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

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RTI INTERNATIONAL

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

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1.0 Procedural Section

1.1 Purpose and Applicability

This document outlines procedures for the extraction and subsequent determination of ammonium, sodium, and potassium ions in filter extracts. Analytical procedures outlined are specific to the ion chromatographs used in RTI's ion analysis laboratories.

1.2 Summary of Method

Cations in solution are separated when passed through a surface-sulfonated ion-exchange resin due to the 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- ions. Species are detected and quantified as their hydroxides by a conductivity meter. The eluent is sulfuric acid, which yields deionized water when passed through the suppressor column.

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 sodium, ammonium, and potassium 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)
NH_4^+	99.0 (91.0 - 108.0) n = 59	99.4 (96.4 - 105.9) n = 14
Na^+	104.2 (100.0 - 107.7) n = 20	101.8 (97.0 - 105.1) n = 5
K^+	103.0 (96.6 - 106.3) n = 20	99.2 (97.0 - 102.7) n = 5

*% 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 (Std Dev), n = 7**	**0.05 ppm QC Sample RSD, n = 7**
NH_4^+	0.6 (0.1 - 1.6) for 13 duplicates	0.000 (0.000)	2.0
Na^+	8.0 (0.6 - 19.8) for 17 duplicates	0.001 (0.003)	13.3
K^+	1.1 (0.1 - 3.1) for 17 duplicates	0.000 (0.000)	2.0

** 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 cations eluting close to the ions 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 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

- Disposable centrifuge tubes with screw caps, 50 mL(polypropylene)
- Calibrated Rainin electronic pipette (10-mL capacity) and adjustable Eppendorf pipette (10-100µ)
- Tweezers

- Ultrasonic bath fitted with epoxy-coated test tube rack to hold centrifuge tubes
- Mechanical shaker
- Ion chromatograph complete with workstation (See Table 3.)
- Pressurized eluent reservoirs
- Volumetric flasks in an assortment of sizes
- Dionex autosampler vials with filter caps
- Coldroom at ≤4º C
- Refrigerators.

Table 3. Configurations of Ion Chromatographs Used for Cation Analysis

Instrument ID	C1	C2	C3	C4
Dionex Model	DX-500	DX-600	ICS-2000	DX-600
Chromatography Module	LC20 (no temperature unit)	LC30	None (built in temperature unit)	LC30
Pump	IP20	IP25	IS2000	IS25
Conductivity Detector	CD20 DS1A Cell	CD20 DS3 Cell	Built-in DS6 cell	CD25 DS3 Cell
Autosampler	AS40	AS40	AS40	AS40
Software	Windows 2000 Dionex PeakNet 5.2	Windows 2000 Dionex PeakNet 5.2	Windows XP Dionex Chromeleon	Windows 2000 Dionex Chromeleon
Guard Column	none	none	none	none
Separator Column	CS12A	CS12A	CS12A	CS12A
Suppressor Column	CSRS-300 auto regenerator	CSRS-ultra auto regenerator	CSRS-ultra auto regenerator	CSRS-ultra auto regenerator
Other	-	-	Built-in eluent regenerator (not used)	EG50 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 Stock Solution: 5N H_2SO_4, purchased from VWR Scientific
2. Working Eluent, 22mN Sulfuric Acid: Dilute 4.4 mL 5N H_2SO_4 to 1 liter using deionized water. Sonicate for 15 minutes just prior to use to de-gas the solution.

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. Calibration Standard Stock Solution, 1000 mg/L each NH_4^+, Na^+, and K^+: Dissolve 2.9654 g NH_4Cl, 2.5422 g NaCl, and 2.2284 g K_2SO_4 in 1 liter deionized water.
2. Standard Solution A: Dilute 10 mL stock solution to 100 mL with deionized water (100 mg/L NH_4^+, Na^+, K^+).
3. Standard Solution B: Dilute 10 mL Standard Solution A to 100 mL with deionized water (10 mg/L NH_4^+ , Na^+, K^+).
4. 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.

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 (QC) solutions must be prepared independent of the calibration solutions.

1. Sodium QC Stock Solution, 1000 mg/L Na^+: Dissolve 1.2711 g NaCl in 500 mL of deionized water
2. Ammonium QC Stock Solution, 1000 mg/L NH_4^+: Dissolve 1.4827 g NH_4Cl in 500 mL of deionized water
3. Potassium QC Stock Solution, 1000 mg/L K^+: Dissolve 1.1142 g K_2SO_4 in 500 mL of deionized water
4. QC-Intermediate Solution, 100 mg/L each Na^+, NH_4^+, and K^+: Pipette 10 mL of 1000 mg/L Na^+, 10 mL of 1000 mg/L NH_4^+, and 10 mL of 1000 mg/L K^+ into a 100-mL volumetric flask and dilute to the mark with deionized water.
5. QC Samples: Using the QC-intermediate solution, prepare QC samples with deionized water in 100-mL volumetric flasks, as shown in Table 5. Prepare fresh QC samples as needed.

Table 4. Preparation of Cation Calibration Standards

Standard	NH_4^+, Na^+, K^+ (mg/L each)	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
5	0.3	3.0
1 mg/L STANDARD (Standard 4)		
6	0.1	10.0
7	0.05	5.0

1.11 Quality Assurance Solutions

Use commercially prepared, NIST-traceable solutions to prepare an intermediate QA solution with known concentrations of Na^+, NH_4^+, and K^+. Solutions can be purchased from CPI (www.cpichem.com) or GFS Chemicals (www.gfschemicals.com).

1. QA-Intermediate Solution, 100 mg/L each Na^+, NH_4^+, and K^+: Pipette 10 mL of 1000 mg/L Na^+, 10 mL of 1000 mg/L NH_4^+, and 10 mL of 1000 mg/L K^+ into a 100-mL volumetric flask and dilute to the mark with deionized water
2. Prepare QA samples with deionized water in 100-mL volumetric flasks, as shown in Table 6. Prepare fresh QA samples as needed.

Table 5. Preparation of Anion Quality Control Samples

QC Sample ID	mL QC-Intermediate	Final Volume, mL (volumetric flask size)	Na^+, NH_4^+, and K^+ Conc (mg/L)
RTI 2 ppm QC	2.0	100	2.0
RTI 5 ppm QC	5.0	100	5.0

Table 6. Preparation of Anion Quality Assurance Samples

QA Sample ID	Dilute	Final Volume, mL (volumetric flask size)	Na^+, NH_4^+, and K^+ Conc (mg/L)
GFS 4.0 ppm QA	4.0 mL QA-Intermediate	100	4.0
GFS 0.4 ppm QA	10 mL GFS 4.0 ppm QA	100	0.4

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 SOP *Sample Receiving, Shipping, and Archiving Procedures for the $PM_{2.5}$ Chemical Speciation Program*, RTI International, Center for Environmental Measurements and Quality Assurance, 1999.

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.

Upon initial receipt of filters, RTI will prepare a Filter Inventory Sheet containing the filter identification numbers, box numbers, date received, date inspected, and number of filters rejected. This form 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: Filters to be analyzed for anions and cations or for cations only will be extracted with deionized water.

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 a 50-ml extraction tube as "Reagent Blank DI H_2O."
4. Add 25.0 mL of deionized water to each tube using a calibrated automatic pipette.
5. Screw the cap tightly on the centrifuge tube.
5. Ensure that the filter is completely submerged in the extraction solution.
6. 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.

7. Install the extraction racks on the mechanical shaker and shake overnight in a cold room (≤4°C) at approximately 60 cycles per minute.
8. Record the date of extraction on the RTI Sample Log Form.
9. 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 polypropylene centrifuge tube that has been labeled with the sample ID printed on a durable (water-resistant) label.
3. Label a 50-ml extraction tube as "Reagent Blank DI H_2O."
4. Remove the caps from all 50-ml extraction tubes. To prevent contamination, place the caps in an upside-down position.
5. 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 DI H_2O" 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.
6. 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.

7. 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.

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

1.15 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 four 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 the GFS 4.0 ppm QA sample. If the observed value for any cation differs by more than 10% 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 NH_4^+, Na^+, or K^+ 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.

1.16 Calculations and Data Reduction

For ion chromatographs using Dionex PeakNet® sofrware, peak areas are automatically 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 cation concentration, µg/L
x	=	the instrument response

For ion chromatographs using Chromeleon® software, NH_4^+ peak areas are automatically entered into the computer where calculations are performed using a cubic fit to the calibration data. The quadratic fit yields the following:

$$y_i = ax_i^3 + bx_i^2 + cx_i + d$$

where

y	=	the calculated NH_4^+ concentration, µg/L
x	=	the instrument response

The cubic fit for NH_4^+ is used at the recommendation of Dionex. Na^+ and K^+ concentrations are calculated using a quadratic fit as described above.

The calibration curve from 0.05 to 10.0 ppm is used for the calculation of the extract NH_4^+, Na^+, and K^+ concentrations. If a cation concentration exceeds 10 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 samples (see Section 1.13) 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.