

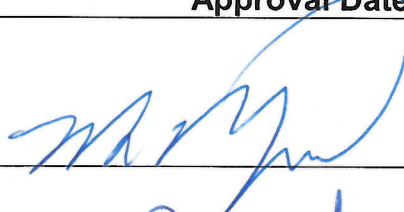



CALIFORNIA
AIR RESOURCES BOARD

Standard Operating Procedure for the Analysis of Anions and Cations in PM_{2.5} Speciation Samples by Ion Chromatography

MLD064
Revision 1.0

Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
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Disclaimer: Mention of any trade name or commercial product in this standard operating procedure does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the standard operating procedure are for equipment used by the Air Resources Board's laboratory. Any functionally equivalent instrumentation is acceptable.

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Standard Operating Procedure for the Analysis of Anions and Cations in PM_{2.5} Speciation Samples by Ion Chromatography

1. Introduction

In 1997, the U.S. Environmental Protection Agency created new federal air quality standards for particulate matter under 2.5 microns (PM_{2.5}) and ozone, and proposed new requirements to reduce the regional haze that impairs visibility. The PM_{2.5} standards complement existing federal and state standards that target the full range of inhalable particulate matter (PM). Efforts to characterize PM_{2.5} and comply with the federal standards will further progress toward California's own particulate matter under 10 microns (PM₁₀) standards.

The goal of the PM_{2.5} speciation monitoring program is to provide ambient data that supports the nation's air quality program. These data include mass measurements and chemically resolved, or speciated data. Mass measurements are used principally for comparison to the PM_{2.5} National Ambient Air Quality Standards (NAAQS). These comparisons identify areas that do or do not meet the PM_{2.5} NAAQS, thereby allowing areas to be designated as attainment or nonattainment. Speciated data support the development of emission mitigation strategies intended to reduce ambient PM_{2.5} levels. The data are used to evaluate emission inventory and air quality models, analyze source attribution, and track the success of emission control programs.

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 SOP should be used in conjunction with the applicable equipment manuals.

3. Acronyms and Definitions

Acronym or Term	Definition
ARB	California Air Resources Board
ASTM	American Society for Testing and Materials
IC	Ion Chromatography
ICS	Ion Chromatography System
KOH	Potassium hydroxide
LCL	Lower control limit
LIMS	Laboratory Information Management System
LOQ	Limit of quantitation
LSS	Laboratory Support Section
LWL	Lower warning limit
MΩ-cm	Mega Ohm-centimeter
MDL	Method detection limit
μL	Microliter
μm	Micrometer
mL	Milliliter
mm	Millimeter
MSA	Methanesulfonic acid
MSDS	Material 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
QMB	Quality Management Branch
QMS	Quality Management Section
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 a 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 MSDS 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 should be disposed of properly. Contact the NLB hazardous waste coordinator as needed.

8. Equipment, Supplies, and Chemicals

8.1. Instrumentation

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

8.1.2. Capillary ICS5000 Operating conditions:

Sample volume	1.0 mL
Analytical columns: Anions Cations	Dionex IonPac AS18-Fast Capillary Dionex IonPac CS16 Capillary
Guard columns: Anions Cations	Dionex IonPac AG18-Fast Capillary Dionex IonPac CG16 Capillary
Suppressors: Anions Cations	ACES300 Capillary CCES300 Capillary
Eluent solutions: Anions Cations	30 mM KOH 30 mM MSA
Eluent flow rates: Anions Cations	0.01 mL/min 0.01 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 μ L and 100 – 5000 μ L
3. Ultrasonicator
4. Shaker table
5. Refrigerator
6. Nanopure water filtration system

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
5. 5 mL Syringes
6. 0.45 μm IC Acrodisc 13mm syringe filters
7. Disposable gloves
8. Kimwipes and towels

8.4. Chemicals:

1. Methanesulfonic acid (MSA)
2. Potassium hydroxide (KOH)
3. Two containers of different lot numbers of National Institute of Science and Technology traceable (NIST-Traceable) 300 $\mu\text{g}/\text{mL}$ nitrate and 120 $\mu\text{g}/\text{mL}$ sulfate standard stock solution.
4. Two containers of different lot numbers of NIST-Traceable 40 $\mu\text{g}/\text{mL}$ sodium, 40 $\mu\text{g}/\text{mL}$ ammonium, 40 $\mu\text{g}/\text{mL}$ potassium standard stock solution.
5. Nanopure ASTM Type 1 deionized water(>16 M Ω -cm)

9. Procedures

9.1. Preparation of eluents

- 9.1.1. 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 $\mu\text{g}/\text{mL}$ nitrate and 120 $\mu\text{g}/\text{mL}$ sulfate. The cation standard and control stock solutions both contain 40 $\mu\text{g}/\text{mL}$ 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. Contact the hazardous waste coordinator to dispose of expired stock solutions.

- 9.2.1. 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 7 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	0.015	0.006	Add 0.1 mL of standard 10. Bring to 100 mL using Nanopure water.
Standard 2	0.030	0.012	Add 0.2 mL of standard 10. Bring to 100 mL using Nanopure water.
Standard 3	0.075	0.03	Add 0.5 mL of standard 10. Bring to 100 mL using Nanopure water.
Standard 4	0.15	0.06	Add 1.0 mL of standard 10. Bring to 100 mL using Nanopure water.
Standard 5	0.30	0.12	Add 0.1 mL of stock. Bring to 100 mL using Nanopure water.
Standard 6	0.60	0.24	Add 0.2 mL of stock. Bring to 100 mL using Nanopure water.
Standard 7	1.5	0.6	Add 1.25 mL of stock. Bring to 250 mL using Nanopure water.
Standard 8	3.0	1.2	Add 1.0 mL of stock. Bring to 100 mL using Nanopure water.

Standard 9	6.0	2.4	Add 2.0 mL of stock. Bring to 100 mL using Nanopure water.
Standard 10	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.

9.2.2. 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 7 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 2	0.004	Add 0.2 mL of standard 10. Bring to 100 mL using Nanopure water.
Standard 3	0.01	Add 0.5 mL of standard 10. Bring to 100 mL using Nanopure water.
Standard 4	0.02	Add 1.0 mL of standard 10. Bring to 100 mL using Nanopure water.
Standard 5	0.04	Add 0.1 mL of stock. Bring to 100 mL using Nanopure water.
Standard 6	0.08	Add 0.2 mL of stock. Bring to 100 mL using Nanopure water.
Standard 7	0.2	Add 1.25 mL of stock. Bring to 250 mL using Nanopure water.

Standard 8	0.4	Add 1.0 mL of stock. Bring to 100 mL using Nanopure water.
Standard 9	0.8	Add 2.0 mL of stock. Bring to 100 mL using Nanopure water.
Standard 10	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. Filter Extraction

- 9.3.1. Filters received from the field are placed into centrifuge tubes by Laboratory Support Section staff using procedures documented in SOP MLD062. 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. Place unused filters in the filter blank and spike centrifuge tubes.
- 9.3.2. Prepare a sequence for the analytical run that begins with a water rinse, 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. At the end of the samples, an extraction water blank, a filter blank, anion spike, and cation spike are analyzed. The last analysis of each run is another check standard.
- 9.3.3. Using a bottle-top water dispenser, add 25 mL of Nanopure deionized water to each centrifuge tube.
- 9.3.4. For the spikes, use the pipettor to add 0.125 mL of the corresponding stock standard solution.
- 9.3.5. 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.
- 9.3.6. After 60 minutes of sonication, remove the samples from the ultrasonicator and place them on the shaker table. Set the timer for 60 minutes.

9.3.7. After shaking for 60 minutes, remove the samples from the shaker table and store in the refrigerator at 4 °C overnight. The samples are now ready for IC analysis.

9.4. Filter Analysis

9.4.1. Transfer approximately 3 mL of working standards, controls, check standards, blanks, spikes, and extracted samples to 10 mL autosampler vials. Extracts should be filtered using a 0.45 µm Acrodisc syringe filter in order to prevent instrument blockages. Pull approximately 4 mL of extract into a 5 mL syringe, place the Acrodisc syringe filter onto the syringe, filter approximately 1 mL of extract to waste, and filter the remaining portion of sample into the autosampler vial. 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.

9.4.2. Samples should be analyzed within 30 days from the sampling date.

9.4.3. After analysis, the samples are stored in the refrigerator for one 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 must be completed. All QC is performed as prescribed by the Laboratory Quality Control Manual.

QC	Acceptance Criteria	Failed 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 $\pm 20\%$ 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 the analyses.

		All analyses must be bracketed by valid QC.
Controls	<p>Anion and cation controls are analyzed after the calibration is complete. The initial limits are $\pm 8\%$ for the warning limits and $\pm 10\%$ 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:</p> <ul style="list-style-type: none"> • 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 	<p>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.</p> <p>Three consecutive control standards falling between the warning and control limits should be investigated and the control limits adjusted if necessary.</p> <p>If the control limits needs to be adjusted, the changes should be documented and approved by the laboratory supervisor.</p>
Nanopure deionized water blank	Nanopure deionized water blank results must be below the RL.	If a blank result is higher than the reporting limit (RL), the results should be verified. Refer to the Laboratory Quality Control Manual for blank corrective action criteria.
Extraction water blank	Extraction water blank results must be below the RL.	If a blank result is higher than the reporting limit (RL), the results should be verified. Refer to the Laboratory Quality Control Manual for blank corrective action criteria.

Filter blank	Filter blank results must be below the RL.	If a blank result is higher than the reporting limit (RL), the results should be verified. Refer to the Laboratory Quality Control Manual for blank corrective action criteria.
Spikes	The spike recovery limit is $\pm 20\%$ of the expected value.	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 $\mu\text{g}/\text{filter}$ for all analytes.	If results are above the field blank limit, the results should be verified. Results above the criteria limit are documented in the monthly data package.
Filter acceptance testing	Extract and analyze a random set of three filters per box of filters. Results must be below 1 $\mu\text{g}/\text{filter}$ for all analytes.	If the levels are above the limit, discard the filter batch.
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 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.	If the replicate results exceed the QC criteria, the samples in the associated batch should be reanalyzed, or invalidated for the affected analytes if reanalysis is not possible.

MDL	<p>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, eluent water blank, filter blank, and meet the following acceptance criteria:</p> <ul style="list-style-type: none"> • Calculated MDL < Spike Concentration • Spike Concentration < 10 x Calculated MDL <p>See QC manual for additional details.</p>	<p>If the MDL acceptance criteria is not met, prepare MDL spikes at a different concentration to recalculate a new MDL.</p>
RL	<p>Reporting limits (RL) should be verified annually and meet the following criteria:</p> <ul style="list-style-type: none"> • RL is greater than or equal to the LOQ. • RL should be greater than or equal to the lowest calibration standard. <p>See QC manual for additional details.</p>	<p>During the annual 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.</p>

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 the sample run. 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 for five years plus the current year.
- 11.2. Refrigerate sample extracts for one year plus the current year.

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 the following:

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

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

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

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

$\mu\text{g/mL} = 25 \text{ mL} \times (\mu\text{g/mL}) / \text{sampler volume in m}^3$

13. Revision History

MLD064 Revision History

	Date	Updated Revision (2018)	Original Procedure (2002)
1		Description: Method Change	
		<ul style="list-style-type: none"> • 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 • Eluents generated by eluent generator cartridges • Samples filtered using 0.45 µm Acrodisc syringe filters 	<ul style="list-style-type: none"> • 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 • Eluents manually prepared • Samples filtered using vial caps

		<ul style="list-style-type: none"> • 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. 	<ul style="list-style-type: none"> • 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
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14. References

- 14.1. California Air Resources Board SOP MLD064: Standard Operating Procedure for the Analysis of Anions and Cations in PM_{2.5} Speciation Samples by Ion Chromatography, June 2002.
<https://www.arb.ca.gov/aaqm/sop/mld064.pdf>
- 14.2. California Air Resources Board MLD Northern Laboratory Branch: Laboratory Quality Control Manual, Revision 4.0, September 2018.
<https://www.arb.ca.gov/aaqm/sop/nlbqcm.pdf>
- 14.3. California Air Resources Board MLD Northern Laboratory Branch: Final Chemical Hygiene Plan for Northern Laboratory Branch 1927 13th Street, 1900 14th Street, March 2016.
- 14.4. California Air Resources Board SOP MLD062: Standard Operating Procedure for Filter and Canister Preparation for PM_{2.5} Speciation Samples, June 2002.
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