

**APPENDIX A**

**STANDARD OPERATING  
PROCEDURES FOR  
NATIONAL PARK SERVICE FILTER  
PREPARATION, EXTRACTION,  
AND ANION ANALYSIS**

## **Standard Operating Procedure for National Park Service Filter Preparation, Extraction, and Anion Analysis**

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## 1.0 PROCEDURAL SECTION

### 1.1 Purpose and Applicability

This document outlines procedures for the filter preparation and extraction, and the subsequent determination of anions in filter extracts. Analytical procedures outlined are specific to the Dionex Model DX-500 Ion Chromatographs located in Research Triangle Institute's Center for Environmental Measurements and Quality Assurance.

### 1.2 Summary of Method

Nylon filters for collection of anions do not require pretreatment. Quartz fiber filters are impregnated with  $K_2CO_3$  glycerol solution for collection of gaseous  $SO_2$ . Exposed filter samples are extracted by a method appropriate for the analyte(s) of interest. Nylon filters to be analyzed for anions only will be extracted with the eluent used for IC analysis, a dilute sodium carbonate/sodium bicarbonate buffer. Nylon filters to be analyzed for anions and cations will be extracted with deionized water. Carbonate-impregnated quartz fiber filters are extracted with a 0.1% peroxide solution that oxidizes the  $SO_2$  to sulfate ion.

Sample extracts are passed through a column of ion chromatographic resin consisting of polymer beads coated with quaternary ammonium active sites. During passage through the column, anion separation occurs due to the different affinities of the anions for the active resin sites. Following separation, the anions pass through a suppressor column which exchanges all cations for  $H^+$  ions. An eluent which yields a low conducting acid is used. Species are detected and quantified as their acids (e.g., HCl) by a conductivity meter.

### 1.3 Health and Safety Warnings

The NPS ion analysis operations do not involve unusual risks from electrical equipment or chemical exposures. Standard RTI laboratory health and safety precautions will be followed.

### 1.4 Cautions

Laboratory personnel should always wear clean clothes and wash hands thoroughly before performing filter handling and analysis procedures. The use of cleanroom gloves is required and will minimize the potential for laboratory contamination.

### 1.5 Interferences

Large amounts of anions eluting close to the ions of interest will result in an interference. No interferences have been observed in nylon filters samples analyzed to date. If interferences are observed, several steps to increase separation can be taken, such as reducing eluent strength and/or flow rate or replacing the columns.

Analysis of the extracts of  $K_2CO_3$ /glycerol coated filters, which are used for  $SO_2$  collection, requires careful quantitation of the sulfate peak. The sulfate peaks of undiluted extracts are broad and asymmetrical compared to the sulfate peaks of the standards, resulting in low concentrations when peak height is used for quantitation. A 5-fold dilution of the extract reduces the  $K_2CO_3$ /glycerol matrix



interference sufficiently to produce a sulfate peak that is symmetrical and quantifiable. This method is used for all extracts of  $K_2CO_3$ /glycerol coated filters, with careful monitoring of recoveries through the use of spiked extracts.

## 1.6 Personnel Qualifications

Personnel employed to perform ion analysis operations will have at least a Bachelor's Degree in a laboratory science, and will be trained by a supervisor before being allowed to process client samples for the NPS program.

## 1.7 Apparatus and Materials

### 1.7.1 Carbonate-Impregnated Filter Preparation

- Quartz fiber filters (Pallflex NO. 2500 AT-UP, 25 mm, or equivalent)
- Volumetric flask, 1000 mL
- Crystallizing dish (flat bottom and straight sides), 150 mm x 75 mm
- Tweezers
- Glass rod drying racks
- Vacuum drying oven

### 1.7.2 Filter Extraction and Analysis

- Monovettes® (Nalgene)
- Tweezers
- Pipets - an assortment of sizes
- Ultrasonic bath fitted with epoxy-coated test tube rack to hold Monovettes
- Ion chromatograph (Dionex Model DX-500 with LC20 chromatography module, one IP25 isocratic pump, one GP50 gradient pump, two CD20 conductivity detectors, a Dionex AS40 automated sampler and PeakNet Control Windows 95 Workstation) with Dionex AG12A anion guard column, Dionex AS12A anion separator column, and Dionex ASRS-ULTRA anion self-regenerating suppressor column.
- Pressurized eluent reservoirs.
- Volumetric flasks - an assortment of sizes
- Dionex autosampler vials with filter caps

## 1.8 Reagents

Use ACS reagent grade chemicals for the preparation of all solutions. Dry chemicals used for the preparation of calibration standards at 105°C for 2 hours and cool in a desiccator immediately before weighing.

### 1.8.1 Carbonate-Impregnated Filter Preparation

1.8.1.1  $K_2CO_3$ /2% glycerol solution: Mix 200 grams reagent grade potassium carbonate, 100 mL glycerol, and dilute to 1000 mL in a volumetric flask.

### 1.8.2 Carbonate-Impregnated Filter Extraction

1.8.2.1 0.1%  $H_2O_2$ : Dilute 6.68 mL 30% reagent grade  $H_2O_2$  to 2000 mL using deionized water. (Prepare fresh each extraction day.)

### 1.8.3 Anion Analysis

1.8.3.1 Eluent, 0.3mM  $NaHCO_3$ /2.7mM  $Na_2CO_3$ : Dissolve 0.5041 g  $NaHCO_3$  and 5.7235 g  $Na_2CO_3$  in 20 liters deionized water.

1.8.3.2 Mixed Stock Solution, 1000 mg/L  $NO_2^-$ ,  $NO_3^-$ , and  $SO_4^{2-}$ , and 200 mg/L  $Cl^-$ : Dissolve 1.4998 g  $NaNO_2$ , 1.6305 g  $KNO_3$ , 1.8142 g  $K_2SO_4$ , and 0.3297 g  $NaCl$  in 1 liter deionized water.

1.8.3.3 Standard Solution A: Dilute 10 mL mixed stock solution to 100 mL with eluent (100 mg/L  $NO_2^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ , and 20 mg/L  $Cl^-$ ).

1.8.3.4 Standard Solution B: Dilute 10 mL Standard Solution A to 100 mL with eluent (10 mg/L  $NO_2^-$ ,  $NO_3^-$ , and  $SO_4^{2-}$ , and 2 mg/L  $Cl^-$ ).

1.8.3.5 Calibration Standards: Using Standard Solutions A and B, prepare calibration standards with deionized water in 100 mL volumetric flasks as shown in Table 1. Prepare fresh calibration standards weekly.

1.8.3.6 Quality Assurance Stock Solutions: Purchase from CPI International, GFS (Columbus, OH), and/or EM Science (Gibbstown, NJ).

**TABLE 1. PREPARATION OF ANION CALIBRATION STANDARDS**

Standard	Cl ( mg/L)	NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> (mg/L)	mL of Standard Solution/100 mL
<b>STANDARD SOLUTION A</b>			
1	5.0	25.0	25.0
2	2.0	10.0	10.0
3	0.6	3.0	3.0
<b>STANDARD SOLUTION B</b>			
4	0.2	1.0	10.0
6	0.1	0.5	5.0
7	0.04	0.2	2.0
<b>1 ppm STANDARD</b>			
8	0.02	0.1	10.0
9	0.01	0.05	5.0

NOTE: Higher concentration standards can be prepared from Standard A or from the mixed stock solution if needed.

### 1.9 Carbonate-Impregnated Filter Preparation

Use the procedures described below to prepare filters for collection of sulfur dioxide. The chemist will wear cleanroom gloves and handle the filter with forceps or tweezers.

- (1) Purchase quartz fiber filters (Pallflex No. 2500 AT-UP, 25 mM, or equivalent for 24-hour sampling).
- (2) Inspect all filters for imperfections. Analyze at least one blank filter from every 100 for sulfate to verify the manufacturer's pre-established specifications. Return rejected filters to the manufacturer for credit.
- (3) Pour approximately 250 mL of filter coating solution (Section 1.8.1.1) into a 150 mm x 75 mm crystallizing dish (with a flat bottom and straight sides).

- (4) Saturate a batch of 50 quartz, 25-mm filters in the filter-coating solution. Using forceps or tweezers, remove the filters one at a time from the coating solution and drain for a few seconds. Place the filters on a clean glass rod drying rack and dry the filters in an SO<sub>2</sub>-free oven under vacuum at 60 C for 30 minutes, or until dry. Place the filters in a clean, resealable polyethylene bag, then store the bag in a refrigerator.
- (5) Extract and analyze 1% of the newly-made filters for SO<sub>4</sub><sup>2-</sup> background. Reject the batch if the standard deviation of the mean sulfate concentration is more than half the lower quantifiable limit of sulfate.

## 1.10 Sample Collection

Sample collection is not applicable to this SOP because samples are acquired by the PMCC.

## 1.11 Sample Handling

RTI will provide chain-of-custody documentation with all sample shipments to track and ensure that filter samples are collected, transferred, stored, and analyzed by authorized personnel; sample integrity is maintained during all phases of sample handling and analysis; and an accurate written record is maintained of sample handling and treatment from the time of its collection, through the laboratory analytical process, to the eventual relinquishing of all data to the NPS.

## 1.12 Filter Extraction Procedure

### 1.12.1 Nylon Filters

**NOTE:** Nylon filters to be analyzed for anions only will be extracted with the eluent used for IC analysis, a dilute sodium carbonate/sodium bicarbonate buffer. Filters to be analyzed for anions and cations will be extracted with water. The anion eluent produces a large sodium peak in the cation chromatogram that precludes quantitation of the sodium ion in the filter extract and interferes with the quantitation of ammonium ion.

To extract the filters, the analyst will do the following:

- (1) Remove filters to be extracted from the freezer and allow them to equilibrate to room temperature.
- (2) Using gloved hands and tweezers, place each filter in a Nalgene Monovette that has been labeled with the sample I.D. (The label is carefully taped near the top of the Monovette to prevent loss during sonication.)
- (3) Add exactly 10 mL of extraction solution (0.3 mM NaHCO<sub>3</sub>/2.7 mM Na<sub>2</sub>CO<sub>3</sub> or deionized water) using a repipet. (The repipet will be calibrated against a 10 mL Class A volumetric pipet.)
- (4) Push up the Monovette plunger so that no air space remains above the filter.
- (5) Place the batch of Monovettes in an epoxy-coated wire test tube rack, expose them to ultrasonic energy in a bath for 30 minutes, and then allow them to sit at room temperature overnight.



- (6) Record the date of extraction on the RTI Sample Filter Processing Form.

Refrigerate samples that will not be analyzed the following day. Just prior to analysis, re-sonicate for thirty minutes the filters and extracts that have been refrigerated. This will also serve to bring the samples to room temperature.

### 1.13 IC Procedure

- (1) Fill the eluent reservoirs with the eluent.
- (2) Start the eluent flow, activate the self-regenerating suppressor, and allow the baseline to stabilize.
- (3) Inject two eluent blanks to flush the system and to ensure that the system is operating properly.
- (4) Using the calibration schedule, perform the daily multipoint calibration over the range 0.05 to 25.0 ppm  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  (0.01 to 5.0 ppm  $\text{Cl}^-$ ) followed by quality assurance/quality control (QA/QC) samples listed below:
  - QC sample containing concentrations of  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  typical of those found in the mid-range of actual filter extract concentrations.
  - QC sample containing concentrations of  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  typical of those found at the lower end of actual filter extract concentrations.
  - Commercially prepared, NIST-traceable QA sample containing known concentrations of  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ .

If the observed value for any ion differs by more than 10 percent from the known values, identify and correct the problem before analyzing samples.

- (5) Load the sample extracts into the autosampler vials according to the schedule prepared for that day. Typically, fifty field samples are analyzed per day. The daily schedule includes, at a minimum, 3 duplicate samples, 2 spiked samples and 5 QA/QC samples.
- (6) Begin the analysis run, occasionally checking to ensure that the system is operating properly.
- (7) Examine the data at the end of the run. If the concentration of any ion exceeds the upper end of the calibration curve, dilute the sample appropriately and include with the samples to be analyzed the following day.



## 1.14 Calculations and Data Reduction

Peak areas are entered into the computer automatically by the PeakNet software where calculations are performed using a quadratic fit to the calibration data. The quadratic fit yields the following:

$$y_i = ax_i^2 + bx_i + c$$

where:

y = the calculated anion concentration, mg/L

x = the instrument response

Initially, the calibration curves from 0.05 to 10.0 ppm NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> (0.01 to 2.0 ppm Cl<sup>-</sup>) are used for the calculation of the extract anion concentrations. All nitrite, nitrate, and sulfate concentrations that exceed 10 ppm and all chloride concentrations that exceed 2 ppm are recalculated with the 25.0 ppm NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> (5 ppm Cl<sup>-</sup>) standard added to the calibration curve. If a recalculated nitrite, nitrate or sulfate concentration exceeds 25 ppm or a recalculated chloride concentration exceeds 5 ppm, the extract is diluted appropriately (usually 5-fold) to bring the ion concentration into the calibration range and reanalyzed.

## 2.0 QUALITY ASSURANCE AND QUALITY CONTROL

If correlation coefficient does not exceed 0.998, stop the analysis and identify the problem.

Analyze QC samples (see Section 1.14) at the beginning of every analytical run. Compare the results with those obtained during previous QC tests. If the observed concentration of any ion differs from the known value by greater than 10%, stop the analysis until the problem is identified and corrected. Analyze a duplicate sample, a QA/QC sample, and a spiked sample after at least every 20 field samples.

## 3.0 REFERENCE

DRI Document No. 8068.1F4, Appendix D, Section 4.2

# APPENDIX B

## STANDARD OPERATING PROCEDURE FOR NATIONAL PARK SERVICE CATION ANALYSIS



## Standard Operating Procedure for National Park Service Cation Analysis

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Prepared by: \_\_\_\_\_ Date: \_\_\_\_\_

Reviewed by: \_\_\_\_\_ Date: \_\_\_\_\_

Approved by: \_\_\_\_\_ Date: \_\_\_\_\_



## 1.0 Procedural Section

### 1.1 Purpose and Applicability

This document outlines procedures for the extraction and subsequent determination of ammonium, sodium, potassium, calcium, and magnesium ions in nylon filter extracts. Analytical procedures outlined are specific to the Dionex Model DX-500 Ion Chromatograph located in Research Triangle Institute's Center for Environmental Measurements and Quality Assurance.

### 1.2 Summary of Method

Nylon filters for collection of ions do not require pretreatment. Exposed filter samples are extracted by a method appropriate for the analyte(s) of interest. Nylon filters to be analyzed for cations as well as anions will be extracted with deionized water.

Cations in solution are separated when passed through an ion chromatographic column containing surface-sulfonated ion exchange resin; separation is caused by differing affinities of the cations for the active sites on the resin. After separation, the cations pass through a suppressor column which exchanges all anions for OH<sup>-</sup> ions. Species are detected and quantified as their hydroxides by a conductivity meter. The eluent is hydrochloric acid which yields deionized water when passed through the suppressor column.

### 1.3 Health and Safety Warnings

The NPS ion analysis operations do not involve unusual risks from electrical equipment or chemical exposures. Standard RTI laboratory health and safety precautions will be followed.

### 1.4 Cautions

Laboratory personnel should always wear clean clothes and wash hands thoroughly before performing filter handling and analysis procedures. The use of cleanroom gloves is required and will minimize the potential for laboratory contamination.

### 1.5 Interferences

Large amounts of extraneous cations eluting close to the cations of interest will result in an interference. No interferences have been observed in extracts analyzed by RTI to date. If interferences are observed, several steps to increase separation can be taken, such as reducing eluent strength and/or flow rate, or replacing the columns.

### 1.6 Personnel Qualifications

Personnel employed to perform ion analysis operations will have at least a Bachelor's degree in a laboratory science, and will be trained by a supervisor before being allowed to process client samples for the NPS program.



## 1.7 Apparatus and Materials

- Ion chromatograph (Dionex Model DX-500 with LC20 chromatography module, two IP20 isocratic pumps, two CD20 conductivity detectors, a Dionex AS40 automated sampler and PeakNet software) with Dionex CG12A cation guard column, Dionex CS12A cation separator column, and cation self-regenerating suppressor
- Pressurized eluent reservoirs
- Volumetric flasks - an assortment of sizes
- Dionex Autosampler Vials with filter caps

## 1.8 Reagents

Use ACS reagent grade chemicals for the preparation of all solutions

1. Concentrated Eluent Stock Solution, 1 N Methanesulfonic Acid (MSA): Dilute 96.1 g (~65 mL) of 99% MSA to 1 liter with deionized water.
2. Eluent, 20mN Methanesulfonic Acid: Dilute 20 mL 1N MSA to 1 liter using deionized water.
3. Calibration Standard Stock Solutions, 1000 mg/L each  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ , NIST Traceable : Purchase from GFS, Columbus, Ohio.
4. Standard Solution A: Add 10 mL of each stock solution ( $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) to a 100 mL volumetric flask and dilute to the mark with deionized water and mix thoroughly (100 mg/L  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ).
5. Standard Solution B: Dilute 10 mL Standard Solution A to 100 mL with deionized water (10 mg/L  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ).
6. Calibration Standards: Using Standard Solutions A and B, prepare calibration standards with deionized water in 100 mL volumetric flasks as shown in Table 1. Prepare fresh calibration standards weekly.
7. Quality Assurance Stock Solutions: 1000 mg/L each  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ , NIST Traceable : Purchase from CPI International and/or EM Science, Gibbstown, NJ.

**TABLE 1. PREPARATION OF CATION CALIBRATION STANDARDS**

Standard	NH <sub>4</sub> <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup> (mg/L each)	mL of Standard Solution/100 mL
<b>STANDARD SOLUTION A</b>		
1	25.0	25.0
2	10.0	10.0
3	3.0	3.0
<b>STANDARD SOLUTION B</b>		
4	1.0	10.0
5	0.3	3.0
<b>1 ppm STANDARD</b>		
6	0.1	10.0
7	0.05	5.0

### 1.9 Sample Collection

Sample collection is not applicable to this SOP because samples are acquired by the PMCC.

### 1.10 Sample Handling

RTI will provide chain-of-custody documentation with all sample shipments to track and ensure that samples are collected, transferred, stored, and analyzed by authorized personnel; sample integrity is maintained during all phases of sample handling and analysis; and an accurate written record is maintained of sample handling and treatment from the time of its collection, through the laboratory analytical process, to the eventual relinquishing of all data to the client.

### 1.11 Filter Extraction Procedure

Anion and cation analyses will be performed on the same filter extract. Filters to be analyzed for anions and cations will be extracted with deionized water. The anion eluent (sodium carbonated, bicarbonate solution) produces a large sodium peak in the cation chromatogram that precludes



quantitation of the sodium ion in the filter extract and interferes with the quantitation of ammonium ion. Extraction procedures are detailed in the RTI SOP "Standard Operating Procedure for NPS Filter Preparation, Extraction, and Anion Analysis."

### 1.12 IC Procedure

1. Fill the eluent reservoirs with eluent.
2. Start the eluent flow, activate the self-regenerating suppressor, and allow the baseline to stabilize.
3. Inject two eluent blanks to flush the system and to ensure that the system is operating properly.
4. Using the calibration schedule, perform the daily multipoint calibration over the appropriate range followed by quality assurance/quality control (QC/QA) samples listed below:
  - a QC sample with  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  concentrations typical of the higher concentrations found in actual filter extracts.
  - a QC sample with  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  concentrations typical of the lower concentrations found in actual filter extracts.
  - a commercially prepared, NIST-traceable QA sample containing known concentrations of  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ .If the observed value for any cation differs by more than 10 percent from the known value, identify and correct the problem before analyzing samples.
5. Load the filter extracts into the autosampler vials according to the schedule prepared for that day. The daily schedule includes duplicate samples, spiked samples and QA/QC samples.
6. Begin the analysis run, occasionally checking to ensure that the system is operating properly.
7. Examine the data at the end of the run. If the  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , or  $\text{Mg}^{2+}$  concentration of any extract exceeds the upper end of its calibration curve, dilute the extract appropriately and analyze that day or include with the samples to be analyzed the following day.

### 1.13 Calculations and Data Reduction

Peak areas are entered into the computer automatically where calculations are performed using a quadratic fit to the calibration data. The quadratic fit yields the following:

$$y_i = ax_i^2 + bx_i + c$$

where:

y = the calculated cation concentration, mg/L

x = the instrument response

Initially, the calibration curve from 0.05 to 10.0 ppm is used for the calculation of the extract  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  concentrations. All cation concentrations that exceed 10 ppm are recalculated with the 25.0 ppm standard added to the calibration curve. If a recalculated cation concentration exceeds 25 ppm, the extract is diluted appropriately (usually 5-fold) to bring the cation concentration into the calibration range and reanalyzed.

### 2.0 Quality Control and Quality Assurance

Compare the regression parameters (a, b, c and correlation coefficient) for the standard curves with those obtained in the past. If they exceed the control limits, stop the analysis and identify the problem.

Analyze QC data (see Section 1.12) at the beginning of every analytical run. Compare the results with those obtained during previous QC tests. If the observed concentration of any cation differs from the known value by greater than 10%, stop the analysis until the problem is identified and corrected. Analyze a duplicate sample, a QA/QC sample, and a spiked sample after at least every 20 field samples.

### 3.0 Reference

DRI Document No. 8068.1F4, Appendix D, Section 4.2