Standard Operating Procedure for $PM_{2.5}$ Anion Analysis

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1.0 Procedural Section

1.1 Purpose and Applicability

This document outlines procedures for the extraction and subsequent determination of anions in filter extracts. Analytical procedures outlined are specific to the ion chromatographs used in RTI's Ion Analysis Laboratory.

1.2 Summary of Method

Collected aerosol filter samples are extracted by a method appropriate for the analyte of interest. Sample extracts are passed through a resin consisting of polymer beads coated with quaternary ammonium active sites. Anion separation is 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 that yields a low-conducting acid is used. Species are detected and quantified as their acids by use of a conductivity meter.

In a laboratory evaluation of the accuracy of the method, spiked $PM_{2.5}$ filter extracts and quality assurance/quality control (QA/QC) samples were analyzed for sulfate and nitrate ions. The accuracy (expressed as % recovery) achieved using the subject method is presented in Table 1.

To test the precision of the method, $PM_{2.5}$ filter extracts were analyzed in duplicate, and the blank extracting solution and a low-level QC sample were analyzed seven times each. The results are summarized in Table 2.

Table 1. Accuracy Values for QA/QC Samples and Spiked $PM_{2.5}$ Filter Extracts

Analyte	QA/QC Sample Average % Recovery* (range)	Spiked Extract Average % Recovery* (range)
SO_4	100.5 (97.5–104.2) n = 187	99.9 (98.2–100.7) n = 61
NO_3^-	99.6 (96.9–103.0) n = 187	99.3 (97.5–103.3) n = 61

* % Recovery = (concentration found/concentration expected) × 100

Table 2. Precision Values for $PM_{2.5}$ Filter Extracts, Extracting Solution, and QC Samples

Analyte	Sample Type		
	$PM_{2.5}$ Filter Extracts Average RSD (range)**	**Blank Extracting Solution Average (Standard Deviation), n = 7**	**QC Sample (0.600 ppm NO_3, 1.200 ppm SO_4) RSD, n = 7**
$SO_4^{=}$	0.2 (0.0–1.4)	0.000 (0.000)	0.3
NO_3^-	0.3 (0.0–1.7) for 86 duplicates for 86 duplicates	0.000 (0.000)	0.2

** RSD = relative standard deviation (the standard deviation divided by the average value and expressed as a percentage)

1.3 Health and Safety Warnings

The $PM_{2.5}$ 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 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 or Teflon filter 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 guard and/or separator column.

1.6 Personnel Qualifications

Personnel employed to perform ion analysis operations will have at least an associate's degree in a laboratory science and will be trained by a supervisor before being allowed to process client samples for the $PM_{2.5}$ program.

1.7 Apparatus and Materials

1. Disposable centrifuge tubes with screw caps, 50 mL (polypropylene).
2. Calibrated Rainin electronic pipette (10 mL capacity) and adjustable Eppendorf pipette (10–100μL).
3. Tweezers.
4. Ultrasonic bath fitted with epoxy-coated test-tube rack to hold centrifuge tubes.

5. Mechanical shaker.
6. Ion chromatograph complete with workstation (see Table 3).
7. Pressurized eluent and regenerant reservoirs.
8. Volumetric flasks (an assortment of sizes).
9. Dionex autosampler vials with filter caps.
10. Coldroom at ≤4ºC.
11. Refrigerators.

Table 3. Configurations of Ion Chromatographs Used for Anion Analysis

Instrument ID	A1	A2	A3	A4	A5	A6
Dionex Model	DX-500	DX-500	DX-500	DX-600	DX-600	ICS-2000
Chromatography Module	LC20	LC20	LC20	LC30	LC30	None
Pump	GP50	IP25	IP20	IP25	IS25	IS2000
Conductivity Detector	CD20 DS3 Cell	CD20 DS3 Cell	CD20 DS1A Cell	CD20 DS3 Cell	CD25 DS3 Cell	Built-in DS6
Autosampler	AS40	AS40	AS40	AS40	AS40	AS40
Software	Windows 2000 Dionex PeakNet 5.2	Windows 2000 Dionex PeakNet 5.2	Windows 2000 Dionex PeakNet 5.2	Windows 2000 Dionex PeakNet 5.2	Windows 2000 Dionex Chromeleon	Windows XP Dionex Chromeleon
Guard Column	AG12A	AG12A	AG12A	AG12A	AG12A	AG12A
Separator Column	AS12A	AS12A	AS12A	AS12A	AS12A	AS12A
Suppressor Column	AMMSIII	AMMSIII	AMMSIII	AMMSIII	ASRS Ultra Auto-regen mode	ASRS Ultra Auto-regen mode
Other	—	—	—	—	—	Built-in eluent generator (not used)

1.8 Ion Chromatography Reagents

Use ACS reagent-grade chemicals and 18.2MΩ-cm deionized water for the preparation of all solutions.

1. Concentrated eluent (100X), 30mM $NaHCO_3$/270mM Na_2CO_3: Dissolve 2.5209 g $NaHCO_3$ and 28.6178 g Na_2CO_3 in 1 L of deionized water (Note: Do NOT dry the salts that are used to prepare the eluent).

2. Working eluent, 0.3mM $NaHCO_3$/2.7mM Na_2CO_3: Dilute 200 mL concentrated eluent to 20 L with deionized water.
3. Regenerant, 0.025N H_2SO_4: Dilute 100 mL 5.0N H_2SO_4 to 20 L with deionized water (Note: This reagent is not used for an IC system equipped with a self-regenerating suppressor.).

1.9 Calibration Standards

Use ACS reagent-grade chemicals and 18.2MΩ-cm deionized water for the preparation of all solutions. Dry the salts used for the preparation of calibration standards at 105°C for 2 hours and cool in a desiccator immediately before use.

1. Mixed Stock Solution, 1000 mg/L NO_2^-, NO_3^-, and SO_4^{2-}, and 200 mg/L $C1^-$: Dissolve 1.4998 g $NaNO_2$, 1.3708 g $NaNO_3$, 1.8142 g K_2SO_4, and 0.3297 g NaCl in 1 L of deionized water (Note: These are the four anions typically analyzed in the Ion Analysis Laboratory. $PM_{2.5}$ filter extracts will be analyzed using standards prepared from this mixed-stock solution.).
2. Standard Solution A (100 mg/L NO_2^-, NO_3^-, SO_4^{2-}, and 20 mg/L $C1^-$): Dilute 10 mL mixed-stock solution to 100 mL with deionized water.
3. Standard Solution B (10 mg/L NO_2^-, NO_3^-, and SO_4^{2-}, and 2 mg/L $C1^-$): Dilute 10 mL Standard Solution A to 100 mL with deionized water.
4. Calibration Standards: Using Standard Solutions A and B, prepare calibration standards with deionized water in 100 mL volumetric flasks as shown in Table 4. Prepare fresh calibration standards weekly.

Table 4. Preparation of Anion Calibration Standards

Standard	NO_3^-, SO_4^{2-} (mg/L)	mL of Standard Solution/100 mL
Standard Solution A		
1	25.0	25.0
2	10.0	10.0*
3	3.0	3.0
Standard Solution B		
4	1.0	10.0*
6	0.5	5.0
7	0.2	2.0
1 mg/L STANDARD (Standard 4)		
8	0.1	10.0*
9	0.05	5.0*

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

*For these solutions, use two times the stated mL of standard solution in a 200 L flask.

1.10 Quality Control Solutions

Use ACS reagent-grade chemicals and 18.2MΩ-cm deionized water for the preparation of all solutions. Dry the salts used for the preparation of calibration standards at 105°C for 2 hours and cool in a desiccator immediately before use. Quality control solutions must be prepared independent of the calibration solutions.

1. Chloride Stock Solution, 1000 mg/L $C1^-$: Dissolve 0.8243 g NaCl in 500 mL of deionized water.
2. Nitrite Stock Solution, 1000 mg/L NO_2^-: Dissolve 0.7499 g $NaNO_2$ in 500 mL of deionized water.
3. Nitrate Stock Solution, 1000 mg/L NO_3^-: Dissolve 0.6854 g $NaNO_3$ in 500 mL of deionized water.
4. Sulfate Stock Solution, 1000 mg/L SO_4^{2-}: Dissolve 0.9071 g K_2SO_4, in 500 mL of deionized water.
5. QC-Intermediate Solution, 10 mg/L $C1^-$, 20 mg/L NO_2^-, 30 mg/L NO_3^-, and 60 mg/L SO_4^{2-}: Pipette 1 mL of 1000 mg/L $C1^-$, 2 mL of 1000 mg/L NO_2^-, 3 mL of 1000 mg/L NO_3^-, and 6 mL of 1000 mg/L SO_4^{2-} into a 100 mL volumetric flask and dilute to the mark with deionized water.
6. QC Samples: Using the QC-intermediate solution, prepare calibration standards with deionized water in 100 mL volumetric flasks as shown in Table 5. Prepare fresh calibration standards weekly.

Table 5. Preparation of Anion Quality Control Samples

QC Sample ID	mL QC-Intermediate Solution	Final Volume, mL (Volumetric Flask Size)	NO_3^- Conc (mg/L)	SO_4^{2-} Conc (mg/L)
QC-LOW	2.0	100	0.6	1.2
QC-MED	5.0	100	1.5	3.0
QC-HIGH	10.0	50	6.0	12.0

1.11 Quality Assurance Solutions

Use commercially prepared, NIST-traceable solutions to prepare an intermediate quality assurance solution known concentrations of $C1^-$, NO_2^-, NO_3^-, and SO_4^{2-}. Solutions can be purchased from CPI (www.cpichem.com) or GFS Chemicals (www.gfschemicals.com).

1. QA-Intermediate Solution, 10 mg/L $C1^-$, 20 mg/L NO_2^-, 30 mg/L NO_3^-, and 60 mg/L SO_4^{2-}: Pipette 1 mL of 1000 mg/L $C1^-$, 2 mL of 1000 mg/L NO_2^-, 3 mL of 1000 mg/L NO_3^-, and 6 mL of 1000 mg/L SO_4^{2-} into a 100 mL volumetric flask and dilute to the mark with deionized water.

2. Using the QA-intermediate solution, prepare calibration standards with deionized water in 100 mL volumetric flasks as shown in Table 6. Prepare fresh quality assurance samples as needed.

Table 6. Preparation of Anion Quality Assurance Samples

QC Sample ID	mL QA-Intermediate Solution	Final Volume, mL (Volumetric Flask Size)	NO3- Conc (mg/L)	SO42- Conc (mg/L)
QA-CPI_LOW	2.0	100	0.6	1.2
QA-CPI_MED-HI	10.0	100	3.0	6.0

1.12 Sample Collection

Sample collection is not applicable to this SOP because samples are acquired by the state agency responsible for exposing the filters.

1.13 Sample Handling

Note: Additional information on this topic can be found in the *Standard Operating Procedure for the Sample Handling and Archiving Laboratory (SHAL)*, Research Triangle Institute, Center for Environmental Measurements and Quality Assurance, 2001.

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 will be maintained during all phases of sample handling and analysis; and an accurate written record will be 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.

Upon initial receipt of filters, RTI will prepare a Filter Inventory Sheet containing the filter identification numbers, box numbers, date received, date inspected, and the number of filters rejected. This sheet will allow laboratory personnel to select and use the filter boxes in the proper sequence.

1.14 Filter Extraction Procedure

1.14.1 Nylon Filters

Note: Nylon filters to be analyzed for nitrate 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 18.2MΩ-cm deionized 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 polypropylene centrifuge tube that has been labeled with the sample ID printed on a durable (water-resistant) label.
3. Label two 50-mL extraction tubes as Reagent Blank DI H_2O and Reagent Blank Eluent. The eluent blank will not be prepared if there are no "nitrate only" samples to be analyzed with the batch.
4. Add 25.0 mL of extraction solution (2.7 mM Na_2CO_3/0.3 mM $NaHCO_3$ for subsequent anion analysis or deionized water for subsequent anion and cation analysis) using a calibrated automatic pipette.
5. Screw the cap tightly on the centrifuge tube.
6. Ensure that the filter is completely submerged in the extraction solution.
7. Place the batch of centrifuge tubes in an epoxy-coated wire test-tube rack and place the extraction rack in the ultrasonic bath. Make sure that the water level of the ultrasonic bath is higher than the extraction solution level but below the screw cap. Sonicate for 60 minutes.

CAUTION:	Monitor the bath temperature during sonication. The temperature should not exceed 27°C. Add ice initially to lower the temperature, and add ice as necessary during the sonication to maintain an acceptable temperature.

8. Install the extraction racks on the mechanical shaker and shake overnight in a cold room (≤4°C) at approximately 60 cycles per minute.
9. Record the date of extraction on the RTI Sample Log Form.
10. Store the extracts in a refrigerator until analysis.

1.14.2 Teflon Filters

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 polypropylene centrifuge tube that has been labeled with the sample ID printed on a durable (water-resistant) label.
3. Label one 50-mL extraction tube as "Reagent Blank DI H_2O." Remove the caps from all 50-mL extraction tubes. To prevent contamination place the caps in an upside-down position.
4. Using an Eppendorf 100-μL pipette, wet the entire surface of each Teflon filter with 100 μL of nanopure ethanol. This is done by very slowly pipetting the ethanol on the center of the filter. Capillary action will distribute the ethanol over the entire surface. The "reagent blank" tube will not contain a filter. Add the 100 μL of ethanol directly to the bottom of the tube.

   Note: Before proceeding, visually inspect each filter to be sure that the entire filter surface is wet.

5. Using a calibrated automatic pipette, add 25.0 mL of deionized water to each extraction tube. The deionized water must have a resistance of at least 18.2MΩ-cm.
6. Recap all extraction tubes tightly to prevent leakage during the extraction procedure. Be sure that the exposed area of the filter is completely immersed in the extraction solution.
7. Place the extraction rack in the ultrasonic bath. Make sure that the water level of the ultrasonic bath is higher than the extraction solution level but below the screw cap.

CAUTION:	Monitor the bath temperature during sonication. The temperature should not exceed 27°C. Add ice initially to lower the temperature, and add ice as necessary during the sonication to maintain an acceptable temperature.

8. Install the extraction racks on the mechanical shaker and shake overnight in a cold room (≤4°C) at approximately 60 cycles per minute.
9. Record the date of extraction on the RTI Sample Log Form.
10. Store the extracted filters in the refrigerator prior to analysis.

1.15 IC Procedure

1. Fill the eluent reservoirs with the eluent and the regenerant reservoirs with regenerant and pressurize the reservoirs.
2. Start the eluent flow at 1.5 mL/min, and if using a self-regenerating suppressor, activate it. Allow the baseline to stabilize.
3. Inject two deionized water 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 NO_3^- and SO_4^{2-} followed by QA/QC samples listed below.

   - A QC sample containing concentrations of NO_3^- and SO_4^{2-} typical of those found in the mid-range of actual filter extract concentrations (QC-MED).
   - A QC sample containing concentrations of NO_3^- and SO_4^{2-} typical of those found at the lower end of actual filter extract concentrations (QC-LOW).
   - A commercially prepared, NIST-traceable QA sample containing known concentrations of NO_3^- and SO_4^{2-} (QA-CPI_LOW).

   If the observed value for nitrate or sulfate differs by more than 10% from the known values, identify and correct the problem before analyzing samples.
5. Remove sample extracts from the refrigerator and allow to equilibrate to room temperature (Note: This should be performed while the system is stabilizing and the calibration is being conducted.)
6. Load the sample extracts into the autosampler vials according to the schedule prepared for that day. Typically, 50 field samples are analyzed per day. The daily schedule includes, at a minimum, 3 duplicate samples, 2 spiked samples, and 5 QA/QC samples.
7. Begin the analysis run, occasionally checking to ensure that the system is operating properly.
8. 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.

1.16 Calculations and Data Reduction

Peak areas are entered into the computer 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, μg/L
x = the instrument response

Initially, the calibration curve from 0.05 to 10.0 ppm is used for the calculation of the extract nitrate and sulfate concentrations. All sulfate and/or nitrate concentrations that exceed 10 ppm are recalculated with the 25.0 ppm standard added to the calibration curve. If a recalculated nitrate or sulfate concentration exceeds 25 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

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 QA/QC samples (see Sections 1.10 and 1.11) at the beginning of every analytical run. Compare the results with those obtained during previous QA/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.