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Adapted from DRI SOP#2-228r2

Determination of Inorganic Anions in Water by Ion Chromatography V1.0

I. Principle of the method.

The purpose of this method is the determination of inorganic anions such as Fluoride, (F^-) Chloride (Cl^-), Bromide (Br^-), Nitrate (NO_3^-), phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}) at low level of concentration, µg/L or ppb. For the purpose of supporting reaeration analyses by NEON, this method is used to measure Bromide and Chloride, which are are used as aqueous chemical tracers in streams where reaeration measurements are made. These anions are analyzed using Ion Chromatography (IC) using the Dionex ICS-5000+ with a liquid chromatographic technique based on an ion exchange mechanism and suppressed conductivity detection for the separation and determination of anions.

II. Safety

Adequate gloves are required for the preparation of the mobile phase, the samples and the standards. A reference file of Material Safety Data Sheets is available and a Laboratory Chemical Hygiene Plan is in place.

III. Reagents and Standards

Reagents

Potassium hydroxide (KOH) Eluent generator (ThermoScientific PN 060553)
Double-deionized water (DDW) having a resistance of at least 18 megaohm per cm, is required for all analyses.

Primary Standards

Certified Standards obtained from ThermoScientific are used for preparation of calibration and check standards.

Dionex Seven Anion Standard (Product Number: 056933)

American Society for Testing Materials (ASTM) Specification D1193-91, Type I (ASTM Standards, 1996).

IV. Equipment

The Dionex ICS-5000+ system has two isocratic pumps (System 1 and System 2) for separate and simultaneous anion and cation analysis. It is equipped with an eluent generator, chromatographic column, electrolytically regenerated suppressor (CRC), and a conductivity detector for each system. System 1 governs anion analyses and is used for Bromide and Chloride as part of NEON reaeration measurements. The eluent generation module of System 1 provides on-line generation of potassium hydroxide. Samples are injected using an automated Sampler (AS/AP). In routine operation, the automated sampler system is used to deliver 25 µL of sample.
Anions are separated using the chromatographic columns Ion Pac AS18 analytical column (2× 250 mm), and Ion Pac AG12 guard column (2 × 250 mm),

V. Preparation of Standard Solutions

The Stock and Working standard solutions are purchased as certified solutions and diluted to concentration by mass(g). (Appendix)

Calibration Standard Levels 1-11(Appendix) are prepared according to Table 1. Digital micropipettes are externally calibrated and certified annually.

Working Standards
Calibration standards are aliquoted at 2mL to instrument vials, capped tightly and stored at room temperature until use. Working standards are remade when the volume available is not sufficient for the next sample batch, usually every two weeks during routine operation.

External Standard: The Quality Control Standard (QCI) is a primary NIST certified QC standard purchased from NSI lab solutions (PN QCI-138) to evaluate instrument accuracy.

QCI standard is prepared by diluting the commercial stock solution 1:100 by weight. Weigh 10.00 g of the QCI concentrate into a 1000.00 mL volumetric flask. Bring to weight with DDW and mix thoroughly. Prepared standard should be stored in the refrigerator and used within 2 weeks.

Table 1. Calibration Standards for Anion Analysis
DIONEX Seven Anion Standard P/N 56933 is diluted as in the table below. Final concentrations are given in the Appendix.

Cal Level	Stock vol (mL)	Working Stock	Final Mass (g)
1	0.25	Cal Level 5	10
2	0.5	Cal Level 5	10
3	0.25	DIONEX	100
4	0.5	DIONEX	100
5	1	DIONEX	100
6	0.25	DIONEX	10
7	0.5	DIONEX	10
9	1	DIONEX	10
10	2.5	DIONEX	5
11		DIONEX	2

Check Standards: Varied mid-level calibration standards are used to monitor instrument consistency through a run sequence. See section VII for further details.

The accuracy of calibration standards is primarily limited by the uncertainties or

variabilities of the standard solution preparation. See section IX for additional details about QC.

VI. Sample Preparation

Samples are sonicated for 5 minutes to mix.

Frozen samples are thawed then sonicated for 10 minutes.

Samples are aliquoted at 2mL into labeled instrument vials.

Duplicate samples are made for every 10 samples in the sample set.

Spiked duplicate samples are made for every 10 samples in the sample set
1mL Sample:1mL Cal Level 5. One each for cations and anions.

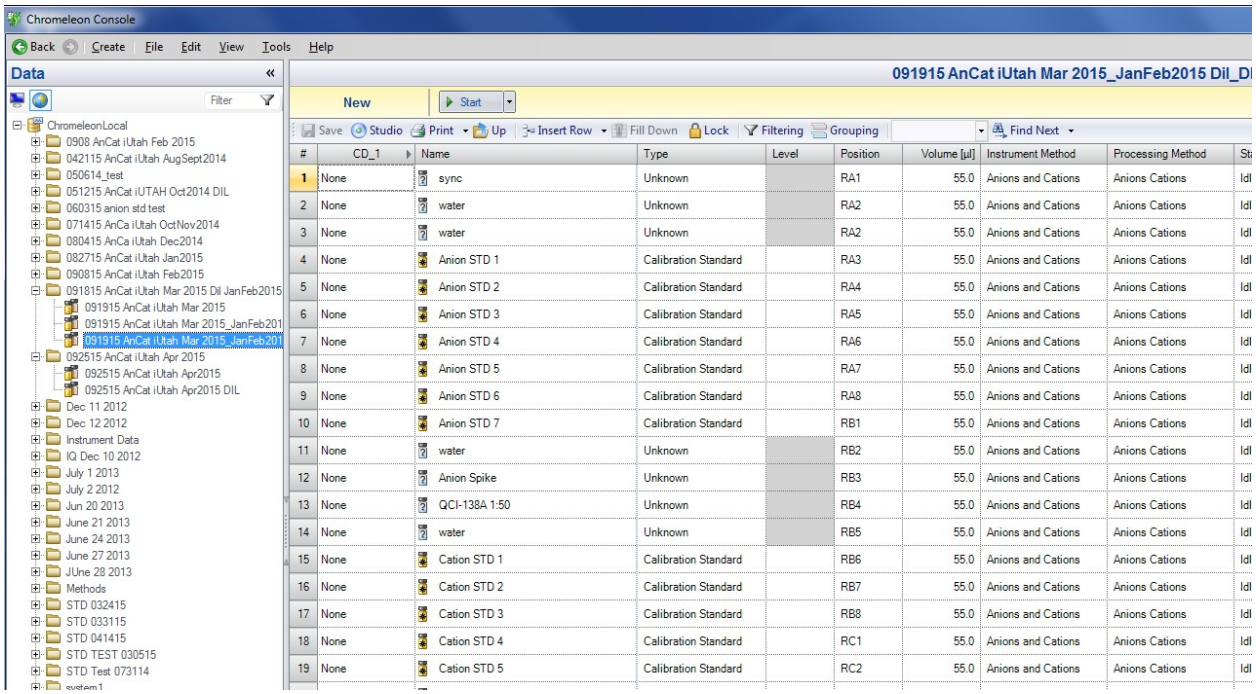
Sample sets with more than 25 samples have a second set calibration standards run at the end of the sequence.

Calibration Standards, Laboratory Blanks, Qualifying Standards, Samples and Duplicates are placed in Automated Sampler trays according to the Sequence Table

VII. Creating a Sequence Table

Create sample list in Chromeleon software.

On the Desktop open Chromeleon Console.
Instrument/Data/Report tab buttons on bottom right of console
Data View
Create a new Sequence
Chromeleon Wizard
Create > Sequence
Update old Sequence
Highlight Sequence in right panel directory
File>SaveAs



Update and fill in the Sample Name, Type and Vial Positions

Standard must be selected as calibration standards in the Type column

Each Standard must be given a "Level" corresponding to the concentrations listed in the processing method. The processing method will update for each sequence according to calibration standards.

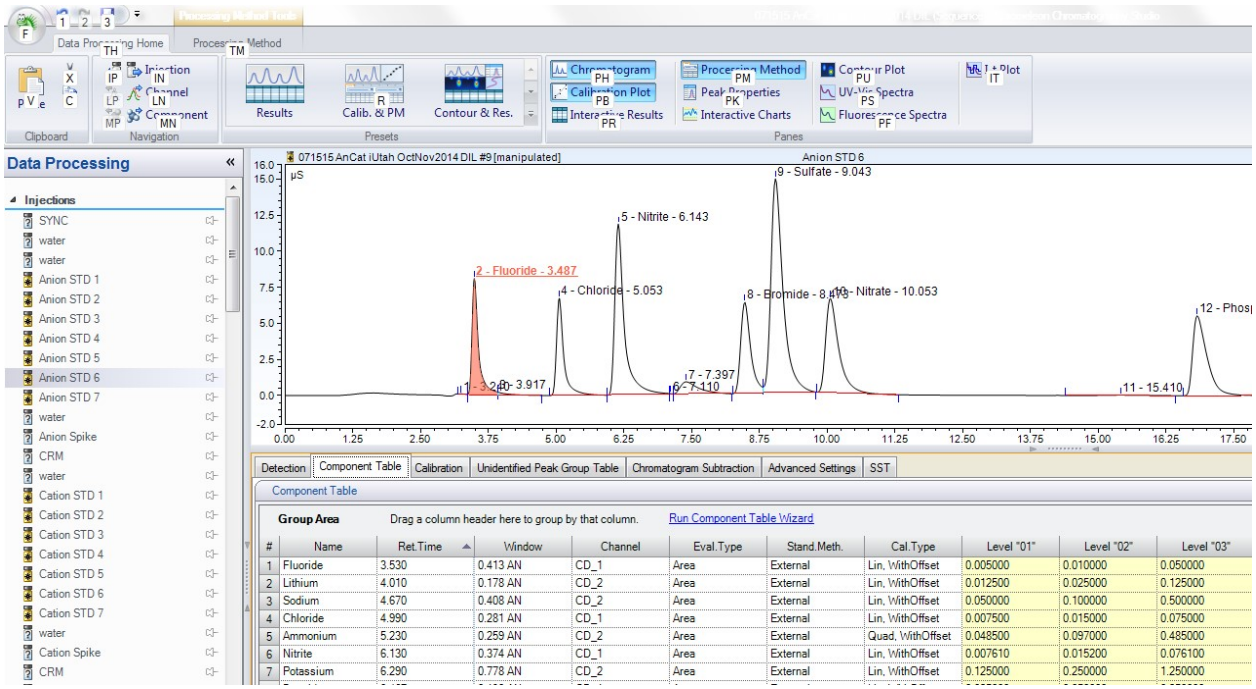
Run a new standard curve in every sequence

Samples are placed in sequences in the following format:

Instrument Sync
Method Blank (DDW)
Calibration Standards
QCI-Quality control standard
Sample Batch:10 samples
Calibration Check Standards (mid-level, three replicates)
QCI Standard
Method Blank
Sample Duplicate
Spiked Replicate

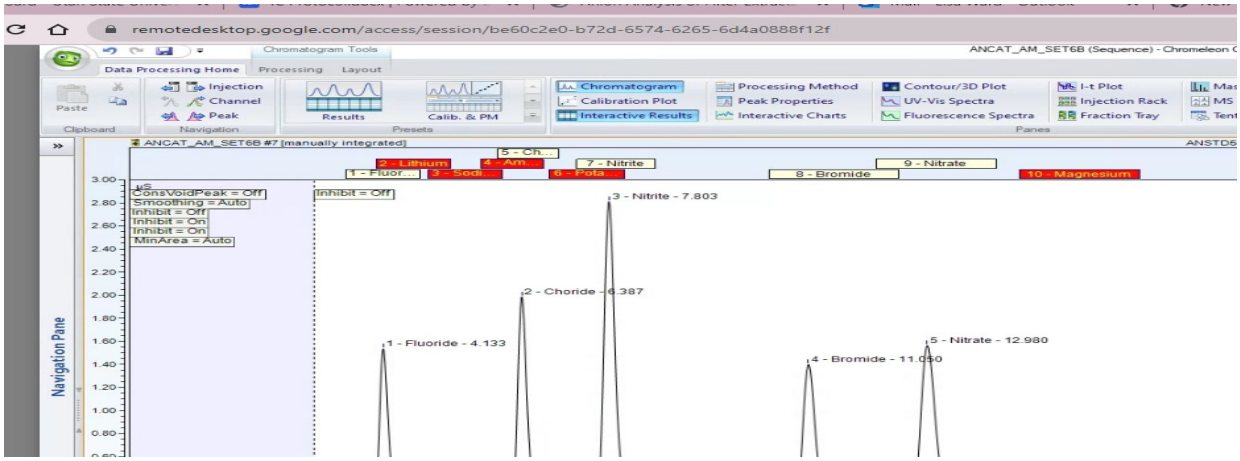
VIII. Data Processing

Double click on any file from the already run parts of the sequence and it will open a Data Processing window.
Check that the retention times are updated and there are no interferents in the standards in the Calib. & PM view setting under the Component Table tab.
Changing to the Results view setting will show what peaks were found and identified by the program.



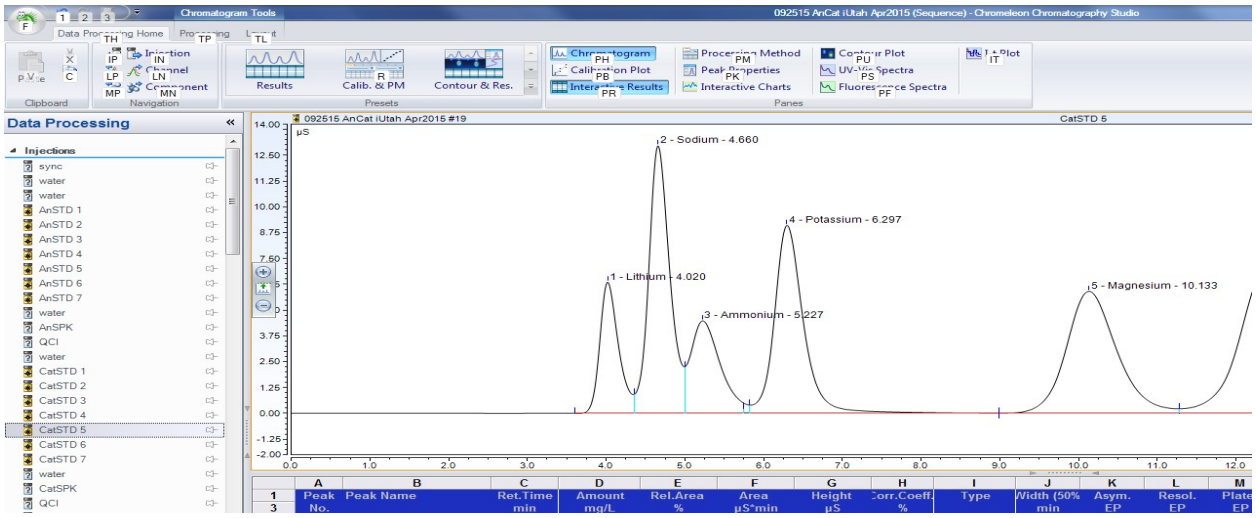
#	Name	Ret.Time	Window	Channel	Eval.Type	Stand.Meth.	Cal.Type	Level "01"	Level "02"	Level "03"
1	Fluoride	3.530	0.413 AN	CD_1	Area	External	Lin, WithOffset	0.005000	0.010000	0.050000
2	Lithium	4.010	0.178 AN	CD_2	Area	External	Lin, WithOffset	0.012500	0.025000	0.125000
3	Sodium	4.670	0.408 AN	CD_2	Area	External	Lin, WithOffset	0.050000	0.100000	0.500000
4	Chloride	4.990	0.281 AN	CD_1	Area	External	Lin, WithOffset	0.007500	0.015000	0.075000
5	Ammonium	5.230	0.259 AN	CD_2	Area	External	Quad, WithOffset	0.048500	0.097000	0.485000
6	Nitrite	6.130	0.374 AN	CD_1	Area	External	Lin, WithOffset	0.007610	0.015200	0.076100
7	Potassium	6.290	0.778 AN	CD_2	Area	External	Lin, WithOffset	0.125000	0.250000	1.250000

. *Example Anion Chromatogram (Channel 1)*

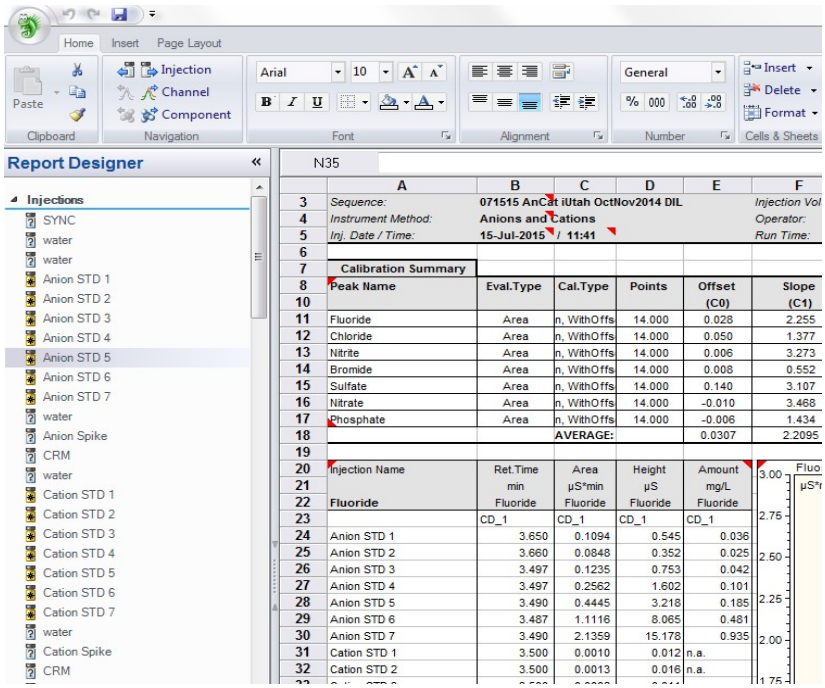


Note that there is a Sulfate peak before Bromide and a Carbonate peak after Nitrite and before Bromide peaks that is not qualitatively analyzed.

Example Cation Chromatogram (Channel 2)



Verify that all appropriate standards are used to make the curves for each component in the Calib. & PM view setting on the Calibration tab.

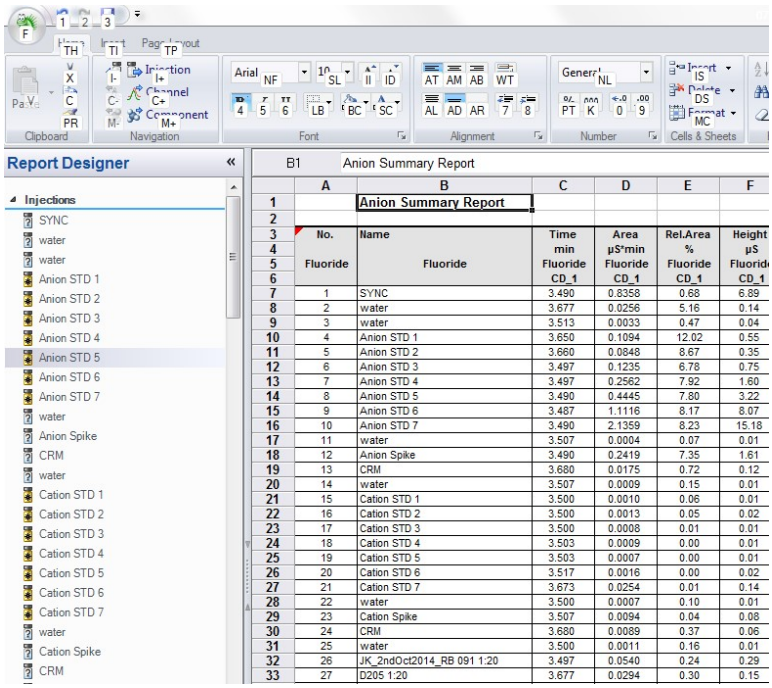


Example Calibration Table

Double click near the check box to be Enable to open the Select Component dialog box and only have the appropriate analytes selected.

This is done for each individual standard.

Check integrations for analytes of samples, standards, and controls and modify if necessary.



Report Designer

Injections
- SYNC
- water
- water
- Anion STD 1
- Anion STD 2
- Anion STD 3
- Anion STD 4
- Anion STD 5
- Anion STD 6
- Anion STD 7
- water
- Anion Spike
- CRM
- water
- Cation STD 1
- Cation STD 2
- Cation STD 3
- Cation STD 4
- Cation STD 5
- Cation STD 6
- Cation STD 7
- water
- Cation Spike
- CRM

B1 Anion Summary Report

Anion Summary Report

No. Fluoride	Name Fluoride	Time min Fluoride CD_1	Area µS*min Fluoride CD_1	Rel.Area % Fluoride CD_1	Height µS Fluoride CD_1
1	SYNC	3.490	0.8358	0.68	6.89
2	water	3.677	0.0256	5.16	0.14
3	water	3.513	0.0033	0.47	0.04
4	Anion STD 1	3.650	0.1094	12.02	0.55
5	Anion STD 2	3.660	0.0848	8.67	0.35
6	Anion STD 3	3.497	0.1235	6.78	0.75
7	Anion STD 4	3.497	0.2562	7.92	1.60
8	Anion STD 5	3.490	0.4445	7.80	3.22
9	Anion STD 6	3.487	1.1116	8.17	8.07
10	Anion STD 7	3.490	2.1359	8.23	15.18
11	water	3.507	0.0004	0.07	0.01
12	Anion Spike	3.490	0.2419	7.35	1.61
13	CRM	3.680	0.0175	0.72	0.12
14	water	3.507	0.0009	0.15	0.01
15	Cation STD 1	3.500	0.0010	0.06	0.01
16	Cation STD 2	3.500	0.0013	0.05	0.02
17	Cation STD 3	3.500	0.0008	0.01	0.01
18	Cation STD 4	3.503	0.0009	0.00	0.01
19	Cation STD 5	3.503	0.0007	0.00	0.01
20	Cation STD 6	3.517	0.0016	0.00	0.02
21	Cation STD 7	3.673	0.0254	0.01	0.14
22	water	3.500	0.0007	0.10	0.01
23	Cation Spike	3.507	0.0094	0.04	0.08
24	CRM	3.680	0.0089	0.37	0.06
25	water	3.500	0.0011	0.16	0.01
26	JK_2ndOct2014_RB 091 1:20	3.497	0.0540	0.24	0.29
27	D205 1:20	3.677	0.0294	0.30	0.15

Example Summary Report

Once data is ready to be exported, change view to Report Designer and apply the Anion Summary Report to the data set.

With the summary report open, copy the calibration information from the Calibration tab into a blank Excel workbook.

Make sure the one of the standards is selected so that all analytes will be seen on the summary report.

Changing to the Summary INJ vs ANION tab will give the calculated amounts for each individual component from that data channel.

Copy the Summary Report into another sheet of the previous Excel workbook.

Make sure the one of the standards is selected.

Go to the next Component to copy that data into the Excel workbook and continue until all of the analytes have been selected and copied.

Repeat the Summary Report process on the other channel of data copying both the calibration information and individual component amounts into new tabs in the Excel workbook.

IX. QA/QC Processes and Method Detection Limit

Check that method blanks are true blanks. If analyte is detected above 5% of MDL, then re-run.

Verify that check standard deviations are <2% for Bromide, if between 2-5% report data with a flag. If >5%, re-run batch. For Chloride, verify that check standards are within ±10%, re-run if >10%. Calculate deviation from expected concentration as

$$\%DEV = (Ccheck - Cstd)/Cstd * 100\%$$

For each run, calculate precision from a minimum of 3 replicate values (e.g. check standards) as the coefficient of variation (standard deviation/mean)*100%

Collect mid-level check standards from multiple runs, recording the expected and observed concentration for each analyte. From seven replicates collected across multiple runs, calculate the method detection limit (MDL) as the standard deviation of the observed concentration times the t-value from a one-sided t-distribution at the 99% level. For 7 replicates, the t-value is 7-1= 6 degrees of freedom = 3.143. Calculate MDL annually if not more frequently.

Check that sample concentrations are within the range of the standard curve. If sample concentration falls below the lowest standard, flag the value and re-run with a lower concentration range. If sample values exceed that of the highest standard, then dilute the sample OR increase the value of the highest standard and re-run.

X. References

1. American Society for Testing and Materials. 2000. Test Method for Anions in Water by Ion Chromatography, D4327-91, Annual Book of ASTM Standards, Vol. 11.01, Philadelphia, PA.

2. American Public Health Association. American Water Works Association, Water Environment Federation. 1998. Standard Methods for the Examination of Water and Wastewater, 20th Ed. CL. S. Clesceri, A. E. Greenberg, A. D. Eaton, eds., Method 4110. Determination of anions by ion chromatography. p. 4-2 to 4-8. American Public Health Association, Washington, DC.

3. Dionex. Determination of Inorganic Anions in Drinking Water by Ion Chromatography. Application Note 133. Dionex Corporation, Sunnyvale, CA.

4. Dionex. Determination of Nitrite and Nitrate in drinking water using ion chromatography with direct UV detection AU132. Application Note 132. Dionex Corporation, Sunnyvale, CA.

5. Dionex. Determination of Nitrite and Nitrate in drinking water using chemically suppressed ion chromatography AU131. Application Note 131. Dionex Corporation, Sunnyvale, CA.

6. USEPA. 1993. Method 300.0,Test Method for the determination of inorganic anions in water by ion chromatography. Environmental Monitoring Systems Laboratory, ORD, USEPA, Cincinnati, Ohio 45268

Appendix

Components	Concentration	
	Labeled (mg/L)	Measured (mg/L)
Fluoride	20	20.1
Chloride	30	29.8
Nitrite	100	100.0
Bromide	100	101.0
Nitrate	100	102.0
Phosphate	150	151.0
Sulfate	150	150.0
Components	**Concentration**	
	Labeled (mg/L)	**Measured (mg/L)**
Lithium	50	50.3
Sodium	201	201.1
Ammonium	254	254.3
Potassium	507	507.4
Magnesium	252	252.1
Calcium	505	505.3

Final Concentration (mg/L)

Cal Level	Fluoride	Chloride	Nitrite	Bromide	Nitrate	Phosphate	Sulfate	Lithium	Sodium	Ammonium	Potassium	Magnesium	Calcium
1	0.005	0.0075	0.025	0.025	0.025	0.0375	0.0375	0.0125	0.05025	0.0635	0.12675	0.063	0.12625
2	0.01	0.015	0.05	0.05	0.05	0.075	0.075	0.025	0.1005	0.127	0.2535	0.126	0.2525
3	0.05	0.075	0.25	0.25	0.25	0.375	0.375	0.125	0.5025	0.635	1.2675	0.63	1.2625
4	0.1	0.15	0.5	0.5	0.5	0.75	0.75	0.25	1.005	1.27	2.535	1.26	2.525
5	0.2	0.3	1	1	1	1.5	1.5	0.5	2.01	2.54	5.07	2.52	5.05
6	0.5	0.75	2.5	2.5	2.5	3.75	3.75	1.25	5.025	6.35	12.675	6.3	12.625
7	1	1.5	5	5	5	7.5	7.5	2.5	10.05	12.7	25.35	12.6	25.25
9	2	3	10	10	10	15	15	5	20.1	25.4	50.7	25.2	50.5
10	10	15	50	50	50	75	75	25	100.5	127	253.5	126	252.5
11	20	30	100	100	100	150	150	50	201	254	507	252	505

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