Illinois State Water Survey
Health and Environmental Applications Laboratory

Standard Operating Procedure For the Determination of Cl^-, Br^-, NO_3^-, and SO_4^{2-} using Thermo Scientific DIONEX ICS-5000 and Integrion Ion Chromatographs, and Chromeleon Software

SOP Number AN.HEAL.IN.IC-anions (AN-0018)

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NOTE THE HEALTH AND SAFETY WARNINGS IN SECTION 4.0

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Contents

1.0 Scope & Applicability

Chloride (Cl^-), sulfate (SO_4^{2-}), bromide (Br^-), and nitrate (NO_3^-) are determined by Thermo Scientific Autosuppressed Ion Chromatography (IC) for the wet deposition samples. The applicable calibration range for NO_3^- and SO_4^{2-} is 0.015-6.000 mg/L; 0.015-4.000 mg/L for Cl^-; and 0.015 – 0.500 mg/L for Br^-. The Method Detection Limit for NO_3^- is 0.003 mg/L, for SO_4^{2-} is 0.002 mg/L, for Cl^- is 0.003 mg/L, and for Br^- is 0.002 mg/L.

2.0 Summary of Method

This ion chromatography (IC) method closely follows EPA Method 300.1. This ion chromatography method combines conductivity detection with the separation capabilities of Thermo Scientific AG18/AS18 columns. A 25 µL aliquot of sample is pumped through an ion exchange column. Because different ions have different migration rates, the sample ions of interest (Cl^-, Br^-, SO_4^{2-}, NO_3^-) elute from the column as discrete bands. Each ion is identified by its retention time. The sample ions are selectively eluted off the separator column and into an anion self-regenerating suppressor (ASRS). The eluent ions are neutralized and the sample ions are converted to their corresponding strong acids which are detected in a conductivity cell. The ion chromatographs are calibrated with standard solutions containing known concentrations of anions. The raw peak area data is collected by the computer. The electronically produced Chromatogram is a picture of the raw data. The Chromeleon software is used to control each IC system and to calculate the concentration of the anions for each sample using the raw data. IC operating conditions are as follows:

Guard column - Thermo Scientific AG18 (for ICS-5000) and AG18-4 µm (for Integrion)
Separator column - Thermo Scientific AS18 (for ICS-5000) and AS18-4 µm (for Integrion)
Anion Suppressor - Thermo Scientific ASRS - Ultra II
Detector - Thermo Scientific Conductivity Detector CD1 cell (for ICS-5000) and Integrion CD Conductivity Detector (for Integrion)
Eluent - 31 mM Potassium Hydroxide
ASRS - Ultra II current = 87 mA
Column Temp = 30˚C
Cell Temp. = 35˚C
Sample loop - 25 µL
Flow rate - 1.0 mL/min

3.0 Definitions*

ACS	American Chemical Society
AG18/AG18-4µm	Anion Guard columns
AS18/AS18-4µm	Anion Separator columns
ASRS	Anion Self Regenerating Suppressor
ECG	Eluent Generator Cartridge
FH	An in-house prepared quality control sample targeting the high end of the calibration curve
FL	An in-house prepared quality control sample targeting the low end of the calibration curve

FM	An in-house prepared quality control sample targeting the middle of the calibration curve
FR50	An in-house prepared quality control synthetic sample targeting the 50th percentile concentration of the precipitation samples analyzed for the NADP/NTN
IC	Ion Chromatography
IDT	Instrument Data Tool
Laboratory spike	A known concentration of analyte is added to a sample for identification or quality control purposes
LIMS	Laboratory Information Management System
MDL	Method Detection Limit
MSDS	Material Safety Data Sheet
OOR	Out Of Range: samples with a greater than 6.000 ppm NO_3- and SO_4^{2-}, 4.000 ppm Cl^-, and 0.500 ppm Br^-
QA	Quality Assurance
QC	Quality Control
QCS	Quality Control Solutions
R^2	Coefficient of Determination displayed as a percentage reflecting the deviation of the measured data points from the calibration curve
STD	Laboratory standards
Wet Deposition Samples	Rain, snow, dew, sleet, and hail

*See Thermo Scientific, ICS-5000, Integrion and Chromeleon manuals/glossaries for other IC and software definitions

4.0 Health & Safety Warnings

4.1 Standards, samples, and most reagents used in this method pose no hazard to the analyst. Use a fume hood, protective clothing, and safety glasses when handling concentrated acids.

4.2 Always wear eye protection in the laboratory.

4.3 No food or drinks are allowed in the lab.

4.4 Safety Data Sheets (SDS) applicable to this SOP can be found by searching the University of Illinois SDS page at: https://www.drs.illinois.edu/Programs/Safety Data Sheets.

4.5 The Illinois State Water Survey Chemical Hygiene Plan covers the ISWS laboratory safety program, including, but not limited to, personal protective equipment used, control equipment inventory and operations (such as vented hoods), employee training programs, medical programs, and safety. The ISWS Chemical Hygiene Plan is available at http://isws.illinois.edu/staffonly/resources/manuals.asp. Procedural notes are included in test methods used (e.g. ASTM International, United States Environmental Protection Agency (USEPA), or Standard Methods for the Examination of Water and Wastewater).

4.6 The University of Illinois Division of Research and Safety requirements for chemical safety can be found at http://www.drs.illinois.edu.

4.7 The HEAL has listed known health and safety warnings for this SOP, but this list should not be assumed to comprise all health and safety issues.

5.0 Cautions

5.1 Wear eye protection and gloves when handling the Eluent Generator Cartridge (EGC).

5.2 Do not cap EGC waste container; small amounts of oxygen and hydrogen gas are produced.

5.3 Wait 15 seconds after turning off equipment before turning it on again. This will prevent damage to pump circuitry and components.

5.4 Electrical precautions: turn off power and unplug electrical cords when replacing fuses, circuit board, and other electrical parts.

5.5 No food or drinks are allowed in the sample processing and equipment area to protect the sample integrity.

5.6 The HEAL has listed known cautions for this SOP, but this list should not be assumed to cover all issues.

6.0 Interferences

6.1 To prevent interferences use chemicals of high purity 99% or better.

6.2 Air bubbles in the eluent can cause the pump to lose prime as well as noise in the detector cell.

6.3 Use DI with a resistivity of 18.0 megohms-cm or greater and a 0.20 µm point of use filter to help prevent contamination problems.

6.4 Occasionally a peak with a retention time similar to Cl^-, NO_3^-, Br^-, or SO_4^{2-} interferes with peak integration. The sample can be diluted to separate the peaks better, or a sample aliquot can be spiked to determine the correct peak. If a Cl^-, NO_3^-, Br^-, or SO_4^{2-} peak cannot be completely resolved, notify the Quality Control Specialist and Lab Manager by email or phone before the data is released to data management.

7.0 Personnel Qualifications

- Bachelor Degree with one year chemistry course work. The course work must include laboratory experience. One year laboratory work experience may be substituted for laboratory course work.
- Basic knowledge of Ion Chromatography, Thermo Scientific ICS-5000 and ICS-Integrion IC operation, and Windows software is helpful. Other computer software skills are also helpful.
- Ability to coordinate analysis of many precipitation samples and keep data organized.

8.0 Equipment and Materials (see Appendix A – Ion Chromatography Ordering Guide)

8.1 Current Equipment

8.1.2 Two IC 5000 Ion Chromatograph, purchased 7/2011 and 3/2014

8.1.2 One Integrion Ion Chromatograph, purchased 12/01/2017

8.1.3 Three Thermo Scientific ASDV autosamplers, purchased 11/2011

8.2 Supplies

8.2.1 Materials purchased from Thermo Scientific

8.2.1.1 AG18/AS18 (AG18-4µm/AS18-4µm) Guard/Separator Columns

8.2.1.2 ASRS (ULTRA II - 4mm) Anion Supressors

8.2.1.3 Sample vials without filter caps

8.2.1.4 Piston seals

8.2.1.5 Peak Tubing

8.2.1.6 Eluent Generator Cartridge - Anions (EGC)

8.2.1.7 Continuously Regenerated Anion Trap Column (CR-ATC)

8.2.2 Lab Materials

8.2.2.1 Eppendorf adjustable pipettes and tips - 100 to 1000 µL

8.2.2.2 Eppendorf adjustable pipettes and tips - 10 to 100 µL

8.2.2.3 Class A Volumetric flasks

8.2.2.4 Whatman filter paper (grade 211)

8.3 Chemicals and Solutions

Certified stock solutions (1000 ppm) are purchased from SPEXCertiPrep (for calibration standards) and High Purity Standards (for QC standards) yearly.

9.0 Method Calibration

9.1 Certified Stock Solutions

Certified stock solutions (1000 ppm) are purchased yearly on or before the expiration dates of the previous set of stock solutions. Verify new certified solutions with standards analyzed previously, certified reference solutions, and internal QCS (see section 18.2).

Laboratory prepared stocks can be used with the approval of the QA specialist if there is a discrepancy between two purchased lots of stocks (see section 18.1).

9.2 Calibration Standards

Prepare Calibration Standards using DI water with a specific resistance of 18.0 megohms-cm or greater and a 0.20 µm point of use filter. Use only class A volumetric flasks (see section 18.1). Verify new calibration standards with standards analyzed previously or their area counts and internal QCS (see section 18.2).

9.2.1

Standard	Volumetric Size	**Cl^-** Value ppm	Amount of Stock to use	**NO_3^-** Value ppm	Amount of Stock to use
S0	1 L	0.015	15 µL	0.015	15 µL
S1	1 L	0.025	25 µL	0.050	50 µL
S2	1 L	0.050	50 µL	0.100	100 µL
S3	1 L	0.100	100 µL	0.200	200 µL
S4	1 L	0.200	200 µL	0.500	500 µL
S5	1 L	0.500	500 µL	1.00	1.00 mL
S6	500 mL	1.000	500 µL	2.50	1.25 mL
S7	500 mL	1.500	750 µL	4.00	2.00 mL
S8	500 mL	2.500	1.25 mL	5.00	2.50 mL
S9	500 mL	4.000	2.00 mL	6.00	3.00 mL

Standard	Volumetric Size	**SO_4^{2-}** Value ppm	Amount of Stock to use	**Br^-** Value ppm	Amount of Stock to use
S0	1 L	0.015	15 µL	0.015	15 µL
S1	1 L	0.050	50 µL	0.025	25 µL
S2	1 L	0.100	100 µL	0.050	50 µL
S3	1 L	0.200	200 µL	0.100	100 µL
S4	1 L	0.750	750 µL	0.200	200 µL
S5	1 L	1.500	1.5 mL	0.500	500 µL
S6	500 mL	2.500	1.25 mL		
S7	500 mL	4.000	2.00 mL		
S8	500 mL	5.000	2.50 mL		
S9	500 mL	6.000	3.00 mL		

9.2.2 Standards 0-6 are used to calculate samples that fall in the range 0 - 1.000 ppm for Cl^- , 0 – 0.500 ppm for Br^- and 0 - 2.500 ppm for NO_3^- and SO_4^{-2}. Standards

6-9 are used to calculate samples that fall in the range 1.000-4.000 ppm for Cl^- and 2.500 - 6.000 ppm for NO_3^- and SO_4^{-2}.

9.2.3 Pipettes should be checked before calibration standards are made, measuring the highest and lowest range used at least three times. Record measurements in IC notebook (see section 18.6).

9.2.4 For other volumetric sizes, use the equation in section 18.3.

Or use:

$$\text{Amount of stock solution to use (mL)} = \frac{\text{desired end volume (mL)} \times \text{desired concentration (mg/mL)}}{\text{stock solution concentration (mg/L)}}$$

Example: $1.5\ \text{mL} = \frac{500\ \text{mL} \times 3\ \text{ppm}}{1000\ \text{ppm}}$

9.2.5 Calibration and quality control check solutions are stable for up to three months.

9.3 Calibration

9.3.1 Set up IC according to the directions given in Sample Preparation and Analysis (see section 12.0)

9.3.2 Pour each standard 0-9. Pour a DI (FB) blank to check DI and system operation. This is followed by FH, FM, FL, and FR50 QC check solutions.

9.3.3 After the calibration standards are analyzed, check the Coefficient of Determination values in the method.

10.0 Sample Collection

Refer to the Quality Assurance Plan.

11.0 Handling & Preservation

11.1 The IC operator should be careful when handling vials, caps, samples and standards to prevent standard and sample contamination.

11.2 Always use the cover on the samplers to keep particulate matter out of the samples.

11.3 Samples are refrigerated at 4˚ C (see section 18.2). Samples are always refrigerated, except to pour them. Time and frequency of sample pouring should be minimized.

12.0 Sample Preparation & Analysis

12.1 DI Water

12.1.1 Use DI water with a specific resistance of 18.0 megohms-cm or better and a 0.20 µm point of use filter.

12.1.2 Change DI water cartridges as needed.

12.1.3 Record daily resistance readings in IC lab in DI Water Notebook.

12.2 Vials and Caps

Soak vials and caps separately in test tube rack and cap containers with DI for at least 1 hour, and rinse 3 times. Dry in clean area in racks. Cover top of test tubes with parafilm while soaking and drying. Avoid contact with vials and caps to prevent contamination.

12.3 IC Start-up Procedures

Fill eluent reservoir container(s) with DI water.

Connect the pump with the system. Prime the pump - loosen the knob on the left pump head, and click the **Prime** button on the pump control section of the control panel. The system will tell the operator to loosen the prime valve - click **OK**. After about 1 minute of priming, click the **Off** button for the pump, close the priming valve and click the **Pump on**, **Supressor on** (87 mA), **Heater on** (30 °C), **Eluent Generator on** (31 mM), **CR-TC on**, and **Cell Temp on** (35 °C) buttons. **Flow rate** should be 1.0 mL/min.

12.4 Retrieving Lab numbers for Daily Runs and Preparing Sequences

12.4.1 Create run sequences in Chromeleon by first opening the template sequences (found in the Chromeleon Console (see Appendix B) under the data option, Chromeleon Local Directory, in the folder for the current month. Scan sample bar codes into the template to create the run sequence.

12.4.2 Each run should start and end with all QC solutions, which are standards: FH, FM, FL and FR50. A DI water blank (FB) is also run at the beginning and end of each run. Every 12 samples, either two QCs or one QC and a replicate sample are run. Replicate samples are run as QCs throughout the run and are randomly picked samples from the day's sample list.

12.4.3 When edits to the temp file are complete, click File, Save As and save the sequence in the folder for the current month. Use the format MoDaYeSys3, MoDaYeSys4, or MoDaYeSys5 as the file name. For example: ChromeleonLocal/ICS5000/February/020118Sys3.

12.4.4 Check that the appropriate program and method are being used. System 5000 methods are used for system 3 and system 4. System Integrion methods are used for system 5.

12.5 Starting Analysis

12.5.1 Check the ICs for any leaks, high pressure readings, and correct conductivity reading (< 2uS). Check that the cell heater is set to 35˚C, column temperature = 30˚C, eluent concentration is set to 31 mM, and that the ASRS is on and set to 87 mA. Monitor the baseline by clicking the **Monitor Baseline** command at the top of the Instrument Chromeleon Console. Once the baseline has flat-lined, the instrument is ready to analyze samples

12.5.2 While the system is warming up, begin pouring samples. At least 2 mL of sample is required for testing. Pour calibration standards from lowest to highest concentrations, and then pour FB, FH, FM, FL, and FR50 standards. Put these in the autosampler and continue to pour samples in order on sequence sheet. After the samples are poured, the sample bottles are marked with a green permanent marker.

12.5.3 Right before beginning analysis, record the date, background conductivity, back pressure and EGC life remaining in the ICS 5000/Integrion hardware logbook.

12.5.4 To start the analysis, make sure the carousel on the AS-DV is locked. If the carousel is not locked, press the **Release Carousel** button on the inside of the autosampler. Click the **Start** button from the top of the sequence.

13.0 Troubleshooting and Maintenance

13.1 IC System Maintenance & Troubleshooting

13.1.1 Change any dirty or crimped lines. This can cause increased system pressure and poor chromatograms.

13.1.2 If IC pressure is running high, greater than about 5000 psi, change the column filters.

13.1.3 Change the pistons seals in the pump yearly, or sooner if needed, to prevent leaks & pump damage.

13.1.4 Change AS18/AS18-4 µm separator columns once a year, or sooner if needed. This helps to ensure good peak shapes and good peak separation.

13.1.5 For ASRS Ultra II cleaning and troubleshooting refer to Thermo Scientific ASRS instruction and Troubleshooting Guide. These are located in Thermo Scientific troubleshooting guide notebook in room 302. Change ASRS as needed.

13.1.6 Clean stator in Rheodyne valve (injection valve) when the sampler starts becoming noisier than normal (caused by blockage in stator) (Refer to Rheodyne injector operating instructions in the Thermo Scientific users guide notebook in room 309). Note: If the high pressure alarm goes off after reassembling valve, the stator and rotor seal may be out of alignment. Make one injection to correct this.

13.1.7 If eluent does not measure < 1µS, check the eluent generator (EGC) % availability and suppressor age (ASRS). Change ASRS if used for more than 1 year. Change EGC if less than 5% left.

13.1.8 If the Coefficient of Determination values start dropping below 99.85%, change the CR-ATC. This assumes standards are made correctly and the columns, EGC and suppressors are working properly.

13.1.9 For electrical and other problems contact a Technical Representative of the Thermo Scientific Corporation at (800) 346-6390. The technical representative arranges service calls.

13.2 Methods Maintenance

Refer to Thermo Scientific Chromeleon manual (see 18.8).

13.2.1 Change retention times in IC methods when columns are changed (refer to Thermo Scientific Chromeleon Manual).

13.2.2 Adjust data events and end run time as needed, i.e. when column ages, retention times shorten and run time can be shortened correspondingly.

13.3 Sampler Maintenance

Change sampling tip and tubing yearly (refer to Thermo Scientific sampler manuals located in room 309).

14.0 Data Acquisition and Calculations

Data acquisition parameters are located in Chromeleon Studio (see Appendix D). The software, along with the selected Data Processing file, processes and plots incoming data. The Data Processing file calculates the analytical concentrations and saves the chromatogram and report. The data is reported to three decimal places. The raw data and report are automatically saved on the computer.

14.1 Calibration curve

The calibration curve type is “quadratic with offset” and the evaluation type is “area”. Select 1/amount (*x*) for proportionate weighing of standards and include point (0.0) for curve filling. These parameters are used to construct a calibration curve for each ion (refer to the Chromeleon 7.2 Start Guide https://assets.thermofisher.com/TFS-Assets/CMD/Product-Guides/QS-7229-0004-Chromeleon-7-2-QS72290004-EN.pdf).

14.1.1 Calibration Data Review

The calibration curve is split into high and low curves. The low curve incorporates standards 0 - 6 and has a range of 0.000 - 1.000 ppm for Cl^- , 0.000 – 0.500 ppm for Br^- and 0.000 - 2.500 ppm for NO_3^- and SO_4^{-2}. The high curve incorporates standards 6 - 9 and has a range of 1.000-4.000 ppm for Cl^- and 2.500-6.000 ppm for NO_3^- and SO_4^{-2}.

14.1.2 Checking Calibration Curves

- In Chromeleon Console double click on the run to work with,
- Double-click on **Standard 5** of the set of standards.
- Click on **Processing** tab in the ribbon, then click on **Detection Parameters**.
- Adjust the inhibit off/on parameters. The inhibit off line goes in front of the peak and the inhibit on line goes after the peak.
- Click on Data Processing Home tab in the ribbon, then choose **Calib & P.M.** tool in the ribbon → **Component Table**.
- In the **Component Table** insert the retention times for all ions.
- In the **Calibration** tab ensure that the standards of interest are checked (0-6 for low curve, 6-9 for high curve). Also, ensure that all concentrations for the standards are correct in the table. Click **Save** button at top of page.
- Click on **Results** in the ribbon**.**

- Go to **Calibration** tab at bottom of page.
- Check the linearity of the low and high curve for all ions. Ensure that all analytes have a coefficient of at least 99.9%.

14.2 Samples Chromatograms

- **Double click** on the first sample in a daily sequence to view chromatogram. Go to **Peak Results** tab at the bottom of page.
- Check the chromatogram for proper peak shapes and any mismarked peaks. All peaks should be properly integrated. Special attention should be taken when looking at the bromide peaks.
- Use the arrow buttons to view the next chromatogram.
- While checking all chromatograms, also check QC values. Compare QC values with yearly control limit data.
- Check for samples that need diluting: any samples with values >4.00 ppm Cl^-, > 0.500 ppm Br^- and > 6.00 ppm NO_3^- and SO_4^{2-} need to be diluted.

14.3 Corrective Actions

- If any QCS are outside the control limits and/or if the Coefficient of Determination does not round to 99.9%, then corrective actions must be taken. Samples must be repeated if corrective actions do not solve problems.
- Determine if standards were integrated or made correctly. Comparing standards with previously analyzed standards will help determine preparation errors.
- If problems occur because of equipment errors, see the ICS-5000 (https://tools.thermofisher.com/content/sfs/manuals/Man-065446-IC-ICS-5000+-Operators-Manual.pdf) or Integrion (https://assets.thermofisher.com/TFS-Assets/CMD/manuals/Man-22153-97003-IC-Integrion-Man2215397003-EN.pdf) manuals.

14.4 Creating Excel files (.xls) to export data to Instrument Data Tool (IDT)

If data passes all quality control specifications, make two Excel files – one for low curve A and the other – for high curve B. While in an open chromatogram window, select **Report Designer**. Use month \day\year\A or B sys# for file name (example, “021218ASys5.xls”)**, w**here “A” is the low curve (standards 0-6) and “B” is the high curve (standards 6-9). Click the Chromeleon icon at the top left of the screen and select **Export.** The parent folder is \\pri-fs1\HEAL\Data\Lab Data In\IC\2022 IC Data\current month, and the subfolder is date (MMDDYY), A or B, SYS3, SYS4, or SYS5.

14.5 Sending data to LIMS

Data is checked in Instrumental Chemistry tool to make sure data is complete and correct before sending it to LIMS (Laboratory Information Management System).

- Double click on the ***Instrumental Chemistry*** icon or \\pri-fs1\HEAL\HEAL-IT\Program Install Files\Lims\Instrumental Chemistry.
- Click on **Data, Load Review, IC, IC Review, Data IO, Load Review Table** from Chromeleon.
- Select the directory where the appropriate .xls file is stored. Double click on the .xls file to import.
- Click on the NUMBER column to sort the data. Review the QC data by right-clicking each set of QC data for each analyte and GRAPH.

- Once all the QC data has been validated, each analyte needs to be checked for dilutions. Click on the appropriate analyte column (Cl^-, Br^-, SO_4^{2-}, NO_3^-) to sort the concentrations from highest to lowest. Delete any values that fall outside of the calibration curve (higher than standard 9). These samples will need to be diluted.
- When all QCs have been validated and dilutions have been held back, the data can be transferred to LIMS. Click on **Data IO, Transfer Results to LIMS Results Table**.
- To check completeness of LIMS data, click on **LIMS**, then **Query** (this brings up Query table). Enter sample range and select **Retrieve**. This will bring up data for all ions.

15.0 Computer Hardware and Software

15.1 Computer Hardware

Two Acer Computers for Chromeleon software, ICS – 5000 and Integrion
System properties:
Processor, Pentium7 CPU 3.00 Ghz
Memory, (RAM), 4Gb

15.2 Software

Windows 10
Thermo Scientific Chromeleon 7.2
IDT (Instrument Data Tool)
Excel 2010

15.3 Computer support

The computer support staff are available to help with hardware and software problems.

16.0 Data Management & Records Management

16.1 Daily log books are kept of instrument analysis, troubleshooting, repair, and maintenance. Instrument background conductivity, background pressure, and eluent generator cartridge life remaining are also recorded. This log is shared by all IC analysts

16.2 Logbooks are also used to document information about standards and QC preparations, software issues, solutions, and upgrades. All logbooks are kept permanently.

16.3 Current SOPs and instrument manuals are maintained in each lab where the instrument is located.

16.4 Data files are kept on a PC for 1 year from the date they are sent to the program office, then transferred to CD-ROM for archiving. (See computer support staff for backup and computer program assistance)

16.5 Original raw data, reports, and the IC database are backed up weekly by the systems computer support person. The backed up data is recoverable for three weeks.

16.6 A complete instrument and file backup procedure is performed once a week on each instrument computer. (See Computer Backup and Recovery, SOP #AD-0011)

17.0 Quality Control and Quality Assurance

See Quality Assurance Plan 2019.

17.1 A calibration curve is always used at the start of each run followed by a blank. A Coefficient of Determination of ≥ 99.9% for Cl^-, Br^-, NO_3^-, and SO_4^{2-} is required (see section 18.2).

17.2 One solution of internally prepared simulated rain containing ion concentrations approximating network 50th percentile level is used for chloride, bromide, nitrate, and sulfate to verify calibration curves (FR50). Control limits and warning limits are established at the time of preparations by measuring new QCS standards at least 10 times and calculating the standard deviations (see section 18.1). Control limits and warning limits for FLYYXXX, FHYYXXX, and FMYYXXX are calculated the same way (see section 18.1).

17.3 Blind internal blanks, splits, replicates, and QCS are analyzed. Values are compiled and checked after data has been transferred to LIMS by the QA chemist.

17.4 A DI water blank is analyzed after the calibration curve as a system check and at the end of each run. If Cl^-, Br^-, NO_3^-, or SO_4^{2-} are found at or above the Method Detection Limits (MDL) another DI water blank is analyzed. If the high value still exists, DI water from a separate source will be analyzed. If the DI water from the separate source shows greater than the MDL concentration, further review of the system will be conducted.

17.5 QC control Charts are maintained by the analyst and may be checked in the LIMS upon data transfer to observe fluctuation of these samples over time. The bench analyst can observe real time data generation as well.

17.6 Accuracy is determined on a weekly schedule by reanalyzing selected samples. Report results in the LIMS. If any major differences are determined between the original and the reanalysis, comments should be included to explain the reasons and make suggestions for any changes and refrigerated samples (if available) should be analyzed to compare to the original value.

17.7 Participation in several interlaboratory comparison programs: the National Water Research Institute (NWRI), Norwegian Institute for Air Research (NILU), World Meteorological Organization (WMO), and United States Geological Survey (USGS) Blind Audit.

17.8 The QA chemist oversees all QC data collected and makes suggestions for improvements or correction.

17.9 A standard spiked with oxalate is analyzed every run after the calibration curve to define oxalate and bromide curve. In 60 mL bottles 50 mL of standard 0 and standard 5 each have been spiked with .1mL of stock oxalate to create these and are labeled Std 0+ox and Std 5+ox.

18.0 References

18.1 Peden, M. E., et al., Method Collection and Analysis of Precipitation, ISWS, 1986.

18.2 EPA Method 300.1. DETERMINATION OF INORGANIC ANIONS IN DRINKING WATER BY ION CHROMATOGRAPHY.

18.3 American Society for Testing Materials. Standard Test Method for Determination of Chloride, Nitrate, and Sulfate in Atmospheric Wet Deposition by Chemically Suppressed Ion Chromatography, Method D5085-95, 1998 Annual Book of ASTM Standards, p. 406.

18.4 Bergerhouse, T., Computer Backup and Recovery, SOP #DA-0011, ISWS.

18.5 Bergerhouse, T., NADP/AIRMoN/NTN Database Management, SOP #DA-0037, ISWS.

18.6 ISWS-1, Standard Operating Procedure for Pipettor Performance Verification.

18.78 Chromeleon 7.2 Start Guide https://assets.thermofisher.com/TFS-Assets/CMD/Product-Guides/QS-7229-0004-Chromeleon-7-2-QS72290004-EN.pdf).

18.8 ICS-5000 manual https://tools.thermofisher.com/content/sfs/manuals/Man-065446-IC-ICS-5000+-Operators-Manual.pdf

18.9 Integrion manual https://assets.thermofisher.com/TFS-Assets/CMD/manuals/Man-22153-97003-IC-Integrion-Man2215397003-EN.pdf

Appendix A Ion Chromatography Ordering Guide

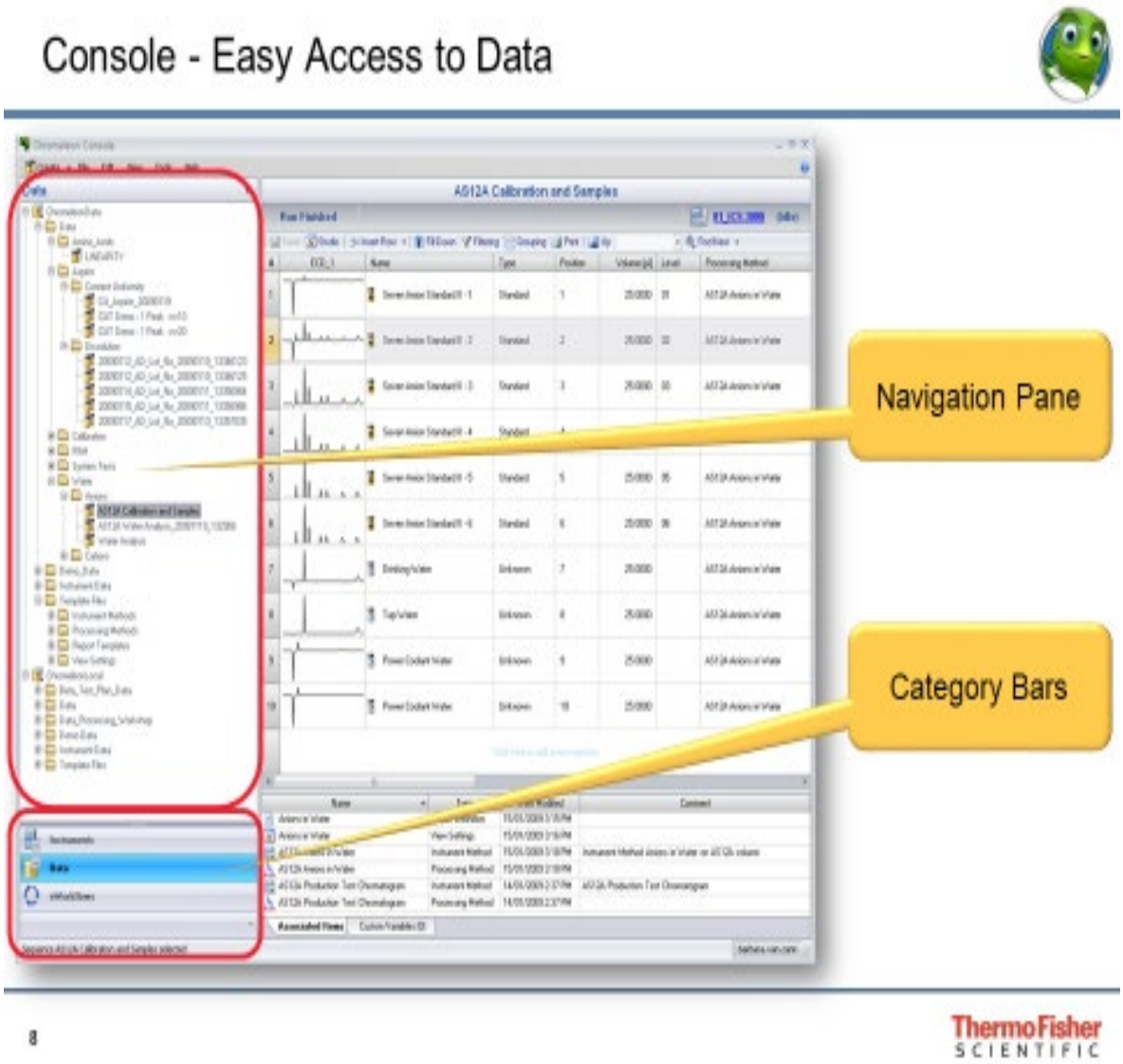
NOTE: Call supplier before ordering to verify order number and current price

Supplier Information	Part Number	Fisher Scientific Number	Name	Description	Instrument
Thermo Electron North America	039532		Autosampler Vials	PolyVials and Plain Caps 5.0 mL 250 per box	ICS 5000/Integrion
1228 Titan Way	060551		Guard Column	IonPac AG18 4mm Guard Column 4x50mm	ICS 5000
Sunnyvale, CA 94988	060549		Analytical Column	IonPac AS18 4mm Analytical Column 4x250mm	ICS 5000
	076035		Guard Column	IonPac AG18 4um Guard Column 4x30mm	Integrion
	076034		Analytical Column	IonPac AS18 4um Analytical Column 4x150mm	Integrion
800.346.6390	082540		Suppressor	ASRS 500	ICS 5000/Integrion
	074532	NC9041253	EGC-II KOH	Potassium Hydroxide Eluent Generator Cartridge	ICS 5000
	075778		EGC-II KOH	Potassium Hydroxide Eluent Generator Cartridge	Integrion
	060477		CR-ATC	Continuously Regenerating Anion Trap Column	ICS 5000
	088662		CR-ATC	Continuously Regenerating Anion Trap Column	Integrion
	074373		Peek Tubing Ferrules	Ferrules, Double Cone	ICS 5000/Integrion
	045987		End line Filters	End line filters	ICS 5000
	036521		35u Filters	35micron filters for in-line autosampler filter	ICS 5000/Integrion
	036522		5u Filters	5 micron filters for in-line autosampler filter	ICS 5000/Integrion
	044105		InLine Filters	Hi-Pressure filter housing (10/32) with filters	ICS 5000/Integrion
			Piston	Pump Head Piston	
	AAA-061795	NC0386590	PM Kit	ICS-3000/5000 Single Pump Maintenance Kit	ICS 5000
	AAA-061796		PM Kit	ICS-3000/5000 Detector Maintenance Kit	ICS 5000
	071575	NC0334443	PM Kit	AS-DV Maintenance Kit	ICS 5000/Integrion
	064946		each	Main Piston Seal (ICS5000)	ICS 5000
	063382		each	Pison Seal Wash Seal, Priming Valve Knob Seal (ICS5000)	ICS 5000
	061830		each	Conductivity Cell for ICS 5000	ICS 5000
	063292		each	4L Plastic Bottle	ICS 5000/Integrion
	042949		each	10uL Sample Loop	ICS 5000/Integrion

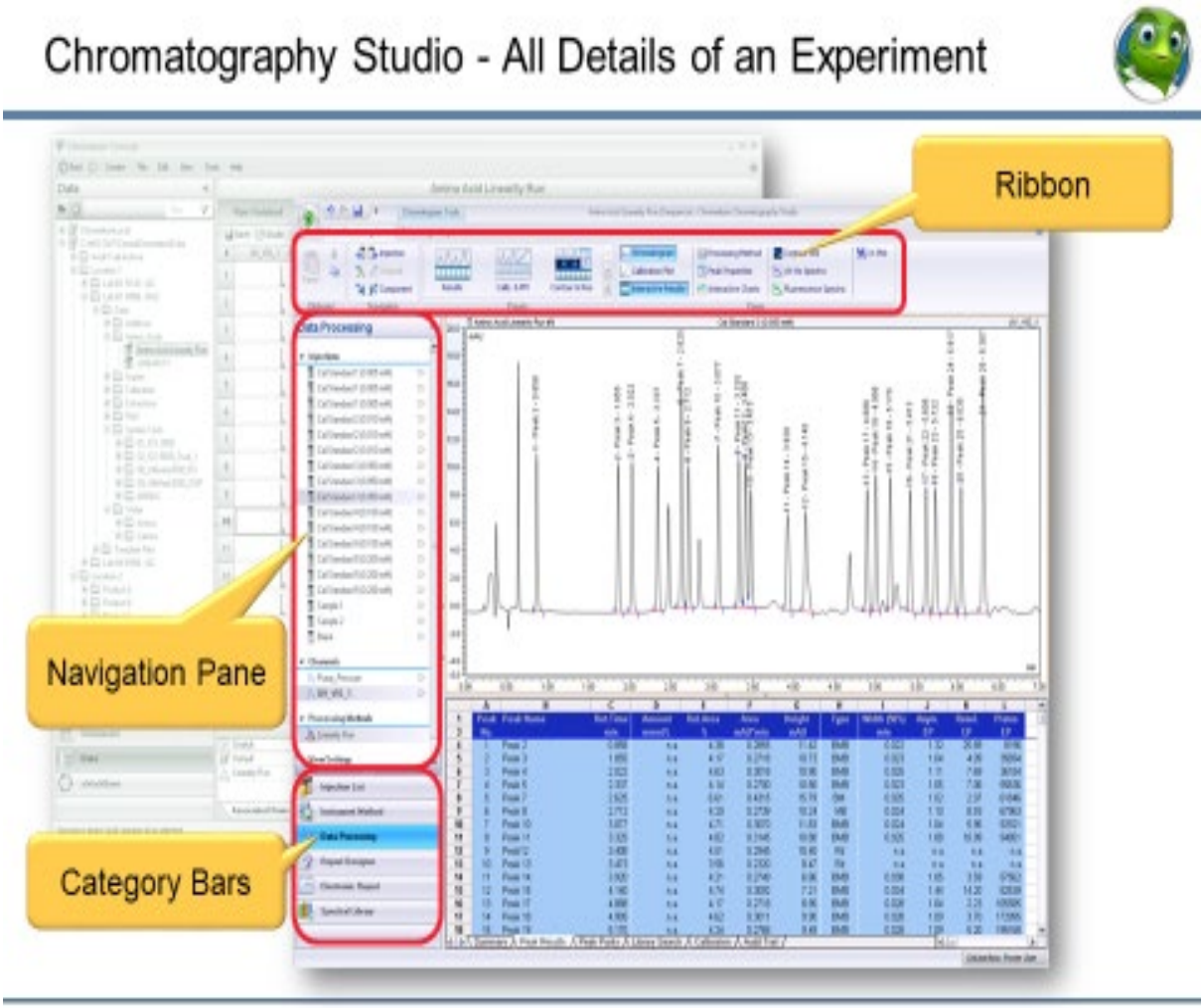
Appendix A Ion Chromatography Ordering Guide (continued)

Supplier Information	Part Number	Fisher Scientific Number	Name	Description	Instrument
SPEX CertiPrep	Calibration Stocks	Catalog Number			ICS 5000/Integrion
	Cl	AS-CL9-2X	1000 mL		ICS 5000/Integrion
	Br	AS-BR9-2X	1000 mL		ICS 5000/Integrion
	NO3	AS-NO39-2X	1000 mL		ICS 5000/Integrion
	SO4	AS-SO49-2X	1000 mL		ICS 5000/Integrion
High Purity Standards	Secondary Stocks	Catalog Number			ICS 5000/Integrion
	Cl	IC-CL-M	1000 mL		ICS 5000/Integrion
	Br	IC-BR-M	1000 mL		ICS 5000/Integrion
	NO3	IC-NO-M	1000 mL		ICS 5000/Integrion
	SO4	IC-SS-M	1000 mL		ICS 5000/Integrion

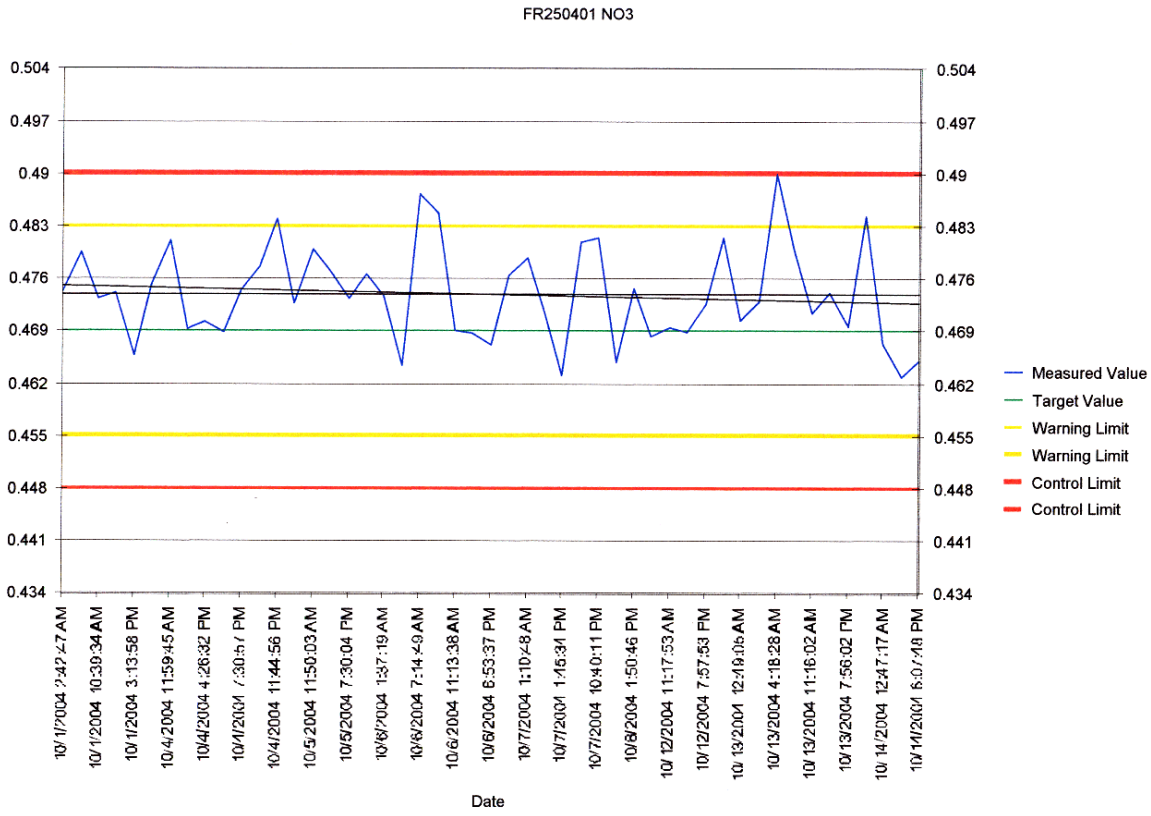
Appendix B. Chromeleon Console view



Appendix C. Chromeleon Studio view



Appendix D. Control Chart Example



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