California Environmental Protection Agency

Air Resources Board

STANDARD OPERATING PROCEDURE (SOP) FOR THE ANALYSIS OF ANIONS AND CATIONS IN PM_{10} SAMPLES BY ION CHROMATOGRAPHY

SOP MLD 068

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Monitoring and Laboratory Division

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STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF ANIONS AND CATIONS IN PM_{10} SAMPLES BY ION CHROMATOGRAPHY

1 Scope

This document describes the methodology used by Monitoring and Laboratory Division (MLD) Inorganics Laboratory Section (ILS) staff to determine anions (chloride, nitrate, and sulfate) and cations (ammonium and potassium) collected on quartz microfiber filters exposed to particulate matter less than or equal to ten micrometers in aerodynamic diameter (PM_{10}).

2 Summary of Method

Method MLD068 determines anions (chloride, nitrate, and sulfate) and cations (ammonium and potassium) collected on 8 x 10 inch quartz fiber filters exposed to PM_{10}. A quarter of the filter is extracted in deionized water, filtered, and stored overnight in a refrigerator. The extract is analyzed by ion chromatography using a dual channel system with each channel containing the following components: a guard column, analytical column, self-regenerating suppressor, eluent generator, and a conductivity detector. Peak analysis is determined using Chromeleon Chromatography software.

3 Interferences and Limitations

3.1 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 decrease in eluent concentration can reduce these co-elution interferences.

3.2 Interferences may be caused by contaminants in the reagent water, reagents, glassware, quartz fiber 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.

3.3 Losses in retention time and resolution can be signs of column deterioration. Monitoring analyte retention times and column back pressure will assist in

determining when an analytical column or guard column may need to be replaced.

3.4 Nitrate losses from PM_{10} filters occur with time. Samples should be extracted as soon as possible to minimize nitrate losses.

4 Personnel Qualifications

Personnel should be trained to operate an Ion Chromatography (IC) System, including routine maintenance and troubleshooting techniques, and to operate both Chromeleon Chromatography Workstation software and the Laboratory Information Management System (LIMS).

5 Safety Statement

All personnel shall follow the general health and safety requirements found in the Air Resources Board's (CARB or ARB) Chemical Hygiene Plan. For additional instrument safety concerns, refer to the safety section of the ICS-3000 Ion Chromatography System Operator's Manual.

6 Equipment and Supplies

6.1 Instrumentation

This SOP assumes familiarity with the installation and operation of the Dionex Ion Chromatography system (ICS). For detailed instructions in the operation of the Dionex IC, refer to the Dionex operations manual.

6.1.1 The Dionex ICS is comprised of modular units for each of the following:

1. Gradient pump
2. Chromatography enclosures
3. Suppressors
4. Conductivity detectors
5. Automated sampler
6. Eluent Generator cartridges

6.1.2 ICS-3000 Operating conditions:

Sample loop volume	25µL for Anions and Cations
Analytical columns: Anions Cations	 Dionex, IonPac AS11-HC Dionex, IonPac CS12A
Guard columns: Anions Cations	 Dionex, IonPac AG11-HC Dionex, IonPac CG12A
Suppressors: Anions Cations	 ASRS300, 4mm CSRS300, 4mm
Eluent solutions: Anions Cations	 30 mM Potassium Hydroxide 18 mM Methanesulfonic Acid
Eluent flow rates: Anions Cations	 1.0 mL / minute 1.5 mL / minute
Acquisition Software	Chromeleon Chromatography Workstation software

6.2 Other Equipment:

1. Analytical Balance
2. Pipettors with disposable pipette tips: 50 – 1000 µL and 100 – 5000 µL
3. Water dispenser with a minimum precision in the 100mL range of 0.3 mL (Wheaton Unispense II)
4. Shaker table
5. Refrigerator

6.3 Materials:

1. Volumetric flasks: 200 and 500 mL sizes
2. Erlenmeyer flasks, 250 mL, with ground-glass stoppers
3. Sample bottles, 125 mL, polypropylene or high-density polyethylene, with screw-top lids
4. Polyethylene storage bottles: 250 and 500 mL sizes
5. Cutting board with ruled edges
6. Scissors
7. Filter base with O-ring

8. 2000 mL filter dome tolled to accept a 300 mL capacity polysulfone magnetic filter funnel
9. Sterile filtration membranes, 47 mm diameter, 0.45 µm pore diameter
10. Dionex 10 mL autosampler vials and caps with septa
11. Kimwipes and towels
12. Powder-free gloves, disposable
13. Glassine envelopes, 11 x 8"

6.4 Chemicals: All chemicals are at least reagent grade.

1. Potassium Hydroxide (KOH)
2. Methanesulfonic Acid (CH_3SO_2OH)
3. Two containers of different lot numbers of National Institute of Science and Technology traceable (NIST-Traceable) 1000 µg/mL nitrate (NO_3^-) and sulfate (SO_4^{2-}), 220 µg/mL potassium (K^+), and 200 µg/mL chloride (Cl^-) and ammonium (NH_4^+) standard stock solution.
4. Nanopure ASTM Type 1 deionized water (>16 MΩ-cm)

7 Procedures

7.1 Preparation of Eluents

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

7.2 Preparation of Standards and Controls

The standard and control stock solutions both contain 1000 µg/mL nitrate, 1000 µg/mL sulfate, 220 µg/mL potassium, 200 µg/mL chloride, and 200µg/mL ammonium. Both standard and control 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.

7.2.1 Working standards: The stock solution is diluted to give working standards for nitrate and sulfate from 2.0 µg/mL to 60.0 µg/mL, for chloride and ammonium from 0.4 µg/mL to 12.0 µg/mL, and for potassium from 0.44 µg/mL to 13.2 µg/mL. All dilutions are made using nanopure deionized water. Store the working standards in polyethylene bottles in the refrigerator. Standards should be labeled with the date they were prepared and the initials of the preparer. Working standards are usable for up to 30 days before they must be prepared again from the stock solution.

7.2.1.1 Table 7.2.1.1 shows the concentrations of the working standards used for the calibration curve. Standard 5 is also used as the check standard.

Table 7.2.1.1

Analyte	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6
NO_3^- Standard Concentration (µg/mL)	2.0	5.0	10.0	20.0	40.0	60.0
SO_4^{2-} Standard Concentration (µg/mL)	2.0	5.0	10.0	20.0	40.0	60.0
Cl^- Standard Concentration (µg/mL)	0.4	1.0	2.0	4.0	8.0	12.0
NH_4^+ Standard Concentration (µg/mL)	0.4	1.0	2.0	4.0	8.0	12.0
K^+ Standard Concentration (µg/mL)	0.44	1.1	2.2	4.4	8.8	13.2

7.2.1.2 Table 7.2.1.2 shows the volume of stock standard needed to produce the working standards shown in Table 7.2.1.1. Working standards are diluted to a volume of 200 mL with the exception of Standard 5 which is diluted to 500 mL. To prepare each standard, use the amount of the stock solution indicated in Table 7.2.1.2 below and dilute to the line etched in the volumetric flask with nanopure water.

Table 7.2.1.2

	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6
Volume of Stock needed (mL)	0.4	1.0	2.0	4.0	20.0	12.0

7.2.2 Controls: The controls are prepared from a secondary source stock standard. The control concentrations are 20.0 µg/mL for nitrate and

sulfate, 4.0 µg/mL for chloride and ammonium, and 4.4 µg/mL for potassium. To prepare use 4.0 mL of the control stock solution and dilute to the line etched in the volumetric flask with nanopure water in a 200 mL volumetric flask. Store the controls in polyethylene bottles in the refrigerator. Controls should be labeled with the date they were prepared and the initials of the preparer. Controls are usable for up to 30 days before they must be prepared again from the stock solution.

7.3 Filter Extraction

7.3.1 Print out an IC worklist from LIMS of samples to be analyzed. Samples should be extracted within 20 business days after receipt in the laboratory.

7.3.1.1 Samples not extracted within 20 business days will be flagged.

7.3.2 Create a set of extraction labels with the barcodes that correspond to the extraction worklist. Include labels for an extraction water blank, a filter blank, a spike, and duplicates.

7.3.2.1 Duplicates need to be logged into LIMS prior to extraction. The duplicate percentage must be ≥ 10%.

7.3.3 Affix extraction labels to Erlenmeyer flasks.

7.3.4 Using a clean, dry laboratory wipe, thoroughly clean the cutting board blade and scissors. Place clean, dry laboratory wipes around the immediate cutting area to prevent contamination. Wear gloves throughout the entire cutting process to prevent contamination. Be careful not to touch the sampled portion of the filter.

7.3.5 Use the cutting board to cut a 4" x 5" section of each filter. Remove a filter from its manila envelope and place it lengthwise on the cutting board, exposed-side up, with the factory-stamped number on the right side. Line the left margin of the exposed area up with the 5" line of the cutting board and cut the filter. Rotate the left half of the filter 90 degrees counter-clockwise, line the left margin of the exposed area up with the 4" line of the cutting board and cut the filter. These two cuts will produce a section of filter containing one

quarter of the original exposed area. Place the remaining three-quarters of the filter back into the glassine envelope.

7.3.6 Fold the 4" x 5" section in half with the exposed area facing inwards. Roll the section of filter into a roughly cylindrical shape. Using the long-edge scissors, cut the filter into approximately equal-sized pieces directly into the appropriate Erlenmeyer flask.

7.3.7 For duplicate samples, use the additional quarter piece of filter created in step 7.3.5.

7.3.8 For the filter blank and spike, there are unexposed filter quarters located in the extraction lab that are used as background media. Repeat step 7.3.6 for the filter blank and spike using these unexposed filter quarters.

7.3.9 Verify that the Wheaton Unispense is delivering the appropriate amount of water by weighing on an analytical balance.

7.3.9.1 The acceptable volume range is 99.5 – 100.5 mL.

7.3.10 Dispense 100.0 mL of nanopure water into each Erlenmeyer flask and seal it with a ground glass stopper.

7.3.11 For spikes, use the micropipettor to remove 1.0 mL of water from the flask and add 1.0 mL of the stock standard solution.

7.3.11.1 The target spike concentrations are as follows: 2.0 µg/mL for chloride and ammonium, 10.0 µg/mL for nitrate and sulfate, and 2.20 µg/mL for potassium.

7.3.12 Secure the stoppered Erlenmeyer flasks on the shaker table and shake them for 60 minutes at low speed (approximately 120 excursions/minute).

7.3.13 After the samples, blanks, and spike have shaken for 60 minutes, the extraction solutions are vacuum filtered. Gloves should be worn throughout the vacuum filtration process in order to prevent contamination.

7.3.13.1 Thoroughly rinse the magnetic filter funnel with nanopure water. With the vacuum on, insert the bottom piece of the magnetic filter funnel into the filter dome. Then add the

filtration membrane and the top piece of the filter funnel. Pour approximately 75- 100 mL of nanopure water into the funnel to wet and rinse the surface of the membrane. Ensure that all rinse water is removed by breaking the vacuum and re-applying it one or more times as necessary. Discard the rinse water down the drain.

7.3.13.2 Immediately prior to filtering, transfer the label from the samples' Erlenmeyer flask directly to the individual sample bottle into which the filtrate will be stored. Place the labeled bottle underneath the filter funnel.

7.3.13.3 Swirl the contents of the flask and then pour the solution into the filter funnel. Let the vacuum pull the liquid through the membrane into the sample bottle.

7.3.13.4 After the liquid has been pulled through, disconnect the apparatus carefully and seal the labeled bottle with a clean lid.

7.3.13.5 Discard the used membrane and rinse both parts of the filter funnel thoroughly with nanopure water in order to remove any filter residue or particles.

7.3.13.6 Repeat Sections 7.3.13.1 through 7.3.13.5 for the remaining filtrates.

7.3.14 After extraction, filter samples are stored in a refrigerator at 4°C until analysis.

7.3.14.1 Filter extracts do not have a holding time, but should be analyzed as soon as possible to avoid clogging the instrumentation.

7.4 Filter Analysis

7.4.1 Prepare an analytical run sequence on the Chromeleon software.

7.4.1.1 The sequence begins with a water rinse, then the calibration standards in order of increasing concentration, followed by a control and a check standard.

7.4.1.2 Follow these with the list of samples, including at least 10% duplicates, at least 10% replicates and, after each

10 analyses, another check standard. An extraction water blank, a filter blank, and a spike must also be included and analyzed. The last analysis of each run is another check standard.

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

7.4.3 After analysis, the samples are stored in a refrigerator for as long as the chemist deems necessary.

7.5 Preventative Maintenance and Repairs

7.5.1 The IC system should be covered by a contract with a certified vendor that includes preventative maintenance and repairs.

7.5.1.1 Preventative maintenance should be performed annually on the IC system and autosampler.

7.5.2 Consumables (i.e. columns, suppressors, etc.) are replaced as needed.

7.6 Troubleshooting

7.6.1 Increased noise in the baseline may indicate a problem with the suppressor.

7.6.2 Decreasing peak retention times may indicate deterioration of the columns.

7.6.3 An increase in system pressure may indicate a blockage in the system.

7.6.4 The analyst may call the technical assistance line of the contracted vendor for more complex problems that may arise.

8 Data Handling

8.1 Data handling for this method assumes a familiarity with the operation of both Chromeleon Ion Chromatography software and the Laboratory Information Management System (LIMS).

8.2 Extraction dates are transferred into LIMS using the Instrument Design Module (IDM) LimsLink.

8.3 Analytes are identified and quantified by the Chromeleon Ion Chromatography software.

8.4 After each analysis run, reports are printed from Chromeleon which include a summary, calibration curves for each analyte, and a chromatogram for each sample analyzed. This report is reviewed by the analyst and a copy is archived for three years.

8.5 After samples are analyzed and the data has been reviewed by the analyst, an excel file containing the data results is created from Chromeleon. Any samples that should not be reported to LIMS are removed from this file before a .csv file is created. The .csv file is transferred into LIMS using IDM LimsLink.

8.6 When samples have been transferred the analyst generates a summary report from LIMS which is reviewed, initialed and dated by the analyst. This summary report is archived with the corresponding report from Chromeleon.

8.7 A paper copy of the raw data is stored in the laboratory. An electronic copy of the raw data is stored on the instrument controller.

8.8 Data is compiled into monthly reports which are reviewed at multiple levels in accordance with criteria stated in the NLB Quality Control Manual.

9 Quality Control

9.1 Each year, the Limit of Detection (LOD) for the method must be verified. The LOD is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and statistically different from a blank. The calculated limit of detection for the method is determined from analysis of a sample in a given matrix (including the sampling media) containing the analyte of interest seven times according to 40 CFR, Appendix B, as follows:

$$LOD = T_{(n-1,1-\alpha=0.99)}(sd)$$

where (sd) is the standard deviation and is calculated for the seven replicates. T is the Students T-value at the 99% confidence level for a particular number of replicates. The standard number of replicates used for this method is 7, which equates to a T-value of 3.143.

The Limit of Quantitation (LOQ) is the minimum concentration or amount of an analyte that a method can measure with a degree of precision. The LOQ is based on the calculated LOD and the chemist's experience of the method and instrument and takes into account variation of instrument performance over time. An annual check of the LOD verifies that the LOQ remains acceptable.

The verified LOD = 3.143 x standard deviation and the LOQ = 10 x standard deviation. The verified LOD and LOQ values are rounded off to the nearest hundredth (0.01) µg/mL.

The concentration of the analytes of interest in each of the 7 samples used for the annual LOD verification must be no greater than five times the value of the LOQ. The new verified LOD must also be less than the LOQ.

9.1.1 If the LOQ is lower than the lowest standard used for the calibration, a reporting limit (RL) will be applied equal to the value of the lowest standard. Data will not be reported below this limit.

9.2 All standards, blanks, spikes, replicates, duplicates, and samples are analyzed using the same analytical method.

9.3 In order for the calibration curve to be acceptable, the correlation coefficient must be greater than or equal to 0.980. If the correlation coefficient is less than 0.980, the standards are re-analyzed.

9.4 A control is analyzed after the calibration is complete. The allowable QC criteria are ±8% for the warning limits and ±10% for control limits from the target value.

If the control value is out of the acceptable limits, the instrument is evaluated for problems and a control reanalyzed successfully before samples are analyzed.

If the control value limits need to be adjusted, the changes should be documented and approved by the Laboratory Supervisor.

9.5 The check standard is analyzed before any samples, again after each group of ten analyses, and finally at the end of the analysis. The acceptable limits for the check standards ± 20% of the expected value.

If the check standard is not within acceptable limits, the instrument is evaluated for problems and a control sample is reanalyzed successfully before samples are analyzed.

9.6 Extraction water blanks and filter blanks are analyzed with each set of extracted filters. Blank levels are monitored to assure that contamination from reagents or from sampling processing techniques are not affecting sample results.

9.6.1 If the blank result is greater than the LOQ or reporting limit, the blank should be reanalyzed to verify the high value. Once verified, the following corrective action criteria apply:

9.6.1.1 If the sample results are at least ten times higher than the blank result, no action is taken.

9.6.1.2 If the sample results are less than ten times higher than the blank result, the analysis result should be invalidated for those samples associated with the blank.

9.7 Spikes are run to measure the accuracy of the entire process. Spikes are prepared from unexposed filters and extraction water with 1.0 mL of standard stock solution added. A spike is extracted and analyzed with each sample set. The spike recovery limits are ± 20% of the expected value.

9.7.1 If the spike value is outside of the recovery limits, the spike should be reanalyzed to verify the value. Once verified, the samples associated with the spike should be invalidated for the analyte(s) that were outside of the acceptable range.

9.8 Duplicates are made from two separate quarters of the PM10 filter and are run at a frequency of at least 10%. The relative percent difference (RPD) is calculated when both of the duplicate samples are above the RL or LOQ, whichever is greater. The RPD between duplicates should be less than 20%. Duplicate samples are used to assess variance of the total method including sampling and analysis.

9.8.1 Since duplicate results are impacted by the sampling process, there are no corrective actions for duplicate results that exceed the percent difference criteria. However, the site operator should be notified of duplicates that exceed the criteria.

9.9 Replicates are an additional analysis of the same sample extract and are run at a frequency of at least 10%. The sample extract used for replicate

analyses must be chosen at random. The RPD between replicates is calculated when both of the replicate samples concentration values are above the RL or LOQ, whichever is greater. The RPD should be less than 10% for samples whose concentration is more than twenty times above the RL or LOQ, whichever is greater, and less than 25% for samples whose concentration is less than twenty times the RL or LOQ, whichever is greater. Replicate analyses results are used to evaluate analytical precision.

9.9.1 If the replicate results do not meet specified QC criteria, the samples in the associated batch should be reanalyzed, or invalidated for the analytes that are out of range if reanalysis is not possible.

10 SOP History

10.1 This method combines MLD 007, MLD 023, and the extraction procedure from MLD 016.

11 References

1. Method MLD007 Standard Operating Procedure for the Determination of Sulfate, Nitrate, and Chloride Using Ion Chromatography, Northern Laboratory Branch, Monitoring and Laboratory Branch, Revision 4.1.
2. Method MLD023 Standard Operating procedure for the Determination of Ammonium Using Ion Chromatography, Northern Laboratory Branch, Monitoring and Laboratory Division, Revision 1.0.
3. Laboratory Quality Control Manual, Northern Laboratory Branch, Monitoring and Laboratory Division, Revision 3.0.
4. Chemical Hygiene Plan for 13th & T Facility, Monitoring and Laboratory Division, July 2005.
5. Laboratory Information Management System Standard Operating Procedure, Northern Laboratory Branch, Monitoring and Laboratory Division, 2014.
6. ICS-3000 Ion Chromatography System Operator's Manual, Revision 4.0, January 2008.
7. Method MLD016 Standard Operating Procedure for the Mass Analysis and Subsequent Extraction of SSI-Sampled PM_{10} from Exposed Quartz Microfiber Filters, Revision 5.0, January 2002.