STANDARD OPERATING PROCEDURES

Determination of Anions and Cations Extracted from PTFE® Filters by Ion Chromatography

Washington University
St. Louis, Missouri, USA

Prepared by: Crystal Weagle, Emily Stone
Revision 3.0
Updated March 12th 2020

TABLE OF CONTENTS

1.0 SCOPE AND APPLICATION

The method described is used for the quantitative determination of anions (defined as chloride (Cl^-), nitrite (NO_2^-), bromide (Br^-), nitrate (NO_3^-), and sulfate (SO_4^{2-})) and cations (defined as sodium (Na^+), ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+})) in air samples collected on 25 mm PTFE® filters. Each 25 mm filter sample is extracted with deionized water and HPLC-grade methanol. The samples are sonicated for 30 minutes following the addition of methanol and deionized water. After sonication, 2 mL of each sample is transferred to a baked 4 mL glass vial and the remaining volume (3.5 – 4.0 mL) is transferred to a clean and dry 8 mL amber plastic vial. Extracts stored in glass vials are sealed in plastic bags grouped by cartridge number and frozen immediately following extraction. Extracts stored in amber vials are refrigerated in sealed plastic bags and grouped by cartridge number. The refrigerated extracts in amber vials will be analyzed for anions and cations using Ion Chromatography (IC).

REVISION HISTORY			
Revision No.	Change Description	Date	Authorization
1.0	Written for mesh Teflon and Nuclepore filters, includes filter cutting and 3 mL extractions.	December 12, 2018	Crystal Weagle
2.0	Edited for stretch Teflon. Removal of filter cutting, addition of 6 mL extraction volume and preservation of filter after extractions.	January 25, 2019	Emily Stone Crystal Weagle
3.0	Updated for use with new Integrion systems, Washington University.	March 12, 2020	Emily Stone

2.0 SUMMARY OF METHOD

Once filters have returned from sampling in the field and have been analyzed through all non-destructive methods (post-weighing, FTIR, HIPS, SSR, UV-Vis, XRF) they are extracted as the final stage in chemical analysis. All filters are extracted using HPLC-grade methanol and 18 MΩ·cm deionized water, making it possible to analyze extracts for anions and cations using IC, and organics with an aerosol mass spectrometry (AMS).

For analysis by IC, sample extracts pass through a column coated with quaternary ammonium active sites for anion analysis and through a column coated with carboxyl active sites for cation analysis. Ion separation occurs as extracts pass through the column due to different affinities of the various ions for the active sites. Following separation, the ions pass through a

suppressor that lowers the background signal from ions in the eluent and increases the signal-to-noise ratio. Species are detected and quantified by a conductivity detector. Accuracy and precision of the method is monitored by routine analysis of quality control (QC) standards.

3.0 CONTAMINATION CONTROL

Contaminants in reagents, plastic and glass labware, pipette tips, and other components used in sample processing have the potential to cause erroneously high results. Therefore, all samples and standards are prepared using plastic and glass labware that has been rinsed once with methanol and then in triplicate with 18 MΩ·cm deionized water. As a portion of each extract is destined for organic analysis by AMS, all 25 mL and 4 mL borosilicate glass vials used during the extraction process are soaked in 1 % ACS-grade nitric acid overnight, rinsed with deionized water, then wrapped in aluminum foil and baked at 500 °C for 5 hours. Following extraction, sample storage vials are capped and remain unopened unless for analysis. Extracts are recapped immediately after the volume required for analysis is removed from the storage vial. See section 5.0 for details on labware preparation.

4.0 SAMPLE STORAGE AND RECORDKEEPING

4.1 Sample Storage

Filters are received at room temperature in sets of 8 according to a preassigned cartridge number. Samples are stored in petri dishes at room temperature prior to extraction and are extracted at room temperature.

The glass vials containing 2 mL of the extract are frozen immediately after extraction at -20 °C. The remaining volume (~3.5 – 4.0 mL) from each filter extract is stored in plastic, 8 mL amber vials and refrigerated at approximately 4 °C prior to analysis. Unused portions of sample extracts are stored for one year from the extraction date. After one year, one sample from each filter cartridge is archived for long-term storage and the remaining samples are discarded.

4.2 E-Logs

Following extraction, the extraction volume, post-weight date, and date of extraction are all recorded in an IC log.

5.0 EQUIPMENT, ELUENTS, AND STANDARDS

5.1 Laboratory Equipment

5.1.1 Labware

- Volumetric flasks; 10 mL, 25 mL
- Pipette tips, plastic, disposable; 1- 100 µL, 10 – 1000 µL, 1 – 10 mL
- Thermo Dionex 500 µL Ion Chromatography autosampler vials
- Glass syringes; 100 µL, 5 mL
- Plastic amber vials, 8 mL
- Borosilicate glass vials with PTFE®-lined caps; 4 mL, 25 mL
- Storage bottles, HDPE, 500 mL
- PTFE®-coated tweezers
- Aluminum foil
- 2 µm Polypropylene filter-heads

5.1.2 Equipment

- Micropipettes, variable volume
- Refrigerator (4 – 10 °C, nominal)
- Freezer (≤ -18 °C, nominal)
- Ultrasonic bath
- Ion Chromatography Systems (Thermo Scientific: Dionex Integrion RFIC)
- 18 MΩ·cm deionized water (Millipore Sigma Milli-Q IQ 7000)

5.2 Preparation of Labware

5.2.1 General Labware

- All plastic labware is rinsed once with ACS-grade methanol followed by a triplicate rinse with 18 MΩ·cm deionized water.
- All washed plastic labware is placed on a Kimwipe® to air-dry and is covered with a Kimwipe® to prevent dust settling on clean labware.
- All clean plastic labware is stored in sealed plastic bags labeled “clean”, with the date of cleaning written on the exterior of the bag in permanent marker.
- Glass volumetric flasks used for making standards are rinsed six times with 18 MΩ·cm deionized water, and stored upside down in a drying rack.

- Tweezers are wiped with an ACS-grade methanol soaked Kimwipe® prior to each use.

5.2.2 Baking Glass Labware: 25 mL vials, 4 mL vials

- The 25 and 4 mL glass vials, as well as the glass containers used to hold 18 MΩ·cm deionized water and HPLC-grade methanol during IC extractions are soaked overnight in 1 % ACS-grade nitric acid solution. This is followed by two rinses of the outside of the vial with 18 MΩ·cm deionized water prior to a triplicate rinse of the inside with 18 MΩ·cm deionized water.
- Once clean, all glass vials and containers are left to dry on a Kimwipe® overnight. They are then wrapped in aluminum foil in sets of 9 and baked at 500 °C for 5 hours. Following this, they are left overnight in the oven to cool to room temperature before being removed.
- Once baked, glass vials remain in the aluminum foil pouches and are placed inside a sealed plastic bag with "Clean and Baked" and the date which they finished the baking procedure is written on the exterior of the bag with permanent marker.
- *NOTE*: The 18 MΩ·cm deionized water and HPLC-grade methanol containers should be cleaned and baked approximately every two weeks.

5.2.3 Aluminum Foil Squares

- For the 25 mL glass vials, small squares of baked aluminum foil are used as a barrier between the glass vial and its plastic lid to keep them from touching. On a day that glassware will be baked, also cut out sets of 10 small foil squares (one for each vial and 1 extra in case a square is torn, etc.) and wrap them in a small foil pouch. Foil squares should also be cut and baked for the lid of the deionized water container. All squares should be baked in same conditions as glass vials for 5 hours.

5.2.4 Glass Syringes

- The plungers are removed from the 5 mL glass syringes and both pieces (the syringe and the plunger) are rinsed once with ACS-grade methanol, and then twice with 18 MΩ·cm deionized water in a Tupperware® container. The plungers are placed back in the syringes and 3 full volumes of 18 MΩ·cm deionized water are pushed through each syringe.
- The 100 µL syringes are used exclusively for HPLC-grade methanol and are rinsed in triplicate with HPLC-grade methanol prior to each use.

5.2.5 Polypropylene Filter-heads

- Polypropylene filter heads are only used once before discarding. They are not cleaned before use.

5.2.6 Autosampler Vials and Pipette Tips

- Autosampler vials for use with Thermo Scientific equipment are available commercially and are used without rinsing.
- Disposable pipette tips for use with micropipettes are available commercially and are used without rinsing.
- If quality control blank analyses consistently show measurable ions, contamination due to autosampler vial and/or pipette tip will be investigated.

5.3 Eluent Generation

The Integrion RFIC Ion Chromatography system generates eluent through electrolysis using 18 MΩ·cm deionized water. To do this, the systems require eluent generation cartridges. For cations, the Thermo Scientific Dionex EGC III MSA cartridge is used for the generation of methanesulfonic acid eluent, and for anions the Thermo Scientific Dionex III KOH cartridge is used to generate potassium hydroxide eluent. See Dionex Eluent Generator Cartridge Manual available online for EGC installation instructions.

Any time the Ion Chromatography systems will be used, the eluent bottle must be filled with fresh 18 MΩ·cm deionized water, so that eluent can be generated. It is important to use fresh deionized water each day the ICs will be used and not water that has been sitting for long periods of time in the eluent bottle in order to prevent potential leaching of ions from the bottle into the water.

5.4 Calibration Standards

A minimum of 8 calibration standards are prepared for both anion and cation IC analysis as outlined in section 5.4.1 and 5.4.2, respectively. These standards are used that day or refrigerated for use within the next seven days. If stored for longer than seven days, prepared standards will be discarded and remade.

5.4.1 Anion Calibration Standards

Anion calibration standards are prepared directly from the Dionex® Seven Anion Standard (Product No. 056933) as shown in Table 1. Only 18 MΩ·cm deionized water is used to dilute to the volumes specified in Table 1. The resulting concentrations of the anions in each standard solution are shown in Table 2.

Table 1. Preparation method summary for anion calibration standards

Standard Label	Method of preparation
STD 3.0	750 µL anion stock solution in 25 mL flask
STD 2.0	500 µL anion stock solution in 25 mL flask
STD 1.5	375 µL anion stock solution in 25 mL flask
STD 1.0	250 µL anion stock solution in 25 mL flask
STD 0.75	188 µL anion stock solution in 25 mL flask
STD 0.5	125 µL anion stock solution in 25 mL flask
STD 0.25	63 µL anion stock solution in 25 mL flask
STD 0.1	2.00 mL of STD 0.5 in 10 mL flask

Table 2. Final anion concentrations in calibration standards (µg/mL)

Standard Label	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^-	SO_4^{2-}
STD 3.0	0.60	0.90	3.00	3.00	3.00	4.50	4.50
STD 2.0	0.40	0.60	2.00	2.00	2.00	3.00	3.00
STD 1.5	0.30	0.45	1.50	1.50	1.50	2.25	2.25
STD 1.0	0.20	0.30	1.00	1.00	1.00	1.50	1.50
STD 0.75	0.15	0.225	0.75	0.75	0.75	1.125	1.125
STD 0.5	0.1	0.15	0.50	0.50	0.50	0.75	0.75
STD 0.25	0.05	0.075	0.25	0.25	0.25	0.375	0.375
STD 0.1	0.02	0.03	0.10	0.10	0.10	0.15	0.15

5.4.2 Cation Calibration Standards

Cation calibration standards are prepared directly from the Dionex® Six Cation-II Standard (Product No. 046070) as described in Table 3. Only 18 MΩ·cm deionized water is used to dilute to the volumes specified in Table 3. The resulting concentrations of the cations in each standard solution are shown in Table 4.

Table 3. Preparation method summary for cation calibration standards

Standard Label	Method of preparation
STD 3.0	300 µL cation stock solution in 25 mL flask
STD 2.0	200 µL cation stock solution in 25 mL flask
STD 1.5	150 µL cation stock solution in 25 mL flask
STD 1.0	100 µL cation stock solution in 25 mL flask
STD 0.75	75 µL cation stock solution in 25 mL flask
STD 0.5	50 µL cation stock solution in 25 mL flask
STD 0.25	25 µL cation stock solution in 25 mL flask
STD 0.1	2.00 mL of STD 0.5 in 10 mL flask

Table 4. Final cation concentrations in calibration standards (µg/mL)

Standard Label	Li^+	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
STD 3.0	0.60	2.40	3.00	6.00	3.00	6.00
STD 2.0	0.40	1.60	2.00	4.00	2.00	4.00
STD 1.5	0.30	1.20	1.50	3.00	1.50	3.00
STD 1.0	0.20	0.80	1.00	2.00	1.00	2.00
STD 0.75	0.15	0.60	0.75	1.50	0.75	1.50
STD 0.5	0.10	0.40	0.50	1.00	0.50	1.00
STD 0.25	0.05	0.20	0.25	0.50	0.25	0.50
STD 0.1	0.02	0.08	0.10	0.20	0.10	0.20

5.5 Quality Control Standards

An intermediate range anion and cation quality control (QC) standard is prepared using the Dionex® Seven Anion Standard and Dionex® Six Cation-II Standard stock solutions, respectively, as described in Table 5. Only 18 MΩ·cm deionized water is to be used to dilute to the volumes specified in Table 5.

Table 5. Preparation method summary for anion and cation quality control standards

Standard Label	Method of preparation
Anion QC STD 1.25	313 µL anion stock solution in 25 mL flask
Cation QC STD 1.25	125 µL cation stock solution in 25 mL flask

6.0 SAMPLE PREPARATION

6.1 Filter Extraction Procedure

- Label 25 mL glass vials, 4 mL glass vials, and 8 mL plastic amber vials 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. ILNZ-027-LB). The lab blanks are prepared following the same procedure as filter extractions.
- Put on gloves and clean the PTFE®-coated tweezers with a methanol-soaked Kimwipe®.
- Using tweezers, place each filter in the 25 mL glass vial that has been labelled with the corresponding filter label. (Note: make sure that the label on the vial matches the label on the petri dish.)
- Using a 100 µL glass syringe, transfer 240 µL of HPLC-grade methanol directly onto the filter in each glass vial.
- Using a 5 mL glass syringe, transfer 5.8 mL of 18 MΩ·cm deionized water into each 25 mL glass vial.

- Using the tweezers, place a baked aluminum foil square over the top of the 25 mL glass vial and then tightly screw on the cap. The foil square prevents any liquid from touching the inside of the unbaked plastic cap.
- Place the 25 mL glass vials upright in a plastic container and plastic bag, and place in the ultrasonic bath. Sonicate for 30 minutes. Remove the vials from the ultrasonic bath.
- Using a new 5 mL glass syringe and 2 µm Polypropylene filter-head for each sample, transfer 2 mL of each extract to the baked 4 mL glass vials. (Note: make sure that the label on the 4 mL vial matches the label on the 25 mL vial). Be sure to put the 2 µm Polypropylene filter-head on the tip of the syringe AFTER the 2 mL aliquot is inside the syringe. Ensure that the filter head is not punctured while you extract the sample.
- Using the 5 mL glass syringe and 2 µm Polypropylene filter-head, transfer the remaining volume in the 25 mL glass vial (3.5 – 4.0 mL) to the 8 mL plastic amber vial. (Note: make sure that the label on the 8 mL amber vial matches the label on the 25 mL vial).
- The filter should be carefully removed and saved for ICP-MS extraction.

6.2 Sample Storage

- The 2 mL aliquot of the extract that is stored in a 4 mL glass vial is frozen immediately following extraction. Wrap the cap with approximately 10 cm of PTFE® tape, then freeze on a 45° angle to prevent the vial from bursting.
- The remaining extract in the 8 mL plastic amber vials will remain refrigerated until analysis and for a minimum of 1 year.

7.0 ANALYSIS BY ION CHROMATOGRAPHY

- Typically, 50 samples (including waters, blanks, standards, and filter extracts) complete an IC batch.
- Fresh 18 MΩ·cm deionized water is put into the IC eluent jugs so that new eluent can be generated on each day the IC is being used.
- The eluent will be run through the IC prior to starting an IC batch until a stable baseline is obtained and a consistent pressure is reported.
- The analysis is set up to run a complete calibration curve at the beginning of each anion and cation IC batch. Two 18 MΩ·cm deionized water blanks will be run prior to the calibration curve for sample loop rinsing.
- The QC standard will be run following the calibration standards, at the end of the sample queue, and after every 10-12 samples to ensure instrument stability.
- Waters (18 MΩ·cm deionized water) will be run intermittently throughout each IC batch for sample loop rinsing and assessment of contamination, as well as at the beginning and end of the sequence.

- The Dionex Chromeleon® software is set up to use a linear function to produce a calibration curve for all anions. The Dionex Chromeleon® software is set up to use a linear function to produce a calibration curve for all cations, except ammonium, which uses a cubic function. Peak areas obtained for each ion in each sample are converted to concentration (µg/mL) using the calibration curve obtained for each IC batch.

8.0 DATA VALIDATION

8.1 Level 1 Data Validation

Level 1 data validation of each IC batch involves manual inspection of each chromatogram. After each IC batch is complete, each chromatogram is examined for proper peak identification by the Dionex Chromeleon® software. If necessary, the peak shapes are corrected, and integration windows adjusted. Peak overlaps are also examined and corrected when possible.

Additional level 1 data validation checks for each IC batch include:

- Ensuring that all samples fall within the range of the standards used for the IC batch.
- Investigation and flagging of outliers (e.g. large sulfate peak).
- Examining the consistency between QC standards and the calibration standards.
- Assuring the correlation coefficient is > 0.995 for all relevant ions.
- Verifying that the peak areas in water blanks do not exceed the method detection limits for relevant ions.

8.2 Level 2 Data Validation

After both anion and cation data are placed in the master data base for a given filter, level 2 data validation is performed based on known physical relationships. For level 2 data validation, check the following:

- Comparison of the new values for consistency with long-term concentrations at a given sampling site, particularly with other close data points in the time series.
- Linearity between ammonium and the sum of sulfate and nitrate for filters in each cartridge.
- When possible, comparison with concentrations of the same species measured by a different method (e.g. XRF).
- Comparison of the mass concentration for a filter to the sum of measured chemical species.