STANDARD OPERATING PROCEDURES

Determination of Trace Metals Extracted from PTFE® Filters by ICP-MS

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Revision 2.1
Updated: April 28, 2019

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1.0 SCOPE AND APPLICATION

Particulate matter with an aerodynamic diameter of 2.5 μm and less ($PM_{2.5}$) has been identified as a potent cause of morbidity and mortality on a Global scale. Currently, the most robust metric for predicting mortality associated with $PM_{2.5}$ exposure is total mass concentration, however there is emerging evidence that the trace-metal component of $PM_{2.5}$ can lead to cellular damage via oxidative stress, while heavy metals such as Pb and As are known carcinogens. Beyond the potential health effects of exposure to trace-metals in $PM_{2.5}$, there is the potential to use the concentrations of different elements as indicators for emission sources.

Due to the inherently low concentrations of trace-metals, it is important that great care is taken to avoid contamination or sample loss during the handling, extraction and quantification steps. Samples are collected on either 25 mm PTFE® filters or 25 mm PF03A stretched Teflon filters from MTL, with the change over to the latter type occurring roughly June 2018. The procedure for analyzing the elemental metal component of $PM_{2.5}$ and PM_{10} is described in the following method. Filters are labeled and pre-weighed, deployed in the field and then returned to the central Dalhousie facility. They are then extracted using a hot acid digestion method and those extracts are analyzed with inductively coupled plasma (ICP) mass spectroscopy (MS). Operation of the ICP-MS instrument is done by the water lab facility in the faculty of engineering on the sexton campus.

REVISION HISTORY			
Revision No.	Change Description	Date	Authorization
2.0	General reorganization and clarification; addition of the aqua regia digestion conditions; introduction of method validation procedure with SRM; updating contamination control and preparation of labware.	July 11, 2018	Paul Bissonnette
2.1	Removed methodology for aqua regia acid digestions since this is no longer performed. Updated data validation to include blank correction	April 28, 2019	Crystal Weagle

2.0 SUMMARY OF METHOD

With the exception of stretched PFTE® filters, the PTFE® filters are cut in half prior to extraction for analysis by ICP-MS. All filters are extracted using TraceMetal™ grade HCl and HNO_3 and 18 MΩ·cm deionized water. This mixture removes the trace metals from the solid PM matrix and solubilizes them allowing the extracts to be analyzed with ICP-MS to quantify the

concentrations of 21 elements.

The sample is introduced into the ICP-MS through a nebulizer, creating an aerosol that encounters the ICP torch. Once introduced to the ICP torch, the sample is completely desolvated and the elements are converted to a gas and then into ions due to the high temperature of the plasma. The ions are then separated based on mass to charge ratios and detected in the mass spectrometer. Accuracy and precision of these measurements is ensured using quality control (QC) standards in each sample batch and periodic recalibration of the instrument to account for any signal drift over time.

3.0 CONTAMINATION CONTROL

Contaminants in reagents, plastic and glass labware, pipet tips, and other components used in sample processing all have the potential to introduce contaminants into samples or extracts. Therefore, all samples and standards are prepared using plastic and glass labware that has been rinsed once with methanol and then soaked in 2% v/v ACS-grade HNO_3 for ≥ 24 hours followed by triplicate rinses with 18 MΩ·cm deionized water. It is important to use only acid-safe plastic forceps or tweezers when handling filters to avoid potential contamination from metallic instruments.

4.0 SAMPLE STORAGE AND RECORDKEEPING

Filters are received at room temperature in sets of 8 or 16 according to a preassigned cartridge number. Samples are stored at room temperature prior to extraction. Following extraction, the extraction volume and date is recorded in the Sample Extraction Log. The plastic sample vials containing the final extract are capped and individually labeled and refrigerated at ~4 °C until they are submitted for ICP-MS analysis.

5.0 EQUIPMNET, ELUENTS, AND STANDARDS

5.1 Laboratory Equipment

5.1.1 Labware

- Volumetric flasks; 10 mL
- Ceramic scalpel
- Pipette tips, plastic, disposable; 1- 100 μL, 10 – 1000 μL, 1 – 10 mL
- 10 mL HDPE sample vials with caps
- Acid-resistant HDPE plastic tweezers
- 50 mL water bath tubes for digestion block

- Lint-free tissue wipes (e.g. Kimwipe®)

5.1.2 Equipment

- Micropipettes, variable volume
- Refrigerator (4 – 10 °C, nominal)
- Freezer (≤ - 18 °C, nominal)
- 24 sample digestion block (SmartBlock) with programable temperature controller
- ICP-MS instrument
- Fume hood

5.2 Preparation of Labware

5.2.1 General Labware

- All plastic labware will be rinsed once with ACS-grade methanol followed by a triplicate rinse with 18 MΩ·cm deionized water.
- Plastic sample vials are to be cleaned with a 2 % v/v HNO_3 solution for ≥ 24 hours prior to use to prevent leaching of elements into solution during acid digestion. Following the acid bath sample vials are to be rinsed in triplicate with 18 MΩ·cm deionized water.
- All washed plastic labware will be allowed to air-dry at room temperature. This will occur while sitting on a Kimwipe and will also be covered with a Kimwipe to prevent dust settling on clean labware.
- All clean plastic labware will be stored in sealed plastic bags with "Clean", as well as the date of cleaning, written on the exterior of the bag in permanent marker.
- Glass volumetric flasks will be cleaned with a 2 % v/v HNO_3 soak for the 24 hours prior to use followed by triplicate rinses with 18 MΩ·cm deionized water. It is important to not let the acid mixture sit in the acid bath for longer than 1 day as the glass from the volumetric flask may begin to get etched. Following the acid cleaning, glassware should be rinsed in triplicate with 18 MΩ·cm deionized water.
- To reuse volumetric flasks during a single set of samples, the 24-h acid soaking procedure does not need to be repeated. Rinse each volumetric with 18 MΩ·cm deionized water 6 times before using it for another sample.
- Tweezers will be wiped with ACS-grade methanol prior to each use.

5.2.2 Pipette Tips

- Disposable pipette tips for use with micropipettes are available commercially and will be used without rinsing.
- If quality control blank analyses consistently show measurable elements, contamination due to pipette tips will be considered.

5.3 Solutions and Standards

The operation and maintence of the ICP-MS instrument is done by a technician in the Clean Water Lab in the Dalhousie University Department of Engineering. Thus, all the details provided in this section (5.3 Solutions and Standards) are extracted from the SOPs published by this group. The document referenced here is "Determination of Elements by Inductively Coupled Plasma Mass Spectrometry" version 1, revision 1.

5.3.1 Tune solution (10 µg/L)
- Add 500 µL of Multi-Element Custom Standard (SCP Science cat# C00-081-101) to a 500 mL volumetric flask container about 300mL ultra-pure water and 10mL concentrated nitric acid (trace metal). Top up to line with ultra-pure water, cover and mix well. Transfer to two 250 mL labelled HDPE bottles. Solutions can be stored at room temperature for 3 months.

5.3.2 Mass Calibration Solution (50 µg/L)
- Add 250 µL of multi-element stock calibration standard 10000 µg/L (from section 5.3.3) and 2.5 µL of the Indium Internal Standard 1000ug/mL (SCP Science 140-051-491) to a 50 mL volumetric flask containing about 25 mL ultra-pure water and 500 µL concentrated nitric acid (trace metal). Top up to line with ultra-pure water, cover and mix well. Transfer to 50 mL mass calibration centrifuge tube in autosampler tray. Solution can be stored at room temperature for 1 month.

5.3.3 Multi element stock calibration standard (10000 µg/L)
- Add 1 mL of each single element standard (Al, Sb, As, Ba, Cd, Ca, Ce, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Ni, P, K, Se, Ag, Na, Ti, U, V, Zn) to one 100 mL volumetric flask containing about 20 mL ultra-pure water and 1mL concentrated nitric acid (trace metal). Top up to the line with ultra-pure water, cover and mix well. Transfer to a 125 mL HDPE bottle. This solution can be store at room temperature for 3 months.

- Note – Some elements don't interact well together in a standard solution so have to be made separately. Two of those elements are gold and tin.

5.3.4   Multi element working calibration standards (25, 50, 100, 250, 500 µg/L)

- Following the table below add a volume of multi-element stock calibration standard to a 250 mL volumetric flask containing about 150 mL ultra-pure water and 5 mL concentrated nitric acid (trace metal). Fill to the line with ultra-pure water, cover and mix well. Transfer each to 250 mL HDPE bottles. Solution can be stored at room temperature for 3 months.

Table 1: Standard concentrations and volumes required to make each standard

Standard	Concentration	Volume of Multi element stock calibration standard (10000ug/L)
Standard 1	25ug/L	625uL
Standard 2	50ug/L	1.25mL
Standard 3	100ug/L	2.50mL
Standard 4	250ug/L	6.25mL
Standard 5	500ug/L	12.50mL

5.3.5   Multi element stock external QC (5000 µg/L)

- Add 500 µL of each single element standard (Al, As, Sb, Cd, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, V, Zn) to one 100 mL volumetric flask containing about 50 mL ultra-pure water and 1 mL concentrated nitric acid (trace metal). Top up to the line with ultra-pure water, cover and mix well. Transfer to a 125 mL HDPE bottle. Solution can be store at room temperature for 3 months.

5.3.6   Internal Standard (100 µg/L)

- Add 100 µL of Sc, In and Tb to one 1L volumetric flask containing about 700 mL ultra-pure water and 20 mL concentrated nitric acid (trace metal). Fill to the line with ultra-pure water, cover and mix well. Transfer to 1L HDPE internal standard bottle. Solution can be stored at room temperature for 3 months but typically needs to be made every few days depending on instrument use.

6.0 SAMPLE PREPARATION

6.1 Filter Extraction Procedure

- Label each 10 mL HDPE sample vial using permanent marker with the filter labels of the cartridge(s) to be extracted. For each cartridge, one lab blank will also be prepared and labeled according to the cartridge number (e.g. CAHA-006-LB). Lab blank preparation is to follow the same procedure as the filter extracts.
- Put on Nitrile gloves and clean the HDPE tweezers with a Kimwipe and methanol.

- Using the tweezers, place each half-filter into the appropriately labeled 10 mL sample vial. Cleaning tweezers between each use.
- Using the micropipette, pipet 10 μL of isopropyl alcohol (IPA) onto each filter. Attempting to wet each filter with the IPA. The purpose of this step is to make the hydrophobic PTFE filter stay more easily submerged in the aqueous solution.
- Add 2.75 mL of 18 MΩ·cm deionized water to every sample vial. Ensure the water is added to the sample tube **before** adding any concentrated acids.
- Working with concentrated acids is dangerous and should be only be done while wearing gloves and a lab coat and working in a well-ventilated fume hood. Add 250 μL of 68 % TraceMetal^{TM} Grade Nitric acid to create a 5 % v/v acid solution. See **Table 2** for a summary of reagent volumes.
- Fill the water bath tubes with 18 MΩ·cm deionized water to the 30 mL mark and insert into heating block. Once this step is complete, the sample vials can be placed into the water baths.
- Set the heating block to run for 2 hours at 97 °C with a 30-minute ramp-up time.
- Once the run is complete, carefully remove each filter and transfer it into a sample vial cleaned by the same acid rinse procedure and with the same label amended with an "A" at the end to distinguish the two digestion extracts (eg, CAHA-015 becomes CAHA-015-A on the second sample vial).
- Top-up all sample vials to a total volume of 3 mL drop-wise with 18 MΩ·cm deionized water to account for any volume that may have evaporated off. This extract is now ready to be submitted for analysis.
- Record the volume and date for each filter extract in the Sample Extraction Logbook

Table 2: Volumes of reagents for hot acid digestion of filters

Digestion Conditions	Volume of IPA (μL)	Volume of deionized water (mL)	Volume of HNO$_3$ (mL)	Volume of HCl (mL)	Total Volume (mL)
5 % Nitric Acid Digestion	10	2.75	0.25	0	3.00

6.2 Sample Storage

- The sample vials are to be refrigerated at ~ 4 °C until they are submitted to the clean water lab for ICP-MS analysis. No further sample storage is required after that point.

7.0 DATA VALIDATION

- To validate the extraction efficiency for each element using this method the NIST standard reference material (SRM) SRM-1648a urban particulate matter is used. Using known masses of the SRM, the extraction and analysis procedures outlined above are used and the concentrations of each element determined by ICP-MS are compared to the certificate values. All samples are run in triplicate and must have an RSD of less than or equal to 10 % or the tests will be re-run.

- The concentrations of trace metals in the lab blanks are used as an indicator of potential contamination in the method. The average concentration of elements in the lab blanks is calculated and if a blank from a particular sample set is one standard deviation above that mean, this sample is flagged as suspect for contamination. If the blank concentration is not flagged as suspect, all trace element concentrations from sampled filters are blank-corrected.