Trace Metals Analysis by ICP-MS – PBM

Parameter   Metals including major ions and trace metals.

Analytical Method   Analysis by ICP-MS.

Introduction   This method is applicable to metals in filtered or digested waters, and to total recoverable metals in solid samples, tissues, and other matrices which have gone through appropriate digestion procedures.

Method Summary   This method describes the multi-elemental determination of trace elements by ICP-MS. It is used to measure dissolved metals in water, total metals in water, total recoverable metals in solid samples such as soil, sediment, and vegetation from a Strong Acid Leachable (SALM) digestate, or other acceptable digestion procedures.

The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The metal ions produced are entrained in the plasma gas and extracted, by means of a differentially pumped vacuum interface, into a mass spectrometer. The metal ions produced in the plasma are sorted according to their mass-to-charge ratios by a quadrupole or magnetic sector mass spectrometer having a minimum resolution capability of 1 AMU peak width at 5% peak height. The ions transmitted through the quadrupole are quantified by a detector and the ion information is processed by a data handling system.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

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-x	Molybdenum	7439-98-7	MO-x
Antimony	7440-36-0	SB-x	Nickel	7440-02-0	NI-x
Arsenic	7440-38-2	AS-x	Phosphorus	7723-14-0	P-x
Barium	7440-39-3	BA-x	Potassium	7440-09-7	K-x
Beryllium	7440-41-7	BE-x	Selenium	7782-49-2	SE-x
Bismuth	7440-69-9	BI-x	Silicon	7440-21-3	SI-x
Boron	7440-42-8	B-x	Silver	7440-22-4	AG-x
Cadmium	7440-43-9	CD-x	Sodium	7440-23-5	NA-x
Calcium	7440-70-2	CA-x	Strontium	7440-24-6	SR-x
Chromium	7440-47-3	CR-x	Sulfur	7704-34-9	S-x
Cobalt	7440-48-4	CO-x	Thallium	7440-28-0	TL-x
Copper	7440-50-8	CU-x	Thorium	7440-29-1	TH-x
Iron	7439-89-6	FE-x	Tin	7440-31-5	SN-x
Lead	7439-92-1	PB-x	Titanium	7440-32-6	TI-x
Lithium	7439-93-2	LI-x	Tungsten	7440-33-7	W-x
Magnesium	7439-95-4	MG-x	Uranium	7440-61.1	U-x
Manganese	7439-96-5	MN-x	Vanadium	7440-62-2	V-x
Mercury	7439-97-6	HG-x	Zinc	7440-66-6	ZN-x

"x" in EMS codes may be T or D dependent upon Total or Dissolved as reported parameter.

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 or codes not provided.

| **Matrix** | Water, Soils, Sediments, Sludges, Solids, Air Filters, Animal and Plant Tissues with appropriate digestion or leachate procedures applied. |

Interferences and Precautions

Interferences associated with ICP-MS analysis may be classified as physical, isobaric (elemental or polyatomic), memory (carryover) or contamination in nature.

a) Physical interferences can be reduced by using internal standards which compensate for the matrix effect. High levels of dissolved solids in the sample will increase deposition of material on the extraction and/or skimmer cones, reducing the effective diameter of the orifices and therefore ion transmission. Dissolved solids of no more than 0.2% have been recommended.

b) Both the isobaric and molecular ion interferences must be fully investigated and understood prior to the introduction of this methodology. When they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence, as the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions.

c) Memory effects can result from sample deposition on the extraction and skimmer cones, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element should be estimated prior to analysis.

d) Interferences may also result from contaminants in acids, reagents, glassware, and other sample processing hardware that lead to artifacts and/or elevated baseline. All materials used should be routinely monitored and demonstrated to be free of interferences under the conditions of the analysis.

Sample Handling and Preservation

Refer to the "Summary of Sample Preservation and Hold Time Requirements" table found in Section A of the British Columbia Environmental Laboratory Manual.

Stability

Refer to the "Summary of Sample Preservation and Hold Time Requirements" table found in Section A of the British Columbia Environmental Laboratory Manual.

Procedure

Reagents:

Reagents may contain elemental impurities that might affect the integrity of analytical data. Owing to the high sensitivity of ICP-MS, high-purity reagents should be used whenever possible.

Digestion:

Refer to British Columbia Environmental Laboratory Manual for appropriate sample preparation procedures.

Where the Laboratory Manual does not prescribe digestion procedures, other appropriate digestion methods may be used provided performance requirements are met.

Instrumental Analysis:

Detailed instrumental procedures are not provided in this method. The procedures described in the following reference are suitable for general guidance:

- 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.

- EPA SW846 Method 6020A "Inductively Coupled Plasma - Mass Spectrometry", Revision 1, U.S. Environmental Protection Agency, February 2007.

This method is applicable only to ICP-MS analysis. Refer to USEPA Method 200.8 or 6020A for guidelines on establishing quantitation and confirmation ions for trace metal analytes.

The use of internal standards is required. Internal standards can vastly improve method accuracy and precision. Instrument drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected for by the use of internal standards. Refer to EPA Method 200.8 for recommended internal standard criteria.

Performance Requirements

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

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 certified reference materials (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: Refer to British Columbia Environmental Laboratory Manual for appropriate sample preparation procedures.

Precision Requirement: Refer to British Columbia Environmental Laboratory Manual for appropriate sample preparation procedures.

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.

Linear Dynamic Range: Linear range studies are to be performed during the initial validation of the method to determine the upper limit of linearity on the specific ICP-MS instrument. It must be determined from a linear calibration. The LDR should be determined by analysing at least 3 different standard concentrations for each analyte and the observed analyte concentration is within 90-110% of the stated concentration of the standard. Note that the LDR concentration may not be the upper limit of the element, but rather the upper concentration examined. If a sample concentration exceeds the LDR, it must be diluted and reanalysed. The frequency of the LDR determination is subject to the individual laboratory's Quality Management System.

Internal Standard Recovery Range: The absolute response of any internal standard must not deviate more than 50-130% from the original response in the calibration blank. Deviations outside this range must be investigated and reanalysed.

Interference Analysis: Laboratories must show evidence that elemental isobaric and polyatomic interference have been fully investigated and corrected for in the reporting of data by this technique.

Elemental Isobaric Interference: Atoms or elements having the same atomic weights are naturally occurring and therefore must be compensated for isobaric overlap. This should be automatically corrected in the instrument software or using post analysis corrections.

Polyatomic Isobaric Interference: Polyatomic ions are formed from samples containing high concentrations of particular elements (i.e. Oxides, Halides, etc.). These interferences may be automatically corrected in the instrument software, or using post analysis corrections, while others may be corrected by using an alternative isotope, or removed by collision/reaction cell or high resolution technologies. Daily optimisation of the nebulizer gas pressure reduces the formation of oxides.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives**
Instrument Blank (IB)	One per 20 samples	Less than reported DL
Calibration Verification Standard (CVS)	One per batch	90-110% recovery (after internal standard correction)
Continuing Calibration Verification (CCV)	1 per 20 samples and at the end of each run.	85-115% recovery (after internal standard correction) for mid-level standards.
If DQOs are not met, repeat testing for bracketed samples or report qualified test results.		

Instrument Blank: Required. Minimum one per batch of 20 samples or less, or as necessary to ensure contamination control.

Calibration Verification Standard (CVS): Required. A control standard from a source separate from the calibration standard must be analyzed to monitor calibration accuracy.

Continuing Calibration Verification (CCV): Required. Calibration standards (typically a mid-point standard) must be analyzed periodically throughout the instrument run to monitor calibration drift (at least 1 per 20 samples). A control standard may serve the same purpose.

Prescribed Elements   The following components of this method are mandatory:

a)   This method is applicable only to analysis by ICP-MS.
b)   Initial calibrations must be done daily.
c)   Internal standards must be used. Internal standards must cover all analytes within a 70 amu range, except for analytes with masses ≥ 210 amu, where interal standard mass must be within 80 amu. Where practical, internal standards used should generally have masses within 50 amu of assigned analytes.
d)   All Performance Requirements and Quality Control requirements must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order 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.   EPA SW846 Method 6020B "Inductively Coupled Plasma - Mass Spectrometry", Revision 2, U.S. Environmental Protection Agency, July 2014.

Revision History

Sept 15, 2017   Added tungsten (a new substance in the 2017 CSR). Added thorium as it is already in the Total Metals in Water digestion method and sulfur as it is already in the SALM method. Made minor updates to the QC table to reflect current naming convention (CVS added). Internal standard amu range changed to 70 amu, and 80 amu for high mass analytes (≥ 210 amu). Internal standard acceptance limits changed to 50-130% (composite value between EPA 200.8 and EPA 6020B limits).

Oct 1, 2013   Trace Metals Analysis by ICP-MS – PBM method added to 2013 version of BC Lab Manual, effective October 1, 2013

May 24, 2011   First version of BC Lab Manual ICPMS method (PBM format).