

Title: Determination of Near-Total Trace Elements in Airborne Particulate Matter by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)		Copy No: ##
Method No.: 6.11/3.0/M	Effective Date: May 17, 2013	Location: ###

QSM Approval: _____

Determination of Near-Total Trace Elements in Airborne Particulate Matter 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 airborne particulate matter (PM) collected on Teflon, quartz fiber and other types of filter media, after microwave assisted acid digestion using HNO₃. It is also applicable to the determination of lead isotopes ratios in digested samples.

Table 1. Near-Total trace elements determined in this method

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

^(a)Elements for monitoring in He mode only when a high concentration (> 14 ppm) of chloride is expected. ^(b)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

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ppm) of chloride is expected, He mode should be used. ⁶³Fe can be determined in both He and H₂ mode. When information on Se is needed, H₂ mode is used.

- 1.2 Method detection limits (MDLs) for the analyzed elements range from 0.2 to 100 ng/filter (based on a 20 mL dilution volume). Expanded measurements uncertainties (k = 2) at concentrations above the method quantitation limits (MQLs = 3 × MDLs) are in the range of 10 to 20%.
- 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 Besides the quantification of elements, the quadrupole ICP-MS provides a fast, convenient and precise method to determine isotope ratios.
- 2.3 Near-total metals are extracted from PM collected on filters, by means of a microwave-assisted acid digestion procedure (SOP 6.20/*.*/*). The digested samples are used for both quantitation of elements and isotope analysis.

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).
- 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

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components. Typical examples are the interference of $^{40}\text{Ar}^{16}\text{O}$ on ^{56}Fe , $^{40}\text{Ar}^{35}\text{Cl}$ on ^{75}As , $^{35}\text{Cl}^{16}\text{O}$ on ^{51}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}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 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 supply (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 (100mL) 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 in the preparation of standards and for 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 **2% HNO₃¹** is used as a rinsing solution for the autosampler rinsing port: dilute 80 mL of concentrated HNO₃ (Trace Metal Grade) to 4 L with DDW. Store in the designated bottle.

5.2.2 **1% HNO₃** is used as a rinsing solution in a designated autosampler vial: dilute 10 mL of concentrated sub-boiled HNO₃ to 1 L with DDW. Store in the designated bottle.

5.2.3 TraceMetal Grade HCl is used directly as purchased

5.2.4 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 expiry date of the intermediate and working solutions should not be longer than the parent stock solutions.

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

- Intermediate TS (5 mg/L in 5% HNO₃): Dilute 0.5 mL of each 1000 mg/L single-element stock solutions of Li, Y, Ce and Tl, and 5 mL of concentrated HNO₃ in a 100 mL volumetric flask with DDW (expiration time is one year).
- Working TS for Normal and H₂ mode (1 µg/L in 2% HNO₃): Dilute 20 µL of Intermediate TS and 2 ml of concentrated HNO₃ in a 100 mL volumetric flask with DDW (expiration time is six months).

¹ All acid 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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- Working TS for He mode (1 µg/L in 2% HNO₃ and 2% HCl): Dilute 20 µL of Intermediate TS, 2 mL of concentrated HNO₃ 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% HNO₃): Dilute 1 mL of each 100 mg/L single-element stock solutions of Y, In and Ho, and 10 mL of concentrated HNO₃ in a 200 mL volumetric flask with DDW. **NOTE:** Other elements such as Scandium (⁴⁵Sc), Rhodium (¹⁰³Rh), Terbium (¹⁵⁹Tb) or Bismuth (²⁰⁹Bi) 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% HNO₃. **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 standards** stock solutions containing 1000 mg/L of Ce, La and U in 5% HNO₃
- 5.3.5 Intermediate and calibration standards:
- 5.3.6 Intermediate Calibration Standard 1 ppm (InCalStd 1ppm NT) containing 1 mg/L of all elements in 2% HNO₃: Dilute 1 mL of multi-element Calibration Standard stock solution, 100 µL of each of single-element stock solutions and 2 mL of concentrated HNO₃ in a 100 mL volumetric flask (expiration time is six months).
- 5.3.7 Intermediate Calibration standard 10 ppm (InCalStd 10ppm NT) containing 10 mg/L of all elements in 2% HNO₃: Dilute 10 mL of multi-element Calibration Standard stock solution, 1 mL of each of single-element stock solutions and 2 mL of concentrated HNO₃ in a 100 mL volumetric flask (expiration time is six months).
- 5.3.8 Calibration standards are prepared from the intermediate calibration standards, to cover the 0.5 to 200 µg/L concentrations range that is typical for analysis of trace elements in acid digested airborne PM. All standards and the calibration blank should be prepared in 4% HNO₃ 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	0.5	1	2	5	10	20	50	100	200
10 ppm standard, mL	-	-	-	-	-	-	0.2	0.5	1	2
1 ppm standard, mL	-	-	-	0.2	0.5	1	-	-	-	-
100 ppb standard, mL	-	0.5	1	-	-	-	-	-	-	-

To each flask add 4 mL of concentrated HNO₃ and dilute to 100 mL using DDW

5.3.9 **Multi-Element Control Standard (MES-NT)** is a synthetic mixture of analytes of interest prepared in 2% HNO₃ (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-NT-A, MES-NT-B and so on.

- **Intermediate MES-NT (InMES-NT in 2% HNO₃):** Dilute 1 mL of each of MES-NT standard mixtures and 1 mL of concentrated HNO₃ in a 50 mL volumetric flask with DDW (expiration time is one month).
- **LCS-NT (low control standard in 4% HNO₃):** Dilute 200 µL of InMES-NT and 4 mL of concentrated HNO₃ to 100 mL using DDW (expiration time is one week).
- **CS-NT (control standard in 4% HNO₃):** Dilute 1 mL of InMES-NT and 4 mL of concentrated HNO₃ to 100 mL using DDW (expiration time is one week).

5.3.10 **Spiked Digested Samples:** Add 40 µL of spiking solution for near total analysis (SPK-NT) to 9.96 mL of digested sample (SOP 6.20/*.*S).

5.3.11 **SRM981** (NIST, USA) common lead isotopic standard consisting of 1 gram of a commercially available, high purity lead metal of 99+% purity, that was extruded into wire form. The certified atomic abundance ratios are 0.059042 ± 0.000037 , 0.91464 ± 0.00033 and 2.1681 ± 0.0008 for the ²⁰⁴Pb/²⁰⁶Pb, ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb ratios, respectively.

5.3.11.1 **Stock calibration solution SRM981 (~1000 mg/L Pb in 3% HNO₃):**

- Weigh ~0.1 g of wire in a Petri dish and clean its surface by dipping in 5% (v/v) HNO₃ for 15 to 20 min.

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- Rinse the etched wire with plenty of DDW, let it dry and weigh it in a centrifuge tube. Record the exact mass.
- Add 3 mL of concentrated HNO₃ and 50 µL of concentrated □HCl. The wire dissolves in few minutes.
- Quantitatively transfer the solution to a 100 mL volumetric flask and dilute to the mark with DDW.
- Record the exact concentration of the solution.

5.3.11.2 Intermediate Calibration Standard SRM981 (~ 1000 µg/L Pb in 2% HNO₃): dilute 0.1 mL of stock calibration solution SRM981 and 2 mL of concentrated HNO₃ to 100 mL with DDW (expiration time is six months).

5.3.11.3 Calibration Standard SRM981 (~ 20 µg/L in 4% HNO₃): dilute 2 mL of the intermediate calibration standard SRM981 and 4 mL of concentrated HNO₃ to 100 mL with DDW (expiration time is one month).

5.3.12 **SRM982** (NIST, USA) equal-atom lead isotopic standard consists of 1 gram wire of at least 99+% purity. The certified atomic abundance ratios are 0.027219 ± 0.000027 , 0.46707 ± 0.00020 and 1.00016 ± 0.00036 for the ²⁰⁴Pb/²⁰⁶Pb, ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb ratios, respectively.

5.3.12.1 Stock solution SRM982 (~1000 mg/L Pb in 3% HNO₃): prepare in the same way as SRM981 stock standard solution

5.3.12.2 Intermediate QC solution SRM982 (~ 1000 µg/L Pb in 2% HNO₃): dilute 0.1 mL of stock solution SRM 982 and 2 mL of concentrated HNO₃ to 100 mL with DDW (expiration time is six months).

5.3.12.3 QC sample SRM982 (~ 20 µg/L in 4% HNO₃): dilute 2 mL of the intermediate QC solution SRM982 and 4 mL of concentrated HNO₃ to 100 mL with DDW (expiration time is one month).

6 SAMPLE REQUIREMENT AND PREPARATION

Consult SOP 6.20/*.*S for the storage conditions of samples and the digestion procedures.

7 QUALITY CONTROL (QC) SAMPLES

7.1 Blanks

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- 7.1.1 Calibration blank (Calblk) is used in establishing the calibration curve before analysis of samples: prepare a 4% HNO₃ solution in a volumetric flask. Analyze at least twice at the beginning of analytical run.
- 7.1.2 Rinse Blank (Blank) consists of 1% HNO₃. It is used to flush the system between 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-NT) is used to verify calibration accuracy at concentrations less than 10 times MDLs (see 5.3.6).
- 7.2.3 Control Standard (CS-NT) 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 1.6 mL of concentrated HNO₃). The following CRMs may be used as QC samples; however, other commercial certified reference materials with similar composition and concentration of analytes can be used.
- 7.2.5 LTM_{xxx} in 4% HNO₃: Low-level fortified certified reference material for trace elements, made in filtered and diluted Lake Ontario water and preserved in 0.2% HNO₃ (National Water Research Institute, Burlington, ON, Canada). Concentrations after dilution are up to 1 µg/L for most elements.
- 7.2.6 MTM_{xxx} in 4% HNO₃: Medium-level trace element fortified certified reference material made in filtered and diluted Lake Ontario water and preserved in 0.2% HNO₃ (National Water Research Institute, Burlington, ON, Canada). Concentrations are 1 to 10 µg/L for most elements.
- 7.2.7 HTM_{xxx} in 4% HNO₃: High-level trace element fortified certified reference material made in filtered and diluted Lake Ontario water and preserved in 0.2% HNO₃ (National Water Research Institute, Burlington, ON, Canada). Concentrations are 10 to 100 µg/L for most elements.
- 7.2.8 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.
- 7.2.9 Spiked Digested Samples are used to monitor the sample matrix interferences during ICP-MS measurements (see 5.3.7).

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7.3 QC samples for lead isotopes analysis (other commercial lead isotopes standards and CRMs with similar composition can be used).

7.3.1 SRM981 has lead isotopes ratios similar to samples and is used as an isotopic standard for mass bias and drift correction.

7.3.2 SRM982 has essentially equal-atom amounts of ²⁰⁶Pb and ²⁰⁸Pb and is used as control standard for estimation of accuracy and reproducibility.

7.4 QC samples for sample preparation procedure: consult **6.20/*.*S for details**

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).

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 following the calibration standard 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.

8.6 Lead isotopes calibration standard SM981 is run at the beginning of the sequence and every 10 samples; the lead isotopes control standard SRM982 is also measured alternately every 10 samples.

9 SAMPLES ANALYSIS AND DATA REPORTING

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- 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).

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, duplicates and lead isotopes SRMs (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_NT and CS_NT) should be run at the beginning of the analysis immediately after calibration is completed.
- 10.5 The lead isotopes standard SRM981 should be run at the beginning of analysis, and every 10-15 samples.
- 10.6 Procedural CRMs and lead isotopes SRM982 should be run once every 10-15 samples and 5-10 samples respectively.
- 10.7 Duplicates of digested samples should be run at least every 10 to 15 samples.
- 10.8 At least one digested sample should be spiked and analyzed with each batch of 35 samples

11 DATA ACCEPTANCE

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11.1 Control Standards and procedural CRMs at concentrations above the MQLs, 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 the 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 The recovery of elements determined in NIST 1648a should be within the limits specified in Appendix A (Table A1).

11.7 Mass bias for lead isotopes in SRMs should be less than 1% (as % relative error) and the precision less than 3% (as %RSD).

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

11.9 View 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 up to three months.

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

12 METHOD DETECTION LIMIT AND METHOD VALIDATION

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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 standards².

12.1.1 Based on the historical data of the digested reagent blanks analysis (SOP 6.20/*.*./S) calculate the MDL_B 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 analyses.

12.1.2 Based on historical data of repeated measurements of the digested MDL-spikes (SOP 6.20/*.*./S) at concentrations not higher than 10 times MDL, calculate the MDL_{Std}:

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

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 analysis.

12.1.3 Estimate MDLs based on the analyst's experience, and the maximum of MDL_B and MDL_{Std}.

12.2 MDLs should be checked at least once a year, and/or after any major modification of the instrument and/or method.

12.2.1 Using separate digestion vials, prepare at least seven MDL-spikes at concentrations not higher than 10 times the actual MDLs (SOP 6.20/*.*./S).

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

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

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 Method validation/verification is accomplished by using the QC samples described in Section 7, by intra-laboratory studies, and by participating in Proficiency Testing (PT)

² Grubbs Test can be used to remove outliers

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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 The possible sources of uncertainty and QC data used for uncertainty estimation are listed in Appendix B.
- 13.3 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 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 and the Microwave oven, consult Safe Working Procedures and Policies SWP-001/*.*/*.

16 APPLICABLE DOCUMENTS

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

SOP 6.20/*.*/*S “Microwave Digestion of Airborne Particulate Matter Collected on Filters using CEM MARS Xpress”

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”

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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 6.11/1.0/M

January 2006: Reviewers, Ewa Dabek and Valbona Celo

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 (4oC) is removed throughout the document.

April 2007: Reviewers, Valbona Celo, Irina Okonskaia

Section 1.1. The scope of the method is changed to include lead isotopes analysis and analysis of samples collected on Teflon, quartz and other types of filters. Changes related to this new scope are made in all other section; Section 5.2 is re-arranged; Section 6.2.1 and 6.2.2 are added to include preparation of 2% and 1% HNO₃ solutions, respectively ; Section 6.2.3 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 mixed tuning solutions are prepared in 2% HNO₃; 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 7 is divided in two subsections describing the QC samples for ICP-MS performance and QC samples for digestion procedures; Section 7.1.1: Blanks descriptions are changed; Section 7.2.4: TM23.3 and TMDA-61 are used instead of TM24.2 and TMDW respectively; Section 9.2 and 9.3: the note is deleted; Section 10.4.5 is added; Section 10.5 is changed; 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; Section 11.2.8 is added; Section 12 is changed to include details on MDL calculations; Section 13.1 is added; Section 14: details on cleaning solutions are removed; Appendices: Table A1, Table B2, Table E1, 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.

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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 and further: 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 6.4: Concentrations of all tuning solutions and P/A factor solution are changed to 50 µg/L; Section 6.5.3: 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 6.5.4.1: Calibration standard concentration is changed to 50 µg/L, and the note is added; Section 6.5.5: Composition of the custom-made multi-element standard (CMS) is changed; the sections referring to this standard are changed accordingly; Section 6.5.8 is removed; sections referring to SRM 983 are removed; Section 7.1.2.3 is added; Section 7.1.2.3 is changed to 7.1.2.4: the paragraph referring to SLRS4 is removed and TM23.3 is changed to TM28.3; Section 7.1.2.6 is added; Section 10.1: the pump speed is changed to 0.10 rps; Section 10.7 is added; Section 18: Agilent Technologies manuals are updated to the latest versions ; Appendices: Tables A1, B2, B3 (Spike 2) and E2 are changed after the validation of the MARS Xpress system and the new ICP-MS configuration; Table B1 is changed to reflect the new CRMs; Table C1 is changed to reflect new autosampler tray configuration, and new standards and CRMs;

December 2009: Reviewer Valbona Celo

Section 4.1 is changed to add the storage conditions of samples and extracts; Section 10.10.5: A paragraph on validation and protection of EXCEL templates is added (referring to the SOP 2.11/*.*S); Section 13.3 is changed and section 13.4 is added; Applicable SOPs: the SOP 2.11/*.*S is added; Reference: US EPA, Compendium Method IO-3.1, is added; Table E is removed and a note is added at Table E1.

July 2011: Reviewers, Valbona Celo, Irina Okonskaia

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 206Pb²⁺ on 103Rh” is added; Section 6.1: Specifications of water purification systems are removed; Sections 6.2. and 6.3: Specifications of HNO₃ grade are added; Section 6.3.7: reference to Appendix B is removed; Sections 6.3.9 and 6.3.10: specific SRM names, respectively SRM981 and SRM982, are added; Section 7.1.2: Title is changed to “QC standards and CRMs for ICP-MS analysis”; Section 8.1: a NOTE is added; Section 7.1.2.4 and throughout the text: specifications of the CRMs are removed; instead LTM_{xxx}, MTM_{xxx} and HTM_{xx} are added for the low, medium and high concentration CRMs, respectively; Section 10.6 and throughout the text: referring to ETC08 and

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other specific shared drives locations are deleted; Section 10.7: "...or the external hard drive" is added; Section 12.1: "The single laboratory (ICP-MS lab, Particulate Characterization Unit, AAQS, AQRD" and "tabulated in Appendix A" are deleted; Sections 12.1.1 and 12.1.2 are changed; Sections 12.2.4 and 12.2.5 are added; Section 12.3 is changed and "For the records of the precision and accuracy of measurements, refer to the latest Method Verification Binder (Room 172)" is added; Section 13.3: "For the records of estimated uncertainties refer to the latest Method Verification Binder (Room 172)" is added (deleted from the NOTE in Table E1); Appendix A (Table A1) and Appendix B, (Tables B1 and B3) are removed.

May 2013: Reviewers, Valbona Celo, Irina Okonskaia

Section 1.1: The "after microwave assisted acid digestion using HNO₃" is added for a description of Near-Total digestion; also new analytes (Al, Ce, La and Ti) are added to the scope; Section 1.3 is re-phrased; Sections 4, 5 and 6 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; Sections 4.8.1 and 4.8.2 are added; Section 6.3.1 (5.3.1 in this version): Working TS term is used instead of Mixed TS; Section 6.3.2 (5.3.2 in this version): Table with composition of ISTD is removed; Section 6.3.4 (5.3.4 in this version) is changed to include La and Ce single-elements stock standards; Section 5.3.5: intermediate and calibration standards are added; Section 6.3.6 (5.3.6 in this version): The NOTE is added; Section 7: numbering is changed; Section 7.1.1: description of blanks is not in tabular form; Section 7.1.2.4: 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 12.1.5, (Section 11.5 in this version) is changed to: "For analyte values greater than Method Quantitation Limit (MQL = 3 x MDL) the RPD% of duplicates should be less than 30%"; Section 12.1.8 (Section 11.8 in this version) is changed in order to specify the actions that are taken when the Data Acceptance criteria are not met; Reference to the SOPs describing the operations of both ICP-MS instruments are added throughout the text; The SOP 6.22/*.*S is added to Section 16; Appendix A: Table A1 updated with more recent values; Appendices B and C are removed. These and other details specific to the ICP-MS systems 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

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US EPA, *Inorganic Analytes*, Draft Update IVA of SW-846 On-Line, Chapter 3, Revision 4, November, 2000

US EPA, *Compendium Method IO-3.5, Determination of Metals in Ambient Particulate Matter using Inductively Coupled Plasma/Mass Spectrometry*, June, 1999

US EPA, *Compendium Method IO-3.1, Selection, Preparation and Extraction of Filter Material*, June 1999

US EPA, *Revised Assessment of Detection and Quantitation Approaches*, October 2004

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

Celo, V., Dabek-Zlotorzynska, E., Mathieu, D., Okonskaia, I., (2010) "Validation of a Simple Microwave-Assisted Acid Digestion Method using Microvessels for Analysis of Trace Elements in Atmospheric PM_{2.5} in Monitoring and Fingerprinting Studies", *The Open Chem. Biomed. Methods J.*, 3, 141-150

Watters, R. L. Jr, Eberhardt, K. R, Beary, E. S., Fassett, J. D., (1997), "Protocol for isotope dilution using ICP-MS for the determination of inorganic elements", *Metrologia*, 34, 87-96

Lead Reviewer: Valbona Celo

Title: ICP-MS Lab Supervisor, Particulate Characterization Unit

Approved by: Ewa Dabek

Title: Head, Particulate Characterization Unit

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APPENDIX A

Table A1. Average concentrations (in mg/kg, unless noted as %) and recoveries obtained for the NIST 1648a standard reference material based on the 2010-2013 measurements (N = 65)

Element	Certified * concentration	Measured concentration ^(a)	Recovery ^(b) [%]
Be	NC	2 ± 121	NA
Al	3.43%	(1.57 ± 11)%	46 ± 2
Ti	4021	1058 ± 13	26 ± 2
V	127	103 ± 5	80 ± 2
Cr	402	92 ± 10	23 ± 2
Mn	790	690 ± 6	90 ± 3
Fe	3.92%	(2.91 ± 13)%	74 ± 4
Co	17.93	14 ± 7	75 ± 4
Ni	81.1	67 ± 6	83 ± 3
Cu	610	554 ± 6	92 ± 2
Zn	4800	5264 ± 11	110 ± 6
As	115.5	126 ± 9	109 ± 3
Se*	28.4	28 ± 17	99 ± 8
Sr	215	159 ± 6	74 ± 2
Mo	NC	15 ± 9	NA
Ag*	6	6 ± 8	102 ± 4
Cd	73.7	76 ± 9	103 ± 4
Sn	NC	84 ± 10	NA
Sb	45.4	27 ± 20	60 ± 6
Ba	NC	565 ± 6	NA
La	39	24 ± 10	61 ± 5
Ce	54.6	34 ± 10	63 ± 5
Tl	NC	2 ± 12	NA
Pb	0.655%	(0.61 ± 8)	92 ± 5
U	NC	4 ± 9	NA

NC: not certified; ^(a) values in parenthesis are the RSD%; ^(b) values in parenthesis correspond to 95% confidence limit; *Reference values

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APPENDIX B

Table B1. Major Sources of Uncertainty in the Analysis of the Near Total Metals in PM Collected on Filters

Measurement Steps	Uncertainty Sources	QC Data May Be Used
Sample Preparation Filter Preparation Microwave Digestion	Filter Support Ring Cut Acid Volume Digestion Condition	Spiked Filter Blanks Weight of Water Recovery of Spiked Filter Blanks Recovery of Spiked Blank Solutions Duplicates Digested SRMs (for example NIST1648) recovery
ICP-MS Analysis	Analyst Standard Solution Preparation Calibration Instrument Drift and Internal Standard Correction Data Process	CRMs at three concentration levels, higher than MQLs