Digestion for Total Metals in Water - Prescriptive

Parameter

Total Metals in Water.

Analytical Method

Nitric – Hydrochloric acid digestion, Instrumental analysis.

Introduction

This method was prepared for BC MOE by the BCELTAC to provide improved consistency of results for total metals in water. All definitive elements of the method have been prescribed to minimize inter-laboratory variability.

This method uses a prescribed mixture of nitric and hydrochloric acids with a standardized digestion time and temperature. Laboratories are allowed some flexibility regarding apparatus and heating methods, but variations in acid type or concentration, digestion time, or digestion temperature are not permitted.

This method is BC MOE approved for the digestion of 36 metals in waters, including mercury (subject to performance requirements being met). However, other methods are also available for mercury, including potassium permanganate / potassium persulfate digestion and bromine monochloride oxidation.

Method Summary

Samples are digested with a mixture of nitric and hydrochloric acids. 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. Total metals include all metals, inorganically and organically bound, both dissolved and particulate (APHA 3030A). The terms total metals and total recoverable metals are used interchangeably, and are defined as the concentration of analyte measured in an unfiltered aqueous sample following treatment by refluxing with hot dilute mineral acid (US EPA 200.2).

Digestion by this procedure is required for total metals analysis of any water sample with turbidity >1 NTU, or for any sample that is visibly coloured, or that has any noticeable odour. Colourless samples with no apparent odour that are verified by measurement to have turbidity <1 NTU are either analyzed as received, or are digested.

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

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

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.
Method Limitation	This digestion procedure may not be sufficiently vigorous to solubilize all particulate metals in the sample. Even in these cases, this method does provide a conservative measure of environmentally or ecologically available metals. This method is suitable for digestion of water samples containing silver concentrations of up to 0.1 mg/L (US EPA 200.2). Samples containing higher levels of silver must be diluted prior to digestion by this procedure. The solubility and stability of barium is limited in the presence of free sulfate using this method (US EPA 200.2). This method is not suitable for the determination of volatile low boiling point organo-mercury compounds (US EPA 200.2). Some volatile selenium species (e.g. dimethyl selenide) may be lost or only partially recovered by this procedure.
Matrix	Water, including fresh water, marine water, brackish water, and waste water.
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. **Metals other than Mercury:** Collect samples in clean high density polyethylene (HDPE), glass, or Polytetrafluoroethylene (PTFE) containers. Preserve in the field with nitric acid to pH < 2. Treatment of samples with approximately 3 mL of 1:3 HNO3 : Deionized water per 250 mL sample is recommended. Adding nitric acid to the original sample container at the laboratory within 14 days of sampling is an acceptable alternative to field preservation (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 ≥ 5 mL BrCl solution per litre of sample, equilibrate ≥ 24 hours prior to sub-sampling).
Stability	**Holding Time:** Metals (excluding Mercury): 6 months Mercury: 28 days Results reported for samples digested beyond holding times must be qualified. **Storage:** No storage temperature requirement (US EPA 40CFR May 18, 2012).
Equipment and Supplies	1. Heating source (e.g. block digester, hotplate, water bath) capable of maintaining a sample extract temperature of 95 ± 5°C). 2. Acid dispensers. 3. Vapour refluxing cover to fit digestion vessel (e.g. reflux cover, watch glass, etc.). 4. Digestion Vessels (e.g. block digester tube, beaker, flask, etc.). 5. Gloves. 6. Filters (optional; filtration through large pore size filters, e.g. 20 – 25 µm, may be necessary for filtration of some samples prior to analysis). 7. Filter funnels (optional). 8. Glass thermometer or suitable temperature sensor.
Reagents	1. Nitric acid (HNO3), concentrated (67 - 70%), ACS or reagent grade minimum. 2. Hydrochloric Acid (HCl), concentrated (36 - 40%), ACS or reagent grade minimum. 3. Water, de-ionized (ASTM Type I or equivalent recommended).

Safety

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

Procedure

Samples are prepared and digested using the following procedures:

No-Digestion Option for Samples with Low Turbidity

Digestion is not required for single-phase samples with measured turbidity <1 NTU with no visible colour and no discernable odour. To qualify for this exception, measured turbidity values from the raw (unacidified) cut, or from the acidified total metals cut must be measured and recorded. If the raw cut is used for turbidity measurement, visually confirm that no precipitates exist in the acidified portion.

For samples that were not acidified in the field, acidify with HNO_3 to pH <2. Shake the sample to mix. Let samples stand in their original containers for at least 16 hours prior to analysis to allow potentially adsorbed metals to re-dissolve. Apply appropriate qualifiers to any total metals samples that have not been allowed to equilibrate for this time. No further preparation is required.

Digestion is required for all samples that do not meet the above criteria for turbidity, colour, odour and phase.

Sample Preparation - Digestion

For samples that were not acidified in the field, acidify with HNO_3 to pH < 2. Shake the sample to mix. Let samples stand in their original containers for at least 16 hours prior to analysis to allow potentially adsorbed metals to re-dissolve. Apply appropriate qualifiers to any total metals samples that have not been allowed to equilibrate for this time.

The following procedure uses a 50 mL sub-sample. Sample volume may be scaled up or down if the ratios of HNO_3 or HCl to sample are not changed.

1. Shake the sample well to homogenize before sub-sampling for digestion.
2. Take a 50 ± 1 mL sub-sample and dispense the sample into a digestion vessel, which must be fitted with a reflux cap and which must be capable of supporting open vessel reflux action. Examples of digestion vessels fitted with a reflux cap include a beaker fitted with a watch glass, or an Erlenmeyer flask or digestion tube fitted with a reflux cover or watch glass. Include Method Blanks, Lab Duplicates and Reference Materials or Laboratory Control Samples with each batch of samples.
3. Add 1.0 ± 0.1 mL conc. HNO_3 and 0.50 ± 0.05 mL conc. HCl to each sample (assuming 50 mL sample size).
4. Prepare a Method Blank for every batch of samples. Add 50 ± 1 mL of de-ionized water into a digestion vessel. Add 1.0 ± 0.1 mL of conc. HNO_3 and 0.50 ± 0.05 mL conc. HCl to the water.
5. Prepare a Reference Material or Laboratory Control Sample for every batch of samples. Add 50 ± 1 mL of the RM or LCS solution into a digestion vessel. Add 1.0 ± 0.1 mL of conc. HNO_3 and 0.50 ± 0.05 mL conc. HCl to the water.
6. Prepare at least one duplicate for every batch of samples.
7. Cover samples with a reflux cover or watch glass and digest for 2.0 – 2.5 hours at 95 ± 5°C (this excludes the time needed to pre-heat the samples to 95°C). The heat for digestion must maintain the sample extract temperature at 95 ± 5°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, using 50 ± 1 mL de-ionized water with 1.0 ± 0.1 mL conc. HNO_3 and 0.50 ± 0.05 mL conc. HCl.
8. After 2.0 – 2.5 hours at 95 ± 5°C, remove the samples from heat source and let cool for at least 30 minutes (this will reduce any potential harmful fumes from the sample).
9. Remove the reflux cover or watch glass and reconstitute sample(s) back to 50 ± 1 mL with de-ionized water. Shake samples to mix. It is not necessary to rinse the

condensation from the reflux cover or watch glass back into the sample tube.

10. Analyze the digested sample using appropriate analytical methods. If significant solids are present in the sample after digestion, decant, centrifuge, or filter the sample prior to analysis to prevent sample introduction issues. If any sample extracts are filtered, the method blank must also be filtered.
11. Record and report any anomalies observed during the digestion and analysis.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
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% (recommended)
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.		

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 a Reference Material or Laboratory Control Sample.

Where the above Reference Material or Laboratory Control Sample is 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 Difference from the targets for the Reference Material or Laboratory Control Sample. For each metal, average accuracy must be within 90-110% of the targets, for results ≥ 5 times the Reported Detection Limit. Precision must be <10% RSD for results ≥ 5 times the Reported Detection Limit.

References

1. 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.
2. APHA 3030A, Preliminary Treatment of Samples – Introduction, 2004.
3. US EPA 40CFR, Table II, Required Containers, Preservation Techniques, and Holding Times, May 18, 2012.

Revision History

Dec 29, 2016	Added tungsten and zirconium which are new substances in the 2017 CSR.
Nov 6, 2015	Updated “total metals” definition reference to APHA 3030A. Updated EPA 40CFR reference to 2012 version. Removed requirement that 1% solids by weight must be digested with SALM procedure. Added recommendation for Matrix Spike in QC section. Updated preservations for mercury to current BC MOE requirements.
Oct 1, 2003	Replaces BC Lab Manual Methods (December 31, 2000) “Nitric Acid Digestion for Water Samples” and “Nitric Acid Digestion for Turbid

Water Samples". Effective October 1, 2013, the use of this method is required for listed metals, other than mercury, for BC CSR analysis purposes.