

Title: Determination of Total Trace Elements and Lanthanoids in Airborne Particulate Matter by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)		Copy No: ##
Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

QSM Approval: _____

Determination of Trace Elements and Lanthanoids 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 with a mixture of HNO₃/HCl/HF acids. It is also applicable to the determination of lead isotopes ratios¹ in digested samples.

Table 1. Trace elements determined in this method

No gas mode		Reaction gas mode	
		He Mode	H ₂ Mode
Aluminum (Al)	Molybdenum (Mo)		
Antimony (Sb)	Nickel (Ni)		
Arsenic (As)	Niobium (Nb)	Arsenic (As) ^(a)	Chromium (Cr)
Barium (Ba)	Rubidium (Rb)	Chromium (Cr) ^(b)	Iron (Fe)
Beryllium(Be)	Silver (Ag)	Iron (Fe) ^(c)	Selenium (Se)
Bismuth (Bi)	Strontium (Sr)	Vanadium (V) ^(a)	
Cadmium (Cd)	Thallium (Tl)		
Chromium (Cr)	Tin (Sn)		
Cobalt (Co)	Titanium (Ti)		
Copper (Cu)	Tungsten (W)		
Germanium (Ge)	Uranium (U)		
Lanthanoids (La to Lu) ^(d)	Vanadium (V)		
Lead (Pb)	Zinc (Zn)		
Manganese (Mn)	Zirconium (Zr)		

^(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

¹ If determination of Pb isotopes is required, refer to method 6.11/*:*/M

Title: Determination of Total Trace Elements and Lanthanoids in Airborne Particulate Matter by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)		Copy No: ##
Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

ppm) of chloride is expected, He mode should be used. ^(c)Fe can be determined in both He and H₂ mode. When information on Se is needed, H₂ mode is used. ^(d)Lanthanoids (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) are determined using the high matrix introduction (HMI) mode (SOP 6.14/*.*/*S and 6.22/*.*/*S).

- 1.2 Method detection limits (MDLs) range from 0.1 to 0.4 ng/filter for lanthanoids and 0.1 to 500 ng/filter for other trace elements (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 Trace metals are extracted from PM collected on filters, by means of a microwave-assisted acid digestion procedure (SOP 6.20/*.*/*S). The digested samples were 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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Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

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. Ba and almost all light lanthanoids form at least one polyatomic ion that overlaps with the mass spectra of the heavier elements.

- Doubly-Charged Ion Interferences are caused by ions consisting of more than one charge. Typical examples are the interferences of $^{206}\text{Pb}^{2+}$ on ^{103}Rh and $^{138}\text{Ba}^{2+}$ on ^{69}Ga .

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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--	--------------------------------

Title: Determination of Total Trace Elements and Lanthanoids in Airborne Particulate Matter by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)		Copy No: ##
Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

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% HNO₃²** 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 TraceMetal Grade HF 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 expiry date of the intermediate and working solutions should not be longer than 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% 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 (5 µg/L in 2% HNO₃): Dilute 0.1 mL of Intermediate TS and 2 ml of concentrated HNO₃ in a 100 mL volumetric flask with DDW (expiration time is six months).

² 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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--	--------------------------------

Title: Determination of Total Trace Elements and Lanthanoids in Airborne Particulate Matter by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)		Copy No: ##
Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

- Working TS for He mode (5 µg/L in the digestion matrix³): Dilute 0.1 mL of Intermediate TS, in a 100 mL volumetric flask with the digestion matrix (expiration time is six months).
 - Intermediate TS for HMI mode (1mg/L Ba, Pr, Dy, Tm, Lu in 2% HNO₃): Dilute 0.1 mL of each 1000 mg/L single-element stock standard solutions and 2 mL of concentrated HNO₃ in a 100 mL volumetric flask with DDW (expiration time is one year).
 - Working TS for HMI mode (5 µg/L in 2% HNO₃): Dilute 0.5 mL of Intermediate TS for HMI mode, and 2 mL of concentrated HNO₃ in a 100 mL volumetric flask with DDW (expiration time is six months).
- 5.3.2 **Internal Standard (ISTD) solution for analysis in no gas, H₂ and He modes (0.5 mg/L in 2% 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 (expiration time is one year).
- 5.3.3 **Internal Standard (ISTD) solution for analysis in HMI mode (0.5 mg/L in 2% HNO₃):** Dilute 1 mL of each 100 mg/L single- element stock solutions of Rh and In and 10 mL of concentrated HNO₃ in a 200 mL volumetric flask with DDW (expiration time is one year). **NOTE:** Make sure that the counts of Ho are at the background level before switching to HMI mode analysis.
- 5.3.4 **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).
- 5.3.5 **Single-element calibration standards** stock solutions containing 1000 mg/L of Bi, Ge, Nb, Rb, W, Zr and U in 5% HNO₃.
- 5.3.6 **Multi-element Intermediate and calibration standards:**
- Intermediate Calibration Standard 1 ppm (InCalStd 1ppm T) 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).
 - Intermediate Calibration standard 10 ppm (InCalStd 10ppm T) containing 10 mg/L of all elements in 2% HNO₃: Dilute 10 mL of multi-element Calibration Standard

³ The preparation of the digestion matrix is described in SOP 6.20/*.*S

Title: Determination of Total Trace Elements and Lanthanoids in Airborne Particulate Matter by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)		Copy No: ##
Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

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).

- Calibration standards are prepared from the intermediate calibration standards, to cover the 0.5 to 200 µg/L concentration range that is typical for analysis of trace elements in acid digested PM. All standards and the calibration blank should be prepared in the total digestion matrix⁴ (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.

Table 2. Preparation of calibration standards

Concentrations, µg/L	0	0.5	1	2	5	10	20	50	100	200
InCalStd_10ppm_T, µL	-	-	-	-	-	-	40	100	200	400
InCalStd_1ppm_T, µL	-	-	-	40	100	200	-	-	-	-
100 ppb standard, µL	-	100	200	-	-	-	-	-	-	-

Dilute to 20 mL using the total digestion matrix

5.3.7 **Lanthanoids Calibration Standard** stock solution containing 10 mg/L of Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm and Yb in 5% HNO₃. **NOTE:** Single-element stock solutions can also be purchased and used for preparation of stock calibration standard. Calculate the dilution factor for each standard every time, since concentrations of stock solutions may differ depending on the vendor and availability.

- Intermediate Calibration Standard for Lanthanoids (InCalStd 100ppb LA) containing 100 µg/L of all lanthanoids in 5% HNO₃: Dilute 1 mL of Lanthanoids Calibration Standard stock solution and 5 mL of concentrated HNO₃ in a 100 mL volumetric flask with DDW (expiration time is six months).
- Lanthanoids calibration standards are prepared from the intermediate calibration standard to cover the 0.01 to 10 µg/L concentrations range is typical for analysis of lanthanoids in acid digested PM. All standards and the calibration blank should be prepared in 4% HNO₃ (Table 3). If a single multi-element standard will be used (SOP 6.14/*.*S), prepare only the 0.1 µg/L standard. If samples are expected to have concentrations higher than 5 µg/L, a higher calibration standard should be prepared.

⁴ If deemed necessary, the calibration standards and QC samples can be digested and treated the same way as samples (SOP 6.20/*.*S)

Title: Determination of Total Trace Elements and Lanthanoids in Airborne Particulate Matter by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)		Copy No: ##
Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

Table 3. Preparation of lanthanoids calibration standards

Concentrations, µg/L	0	0.01	0.05	0.1	0.5	1	5	10
InCalStd_100ppb_LA, mL	-	0.01	0.05	0.1	0.5	1	5	10

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

5.3.8 **Multi-element Control Standard (MES-T)** 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-T-A, MES-T-B and so on.

- Intermediate MES-T (InMES-T in 2 % HNO₃): Dilute 1 mL of each of MES-T standard mixtures and 1 mL of concentrated HNO₃ in a 50 mL volumetric flask with DDW (expiration time is one month).
- LCS-T (low control standard in total digestion matrix): Dilute 40 µL of Intermediate MES-T to 20 mL using the digestion matrix (expiration time is two weeks).
- CS-T (control standard in total digestion matrix): Dilute 200 µL of Intermediate MES-T to 20 mL using the digestion matrix (expiration time is two weeks).
- LCS-LA (low control standard for lanthanoids, in 4% HNO₃): Dilute 40 µL of Intermediate MES-T and 0.8 mL of concentrated HNO₃ to 20 mL with DDW (expiration time is two weeks).
- CS-LA (control standard for lanthanoids, in 4% HNO₃): Dilute 200 µL of Intermediate MES-T and 0.8 mL of concentrated HNO₃ to 20 mL with DDW (expiration time is two weeks).

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

6 SAMPLE REQUIREMENT AND PREPARATION

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

Title: Determination of Total Trace Elements and Lanthanoids in Airborne Particulate Matter by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)		Copy No: ##
Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

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. It is prepared together with samples (SOP 6.20/*.*S) and used as the matrix to prepare the calibration standards and CRMs.

7.1.2 Rinse Blank (Blank) consists of 1% HNO₃. It is used to flush the system between all samples and standards and to monitor possible carry-over contamination.

7.2 Quality Control Samples and CRMs

7.2.1 Verification standard (VS) is the same as one 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-T or LCS-LA) is used to verify calibration accuracy at concentrations 5 to 10 times MDLs for most analytes (see 5.3.8).

7.2.3 Control Standard (CS-T or CS-LA) is used to verify calibration accuracy at concentration close to quantitation limits for most of the elements (see 5.3.8).

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. dilute 1 mL of CRM to 10 mL using the total digestion matrix). 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.

- LTM_{xxx} in digestion matrix: 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.
- MTM_{xxx} in digestion matrix: 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 after dilution are 1 to 10 µg/L for most elements.
- HTM_{xxx} in digestion matrix: 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 after dilution are 10 to 100 µg/L for most elements.

7.2.5 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.

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Page:
8 of 17

Title: Determination of Total Trace Elements and Lanthanoids in Airborne Particulate Matter by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)		Copy No: ##
Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

7.2.6 Spiked Digested Samples are used to monitor the sample matrix interferences during ICP-MS measurements (see 5.3.9).

7.3 Quality Control 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, reaction/collision gas and HMI). 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 ($RSD\% \leq 10\%$).
- 8.4 All analyses require that a calibration curve be prepared to cover the appropriate concentration range based on the intended application. 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 control standards, quality control samples and 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.

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

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--	--------------------------------

Title: Determination of Total Trace Elements and Lanthanoids in Airborne Particulate Matter by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)		Copy No: ##
Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

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 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, 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 At least one of the control standards (for example LCS-T and CS-T or LCS-LA and CS-LA) should be run at the beginning of the analysis immediately after calibration is completed.
- 10.5 Duplicates of digested samples should be run at least every 10 to 15 samples.
- 10.6 At least one digested sample should be spiked and analyzed with each batch of 35 samples.

11 DATA ACCEPTANCE

- 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:

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

Title: Determination of Total Trace Elements and Lanthanoids in Airborne Particulate Matter by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)		Copy No: ##
Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

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

- 11.6 The recovery of elements of interest from digested standard reference materials (for example NIST 1648 PM and BCR-677) should be within the limits specified in Appendix A (Table A1 and Table A2).
- 11.7 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).
- 11.8 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.
- 11.9 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.⁵

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

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

where C_B and S_{blk} are respectively, the average concentration and standard deviation of blanks, $t_{(0.99, n-1)}$ 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 historical data of repeated measurements of the digested MDL-spikes (SOP 6.20/*.*./S) at concentrations not higher than 10 times MDL, estimate 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 analyses.

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

⁵ Grubbs Test can be used to remove outliers

Title: Determination of Total Trace Elements and Lanthanoids in Airborne Particulate Matter by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)		Copy No: ##
Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

12.2 MDLs should be checked at least once a year, and/or after major modification to 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) 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

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Title: Determination of Total Trace Elements and Lanthanoids in Airborne Particulate Matter by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)		Copy No: ##
Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

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”

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

May 2013: Authors, Valbona Celo and Irina Okonskaia. New document 6.13/1.0/M

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--	---------------------------------

Title: Determination of Total Trace Elements and Lanthanoids in Airborne Particulate Matter by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)		Copy No: ##
Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

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Author: Valbona Celo **Date**

Title: ICP-MS Lab Supervisor, Particulate Characterization Unit

Approved by: Ewa Dabek **Date**

Title: Head, Particulate Characterization Unit

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Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

APPENDIX A

Table A1. Average concentrations (in mg/kg, unless noted as %) and recoveries obtained for the NIST 1648a standard reference material based on 2011-2012 measurements (N = 33)

Element	Certified concentration	Measured concentration ^(a)	Recovery ^(b) [%]
Be	NC	2 ± 14	NA
Al	3.43%	(3.31 ± 11)%	96 ± 4
Ti	4021	3578 ± 9	89 ± 3
V	127	122 ± 5	96 ± 2
Cr	402	171 ± 13	43 ± 2
Mn	790	767 ± 14	97 ± 5
Fe	3.92%	(3.66 ± 15)%	93 ± 5
Co	17.93	16 ± 12	89 ± 4
Ni	81.1	76 ± 8	94 ± 3
Cu	610	544 ± 7	89 ± 2
Zn	4800	4296 ± 8	89 ± 3
As	115.5	102 ± 20	88 ± 7
Se*	28.4	19 ± 10	68 ± 9
Sr	215	195 ± 9	91 ± 3
Mo	NC	16 ± 11	NA
Ag*	6	6 ± 9	100 ± 4
Cd	73.7	66 ± 6	89 ± 2
Sn	NC	94 ± 8	NA
Sb	45.4	34 ± 11	74 ± 3
Ba	NC	655 ± 7	NA
Tl	NC	2 ± 24	NA
Pb	0.655%	(0.585 ± 6)%	89 ± 2
U	NC	5 ± 20	NA

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

Title: Determination of Total Trace Elements and Lanthanoids in Airborne Particulate Matter by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)		Copy No: ##
Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

Table A2. Average concentrations (in mg/kg) and recoveries of lanthanoids obtained for the BCR 667 standard reference material based on 2011-2012 measurements (N = 33)

Element	Certified concentration [mg/kg]	Measured concentration ^(a) [mg/kg]	Recovery ^(b) [%]
La	28	29 ± 14	106 ± 6
Ce	56.7	56 ± 12	99 ± 5
Pr	6.1	6.5 ± 12	107 ± 5
Nd	25	22 ± 12	89 ± 4
Sm	4.66	4.8 ± 11	104 ± 5
Eu	1	1.0 ± 13	102 ± 5
Gd	4.41	4.4 ± 12	100 ± 5
Tb	0.68	0.64 ± 12	94 ± 5
Dy	4.01	3.6 ± 13	89 ± 5
Ho	0.8	0.69 ± 13	87 ± 5
Er	2.35	1.9 ± 13	83 ± 4
Tm	0.33	0.27 ± 12	82 ± 4
Yb	2.2	1.8 ± 13	80 ± 4
Lu	0.33	0.25 ± 14	76 ± 4

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

Title: Determination of Total Trace Elements and Lanthanoids in Airborne Particulate Matter by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)		Copy No: ##
Method No.: 6.13/1.0/M	Effective Date: May 17, 2013	Location: ###

APPENDIX B

Table B1. Major Sources of Uncertainty in the Analysis of the Total Metals and Lanthanoids 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 recoveries of NIST 1648a or BCR-677)
ICP-MS Analysis	Analyst Standard Solution Preparation Calibration Instrument Drift and Internal Standard Correction Data Process	CRMs at three concentration levels