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Standard Operating Procedure for the Analysis of Anions and Cations in PM2.5 Speciation Samples by Ion Chromatography

MLD064
Revision 2.0

Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
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Standard Operating Procedure for the Analysis of Anions and Cations in PM2.5 Speciation Samples by Ion Chromatography

1. Introduction

This document describes the methodology used by the Monitoring and Laboratory Division (MLD) Inorganics Laboratory Section (ILS) staff to analyze anions and cations in PM2.5 samples by ion chromatography (IC).

2. Summary of Method

Method MLD064 determines anions (nitrate and sulfate) and cations (sodium, ammonium, and potassium) collected on nylon filters exposed to ambient air, which are submitted to the laboratory by site operators. The filters are extracted in Nanopure water by sonicating for one hour, shaking for one hour, and storing overnight in a refrigerator. The extract is analyzed by ion chromatography using a system comprised of a guard column, analytical column, self-regenerating suppressor, eluent generator, and a conductivity detector. Peak analysis is determined using Chromeleon Chromatography software. This standard operating procedure (SOP) should be used in conjunction with the applicable equipment manuals.

3. Acronyms and Definitions

Acronym or Term	Definition
ASTM	American Society for Testing and Materials
EGC	Eluent Generator Cartridge
IC	Ion Chromatography
ICS	Ion Chromatography System
KOH	Potassium hydroxide
LCL	Lower control limit
LIMS	Laboratory Information Management System
LOQ	Limit of quantitation
LWL	Lower warning limit
MΩ-cm	Mega Ohm-centimeter
MDL	Method detection limit
µL	Microliter

Acronym or Term	Definition
µm	Micrometer
mL	Milliliter
mm	Millimeter
MSA	Methanesulfonic acid
SDS	Safety Data Sheets
NAAQS	National Ambient Air Quality Standards
NIST	National Institute of Science and Technology
NLB	Northern Laboratory Branch
PM2.5	Particulate Matter with diameter of less than 2.5 micrometers
QC	Quality control
QCM	Quality control manual
RL	Reporting limit
RPD	Relative percent difference
SOP	Standard operating procedure
UCL	Upper control limit
UWL	Upper warning limit

4. Interferences and Limitations

4.1. Co-elution interference can be caused by ions with retention times that are similar to and thus overlap those of the ions of interest, or by large amounts of any one anion or cation that interferes with the peak resolution of an ion with closely matching retention time. Sample dilution or a change in eluent concentration can reduce these co-elution interferences.

4.2. Interferences may be caused by contaminants in the reagent water, reagents, glassware, nylon filters, and other sample processing apparatus that could lead to an elevated baseline or detectable concentrations of any of the ions of interest. A reagent water blank, extraction water blank, and a filter blank are run with each set of samples to monitor these possible sources of contamination.

4.3. Losses in retention time and resolution can be signs of column deterioration. Monitoring analyte retention times and system backpressure will assist in determining when an analytical column or guard column may need to be replaced.

5. Personnel Qualifications and Training

Prior to performing this method, new personnel must be trained by staff with expert knowledge of this method. Personnel must be trained to understand the program's requirements per any applicable State and federal regulations and guidance, and this SOP. Personnel will also be trained on how to safely and properly operate the equipment needed to perform the method, the quality assurance components, and LIMS functionality pertaining to the program.

Personnel should provide an initial demonstration of capability prior to performing this method on real-world samples (i.e., data for record).

Training will be documented and maintained by the laboratory supervisor.

This SOP assumes familiarity with the operation of Dionex ion chromatography systems. For detailed operation instructions refer to the Dionex operations manual.

6. Safety Requirements

All personnel must follow the general health and safety requirements found in NLB's Chemical Hygiene Plan.

Analyst must read the safety data sheets (SDS) for all chemicals they use. Analyst can reference additional instrument safety concerns in the safety section of the ion chromatography system operator's manual.

7. Hazardous Waste

Eluent generator cartridges contain methane sulfonic acid (MSA) or potassium hydroxide (KOH), and therefore should be disposed of during hazardous waste pickups. Contact the NLB hazardous waste coordinator to have waste included during pickup.

8. Equipment, Supplies, and Chemicals

8.1. Instrumentation

8.1.1. Dionex Ion Chromatography System 6000 (ICS6000) comprised of the following: chromatography enclosures, gradient pumps, suppressors, conductivity detectors, eluent generator cartridges, and an automated sampler.

8.1.2. ICS6000 Operating conditions:

Sample loop volume	10 µL each
Analytical columns: Anions Cations	 Dionex IonPac AS18 - 4µm Dionex IonPac CS12A - 5µm
Guard columns: Anions Cations	 Dionex IonPac AG18 – 4µm Dionex IonPac CG12A - 5µm
Suppressors: Anions Cations	 ADRS600 CDRS600
Eluent solutions: Anions Cations	 23 mM KOH 20 mM MSA
Eluent flow rates: Anions Cations	 0.25 mL/min 0.5 mL/min
Acquisition software	Chromeleon Chromatography software

8.2. Other Equipment:

1. Bottle-top dispenser, 25.0 mL volume
2. Pipettors with disposable tips: 50 – 1000 µL and 100 – 5000 µL
3. Ultrasonicator
4. Shaker table
5. Refrigerator
6. Nanopure water filtration system capable of dispensing ultrapure type I (18.2 MΩ.cm) water

8.3. Supplies:

1. Volumetric flasks: 100 and 250 mL sizes
2. Polyethylene storage bottles: 125 and 250 mL sizes
3. Plastic centrifuge tubes with caps, 50 mL size
4. 10 mL autosampler vials with caps and blue septa
5. 46.2 mm washed nylon filters, 1 µm pore size, such as MTL NY47P

6. Kimberly-Clark Nitrile Powder-Free disposable gloves
7. Kimwipes and towels

8.4. Chemicals:

1. Dionex EGC 500 MSA, such as product number 075779
2. Dionex EGC 500 KOH, such as product number 075778
3. Two containers of different lot numbers of National Institute of Science and Technology traceable (NIST-Traceable) 300 µg/mL nitrate and 120 µg/mL sulfate standard stock solution.
4. Two containers of different lot numbers of NIST-Traceable 40 µg/mL sodium, 40 µg/mL ammonium, 40 µg/mL potassium standard stock solution.
5. Nanopure ASTM Type 1 deionized water (>18 MΩ.cm)

9. Procedures

9.1. Preparation of Eluents

Anion and cation eluents are generated by an eluent generator module and requires no preparation other than keeping the reservoirs filled with Nanopure water.

9.2. Preparation of Standards and Controls

The anion standard and control stock solutions both contain 300 µg/mL nitrate and 120 µg/mL sulfate. The cation standard and control stock solutions both contain 40 µg/mL each sodium, ammonium, and potassium. All standard and control stock solutions are NIST traceable in addition to each having different lot numbers. All standard and control solutions are stored in the refrigerator until ready for use. Stock solutions are not used past the expiration date listed by the manufacturer.

Anion working standards and controls: Prepare anion working standards and controls from a NIST traceable stock. Store the anion working standards and controls in polyethylene bottles in the refrigerator. Label solutions with the date they were prepared and the initials of the preparer. Anion working standards and controls are usable for up to 90 days before they must be prepared again from the stock solution. The following table directs the preparation of anion standards. Standard 3 is also used as the check standard.

Stock and Standards	Nitrate Target Concentration (µg/mL)	Sulfate Target Concentration (µg/mL)	Preparation
Stock	300	120	Prepared by Vendor & NIST Traceable
Standard 1	0.030	0.012	Add 0.2 mL of standard 5. Bring to 100 mL using Nanopure water.
Standard 2	0.30	0.12	Add 0.1 mL of stock. Bring to 100 mL using Nanopure water.
Standard 3	1.5	0.6	Add 1.25 mL of stock. Bring to 250 mL using Nanopure water.
Standard 4	6.0	2.4	Add 2.0 mL of stock. Bring to 100 mL using Nanopure water.
Standard 5	15.0	6.0	Add 5.0 mL of stock. Bring to 100 mL using Nanopure water.
Control	1.5	0.6	Add 0.5 mL of stock. Bring to 100 mL using Nanopure water. Note: Control is prepared from a separate source or has a different lot number.

Cation working standards and controls: Prepare cation working standards and controls from a NIST traceable stock. Store the cation working standards and controls in polyethylene bottles in the refrigerator. Label solutions with the date they were prepared and the initials of the preparer. Cation working standards and controls are usable for up to 90 days before they must be prepared again from the stock solution. The following table directs the preparation of cation standards. Standard 3 is also used as the check standard.

Stock and Standards	Sodium, Ammonium, and Potassium Target Concentration (µg/mL)	Preparation
Stock	40	Prepared by Vendor & NIST Traceable
Standard 1	0.02	Add 1.0 mL of standard 5. Bring to 100 mL using Nanopure water.
Standard 2	0.08	Add 0.2 mL of stock. Bring to 100 mL using Nanopure water.
Standard 3	0.2	Add 1.25 mL of stock. Bring to 250 mL using Nanopure water.
Standard 4	0.8	Add 2.0 mL of stock. Bring to 100 mL using Nanopure water.
Standard 5	2.0	Add 5.0 mL of stock. Bring to 100 mL using Nanopure water.
Control	0.2	Add 0.5 mL of stock. Bring to 100 mL using Nanopure water. Note: Control is prepared from a separate source or has a different lot number.

9.3. Preparation of Quality Control Samples

QC Sample	Target Concentration	Preparation
Water blank	< RL	Dispense Nanopure deionized water directly from the bottle-top dispenser into an autosampler vial. This sample does not go through the extraction process.
Extraction water blank	< RL	Add 25 mL of Nanopure deionized water to a centrifuge tube.
Filter blank	< RL	Place an unused filter in a centrifuge tube and add 25 mL of Nanopure deionized water.
Anion spike	1.5 µg/mL nitrate 0.6 µg/mL sulfate	Place an unused filter in a centrifuge tube and add 25 mL of Nanopure deionized water. Use the pipettor to add 0.125 mL of the anion stock standard solution.
Cation spike	0.2 µg/mL for each analyte	Place an unused filter in a centrifuge tube and add 25 mL of Nanopure deionized water. Use the pipettor to add 0.125 mL of the cation stock standard solution.

9.4. Filter Extraction

9.4.1. Transfer the centrifuge tubes containing the samples from the refrigerator to a centrifuge tube rack. Label four empty centrifuge tubes as follows: extraction water blank, filter blank, anion spike, and cation spike. Preparation of these quality control samples is explained in section 9.3.

9.4.2. Prepare the sequences for the anion and cation analytical runs. Both sequences begin with a water rinse to flush the system, then the calibration standards, followed by a water blank, a control, and a check standard. Follow these with the list of samples, including at least 10% replicates, and after each 10 analyses, another check standard. Included with these samples will be an extraction water blank, a filter blank, and an anion and cation spike. The last analysis of each run is a check standard.

9.4.3. Using a bottle-top water dispenser, add 25 mL of Nanopure deionized water to each centrifuge tube.

9.4.4. Securely replace the lids on each centrifuge tube, place the centrifuge rack inside of the ultrasonicator and fill with water to the fill line. Turn on the sonication function for 60 minutes.

9.4.5. After 60 minutes of sonication, remove the samples from the ultrasonicator and place them on the shaker table. Set the timer for 60 minutes.

9.4.6. After shaking for 60 minutes, remove the samples from the shaker table. The samples are ready for IC analysis. Samples are stored in the refrigerator.

9.5. Filter Analysis

9.5.1. Transfer approximately 3 mL of working standards, controls, check standards, blanks, spikes, and extracted samples to 10 mL autosampler vials. Place a cap with a blue septa onto each vial and place them into the autosampler tray. Place the autosampler tray into the autosampler and begin analysis.

9.5.2. After analysis, the sample and/or the sample extract are stored in the refrigerator for one year plus the current year from the sampling date.

10. Quality Control

Quality control measures include anion and cation calibration curves, secondary source controls, check standards, Nanopure deionized water blanks, extraction water blanks, filter blanks, spikes, and field blanks. Furthermore, an annual method detection limit verification must be completed.

QC	Acceptance Criteria	Corrective Action
Calibrations	Multi-point calibration using all of the concentrations listed in sections 9.2.1 and 9.2.2. Calibration correlation coefficient must be ≥ 0.990.	Re-prepare standards and re-run the analysis.
Check standards	Check standards must fall within ± 20% of the target concentration. Check standards must be analyzed before any samples, again after each group of ten analyses, and finally at the end of the analysis.	If the check standard is outside of the criteria limit, the sample results are invalid. Take action to bring the system back into control and repeat analysis of the associated samples. All analyses must be bracketed by valid QC.
Controls	Anion and cation controls are analyzed after the calibration is complete. The initial limits are ± 8% for the warning limits and ± 10% for control limits from the target value. Once a minimum of 20 control values are obtained, the limits for tolerance of the control results around the mean should be set as follows: • Upper Control Limit (UCL) = Mean + 3 Standard Deviations • Upper Warning Limit (UWL) = Mean + 2 Standard Deviations • Lower Warning Limit (LWL) = Mean - 2 Standard Deviations • Lower Control Limit (LCL) = Mean - 3 Standard Deviations	If the controls are outside of the criteria limit, the sample results are invalid. Take action to bring the system back into control and repeat the analyses. Three consecutive control standards falling between the warning and control limits must be investigated and the control limits adjusted if necessary. If the control limits needs to be adjusted, the changes must be documented and approved by the laboratory supervisor.
Water blank	Water blank results must be below the RL. A water blank must be run with each analytical sequence.	If a blank result is higher than or equal to the reporting limit (RL), the results must be verified by reanalysis. Refer to the NLB Laboratory Quality Control Manual for

QC	Acceptance Criteria	Corrective Action
		blank corrective action criteria.
Extraction water blank	Extraction water blank results must be below the RL. An extraction water blank must be included with each extraction batch.	If a blank result is higher than or equal to the reporting limit (RL), the results must be verified by reanalysis. Refer to the NLB Laboratory Quality Control Manual for blank corrective action criteria.
Filter blank	Filter blank results must be below the RL. A filter blank must be included with each extraction batch.	If a blank result is higher than or equal to the reporting limit (RL), the results must be verified by reanalysis. Refer to the NLB Laboratory Quality Control Manual for blank corrective action criteria.
Spikes	The spike recovery limit is ± 20% of the expected value. An anion and cation spike must be included with each extraction batch.	If the spike fails, re-run the spike to verify the results. If the spike fails again, the samples associated with the spike are invalid for the analytes outside of the criteria limit.
Field blank	The field blank limit is 1 µg/filter for all analytes.	If results are above the field blank limit, the results must be verified by reanalysis. Results above the criteria limit are documented in the monthly data package and flagged.
Filter acceptance testing	Extract and analyze two random filters for every 50 filters before they are sent to the field for sampling. Results must be below 1 µg/filter for all analytes.	If the levels are above or equal to the limit, discard the associated filters.
Replicate	Replicates are run at a frequency of at least 10% and consist of a separate aliquot of the filter extract. The relative percent difference between replicates should be less than 10% for samples whose concentration is more than	If the replicate results exceed the QC criteria, the samples in the associated batch must be reanalyzed, or invalidated for the affected

QC	Acceptance Criteria	Corrective Action
	twenty times above the RL, and less than 25% for samples whose concentration is less than twenty times above the RL. Samples whose concentration is less than five times the RL are not evaluated for relative percent difference.	analytes if reanalysis is not possible.
MDL	Method Detection Limit (MDL) verifications should be performed at least annually or as required by the NLB QC manual. As part of the verification, an LOQ is calculated and compared to the RL. For an MDL to be valid it must have valid calibrations, check standards, controls, water blank, extraction water blank, filter blank, and meet the following acceptance criteria: • MDL < Spike Concentration • Spike Concentration < 10 x MDL • MDL spike recovery within 50%-150% See QC manual for additional details.	If the MDL acceptance criteria is not met, prepare MDL spikes at a different concentration to recalculate a new MDL.
RL	Reporting limits (RL) should be verified annually and meet the following criteria: • RL is greater than or equal to the LOQ. • RL should be greater than or equal to the lowest calibration standard. See QC manual for additional details.	During the annual MDL verification procedure, if the RL is less than the LOQ, then the RL should be raised to an appropriate limit. If the RL is more than two times the LOQ, then consideration should be given to lower the RL. Any changes to the RL must be approved by management.

11. Sample and Data Management

Data management consists of samples logged into the Laboratory Information Management System (LIMS), documentation of unusual occurrences and their resolutions, creation of data packages (monthly, amendments, and special projects) for peer review and management approval, submittal of data to clients, and archival procedures for sample media and respective chains of custody. Keep program and maintenance notebooks and/or logbooks with the instrumentation at all times.

11.1. After samples are analyzed, print and review all calibration curves, chromatograms, and associated QC prior to transferring the data to LIMS. Add the LIMS transfer summary to the documentation. Maintain these records in the laboratory for five years plus the current year.

11.2. Refrigerate samples and/or sample extracts for one year plus the current year from the sampling date.

11.3. Data packages undergo a multi-level data validation process. This process includes analyst review, peer review, and laboratory management review and approval in line with Laboratory Quality Control Manual. Data packages created by the analyst must consist of at least the following:

11.3.1. Documentation of the method and program name, standards expiration dates, MDL verification dates, and criteria limits

11.3.2. Summary of the data generated for a sample date period, blank data, and a graph showing nitrate vs. ammonium values

11.3.3. Summary of QC data, sample transfer summaries, calibration curves, and any additional QC documentation

12. Calculations

12.1. Spiked Samples

Spike Percent Recovery= (Spike Result / Target Concentration) x 100

12.2. Replicates Relative Percent Difference (RPD)

$$RPD = \frac{|(Y - X)|}{((Y + X)/2)} \times 100$$

Where:

X = sample result

Y= replicate result

12.3. Conversion of Aqueous Units to Aerometric Units

µg/mL = 25 mL x (µg/mL) / sampler volume in m^3

Where 25 mL is the extraction volume.

13. Revision History

	Date	Previous Procedure	Updated Procedure
1	**Description**: Standard Operating Procedure for the Analysis of Anions and Cations in PM2.5 Speciation Samples by Ion Chromatography, Revision 0, June 18, 2002		
	Approval Date: June 18, 2002	New SOP	New SOP
	Description: Method Change California Air Resources Board SOP MLD064: Standard Operating Procedure for the Analysis of Anions and Cations in PM2.5 Speciation Samples by Ion Chromatography Revision 1.0, October 2018.		
	Approval Date: October 8, 2018	• Two separate Analytical IC systems • AS4A Analytical Column • CS12A Analytical Column • AG4A Guard Column • CG12A Guard Column • Anion eluent: 1.5 mM carbonate / 1.7 mM bicarbonate • Cation eluent: 20mM MSA • Anion flow rate = 2.0 mL / minute • Cation flow rate = 1.0 mL / minute • Dionex Peaknet Chromatography Workstation software	• One Capillary ICS5000 • AS18-Fast Capillary Column • CS16 Capillary Column • AG18- Fast Capillary Guard Column • CG16 Capillary Guard Column • Anion eluent: 30 mM KOH • Cation eluent: 30 mM MSA • Anion flow rate = 0.01 mL / minute • Cation flow rate = 0.01 mL / minute • Chromeleon Chromatography software

<table>
<tr><th></th><th>Date</th><th>Previous Procedure</th><th>Updated Procedure</th></tr>
<tr><td></td><td></td><td>• Eluents manually prepared
• Samples filtered using vial caps
• Anion working standards range from 0.02 µg/mL to 20.0 µg/mL for both analytes
• Cation working standards range from 0.02 µg/mL to 20.0 µg/mL for all analytes
• Working standards usable for 21 days
• Sample extracts stored refrigerated for 6 months after analysis</td><td>• Eluents generated by eluent generator cartridges
• Samples filtered using 0.45 µm acrodisc syringe filters
• Anion working standards range from 0.015 µg/mL to 15.0 µg/mL for nitrate and 0.006 µg/mL to 6.0 µg/mL for sulfate
• Cation working standards range from 0.004 µg/mL to 2.0 µg/mL for all analytes
• Working standards usable for 90 days
• Sample extracts stored refrigerated for one year from the sampling date.</td></tr>
<tr><td>2</td><td colspan="3">Description: Amendment

California Air Resources Board SOP MLD064: Standard Operating Procedure for the Analysis of Anions and Cations in PM2.5 Speciation Samples by Ion Chromatography with Addendum 30, February 2019.</td></tr>
<tr><td></td><td>Approval Date:

February 7, 2019</td><td>• Cation eluent: 30mM MSA
• Anion working standards range from 0.015 µg/mL to 15.0 µg/mL for nitrate and 0.006 µg/mL to 6.0 µg/mL for sulfate
• Cation working standards range from 0.004 µg/mL to 2.0 µg/mL for all analytes</td><td>• Cation eluent: 25mM MSA
• Anion working standards range from 0.030 µg/mL to 15.0 µg/mL for nitrate and 0.012 µg/mL to 6.0 µg/mL for sulfate
• Cation working standards range from 0.02 µg/mL to 2.0 µg/mL for all analytes</td></tr>
</table>

	Date	Previous Procedure	Updated Procedure
3	**Description**: Method Change California Air Resources Board SOP MLD064: Standard Operating Procedure for the Analysis of Anions and Cations in PM2.5 Speciation Samples by Ion Chromatography Revision 2.0.		
	Approval Date: July 12, 2021	• Capillary ICS5000, running samples simultaneously • AS18-Fast Capillary Column • CS16 Capillary Column • AG18- Fast Capillary Guard Column • CG16 Capillary Guard Column • Anion eluent: 30 mM KOH • Cation eluent: 30 mM MSA • Anion flow rate = 0.01 mL / minute • Cation flow rate = 0.01 mL / minute • Samples filtered using 0.45 µm Acrodisc syringe filters • 9 Anion working standards range • 7 Cation working standards	• Analytical ICS6000, running samples sequentially • AS18 4µm Analytical Column • CS12A 5µm Analytical Column • AG18 4µm Guard Column • CG12A 5µm Guard Column • Anion eluent: 23 mM KOH • Cation eluent: 20 mM MSA • Anion flow rate = 0.25 mL / minute • Cation flow rate = 0.5 mL / minute • Samples not required to be routinely filtered • 5 Anion working standards • 5 Cation working standards

14. References

14.1. Laboratory Quality Control Manual, Northern Laboratory Branch, MLD Revision 4.0, September 2018.

https://ww2.arb.ca.gov/sites/default/files/2018-10/nlbqcm.pdf

14.2. Final Chemical Hygiene Plan for Northern Laboratory Branch 1927 13th Street, 1900 14th Street, June 2019.

14.3. Dionex ICS-6000 Ion Chromatography System Operator’s Manual, Revision 01, February 2018.