

Title: Determination of Anions and Cations on Multi (2) - Ion Chromatography System		Copy No: ##
Method No.: 6.03/6.4/M	Effective Date: December 28, 2012	Location: ###

QSM Approval: _____

Determination of Anions and Cations on Multi (2) - Ion Chromatography System

1. INTRODUCTION and SCOPE

- 1.1. This method is applicable to automatic simultaneous determination of inorganic and organic anions and inorganic cations listed in Table 1 in aqueous extracts of atmospheric aerosols and other aqueous solutions.
- 1.2. Method detection limits (MDLs) for the analyzed ions are in the range of low µg/filter (based on 15 mL dilution volume). Expanded measurements uncertainties ($k = 2$) at the concentrations above method quantitation limits (MQLs = 3xMDLs) are in the range of 5-25%.
- 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.

2. SUMMARY of METHOD

2.1. Ion chromatography combines suppressed-conductometric detection with the separation capabilities of ion exchange resins. Anions and cations of interest are separated and measured, using a system comprising guard columns, analytical columns, suppressor devices, and conductivity detectors (Table 1). 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 simultaneous determination of anions and cations:

Anions_System: to start AS15 method (anion gradient elution).

Cations_System: to start CS12A method (cation isocratic elution).

Stop_Anions and Stop_Cations programs automatically turn off all parts of the IC System.

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Table 1. Experimental Conditions

Parameter	AS15 method (Gradient Anion System)	CS12A method (Isocratic Cation System)
Ions	F ⁻ , Cl ⁻ , NO ₂ ⁻ , Br ⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ , acetate, propionate, formate, MSA*, oxalate	Li ⁺ , Na ⁺ , NH ₄ ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , Ba ²⁺
Separation column	IonPac-AS15 (4 mm x 250 mm)	IonPac-CS12A (4 mm x 250 mm)
Guard column	IonPac-AG15 (4mm x 50 mm)	IonPac-CG12A (4 mm x 50 mm)
Suppressor	ASRS 300 (4 mm)	CSRS 300 (4 mm)
Eluent	DI water (KOH cartridge)	18 mM MSA*
Eluent flow-rate	1.4 mL/min	1.0 mL/min
Sample loop	100 µL	50 µL

* methanesulfonic acid

Note: The temperature of the autosampler compartment is set to 10 °C.

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. lactic acid coeluts with acetic acid).

3.1.2 Large amounts of an ion can interfere with the peak resolution of an adjacent ion (e.g. sulphate-oxalate).

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).

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4. SAMPLE REQUIREMENT and PREPARATION

4.1 Consult SOP 6.06/*.*S for the storage conditions of samples and extraction procedures.

5. EQUIPMENT and SUPPLIES

5.1. All ion chromatography equipment, columns 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), eluent generator (EG) with KOH cartridge, 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. Pipettes and Bottle Dispenser.

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.

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6.1. Reagent water: High-purity degassed, deionized water (resistance > 18 MOhm cm) is used for reagent and standards makeup to prevent gas bubbles forming in the reagent line and pump.

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

6.2. Eluent

6.2.1 **1 M methanesulphonic acid (MSA)** stock cation eluent: Weigh out 96.10 g of MSA. Carefully add this amount to a 1-liter volumetric flask containing about 500 mL of deionized water. Dilute to the mark and mix thoroughly.

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

6.3. Standard Solutions

6.3.1 Anion Mixed Standard Solutions

- **Stock A-1:** Prepare a mixed standard solution from single stock anion standard solutions (10,000 mg/L) in 50 mL volumetric flask.
- **Stock A-2:** Prepare a mixed standard solution from single stock anion standard solutions (10,000 mg/L) in 50 mL volumetric flask. **Add 75 µL 50% NaOH to stabilize nitrite.**
- **Stock A-3:** Prepare a mixed standard solution from single stock anion standard solutions (10,000 mg/L – acetate, formate, oxalate; 1000 mg/L – MSA, propionate) in 50 mL volumetric flask.

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

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Table 2. Preparation of Anion Mixed Standard Solutions

Stock A-1 (50 mL)		
Every year		
Ion	Stock (mL)	Concentration (mg/L)
Chloride	5	1000
Nitrate	5	1000
Sulphate	5	1000

Stock A-3 (50 mL)		
Every 3 months		
Ion	Stock (mL)	Concentration (mg/L)
MSA	5	100
Propionate	5	100
Acetate	0.5	100
Formate	0.5	100
Oxalate	1	200

Stock A-2 (50 mL)		
Every 3 months		
Ion	Stock (mL)	Concentration (mg/L)
Fluoride	0.25	50
Nitrite	1	200
Bromide	2	400
Phosphate	2	400
50% NaOH, 75 µL		

6.3.1.1 Anion Calibration Standards

The calibration standards (Cal-0A – Cal-6A) should be prepared fresh prior to analysis; Cal-7A & Cal-8A should be prepared fresh every 3 months, or when any deterioration of anions (e.g. nitrate) is observed. Store Cal-7A & Cal-8A in refrigerator at 4±2°C.

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

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Table 3. Preparation of anion calibration standards

	Cal-0A	Cal-1A	Cal-2A	Cal-3A	Cal-4A*	Cal-5A	Cal-6A	Cal-7A	Cal-8A
Final Vol. (mL)	50	200	100	50	50	50	50	50	50
Stock A-1 (µL)	---	20	50	50	100	250	500	1500	2500
Stock A-2 (µL)	---	100	100	100	200	250	500	---	---
Stock A-3 (µL)	---	100	100	200	400	800	1000	---	---
Isopropanol (µL)	330	1320	660	330	330	330	330	330	330

* verification standard (VS-A = Cal-4A) is used to monitor system stability

Table 4. Concentrations of anion calibration standards (mg/L)

	Cal-0A	Cal-1A	Cal-2A	Cal-3A	Cal-4A*	Cal-5A	Cal-6A	Cal-7A	Cal-8A
Fluoride	0	0.025	0.05	0.10	0.20	0.25	0.50	-	-
Acetate	0	0.05	0.10	0.40	0.80	1.6	2	-	-
Formate	0	0.05	0.10	0.40	0.80	1.6	2	-	-
MSA	0	0.05	0.10	0.40	0.80	1.6	2	-	-
Propionate	0	0.05	0.10	0.40	0.80	1.6	2	-	-
Chloride	0	0.10	0.5	1	2	5	10	30	50
Nitrite	0	0.10	0.20	0.40	0.80	1	2	-	-
Sulphate	0	0.10	0.5	1	2	5	10	30	50
Oxalate	0	0.10	0.20	0.8	1.6	3.2	4	-	-
Phosphate	0	0.20	0.40	0.8	1.6	2	4	-	-
Bromide	0	0.20	0.40	0.8	1.6	2	4	-	-
Nitrate	0	0.10	0.5	1	2	5	10	30	50

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6.3.1.2. Anion Control Standards (CS-A)

- CS-A1:** a mixture of F⁻ (0.1 mg/L), Br⁻; NO₃⁻; SO₄²⁻ (each 0.4 mg/L); phosphate (0.6 mg/L); Cl⁻ (0.2 mg/L), acetate, formate, oxalate (each 0.5 mg/L). Prepare CS-A1 by diluting **100 µL** of the reference mixed anion standard ICMIX2-100, **50 µL** of each IC-FORM-10X-1 (1000 mg/L), IC-ACET-10X-1 (1000 mg/L) and IC-OXAL-10X-1 (1000 mg/L) in a 100 mL volumetric flask with degassed, deionized water.

Note: CS-A1 standard is prepared **daily** from the commercially available certified standards e.g. SPEXCertiPrep Standards.

- CS-A2:** a mixture of Cl⁻, NO₃⁻, SO₄²⁻ (each 8.0 mg/L). Prepare CS-A1 by diluting **2 mL** of the NIST anion reference single standards (1000 mg/L) in a 250 mL volumetric flask with degassed, deionized water.

Note: CS-A2 standard is prepared **every 6 months**.

Anion Control Standards should be prepared fresh as specified above, or when any deterioration of anions (e.g. nitrate) is observed, and stored in the refrigerator at 4±2°C.

6.3.2 Cation Mixed Standard Solutions

Prepare stock solutions from the single stock standards (each at concentration 1000 mg/L, and ammonium - 10,000 mg/L) in 50 mL volumetric flasks (Consult SOP 6.03/*.*S). All mixed cation standards should be prepared every **6 months** and stored in the refrigerator at 4±2°C.

Table 5. Preparation of Cation Mixed Standard Solutions

Stock C-1 (50 mL)			Stock C-2 (50 mL)		
	Stock (mL)	Concentration (mg/L)		Stock (µL)	Concentration (mg/L)
Sodium	5	100	Lithium	250	5
Ammonium	0.5	100	Potassium	1000	20
Calcium	5	100	Magnesium	1000	20
			Strontium	1000	20
			Barium	1000	20

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6.3.2.1 Cation Calibration Standards

Calibration standards (Cal-0C – Cal-6C) should be prepared fresh prior to analysis; Cal-7C and Cal-8C should be prepared every 6 months; all standard solutions should be stored in the refrigerator at 4±2°C.

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

Table 6. Preparation of cation calibration standards

	Cal-0C	Cal-1C	Cal-2C	Cal-3C	Cal-4C*	Cal-5C	Cal-6C	Cal-7C**	Cal-8C***
Final Vol. (mL)	25	25	25	25	25	25	25	50	50
Stock C-1 (µL)	---	500 µL of Cal-4C	25	250	250	625	1250	---	---
Stock C-2 (µL)	---		125	250	625	1250	---	---	
Isopropanol (µL)	165	165	165	165	165	165	165	330	330

* verification standard (VS-C = Cal-4C) is used to monitor system stability;

** Add 500µL of each single stock ammonium and sodium standards (1000 mg/L)

*** Add 1000µL of each single stock ammonium and sodium standards (1000 mg/L)

Table 7. Concentrations of cation calibration standards (mg/L)

	Cal-0C	Cal-1C	Cal-2C	Cal-3C	Cal-4C*	Cal-5C	Cal-6C	Cal-7C**	Cal-8C***
Lithium	0	0.0025	0.025	0.05	0.125	0.25	-	-	-
Sodium	0	0.01	0.1	1	0.5	2.5	5	10	20
Ammonium	0	0.01	0.1	1	0.5	2.5	5	10	20
Potassium	0	0.01	0.1	0.2	0.5	1	-	--	--
Magnesium	0	0.01	0.1	0.2	0.5	1	-	--	--
Calcium	0	0.01	0.1	1.0	0.5	2.5	5	-	-
Strontium	0	0.01	0.1	0.2	0.5	1	-	--	--
Barium	0	0.01	0.1	0.2	0.5	1	-	--	--

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6.3.2.2 Cation Control Standards (CS-C)

- CS-C1:** a mixture of Li (0.25 mg/L) Na, K, Mg (each 1 mg/L), Ca (5 mg/L), NH₄ (2 mg/L) and Sr, Ba (each 0.5 mg/L). Prepare CS-C1 by diluting **500 µL** of the reference mixed cation standard ICMIX3-100, **50 µL** of PLSR2-2T (Sr, 1000 µg/mL) and **50 µL** of PLBA2-2T (Ba, 1000 µg/mL) in a 100 mL volumetric flask with degassed, deionized water.

Note: CS-C1 standard is prepared **every 3 months**, or when any deterioration of cations (e.g. ammonium) is observed, from the commercially available standards (e.g. SPEXCertiPrep Standards), and stored in the refrigerator at 4±2°C.

- CS-C2:** a mixture of Li (0.05 mg/L) Na, K, Mg (each 0.2 mg/L), Ca (1.0 mg/L), NH₄ (0.4 mg/L) and Sr, Ba (each 0.2 mg/L). Prepare CS-C2 by diluting **100 µL** of the reference mixed cation standard ICMIX3-100, **20 µL** of PLSR2-2T (Sr, 1000 µg/mL) and **20 µL** of PLBA2-2T (Ba, 1000 µg/mL) in a 100 mL volumetric flask with degassed, deionized water.

Note: CS-C2 standard is prepared **daily** from the commercially available standards (e.g. SPEXCertiPrep Standards), and stored in 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 concentration of verification and control standards being analyzed are within the specified limits.

7.1.1 The calibration uses the external standard quantitation method. For each analyte of interest, prepare a multi-point calibration with concentration 0 as indicated in Section 6.3. Past experience shows that adequate linear or quadratic response (peak area/height) can be established within this concentration range. If the coefficient of correlation for the calibration curve is better than 0.995 (99.5%) then calibration curves for the working range are established. A high-concentration calibration curve includes Cal-7 and Cal-8, and is used for highly concentrated samples.

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- 7.2. Verify calibration accuracy by analyzing quality control standards at two different concentration ranges (CS-A/CS-C). If the response for major ions varies from the expected values by more than $\pm 10\text{-}25\%$ (See Section 10.2), fresh control standards have to be prepared. If the results are still outside of the specified limits, a new calibration curve must be prepared. If the value still exceeds the warning limits, the analyses should be terminated until the source of the problem is identified and corrected.
- 7.3. Verify the system calibration daily through the analysis by intermittently analyzing control standards (i.e.: every fifteen samples; See Appendix A). If the concentrations of determined analyte fall outside acceptable 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.
- 7.4. Verify system stability by analyzing a verification standard (VSA = Cal-4A; VS-C = Cal-4C) on each working day. The concentration must fall within limits (See Section 10.2). If results fall outside the limit, analyze an additional aliquot of the standard. If unacceptable results persist, then recalibrate the instrument and reanalyse all samples measured after the last acceptable control standard.

8. ANALYSIS

- 8.1. Make sure that all necessary maintenance procedures of instruments are done before weekly analyses. **Note:** in general every batch (usually less than 100 samples) is analyzed without any shutting down of the multi-IC system.
 - 8.1.1 Check eluents 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.

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- 8.2.** Start-up instruments and let the chromatography system and columns equilibrate for at least 90 min (1st day of batch analysis). Check background conductivity and backpressure after the system stabilizes (record values daily in **Control Charts**).
- 8.3.** Prepare the sequences (Appendix A) for the automated run, which include samples, calibration standards, method blank (MetBlank), spiked blanks (SP-MDL-A/SP-MDL-C, SP-VSA/SP-VSC), control standards (CS-A/CS-C), verification standards (VS-A/VSC) and duplicate samples.
- 8.4.** Extract filters (Consult SOP 6.06/*.*S).
- 8.4.1 Prepare spiked blanks:
- **SP-MDL-A & SP-MDL-C:** Place blank Teflon filters in labeled extraction bottles. Wet filters with 100 µL of isopropanol and spike them with 15mL of the lowest calibration standard (Cal-1A and Cal-1C). Sonicate SP-MDL-A & SP-MDL-C together with samples.
 - **SP-VSA & SP-VSC:** Place blank Teflon filters in labeled extraction bottles. Wet filters with 100 µL of isopropanol and spike them with 15mL of the verification standard (Cal-4A and Cal-4C). Sonicate SP-VSA & SP-VSC together with samples.
- 8.5.** Fill the sample vials (2 mL) with the calibration standards, quality control and unknown samples and place them in the sample tray according to the schedule (sample shown in Appendix A).
- 8.5.1 Start sequences for both **Cations_System** and **Anions_System**.
- 8.5.2 **NEVER OPEN THE AUTOSAMPLER** before checking its mode (should be on **IDLE**) and if there is enough time before the next sample loading.
- 8.6.** After run of Cal-5 (system performance check), compare values for retention time and peak area (sulphate and ammonium) with that of most recent one by overlapping chromatograms. If value of retention time or peak area exceeds a ±10%, stop the run and eliminate the source of the problem (e.g. prepare new calibration standards and/or eluents, and/or change column).
- 8.7.** Check system calibration and stability daily through the analysis as described in Section 7.

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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. Using Chromeleon Chromatography Software prepare a calibration curve for each analyte by plotting instrument response (peak area/height) against standard concentration. 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 eventually correct them. 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. 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).

10. QUALITY CONTROL

- 10.1. The QC samples normally comprise 10-25 % of total sample through put.
 - 10.1.1 Each batch of approximately 100 samples includes various blanks, control/verification standard, spikes, and duplicates (See Appendix A).

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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.

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

10.1.1.4 Verification Standard (VS) – standard from calibration (STD4) is used to monitor system stability.

10.1.1.5 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.

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

10.2. Data Acceptance

10.2.1 Control Standards, Verification Standards, and Spikes should be within 10-25% 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 LIMIT and METHOD VALIDATION

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

11.1.1 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_i is the number of repeats, and S_{Std} is their standard deviation.

11.1.2 MDLs for the analyzed ions are in the range of low µg/filter (based on 15 mL dilution volume). For the record of calculated and reported MDLs refer to the latest Method Verification Binder (Room 172).

11.1.3 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 record of precision and accuracy of measurement refer to the latest Method Verification Binder (Room 172).

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12. ESTIMATION of MEASUREMENT UNCERTAINTY

- 12.1. The measurement of uncertainty is calculated based on Type A approach recommended by 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.
- 12.3. The overall uncertainties at concentrations above method quantitation limits (MQLs = 3xMDLs) for determined ions are in the range of 5-25%. For the record 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 8. 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 valves after systems were shut down • Clean or replace when pump lost prime or it is difficult to re-prime
Detector/Chromatography Module	
Leak	<ul style="list-style-type: none"> • Periodically check for leaks or spills inside modules and for crimping of gas and 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 separator 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
Eluent generation	<ul style="list-style-type: none"> • Replace cartridge when exhausted (<5% capacity) or if it leaks • Replace trap column (CR-ATC) when loss of performance is observed • 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 • Annually perform preventive maintenance procedure (see Product Manual, Dionex Corporation)

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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”
- 19.02/*.*/*S “Volumetric Measurement- Micro Pipettes and Bottle-Top Dispensers”
- SWP-001/*.* “Safe Working Procedure and Policies”

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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

16. REVISIONS

September 1997: Author: Ewa Dabek

New document

July 1999: Reviewers: Ewa Dabek, Nicole Houle

Addition of storage conditions for standards; control standards; STD 6 added to standards; new introduction; new section on calibration and standardization; minor changes to the procedure section; changes to method performance (10%) and equipment sections; reference applicable SOPs; new section on sample requirements; removal of certain sections (filter analyses); minor changes to Table 1; Quality Control (number of samples changed from 25-45 to 56; samples comprise 15-25% of total sample through put; Table in 3.3.3, concentration of anions in working standards: each value for Br, multiplied by 2.

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September 2001: Reviewers: Ewa Dabek, Nicole Houle

Major changes due to installation of new Multi-IC System (DX-500, autosampler, eluent generation, software etc), IonPacAS15 column instead of IonPacAS10 column used for the anion separation with gradient elution; new composition of stock standard solutions; reagent blank (CAL0), STD-7 and STD-8 included in the calibration; samples comprise 10-25% of total sample through put, one more control standard included.

September 2003: Reviewers: Maria Piechowski, Nicole Houle

Appendix A is renamed to Appendix B; new Appendices A, C, D are added; through text instead of temperature below 10°C is 4°C, and instead <-10°C is -20°C; in section 4.1 storage condition and holding time are included; in section 4.2.5 “..up to 1 year..” is changed to “..up to 6 months..”; new verification standards have been chosen (STD-4A and STD-4C); in sections 7.2 and 7.3 the control limits from ±20% and ±10% are changed to “warning limits (See Appendix D)”; changes in the sections numbering due to addition of “Estimation of Measurement Uncertainty” (Section 12); in section 14: 2.10/*.*/*S “Estimation of Uncertainty in Chemical Analysis” is added, and 6.4/*.*/*S “Data Backup and Storage” is removed.

September 2005: Reviewer: Maria Piechowski

US EPA methods are added in Section 15.

July 2007: Reviewers: Maria Piechowski, Nicole Houle

Changes in Title and through text due to removing Anion Isocratic System from Multi (3) Ion Chromatography System. Duplicate samples - added; Data Acceptance (10.2) – added; (4°C) – removed through text; Sections: 13, 14, and 15 – updated; Appendices: E, F - added.

July 2009: Reviewers: Maria Piechowski, Nicole Houle

Text edited to reflect changes in division/section/lab structure/name; Sections: 2, 13 – “..(DX600)..” and/or “..(ICS3000)..” – added; Sections: 5, 8, 10, 14 – updated; Appendix D – value of reported uncertainty changed for: Sodium (from 10 to 15%), Potassium (from 20 to 25%), Propionate (from 25 to 15%).

December 2009: Reviewers: Maria Piechowski, Nicole Houle

Section 4.2 “Filter Extraction” moved to the SOP: 6.06/*.*/*S; Section 6.3 – “fresh as required” changed to “fresh prior to analysis”; Section 7 and 9 – “See Appendix D” changed to “See Section 10.2” ; Section 7.2 – “warning limits” changed to “±10-15%”; Section 8.3 – “spiked blank (MetBlank-SP)” added; Section 8.4 – “spikes” added; Section 9.5 – information about EXCEL templates validation – added; Section 10.1.1.2 and 10.1.1.7 – new; Section 10.2.1 – “and spikes” added; Section 11.3 – information about CALA – added; Section 12.3 and 12.4 – new; Section 14 – 2.11/*.*/*S and 6.06/*.*/*S – added; Section 15.8 – added; Appendix A – edited; Appendix B – “VialBlank” and “MetBlank-SP” added; Appendix C – “Duplicate” and “PT

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studies results” added; Appendix D – removed; Appendix E – changed to D; Appendix F – changed to E.

July 2011: Reviewers: Maria Piechowski, Michal Suski

Section 1.2 “tabulated in Appendix A” removed – range of MDLs values and Note added; Section 2.3 new – DX600 removed through text; Table 1 – Manganese removed - also from tables through text, “ASRS” and “CSRS” changed to “ASRS 300” and “CSRS 300”, “EG40” removed; Section 5 – new editing – DX600 information removed; Section 8.1.1 removed - new numbering; Section 8.3 “reagent blank” removed; Section 8.6 and 9.5 new; Section 9.6 name of the Network backup drive changed; Section 10.1.1.1 removed – new numbering; Section 11 – new; Section 12.3 – new editing; Section 13 new editing within section – DX600 info removed; Section 14 – SOP 6.08 removed; Appendix A removed; Appendix B new. All Appendices renamed accordingly and their references changed throughout the text.

December 2012: Reviewers: Michal Suski

Replaced “store in refrigerator” with “store in refrigerator at 4±2°C” throughout the text; Section 2.1 and 2.2 combined into one; Section 5.1.1 – eluent generator added, reference to gradient pump removed; Section 6.3.2.1 – flask volumes and corresponding stock amounts changed; Section 6.3.2.2 – CS-SR2-2Y replaced with PLSR2-2T and CS-BA2-2Y replaced with PLBA2-2T (replacement standards, original no longer available); Section 8.1.3 – removed; Section 8.3 - added SP-MDL, renamed MetBlank-SP to SP-VSA/SP-VSC; Section 8.5.1 and 8.5.2 – removed; Section 9.1 – updated, raw data backup added; Section 9.5.1 – removed; Section 9.5.2 renumbered to 9.5.1; Section 10.1.1.6 - – changed QC sample names as per Section 8.3; Section 13 – Eluent generator maintenance updated with instructions for replacement of CR-ATC; Appendices updated with most recent examples of forms and chromatograms; formatting changes throughout the text.

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)

Name	Type	Pos.	Program	Method
test	Unknown	1	Anions_System	AS15
test	Unknown	2	Anions_System	AS15
Cal-0A	Standard	3	Anions_System	AS15
Cal-5A	Standard	5	Anions_System	AS15
Cal-1A	Standard	7	Anions_System	AS15
Cal-2A	Standard	9	Anions_System	AS15
Cal-3A	Standard	11	Anions_System	AS15
Cal-4A	Standard	13	Anions_System	AS15
Cal-6A	Standard	15	Anions_System	AS15
Cal-7A	Standard	17	Anions_System	AS15
Cal-8A	Standard	19	Anions_System	AS15
VialBlank 1	Unknown	20	Anions_System	AS15
MetBlank	Unknown	21	Anions_System	AS15
SP-MDL-A	Unknown	23	Anions_System	AS15
CS-A1	Validate	25	Anions_System	AS15
SAMPLE 1-16	Unknown	26-40	Anions_System	AS15
Duplicate 1	Unknown	41	Anions_System	AS15
CS-A2	Validate	43	Anions_System	AS15
SAMPLE 17-32	Unknown	44-58	Anions_System	AS15
Duplicate 2	Unknown	59	Anions_System	AS15
SP-VSA	Validate	61	Anions_System	AS15
SAMPLE 33-48	Unknown	62-76	Anions_System	AS15
Duplicate 3	Unknown	77	Anions_System	AS15
VialBlank 2	Unknown	78	Anions_System	AS15
VS-A	Validate	80	Anions_System	AS15
SAMPLE 49-64	Unknown	81-95	Anions_System	AS15
Duplicate 4	Unknown	96	Anions_System	AS15
CS-A1	Validate	98	Anions_System	AS15
SAMPLE 65-80	Unknown	99-13	Anions_System	AS15
Duplicate 5	Unknown	14	Anions_System	AS15
CS-A2	Validate	16	Anions_System	AS15
SAMPLE 81-96	Unknown	17-31	Anions_System	AS15
Duplicate 6	Unknown	32	Anions_System	AS15
VialBlank 3	Unknown	33	Anions_System	AS15
VS-A	Validate	35	Anions_System	AS15
SHUT	Unknown	100	Stop_Anions	AS15

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Table A2. Proposed sequence (cations)

Name	Type	Pos.	Program	Method
test	Unknown	1	Cations_System	CS12A
test	Unknown	2	Cations_System	CS12A
Cal-0C	Standard	3	Cations_System	CS12A
Cal-5C	Standard	4	Cations_System	CS12A
Cal-1C	Standard	6	Cations_System	CS12A
Cal-2C	Standard	8	Cations_System	CS12A
Cal-3C	Standard	10	Cations_System	CS12A
Cal-4C	Standard	12	Cations_System	CS12A
Cal-6C	Standard	14	Cations_System	CS12A
Cal-7C	Standard	16	Cations_System	CS12A
Cal-8C	Standard	18	Cations_System	CS12A
VialBlank 1	Unknown	20	Cations_System	CS12A
MetBlank	Unknown	21	Cations_System	CS12A
SP-MDL-C	Unknown	22	Cations_System	CS12A
CS-C1	Validate	24	Cations_System	CS12A
SAMPLE 1-16	Unknown	26-40	Cations_System	CS12A
Duplicate 1	Unknown	41	Cations_System	CS12A
CS-C2	Validate	42	Cations_System	CS12A
SAMPLE 17-32	Unknown	44-58	Cations_System	CS12A
Duplicate 2	Unknown	59	Cations_System	CS12A
SP-VSC	Validate	60	Cations_System	CS12A
SAMPLE 33-48	Unknown	62-76	Cations_System	CS12A
Duplicate 3	Unknown	77	Cations_System	CS12A
VialBlank 2	Unknown	78	Cations_System	CS12A
VS-C	Validate	79	Cations_System	CS12A
SAMPLE 49-64	Unknown	81-95	Cations_System	CS12A
Duplicate 4	Unknown	96	Cations_System	CS12A
CS-C1	Validate	97	Cations_System	CS12A
SAMPLE 65-80	Unknown	99-13	Cations_System	CS12A
Duplicate 5	Unknown	14	Cations_System	CS12A
CS-C2	Validate	15	Cations_System	CS12A
SAMPLE 81-96	Unknown	17-31	Cations_System	CS12A
Duplicate 6	Unknown	32	Cations_System	CS12A
VialBlank 3	Unknown	33	Cations_System	CS12A
VS-C	Validate	34	Cations_System	CS12A
SHUT	Unknown	100	Stop_Cations	CS12A

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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:				NOTES:																																																													
General Information Sample Preparation Analytical Instrument Analytical Instrument Model # Method ID Batch # Analyst																																																																	
QA/QC samples checklist				Samples analysis results checklist																																																													
<table border="1"> <thead> <tr> <th>Parameter</th> <th>QC sample</th> <th>Sample name</th> <th>Check (by analyst)</th> </tr> </thead> <tbody> <tr> <td>Calibration: - correlation coefficient >99.5%</td> <td></td> <td></td> <td></td> </tr> <tr> <td rowspan="3">QC Standards (recoveries within limits specified in the method)</td> <td>VS</td> <td></td> <td></td> </tr> <tr> <td>Control Standards</td> <td></td> <td></td> </tr> <tr> <td>Other QCs</td> <td></td> <td></td> </tr> <tr> <td rowspan="2">Blanks (less than MDLs)</td> <td>Vial Blanks</td> <td></td> <td></td> </tr> <tr> <td>Method Blanks</td> <td></td> <td></td> </tr> <tr> <td rowspan="2">Spikes (recoveries within limits specified in the method)</td> <td>MDL spike</td> <td></td> <td></td> </tr> <tr> <td>VS spike</td> <td></td> <td></td> </tr> <tr> <td>Trend analysis</td> <td></td> <td></td> <td></td> </tr> <tr> <td>Duplicates (%RPD within limits specified in the method)</td> <td></td> <td></td> <td></td> </tr> </tbody> </table>	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)				<table border="1"> <thead> <tr> <th>Parameter</th> <th>Check (by analyst)</th> </tr> </thead> <tbody> <tr> <td>Unusual results*</td> <td></td> </tr> </tbody> </table>	Parameter	Check (by analyst)	Unusual results*		Reporting checklist	<table border="1"> <tbody> <tr> <td>Latest Template used for Internal Report</td> <td></td> </tr> <tr> <td>Latest Template used for the Final Report</td> <td></td> </tr> <tr> <td>Sample information taken from: (i.e NAPS site ID, Sampling date, PM mass, Actual air volume, lab comments and codes)</td> <td></td> </tr> <tr> <td>MDLs (latest values)</td> <td></td> </tr> <tr> <td>Units (both reports)</td> <td></td> </tr> <tr> <td>Uncertainties (latest estimation)</td> <td></td> </tr> <tr> <td>Calculations (random samples check)</td> <td></td> </tr> <tr> <td>Cross-check (final vs internal report)</td> <td></td> </tr> <tr> <td>Checklist completed and printed</td> <td></td> </tr> </tbody> </table>	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. Uncertainty -Major Sources

Measurements Steps	Uncertainty Sources	QC Data Used
Sample Preparation (Extraction)	Extraction Volume Extraction Condition	Weight of Water VS + Blank Filter
IC Analysis	Analyst Standard Solution Preparation Calibration Instrument Drift Data Process	CS-1 CS-2 VS Duplicate PT studies results

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APPENDIX D

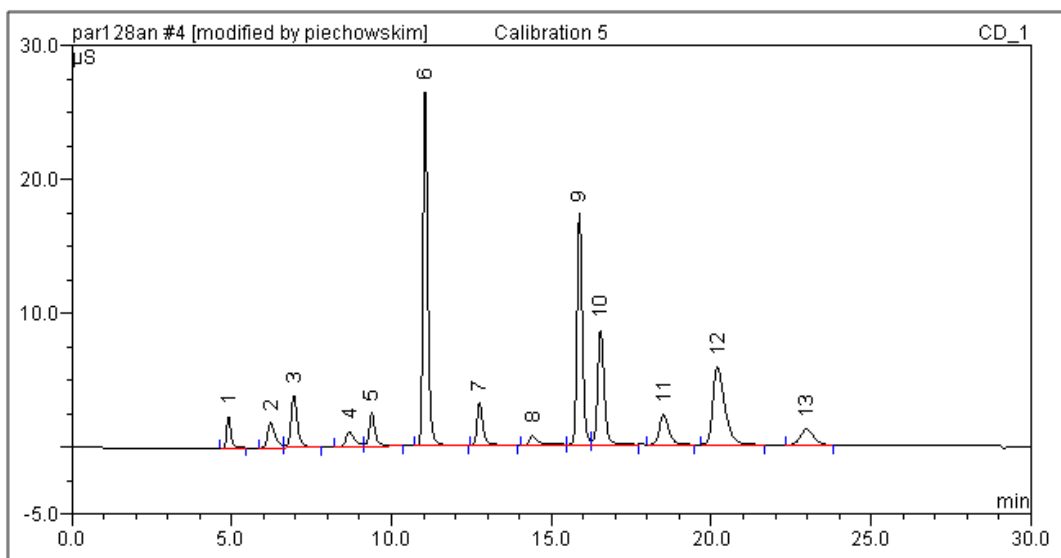
Figure D1. Example chromatogram of anions calibration standard

Particulate Characterization Unit - AAQS, AQRD, STB, EC

Sample Analysis Report - Anions

Sample Name:	Calibration 5	Sample No.:	4
Sequence Name:	par128an	Sample Type:	standard
Program Method:	Anions_System	Injection vol.:	50 µL
Quantitation Method:	AS15	Dilution Factor:	1
Date Time Collected:	09/07/2007 4:11 PM	Modified?	01.Aug.07
Sample I.D.:	par128	Comments:	Prepared: 7/9/2007
Analyst:	N. Houle	Method:	6.03/5.1/M System 3

Peak No.	Component Name	Retention Time min	Area µS*min	Height µS	Amount µg/mL	Modified?	Amnt.Dev.(rel) %
1	Fluoride	4.90	0.366	2.322	0.2473	*	-1.07
2	Acetate	6.22	0.527	1.866	1.5839	*	-1.01
3	Formate	6.95	0.926	3.876	1.5933	*	-0.42
4	Propionate	8.68	0.363	1.117	1.5686	*	-1.96
5	MSA	9.38	0.554	2.490	1.6134	*	0.84
6	Chloride	11.05	4.587	26.362	4.9805	*	-0.39
7	Nitrite	12.75	0.680	3.172	0.9973		-0.27
8	Carbonate	14.40	0.229	0.709	0.3145	*	n.a.
9	Sulphate	15.88	3.345	17.213	4.9620	*	-0.76
10	Oxalate	16.54	2.031	8.516	3.1592	*	-1.27
11	Bromide	18.51	0.759	2.230	1.9736	*	-1.32
12	Nitrate	20.19	2.494	5.767	4.9802		-0.40
13	Phosphate	22.98	0.560	1.164	1.9887		-0.56



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Figure D2. Example chromatogram of cations calibration standard.

PARTICULATE CHARACTERIZATION - AAQS

Sample Analysis Report - CATIONS

Sample Name:	Calibration 5	Sample No.:	4
Sequence Name:	PAR330CA	Sample Type:	standard
Program Method:	Cations_System	Loading vol.:	250
Quantitation Method:	CS12A	Dilution Factor:	1
Date Time Collected:	10/09/2012 3:24 PM	Modified?	14.Sep.12
Sample I.D.:	PAR330	Comments:	
Analyst:	M. Suski	Method:	6.03/6.3/M System 3

Peak No.	Component Name	Retention Time	Area $\mu\text{S}^*\text{min}$	Height μS	Amount $\mu\text{g}/\text{mL}$	Modified?	Amnt.Dev.(rel) %
1	Lithium	3.77	0.503	3.634	0.2511	*	0.44
2	Sodium	4.48	1.619	10.699	2.4414	*	-2.35
3	Ammonium	5.09	1.283	5.886	n.a.	*	n.a.
4	Potassium	6.28	0.427	2.175	0.9918	*	-0.82
5	Magnesium	11.57	1.228	2.603	0.9989	*	-0.11
6	Calcium	14.38	1.925	3.431	2.5172	*	0.69
7	Strontium	16.54	0.359	0.546	1.0016	*	0.16
8	Barium	23.87	0.201	0.227	0.9988	*	-0.12

