Standard Operating Procedure for PM2.5 Anion Analysis

Environmental and Industrial Measurements Division
Research Triangle Institute, Research Triangle Park, North Carolina

Prepared by: Eva D. Hardison Date: 8/14/03

Reviewed by: James B. Flanagan Date: 8-15-03

Approved by: RK Mayanovic Date: 8-15-03

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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 Dionex Model DX-500 Ion Chromatograph.

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 which yields a low conducting acid is used. Species are detected and quantified as their acids by a conductivity meter.

In a laboratory evaluation of the accuracy of the method, spiked PM2.5 filter extracts and quality assurance/quality control samples were analyzed for sulfate and nitrate ions. The accuracy (expressed as %recovery) achieved using the subject method are presented in Table 1.

To test the precision of the method, PM2.5 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 PM2.5 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 (Std Dev), 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 PM2.5 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.

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 PM2.5 program.

1.7 Apparatus and Materials

(1) Centrifuge tubes (Nalgene)
(2) Pipets - an assortment of sizes
(3) Ultrasonic bath fitted with epoxy-coated test tube rack to hold centrifuge tubes
(4) Mechanical shaker
(5) Ion chromatograph (Dionex Model DX-500 with LC20 chromatography module, an IP25 or IP20 isocratic pump or a GP50 gradient pump, a CD20 conductivity detector, a Dionex AS40 automated sampler and PeakNet Control Windows 95 or 98 Workstation) with Dionex AG12A anion guard column, Dionex AS12A anion separator column, and Dionex AMMS-III anion micromembrane suppressor column.
(6) Pressurized eluent and regenerant reservoirs.
(7) Volumetric flasks - an assortment of sizes
(8) Dionex autosampler vials with filter caps

1.8 Reagents

Use ACS reagent grade chemicals and 18.2MΩ-cm deionized water 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 use.

(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 liter deionized water.

(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.

(4) 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 liter deionized water. (Note: These are the four anions typically analyzed in the Ion Analysis Labotatory. PM2.5 filter extracts will be analyzed using standards prepared from this mixed stock solution).

(5) 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.

(6) 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.

1.9 Calibration

Using Standard Solutions A and B, prepare calibration standards with deionized water in 100 mL volumetric flasks as shown in Table 3. Prepare fresh calibration standards weekly.

Table 3. 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.

1.10 Sample Collection

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

1.11 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 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.

1.12 Filter Extraction Procedure

1.12.1 Nylon Filters

NOTE: Nylon filters to be analyzed for anions only (sulfate and nitrate) 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 Nalgene centrifuge tube that has been labeled with the sample ID. (The label is carefully taped near the top of the Centrifuge tube to prevent loss during sonication.)

(3) Label two 50-ml extraction tubes as "Reagent Blank DI H_2O" and "Reagent Blank Eluent".

(4) Add 25.0 mL of extraction solution (2.7mM Na_2CO_3/0.3mM $NaHCO_3$ for subsequent anion analysis or deionized water for subsequent anion and cation analysis) using a calibrated automatic pipette.

(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.

(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.

1.12.2 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 Nalgene centrifuge tube that has been labeled with the sample ID. (The label is carefully taped near the top of the centrifuge tube to prevent loss during sonication.)

(3) Label one 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 Epppendorf 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.

(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.

(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.

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.

(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.

1.13 IC Procedure

1. Fill the eluent reservoirs with the eluent and the regenerant reservoirs with regenerant.

2. Start the eluent flow at 1.5 mL/min, pressurize the regenerant reservoir, and 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 control/quality assurance (QC/QA) 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.
- Aa QC sample containing concentrations of NO_3^- and SO_4^{2-} typical of those found at the lower end of actual filter extract concentrations.
- A commercially prepared, NIST-traceable quality assurance sample containing known concentrations of NO_3^- and SO_4^{2-}.

If the observed value for nitrate or sulfate 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 quality control/quality assurance 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 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 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 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 quality control 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