



Ministry of  
Environment

# ***ANALYTICAL METHOD 9*** ***FOR CONTAMINATED SITES***

## Soluble Barium by Calcium Chloride Extraction

Prepared pursuant to Section 64 of the  
*Environmental Management Act*

Approved:

J Hofweber  
Director of Waste Management

September 20, 2007  
Date

**Version 1.0**

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EMS Method Code:\*\*\*\*\*  
Revision Date: August 16, 2007

**Soluble Barium by Calcium Chloride Extraction – Prescriptive**

**Parameter**

Soluble Barium (CaCl<sub>2</sub>)

**Analytical Method**

1M Calcium Chloride extraction

**Introduction**

This method is intended to provide quantification of soluble barium species, without extracting insoluble and/or sequestered barium (e.g. barite – barium sulphate). It is intended to support the assessment and remediation of barium under the Contaminated Sites Regulation at sites where detailed documentary evidence of barite use exists.

The method uses excess calcium ions to increase barium solubility in solution, and to encourage displacement of barium from cation exchange sites.

**Method Summary**

*This method is prescriptive. It must be followed exactly as described.* Where minor deviations are permitted, this is indicated in the text.

Samples are dried at low temperature and sieved using a 2 mm (10 mesh) sieve. Solid samples are extracted for 2 hours with 1.0 M CaCl<sub>2</sub> at a 10:1 ratio of extraction solvent to solid. The extract is filtered and analyzed for barium using an appropriately sensitive and precise analytical method for barium (e.g. ICP-AES or ICP-MS).

**MDL and EMS Codes**

Analyte	Approx. MDL	EMS Code
Soluble Barium (CaCl <sub>2</sub> )	2 mg/kg	Not available

**Matrix**

Soil, Sediment, Drilling Waste Solids, Waste

### **Interferences and Precautions**

Samples with high petroleum or non-petroleum hydrocarbon content (Oil and Grease) may require specialized sample pre-treatment using solvent extraction.

Extracts from this method are very high in salt content, and normally require dilution prior to analysis by most techniques.

### **Sample Handling and Preservation**

Collect samples in a clean polyethylene or glass container. No preservation is required.

### **Stability**

**Holding and Storage Time:** Soils may be stored at room temperature or refrigerated at  $<6^{\circ}\text{C}$  for up to 6 months.

Extracts must be stored at room temperature, and must be analyzed within 7 days of extraction.

### **Procedure**

Samples are prepared using the following procedures. All procedures are mandatory elements, unless otherwise indicated.

#### **1. Reagents**

- 1.1. **1.0 M CaCl<sub>2</sub>:** Volumetrically prepare the extraction solution by dissolving 147.0 g CaCl<sub>2</sub>·2H<sub>2</sub>O per 1L of laboratory grade water. Test new lots or supplies of calcium chloride for barium background before use.
- 1.2. **Laboratory Grade Water:** Water free of substances that interfere with the analytical method.

#### **2. Sample Preparation**

- 2.1. Inspect the sample and record any unusual or significant characteristics (i.e. foreign material, metals etc.).
- 2.2. Remove any obviously foreign material such as vegetation.
- 2.3. Homogenize the entire sample and sub-sample a sufficient quantity for drying and analysis. Use appropriate sub-sampling techniques and quantities to ensure that the sample has been sufficiently represented.

## 2. Sample Preparation (continued)

- 2.4. Dry sub-samples to constant weight at a temperature of  $<60^{\circ}\text{C}$ . If no other metals or temperature-sensitive analytes are to be determined using the same sub-sample, a drying temperature of up to  $105^{\circ}\text{C}$  may be used.
- 2.5. Disaggregate the dried sample by manual or gentle mechanical action.
- 2.6. Sieve each sample through a 2 mm (10 mesh) sieve. Discard the “greater than 2 mm” fraction.

## 3. Sample Extraction Procedure

- 3.1. Accurately weigh  $5.0 \pm 0.5$  g of dry sample into a vessel appropriate for mechanical mixing (e.g. 250 mL glass Erlenmeyer). Include method blanks, duplicates and at least one reference material per batch of samples. Record sample weights to  $\pm 0.01$  g.
- 3.2. Add  $50 \pm 0.5$  mL of 1.0 M  $\text{CaCl}_2$  extraction solution.
- 3.3. Extract the mixture for 2 hours  $\pm 15$  minutes using a mechanical agitation method such as a shaker table or rotary mixer.
- 3.4. Filter the extract under gravity or suction, using a filter paper fine enough to yield a clear filtrate. Alternatively, extracts can be centrifuged to remove suspended particles.
- 3.5. Accurately dilute the entire sample with laboratory grade water to the volume required for the analysis. The dilution volume will depend on the analysis technique, the detection limit, and the sample concentration.

## 4. Sample Analysis for Barium

- 4.1. Analyze the appropriately diluted extract of samples and QC samples using an appropriate technique for barium, such as ICP-AES or ICP-MS. Report results for soluble barium on a dry weight basis.
- 4.2. Report any anomalies during extraction and analysis.

## Performance Requirements

All laboratories performing this analytical method must conduct validation to confirm that the requirements below are met.

Accuracy and Precision requirements apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples. For Initial Validations, averages of at least 8 spikes or CRMs must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 6 months to 1 year). A

minimum frequency of 2 years is recommended for Ongoing Re-validations.

**Accuracy Requirement:** Laboratories must demonstrate method accuracy (measured as average recovery) of 80% or better for a minimum of 8 clean matrix spikes of barium chloride in clean sand, at concentrations above ten times the MDL.

**Precision Requirement:** Laboratories must demonstrate method precision equal to or better than 15% relative standard deviation for a minimum of 8 clean matrix spikes of barium chloride in clean sand, at concentrations above ten times the MDL.

**Sensitivity Requirement:** Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

### Quality Control - Summary of QC Requirements

QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	One per batch	Less than reported DL
Method Spike or Ref. Material	One per batch	70 - 130% recovery
Lab Duplicates	Approximately 5-10%	40% RPD

\* Minimum DQOs apply to individual QC samples, not averages, and only at levels above 10x MDL. If any DQOs are exceeded at a frequency of more than ~5%, the laboratory's method should be reviewed in an attempt to improve its performance. Laboratories should report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.

**Method Blank:** Required. Minimum one per batch or as necessary to ensure contamination control.

**Lab Duplicates:** Required. Replicate all components of the test from start to finish. Random duplicate selection at an approximate frequency of 5-10% is recommended.

**Reference Material or Method Spike:** Required. Use of a Clean Matrix Spike of Barium Chloride in sand is strongly recommended. In-house prepared RMs are permitted.

### Revision History

June 10, 2007 Draft version for public comment. Prepared for B.C. MOE by the BCLQAAC Barite Task Group (Mark Hugdahl, Darlene Lintott, John Ashworth and Miles Tindal).

August 16, 2007 BCLQACC final approved version 1.0, submitted for Director's approval.

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