

<b>Title: Determination of Trace Elements in Aqueous Extracts of Airborne Particulate Matter and Other Aqueous Solutions by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)</b>		Copy No: ##
Method No.: 6.10/3.0/M	Effective Date: May 17, 2013	Location: ###

QSM Approval: \_\_\_\_\_

## Determination of Trace Elements in Aqueous Extracts of Airborne Particulate Matter and Other Aqueous Solutions by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

### 1 INTRODUCTION AND SCOPE

1.1 This method is applicable to the determination of trace elements (Table 1) in aqueous extracts of airborne particulate matter (PM) collected on filters, and in other aqueous samples (excluding seawater samples).

**Table 1.** Trace elements determined in this method

No gas mode		Reaction gas mode	
		He Mode	H <sub>2</sub> Mode
Aluminum (Al)	Molybdenum (Mo)		
Antimony (Sb)	Nickel (Ni)		
Arsenic (As)	Silver (Ag)	Arsenic (As) <sup>(a)</sup>	Chromium (Cr)
Barium (Ba)	Strontium (Sr)	Chromium (Cr) <sup>(b)</sup>	Iron (Fe)
Beryllium(Be)	Thallium (Tl)	Iron (Fe) <sup>(c)</sup>	Selenium (Se)
Cadmium (Cd)	Tin (Sn)	Vanadium (V) <sup>(a)</sup>	
Chromium (Cr)	Titanium (Ti)		
Cobalt (Co)	Uranium (U)		
Copper (Cu)	Vanadium (V)		
Lead (Pb)	Zinc (Zn)		
Manganese (Mn)			

<sup>(a)</sup>Elements for monitoring in He mode only when a high concentration (> 14 ppm) of chloride is expected. <sup>(b)</sup>Cr can be determined in all three modes. The decision on which mode is to be used depends on the type of sample and application. For example, when a high concentration (> 140 ppm) of chloride is expected, He mode should be used. <sup>(c)</sup>Fe can be determined in both He and H<sub>2</sub> mode. When information on Se is needed, H<sub>2</sub> mode is used.

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- 1.2 Method detection limits (MDLs) for the analyzed elements range from 0.2 to 45 ng/filter (based on a 15 mL dilution volume) for aqueous extracts of PM and from 0.01 to 1 µg/L for other aqueous solution. Expanded measurements uncertainties (k = 2) at concentrations above the method quantitation limits (MQLs = 3 × MDLs) are in the range of 5 to 15%.
- 1.3 This method is restricted to use by, or under supervision of properly experienced and trained personnel, including spectroscopists who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS. Each analyst must demonstrate the ability to generate acceptable results with this method.

## 2 SUMMARY OF METHOD

- 2.1 ICP-MS provides rapid and simultaneous quantitative and semiquantitative analysis of elements present in concentrations ranging from several parts per trillion (ppt) to a few parts per million (ppm). ICP is an electrodeless discharge maintained by energy inductively coupled to it from a radio-frequency generator. The liquid sample which is introduced to the system is firstly nebulised and the resulting aerosol is transported by argon gas into the plasma torch, where the analyte species are desolvated, vaporized, atomized and finally ionized. The produced ions are then transported via an interface to the mass spectrometer where they are separated according to their mass-to-charge ratios and quantified by an electron multiplier detector. Lastly, the ion information is processed by a data handling system.
- 2.2 Water-soluble metals are firstly extracted with water from particulate matter collected on filters (Method 6.03/\*.\*M). The extracts are then acidified with nitric acid to the final concentration of 1% HNO<sub>3</sub><sup>1</sup> and analyzed by ICP-MS.
- 2.3 The other aqueous solutions are analyzed directly when acidic upon receipt, or acidified to the final concentration of 1% HNO<sub>3</sub> when needed.

## 3 INTERFERENCES

### 3.1 Mass Spectroscopic Interferences

- Isobaric Interferences are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z).

<sup>1</sup> Acids concentrations in this document are expressed in % (v/v). Handle concentrated acids with extreme care.

**ACID IS ALWAYS ADDED TO WATER, NEVER THE REVERSE.**

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- Polyatomic Ion Interferences are caused by ions consisting of more than one atom. These ions are usually formed in the plasma from support gases or sample components. Typical examples are the interference of  $^{40}\text{Ar}^{16}\text{O}$  on  $^{56}\text{Fe}$ ,  $^{40}\text{Ar}^{35}\text{Cl}$  on  $^{75}\text{As}$ ,  $^{35}\text{Cl}^{16}\text{O}$  on  $^{51}\text{V}$ , etc.
- Doubly-Charged Ion Interferences are caused by ions consisting of more than one charge. Typical example is the interference of  $^{206}\text{Pb}^{2+}$  on  $^{103}\text{Rh}$ .

### 3.2 Non-Spectroscopic Interferences

- High Total Dissolved Solids will clog the sampling and skimmer cones.
- Matrix Effect, such as the presence of a high concentration of concomitant elements will either enhance or suppress the analyte signal in an unpredictable way.

## 4 EQUIPMENT AND SUPPLIES

### 4.1 The ICP-MS systems used for these analyses consist of:

- the collision/ reaction cell option for measurement in  $\text{H}_2$ , He or other collision/ reaction gas modes;
- a software capable of controlling the instrument, processing the data and reporting the results;
- an autosampler which can provide long-term, unattended operation of the system.

For detailed description of instruments, refer to SOP 6.14/\*.\*/\*S and SOP 6.22/\*.\*/\*S.

### 4.2 Gas supplies:

- 4.2.1 Liquid Argon (ICP grade, 99.998%);
- 4.2.2 Argon gas (Ultra High Purity grade, 99.999%);
- 4.2.3 Hydrogen gas (Ultra High Purity grade);
- 4.2.4 Helium gas (Ultra High Purity grade);

### 4.3 Tygon and PTFE tubing of various diameters.

### 4.4 Milestone duoPur sub-boiling distillation system.

### 4.5 Millipore Super-Q system (SOP 19.04/\*.\*/\*S) and Barnstead NANOpure Diamond water purifying system.

### 4.6 Labconco Purifier Trace Metal Analysis Work Station.

### 4.7 Micropipettes.

### 4.8 All labware used in this laboratory is non-glass, except for some glass beakers that are used during the maintenance of the ICP-MS (SOP 6.13/\*.\*/\*S).

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4.8.1 Class A volumetric (100 mL) flasks (PFA).

4.8.2 Other volumetric flasks (Nalgene).

## 5 REAGENTS AND STANDARDS

5.1 Double deionised water (DDW, resistance >18 MOhm cm) (see 4.5) is used throughout the procedure for the preparation of solutions, dilutions, and for rinsing labware.

5.2 All acids used for the preparation of standards and for the sample processing should be of high purity, either purchased directly or purified through a sub-boiling distillation process (SOP 6.15/\*.\*/\*S).

5.2.1 **15% HNO<sub>3</sub>** is used for sample acidification: Dilute 15 mL of concentrated sub-boiled HNO<sub>3</sub> to 100 mL with DDW. Store in a NALGENE<sup>®</sup> (HDPE) bottle.

5.2.2 **2% HNO<sub>3</sub>** is used as a rinsing solution for the autosampler rinsing port: Dilute 80 mL of concentrated HNO<sub>3</sub> (Trace Metal Grade) to 4 L with DDW. Store in the designated bottle.

5.2.3 **1% HNO<sub>3</sub>** is used as rinsing solution in the designated autosampler vial: Dilute 10 mL of concentrated, sub-boiled HNO<sub>3</sub> to 1 L with DDW. Store in the designated bottle.

5.2.4 TraceMetal Grade HCl is used directly as purchased.

5.2.5 HPLC Grade isopropanol (IP) is used directly as purchased.

5.3 **Standards and other solutions:** All standard solutions and samples should be opened and prepared in the Labconco Purifier Trace Metal Analysis Work Station and stored in the refrigerator. **NOTE:** The expiration date of the intermediate and working solutions should not be later than that of the parent stock solutions.

5.3.1 **Tuning Solutions (TS)** (commercially available stock or working tuning solutions can also be used):

- Intermediate TS (5 mg/L in 5% HNO<sub>3</sub>): Dilute 0.5 mL of each 1000 mg/L single-element stock solutions of Li, Y, Ce and Tl, and 5 mL of concentrated HNO<sub>3</sub> in a 100 mL volumetric flask with DDW (expiration time is one year).
- Working TS for Normal and H<sub>2</sub> mode (1 µg/L in 2% HNO<sub>3</sub>): Dilute 20 µL of Intermediate TS and 2 ml of concentrated HNO<sub>3</sub> in a 100 mL volumetric flask with DDW (expiration time is six months).

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- Working TS for He mode (1 µg/L in 2% HNO<sub>3</sub> and 2% HCl): Dilute 20 µL of Intermediate TS, 2 mL of concentrated HNO<sub>3</sub> and 2 mL concentrated HCl in a 100 mL volumetric flask with DDW (expiration time is six months).
- 5.3.2 **Internal Standard (ISTD) solution** (0.5 mg/L in 5% HNO<sub>3</sub>): Dilute 1 mL of each 100 mg/L single-element stock solutions of Y, In and Ho, and 10 mL of concentrated HNO<sub>3</sub> in a 200 mL volumetric flask with DDW. **NOTE:** Other elements such as Scandium (<sup>45</sup>Sc), Rhodium (<sup>103</sup>Rh), Terbium (<sup>159</sup>Tb) or Bismuth (<sup>209</sup>Bi) at the same concentration and acid matrix can be used as internal standards in specific cases.
- 5.3.3 **Multi-element Calibration Standard** stock solution containing 100 mg/L of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V and Zn in 5% HNO<sub>3</sub>. **NOTE:** Calculate the dilution factor for each standard every time, since concentrations of stock solutions may differ depending on the vendor and availability.
- 5.3.4 **Single-element calibration standard** stock solutions containing 1000 mg/L of U in 5% HNO<sub>3</sub>.
- 5.3.5 **Intermediate and calibration standards:**
  - Intermediate Calibration Standard 1 ppm (InCalStd 1ppm WS) containing 1 mg/L of all elements in 2% HNO<sub>3</sub>: Dilute 1 mL of multi-element Calibration Standard stock solution, 100 µL of U single-element stock solution and 2 mL of concentrated HNO<sub>3</sub> in a 100 mL volumetric flask (expiration time is six months).
  - Intermediate Calibration standard 10 ppm (InCalStd 10ppm WS) containing 10 mg/L of all elements in 2% HNO<sub>3</sub>: Dilute 10 mL of multi-element Calibration Standard stock solution, 1 mL of U single-element stock solution and 2 mL of concentrated HNO<sub>3</sub> in a 100 mL volumetric flask (expiration time is six months).
  - Calibration standards are prepared from the intermediate calibration standards, to cover the 0.1 to 100 µg/L concentrations range that is typical for analysis of trace elements in aqueous extracts of PM. All standards and the calibration blank should be prepared in 1% HNO<sub>3</sub> and 0.67% IP to match the sample matrix (Table 2). If a single multi-element standard will be used (SOP 6.14/\*.\*S), prepare only the 20 µg/L standard (CalStd). If one or more samples have concentrations higher than 100 µg/L, a higher calibration standard should be prepared.

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**Table 2.** Preparation of calibration standards

Concentrations, µg/L	0	0.1	0.5	1	2	5	10	20	50	100
InCalStd_10ppm_WS, mL	-	-	-	-	-	-	-	0.2	0.5	1
InCalStd_1ppm_WS, mL	-	-	-	-	0.2	0.5	1	-	-	-
100 ppb standard, mL	-	0.1	0.5	1	-	-	-	-	-	-

To each flask add 1 mL of concentrated HNO<sub>3</sub> and 667 µL of isopropanol and dilute to 100 mL using DDW

- Calibration standards for other aqueous solutions analysis should cover the 0.1 to 500 µg/L concentrations range and should be prepared in 1% HNO<sub>3</sub>
- 5.3.6 **Multi-Element Control Standard (MES-WS)** is a synthetic mixture of analytes of interest prepared in 2% HNO<sub>3</sub> (expiration time is one year). **NOTE 1:** This is a custom-made, NIST-traceable solution purchased from a provider that is different from the one used for calibration standards. Calculate the composition of this solution so that the final concentrations of all analytes in the low control standard and MDL-Spike solution are 5 to 10 times their respective MDLs. **NOTE 2:** Because some analytes are not compatible, it may be necessary to purchase more than just one standard mixture. In this case, label each bottle as MES-WS-A, MES-WS-B and so on.
- Intermediate MES-WS (InMES-WS in 2 % HNO<sub>3</sub>): Dilute 1 mL of each of MES-WS standard mixtures and 1 mL of concentrated HNO<sub>3</sub> in a 50 mL volumetric flask with DDW (expiration time is one month).
  - LCS-WS (low control standard in 1% HNO<sub>3</sub> and 0.67% IP): Dilute 200 µL of Intermediate MES-WS, 1 mL of concentrated HNO<sub>3</sub> and 667 µL of IP to 100 mL using DDW (expiration time is one week).
  - CS-WS (control standard in 1% HNO<sub>3</sub> and 0.67% IP): Dilute 1mL of Intermediate MES-WS, 1 mL of concentrated HNO<sub>3</sub> and 667 µL of IP to 100 mL using DDW (expiration time is one week).

## 6 SAMPLE REQUIREMENT AND PREPARATION

6.1 Airborne PM samples collected on Teflon filters are extracted in the Ion Analysis laboratory for analysis of water soluble ions by ion chromatography (IC) (SOP 6.06/\*.\*/\*S). The same extracts are used for metal analysis by ICP-MS.

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- 6.1.1 Aqueous extracts of airborne PM must be received and acidified in the ICP-MS laboratory the same day of extraction. Record the date of extraction, acidification and analysis in the Sample Receiving logbook.
- 6.1.2 Pipette 8.0 mL aqueous extracts (SOP 6.06/\*.\*/\*S) into each sample preparation tube (12-mL polypropylene tube).
- 6.1.3 Add 0.56 mL of 15% HNO<sub>3</sub> into each sample preparation tube, cap it immediately and mix well.
- 6.1.4 An extraction batch of about 100 samples should include at least one of each type of blanks and spikes that are prepared as described in the following paragraphs.
- 6.2 Other aqueous samples: analyze as is or after acidification if it is not already acidified, and/or after dilution (depending on the concentration of matrix and analytes).
- 6.3 Acidified samples should be stored in refrigerator until analysis (up to 1 month).

## 7 QUALITY CONTROL (QC) SAMPLES

### 7.1 Blanks:

- 7.1.1 Calibration blank (Calblk) is used in establishing the calibration curve before analysis of samples: Dilute 0.5 mL of concentrated HNO<sub>3</sub> and 334 µL of IP to 50 mL using DDW. Analyze at least once at the beginning of analytical run.
- 7.1.2 ICP-MS Method Blank (ICPbl-M) is used to assess possible contamination from the sample acidification procedure which is done at the ICP-MS lab<sup>2</sup>: Pipette 9.83 mL of DDW, 0.1 mL of concentrated HNO<sub>3</sub> and 66.7 µL of IP to a sample preparation tube. Prepare the same day as the samples.
- 7.1.3 IC Vial Blank (ICblk-R) is used to assess possible contamination from the sample extraction procedure (SOP 6.06/\*.\*/\*S): Pipette 8.0 mL of IC Vial Blank and 0.56 mL of 15% HNO<sub>3</sub> to a sample preparation vial. Prepare the same day as the samples.
- 7.1.4 IC Method Blank (ICblk-M) is used to assess possible contamination from the sample extraction procedure including the filters used for sample collection (SOP 6.06/\*.\*/\*S): Pipette 8.0 mL of IC Method Blank and 0.56 mL of 15% HNO<sub>3</sub> to a sample preparation tube. Prepare the same day as the samples.

<sup>2</sup> For analysis of other aqueous solutions this blank consists of a 1% HNO<sub>3</sub> solution going through the same dilution procedure as samples

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7.1.5 Rinse Blank (Blank) consists of 1% HNO<sub>3</sub>. It is used to flush the system between all samples and standards and to monitor possible carry-over contamination.

## 7.2 QC samples and CRMs

7.2.1 Verification standard (VS) is the same as one (or more) of the calibration standards. It is used at the end of daily analysis to verify that the calibration is still valid.

7.2.2 Low Control Standard (LCS-WS) is used to verify calibration accuracy at concentrations less than 10 times MDLs (see 5.3.6).

7.2.3 Control Standard (CS-WS) is used to verify calibration accuracy at concentrations close to quantitation limits for most of the elements (see 5.3.6).

7.2.4 Procedural CRMs are used to verify the accuracy of ICP-MS measurements in natural matrices at different concentration levels. The purchased CRMs should be prepared in the same matrix as samples (e.g. take 40 mL of CRM and spike with 16.7 µL of IP). CRMs are normally used untreated for the analysis of other aqueous solutions. The following CRMs may be used as QC samples; however, other commercial certified reference materials with similar composition and concentration of analytes can also be used.

- LTM<sub>xxx</sub> in sample matrix: Low-level fortified certified reference material for trace elements, made in filtered and diluted Lake Ontario water and preserved in 0.2% HNO<sub>3</sub> (National Water Research Institute, Burlington, ON, Canada). Concentrations after dilution are up to 1 µg/L for most elements.
- MTM<sub>xxx</sub> in sample matrix: Medium-level fortified certified reference material for trace elements, made in filtered and diluted Lake Ontario water and preserved in 0.2% HNO<sub>3</sub> (National Water Research Institute, Burlington, ON, Canada). Concentrations after dilution are 1 to 10 µg/L for most elements.
- HTM<sub>xxx</sub> in sample matrix: High-level fortified certified reference material for trace elements, made in filtered and diluted Lake Ontario water and preserved in 0.2% HNO<sub>3</sub> (National Water Research Institute, Burlington, ON, Canada). Concentrations after dilution are 10 to 100 µg/L for most elements.
- Lab PT<sub>xxx</sub> (PT<sub>xxx-y</sub>): samples from round robin studies e.g. PT No. xxx, sample No. y, with concentrations ranging from less than MDLs to about 500 µg/L for most elements.

7.2.5 ICP-MS Spike is used to calculate the recoveries of trace elements during the sample preparation procedure performed in the ICP-MS laboratory. This solution is prepared together with samples using a certified reference material or standard and follows the samples in every step of preparation in the ICP-MS laboratory.

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- Into a sample preparation tube add 9.81 mL DDW, 66.7 µL IP, 100 µL of concentrated HNO<sub>3</sub> and 20 µL of the Intermediate MES-WS. Cap the tube, mix well and store in refrigerator together with samples. This solution contains all analytes in concentrations 5 to 10 times method detection limits (MDLs).
- 7.2.6 IC spike solutions are used to calculate the recoveries of trace elements during the sample extraction/acidification procedure, at two levels of concentrations. They are prepared together with samples using a certified reference material or standard and follow the samples in every step of preparation.
- IC- Spike 1: In an extraction vial<sup>3</sup> containing one blank Teflon filter add 15 mL DDW, 100 µL IP and 30 µL of the Intermediate MES-WS solution. Prepare the extract by following SOP 6.06/\*.\*S along with samples. Pipette 8.0 mL of the aqueous extract into a sample preparation tube and add 0.56 mL of 15% HNO<sub>3</sub>. Cap the tube immediately, mix well and store in refrigerator together with samples. This solution contains all analytes in concentrations 5 to 10 times the actual MDLs.
  - IC- Spike 2: In an extraction vial containing one blank Teflon filter, add 15 mL DDW, 100 µL IP and 60 µL of the Intermediate MES-WS solution. Prepare the sample by following SOP 6.06/\*.\*S. Pipette 8.0 mL of aqueous extract into a sample preparation tube and add 0.56 mL of 15% HNO<sub>3</sub>. Cap the tube immediately, mix well and store in refrigerator together with samples. This solution contains all analytes in concentrations 10 to 20 times the actual MDLs.
  - MDL-Spike: In an extraction vial, add 15 mL DDW, 100 µL IP and 30 µL of the Intermediate MES-WS solution. Prepare the sample by following SOP 6.06/\*.\*S. Pipette 8.0 mL of the aqueous extract into a sample preparation tube and add 560 µL of 15% HNO<sub>3</sub>. Cap the tube immediately, mix well and store in refrigerator together with samples. This solution contains all analytes in concentrations 5 to 10 times the actual MDLs.
- 7.2.7 Duplicates are used to monitor the precision of the ICP-MS analysis. If enough sample solution is available, analyze every tenth to fifteenth sample as a duplicate.

## 8 CALIBRATION AND STANDARDIZATION

- 8.1 Set up the instrument with proper operating parameters as detailed below, and as described in the appropriate SOPs (SOP 6.14/\*.\*S and SOP 6.22/\*.\*S ) and manufacturer's manuals. The instrument should be allowed to become thermally stable before starting the analysis (usually requiring at least 30 min of operation prior to calibration).

<sup>3</sup> Extraction vials are received from the Ion Analysis lab

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- 8.2 Tune the instrument or check its performance in all analysis modes (normal and/or reaction/collision gas modes). Make sure that the sensitivity, signal stability (RSD%), peak width and resolution, oxides and doubly charged ions yields, and background counts are within acceptance limits (SOP 6.14/\*.\*S and SOP 6.22/\*.\*S). Record the instrument performance parameters in the designated logbooks.
- 8.3 Internal standard is added on line and is used to correct for the effect of instrument signal drift. Before starting the analysis, make sure that the signal for each element present in the internal standard solution is stable (RSD% ≤ 10%).
- 8.4 All analyses require a calibration curve that covers the expected concentration range. To be considered acceptable, the calibration curve should have a correlation coefficient greater than or equal to 0.998. Single-point calibrations are also accepted when the recoveries of check standard and all CRMs are within acceptance limits (Section 11.2).
- 8.5 Calibration accuracy is verified immediately after measuring the calibration standards by analyzing the control standards; other quality control samples/standards at different concentration levels are analysed in between samples, and the verification standard is measured at the end of daily analysis.

## 9 SAMPLES ANALYSIS AND DATA REPORTING

- 9.1 Set up and print the sequence for automated run, including calibration standards, unknown samples and QCs. Load the autosampler and run the sequence (SOP 6.14/\*.\*S and SOP 6.22/\*.\*S).
- 9.2 Analyse the samples and save and backup the raw data files (SOP 6.14/\*.\*S and SOP 6.22/\*.\*S).
- 9.3 Prepare the internal and final reports using the templates available in the ICP-MS Lab sub-directory of the INORG\$ shared drive. Validate the EXCEL templates containing formulas and/or macros at least once a year or after major changes of the acquisition method (SOP 2.11/\*.\*S). The validated templates should be password-protected (Read Only). Record the file name and the validation date in the designated logbook.
- 9.4 After the internal and final reports are completed, print, fill-out and sign the Data Validation Checklist. The approved reports shall be password-protected and the hardcopy of the signed Data Validation Checklist shall be stored for at least one year (e.g. in the Room 172).

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## 10 QUALITY CONTROL

- 10.1 The QC samples normally comprise 10 - 25% of total sample throughput. Each daily batch includes various blanks, control standards, procedural CRMs, verification standard, spikes, and duplicates (Section 7).
- 10.2 Rinse blanks should be analyzed after high concentration standards and CRMs (e.g., concentration > 50 µg/L), and before the analysis of other blanks.
- 10.3 Other blanks (for example laboratory and field blanks) should be analyzed at the beginning of the daily runs.
- 10.4 Control standards (for example LCS-WS and CS-WS) should be run at the beginning of the analysis immediately after calibration is completed.
- 10.5 Procedure CRMs should be run once every 10 to 15 samples.
- 10.6 Duplicates should be run at least every 10 to 15 samples.
- 10.7 At least one ICP-MS spike (ICP-Spike), two IC spikes (IC-Spike1 and IC-Spike2) and two MDL-Spike should be run every 100 samples.

## 11 DATA ACCEPTANCE

- 11.1 Control Standards and procedure CRMs with concentrations above the method quantitation limit, should be within 10% -20% of target values.
- 11.2 Verification Standards should be within 5% of the target concentration.
- 11.3 Blanks should be below MDLs.
- 11.4 Spikes recovery should be within 80% -120% of the expected value.
- 11.5 For analyte values greater than MQL the relative percent difference (RPD%) of duplicates should be less than 30%. RPD% is calculated as follows:

$$RPD\% = \frac{x_1 - x_2}{(x_1 + x_2)/2} \times 100$$

where  $x_1$  and  $x_2$  are the concentrations determined for the first and second measurement, respectively.

- 11.6 If the above data acceptance criteria are not met, investigate the reason and correct the cause if possible. If deemed correctable, then re-analyze any samples and QCs analyzed during the out-of-limit conditions (SOP 19.03/\*.\*S).

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11.7 View the data for inconsistencies such as data missing, unusually high values, and large deviations between sample duplicates. If it is possible, repeat any suspicious sample using the extract which is kept in the fridge for less than a month.

11.8 All quality control data should be maintained and available for easy reference or inspection.

## 12 METHOD DETECTION LIMIT AND METHOD VALIDATION

12.1 MDLs for elements analyzed in the aqueous extracts of PM, are calculated based on historical (for example, the latest year of analysis) and recent measurements of blanks and low control standards<sup>4</sup>.

12.1.1 Based on the historical data of IC-Vial Blank analysis, calculate the MDL<sub>B</sub> as follows:

$$MDL_B = C_B + t_{(0.99, n-1)} S_{blk} \quad (1)$$

where  $C_B$  and  $S_{blk}$  are the average concentration and standard deviation of blanks respectively,  $t_{(0.99, n-1)}$  is the single-tailed Student's test for 99% confidence level and  $n-1$  degrees of freedom, where  $n$  is the number of replicate blank analysis.

12.1.2 Based on the historical data of repeated measurements of the MDL-Spike at concentrations not higher than 10 times the actual MDLs, estimate the MDL<sub>Std</sub>:

$$MDL_{std} = t_{(0.99, n-1)} S_{Std} \quad (2)$$

where  $t_{(0.99, n-1)}$  is the single tailed Student's test for 99% confidence level and  $n-1$  degrees of freedom,  $n$  is the number of historical repeats, and  $S_{Std}$  is the standard deviation of replicate analyses.

12.1.3 Estimate MDLs based on the analyst's experience, and the maximum of MDL<sub>B</sub> and MDL<sub>Std</sub>

12.2 MDLs should be checked at least once a year, and/or after major modification of the method and/or the ICP-MS systems.

12.2.1 Using separate sample preparation vials, prepare at least seven MDL-Spike solutions (see 7.3.2).

12.2.2 Analyze these samples at least three times on three non-consecutive days and/or using three separate calibration standards and other QC samples.

12.2.3 Calculate the MDLs using equation (2) and compare with the actual MDLs.

<sup>4</sup> Grubbs Test can be used to remove outliers

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12.2.4 The supervisor will assess the MDL data versus actual values and determine if any corrective action is required to restore detection limits to acceptable levels or change the reported values.

12.3 MDLs for trace elements determined in the other aqueous solution are calculated based on reagent blanks and low control standards prepared the same way as samples and as described in Section 12.1.

12.4 Method validation/verification is accomplished by using the QC samples described in Section 11 and by participating in Proficiency Testing (PT) Programs. For the records of the precision and accuracy of measurements, refer to the latest Method Verification Binder (Room 172).

### 13 ESTIMATION OF MEASUREMENT UNCERTAINTY

13.1 The measurements uncertainty is calculated based on the Type A approach recommended by the CALA. For detailed estimation approach refer to SOP 2.10/\*.\*S.

13.2 For the water soluble metals in PM, the uncertainty is calculated using the repeated measurement of spikes, sample duplicates and laboratory CRMs analyzed together with the samples during one year. For the other aqueous solution, the laboratory CRMs and PT studies analysis are used. For the detailed estimation approach refer to SOP 2.10/\*.\*S.

13.3 The possible sources of uncertainty and QC data used for uncertainty estimation are listed in Appendix A.

13.4 The uncertainty should be estimated at least once a year, and/or after any major modification of the method. The most recent estimated values should be reported to the client. For the records of estimated measurements uncertainties refer to the latest Method Verification Binder (Room 172).

**This method is fit for the intended use.**

### 14 MAINTENANCE

Refer to instrument hardware manuals, SOP 6.14/\*.\*S and 6.22/\*.\*S for details.

### 15 SAFETY

For safety procedures while operating the ICP-MS consult Safe Working Procedures and Policies SWP-001/\*.\*.

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## 16 APPLICABLE SOPs

SWP-001/\*.\* “Safe Working Procedures and Policies”

SOP 6.06/\*.\* /S “Extraction of Filters”

SOP 6.13/\*.\* /S “Labware Cleaning in ICP-MS Laboratories”

SOP 6.14/\*.\* /S “Agilent 7500ce Inductively Coupled Plasma Mass Spectrometer operation, data acquisition, processing and reporting”

SOP 6.22/\*.\* /S “Agilent 7700x Inductively Coupled Plasma Mass Spectrometer operation, data acquisition, processing and reporting”

SOP 6.15/\*.\* /S “Acid Purification Using MILESTONE duoPUR “Subboiling” Distillation System”

SOP 2.10/\*.\* /S “Estimation of Uncertainty in Chemical Analysis”

SOP 2.11/\*.\* /S “Electronic Systems Validation and Maintenance”

SOP 19.03/\*.\* /S “Control Charts”

SOP 19.04/\*.\* /S “AAQS Water Purification System”

## REVISIONS

**September 2005:** Authors, Heidi Chen and Xiangjun Liao. New document 6.10/1.0/M

**January 2006:** Reviewers, Ewa Dabek, Valbona Celso

Section 6.3.1: NOTE is added; Section 6.3.8 is added; Section 7.2.2 (L-CS) is added; Section 8.2: L-CS is included; Section 11.1.3: is modified by including CS-L; Appendix B: the concentration of custom-made multi-element standard is included; Appendix C: The proposed sequence is modified by including L-CS; Temperature specification for refrigerator (4°C) is removed throughout the document.

**April 2007:** Reviewers, Valbona Celso, Irina Okonskaia

Section 2.3 is added; Section 4: sample volume is changed to 8.0 mL and the amounts of HNO<sub>3</sub> and isopropanol are changed accordingly; Section 4.1.3 is added; Section 5.2 is re-arranged; Section 6.2.2 and 6.2.3 are added to include preparation of 2% HNO<sub>3</sub> and 1% HNO<sub>3</sub> respectively; section 6.2.4 is added; Sections 6.3.2 and 6.3.3 are deleted and the expiration times are added for each solution; Section 6.3.4 table is removed and the mixed tuning solutions are prepared in 2% HNO<sub>3</sub>; Section 6.3.6: table is changed to include the stock solutions only and a NOTE is added; Section 6.3.8: the table is deleted and added in the Table B1; Section 6.3.7 on spike solutions is added; Section 7.1: Blank description is changed; Section 7.2.3: TM23.3 and

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TMDA-61 are used instead of TM24.2 and TMDW respectively; Sections 7.2.3 about spikes and 7.2.5 about duplicates are added; Section 10.4.4 is added; Section 10.5 is changed by adding more details; Section 10.9 is changed to prepare the final reports using the templates available in the ICP-MS lab sub-directory of the INORG\$ on the ETC08 drive; Section 11.2 on data acceptance criteria is changed based on the updated uncertainty values; Sections 11.2.5 and 11.2.6 are added; Section 11.3: a sentence for repetition of suspicious samples is added; Section 12 is changed to include details on MDL calculations; Sections 13.1 and 13.2 are added. Section 14: details about cleaning solutions are deleted; Appendixes: Table A1 and Table E2 are updated with estimations based on 2005-2006 data; Table B1: the CMS composition is changed; Table D1: the NOTE for Bi determination is added; Table E1: the use of PT studies results for estimation of uncertainty is added.

**September 2009:** Reviewers, Valbona Celo, Irina Okonskaia

Section 1.1 Table 1: Heading is changed to “No gas mode” and “Reaction gas mode”. Uranium is added in this table and in the other sections ; Section 1.2: Lab location is changed to “ICP-MS lab, Particulate Characterization Unit, AAQS, AQRD” ; Section 5.1: The instrument is changed to “Agilent 7500ce ICP-MS system”; Section 6.1 The DW system is changed to Millipore RIOS 30; Section 6.3.2: Concentrations of all tuning solutions and P/A factor solution are changed to 50 µg/L; Section 6.3.4: Concentration of the mixed Internal standard (ISTD) solution is changed to 0.5 mg/L and Sc is described as an optional component of ISTD; Section 6.3.6 is added; Section 6.3.5.1: Calibration standard concentration is changed to 50 µg/L, and the NOTE is added Section 6.3.6: Composition of the custom-made multi-element standard (CMS) is changed; the sections referring to this standard are changed accordingly; Section 7.3.2 is added; Section 7.2.4 is changed to 7.2.5: LabSLRS4 is removed and TM23.3 is replaced with TM 28.3; Section 10.1: the pump speed is changed to 0.10 rps ; Section 10.7 is added; Section 11.1.6 is added; Section 18: Agilent Technologies manuals are updated to the latest versions; Appendixes: Tables A1, E2, and E3 are changed after the validation of the new ICP-MS configuration; Table B1 is changed to reflect the new CRMs; Table C1 and C2 are changed to reflect new autosampler tray configuration, and new standards and CRMs;

**December 2009:** Reviewer, Valbona Celo

Section 4.1 is changed to “Aqueous extracts of airborne PM samples collected on Teflon filters (see SOP 6.06/\*.\*S)”; Section 4.1.1 is added; Section 4.2: The sample storage time is added; Section 7.2.1: IC Method Blank and IC Vial Blank are added; Section 10.10: A paragraph on validation and protection of EXCEL templates is added (referring to the SOP 2.11/\*.\*S); Section 13.4 is changed and section 13.5 is added; Applicable SOPs: the SOP 2.11/\*.\*S is added; Tables E2 and E3 are removed and a NOTE is added at Table E1.

**July 2011:** Reviewers, Valbona Celo, Irina Okonskaia

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Section 1.2: Reference to Appendix A is deleted and ranges of MDLs and measurements uncertainties are added; Section 3.1, Polyatomic Ion Interferences bullet: “These ions are usually formed in the plasma from support gases or sample components” is added; Doubly-Charged Ion Interferences bullet: “Typical example is the interference of  $^{206}\text{Pb}^{2+}$  on  $^{103}\text{Rh}$ ” is added; Section 4.1.1: “...in the ICP-MS laboratory” is added; Section 4.1.2 is changed to reflect the new procedure followed for sample preparation; Section 4.1.4 is changed to reflect the new blanks and spikes added in the method; Section 6.1: Specifications of water purification systems are removed; Section 6.2.2 to 6.2.3: Specifications of  $\text{HNO}_3$  grade are added; Section 6.3.8: Reference to Appendix B is deleted; Section 6.3.9 is changed to reflect the new procedure followed for preparation of spike solutions; Section 6.3.10 is added; Section 7.1.1 is changed to reflect the new procedure followed for preparation of blanks; Section 7.2.4 and throughout the text: specifications of the CRMs are removed; instead LTMxxx, MTMxxx and HTMxx are added for the low, medium and high concentration CRMs, respectively; Section 7.2.5: Spike name is changed to distinguish the ICP-MS analysis spikes from the IC-Spikes (IC extraction and ICP-MS acidification and measurements); Section 7.2.6 is added; Section 8.1: a NOTE is added; Section 10.6 and throughout the text: referring to ETC08 is deleted; Section 10.7: “...or in the external hard drive” is added; Section 11.1.7 is added; Section 12.1: “The single laboratory (ICP-MS lab, Particulate Characterization Unit, AAQS, AQRD” and “tabulated in Appendix A” are removed; Sections 12.1.1 and 12.1.2 are changed; Section 12.2.4, 12.2.5 and 12.3.1 are added; Section 12.4 is changed and “For the records of the analytical precision and accuracy of measurements, refer to the latest Method Verification Binder (Room 172)” is added; Section 13.4: “For the records of estimated uncertainties refer to the Method Verification Binder (Room 172)” is added (deleted from the NOTE in Table E1); Appendix A (Table A1) and Appendix B (Table B1) are deleted; Table C1 (Table A1 in this version) is changed to reflect the blanks and spikes added in the method.

**May 2013:** Reviewers, Valbona Celo, Irina Okonskaia

Section 1.2: method detection limits are changed to reflect the latest values; MDLs for other aqueous solutions are added; Section 1.3 is re-phrased; Section 2.2: A footnote is added and (v/v) notation is removed throughout the text; Sections 4, 5 and are swapped over; Section 5.1 (4.1 in this version): Reference to the Agilent 7500ce system is removed and a more general description of the ICP-MS system is given; Reference to the SOPs describing the operations of both ICP-MS instruments are added here and throughout the text; Section 4.5: Millipore Super-Q system (SOP 19.04/\* \*/S) is added; Sections 4.8.1 and 4.8.2 are added; Section 6.2.4 (5.2.4 in this version) is changed to “TraceMetal Grade HCl” and Section 5.2.5 is added; Section 6.3.1 (5.3.1 in this version): Working TS term is used instead of Mixed TS; Section 6.3.3: Table with composition of ISTD is removed; Section 6.3.4 (5.3.3 in this version): The “Multi-element Calibration Standard” term is used for the stock calibration standard; Sections 5.3.5 is added and 6.3.6 and 6.3.7 are removed; Section 6.3.8 (5.3.5 in this version) is modified; Sections 6.3.9 and 6.3.10 are moved to Section 7.2; Section 7.1: Preparation of blanks is not in table format; Section 7.2 title is

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changed to “QC Standards and CRMs”; Section 7.2.4: The word “standards” is replaced by “certified reference materials” and the concentration ranges are changed; Section 8 is changed to reflect the option of using other ICP-MS instruments and the full calibration method. Sections 9 and 10 are merged together (under Section 9) and are changed in order to remove specifics of Agilent 7500ce operations and to reflect the option of using other ICP-MS instruments; Section 11.2.6, (Section 11.6 in this version) is changed in order to specify the actions that are taken when the Data Acceptance criteria are not met; Sections 12.2.5 and 12.3.1 are removed; Section 16: Reference to the SOPs describing the operations of both ICP-MS instruments (6.14/\*.\*/\*S and 6.22/\*.\*/\*S) are added throughout the text and in this section; Appendices A and B are removed. These and other details specific to the instruments operations are added to the respective SOPs.

## REFERENCES

- US EPA, Method 6020 A, *Inductively Coupled Plasma – Mass Spectrometry*, Revision 1, January, 1998
- US EPA, *Quality Control*, Draft Update IVA of SW-846 On-line, Chapter 1, Revision 1, July, 1992
- US EPA, *Inorganic Analytes*, Draft Update IVA of SW-846 On-Line, Chapter 3, Revision 4, November, 2000
- US EPA, Compendium of Method IO-3.5, *Determination of Metals in Ambient Particulate Matter using Inductively Coupled Plasma/Mass Spectrometry*, June, 1999
- US EPA, *Revised Assessment of Detection and Quantitation Approaches*, October 2004
- Environment Canada, Air Quality Research Division, Method 6.03/\*.\*/\*M *Determination of Anions and Cations on Multi (2) – Ion Chromatography System*
- Agilent Technologies, *Agilent 7500 Series ICP-MS ChemStation (G1834B) Operator’s Manual*, Rev. A, September 2007, Tokyo, Japan
- Agilent Technologies, *Agilent 7500 Series ICP-MS Hardware Manual*, Rev. A, September 2008, Tokyo, Japan
- Agilent Technologies, *Agilent 7700 Series ICP-MS MassHunter Workstation User Guide*, Rev.A, October 2011

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**APPENDIX A:**

**Table A1.** Major Sources of Uncertainty in the Analysis of Water-Soluble Metals in PM Collected on Teflon Filters and other aqueous solutions

Measurement Steps	Uncertainty Sources	QC Data May Be Used
<u>Sample Preparation</u> (if applicable) Extraction  Acidification	Extraction Volume Extraction Condition  Acid Volume Sample Volume Acidification Condition	Weight of Water Filter blanks  Weight of Water Weight of Water Spiked reagent blanks Duplicates
<u>ICP-MS Analysis</u>	Analyst Standard Solution Preparation Calibration Instrument Drift and Internal Standard Correction Data Process	Lab CRMs <sup>(a,b)</sup> Spiked reagent blanks <sup>(a)</sup> Duplicates <sup>(a,b)</sup> PT studies results <sup>(b)</sup>

<sup>(a)</sup> Used to estimate uncertainty for the analysis of metals in aqueous extracts of PM collected on Teflon filters

<sup>(b)</sup> Used to estimate uncertainty for the analysis of metals in other aqueous solutions