DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 1 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

DRI STANDARD OPERATING PROCEDURE

Cation Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography using the DIONEX ICS-5000$^+$ System for the Chemical Speciation Network

DRI SOP #2-228r2
Febrary 23, 2017

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Prepared By: _Paul M Cropper_   **Date:** _2/28/17_

Reviewed By: _____   **Date:** _2/28/17_

Approved By: _____   **Date:** _2/28/17_

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
            by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 2 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

1.0   GENERAL DISCUSSION

1.1   Purpose of Procedure

The objectives of this standard operating procedure are to:
- Provide a basic understanding of ion chomatography principles and operation
- Detail the implementation of a state-of-the-art ion chromatography measurement process, including interferences and technical problems that may arise while using the Dionex ICS-5000$^+$ Ion Chromatography System
- Describe routine analysis of aqueous filter extracts or precipitation samples using the Dionex ICS-5000$^+$ Ion Chromatography System for the following cations:
    Sodium (Na$^+$)
    Ammonium (NH4$^+$)
    Magnesium (Mg^{2+})
    Potassium (K$^+$)

This procedure will be followed by all analysts in the Environmental Analysis Facility (EAF), Division of Atmospheric Sciences, at the Desert Research Institute.

1.2   Measurement Principle

Ion Chromatography (IC) using the Dionex ICS-5000+ is a liquid chromatographic technique based on an ion exchange mechanism and suppressed conductivity detection for the separation and determination of cations. Its separation principle is similar to that of all chromatographic methods. Each ion's affinity for the exchange site, known as its selectivity quotient, is largely determined by its radius and its valence. As a consequence of differences in the equilibrium distribution of sample components between the mobile (sample/eluent flow) and stationary (ion exchange column) phases, the analyte ions elute from the column as discrete bands based upon their migration velocities. Each ion is identified by its retention time within the ion exchange column.

During routine operation, an aliquot of sample is pumped through an ion exchange column where the ions are separated. The eluent ions from this separator column are then neutralized in the cation electrolytically regenerated suppressor, and the sample ions are converted to their corresponding strong acids for detection with a conductivity detector. The conductivity responses are associated with ionic species by their elution times. Ionic concentrations are quantitatively determined from conductivity peak heights or areas (Small et al., 1975).

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
          by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 3 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

1.3   Measurement Interferences and their Minimization

The presence of air bubbles in the columns, tubing, or conductivity detector cell may cause baseline and peak variability. Introducing air into the system when injecting samples and standards should be avoided.

Unresolved peaks will result when the ion concentration of one of the sample components is 10 to 20 times higher than another component that appears in the chromatogram as an adjacent peak. Decreasing the eluent concentration or the flow rate may correct this problem. Decreasing the flow rate will, however, lengthen the retention time.

Interferences may be caused by ions with retention times that are similar to each other, resulting in overlapping peaks. Decreasing the eluent concentration or the flow rate may result in improved peak resolution and minimize the positive interferences (Bachman et al., 1986).

Injection of samples with total ionic concentrations greater than 200 µg/mL or the use of sample loop volumes greater than 25 µL may result in column overloading, causing the loss of the sample since it cannot be retained on an overloaded column. Non-quantifiable responses will also occur. Dilution of samples or decreasing the sample loop volume will prevent column overloading.

Column performance deterioration can result from the accumulation of contaminants on the exchange resin. Changes in retention times and in resolution are symptoms of column deterioration. Refer to the manufacturer's guidelines that are received with each new column or Section 2.1.3 for column replacement instructions.

1.4   Ranges and Typical Values of Measurements

A wide range of ambient concentrations are collected in both filter extracts and precipitation samples. Table 1-1 summarizes the ranges of cation concentrations from past DRI studies. "Typical" values are difficult to express except in terms of ranges, because µg/mL measurements depend on volume of extract or sample, area of filter extracted, type of sample (i.e., urban or rural ambient, direct or diluted source), volume of air sampled, and filter deposit area. All of these factors may be adjusted to compensate for unusually low or high concentrations.

1.5   Typical Lower Quantifiable Limits, Precision, and Accuracy

The Dionex ICS-5000$^+$ is capable of measuring the cations Na^+, NH_4^+, K^+ Mg^{2+}, and down to the ppb range. The minimum detection limit (MDL) is determined as three times the standard deviation of seven or more laboratory blank analyses. Table 1-2 lists the typical

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
            by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 4 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

MDLs from various ion chromatography analyses. The lower quantifiable limit (LQL) for each of the ionic species is determined by variability in field blank analyses or the minimum detection limit - whichever is greater. Table 1-3 lists the LQLs resulting from various ion chromatography analyses. MDLs and LQLs are determined periodically, depending on the project. Usually, they are determined annually or quarterly. The accuracy is primarily limited by the uncertainties in the standard solution preparation and is typically within ± 5%. Precision as estimated by replicate analyses is in the range of ± 10% to ± 30%, depending on the analyte and the concentration of the analyte (see section 6.3).

Table 1-2. Minimum Analytical Detection Limits of Cations Determined by Ion Chromatography

Ionic Species	MDL^a (μg/mL)^b
Na$^+$	0.015
NH$_4^+$	0.0014
Mg^{2+}	0.00009
K$^+$	0.006

^{a} Minimum Detection Limit (MDL) equals three times the standard deviation of laboratory blanks as determined from recent monitoring programs.
^{b} Values given are per filter assuming no dilution factor and 15 mL extraction volume.
^{c} nd is non detected

1.6   Personnel Responsibilities

All analysts in the laboratory should read and understand the entire standard operating procedure, obtain proper training, and have a fundamental knowledge of the instrument's mechanical systems and software before performing IC analysis. The analyst is expected to follow this procedure step by step to perform routine system calibrations, chemical analyses, and performance tests. The laboratory manager is responsible for ensuring that the IC procedures are properly followed; examining all replicate, standard, and blank performance test data; designating samples for re-analysis; and delivering the analysis results to the project manager within the specified time period.

The EAF quality assurance (QA) officer is responsible for: 1) determining the QA methods to be applied to each project; ; 2) identifying the appropriate personnel to perform QA tasks; 3) updating QA procedures; and 4) ensuring that QA tasks are budgeted and carried out as part of contract performance.

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
            by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 5 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

1.7   Definitions

The following terms are used in this document:

CERS 500:	A device used to continuously minimize eluent conductivity and convert sample species to a high conductivity form, thus increasing detection sensitivity.
Analytical/Separator Column:	The column used to perform the actual chromatographic separation.
Column Capacity:	Related to the total ionic strength of the sample, it is the maximum concentration of sample that may be loaded onto a separator column before overloading occurs.
Conductivity:	A measure of the characteristic of ions in solution to carry electrical current through a liquid between two oppositely charged electrodes. When combined with chemical eluent suppression, it provides excellent selectivity and sensitivity for many ionic species.
Eluent:	The ionic liquid mobile phase used to transport the sample through the guard and analytical columns.
Guard Column/Pre-Column:	A small column that prevents poisoning and contamination of the separator column by removing particles and absorbing organic compounds.
Ion Exchange:	The reversible process by which ions are interchanged between an insoluble material and a liquid with no substantial structural changes of materials.
Ion Exchange Capacity:	The number of active ion-exchange sites in a given weight or volume of resin, often expressed in meq/g or meq/mL.
Ion Exchange Resin:	An insoluble carbon-based polymer matrix containing charged exchange sites (anionic or

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
           by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 6 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

	cationic). The resin used in IC is formed into small spherical particles (i.e., beads).
Laboratory Blank:	A blank Nylon filter, extracted following protocol and analyzed under typical run conditions.
Resolution:	A measure of the ability of a column to separate constituents under specified test conditions. Peak resolution is a function of column efficiency, selectivity, and capacity.
Retention Time:	The interval measured from the point of sample injection to the point of maximum peak height or area; the basis for identification of a species in chromatography.
Theoretical Plates/ Column Efficiency:	A measure of peak dispersion as flow moves through a column proportional to column length for a given column diameter and resin.

1.8   Related Procedures

Related laboratory procedures are specified in the following DRI Standard Operating Procedures:

- Impregnation and Drying of Filters for Sampling Gases in Air (DRI SOP #2-104)
- Filter Sectioning (DRI SOP #2-108)
- Extraction of Ionic Species from Filter Samples (DRI SOP #2-109)
- Anion Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography using the DIONEX ICS-5000$^+$ System (DRI SOP #2-228)

2.0   APPARATUS, INSTRUMENTATION, AND REAGENTS

2.1   Apparatus and Instrumentation

2.1.1   Description

The Dionex ICS-5000$^+$ is a completely inert and metal-free analytical system. The system is composed of an isocratic pump, an eluent generator, a guard column (CG16), a chromatographic column (IonPac CS16), an electrolytically regenerated suppressor (CERS), a conductivity detector, and an autosampler (illustrated in Figure 2.1). The Dionex ICS-5000$^+$ system includes:

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
            by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 7 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

Pump Module (DP): A microprocessor-based eluent delivery system designed to provide isocratic capability at precisely controlled flow rates. It is a dual-piston, direct current motor pump that can be operated with flow rates ranging from 0.1-3.0 mL/min (in increments of 0.1 mL/min) and pressures ranging from 0 to 5000 psi. An eluent degasser (contained in the DP module) provides continuous on-line purging and degassing of the DDW delivered to the eluent generator.

Eluent Generator Module (EG): Provides on-line generation of KOH eluent with a specific concentration.

Sampling System: Samples are introduced into the analyzer with either an automated sampler or a hand-operated syringe.

Automated Sampler (AS): In routine operation, the automated sampler system is used to deliver 25 µL of sample using a 25 µL sample loop. 250 µL of Distilled Deionized Water is used to wash the injection system and sample loop. The sampler compartment can hold up to 24 10.0 mL and 120 1.5 mL vials.

Syringe: A polyethylene syringe with a minimum capacity of 1 mL is used for manual injection of samples. The syringe is equipped with a pre-filter for use with samples that contain insoluble particulate matter.

Detector/Chromatography Compartment (DC): The DC module includes an injection valve (a high-pressure pneumatically operated 6 port valve with a 25 µL sample loop), a column selection valve (a high-pressure 6-port valve that provides switching between two columns), and inter-connecting tubing. Figure 2-1 illustrates the flow through the system. Eluent and the sample are mixed at the injection valve. The mixture of eluent and sample then flows through the column selection valve (valve A), the guard column, the separator column, the corresponding CERS, and finally through the detector cell to the waste reservoir. The DC module is divided into an (upper) detector compartment and a (lower) column compartment, which are individually temperature-controlled, maintaining the temperature at a specific value (e.g., 30 °C), in order to stabilize the peak retention times. Separation of the individual analytes (cations) is achieved on an IonPac CS16 analytical column (5 x 250 mm), preceded by an IonPac CG16 guard column.

Conductivity Detector (CD): A microprocessor-controlled detection system based on electronic signal processing used to increase the signal-to-noise ratio and enhance sensitivity at low concentrations. The system displays conductivities over the full-scale range of 0.01 to 1,000 µS (micro Siemens) and compensates for temperature-induced conductivity variations, with correction factors between 0.0 and 9.9% per °C.

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
          by Ion Chromatography using the DIONEX ICS-5000+ System

Page: 8 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

2.1.2   Characterization

The Dionex ICS-5000+ equilibrates about 60 minutes after the appropriate cation method has been entered and the pumps have started running. The instruments are stable and will produce area counts within ±10% of previous readings of the same standards, using the same eluent conditions.
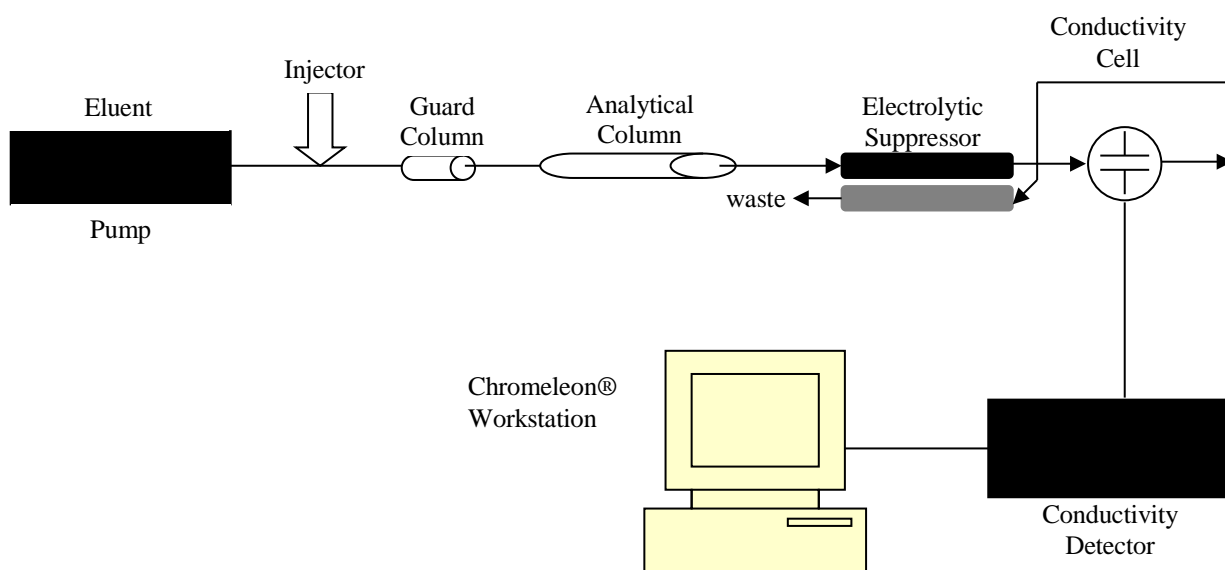
Figure 2.1. Components of the Dionex ICS-5000+ Ion Chromatography System.

2.1.3   Maintenance (Consult the Dionex ICS-5000+Operator's Manual)

Column. Replace the column when retention times decrease by 25% or sooner if peaks of interest cannot be resolved.

Conductivity Detector. Conduct periodic leak checks of the liquid line connections to the cells; the unit itself is not user serviceable.

Pump. Replace the check valves, piston seals, and washer support seals each year or when there is excessive leakage from the pump valves.

CERS: To prevent drying out of the membrane, the unit remains in standby mode with continuous flow at a low flow rate.

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
            by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 9 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

2.2   Reagents

2.2.1   Primary Standards

Certified standards obtained from Environmental Research Associates (ERA, Arvada, CO) are used for preparation of calibration and check standards. All analytes of interest (i.e., Li^+, Na^+, NH_4^+, K^+ Mg^{2+}, and Ca^{2+}) should be included in the 100 µg/mL custom-ordered standard.

2.2.2   Water

Use water conforming to American Society for Testing Materials (ASTM) Specification D 1193-91, Type I (ASTM Standards, 1996). Deionized-distilled water (DDW) having a resistance of at least 18 megaohm per cm, is required for all analyses.

2.2.3   Eluent Solution

8 mM MSA (methanesulfonic acid) generated from the eluent generator (EG) is used to elute ions from the separator/analytical column. The current that goes into the EG produces a constant concentration that is required for the analysis. A concentration gradient can be applied via the EG control panel within the Chromeleon software.

3.0   CALIBRATION STANDARDS

3.1   Preparation of Standard Solutions

The stock standard solutions are purchased as certified solutions and diluted to the proper concentrations by weighing the certified standards, assuming the density is 1 g/mL.

3.1.1   Purchase of Stock Solution

The 6 cation stock solution (100 µg/mL) is purchased custom-mixed and certified from Environmental Research Associates (ERA, Arvada, CO).

3.1.2   Preparation of Working Standards

The stock solution above is diluted to a 10 µg/mL working standard, and both are used to prepare calibration standards. The same calibration standards are used as QC standards during every sequence.

- 10 µg/mL working standard: Weigh 10.00 g of the 100.00 µg/mL stock solution into a 100 mL volumetric flask. Dilute to volume with DDW.

DRI STANDARD OPERATING PROCEDURE   Page: 10 of 29
                                                                    Date: 02/23/17
Title: Cation Analysis of Filter Extracts and Precipitation Samples   Number: 2-228r2
            by Ion Chromatography using the DIONEX ICS-5000$^+$ System   Revision: 2

3.1.3   Preparation of Calibration Standards

These are the standard solutions used to create the calibration curves for the analysis. For increased accuracy, the standards are weighed rather than pipetted. The concentrations are as follows:

Concentration	Standard	Mass of Standard Solution	Final Volume
0.02 µg/mL	10 µg/mL	0.20 g	100 mL
0.05 µg/mL	10 µg/mL	0.50 g	100 mL
0.1 µg/mL	10 µg/mL	1.00 g	100 mL
0.2 µg/mL	10 µg/mL	2.00 g	100 mL
0.5 µg/mL	10 µg/mL	5.00 g	100 mL
1.0 µg/mL	100 µg/mL	1.00 g	100 mL
3.0 µg/mL	100 µg/mL	3.00 g	100 mL

The standards are remade when the volume available is not sufficient for the next sample batch, usually every two weeks during routine operation. Standard solutions are loaded into 10 mL vials with 3-5 mL of standard as explained in section 4 of this SOP.

3.2   Use of External Quality Control (QC) Standards

Three differed QC solutions serve as control checks for ions of interest:
- A primary NIST certified QC standard is purchased from Thermo Scientific (Dionex). The concentrations of Sodium, Ammonium, Magnesium and Potassium cations range from 200 to 500 µg/mL. For the primary QC, prepare a working QC standard by diluting the commercial stock solution 1:200. Prepare the QC standards as follows: Weigh 0.50 g of the QC concentrate into a 100.00 mL volumetric flask. Bring to volume with DDW and mix thoroughly.
- A laboratory check standard is prepared by dissolving 1.666 g NaCl, 1.371g NaNO$_3$, and 1.375 g (NH$_4$)$_2$SO$_4$ in a 1 L volumetric flask. This results in a solution that is 1.03 ppm sodium and 0.375 ppm ammonium.

3.3   The Accuracy of Calibration Standards

The accuracy of calibration standards is primarily limited by the uncertainties or variabilities of the standard solution preparation. QC standards that have a concentration above 0.2 µg/mL should be within ±10% of the certified value, while the QC samples that have a concentration of 0.1 µg/mL or less should be within ±15% of the certified value.

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
          by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 11 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

4.0 PROCEDURES

4.1 General Flow Diagram for the ICS-5000$^+$ system.

Figure 4-1 describes the general flow for filter chain-of-custody, chemical analysis, and data processing/validation. The level of validation and type of report depend on project requirements. Figure 4-2 shows an example of DRI's analysis list. Figure 4-3 is the general flow diagram of routine IC analysis, starting with the initial chromatography adjustment and analysis parameter setup. The samples and replicates are analyzed after the calibration curve is established.

4.2 Startup for the Dionex ICS-5000$^+$ Software and Instrumentation

4.2.1   Software (Chromeleon) Startup

- Start the Server Monitor. When the computer has not been powered down, the server monitor will always be active. The server monitor can be found either in the Chromeleon startup menu or in the lower right corner of the desktop. After the server monitor has been started, click Close, which will save the icon on the Windows Services area of the task bar.
- Start Chromeleon from the desktop shortcut. It will open to the last opened browser window. Select the Data button in the lower left corner and select the anion timebase in the left frame of the browser (Figure 4-4).

4.2.2   Hardware Startup/Shutdown

- In the browser window, click on instruments (Figure 4-5). The control panel will appear and the system status will be displayed in the corresponding tab.
- Startup: In case the instrument has stopped, manually turn on the pumps, the EG cartridge (EGC), the suppressor, and all other modules that have been disconnected. Make sure each module is connected by monitoring the green radio button on the left top corner in each tab.
- Shutdown: Shutdown of the instrument is not recommended; it should be left in standby mode, with low eluent flow at all times. However, shutdown can be accomplished by turning all modules off by pushing the respective ON/OFF buttons.
- Manual shutdown of the hardware and software if the system locks up:
    1. Turn off all modules.
    2. Exit the software and quit the Chromeleon Server in the bottom status bar.
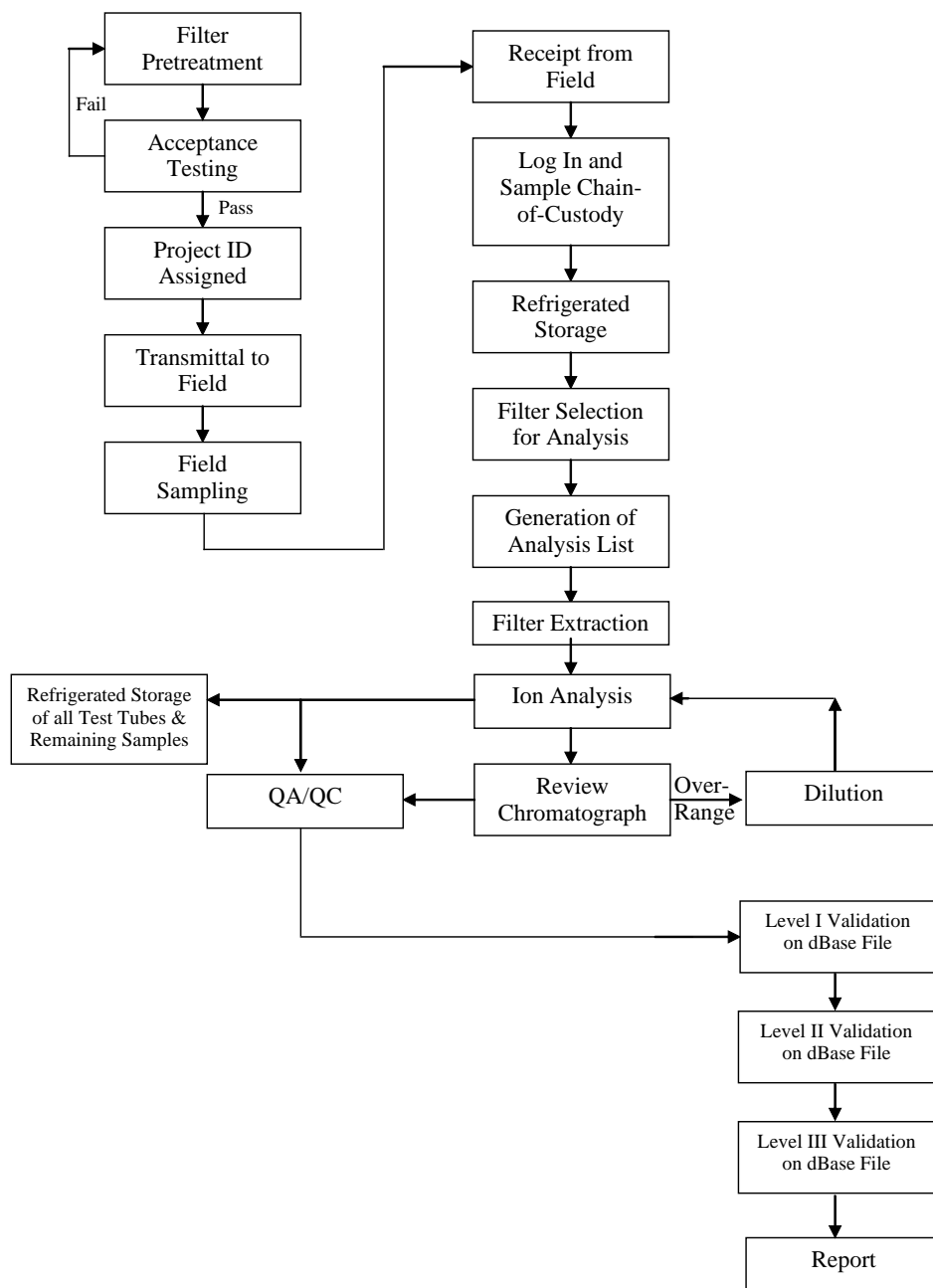   3. Turn the computer off.

DRI STANDARD OPERATING PROCEDURE

Page: 12 of 29
Date: 02/23/17

Title: Cation Analysis of Filter Extracts and Precipitation Samples
by Ion Chromatography using the DIONEX ICS-5000+ System

Number: 2-228r2
Revision: 2

Figure 4-1. General flow diagram for sample pre-treatment and analysis using the Dionex ICS-5000+ system in the Environmental Analysis Facility.

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
           by Ion Chromatography using the DIONEX ICS-5000⁺ System

Page: 13 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

```
                    CSN : Batch Ø8 (Part A) Nylon

  Date    : Ø6/16/16                    Account:       -    -

  From    : K Langford

  To      : D.Trimble
            T.Pascal
            IC Lab
            AC Lab
            AA Lab

  Analysis: Cl-/NO3-/SO4=           by IC : 5ØØ samples, data in CSANIØ8X.DBF
            NH4+                    by AC : 5ØØ samples, data in CSN4CØ8X.DBF
            K+                      by AA : 5ØØ samples, data in CSKPAØ8X.DBF
            Na+                     by AA : 5ØØ samples, data in CSNAAØ8X.DBF

  Sample Overview:

    This analysis list covers samples from the AMEC Ambient Network project.  These
    are 5ØØ PM2.5 samples on 47 mm Nylon filters, including no lab blanks and no
    field blanks.  These samples were collected with an IMPROVE_A sampler.  Filters
    received May 26, 2Ø16 in 3 coolers.

  Analysis Overview:

    Sample deposit area: 1.ØØ cm²
    Analysis start date: asap
    Analysis deadline   :
    Sample location     : Elements Room Refrigerator

  Analysis Details:

    Use Improve_A method.  NOTE THAT THIS RUN HAS Ø LABORATORY BLANKS.

    Sample extractions must be scheduled with Wet Chem Lab personnel.  Whole samples
    will be extracted in 15.Ø ml DDW.  Samples will be sonicated for 6Ø minutes,
    shaken for 6Ø minutes, and left in the refrigerator overnight before analysis
    begins.  Analysis data will be stored in the \CSN\BATCHØ8A\DATA directory.
```

Figure 4-2(a). Example of page 1 of a DRI analysis list – analysis information.

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
         by Ion Chromatography using the DIONEX ICS-5000+ System

Page: 14 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2
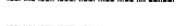
```
                              CSN : Batch Ø8 (Part A) Nylon
                              ******************************
  Date: Ø6/16/16
                                                                              Page 2 of 22

                  Filter      Description   Cl-/NO3-/SO4=    NH4+      K+        Na+

  ||||||||||||    FØØ7688                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ7691                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ7694                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ7697                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ77ØØ                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ77Ø3                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ77Ø6                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ77Ø9                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ7712                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ7715                    Y _____    Y _____   Y _____   Y _____

  ||||||||||||    FØØ7718                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ7721                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ7724                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ7727                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ773Ø                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ7733                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ7736                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ774Ø                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ7743                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ7746                    Y _____    Y _____   Y _____   Y _____

  ||||||||||||    FØØ7749                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ7752                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ7755                    Y _____    Y _____   Y _____   Y _____
  ||||||||||||    FØØ7758                    Y _____    Y _____   Y _____   Y _____
```

Figure 4-2(b). Example of page 2 of a DRI analysis list – barcoded IDs for all samples to be analyzed.

DRI STANDARD OPERATING PROCEDURE

Page: 15 of 29
Date: 02/23/17
Title: Cation Analysis of Filter Extracts and Precipitation Samples Number: 2-228r2
by Ion Chromatography using the DIONEX ICS-5000$^+$ System Revision: 2
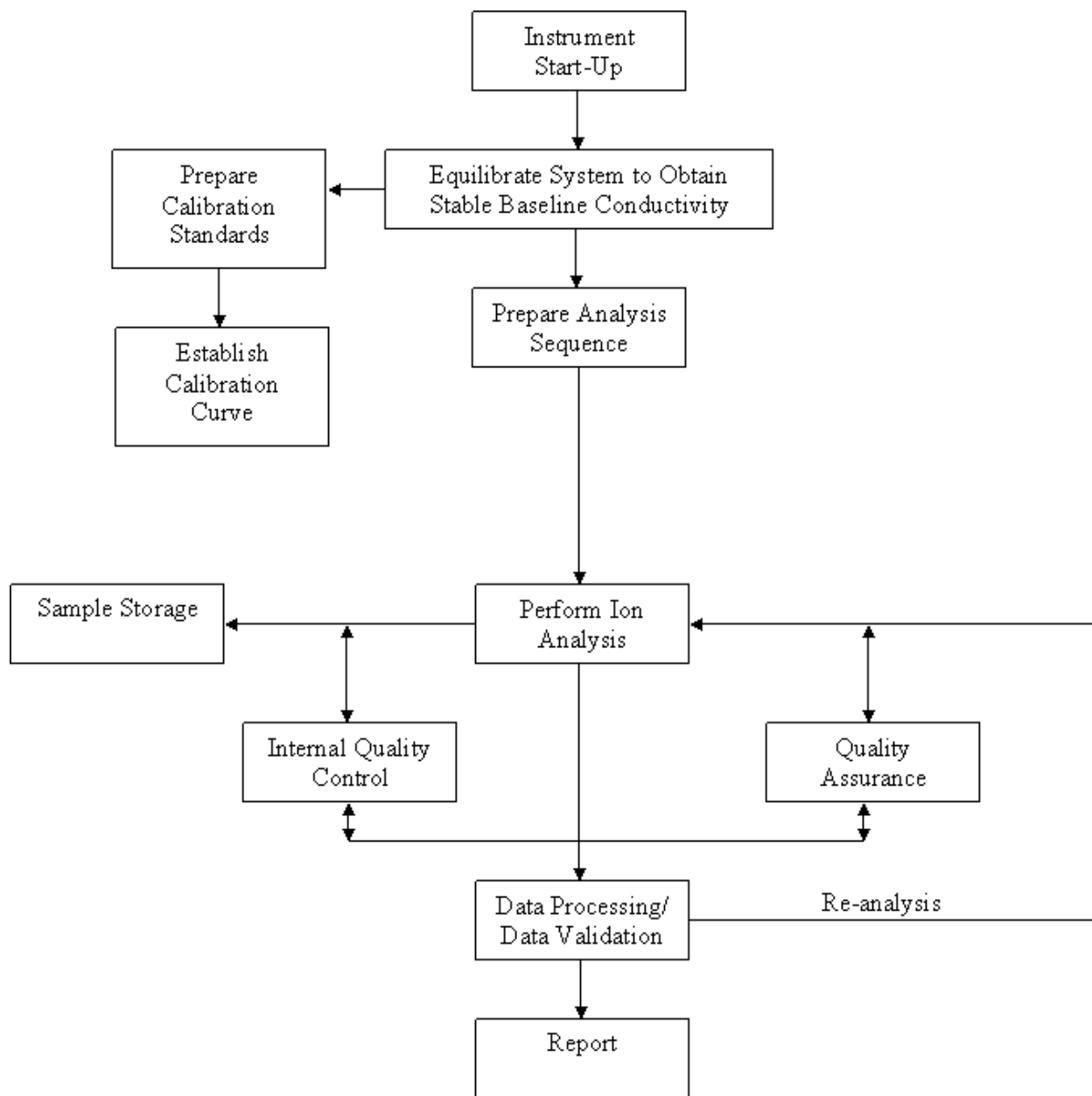
Figure 4-3. Flow diagram for IC analysis.

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
          by Ion Chromatography using the DIONEX ICS-5000+ System

Page: 16 of 29
Date: 02/23/17
Number: 2-228r2
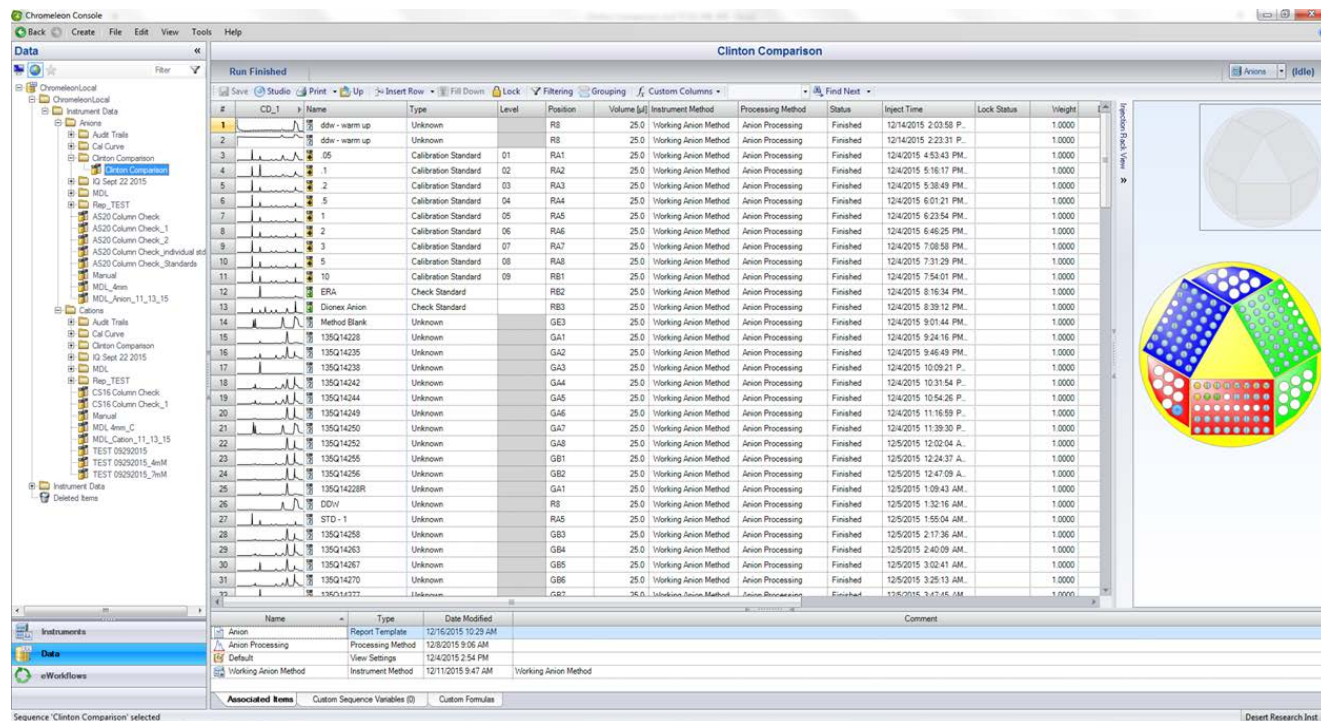Revision: 2

Figure 4-4. Chromeleon Console window with an example of a run list.

- Manual startup if the hardware and software are already off:
    1. Turn on all modules.
    2. Turn on the computer.
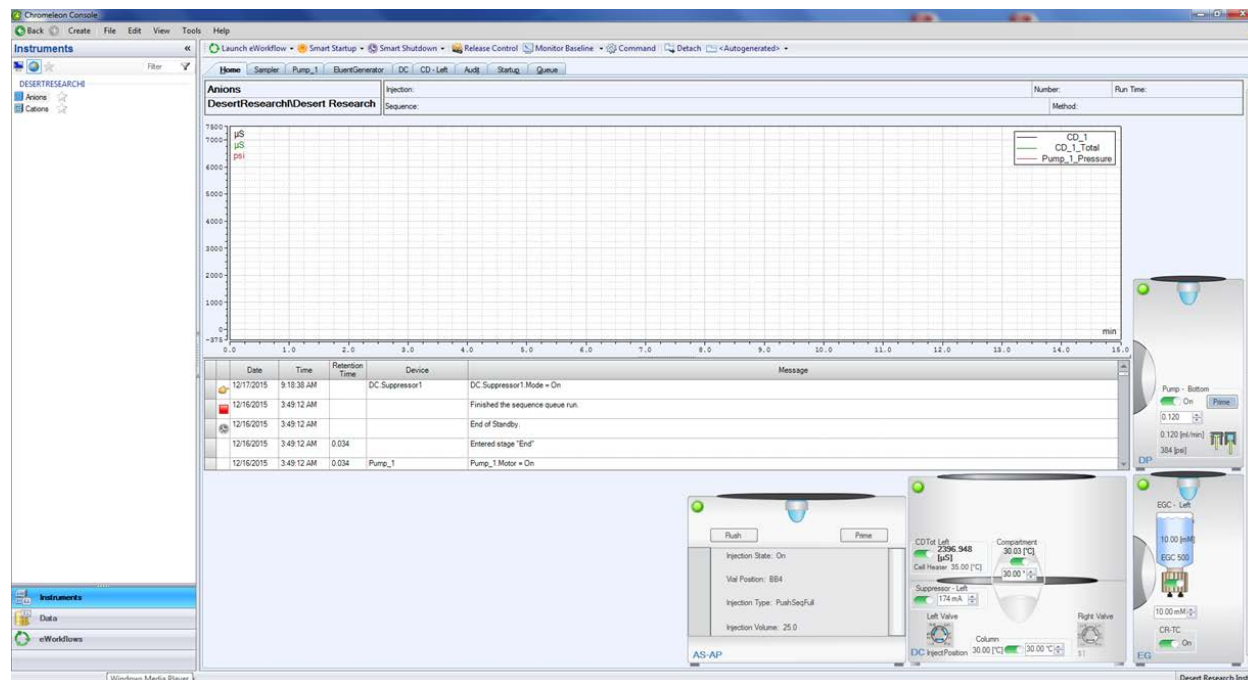   3. Proceed with the software start-up procedure described in 4.2.1.

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
              by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 17 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

Figure 4-5. Instrument control functions in Chromeleon Console.

4.2.3   Creating a Sequence

- From the browser, click **Create** and **Sequence** (using Wizard) and follow the step-by-step instructions.
- Save the sequence as ppmmddyya, where pp is the file code found on the analysis list and "a" indicates cation analysis.

4.2.4   Creating a Quantification Method (Standard Curve)

- From the browser, click **Create** and **Processing Method**. The Method Editor Wizard opens and several options are displayed. Select **Basic Quantitative**. Title the method with the project name and click Finish.
- In the processing method window click on "Run Cobra Wizard". In the wizard, select "Consider Void Peak" and set the minimum peak area detection to 0.001. All other parameters may be left in auto or standard mode. A method called "Cation Processing" has already been created and may be used for future analysis.
- Start the sequence from the data panel window by clicking **Start.** From the drop down menu on the Processing Method column, select the desired method for the sequence (e.g., Cation Processing)
- The sequence does not have to be finished in order to make the standard curve. Standard must be selected as calibration standards in the **Type** column, and each standard must be given a "Level" that represents its concentration. When the standards

DRI STANDARD OPERATING PROCEDURE   Page: 18 of 29
                                                                   Date: 02/23/17
Title: Cation Analysis of Filter Extracts and Precipitation Samples   Number: 2-228r2
          by Ion Chromatography using the DIONEX ICS-5000$^+$ System   Revision: 2

are completed, open any standard in the run by double clicking the selected standard and select the **Calib. & PM** tab. In the group area enter the concentration of each standard below each **Level**. Continue by selecting the "Component Wizard" in order to determine elution times and peak naming.

- Click the **Detection** tab, set the integration parameters as needed. Detection parameters serve to recognize, classify, or suppress peaks, and to determine the baseline contact.
- Click on **Calibration Plot** to open the calibration window. Select the desired component and right click the calibration window that appeared on the top right corner of the screen, and click on **Calibration Type** to fit the standard curve as linear, quadratic, or exponential. In almost all cases, a linear curve is used (ammonium being the exception where a quadratic is used). If any standard is deemed unsuitable, the enabled box can be unmarked by right clicking on the specific point. A red star in the calibration curve will indicate standards that are not included. If r^2 <0.98 the calibration curve is redone.
- Save Method File (standard curve) when completed with the optimization.
- Run a new standard curve in every sequence

4.3   Routine Operation

4.3.1   Daily Operation

Ensure the following:
- The DDW bottle is full.
- The wash reservoir is full.
- Thee waste container has enough capacity for the run.

Perform the following steps:
- Start Chromeleon from the desktop shortcut.
- Select the **Cation** timebase in the Chromeleon Data browser. Start the Server Monitor (if not activated yet). This step is necessary if the computer has been powered down. The Server Monitor can be found in the Windows systems tray.
- Open Instruments panel and click **SmartStartup**. Take the calibration standards out of refrigerator, and prepare fresh standards if the quantities are insufficient for the run.
- The conductivity should stabilize between -1.0 and 1.0 micro-Siemens. If the conductivity is not within these limits, check for leaks; air bubbles may cause variation. (See troubleshooting). The pressure should stabilize between 2000 and 2400 psi with a variation of $\pm$ 20 psi.
- While the instrument is stabilizing, generate the report for the previous day's analyses, make working and calibration standards (if necessary), generate the day's sequence and processing file, and load samples into autosampler vials.

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
            by Ion Chromatography using the DIONEX ICS-5000⁺ System

Page: 19 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

4.3.2   Sequence Setup

Prepare the sequence. Use the Wizard (see 4.2.3) to create a new sequence or save a finished sequence with a new name. Be sure that the cation timebase is used and that the injection volume is 25 µL. In the next window, standards can be imported from a previous sequence. Browse to select the sequence, show the standards, select the ones in the right window that are to be used, select the **Apply** button and the standards of choice will be imported.   Save the sequence as **ppmmddyya**, where **pp** is the file code found on the analysis list and **a** indicates anion analysis. In the new sequence, the status of all samples/standards will be "idle" (no data yet).The samples in a sequence are placed in the following order, starting with water blanks and standards:

- DDW
- DDW
- Calibration Curve
- ERA "Custom Standard"
- Dionex Cation QC

Samples are run in groups of 10, followed by a DDW blank and a check standard. Thus, the sample sequence will have the following repeating format:

- 10 samples
- 1 replicate
- 1 DDW
- 1 check standard
- 10 samples
- 1 replicate
- 1 DDW
- 1 check standard

The concentration of check standards within the sequence usually starts with the 0.02 µg/mL standard and increases sequentially. If the run is short, a random selection may be used, including at least one standard at the lower end and one at the higher end of the calibration range. At the beginning of the first pattern, add the method blank(s). The system will enter standby model after the end of the sequence, or at the end of the queue.

4.3.3   Sample Setup and Analysis

Align the sample vials in the sampling tray according the sequence that is set up. Each sample tray is 5x8 (5 rows and 8 columns each), totaling in 40 samples per tray. Three sample trays can be loaded into the instrument simultaneously (with a capacity of 8 vials each). In addition to the 3 sample trays, 3 large volume trays are also loaded into the

DRI STANDARD OPERATING PROCEDURE   Page: 20 of 29
                                                          Date: 02/23/17
Title: Cation Analysis of Filter Extracts and Precipitation Samples   Number: 2-228r2
            by Ion Chromatography using the DIONEX ICS-5000$^+$ System   Revision: 2

instrument, these contain standard solutions and deionized water. The configuration of the six trays when loaded in the instrument is shown in Figure 4-6.

Load each sample vial with a 1 mL aliquot of the sample extract solution and cap the vial. Ensure that the position in the sample tray corresponds to the position indicated in the sequence. In order to aid the user in aligning the samples on the try with the sequence, the user may print a hard copy of the sequence to use when loading the samples. To do this click **Print** in the Data window. After every 8 samples, draw a line. After the 8 samples are loaded into the vials, check off that set. Alternately the analysis log sheet may be used as shown in Figure 4-7.

Place the prepared sample trays into the auto sampler. Ensure that trays are placed in the correct location, according to the sequence.

Start the analysis from the Data window. Select **Start with SmartStartup.** Green bars indicate no problems. All error messages should be resolved before beginning the run.

Figure 4-6. Photograph of sample vial configuration in the autosampler of Thermo Scientific/Dionex ICS-5000+ system with three 40-vial sample trays and three eight-vial calibration/QC standard trays.

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
           by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 21 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

Figure 4-7. Example of DRI's EAF Ion Analysis Log Sheet for the Thermo Scientific/Dionex ICS-5000+ system (H1 through H95 denotes sample numbers 1 through 95 for PM2.5 samples from the Hong Kong Chemical Speciation Network). The circles denote calibration and QC standards.

4.4   Shut-Down

4.4.1   Routine Instrument Shut-Down

The instrument will enter standby mode once the sequence has finished analyzing all samples.

4.4.2   Waste Disposal

Once the waste container is 70-80% full, neutralize with baking soda solution until it reaches a pH of ~7, and dispose of the waste in a sink. If an EGC reaches the end of its lifetime, detach the EGC pod from the reservoir and dispose of the solution into an appropriate hazardous waste container, following the local hazard material disposable procedure.

4.5   DAILY CHECKLIST

- Check the remaining EGC capacity
- Check the eluent bottles for DDW level
- Check the waste container for fluid level

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
           by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 22 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

- Open Chromeleon and start the instrument
- Prepare standards, if necessary
- Prepare sequence
- Load samples
- Begin run
- Process the data
- Copy the files to the proper directory on the EAF server

4.5   TROUBLESHOOTING

Use the Reference Library CD that is provided by DIONEX to find troubleshooting guides for the various IC instruments and consumables (e.g., columns or suppressors) in the respective manuals. The Technical Support Center can also be consulted by phone (1-800-532-4752) or e-mail (CustomerCare.dionex@thermofisher.com). Common problems and their solutions are:

There is a message that the server is not active. Click on the Chromeleon icon in the lower right corner of the toolbar.

The autosampler doesn't start and there is a "module timed out" message. This means that the computer and the autosampler are not communicating. Use the procedures for power failures (end of section 4.2.2). If there is a run on the cation system, it will need to be stopped after the currently running sample. Make sure that the run is restarted on the proper sample and that the interrupted sample gets run (by changing its status to idle).

There is a leak message on the menu screen. Check the fittings on the DC module. Tighten the leaking nuts one-eighth of a turn at a time until the leaking stops. Dry the affected area, including the area around the leak sensor.

The baseline is not stable. Check that the DDW reservoir has enough DDW in it; if it has run out, prime the pump after filling the reservoir. If this doesn't fix the problem, check for leaks and air bubbles; prime the pump.

Peaks are not sharp. The column may need to be replaced. Try cleaning it first, following the procedure in the respective Dionex column manual.

Overlapping peaks. If the retention times have shifted and peaks are too close to the water dip, some ions will co-elute and overlap, replace the analytical column.

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
           by Ion Chromatography using the DIONEX ICS-5000⁺ System

Page: 23 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

High pump pressure. There may be blockage in the lines. Trace the sample stream from the autosampler, disconnecting and replacing one section at a time until the blockage is cleared.

Low pump pressure. This may be due to air in the line. Check the eluent levels. Prime the pump. There is a **Prime** button on the panel face. Follow the directions.

Leakage from the CERS. If the pump has been off, the membranes may have dried out. Try running at low flow for about 10 minutes. If it still leaks let it sit overnight to allow for rehydration of the membrane. Order another CERS just in case the hydration is not successful.

5.0   DATA COMPILATION AND FILE MANAGEMENT

5.1   Validation of the Chromatograms

Visually inspect every chromatogram to ensure that the samples have run properly, the peaks are identified correctly, there are no errors in the labels of the samples, the peaks are adequately drawn, and the peak areas are completely integrated.

Proper Data Collection: The baseline should be constant before the water dip, return to its baseline position after the water dip and between components. A shifting or noisy baseline may indicate air bubbles in the line caused by leakage at the pump, air leaks affecting the conductivity cell, or running out of eluent.

Peak Identification: Occasionally, the constituents of a sample will be misidentified by the software due to a shift in the retention times during the run. This can be caused by very high concentrations, viscosity of the sample, or deterioration of the column. The peak(s) should be compared with the standard peaks and a determination made of the identity of the peak(s) from comparison with the order of elution. Correct the peak identification by changing the window size in the **Calib. & PM.** tab or by manually assigning the peak name by selecting the peak with a right click and using the peak **properties** window and choosing the correct name from the list of displayed analytes. In case incorrect peak assignment is observed for multiple samples, it is usually due to a retention time window that is too small or not in the correct location. With a sample file open, access the Processing Method file, use the peak table tab, increase the size of the retention window until the ion is identified correctly in the chromatogram, save the Processing Method file and exit.

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
            by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 24 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

Sample Peaks and Integration: Peaks should rise from the baseline and remerge smoothly with it. It is necessary to redraw the baselines if the drawn integration line does not look proper, e.g., if it cuts off the peak prematurely or extends too far from the peak on the baseline (fronting or tailing). To reintegrate a peak, delete original baseline by clicking on it and using the delete key. Re-draw the baseline by moving the mouse to the desired starting point of the baseline and left click, dragging it across the entire peak to the desired end point. A double up-pointing marker indicates the peak start, while a double down-pointing marker indicates the peak end. Left-click and drag the tool until the baseline is in the desired location and consistent with those for peaks of the same analyte.

All peak properties such as area, width, analyte amount, etc. are recalculated. The integration report is immediately updated automatically. Save manipulations by clicking on the **save** icon that appears to the right of the reintegrated sample/standard name in the "Injections" list under the **Data Processing** tab on the left side of the screen.

5.2   Calculation of Concentrations in the Extract Solution

The peaks in the chromatograms are identified and area counts are converted to concentrations in µg/mL and printed on the chromatogram. An example of a typical ion chromatogram for a cation calibration solution is illustrated in Figure 5-1. Any samples that have amounts above the highest standard in the calibration curve must be diluted and re-analyzed, because the calibration curve does not extend indefinitely in a linear manner. These dilutions may be done at the end of the sequence or as part of the next day's run.

5.3   Calculation of Concentrations on the Filter

When the analysis is complete, the sequence is batched to an Excel file. The file is manipulated so that the columns contain the information of interest, i.e., sample names, retention times, and amounts (concentrations).

5.4   Exporting the Sequence

- Open the Sequence file using the browser on the left hand side.
- Select any sample in the sequence, and double click to open.
- Click "Report Designer" on the bottom left hand menu.
- Choose what parameters and analytes are to be included in the report. Double click on the heading to change parameters or analytes.
- Save the file.
- Click the Chromeleon (chameleon) icon in upper left corner of the window and choose "Export".
- Choose the file location (entered under parent folder) and desired format (e.g. excel).
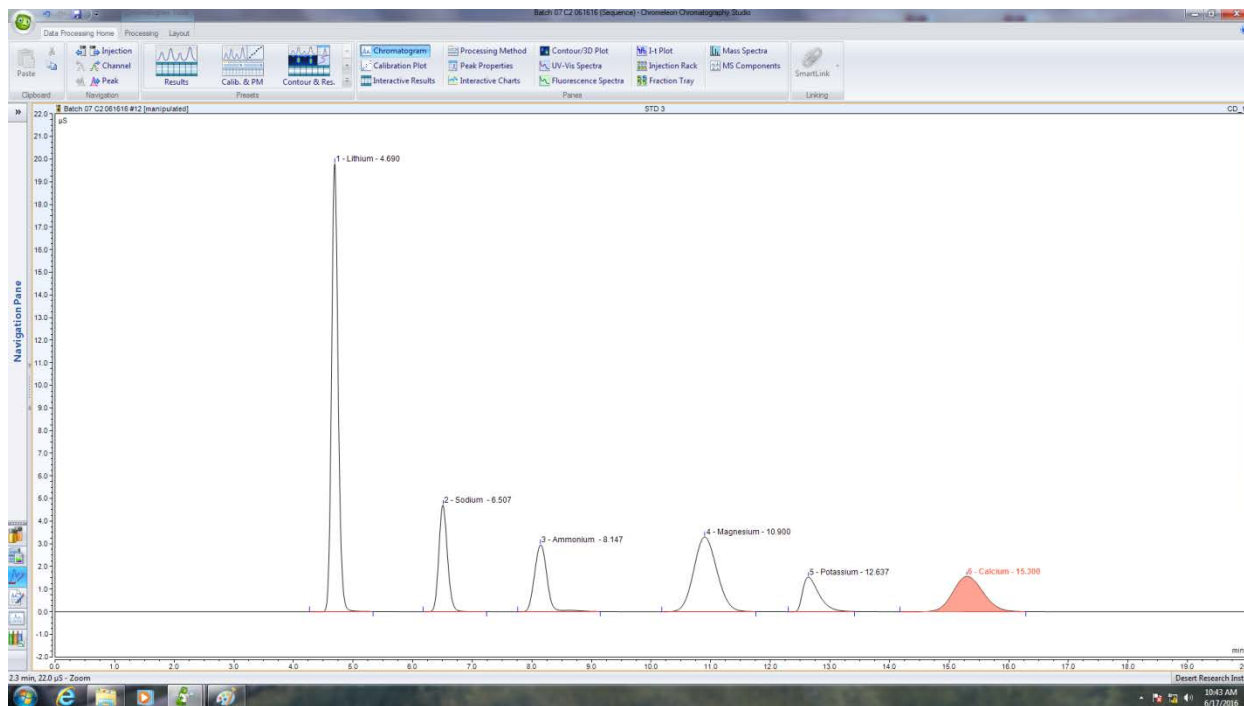
DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
          by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 25 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

Figure 5-1. Example chromatogram of a cation calibration standard.

5.5   Calculations

5.5.1.   Manual Calculation of Concentrations

These steps should be followed if manual calculation of concentrations is necessary.

1.   Determine the linear regression of the calibration curve for each ionic species. The calibration equation is given by the following relationship.

   µg/mL = SLOPE *response (µS) + intercept   (5-1)

2.   Calculate concentrations of sample extracts corresponding to the area counts according to the calibration curve.

3.   Calculate the total amount of ionic species in precipitation samples or in the filter by using the appropriate factors and record on the data sheet, using the following equation:

   µg/filter = µg/mL x V x D x F   (5-2)

   where:

   V = volume of extract

   D = dilution factor

   F = scaling factor, determined by ratio of filter size to the fraction analyzed

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
           by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 26 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

5.5.2   Precision Estimates

Precisions reported in the data bases are propagated from the precision of the replicated analysis and the field blank variability using the methods of Bevington (1969). The following formulas describe the calculation of the precision propagation:

$$B_i = \frac{1}{n}\sum_{j=1}^{n} B_{ij} \qquad\qquad \text{for } B_i > \sigma_{B_i} \qquad (5\text{-}3)$$

$$B_i = 0 \qquad\qquad \text{for } B_i \leq \sigma_{B_i} \qquad (5\text{-}4)$$

$$\sigma_{B_i} = STD_{B_i} = \left[\frac{1}{n}\sum_{j=1}^{n}\left(B_{ij} - B_i\right)^2\right]^{1/2} \qquad\qquad \text{for } STD_{B_i} > SIG_{B_i} \qquad (5\text{-}5)$$

$$\sigma_{B_i} = SIG_{B_i} = \left[\frac{1}{n}\sum_{j=1}^{n}\left(\sigma_{B_{ij}}\right)^2\right]^{1/2} \qquad\qquad \text{for } STD_{B_i} \leq SIG_{B_i} \qquad (5\text{-}6)$$

$$\text{and } B_i \geq SIG_{B_i}$$

$$\sigma_{B_i} = 0 \qquad\qquad \text{for } B_i < SIG_{B_i} \qquad (5\text{-}7)$$

$$D_{M_{ij}} = M_{ijf} - M_{ijr} \qquad (5\text{-}8)$$

$$D_{M_i} = \frac{1}{n}\sum_{j=1}^{n} D_{M_{ij}} \qquad (5\text{-}9)$$

$$\sigma_{M_i} = \left[\frac{1}{n}\sum_{j=1}^{n}\left(D_{M_{ij}} - D_{M_i}\right)^2\right]^{1/2} \qquad (5\text{-}10)$$

where:

M_i = amount of species i on the substrate

M_{ijf} = amount of species i on sample j from routine analysis

M_{ijr} = amount of species i on sample j from replicate analysis

B_i = average amount of species i on field blanks

B_{ij} = the amount of species i found on field blank j

σ_{B_i} = blank precision for species j

σ_{M_i} = precision of amount of species i on substrate

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
           by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 27 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

6.0   QUALITY CONTROL

The QC procedures serve two main purposes: 1) to identify possible problems with the measurement process, and 2) to calculate the precision of ion measurements.

6.1   Performance Testing

In addition to the daily start-up described in Section 4, the analysis sequence for standards, blanks and replicates should be followed as described in Section 4.3.2, resulting in approximately 10% check standards, 10% replicates and 5% blank checks.

6.2   Reproducibility Testing

Reproducibility is examined with the 10% replicate analyses during the routine sample analysis. Each tray holds 40 samples, and 4 replicates from each tray are randomly chosen for replicate analysis using an alternate instrument. Four random numbers are generated to determine which samples are replicated. The replicate analysis will exclude field blanks. The samples are extracted only once, so the replicate analysis refers only to the IC analysis of the extract. The precision of the replicate analysis will be calculated as stated in Section 5.5.2.

6.3   Tolerances and Actions to be Taken

Tolerances are generally ±30% at levels between 0.030 and 0.100 µg/mL; ±20% at levels between 0.100 and 0.150 µg/mL; and ±10% at levels above 0.150 µg/mL. If replicates exceed these tolerances, analyses beyond the last acceptable replicate are suspected to be incorrect. The replicate analysis on the same sample should be repeated again. If the second replicate duplicates the original sample result, the first replicate result can be taken as spurious. Another replicate should be selected from samples within the same set of 10 samples, after that first spurious replicate, and analyzed to verify that assumption. If the second replicate analysis exceeds the tolerance criteria, the cause of the error (probably in the instrument or the chemistry of the analysis) must be determined. In that case, the whole set of 10 samples must be reanalyzed. Notify the laboratory supervisor immediately if sample rerun is to be performed.

6.4   Data Validation Feedback

The sample validation philosophy follows the three-level approach devised by Mueller et al. (1983) in the Sulfate Regional Experiment (SURE):

DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
           by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 28 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

Level I sample validation takes place in the field or laboratory and consists of: 1) flagging samples when significant deviations from measurement assumptions have occurred, 2) verifying computer file entries against data sheets, 3) eliminating values from measurements which are known to be invalid because of instrument malfunctions, 4) replacing data when re-analyses have been performed, and 5) adjusting measurement values for quantifiable calibration of interference biases.

Level II sample validation takes place after data from various measurement methods have been assembled in the master database.

Level III sample validation is part of the data interpretation process and will be performed by each project manager and subsequent data users. The first assumption upon finding a measurement which is inconsistent with physical expectations is that the unusual value is due to a measurement error. If upon tracing the path of the measurement nothing unusual is found, the value can be assumed to be a valid result of an environmental cause.

The laboratory supervisor should review all the QC data as soon as it becomes available and ensure the feedback from the QC results to the routine operations. The project manager should consult with the QA officer to initiate and document changes to the data base as they are needed.

7.0   QUALITY ASSURANCE

Performance and system audits are scheduled for specific projects by the designated QA officer on a project specific basis to ensure that all procedures are followed properly and to verify the precision, accuracy and validity of the data. As a general rule, the EAF encourages inter-laboratory performance audits and participates when possible.

8.0   REFERENCES

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DRI STANDARD OPERATING PROCEDURE

Title: Cation Analysis of Filter Extracts and Precipitation Samples
           by Ion Chromatography using the DIONEX ICS-5000$^+$ System

Page: 29 of 29
Date: 02/23/17
Number: 2-228r2
Revision: 2

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9.0   DOCUMENT CHANGES

01/26/16: r0 – New SOP for ICS-5000$^+$ instrument. This SOP supplements, but does not replace other ion analysis SOPs, using other systems.

06/16/16: r1 – Updated typical values for Table 1-1; added new table for minimum detection limits and updated table for lower quantifiable limits; revised calibration range for calibration standards in Section 3.1.3; updated Figure 4; and clarified what type of calibration curve fit is to be used and acceptable fit. Also, made minor editorial and format changes throughout the document.

02/23/17: r2 – Revised to make document CSN specific.