

SOP #8

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

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1.0 SCOPE AND APPLICATION

The method described is used for the quantitative determination of anions (defined as chloride (Cl⁻), nitrite (NO₂⁻), bromide (Br⁻), nitrate (NO₃⁻), and sulfate (SO₄²⁻)) and cations (defined as sodium (Na⁺), ammonium (NH₄⁺), potassium (K⁺), magnesium (Mg²⁺), and calcium (Ca²⁺)) in air samples collected on 25 mm PTFE[®] filters. After each 25 mm filter sample is cut in half, following SPARTANSOP #7, samples will be extracted with deionized water and HPLC-grade methanol. The samples will be sonicated for 30 minutes following the addition of methanol and deionized water. After sonication, 1 mL of each sample will be transferred to a baked 4 mL glass vial and the remaining volume (1.5 – 2.0 mL) will be transferred to a clean and dry 8 mL amber, plastic vial. Extracts stored in glass vials are 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
2.0	General reorganization and clarification; addition of calibration standard 3.0 for anions and cations; introduction of quality control standards; updating of sample extraction method, contamination control and preparation of labware	May 24, 2018	 Crystal Weagle

2.0 SUMMARY OF METHOD

The PTFE[®] filters are cut in half prior to extraction for analysis for IC, following SPARTAN SOP #7. Otherwise, no pretreatment is required. 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 spectrometer (AMS).

For analysis by IC, sample extracts are passed 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 will be 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 M Ω -cm deionized water. Since 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 then wrapped in aluminum foil and baked at 500 °C for 5 hours. Following extraction, sample storage vials will be capped and remained unopened unless for analysis. Extracts are then recapped immediately after the volume required for analysis is removed from the storage vial.

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 and are extracted at room temperature. Following extraction, the extraction volume and date of extraction is recorded in the Sample Extraction Log. The glass vials containing 1 mL of extract are frozen immediately after extraction at -20 °C. The remaining volume (~1.5 – 2.0 mL) from each filter extract is stored in plastic, 8 mL amber vials and refrigerated at approximately 4 °C until 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 stored long-term and the remaining samples are discarded.

5.0 EQUIPMENT, ELUENTS, AND STANDARDS

5.1 Laboratory Equipment

5.1.1 Labware

- Volumetric flasks; 10 mL, 25 mL, 1 L, 2 L
- Pipette tips, plastic, disposable; 1- 100 μ L, 10 – 1000 μ L, 1 – 10 mL
- Thermo Dionex 500 μ L Ion Chromatography autosampler vials
- Glass syringes; 100 μ L, 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 PTFE filter-heads

5.1.2 Equipment

- Micropipettes, variable volume
- Refrigerator (4 – 10 °C, nominal)
- Freezer (\leq - 18 °C, nominal)
- Analytical balance capable of 0.001 g readability
- Ultrasonic bath
- Ion Chromatography (Thermo Scientific Model ICS-1100 and Aquion) systems

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 M Ω -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 in the same manner as plastic labware, except once dry they will be sealed with parafilm and stored.
- Tweezers will be wiped with ACS-grade methanol prior to each use.

5.2.2 Glass Vials

- The 25 mL glass vials will be soaked overnight in 1 % ACS-grade nitric acid solution followed by one rinse with 18 M Ω -cm deionized water prior to one rinse with ACS-grade methanol and a triplicate rinse with 18 M Ω -cm deionized water.
- All glass vials are wrapped in aluminum foil in sets of 9 and then baked at 500 °C for 5 hours and allowed to cool to room temperature overnight before being removed from the oven.
- Once baked, glass vials remain in the aluminum foil pouches and are placed inside a sealed plastic bag with “Baked” and the date written on the exterior of the bag with permanent marker.

5.2.3 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. Then, the plungers are placed back in the syringes and 3 full volumes of 18 M Ω -cm deionized water are pushed through each syringe.
- The 100 μ L syringes are used exclusively for HPLC-grade methanol and are rinsed in triplicate with HPLC-grade methanol prior to each use.

5.2.4 PTFE Filter-heads

- Prior to and between uses, the PTFE filter-heads are rinsed in triplicate with 18 M Ω -cm deionized water using a 5 mL syringe and allowed to dry at room temperature between clean Kimwipes.
- When pushing water through the filter becomes difficult compared to new filter heads, the filter head is discarded.

5.2.5 Autosampler Vials and Pipette Tips

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

5.3 Eluents

5.3.1 Anion Chromatography Eluent

- Concentrated stock solutions (250 mM) of sodium carbonate (Na₂CO₃) and sodium bicarbonate (NaHCO₃) are used to prepare the eluent. These solutions are kept refrigerated for use over a 6-month period. New stock solutions are made when they have been fully used or every 6 months, whichever comes first. The stock solutions are made following the steps listed below:
 - a. Dissolve 26.50 g of Na₂CO₃ in 1 L of 18 M Ω -cm deionized water, using a volumetric flask.
 - b. Dissolve 11.50 g of NaHCO₃ in 500 mL of 18 M Ω -cm deionized water, using a volumetric flask.
 - c. Once all the salts are dissolved, transfer the solution to one or two, clean and dry 500 mL plastic HDPE storage bottle and refrigerate.
- The anion eluent is 4.5 mM Na₂CO₃ and 0.8 mM NaHCO₃. Fresh eluent is prepared for each anion IC run. To prepare the eluent, add 36 mL of Na₂CO₃ and 6.4 mL of

NaHCO₃ to a 2 L volumetric flask and dilute to the 2 L mark using 18 MΩ·cm deionized water. Transfer the eluent from the volumetric flask to the plastic IC eluent container for use in the IC system.

5.3.2 Cation Chromatography Eluent

- The cation eluent is 20 mM methanesulfonic acid (MSA). Fresh eluent is prepared for each cation run. To prepare the eluent, add 2.62 mL of MSA to a 2 L volumetric flask and dilute to the 2 L mark using 18 MΩ·cm deionized water. Transfer the eluent from the volumetric flask to the plastic IC eluent container for use in the IC system.

5.4 Calibration Standards

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

5.4.1 Anion Calibration Standards

Anion calibration standards will be prepared directly from the Dionex[®] Seven Anion Standard (Product No. 056933) as shown 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 0.12.00 mL of STD 0.5 in **10 mL** flask**Table 2.** Final anion concentrations in calibration standards ($\mu\text{g/mL}$)

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 will be prepared directly from the Dionex[®] Six Cation-II Standard (Product No. 046070) as described in Table 3. Only 18 M Ω -cm deionized water is to be used to dilute to the volume 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 ($\mu\text{g}/\text{mL}$)

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 M Ω -cm deionized water is to be used to dilute to the volume specified in Table 5.

Table 5. Preparation method summary for anion and cation calibration standards

Standard Label	Method of preparation
Anion QC STD 1.25	313 μL cation 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. Make sure the label is easy to read. 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 PTFE-coated tweezers with a methanol-soaked Kimwipe.
- Using tweezers, place each half-filter in a 25 mL glass vial that has been labelled with the 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 120 μL of HPLC-grade methanol directly onto the filter in each glass vial.
- Using a 5 mL glass syringe, transfer 2.9 mL of 18 M Ω -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 caps.
- Place the 25 mL glass vials in a plastic container 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 PTFE filter-head for each sample, transfer 1 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 PTFE filter-head on the tip of the syringe AFTER the 1 mL aliquot is inside the syringe.
- Use the 5 mL glass syringe and 2 μm PTFE filter-head, transfer the remaining volume in the 25 mL glass vial (1.5 – 2.0 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).

6.2 Sample Storage

- The 1 mL aliquot of the extract that is stored in a 4 mL glass vial is to be 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 eluent (2 L), using 18 M Ω -cm deionized water obtained that day, is prepared for each IC batch.
- 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.
 - For cations, a stable baseline is obtained when the total conductivity of is between 0.4 - 0.5 μS for ≥ 20 minutes. A system pressure should be steady at 900 ± 30 psi.
 - For anions, a stable baseline is obtained when the total conductivity of is between 18.4 – 18.8 μS for ≥ 20 minutes. A system pressure should be steady at 1600 ± 50 psi.

- The analysis will be set up to run a complete calibration curve at the beginning of each anion and cation IC batch. Two 18 M Ω -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 M Ω -cm deionized water) will be run intermittently throughout each IC batch for sample loop rinsing and assessment of contamination.
- 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 ($\mu\text{g}/\text{mL}$) using the calibration curve obtained for each IC batch.
- The analyst will follow the maintenance procedures listed in SPARTAN SOP Maintenance of Ion Chromatography Systems v1.0.