

Sample Preparation for Dissolved Metals or Mercury in Water – PBM

Parameter	Dissolved Metals in Water.
Analytical Method	Membrane filtration, acid preservation, instrumental analysis.
Introduction	<p>This method was prepared for the BC Ministry of Environment and Climate Change Strategy (BC ENV) by the BCELTAC to ensure consistency of results for dissolved metals in water. All definitive elements of the method have been prescribed to minimize inter-laboratory variability.</p> <p>This method is BC ENV approved for the preparation of 35 dissolved metals in waters. This method is not applicable to the determination of speciated metals such as hexavalent chromium.</p>
Method Summary	<p>Samples are field-filtered (before preservation) through a 0.45 µm membrane. General metals samples are preserved with nitric acid. Mercury samples are preserved with hydrochloric acid or bromine monochloride (BrCl). BrCl is not recommended for use in the field.</p> <p>Instrumental analysis of sample extracts can be performed by a variety of BC ENV approved analytical methods.</p> <p>Samples must be filtered in the field as close as possible to the time of collection (preferably within 15 minutes). This is particularly important for groundwaters where exposure to atmospheric conditions can trigger redox reactions that cause certain metals to precipitate (particularly iron). If precipitation of iron oxides occurs, many other heavy metals may precipitate or co-precipitate, potentially causing substantially low bias for many metallic elements. In extreme cases, some elements may be 100% removed from solution due to precipitation or co-precipitation caused by delay of filtration.</p> <p>Acid preservation of filtered samples (using nitric acid for general metals, or hydrochloric acid for mercury) is normally performed in the field, but may alternatively be performed in the lab (within 14 days of sample collection for general metals, or within 28 days for mercury using BrCl). BrCl (bromine monochloride) is not normally recommended as a field preservative for safety reasons.</p> <p>Upon arrival at the laboratory, minimal preparation is required for field-filtered and preserved samples, except that additional acid may be added prior to analysis to ensure pH is < 2 and for matrix-matching purposes.</p> <p>If filtration is not possible in the field, samples may be forwarded to the laboratory without filtration or preservation. However, lab-filtered samples may not provide reliable measures of dissolved metals concentrations (particularly for groundwaters and anoxic samples, where results may be significantly low-biased) and must be qualified. <u>Lab-filtered samples are not acceptable for compliance testing for CSR or permittee purposes.</u></p> <p>If a visible precipitate is evident at the laboratory after filtration and preservation, the sample must be digested prior to analysis, using an applicable BC ENV approved digestion method for metals or mercury (as applicable).</p> <p>This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency if all stated performance requirements and prescribed (mandatory) elements are met.</p>

MDL(s) and EMS Analyte Code(s)

This method is applicable to the following parameters:

Parameter	EMS Code	Parameter	EMS Code	Parameter	EMS Code
Aluminum	AL-D	Iron	FE-D	Silver	AG-D
Antimony	SB-D	Lead	PB-D	Sodium	NA-D
Arsenic	AS-D	Lithium	LI-D	Strontium	SR-D
Barium	BA-D	Magnesium	MG-D	Thallium	TL-D
Beryllium	BE-D	Manganese	MN-D	Thorium	TH-D
Bismuth	BI-D	Mercury	HG-D	Tin	SN-D
Boron	B-D	Molybdenum	MO-D	Titanium	TI-D
Cadmium	CD-D	Nickel	NI-D	Tungsten	W-D
Calcium	CA-D	Phosphorus	P-D	Uranium	U-D
Chromium	CR-D	Potassium	K-D	Vanadium	V-D
Cobalt	CO-D	Selenium	SE-D	Zinc	ZN-D
Copper	CU-D	Silicon	SI-D		

Other metals may be analyzed by this method if acceptable performance is demonstrated and validated.

EMS Method Code

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

Matrix

Water, including fresh water, seawater, brackish water, and wastewater.

Interferences and Precautions

The interferences encountered will differ depending on the instrumental method used to analyze the sample extracts. 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. For further details, refer to the BC Field Sampling Manual.

The sample must be filtered through a 0.45 µm pore diameter membrane filter at the time of collection, or as soon thereafter as practically possible (preferably within 15 minutes).

Note: Membrane filters are typically made from polycarbonate or cellulose esters, though other materials are acceptable if demonstrated to be suitable for use. Pre-filters are also acceptable for highly turbid samples if demonstrated to be suitable. To reduce the possibility of false positives from contamination, it is highly recommended that the environmental practitioner either use filters that are supplied by the laboratory or provide the laboratory with samples of their chosen filters for testing prior to use.

Metals other than Mercury: Collect samples in clean high-density polyethylene (HDPE), glass, or Polytetrafluoroethylene (PTFE) containers. Preserve in the field (or in the laboratory) with nitric acid to pH < 2. Treatment of samples with approximately 1 mL of 1:4 HNO₃* per 100 mL sample is recommended. For laboratory preservation, add nitric acid to the original sample container within 14 days of sampling, then equilibrate ≥ 16 hours prior to sub-sampling.

Mercury: Collect samples using only glass or PTFE containers. Field-preserve with HCl to pH < 2. Adding BrCl to the original sample container at the laboratory within 28 days of sampling is an acceptable alternative to field preservation (use ≥ 0.5 mL BrCl solution per 100 mL of sample and equilibrate ≥ 24 hours prior to sub-sampling; prepare BrCl solution as per BC Lab Manual method for Total and Dissolved Mercury in Water by Bromine Monochloride Digestion).

* Note: 1:4 HNO₃ is equivalent to 18 %wt/wtHNO₃. Nitric acid concentrations exceeding 20 wt% triggers additional TDG shipping restrictions (cannot be shipped by passenger airline).

Stability

Holding Time:

Metals, excluding Mercury: 180 days from sampling (if preserved to pH < 2 with HNO₃)
Mercury; 28 days from sampling (if preserved to pH < 2 with HCl or BrCl)

Results reported for samples analyzed beyond the holding time must be qualified.

Storage: No storage temperature requirement (US EPA 40CFR May 18, 2012).

Procedure

If the laboratory's client or sample submission paperwork indicates that the sample was not filtered prior to arrival at the laboratory, proceed with filtration at the laboratory as soon as is practical. Lab-filtered dissolved metals samples must always be qualified due to the potential for low biased results, regardless of how quickly after receipt the filtration is conducted. Dissolved metals or mercury samples that are lab-filtered may be low-biased, and may not reflect conditions at time of sampling.

For filtration (field or laboratory), use 0.45 µm filters that have been previously tested to be metals-free (i.e. < MRL for analytes of interest) by filtering deionized water. Positive pressure (e.g. syringe) or vacuum filtration are acceptable, provided that the materials that contact the sample have been tested for suitability. Use a portion of the sample to rinse the filter assembly, discard this portion and collect the required volume of filtrate. Add the appropriate volume of nitric acid (for general metals) or hydrochloric acid (for mercury) to achieve pH < 2.

If the sample was field-filtered but not acid-preserved prior to arrival at the laboratory, samples may be preserved in the laboratory without consequence (refer to Sample Handling and Preservation section for guidance).

Prior to sub-sampling and analysis, perform a visual assessment of each filtered and acid-preserved sample. If a precipitate is evident, the sample must be digested prior to analysis using an applicable BC ENV approved digestion method, e.g. "Digestion for Total Metals in Water – Prescriptive" or "Total and Dissolved Mercury in Water by Bromine Monochloride Digestion – PBM". Results are still reported as "dissolved" metals or mercury.

Conduct instrumental analysis using an appropriate BC ENV approved method. Specific preparation steps are dependent on the analytical technique.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements, and 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. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. 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 85-125% or better for Lab Control Samples or Reference Materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 10% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) 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
Field Filtration Blank	Strongly Recommended	One per sampling event
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	80 – 120%
Lab Duplicates (DUP)	One per batch (max 20 samples)	≤ 20% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	One per batch (max 20 samples)	70 – 130%
Field Duplicates	Recommended	None specified
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

Prescribed Elements

The following components of this method are mandatory:

1. Dissolved metals samples must be field-filtered for suitability to CSR or permittee applications for compliance testing. Samples that are filtered and preserved in the laboratory must be qualified, e.g. “dissolved metals sample was lab-filtered; test results may be low-biased and are unsuitable for CSR or permittee compliance monitoring”.
2. Samples must not be preserved prior to filtration.
3. Filtration must be performed using 0.45 µm membrane filters. For filtration conducted in the laboratory, filters used must have been previously tested for trace metal impurities, i.e. all results < MRL (method reporting limit).
4. Method Blanks associated with lab-filtered dissolved metals samples must be lab-filtered. When pre-filters are used for filtration of turbid samples in the laboratory, they must be proofed with each usage using the Method Blank or an independent blank.
5. Positive control QC samples associated with lab-filtered dissolved metals samples (LCS, RM, MS) must either be lab-filtered, or the lab must validate and document that filtration media and process does not adsorb targeted metals at high or MRL levels.
6. If a visible precipitate is evident after filtration and preservation, the sample must be digested prior to analysis using an applicable BC ENV approved digestion method for metals or mercury (as applicable). If digestion is conducted due to visible particulate, qualify test results, e.g. “field filtered dissolved metals sample required digestion due to presence of visible particulate”. This may indicate precipitation of dissolved metals has occurred, or could indicate improper field filtration.
7. Samples that are field-filtered but not field-preserved must be preserved at the lab in their original containers. For general metals, add HNO₃ to the original container to achieve pH < 2 within 14 days of sampling, then equilibrate for at least 16 hours prior to sub-sampling or analysis. For mercury, add BrCl to the original container within 28 days of sampling, then equilibrate for at least 24 hours prior to sub-sampling and analysis. If immediate analysis for metals or mercury without equilibration is necessary, preserve in the same manner and qualify appropriately, e.g. “received unpreserved, preserved at laboratory; results may be biased low”.
8. All stated Performance Requirements and Quality Control requirements must be met.
9. Sample container materials, preservation, storage, and hold time requirements may not be modified. Samples analyzed beyond the stated holding time must be qualified. Refer to latest version of “BC MOE Sample Preservation and Hold Time Requirements” for updates.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method to improve quality or efficiency.

References

1. EPA Method 200.8 "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry", Revision 5.4, U.S. Environmental Protection Agency, May 1994.
2. British Columbia Field Sampling Manual – Part E: Water and Wastewater Sampling, 2013
3. APHA 3030 B, Preliminary Treatment of Samples – Filtration for Dissolved and Suspended Metals, 2004.
4. US EPA 40CFR, Table II, Required Containers, Preservation Techniques, and Holding Times, May 18, 2012.

Revision History

Nov 22, 2018 First version of method for publication in BC Lab Manual. This method formalizes BC ENV policy that field filtration is required for dissolved metals (for CSR or permittee compliance monitoring).