieve.
4. Field sampling personnel may pre-screen the samples in the field.

Sample Preparation - Digestion

1. Weigh 1.0 ± 0.1 g (dry weight) of sample into a digestion vessel, which must be fitted with a cap that supports open vessel reflux action (e.g. hotblock digestion tube, beaker, or Erlenmeyer flask with watch glass). At minimum, include Method Blanks, Lab Duplicates, and Reference Materials with each batch of samples. Laboratory Control Samples are also recommended. Weights must be recorded using a minimum 3 place balance.

Note: In cases where one gram of sieved sample is not available, perform the analysis as described, and qualify the results (results for poorly recovered metals like Barium may be increased).

2. Add 5.0 ± 0.5 mL de-ionized water, 2.50 ± 0.25 mL concentrated HNO_3 , and 2.50 ± 0.25 mL concentrated HCl. Alternatively, add 5.0 ± 0.5 mL of HNO_3 (1+1) and 5.0 ± 0.5 mL of HCl (1+1).
3. Add a reflux cap to the top of the digestion vessel. Swirl acid and sample to mix gently. It is permitted to allow samples to cold digest prior to heating to reduce any potential effervescence from reactive samples.
4. Digest samples for 2 hours \pm 15 minutes at a temperature of $95 \pm 5^\circ\text{C}$ at atmospheric pressure. A digestion block or water bath are the preferred methods of heating. The heat for digestion must maintain the sample extract temperature at $95 \pm 5^\circ\text{C}$. This refers to the temperature of the sample extract in a digestion vessel covered with a reflux cap, not the temperature setting on the heating source, and not the temperature of an uncovered digestion vessel. It is recommended that the sample extract temperature be monitored and recorded with each batch.
5. Allow the sample to cool and dilute the entire sample with de-ionized water to the volume required for the analysis. The dilution volume will depend on the analytical method and objectives. Typical final dilution volumes will be 25 mL, 50 mL, or 100 mL. Include all undigested solid material as part of the final diluted volume. Sample extracts should not be stored in glass.
6. When tin and antimony analyses are required, sample extracts must be separated from the undigested solids within 4 hours of diluting to final volume. The decanted or filtered sample extract must be analyzed within 7 days. These steps are necessary to minimize tin and antimony losses due to re-sorption.
7. Analyze the final extract using appropriate analytical methods and report the results on a dry weight basis.

Report any anomalies observed during the digestion and analysis.

Method QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	1 per batch (max 20 samples)	Less than reported DL
Reference Material	1 per batch (max 20 samples)	70 - 130% of the laboratory's long term mean value (see validation section for additional requirements)
Laboratory Control Sample	1 per batch (max 20 samples)	80 - 120%
Lab Duplicates	1 per batch (max 20 samples)	≤ 30% RPD for all metals except those indicated below; [or within 2x reported DL for low level results] ≤ 40% RPD (Ag, Al, Ba, Hg, K, Mo, Na, Pb, Sn, Sr, Ti, W, Zr)
Field Duplicates	Recommended	None Specified

* If DQOs are not met, repeat testing or report qualified test results. The stated recovery DQOs do not apply to RM parameters where target levels are below 10x MDL (use locally derived DQOs).

Reference Material requirements: Any suitable RM (including in-house RMs) may be utilized for this method for routine Quality Control purposes, but the RMs listed below under validation requirements are recommended. RMs provide QC data that includes digestion elements of the method and which is representative of method performance for typical samples.

Laboratory Control Sample: An LCS for this method is a digested spiked Method Blank (no blank matrix exists for metals in soils). An LCS has more precisely defined targets than soil RMs, can cover all parameters reported by the method, and allows for better and more precise Quality Control of basic elements of the method (e.g. volumetric precision and controls and instrumental analysis).

Method Validation Requirements

Initial Method Validation requirements as outlined below must be completed before this method may be used to generate results for unknown samples. The method must be re-evaluated periodically (every two years is recommended as a suitable frequency). Prepared validation samples must be analyzed by all instrument methods used for routine analysis.

Demonstration of Accuracy and Precision:

Prepare and analyze at least 8 replicates of at least two of the following Certified Reference Materials:

- NRC PACS-2
- CCRMP TILL-1
- CCRMP TILL-3
- SCP Science SS-2

Where the above RMs are utilized for routine QC purposes, re-validations should be conducted using all routine QC data available for the review period.

Accuracy is measured as Percent Recovery versus the Interim Targets outlined in Table 1. For each metal, average accuracy must be within 70-130% of the Interim Targets, for results ≥ 5 times the Reported Detection Limit. Precision must be <15% RSD for results ≥ 5 times the Reported Detection Limit.

The Interim SALM Targets and DQOs may be re-assessed in the future if RMs become unavailable or if otherwise required.

References

US EPA Method 200.2, Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements, National Exposure Research Laboratory, Office of Water, US EPA, Cincinnati, OH, October 1999.

Soil Sampling and Methods of Analysis, Carter, M.R., editor, for Canadian Society of Soil

Science, Lewis Publishers, 1993.

The Influence of Sample Drying Procedures on Mercury Concentrations Analyzed in Soils, Maria Hojdova et. al., Bull Environ Contam Toxicol (2015) 94:570–576.

Revision History

Sept 15, 2017	Added tungsten (a new substance in the 2017 CSR). Minor changes for compliance with CCME guidance manual including requirement for LCS QC (previously recommended) and change of storage temperature from ambient to $\leq 6^{\circ}\text{C}$ for Hg (unless dried). Acid and water reagent volume tolerances standardized at +/-10%. Method limitation comment added for elemental sulfur.
Nov 6, 2015	Changed storage temperatures to be consistent with current BC MOE requirements. Removed requirement for minimum one-hour cold digestion (not necessary with version 2 of SALM method). Added LCS to QC and Procedure sections (recommended). Removed unnecessary references.
July 7, 2009	Version 2 of BC SALM Method for 2009 BC Lab Manual. Method revised from performance based to prescriptive. All key defining elements of the method are now prescribed. New interim RM targets assigned.
Feb 2001	Version one of BC SALM Method was introduced. Incorporated into Lab Manual November 2002.

TABLE 1. Interim Target Values for Reference Materials using BC SALM^(a)

Parameter	CCRMP TILL-1 Certified ("Total")	CCRMP TILL-1 SALM Interim Target	CCRMP TILL-3 Certified ("Total")	CCRMP TILL-3 SALM Interim Target	NRC PACS-2 Certified ("Total")	NRC PACS-2 SALM Interim Target	SCP Science SS-2 EPA3050A Digestion Targets	SCP Science SS-2 SALM Interim Target
Aluminum - Al (%)	7.25	1.82	6.45	1.15	6.62	1.75	1.33	1.37
Antimony - Sb (mg/kg)	7.8	6.27	0.9	0.724	11.3	7.3	-	4.16
Arsenic - As (mg/kg)	18	15.4	87	82.1	26.2	23.3	75	88.4
Barium - Ba (mg/kg)	702	80.6	489	40	-	294	215	224
Beryllium - Be (mg/kg)	2.4	0.544	2.0	0.369	1.0	0.408	-	-
Boron - B (mg/kg)	-	-	-	-	-	38.1	-	-
Cadmium - Cd (mg/kg)	< 0.2 ^(b)	-	< 0.2 ^(b)	-	2.11	1.98	-	2.2
Calcium - Ca (%)	1.94	0.332	1.88	0.517	1.96	0.779	11.3	12.3
Chromium - Cr (mg/kg)	65	27.2	123	63.1	90.7	48.1	34	34.6
Cobalt - Co (mg/kg)	18	12.5	15	10.4	11.5	8.75	12	13.1
Copper - Cu (mg/kg)	47	44.9	22	19.8	310	297	191	211
Iron - Fe (%)	4.81	3.33	2.78	2.02	4.09	3.12	2.10	2.53
Lead - Pb (mg/kg)	22	14.4	26	17.3	183	167	126	132
Lithium - Li (mg/kg)	15	-	21	-	32.2	-	14	14.3
Magnesium - Mg (%)	1.30	0.583	1.03	0.609	1.47	0.99	1.11	1.24
Manganese - Mn (mg/kg)	1420	1100	520	315	440	253	457	511
Mercury - Hg (mg/kg)	0.092 ^(b)	0.098	0.107 ^(b)	0.11	3.04	2.88	-	0.33
Molybdenum - Mo (mg/kg)	2	0.738	2	0.619	5.43	4.57	-	2.94
Nickel - Ni (mg/kg)	24	17.4	39	31.7	39.5	31.6	54	63
Phosphorus - P (%)	0.0930	0.0796	0.0490	0.042	0.096	0.0838	0.0752	0.0832
Potassium - K (%)	1.84	0.0619	2.01	0.0965	1.24	0.323	0.342	0.342
Selenium - Se (mg/kg)	-	-	-	-	0.92	-	-	-
Silver - Ag (mg/kg)	0.2 ^(b)	-	1.6 ^(b)	1.75	1.22	-	-	1.1
Sodium - Na (%)	2.01	0.0340	1.96	0.027	3.45	1.86	0.0558	-
Strontium - Sr (mg/kg)	291	11.6	300	20.3	276	68	214	232
Sulfur - S (%)	< 0.05	-	< 0.05	-	1.29	1.22	-	-
Thallium - Tl (mg/kg)	-	-	-	-	0.6 ^(c)	-	-	0.38
Thorium - Th (mg/kg)	5.6	-	4.6	-	-	-	-	-
Tin - Sn (mg/kg)	-	-	-	-	19.8	19.1	-	0.74
Titanium - Ti (%)	0.599	0.0764	0.291	0.0645	0.443	0.09	0.0850	0.0969
Uranium - U (mg/kg)	2.2	-	2.1	-	3 ^(c)	-	-	1.34
Vanadium - V (mg/kg)	99	54.9	62	33.5	133	74.4	34	39.9
Zinc - Zn (mg/kg)	98	67.5	56	40.2	364	337	467	546

(a) Interim Targets from "Report on Results of 2007 Inter-laboratory Study to Re-establish Data Quality Objective for BCMOE Strong Acid Leachable Metals (SALM) in Soil Method, Prepared for the BC Ministry of Environment, JRD Consulting Company, 2007 June 20. Interim Targets for SS-2 RM are single lab values provided to BCLQAAC.

(b) Parameter not listed as "Total". Listed as "Summary of partial extraction elements concentrated HNO₃ – concentrated HCl".

(c) Parameter not certified, provided as informational value.