



PROCEDURE FOR THE ANALYSIS OF PARTICULATE ANIONS AND CATIONS IN MOTOR VEHICLE EXHAUST BY ION CHROMATOGRAPHY

**SOP MV-AEROSOL-142 Version 2.4
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Aerosol Analysis and Methods Evaluation Section
Chemical Analysis and Emissions Research Branch
Mobile Source Laboratory Division

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TABLE OF CONTENTS

1	Introduction	1
2	Interferences and Limitations	1
3	Safety	1
4	Equipment and Supplies	1
5	Materials and Reagents	2
6	Cleanup Procedure	3
7	Procedure	3
8	Ion Chromatography Procedure	5
9	Calculations and Reporting	7
10	Limit of Detection	7
11	Quality Control	9
12	References	11
13	Revision Record	12

SOP No. 142 - PROCEDURE FOR THE ANALYSIS OF PARTICULATE ANIONS AND CATIONS IN MOTOR VEHICLE EXHAUST BY ION CHROMATOGRAPHY

1. Introduction

This document describes a procedure using ion chromatography (IC) to determine water soluble anions (chloride, nitrate and sulfate) and cations (sodium, ammonium, potassium, magnesium and calcium) collected on filters from motor vehicle exhausts. The ions are extracted from the filter by sonication in deionized (DI) water with ~1% isopropyl alcohol. The resulting extracts are stored in a refrigerator in order to settle particles. The extract is analyzed by ion chromatography with a conductivity detector.

2. Interferences and Limitations

- 2.1. Any species with retention times close to those ions of interest will chromatographically overlap and thus interfere. A large peak adjacent to a peak of an analyte can affect the accuracy of the determination of the ion concentration. Diluting the sample may reduce this type of interference.
- 2.2. Teflon[®] filters used to collect particulate matter from exhaust are hydrophobic. By adding 100 µL isopropyl alcohol or other wetting agents onto the Teflon[®] filters improves the extraction efficiency but will result in a baseline elevation and can affect accuracy. The negative effects on the small peaks of target analytes can be reduced by adding the wetting agent to all standards and blanks.
- 2.3. Quartz microfiber filters used for collection may also exhibit contamination.
- 2.4. Contaminants in the reagents, glassware and other sample processing apparatus may cause interferences. DI water blank, and filter blank are extracted and analyzed with each set of samples to monitor these possible sources of contamination.

3. Safety

For general laboratory safety procedures, consult the ARB Laboratory Safety Manual (Chemical Hygiene Plan). Material Safety Data Sheets (MSDS) are available in the laboratory.

4. Equipment and Supplies

The Dionex ICS-5000 Ion Chromatographic System, or equivalent, is used for the analysis of both anions and cations.

- 4.1 Ion chromatograph (Dionex ICS-5000) consists of:
 - 4.1.1 ICS-5000 Ion Chromatography System
 - 4.1.2 Dual pump - Gradient with Degas
 - 4.1.3 ICS-5000 EG Eluent Generators with Potassium Hydroxide (KOH) in EluGen Cartridge and

SOP No. 142 - PROCEDURE FOR THE ANALYSIS OF PARTICULATE ANIONS AND CATIONS IN MOTOR VEHICLE EXHAUST BY ION CHROMATOGRAPHY

Methanesulfonic acid (MSA) in EluGen Cartridge

- 4.1.4 ICS-5000 CD Conductivity Detectors
- 4.1.5 AS-DV Autosampler and vials (5.0 mL) with filter caps
- 4.1.6 PC with acquisition software: Chromeleon, version 7.0

4.2 Dionex ICS-5000 Components and Typical Operating Conditions:

	ANIONS	CATIONS
Sample loop volume	25 µL/mL	25 µL/mL
Analytical columns	Dionex, IonPac AS18	Dionex, IonPac CS12A-5 µm
Guard columns	Dionex, IonPac AG18	Dionex, IonPac CG12A-5 µm
Self-Regenerating Suppressor	ASRS ULTRA II 4mm	CSRS Ultra II 2 mm
Eluent solutions (eluent generator setting)	28 mM Potassium Hydroxide	20 mM Methanesulfonic acid
Eluent flow rates	1.0 mL/min	0.5 mL/min

4.3 Other Equipment:

- 4.3.1 Analytical balance
- 4.3.2 Bottle-top dispenser, 12 mL volume – Calibrated by weight.
- 4.3.3 Automatic pipet with disposable pipette tips: 10-300 µL, 100-1,000 µL, and 100-5,000 µL
- 4.3.4 Ultrasonic water bath filled with laboratory deionized water
- 4.3.5 Water purification system source of DI (deionized) water

5. Materials and Reagents

5.1 Materials:

- 5.1.1 Volumetric flasks: 100 mL sizes. PMP (polymethylpentene) Nalgene[®] flask
- 5.1.2 Disposable plastic centrifuge tubes with caps, 50 mL and 15 mL
- 5.1.3 Plastic test tube rack for 15-mL tubes
- 5.1.4 Disposable plastic pipets
- 5.1.5 Latex Gloves, disposable, class 100 powder free

5.2 Reagents: All chemicals are spectrophotometric grade or better.

- 5.2.1 DI water: the deionized water passed through a 0.2-µm filter with a specific resistance of 18.0 Mohm-cm or better
- 5.2.2 Isopropyl Alcohol (2-Propanol)
- 5.2.3 NIST Traceable Standard stock solutions: Inorganic Ventures or

SOP No. 142 - PROCEDURE FOR THE ANALYSIS OF PARTICULATE ANIONS AND CATIONS IN MOTOR VEHICLE EXHAUST BY ION CHROMATOGRAPHY

equivalent. Two sets of stock standard solutions are purchased for anion and cation standards. The concentration of each ion in the stock solution is 1,000 µg/mL.

6. Cleanup procedure

Clean latex gloves are worn during cleanup and sample handling procedures. New vials, caps, centrifuge tubes, pipets and gloves are cleaned before use and stored in a pre-cleaned covered plastic container.

- 6.1 The following are typically rinsed 3 times with DI water, sonicated for 1 hour, soaked overnight, rinsed 3 times and air dried:

Disposable plastic centrifuge tubes with caps, 50mL or 15mL
Dionex Autosampler Vial (Polyvial®), 5 mL

- 6.2 Dionex filter vial caps for autosampler vials: rinse 3 times, sonicate for 1 hour, and soak overnight. Rinse and sonicate for 1 hour and soak overnight 2 more times.
- 6.3 Disposable plastic pipets and latex gloves: typically rinsed with DI water and air dried.

7. Procedure

Samples for ion analysis are submitted to the laboratory and stored in the freezer until extraction.

- 7.1 Standards:

Calibration and control standard solutions are stored in the refrigerator until ready for use. All dilutions are made with DI water.

- 7.1.1 Calibration standards:

Separate sets of standards are prepared for the anion and cation analyses. Using the stock standard solutions and the 100 mL volumetric flasks, typical calibration standards prepared are shown in the following table.

SOP No. 142 - PROCEDURE FOR THE ANALYSIS OF PARTICULATE ANIONS AND CATIONS IN MOTOR VEHICLE EXHAUST BY ION CHROMATOGRAPHY

Working Standard No.	Concentration (µg/mL)	Stock Concentration (µg/mL)	Volume of Stock Solution Needed (µL)	Final Dilution Volume (mL)
1	0.02	10	200	100
2	0.05	10	500	100
3	0.20	10	2000	100
4	0.50	10	5000	100
5	1.00	1,000	100	100
6	2.00	1,000	200	100
7	10.00	1,000	1000	100

7.1.2 Preparation of standards before analysis:

Label 15-mL centrifuge tubes to be used for each of the calibration and control standards. Pipet 12 mL of the prepared standard solutions to the tubes and add 100 µL of isopropyl alcohol to each one, cap the tubes and mix the solution. Standards are now ready for the analysis.

7.2 Filter Extraction Procedure

7.2.1 Prepare a list of samples to be analyzed.

7.2.2 Remove filters from the freezer and allow them to equilibrate to room temperature.

7.2.3 Label one centrifuge tube for DI water blank.

7.2.4 Use the convention of labeling each tube with the filter ID, test name, test ID number and test phase for the samples. This will also be used as the sample name on the batch list for the analytical sequence.

7.2.5 Using tweezers roll the filter to fit into the 15mL centrifuge tube that has been labeled with filter ID. Ensure that the exposed area of the filter is well below the 12 mL mark.

7.2.6 Place an unused filter of the same type as those used for sampling in a centrifuge tube and label this as laboratory blank filter.

7.2.7 Add 100 µL of isopropyl alcohol to the 47 mm Teflon[®], polytetrafluoroethylene (PTFE) filter, or other filter media used for PM collection. Depending on the size and type of filter, additional isopropyl alcohol may be needed to wet the entire filter. The same

SOP No. 142 - PROCEDURE FOR THE ANALYSIS OF PARTICULATE ANIONS AND CATIONS IN MOTOR VEHICLE EXHAUST BY ION CHROMATOGRAPHY

amount of isopropyl alcohol is added to DI water blank, blank filter and standards.

- 7.2.8 Dispense 12 mL DI water to all centrifuge tubes.
- 7.2.9 Replace and secure the lids on each centrifuge tube. The exposed area on the filter should be completely immersed in solution.
- 7.2.10 Place the rack of tubes in the ultrasonic bath. The bath water should be above the level of the solution inside the tubes. Sonicate for 60 minutes. The bath temperature should not exceed 27 °C (add ice to the bath if necessary).
- 7.2.11 Remove the samples from the ultrasonic bath and store in a refrigerator set at 4 °C.
- 7.2.12 The sample extracts shall be stored overnight to settle particles in the extracts before analysis.

8. Ion chromatography procedure

The analyst must be familiar with the operation of the IC system. Detailed operating procedure is in the IC system manual. This procedure only serves as an outline of steps that must be followed.

- 8.1 Fill the reservoir bottles with “freshly-prepared” DI water when needed. Prime the pumps everyday before use.
- 8.2 Check and empty solvent waste reservoir.
- 8.3 Check the system stability.
 - 8.3.1 The system is stable when the pressure and total conductivity matches those of the last valid set of analysis.
 - 8.3.2 Check the stability of the system by analyzing the water blank and if any aspects of the baseline (e.g. noise or drift) have changed significantly, investigate before continuing.
- 8.4 Analyze control standards twice. The system is ready for analysis when two consecutive analyses show good consistency. See details in section 11.1 for the preparation of the control standards.
- 8.5 A batch analysis consists of blanks, standards, and samples. Each set of calibration standards are analyzed in the order of increasing concentration.

SOP No. 142 - PROCEDURE FOR THE ANALYSIS OF PARTICULATE ANIONS AND CATIONS IN MOTOR VEHICLE EXHAUST BY ION CHROMATOGRAPHY

- 8.6 Prepare the batch list for the analytical run. The naming convention for this list may contain “Anion-Cation, test type, project number, set #, YYMMDD (date of analysis)”.
- 8.7 The analytical sequence of injections is as follows: blank, control standards, cation calibration standards, blank, anion calibration standards, control standards, blank, sample extracts with one replicate for every 10, and the last two are control standards.
- 8.8 Label each vial with sample ID and transfer approximately 5 mL sample extract. The sample extracts will be transferred to the vials only after the calibration and quality control standards meet the quality control criteria.
- 8.9 Cap each vial with a filter cap and load in the autosampler according to the sequence on the list.
- 8.10 The remaining portions of the extracts are stored in the refrigerator for archive.
- 8.11 Verify the calibration curves; check the quality control (QC) standards and water blanks. Refer to the QC criteria in the QC section before proceeding. See details in section 11.
- 8.12 Typical chromatogram of the lowest IC standard is shown in Figure 1 for anions and Figure 2 for cations.

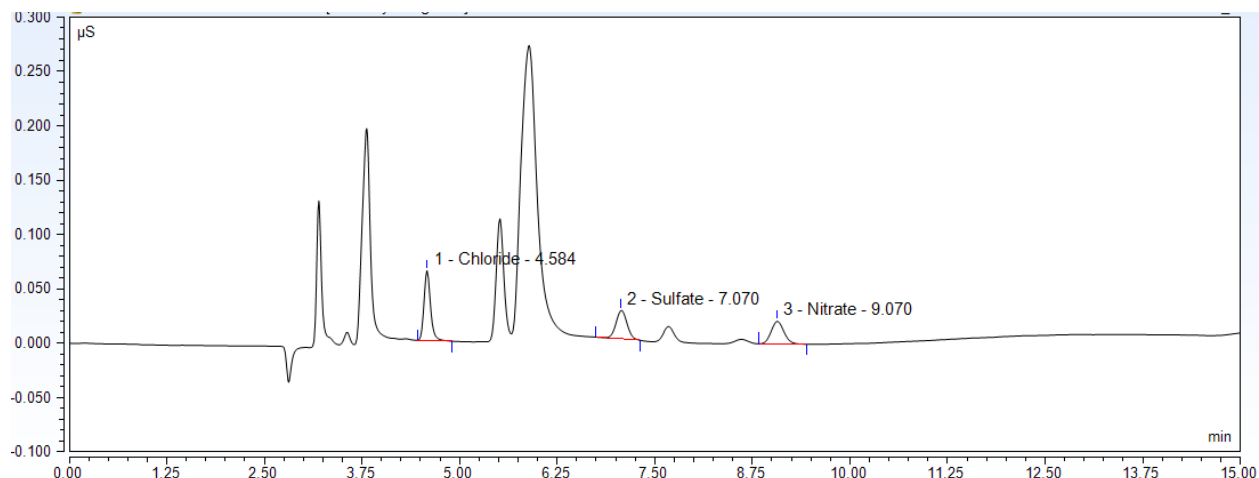


Figure 1 IC chromatogram for anions

SOP No. 142 - PROCEDURE FOR THE ANALYSIS OF PARTICULATE ANIONS AND CATIONS IN MOTOR VEHICLE EXHAUST BY ION CHROMATOGRAPHY

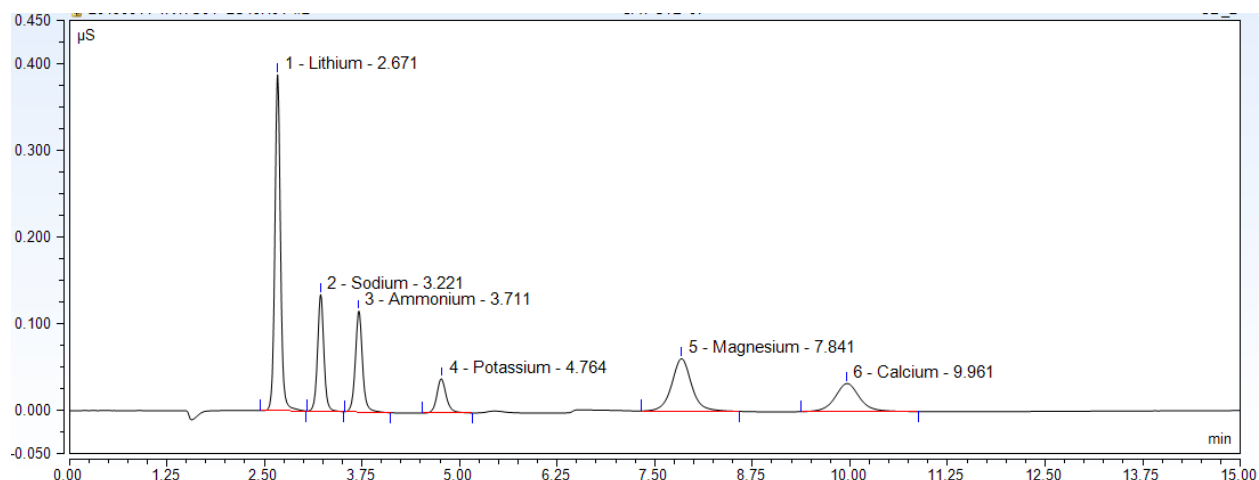


Figure 2 IC chromatogram for cations

9. Calculations and Reporting

- 9.1 Confirm that all QC criteria are met before reporting. Otherwise, fix problems and re-analyze samples. See details in section 11.
- 9.2 The concentration of each ion is calculated by the Dionex software.
- 9.3 Calculate the total amount of anions and cations of each filter, where
 $Mass (\mu g) = Concentration (\mu g / mL) \times Extraction Volume (mL, 12mL)$
- 9.4 Copy the Dionex software generated report sheet to an excel sheet and label it with the naming convention for the file: "YYMMDD (date of analysis) data sheet 1" for export to LIMS.

10. Limit of Detection

- 10.1 The limit of detection (LOD) is defined as the lowest concentration an analyte can be quantified with a defined confidence level. The calculated LOD for this method is determined by analyzing a low concentration standard seven times, as follows:

$$LOD = t_{(n-1, 1-\alpha=0.99)} \times \sigma$$

where σ is the standard deviation and is calculated for the seven replicates, and where t is the Student's t value associated at 99% confidence level. The calculated LOD = 3.143 (n=7) x standard deviation.

- 10.1.1 The Student's t value is dependent upon the degrees of freedom associated with the analysis. The degrees of freedom of the

SOP No. 142 - PROCEDURE FOR THE ANALYSIS OF PARTICULATE ANIONS AND CATIONS IN MOTOR VEHICLE EXHAUST BY ION CHROMATOGRAPHY

analysis are equal to the number of replicate measurements, n, of the lowest concentration standard minus one. An abbreviated table of values of t associated at 99% confidence level is shown below (Ref. 12.5):

Degrees of Freedom (n-1)	t-value
4	3.747
5	3.365
6	3.143
7	2.998

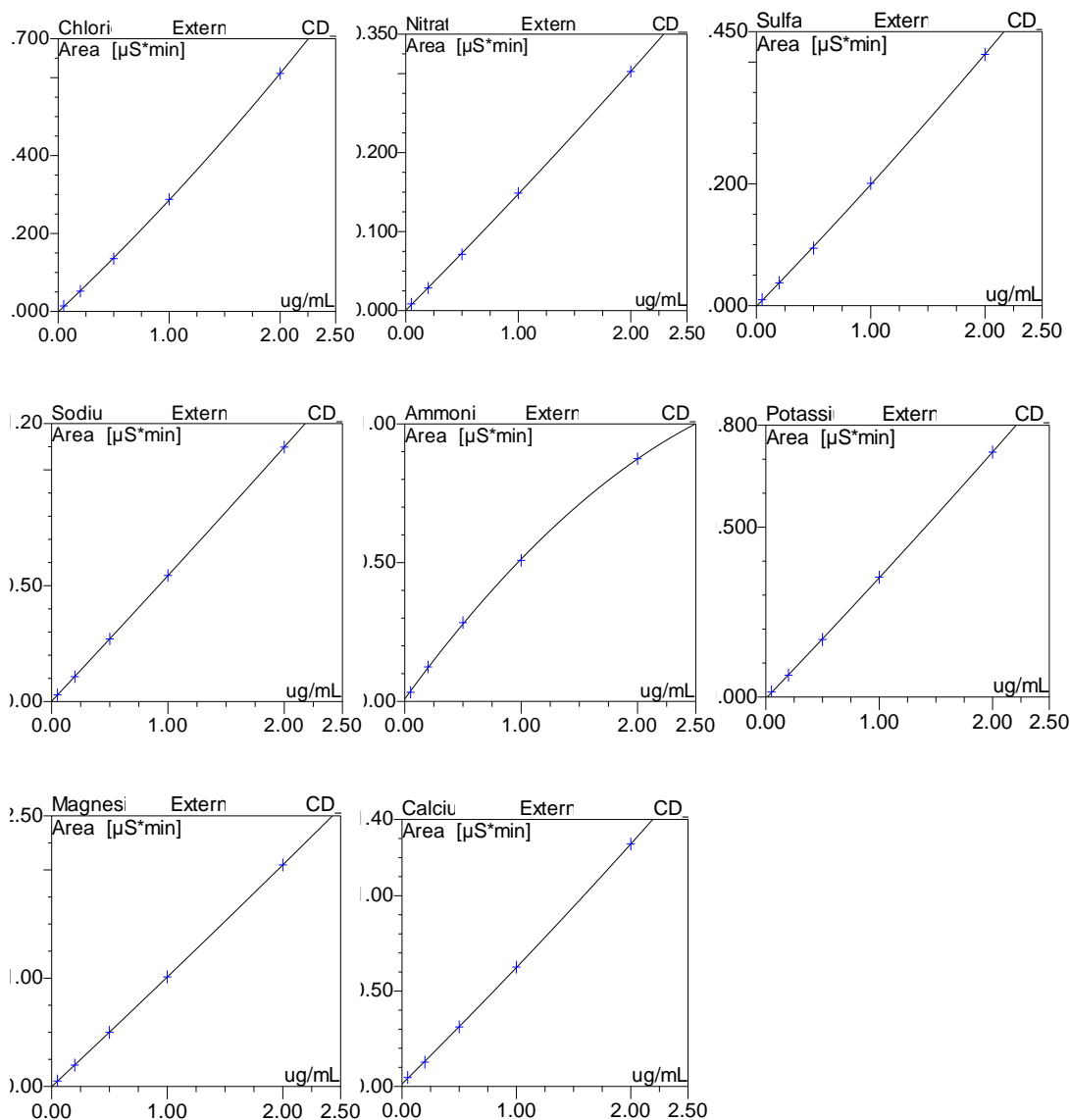
- 10.2 The LOD is determined at least once per year or after modifications or repair on the instruments which can affect the instrument sensitivity.
- 10.3 The reporting limit is at least 10 times the standard deviation of the LOD.
- 10.4 The table below lists the current calculated LOD based on 0.02 ug/mL standard. For the data continuity, the reporting limit remains the same as previous assessment.

	Chloride	Nitrate	Sulfate	Sodium	Ammonium	Potassium	Magnesium	Calcium
Concentration of Lowest Standard Used (µg/mL)	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Standard Deviation	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.005
Calculated LOD (µg/mL)	0.004	0.003	0.003	0.003	0.003	0.003	0.003	0.016
Calculated Reporting limit (10* Std Dev) (µg/mL)	0.014	0.010	0.010	0.010	0.010	0.010	0.010	0.051
Reporting limit with 12 mL sample extraction (µg/filter)	0.40	0.20	0.20	0.40	0.20	0.20	0.20	0.70

- 10.5 A multi-point calibration is typically in the range of 0.02 µg/mL - 2.00 µg/mL. The correlation coefficient of the calibration must be greater than or equal to 99% for all analytes, otherwise, the standards are re-analyzed or re-prepared, or the instrument checked.

SOP No. 142 - PROCEDURE FOR THE ANALYSIS OF PARTICULATE ANIONS AND CATIONS IN MOTOR VEHICLE EXHAUST BY ION CHROMATOGRAPHY

10.6 The following plots are examples of typical calibration curves.



11. Quality Control

11.1 Quality control (QC) standards:

Dilute the stock standard solutions labeled "Second Source" to the 0.50 µg/mL concentration level.

11.2 QC standards are analyzed after both sets of calibration standards are completed and again at the end of the samples. The acceptable limits for the control standards are determined annually using results of control analysis over the previous year. The limits are defined as follows:

SOP No. 142 - PROCEDURE FOR THE ANALYSIS OF PARTICULATE ANIONS AND CATIONS IN MOTOR VEHICLE EXHAUST BY ION CHROMATOGRAPHY

Upper Control Limit (UCL) = average value + 3 times the standard deviation
 Upper Warning Limit (UWL) = average value + 2 times the standard deviation
 Lower Warning Limit (LWL) = average value - 2 times the standard deviation
 Lower Control Limit (LCL) = average value - 3 times the standard deviation

- 11.3 QC values outside the control limit are considered as a “QC failure.”
- 11.4 If any of the QC values is between control and warning limits (UWL or LWL), it is considered a QC “warning”. When warnings occur on two consecutive analyses, the second value is considered a QC failure. A QC failure requires corrective action.
- 11.5 The initial values for control limits were calculated from the results of analysis using the ICS 5000 instrument. These values are shown in the table below as an example.

Table of Control Limits:

	Chloride (µg/mL)	Nitrate (µg/mL)	Sulfate (µg/mL)	Sodium (µg/mL)	Ammonium (µg/mL)	Potassium (µg/mL)	Magnesium (µg/mL)	Calcium (µg/mL)
Number of QC analyzed	8	8	8	8	8	8	8	8
Standard Deviation	0.012	0.025	0.036	0.014	0.014	0.012	0.013	0.020
UCL	0.550	0.597	0.639	0.537	0.551	0.530	0.529	0.547
UWL	0.537	0.572	0.603	0.524	0.537	0.518	0.516	0.527
Average	0.513	0.523	0.531	0.496	0.509	0.493	0.499	0.488
LWL	0.488	0.474	0.459	0.469	0.482	0.469	0.463	0.428
LCL	0.475	0.449	0.498	0.455	0.468	0.456	0.450	0.501

- 11.6 DI water blanks and filter blanks are analyzed with each set of extracted filters. If any water blank shows a peak greater than the LOD, the source of contamination must be investigated and remedied.
- 11.7 Ten percent of sample extracts are randomly selected for replicate analysis. Replicate analysis consists of a double injection of the same filter extract. The relative percent difference (RPD) in concentrations between the pair of analyses is calculated for each of the target ions as the following:

$$RPD = \frac{|\text{Sample Conc.} - \text{Replicate Conc.}|}{\text{Average Conc. of Both Analyses}} \times 100$$

SOP No. 142 - PROCEDURE FOR THE ANALYSIS OF PARTICULATE ANIONS AND CATIONS IN MOTOR VEHICLE EXHAUST BY ION CHROMATOGRAPHY

- 11.8 A limit on the allowable RPD is established based on the average concentration of the replicate runs, as shown in the following table:

Average Measurement for Replicate Runs	Allowable RPD (%)
1 to 5 times reporting limit	Not evaluated
5 to 20 times reporting limit	<25%
Greater than 20 times reporting limit	<15%

- 11.9 If the measured RPD of any of the target ions is greater than the allowable limit, the sample is re-analyzed.

12. References

- 12.1 EPA Method 300.6, Orthophosphate, Nitrate, and Sulfate in Wet Deposition by Chemically Suppressed Ion Chromatography, USEPA, March 1986.
- 12.2 EPA: Quality Assurance Guidance Document, Final, Quality Assurance Project Plan, PM 2.5 Speciation Trends Network Field Sampling, EPA-4154/R-01-001.
- 12.3 EPA: Guideline on Speciated Particulate Monitoring August 1998
<http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/drispec.pdf>
- 12.4 ARB SOP MLD 064: Standard Operating Procedure for the Analysis of Anions and Cations in PM 2.5 Speciation Samples by Ion Chromatography.
- 12.5 Harris, Daniel C., "Quantitative Chemical Analysis", *W.H. Freeman & Co.*, 4th ed., 1995
- 12.6 Yele Sun, Guoshun Zhuang, Aohan Tang, Ying Wang and Zhisheng An[§] "Chemical Characteristics of PM_{2.5} and PM₁₀ in Haze-Fog Episodes in Beijing" *Environ. Sci. Technol.*, 2006, 40 (10), pp 3148–3155

SOP No. 142 - PROCEDURE FOR THE ANALYSIS OF PARTICULATE ANIONS AND CATIONS IN MOTOR VEHICLE EXHAUST BY ION CHROMATOGRAPHY

13. Revision Record

Revision	Date	Responsible Person	Description of Change	Status
Revision 1	May 2006	Norma Castillo	Initial Release modified from MLD 064	Approved
Revision 1.1	August 2006	Yanbo Pang	Addition of the Cation analysis with new IC instrument ICS2000	Approved
Revision 1.2	June 2007	Luzviminda Salazar	7.1.3 Change of sample extraction volume from 25 mL to 12 mL 5.4.3 Quality control standards: Change of concentration of the control standard from 1.0 µg/mL to 0.5 µg/mL 5.4.2 The number of multipoint calibration levels used was changed from 10 levels to 6 levels eliminating some of the higher concentrations 8.6 Spike analysis was eliminated from the analysis	Approved
Revision 2.0	June 2011	Luzviminda Salazar	2 Addition of reportable ions: for anions: chloride, for cations: magnesium and calcium 3.2 Change of sample volume: 25 µL sample instead of 100µL 4 Change to a new instrument from a two system instruments ICS 2500 and ICS 2000 to just one system ICS 3000 dual pump system 4.2 Anion analysis using KOH eluent instead of Na ₂ CO ₃ Change of column: AS18column instead of AS 14A column 5.13 Revised cleaning steps for the autosampler vials and caps 7.1 Addition of 100uL isopropyl alcohol to the Teflon filters before extraction 7.2.2 Remove monitoring of the gas line because it is no longer used with the new instrument 8.1.3 Reporting limits were lowered because detection limits are better with the new instrument configuration.	Approved
Revision 2.1	August 2014	Yilin Ma	Change the SOP name from SOP No. MLD 142 to SOP MV-AEROSOL-142	Approved

SOP No. 142 - PROCEDURE FOR THE ANALYSIS OF PARTICULATE ANIONS AND CATIONS IN MOTOR VEHICLE EXHAUST BY ION CHROMATOGRAPHY

			due to Division and Branch name change	
Revision 2.2	July 2015	Yilin Ma	One lower level of standard solution (0.02 µg/mL) was added to the calibration table, and was used for LOD determination.	Approved
Revision 2.3	March 2016	Yilin Ma	Change of analytical instrument from ICS3000 to ICS5000 due to system replacement	
Revision 2.4	Sept. 2019	Guenter Engling	Change of division name	