Standard Operating Procedure for the X-Series ICP-MS for the Analysis of Particulate Deposits on Teflon Filters

Environmental and Industrial Science Division
RTI International*, Research Triangle Park, North Carolina

Prepared by: _____   Date:_____

Reviewed by: _____   Date:_____

Approved by: _____   Date:_____

* RTI International is a trade name of Research Triangle Institute.

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1.0   SCOPE AND APPLICATION

This standard operating procedure (SOP) addresses the extraction and analysis of selected metals from Teflon filters using inductively coupled plasma mass spectroscopy (ICP-MS).

Table 1. Project-Specific Elements Analyzed for the PM$_{2.5}$ Speciation Program

Aluminum[*]	Antimony	Arsenic	Beryllium	Cadmium
Chromium	Cobalt	Copper	Barium	Lead
Manganese	Mercury	Nickel	Selenium	Silver

*ICP-MS analysis is not recommended using Whatman Teflon filters due to background levels present in the stiffening ring.

1.1   Principle

The sample is extracted into a solution of nitric and hydrochloric acid to solubilize the material deposited on the filter. The resulting solution is aspirated into an argon plasma to generate ions, which are then accelerated through a series of focusing lenses, separated on a mass to charge basis by a quadrapole, and impacted into an electron multiplier detector that reads the resulting voltage and extrapolates the concentration against a known concentration curve.

1.2   Method Overview

Filter samples are removed from cold storage or received after analysis by XRF. Sample information is entered into the extraction logbook. The filters are loaded into 50mL, acid-cleaned centrifuge tubes, with the loaded side facing inward. A 25mL aliquot of extraction solution is added to cover the filter in the tube. The tubes are capped and placed in a heated ultrasonic bath for three hours to extract the metals on the filter. The samples are allowed to cool, centrifuged, and a 5mL aliquot of the supernatant liquid is removed for ICP-MS analysis. The ICP-MS is optimized daily with a tuning solution, and the samples are analyzed against a new calibration curve for each analytical sequence.

2.0   Safety

Because the extraction solution is made from concentrated acids, proper persaonl protective equipment (PPE) must be worn at all times. Safety glasses, gloves, and a laboratory coat must be worn at all times to protect against spills and splashes, which can result from handling liquid samples.

3.0   Filter Sample Considerations

It is important that care be taken when handling the filters so that the deposit is not abraded in any way that would cause the loss of material. Care also needs to be taken to assure that the filters are not contaminated by metal tweezers or any other source as the whole filter, front and back, is extracted. Any contamination present would contribute to the total result for the filter.

4.0   Interferences and Intensity Corrections

The following are potential sources of error in the procedure:

4.1   Polyatomic interferences

Polyatomic interferences exist for several elements; in particular, arsenic and selenium. The polyatomic interferences are overcome using a combination of collision cell technology and kinetic energy discrimination. The collision cell introduces a mixed hydrogen/helium gas into the ion beam, and the resulting collisions break apart the polyatomic species, which have the same mass as a target analyte. Any polyatomic species that remain intact are then slowed by kinetic energy discrimination because the larger polyatomic molecule does not travel as fast as the elemental ion through the lens stack. This approach greatly reduces the impact of polyatomic species such as $^{40}Ar^{35}Cl$ on elements like ^{75}As.

4.2   Sample viscosity

The viscosity of the sample being pumped and aspirated can cause fluctuations in response. This fluctuation is negated by the use of internal standards. The internal standard response is measured on each replicate of the analysis, and the concentration of the analyte is corrected using the following formula:

$$M = A / I$$

Where M = reported concentration, A = measured concentration, and I = internal standard response.

5.0   Instruments

Two Thermo X-Series Inductively Coupled Plasma Mass Spectrometers are used for this procedure. Both instruments are equipped with collision cell technology and the following major components:

- Torch box, RF generator, lens stack, quadrapole, and electron multiplier detector

- Personal computer with the Thermo PlasmaLab software

- Vacuum pump and turbo pump

- Refrigerated water recirculator

- Uninterruptible Power Supply (UPS), which supplies the entire instrument, PC, and chiller with 15 minutes of uninterruptible power in full operation and two hours of vacuum support in standby mode

- 240 position autosampler housed in a HEPA-filtered enclosure to protect against atmospheric contamination.

6.0   Instrument Calibration

6.1   Standards

Standards are prepared from NIST-traceable, commercially purchased stock solutions. A series of concentrations ranging from 0.25 ppb to 500 ppb along with a blank are prepared to bracket expected analyte concentrations. The range of calibration standards will be adjusted based on the indigenous concentration of individual elements in the samples.

6.2   Check Standard

A check standard is prepared from a second source of commercially purchased NIST-traceable stock standards to verify the validity of the calibration curve. The check standard is prepared at a concentration that is not a point on the calibration curve and near the midpoint of the calibration range. The check standard is analyzed following calibration and before the analysis of any samples, at a frequency of one per every ten samples, and at the end of analysis. All sample results to be reported must be bracketed by passing standard checks.

6.3   Method Set-Up

The analysis method is saved as a template that contains the analyte list, acquisition parameters, calibration standards and defined concentrations, and uptake and rinse times. The analyst will click on "create sequence from template" and save the sequence as a new name in the instrument software. The sample names will be filled in on the analysis sequence, and the sequence will be started.

6.4   Calibration Frequency

Calibration is performed at the beginning of each analytical run. The correlation coefficient must be ≥ 0.995 for each element. The result for each standard concentration on the curve must be +/- 10% of the expected value for the point to be valid. The initial calibration check, which is prepared from a separate standard source than the calibrants, must pass at +/- 10% of the expected concentration for each element. The initial calibration blank must be less than the reporting limit for each element. If an element fails to meet the calibration criteria, a new calibration must be run and the associated samples reanalyzed for the given element.

6.5   Detection Limit and Uncertainty

The detection limit for each element is calculated by analyzing seven replicates of a known standard concentration and multiplying the standard deviation of the replicates by three. The uncertainty for the measurement is the percent relative standard deviation, which is calculated by the instrument operating software for the triplicate readings taken on each sample.

7.0   Filter Handling

Teflon filters are received from storage or after analysis by XRF. Custody of the Teflon filters are transferred to the ICP-MS Laboratory by the signing of the appropriate chain of custody forms. The filters are stored in plastic bags in a hood until they are ready for extraction.

8.0   Filter Preparation and Analysis

8.1   Preparation

Filters are removed from their petri dish and placed in a labeled acid-cleaned, 50mL centrifuge tube with the loaded side facing inward using acid-cleaned plastic tweezers. The tubes are gently tapped on the lab bench to settle the filter as low in the tube as possible. 25mL of an 8% $HCl/3\%HNO_3$ extraction solution is added to each tube, and the tubes are capped. All the samples are placed in a heated ultrasonic water bath at 69°C for three hours. After removal from the bath, the samples are allowed to cool to room temperature and are vortex mixed. The samples are placed in a centrifuge at ~2800 RPM for 15 minutes to settle any insoluble particulate, and a 5mL aliquot of sample is removed for ICP-MS analysis.

8.2   Analysis

The sample identifications are typed into the autosampler table in the method, and the samples are loaded in the autosampler according to the table. The instrument is tuned, which consists of maximizing the signal at ^{115}In while minimizing cerium oxide/cerium ratio, and a system suitability check is run to show that the instrument is stable over a 10 replicate analysis. The instrument daily-use benchsheet and system suitability are posted in the instrument notebook. Once the instrument is tuned and the autosampler is loaded, the analyst will queue the experiment and monitor the analysis.

8.3   Archiving

After analysis is completed, the remaining extract will be stored in the sample custody room (Building 6, Room 205) for a period of 6 months. Samples will be stored at ambient temperature. After the 6-month storage period, samples will be discarded as acid waste.

9.0   Data Acquisition and Calculations

After all the samples have all been acquired, the software will display a message "Experiment _____ is no longer in the queue". The analyst will click the OK button and then the Results tab in the software to display all the sample results. The analyst will confirm that the acceptance criteria in Section 10 are met. The dilution factor of 25 is built into the autosampler table, so all results are displayed in units of nanograms per filter. The analyst will transfer the CSV results file to a USB storage device. Any data that does not meet acceptance criteria will be edited out of the file, and the file will be sent for uploading into the PM$_{2.5}$ database.

10.0   Quality Control

Several different quality control activities are performed as part of the analysis procedure. These activities, their frequency, and the measures of acceptable performance are given in the following table.

Activity	Frequency	Measure of Acceptable Performance
Calibration	Every sequence	Correlation coefficient of ≥ 0.995
QC Blank	Analyzed after calibration, every 10 samples, and at the end of the sequence.	All elements below method reporting limit.
QC Check Sample	Analyzed after calibration, every 10 samples, and at the end of the sequence.	90–110% recovery
MDL	Every 6 months	n/a
Duplicate Analysis	One per 20 samples	n/a – flag LDU if >20%

11.0   Data Review and Validation

The analytical data set goes through Level 0 and Level 1 validations. These levels of validation will ensure the data set being reported will be of good quality.

11.1   Level 0 Validation

A Level 0 validation begins with the analyst. The analyst identifies any problems related to the COC, filter, or any mechanical or software problems that might have arisen during analysis of the filters. If such items are identified, validation flags will be applied to single out any problems, and these flags will be considered when using the data.

11.2   Level 1 Validation

A Level 1 validation is a more technical review of the analytical data. This review starts with the analyst, but will primarily be performed by the Technical Area Supervisor. Using the review criteria developed by the QA Manager, the Technical Area Supervisor will check to ensure that the analytical data set is complete, the data is reasonable, the QC sample results are within acceptance limits, and the procedure to analyze the filters was followed. If any discrepancies are noted and would have a direct affect on the data, the Technical Area Supervisor would apply validation flags to the data. A Level 1 checklist is presented as Figure 1. A table of laboratory flags applicable to ICP/MS in shown in Figure 2.

After the analytical data set has gone through the two levels of review, both the analyst and the Technical Area Supervisor sign off on the data set, and it is ready to be submitted for upload into the database. The data file, together with any data flags applied during the review process, will be submitted via e-mail in CSV format for uploading to the database.

Figure 1. ICP-MS Level 1 Elemental Analysis Checklist

COC Form No. _____ Report Date: _____

Data Review:

Sample Filter No. _____Comments: _____

Sample Filter No. _____Comments: _____

Sample Filter No. _____Comments: _____

Sample Filter No. _____Comments: _____

Sample Filter No. _____Comments: _____

Quality Control Review:

Calibration Data Acceptable: Yes __ No___   Notes: _____

_____

QC Data Acceptable: Yes __   No___   Notes: _____

_____

Uncertainty Data Acceptable: Yes __ No___   Notes: _____

_____

File Name: _____

Reviewed by: _____   _____
                                                                              Date

Approved by: _____   _____
                                                                              Date

Figure 2. Data Flags Applicable to ICP/MS

Flag Code	Description	Applicability
4	Possible lab contamination	If results can not be explained after internal investigation.
AAR	Above Analytical Range	If sample exceeds the instrument calibration.
AR	Lab Error	
AS	Poor Quality Assurance Results	Used if QC samples fail to meet specification.
LBL	Laboratory Blank values outside of limits	
LCA	Laboratory calibration out of limits	
LDU	Lab duplicates out of limits	If duplicate analysis falls outside of specified range.
LFH	Filter inspection flags* – Holes in filter	
LFL	Filter inspection flags* – Loose Material	
LFO	Filter inspection flags* – Other (wrinkling, warping, etc.)	
LFP	Filter inspection flags* – Pinholes	
LFS	Filter inspection flags* – Separation of reinforcing ring	
LFT	Filter inspection flags* – Tear	
LLI	ANALYSIS INVALID – Other	

12.0   References

Thermo X-Series II Getting Started Guide, 1995

Plasmalab Version 2.5.3

CARB-MLD 061

TID-TOP-001, Use and Maintenance of the Thermo X-Series ICP-MS