

Title: Determination of Gaseous and Particulate Inorganic Air Pollutants by Ion Chromatography		Copy No: ##
Method No.: 6.05/3.0/M	Effective Date: December 28, 2012	Location: ###

QSM Approval: _____

Determination of Gaseous and Particulate Inorganic Air Pollutants by Ion Chromatography

1. INTRODUCTION AND SCOPE

- 1.1. This method is applicable to the determination of gaseous and particulate inorganic air pollutants (listed in Table 1) in aqueous solutions extracted from different collection media (nylon, Teflon, carbonate-coated filters or denuder, and citric acid-coated filters or denuders).
- 1.2. Method detection limits (MDLs) for the analyzed ions are in the range of low µg/filter and low µg/denuder (see Sec. 11). Expanded measurements uncertainties (k = 2) at the concentrations above method quantitation limits (MQLs = 3xMDLs) are in the range of 5-15% (see Sec. 12).
- 1.3. This method is recommended for use only by, or under the supervision of, analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatograms.

TABLE 1. Inorganic Ions Determined by this Method

Ion	Media	Observation	Extraction Solution*
NH ₄ ⁺	Citric Acid-Coated Filter	Gas Phase	Deionized Water
	Citric Acid-Coated Denuder	Gas Phase	Deionized Water
NO ₃ ⁻ , SO ₄ ²⁻ , NO ₂ ⁻	Teflon Filter	PM 2.5	Deionized Water
NO ₃ ⁻ , NO ₂ ⁻	Nylon Filter	Gas Phase	1.0 mM Bicarbonate/3.5 mM Carbonate
SO ₄ ²⁻	Carbonate-Coated Filter	Gas Phase	0.09% v/v Hydrogen Peroxide
NO ₃ ⁻ , SO ₄ ²⁻ , NO ₂ ⁻	Carbonate-Coated Denuder	Gas Phase	0.09% v/v Hydrogen Peroxide

Consult SOP 6.06/.* /S and SOP 6.09/*.* /S

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2. SUMMARY OF METHOD

2.1. Ion chromatography combines suppressed-conductometric detection with the separation capabilities of ion exchange resins. The ions of interest are separated and measured, using a system comprising guard columns, analytical columns, suppressor devices, and conductivity detectors (Table 2). The suppressor reduces the background conductivity of the eluent to a negligible level. The concentrations of the separated ions are determined by measuring their respective conductivities. Ions are identified by their retention times as compared to the retention times of known standards.

2.2. The following programs are used for automatic determination of anions and cations:

AnionProgram: to start determination of major anions with isocratic elution.

CationProgram: to start determination of ammonium with isocratic elution.

Anion_Stop and **Cation_Stop** programs automatically turn off all parts of the IC System.

TABLE 2. Experimental Conditions

Parameter	Cation	Anions
Ions	NH ₄ ⁺	NO ₃ ⁻ , SO ₄ ²⁻ , NO ₂ ⁻
Separation column	IonPac-CS12A (4 mm x 250 mm)	IonPac-AS14 (4 mm x 250 mm)
Guard column	IonPac-CG12A (4 mm x 50 mm)	IonPac-AG14 (4 mm x 50 mm)
Suppressor	CSRS 300 (4 mm)	ASRS 300 (4 mm)
Eluent	18 mM MSA*	1.0 mM NaHCO ₃ / /3.5 mM Na ₂ CO ₃
Eluent flow-rate	1.0 mL/min	1.2 mL/min
Sample loop	50 µL	50 µL

*MSA - methanesulfonic acid

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3. INTERFERENCES

3.1. Anion method

3.1.1 Interference can be caused by substances with retention times that are similar to, and overlap with, those of the ions of interest (e.g. some dicarboxylic acids coelute with sulphate).

3.2. Cation method

3.2.1 Large amounts of an ion can interfere with the peak resolution of an adjacent ion (e.g. sodium-ammonium-potassium).

4. SAMPLE REQUIREMENT

4.1. Exposed denuders and filters are stored in the refrigerator and analyzed within 3 and 6 months of reception in the Ion Analysis laboratory, respectively.

4.2. Carry out the analysis the same day as the extraction of filters/denuders or as specified in the appropriate procedure (consult SOP 6.06/*.*/*S and SOP 6.09/*.*/*S).

5. EQUIPMENT and SUPPLIES

5.1. All ion chromatography equipment and software are from one manufacturer (Dionex, Sunnyvale, CA, USA). The Dionex ICS-3000 System* for dual-analysis consists of:

5.1.1 Dual pump (DP), two self-regenerating suppressors, two microconductivity detectors (CD), two guard columns, and two separation columns.

5.1.2 Automated sample changer (AS) with tray carrying sample vials with sample size ~2 mL.

5.1.3 Chromeleon Xpress TabletStation containing the operating and processing software (Chromeleon 6.***, Dionex, Sunnyvale, CA, USA).

Note: *Other validated Dionex IC System can also be used.

5.2. Balances

5.2.1 Analytical balance (Mettler AT 400) - sensitivity 0.1 mg;

5.2.2 Technical balance (Mettler PR 1200) – sensitivity 10 mg.

5.3. Ultrasonic bath or mechanical shaker.

5.4. Micropipettes and Bottle Dispensers.

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5.5. Glassware, Sample Vials and Caps. **Note:** All glassware used in the laboratory is Class A (Consult SOP 6.02/*.*S for cleaning of all labware).

6. REAGENTS and STANDARDS

Unless otherwise indicated, it is intended that all reagents are analytical grade, where such specifications are available; otherwise, the best available grade is used.

6.1. **Reagent water:** Use high-purity degassed, deionized water (resistance > 18 MOhm cm) for reagent and standard makeup to prevent gas bubbles from forming in the reagent line and pump.

6.1.1 To degas water, fill 4L reservoir with fresh deionized water and purge with helium for approximately 20 minutes.

6.2. Eluents

6.2.1 **0.5 M sodium bicarbonate (NaHCO₃) stock anion eluent solution:** Dissolve 21.00 g of NaHCO₃ in deionized, degassed water and dilute to 500 mL.

6.2.2 **0.5 M sodium carbonate (Na₂CO₃) stock anion eluent solution:** Dissolve 26.49 g of Na₂CO₃ in deionized, degassed water and dilute to 500 mL.

Note: Store bicarbonate and carbonate stock solutions in the refrigerator at 4±2°C for up to one year.

6.2.3 **Working anion eluent solution (1.0 mM NaHCO₃ / 3.5 mM Na₂CO₃):** Dilute 14 mL of 0.5 M Na₂CO₃ stock solution and 4 mL of 0.5 M NaHCO₃ stock solution to 2 L with deionized, degassed water.

6.2.4 **1 M methanesulphonic acid (MSA) stock cation eluent solution:** Weigh out 96.10 g of MSA. Carefully add this amount to a 1-liter volumetric flask containing about 500 mL of deionized, degassed water. Dilute to the mark and mix thoroughly.

6.2.5 **Working cation eluent solution (18 mM MSA):** Dilute 36 mL of stock solution to 2 L with deionized, degassed water.

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6.3. Standards

6.3.1 Anion Mixed Standard Solutions

Stock A-I: Prepare mixed standard solutions from single stock anion standard solutions (10,000 mg/L) in 50 mL volumetric flask with deionized, degassed water.

Stock A-II: Prepare mixed standard solutions from single stock anion standard solutions (10,000 mg/L) in 50 mL volumetric flask with deionized, degassed water. Add 75 µL of 50% NaOH to stabilize nitrite.

The anion mixed standard solutions should be prepared within time limits specified in Table 3, or when any deterioration is observed, and stored in the refrigerator at 4±2°C. Consult SOP 6.03/*.*S regarding preparation, storage and use of the standard solutions in the laboratory.

TABLE 3. Preparation of Anion Mixed Standard Solutions

Stock A-I <i>(Fresh every 6 months)</i>			Stock A-II <i>(Fresh every 6 months)</i>		
Ion	mL of Stock (in 50 mL)	Concentration, mg/L	Ion	mL of Stock (in 50 mL)	Concentration, mg/L
Sulphate	1	200	Nitrite	1	200
Nitrate	1	200	50 % NaOH, 75 µL		

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6.3.1.1 Anion Calibration Standards

The anion calibration standards (Cal-0A – Cal-4A) should be prepared fresh prior to analysis; Cal-5A & Cal-6A should be prepared fresh every 3 months, or when any deterioration of anions (e.g. nitrate) is observed. Store Cal-5A & Cal-6A in refrigerator at 4±2°C.

Note: The concentration of calibration standards may be adapted to the sample concentration range (See Section 7.1).

TABLE 4. Preparation of Anion Calibration Standards and their concentrations.

	Cal-0A	Cal-1A	Cal-2A	Cal-3A	Cal-4A	Cal-5A *	Cal-6A **
Final vol. (mL)	10	100	100	50	50	50	50
Stock A-I (µL)	0	25	250	500	2000		
Stock A-II (µL)	0	50	125	125	250		
Concentration, mg/L							
Nitrite	0	0.1	0.25	0.5	1	5	10
Nitrate	0	0.05	0.5	2	8	20	40
Sulphate	0	0.05	0.5	2	8	20	40

*Cal-5A - Add 100 µl of each single stock standard (10,000 mg/L) of nitrate and sulphate, and 25 µL of nitrite; and if standard is prepared in water, **add 75 µL of 50% NaOH.**

** Cal-6A - Add 200 µl of each single stock standard (10,000 mg/L) of nitrate and sulphate, and 50 µL of nitrite; and if standard is prepared in water, **add 75 µL of 50% NaOH.**

Note: All calibration standards for analysis of nylon, and carbonate coated filter/denuder extracts are prepared in the 1.0 mM NaHCO₃/3.5 mM Na₂CO₃ buffer. All standards for analysis of Teflon filter extracts are prepared in deionized, degassed water.

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6.3.2 Anion Control Standards

- CS-A1:** prepare mixture of NO_3^- ; SO_4^{2-} (each 0.6 mg/L), and NO_2^- (1 mg/L) from reference mixed/single anion standards, e.g. the AccuIon™ Reference Standards (AccuStandard Inc.).
- CS-A2:** Prepare mixture of NO_3^- , SO_4^{2-} (each 5 mg/L) from NIST anion stock standard solutions.

Control standards CS-A1 and CS-A2 should be prepared within time limits specified in Table 5 and Table 6, or when any deterioration of ions is observed, and stored in the refrigerator at $4 \pm 2^\circ\text{C}$. Consult SOP 6.03/*.*S for preparation, storage and use of standard stock solutions.

Note: Control standard must be prepared in the same matrix as the calibration standards.

TABLE 5. Preparation of Control Standard **CS-A1**

Stock Solution	mL into 50 mL vol. Flask <i>(Fresh biweekly)</i>
IC-MAN-12-1	2
IC-NO2-1X-1	0.5
(add 50% NaOH, 75 μL - for water matrix only)	

TABLE 6. Preparation of Control Standard **CS-A2**

Stock Solution	μL into 100 mL vol. Flask <i>(Fresh every 6 months)</i>
Nitrate, 1000 mg/L	500
Sulphate, 1000 mg/L	500

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6.3.3 Cation Standard Solution

Stock C: Prepare standard solution from ammonium single stock (10,000 mg/L) in 50 mL volumetric flask with deionized, degassed water. Stock C should be prepared every 6 months, or when deterioration of ammonium is observed, and stored in the refrigerator at 4±2°C.

TABLE 7. Preparation of Cation Standard Solution

Ion	mL of Single Stock (in 50 mL)	Concentration, mg/L
Ammonium	2	400

6.3.3.1. Cation Calibration Standards

Note: The concentration of calibration standards may be adapted to the sample concentration range (See Section 7.1).

The cation calibration standards (Cal-0C – Cal-4C) should be prepared fresh prior to analysis; Cal-5C should be prepared fresh every 3 months, or when any deterioration of ammonium is observed. Store Cal-5C in refrigerator at 4±2°C.

TABLE 8. Preparation of Cation Calibration Standards and their concentrations

	Cal-0C	Cal-1C	Cal-2C	Cal-3C	Cal-4C	Cal-5C*
Final vol. (mL)	10	200	100	50	50	50
Stock C (µL)	0	20	200	250	500	
Concentration, mg/L						
Ammonium	0	0.04	0.8	2	4	10

* Cal-5C - Add 50 µl of ammonium stock standard (10,000 mg/L).

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6.3.4 Cation Control Standards

- **CS-C1:** ammonium (1.0 mg/L); prepare CS-C1 by diluting 50µL of reference standard IC-NH4-10X-1 (1000 mg/L), in a 50 mL volumetric flask with degassed, deionized water.

Note: CS-C1 is prepared every 2 weeks, or when deterioration of ammonium is observed, from commercially available certified standards, e.g. the AccuIon Reference Standard (AccuStandard Inc.), and stored the refrigerator at 4±2°C.

- **CS-C2:** ammonium (4 mg/L); prepare CS-C2 by diluting 200µL of reference standard IC-NH4-10X-1 (1000 mg/L), in a 50 mL volumetric flask with degassed, deionized water.

Note: CS-C2 is prepared every 3 months, or when deterioration of ammonium is observed, from commercially available certified standards, e.g. the AccuIon Reference Standard (AccuStandard Inc.), and stored the refrigerator at 4±2°C.

7. CALIBRATION AND STANDARDIZATION

7.1. Calibration of the instruments is performed using working standards before analysis of the first set of samples in any given week. Calibration may also be necessary after unusual performance of the instrument (e.g. suppressor failure). The instruments do not need to be re-calibrated during the remainder of the week as long as the calculated concentrations of verification and control standards are within the specified limits.

7.1.1. The calibration uses the external standard quantitation method. The quadratic dynamic range is established using a multi-point calibration curve constructed for every target analyte (includes Cal-0 – reagent blank to establish calibration baseline). If the coefficient of correlation for the calibration curve is better than 0.995, linearity for the working range is established. A high-concentration calibration curve includes Cal-5, or Cal-5 and Cal-6, and is used for highly concentrated samples.

7.2. Verify calibration accuracy by analyzing quality control standards at two different concentration ranges (CS-A/CS-C). If the response for the major ions varies from expected values by more than ±10% (See Section 10.2), fresh control standards have to be prepared. If the results are still more than the specified limits, a new calibration curve must be prepared. If the results still exceed the known values, the analyses should be terminated until the source of the problem is identified and corrected.

7.3. Verify the system calibration and stability daily throughout the analysis by intermittently analyzing quality control standards (i.e.: every fifteen samples; See Appendix A). If the concentrations of determined analyte fall outside acceptable

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limits (See Section 10.2), then that analyte is deemed to be “out of control”. All samples following the last acceptable control standard should be reanalyzed.

8. ANALYSES

- 8.1. Make sure that all necessary maintenance procedures of instruments are done before batch analysis.
 - 8.1.1. Check eluents every day to see if there are enough to run.
 - 8.1.2. Make sure that water used for flushing the autosampler syringe is replaced every week, and record water change date in the logbook. **Note:** Flush and prime the syringe after replacing the water.
- 8.2. Start up instruments and equilibrate the system for at least 90 min. Check background conductivity and backpressure after the system stabilizes (use control chart to record values).
- 8.3. Prepare the sequence for the automated run (Appendix A), which include samples, calibration standards, blanks, spikes, control standards, verification standards and duplicate samples.
 - 8.3.1. The sample files and sequence are named according to the batch name.
- 8.4. Extract filters and/or denuders (consult SOP 6.06/*.*S and 6.09/*.*S).
 - 8.4.1. Prepare spiked blank denuders (SP-VSA/SP-VSC) for analysis of denuders.
 - **SP-VSA:** blank carbonate coated denuder spiked with Cal-3A – in the sample vial combine 20 µL of Stock A-I and 5 µL of Stock A-II with 1.975 mL of blank denuder extract.
 - **SP-VSC:** blank citric acid coated denuder spiked with Cal-3C - in the sample vial combine 10 µL of Stock C with 1.990 mL of blank denuder extract
 - 8.4.2. Prepare spiked blank filters for analyses of filters
 - **SP-MDL:** Place blank Nylon filter in labeled extraction vial and spike it with 8mL of the lowest calibration standard (Cal-1A)
 - **SP-VSA:** Place blank Nylon filter in labeled extraction vial and spike it with 8mL of the verification standard (Cal-3A)
- 8.5. Fill the sample vials (2 mL) with the calibration standards, quality control and unknown samples and place them in the sample tray (sample schedule shown in Appendix A), and start the sequence run.
- 8.6. After run of Cal-3 (system performance check), compare values for retention time and peak area (sulphate/ammonium) with that of most recent one by overlapping

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chromatograms. If value of retention times or peak area exceeds a $\pm 10\%$ stop the run and eliminate the source of the problem (e.g. prepare new working standards, and/or eluents, and/or change column).

- 8.7. Check system calibration and stability daily throughout the analysis as described in Section 7.

9. DATA PROCESSING

- 9.1. Before reprocessing, copy all files from the lab computer to the analyst's office computer, and create a backup file (backup files should be stored in: Inorg:\IC_raw_data_backup). After making sure that all data has been copied and backed up, delete it from the lab computer.
- 9.2. Prepare a calibration curve for each analyte using Chromeleon Chromatography Software by plotting instrument response (peak area/height) against standard concentration (including Cal-0). Check all calibration curves (See Section 7).
- 9.3. Reprocess all quality control samples and check accuracy of the analytes. Results for control and verification standards should be within specified limits (See Section 10.2). If the results are outside limits, check again the calibration curves and correct them if required. Flag the results that are out of limits. If two out of three successive results are outside limits, control standards and affected samples must be reanalyzed.
- 9.4. Reprocess all unknown samples. Visually check all chromatograms. Any sample exceeding the highest standard should be diluted and reanalyzed.
- 9.5. Use Excel software to prepare a final report based on a template of that project.
- 9.5.1. Before reporting to the client, the authorized lab person must check all results (see Appendix B).
- 9.6. After the final report is completed, approved and password-protected, transfer all files for backup to the Network - Inorg on 'Ncr.int.ec.gc.ca\Lab\Riv' drive - into appropriate directory. Validate the EXCEL templates containing formulas and/or macros at least once a year or after major changes of the acquisition method (SOP 2.11/*.*S). The validated templates should be password-protected (Read Only). Record the file name and the validation date in the designated log book. Store hard copy of the report for at least one year (e.g. in the Room 172).

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10. QUALITY CONTROL

10.1. The QC samples used normally comprise 10-25% of total sample through put.

10.1.1. Each batch of approximately 80 samples includes various blanks, control/verification standards, spikes, and duplicate samples (See Appendix A).

10.1.1.1. Vial Blank (VialBlank) - a volume of analyte-free water/extraction solution, which undergoes processing identical to that carried out for the samples. The blank results are used to assess contamination.

10.1.1.2. Method Blank (MetBlank) – a blank filter in analyte-free water/extraction solution, which undergoes processing identical to that carried out for the samples. The blank results are used to assess contamination.

10.1.1.4. Control Standard (CS) – prepared from certified standard solutions is used to monitor accuracy of the calibration.

10.1.1.5. Verification Standard (VS) – standard from calibration (Cal-3) is used to monitor system stability.

10.1.1.6. Duplicate – a second aliquot of the same sample is used to evaluate the reproducibility of the laboratory procedure during the run of a single batch.

10.1.1.7. Spike (SP-MDL and SP-VSA/SP-VSC) – a blank filter spiked with lowest calibration standard or VS solution, which undergoes processing identical to that carried out for the samples, or blank denuder extract spiked with VS. The Spike results are used to calculate recoveries of analytes during the samples processing, and evaluate matrix interferences.

10.2 Data Acceptance

10.2.1 Control Standards and Verification Standards, and Spikes should be within 10% of target values.

10.2.2 Blanks should be below method detection limits (MDLs).

10.2.3 Duplicate samples should have relative percentage difference (RPD) within 10-15% (for samples at concentration higher than the quantitation limit).

10.2.4 If the above data acceptance criteria are not met, specific control standards and samples are repeated.

10.3 All quality control data should be maintained and available for easy reference or inspection.

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11. METHOD DETECTION LIMITS and METHOD VALIDATION

11.1. The single laboratory (Particulate Characterization Unit - AAQS) MDLs for the analyzed ions are calculated based on historical and/or recent measurements of blanks and/or low concentration standard prepared in the respective matrix.

11.1.1 Citric acid and sodium carbonate coated denuders. Based on the historical data or measurement of blanks (at least 7) calculate the average concentration, standard deviation and estimate the MDL_B:

$$MDL_B = C_B + t_{(0.99, n)} S_{Std}$$

where C_B is the average concentration of blanks, $t_{(0.99, n)}$ is the Student's test for 99% confidence level (single tailed), and $n = n_i - 1$ degrees of freedom, n_i is the number of repeated measurement, and S_{Std} is their standard deviation.

11.1.2 Nylon filters. Based on repeated measurements (at least 7) of the low concentration standard in matrix at concentrations not higher than 5-10 times MDL calculate the standard deviation and estimate the MDL_{LCS}:

$$MDL_{LCS} = t_{(0.99, n)} S_{Std}$$

where $t_{(0.99, n)}$ is the Student's test for 99% confidence level (single tailed), and $n = n_i - 1$ degrees of freedom, n is the number of repeats, and S_{Std} is their standard deviation.

11.1.3 MDLs for the analyzed ions are in the range of low µg/filter and low µg/denuder. For the records of calculated and reported MDLs refer to the latest Method Verification Binder (Room 172).

11.1.4 MDLs should be checked at least once a year, and/or after any major modification of the instrument and/or method.

11.2. Method validation/verification is accomplished by using the QC samples described in Section 10, and by participation in Proficiency Testing (PT) Programs. For the records of precision and accuracy of measurements refer to the latest Method Verification Binder (Room 172).

12. ESTIMATION of MEASUREMENT UNCERTAINTY

12.1. The measurement of uncertainty is calculated based on the Type A approach recommended by the CALA (consult SOP 2.10/*.*/*S).

12.2. The possible sources of uncertainty and QC data used for uncertainty estimation are listed in Appendix C.

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- 12.3. The overall uncertainties at concentrations above method quantitation limits (MQLs = 3xMDLs) for determined ions are in the range of 5-15%. For the records of estimated uncertainties refer to the latest Method Verification Binder (Room 172).
- 12.4 The uncertainty should be estimated at least once a year, and/or after any major modification of the method. The most recent estimated values should be reported to the client.

The method is fit for the intended use.

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13. MAINTENANCE

TABLE 9. Routine maintenance of the IC systems

Pumps	
Pump heads	<ul style="list-style-type: none"> • Clean when loss of performance is observed • See Product Manual, Dionex Corporation
Pistons	<ul style="list-style-type: none"> • Clean or replace as required • See Product Manual, Dionex Corporation
Check valves	<ul style="list-style-type: none"> • Prime pump after system was shut down • Clean or replace when pump has lost prime or it is difficult to re-prime
Detector/Chromatography Module	
Leaks	<ul style="list-style-type: none"> • Periodically check for leaks or spills inside modules and for crimping of liquid lines
Conductivity cells	<ul style="list-style-type: none"> • Clean as required
Sample loops	<ul style="list-style-type: none"> • Clean/replace as required
Injection/diverter valves	<ul style="list-style-type: none"> • Rebuild annually • Clean monthly or as required
Columns	<ul style="list-style-type: none"> • Change bed support, guard and analytical columns when necessary (analytical parameters such as retention time, peak shape or backpressure etc. are changing) • See Product Manual, Dionex Corporation
Suppressor	<ul style="list-style-type: none"> • See Product Manual, Dionex Corporation
Autosampler	<ul style="list-style-type: none"> • Daily: check syringe for air bubbles • Periodically: check alignment of the sampling needle

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14. APPLICABLE SOPs

- 2.01/*.*/*S “Gravimetric Measurement”
- 2.06/*.*/*S “Laboratory Refrigerators and Freezers”
- 2.10/*.*/*S “Estimation of Uncertainty in Chemical Analysis”
- 2.11/*.*/*S “Electronic System Validation and Maintenance”
- 6.02/*.*/*S “Labware Cleaning”
- 6.03/*.*/*S “Preparation, Storage and Use of Standard Solutions”
- 6.06/*.*/*S “Extraction of filters”
- 6.09/*.*/*S “Coating and Extraction of Honeycomb Denuders”
- 19.02/*.*/*S “Volumetric Measurement- Micro pipettes and Bottle-Top Dispensers”
- SWP-001/*.* “Safe Working Procedure and Policies”

15. REFERENCES

- 15.1. Chromatography System. Operator's Manuals, Dionex Corporation
- 15.2. Installation Instructions and Troubleshooting Guide for the Columns, Suppressors, and other Parts, Dionex Corporation
- 15.3. Chromeleon Chromatography Information Management System, Dionex Corporation
- 15.4. US EPA Method 300.6, Chloride, Orthophosphate, Nitrate, and Sulphate in Wet Deposition by Chemically Suppressed Ion Chromatography
- 15.5. US EPA Method 9056A, Inorganic Anions by Ion Chromatography, EPA Report SW-846 Ch 5
- 15.6. US EPA Method 300.7, Dissolved Sodium, Ammonium, Potassium, Magnesium, and Calcium in Wet Deposition by Chemically Suppressed Ion Chromatography
- 15.7. Standard Test Method for Determination of Dissolved Alkali and Alkaline Earth Cations and Ammonium in Water and Wastewater by Ion Chromatography, ASTM D6919-03
- 15.8. US EPA, Compendium Method IO-3.1, Selection, Preparation and Extraction of Filter Material, June 1999

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16. REVISIONS

July 2004: Authors: Ewa Dabek and Maria Piechowski

New document

August 2005: Reviewers: Maria Piechowski, Michal Suski

Minor changes through text: in Table 1..v/v..is added, and in Table 2 ..Ultra II..is removed ..0.25.. is changed to..0.30..; §5.1 is reedited; in §6.3.1.1 note is added; in §6.3.4.1 note is added, and in concentration table..25.. is changed to ..50...50 is changed to 100...125.. to ..250...250.. to..500..; in §6.3.2 information about nitrite is added; §6.3.6 is added; in §10.1.1..water.. is changed to ..water/extraction solution..

September 2005: Reviewers: Maria Piechowski, Michal Suski

In §6.31.1 ... if standard prepared in water add... is added; in §6.3.2 .. (add... - for water matrix only)... is added; in Section 15: US EPA methods are added.

July 2007: Reviewers: Maria Piechowski, Alicia Berthiaume, Michal Suski

Changes through text due to installation of the new Dionex System - ICS3000 in place of DX300. Duplicate samples are added (§10); Data Acceptance (§ 10.2) is added; appendices F and G are added; (4°C) is removed through text; Maintenance Table (§13) and §15 are updated.

July 2009: Reviewers: Maria Piechowski, Michal Suski

Changes through text: §6.3.8 – new; §8, 10, 13, 14, Table 1, and Appendix B – updated; text edited to reflect changes in division/section/lab structure/name.

December 2009: Reviewers: Maria Piechowski, Susannah Krack

§4.1 – holding time of samples added; §6.3 – in the calibration preparation tables “fresh as required” changed to “fresh prior to analysis”, “store ...in the refrigerator“ added, (See Section 7.1.)” added; §7 and §9 – “See Appendix E” changed to “See Section 10.2”; §7.2 – “warning limits” changed to “±10%”; §8.3 – “spiked blank filter or denuder (MetBlank-SP)” added; §8.4.1 – new; §8.5.1 and §10.1.1 – “spike” added; §9.6 – information about EXCEL templates validation – added; §10.1.1.6 – new; §10.2 – “and Spikes” added; §11.1 – new; §11.3 – information about CALA – added; §12.3 and §12.4 – new; §14 – 2.11/*.*/*S added; §15.8 – new; Appendix A – new; Appendix B – “VialBlank” and “MetBlank-SP” – added; Appendix D – “Duplicate” and “PT studies results” and note - added; Appendix E – removed; Appendix F – changed to E; Appendix G – changed to F.

July 2011: Reviewers: Maria Piechowski, Michal Suski

§1.2 – “tabulated in Appendix A” – removed – range of MDLs and uncertainties added; Table 1 - Cl⁻, Br⁻, PO₄³⁻ - removed from column 1, row 3; Table 2 – “CSRS” and “ASRS” changed to “CSRS 300” and “ASRS 300”; §5.1 – “(e.g. DX-600)” removed from note;

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§7.1.1 – “(includes STD0...)” – note in the brackets added; §8.1 – 8.1.1 removed – new numbering; §8.3, “reagent blank” - removed; §8.6 – new; §9.6 – name of the Network backup drive changed; §10.1.1 – 10.1.1.1 removed – new numbering; §10.2.3 – “RPD %” changed to “relative percentage difference (RPD)”; §11 – change in the title – “Method” added; §11.1 – “tabulated in Appendix A” removed; “/or” added; §11.1.1 – “or measurement” and “(at least 7)” added; §11.1.3 – new editing; §11.2 – new; 11.3 - removed;; §12.3 – new editing; §13 – new editing within paragraph - “Injection valves” change to “Injection/diverter valves”. Appendix A removed. All Appendices renamed accordingly and their references changed throughout the text.

December 2012: Reviewers: Michal Suski

Removed references to analysis of Cl, Br and PO4 throughout the text and tables; §1.2 – updated MDL values; replaced all “store in refrigerator” with “store in refrigerator at 4±2°C”; §6 – calibration standards renamed from STD to ‘Cal’; §6.3.3.1 – Cal-6C and Cal-7C removed; §6.3.4 - charts for preparation of cation control standards removed; CS-S3 and CS-S4 removed; §6.3.4 – CS-C1 concentration changed from 0.5 to 1.0mg/L, CS-C2 shelf life changed from 6 to 3 months. §7.4 combined with 7.3; §8.1.2 – removed; §8.1.3 – renumbered to §8.1.2; §8.4 – added SP-MDL to QC samples, renamed MetBlank-SP to SP-VSA/SP-VSC; §8.5 – removed parts referring to AS autosampler, §9.1 – new; §9.5.1 – removed, 9.5.2 re-numbered 9.5.1; §10.1.1.7 – changed QC sample names as per §8.4; Updated all appendices with most recent examples of forms and chromatograms.

Lead Reviewer: Michal Suski **Date:**
Title: Technologist, Particulate Characterization Unit

Approved by: Ewa Dabek **Date:**
Title: Head, Particulate Characterization Unit

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APPENDIX A

TABLE A1. Proposed sequence (Anions – Nylon)

Name	Type	Program	Method
test	Unknown	anionprogram	anions1
test	Unknown	anionprogram	anions1
Cal-0A	Standard	anionprogram	anions1
Cal-3A	Standard	anionprogram	anions1
Cal-1A	Standard	anionprogram	anions1
Cal-2A	Standard	anionprogram	anions1
Cal-4A	Standard	anionprogram	anions1
Cal-5A	Standard	anionprogram	anions1
Cal-6A	Standard	anionprogram	anions1
VialBlank	Unknown	anionprogram	anions1
MetBlank	Unknown	anionprogram	anions1
CS-A1	Validate	anionprogram	anions1
CS-A2	Validate	anionprogram	anions1
SAMPLE 1-16	Unknown	anionprogram	anions1
Duplicate	Unknown	anionprogram	anions1
SP-MDL	Validate	anionprogram	anions1
SAMPLE 17-32	Unknown	anionprogram	anions1
Duplicate	Unknown	anionprogram	anions1
CS-A1	Validate	anionprogram	anions1
SAMPLE 33-48	Unknown	anionprogram	anions1
Duplicate	Unknown	anionprogram	anions1
SP-VSA	Validate	anionprogram	anions1
SAMPLE 49-65	Unknown	anionprogram	anions1
Duplicate	Unknown	anionprogram	anions1
CS-A2	Validate	anionprogram	anions1
SAMPLE 66-80	Unknown	anionprogram	anions1
Duplicate	Unknown	anionprogram	anions1
CS-A1	Validate	anionprogram	anions1
VS-A	Validate	anionprogram	anions1
SHUT	Unknown	anion_stop	anions1

Note 1: if using Dionex AS-AP autosampler, do not load vials into position E8 on any of the trays.

Note 2: SHUT (system shutdown) should only be included if no further anion analyses will be carried out after the sequence is completed.

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TABLE A2. Proposed sequence (Anions – Denuders)

Name	Type	Program	Method
test	Unknown	anionprogram	anions1
test	Unknown	anionprogram	anions1
Cal-0A	Standard	anionprogram	anions1
Cal-3A	Standard	anionprogram	anions1
Cal-1A	Standard	anionprogram	anions1
Cal-2A	Standard	anionprogram	anions1
Cal-4A	Standard	anionprogram	anions1
Cal-5A	Standard	anionprogram	anions1
Cal-6A	Standard	anionprogram	anions1
VialBlank	Unknown	anionprogram	anions1
CS-A1	Validate	anionprogram	anions1
CS-A2	Validate	anionprogram	anions1
SAMPLE 1-16	Unknown	anionprogram	anions1
Duplicate	Unknown	anionprogram	anions1
SP-VSA	Validate	anionprogram	anions1
SAMPLE 17-32	Unknown	anionprogram	anions1
Duplicate	Unknown	anionprogram	anions1
CS-A1	Validate	anionprogram	anions1
SAMPLE 33-48	Unknown	anionprogram	anions1
Duplicate	Unknown	anionprogram	anions1
CS-A2	Validate	anionprogram	anions1
SAMPLE 49-65	Unknown	anionprogram	anions1
Duplicate	Unknown	anionprogram	anions1
CS-A1	Validate	anionprogram	anions1
SAMPLE 66-80	Unknown	anionprogram	anions1
Duplicate	Unknown	anionprogram	anions1
CS-A2	Validate	anionprogram	anions1
VS-A	Validate	anionprogram	anions1
SHUT	Unknown	anion_stop	anions1

Note 1: if using Dionex AS-AP autosampler, do not load vials into position E8 on any of the trays.

Note 2: SHUT (system shutdown) should only be included if no further anion analyses will be carried out after the sequence is completed.

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TABLE A3. Proposed sequence (Cations)

Name	Type	Program	Method
test	Unknown	cationprogram	cation1
test	Unknown	cationprogram	cation1
Cal-0C	Standard	cationprogram	cation1
Cal-3C	Standard	cationprogram	cation1
Cal-1C	Standard	cationprogram	cation1
Cal-2C	Standard	cationprogram	cation1
Cal-4C	Standard	cationprogram	cation1
Cal-5C	Standard	cationprogram	cation1
Cal-6C	Standard	cationprogram	cation1
Cal-7C	Standard	cationprogram	cation1
VialBlank	Unknown	cationprogram	cation1
CS-C1	Validate	cationprogram	cation1
CS-C2	Validate	cationprogram	cation1
CS-C3	Validate	cationprogram	cation1
CS-C4	Validate	cationprogram	cation1
SAMPLE 1-16	Unknown	cationprogram	cation1
Duplicate	Unknown	cationprogram	cation1
SP-VSC	Validate	cationprogram	cation1
SAMPLE 17-32	Unknown	cationprogram	cation1
Duplicate	Unknown	cationprogram	cation1
CS-C1	Validate	cationprogram	cation1
SAMPLE 33-48	Unknown	cationprogram	cation1
Duplicate	Unknown	cationprogram	cation1
CS-C2	Validate	cationprogram	cation1
SAMPLE 49-65	Unknown	cationprogram	cation1
Duplicate	Unknown	cationprogram	cation1
CS-C3	Validate	cationprogram	cation1
SAMPLE 66-80	Unknown	cationprogram	cation1
Duplicate	Unknown	cationprogram	cation1
CS-C4	Validate	cationprogram	cation1
VS-C	Validate	cationprogram	cation1
SHUT	Unknown	cation_stop	cation1

Note 1: if using Dionex AS-AP autosampler, do not load vials into position E8 on any of the trays.

Note 2: SHUT (system shutdown) should only be included if no further cation analyses will be carried out after the sequence is completed.

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APPENDIX B.

FIGURE B1. Data validation checklist

DATA VALIDATION CHECK LIST

Report Header

Client:
 Project:
 Number of samples:
 Checked/Approved by: _____ Date: _____
 Report Prepared:
 Report Version:

General Information

Sample Preparation
 Analytical Instrument
 Analytical Instrument Model #
 Method ID
 Batch #
 Analyst

NOTES:

.....

.....

.....

QA/QC samples checklist

Parameter	QC sample	Sample name	Check (by analyst)
Calibration: - correlation coefficient >99.5%			
QC Standards (recoveries within limits specified in the method)	VS		
	Control Standards		
	Other QCs		
Blanks (less than MDLs)	Vial Blanks		
	Method Blanks		
Spikes (recoveries within limits specified in the method)	MDL spike		
	VS spike		
Trend analysis			
Duplicates (%RPD within limits specified in the method)			

Samples analysis results checklist

Parameter	Check (by analyst)
Unusual results*	

Reporting checklist

Latest Template used for Internal Report	
Latest Template used for the Final Report	
Sample information taken from: (i.e NAPS site ID, Sampling date, PM mass, Actual air volume, lab comments and codes)	
MDLs (latest values)	
Units (both reports)	
Uncertainties (latest estimation)	
Calculations (random samples check)	
Cross-check (final vs internal report)	
Checklist completed and printed	



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APPENDIX C

TABLE C1. Major sources of uncertainty

Measurements Steps	Uncertainty Sources	QC Data Used
Sample Preparation (Extraction)	Extraction Volume Extraction Condition	Weight of Water MetBlank/LabBlank SP-VS SP-MDL
IC Analysis	Analyst Standard Solution Preparation Calibration Instrument Drift	CS-1 CS-2 CS-3 CS-4 VS Duplicate

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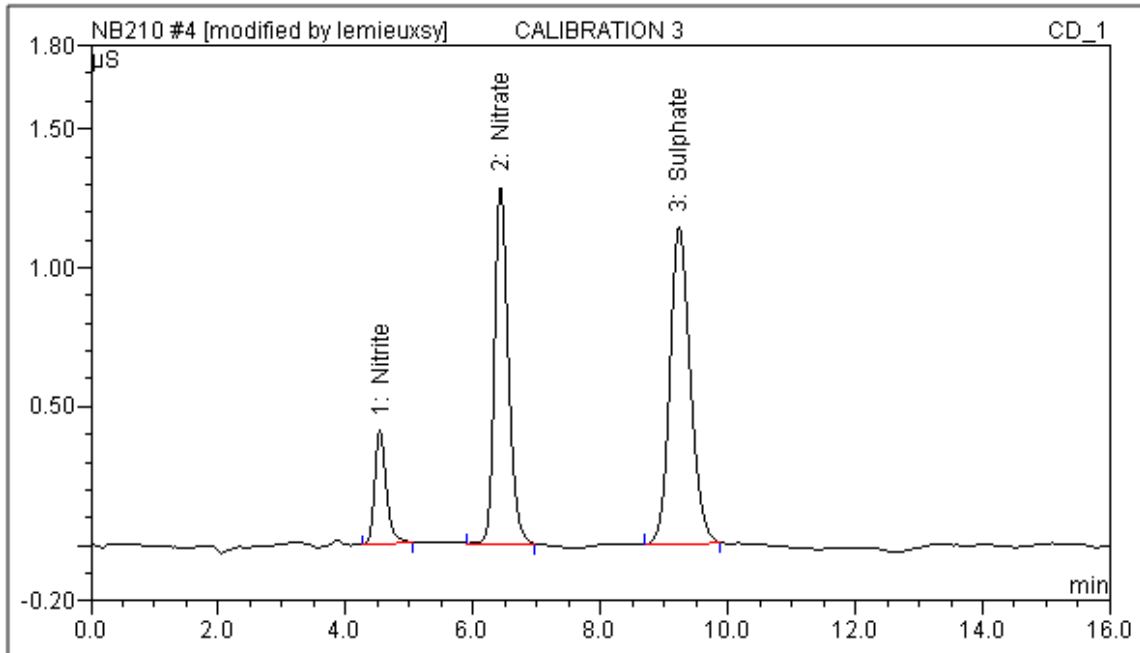
APPENDIX D

FIGURE D1. Sample chromatogram of anions calibration standard

Particulate Characterization Unit - AAQS, AQRD, STB, EC
Sample Analysis Report - ANIONS

Sample Name:	CALIBRATION 3	Sample No.:	4
Sequence Name:	NB210	Sample Type:	standard
Program Method:	anionprogram	Injection vol.:	250
Quantitation Method:	anions1	Dilution Factor:	1
Date Time Collected:	04/06/2012 12:10 PM	Modified?	04.06.12 14:48
System Operator:	M. Suski	Method:	6.05/1.2/M

Peak No.	Component Name	Retention Time	Area $\mu\text{S} \cdot \text{min}$	Height μS	Amount	Amnt.Dev.(rel) %
1	Nitrite	4.54	0.086	0.407	0.5083	1.65
2	Nitrate	6.43	0.321	1.284	1.9730	-1.35
3	Sulphate	9.23	0.422	1.137	2.0051	0.26



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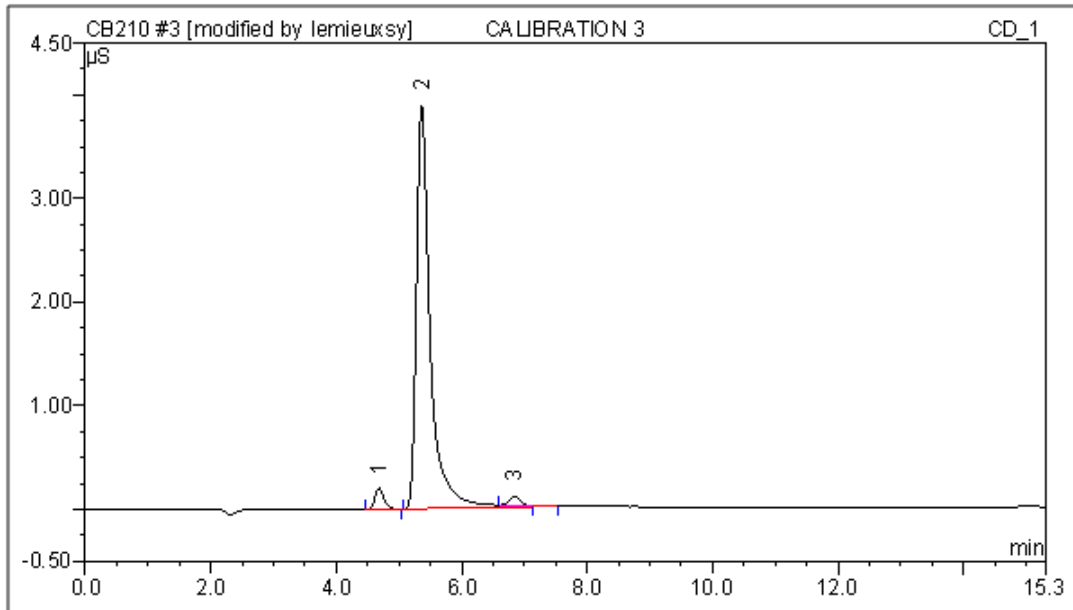
FIGURE D2. Sample chromatogram of cation calibration standard

Particulate Characterization - AAQS

Sample Analysis Report - AMMONIUM

Sample Name:	CALIBRATION 3	Sample No.:	3
Sequence Name:	CB210	Sample Type:	standard
Program Method:	cationprogram	Loading Vol.:	250.0
Quantitation Method:	cation1	Dilution Factor:	1.0000
Date Time Collected:	12/06/2012 10:59 AM	Comment:	
Analyst:	S. Lemieux	Method:	6.05/2.3/M

Peak CD_1 No.	Component CD_1 Name	Retention CD_1 Time	Area CD_1 $\mu\text{S}^*\text{min}$	Height CD_1 μS	Amount CD_1 $\mu\text{g/mL}$	Amnt.Dev.(rel) CD_1 %
1	n.a.	4.68	0.034	0.202	n.a.	n.a.
2	Ammonium	5.36	0.998	3.896	2.0001	0.00
3	n.a.	6.83	0.018	0.085	n.a.	n.a.



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