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Determination of inorganic anions in drinking water using a compact ion chromatography system

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Keywords

Dionex Aquion IC system, Dionex IonPac AS22 column, carbonate/bicarbonate eluent, AS-DV autosampler, U.S. EPA Method 300.1

Goal

To demonstrate inorganic anion determinations in drinking water samples according to U.S. EPA Method 300.1 (A) using a Thermo Scientific™ Dionex™ Aquion™ IC system

Introduction

The determination of inorganic anions in municipal drinking, waste, and bottled waters according to the U.S. Environmental Protection Agency (EPA) Methods 300.0 and 300.1 is one of the most popular and widely used ion chromatography (IC) methods.[1] We used a Thermo Scientific™ Dionex™ Aquion™ ion chromatography system with a Thermo Scientific™ Dionex™ AS-DV Autosampler to determine seven anions (fluoride, chloride, bromide, nitrite, nitrate, phosphate, and sulfate) in drinking water samples. The Dionex Aquion IC system is a simple, inexpensive, and compact platform with straightforward operation for basic ion analysis. In this study, mg/L concentrations of inorganic anions were separated on a 4 × 250 mm Thermo Scientific™ Dionex™ IonPac™ AS22 anion-exchange column using a carbonate/bicarbonate eluent. Eluent was prepared by diluting the Thermo Scientific™ Dionex™ AS22 Eluent Concentrate for ease-of-use and to minimize eluent preparation errors. Following the separation, anions were detected using suppressed conductivity detection with a Thermo Scientific™ Dionex™ AERS™ 500 Carbonate Electrolytically Regenerated Suppressor. This technical note provides detailed instructions for system set up and operation for determining inorganic anions in samples such as drinking water.

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Experimental

Equipment

- Dionex Aquion IC system
- Dionex AS-DV Autosampler equipped for 5 mL vials (P/N 068907) or with 0.5 mL vial adapters (P/N 068908)

Consumables

- Thermo Scientific™ Dionex™ IonPac™ AS22 column, 4 × 250 mm (P/N 064141)
- Thermo Scientific™ Dionex™ IonPac™ AG22 column, 4 × 50 mm (P/N 064139)
- Thermo Scientific™ Dionex™ AERS 500 Carbonate Suppressor, 4 mm (P/N 085029)
- Thermo Scientific™ Dionex™ AS-DV Autosampler PolyVials 5 mL with plain caps: box of 250 (P/N 039532) or Thermo Scientific™ Dionex™ AS-DV Autosampler PolyVials 5 mL with filter caps: box of 250 (P/N 038141)
- Thermo Scientific™ Dionex™ AS-DV Autosampler Vial holders for 5 mL vials (P/N 068947)
- Thermo Scientific™ Nalgene™ Syringe filters, Thermo Scientific (P/N 7252520)
- Thermo Scientific™ PEEK backpressure tubing (P/N AAA-053763)

Reagents and standards

- 18 MΩ·cm resistivity degassed deionized (DI) water
- Dionex AS22 Carbonate/Bicarbonate Concentrate (P/N 063965)
- Thermo Scientific™ Dionex™ Fluoride Standard (1000 mg/L), 100 mL (P/N 037158)
- Thermo Scientific™ Dionex™ Chloride Standard (1000 mg/L), 100 mL (P/N 037159)
- Thermo Scientific™ Dionex™ Sulfate Standard (1000 mg/L), 100 mL (P/N 037160)
- Sodium Nitrite (Crystalline/Certified ACS), Fisher Scientific (P/N S347)
- Sodium Bromide, Sigma-Aldrich (P/N 229981)
- Sodium Nitrate, EMD Millipore (P/N SX0655)
- Sodium Phosphate, monobasic, Sigma-Aldrich (P/N S8282)

Eluent preparation

Dilute the Dionex AS22 Eluent Concentrate 1:100 with DI water, mix thoroughly, and transfer to the eluent bottle on the Dionex Aquion IC system. Alternatively, dissolve 476 ± 1 mg anhydrous sodium carbonate (Na_2CO_3) and 84.0 ± 1 mg of sodium bicarbonate ($NaHCO_3$) in a 1 L volumetric flask containing approximately 500 mL DI water. Dilute to the 1 L mark with DI water, cap, and mix thoroughly by inverting the flask several times before transferring the eluent.

Instrument set up and installation

To set up this application, first connect the Dionex Aquion IC system and Dionex AS-DV Autosampler to the computer with USB cables. Then configure them in the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) as described below.

Configuring the modules in the Chromeleon CDS

To configure the IC system, first start the Chromeleon Instrument Controller program and then select the Configure Instruments link to open the Chromeleon Instrument Configuration Manager. Right-click on the computer connected to the IC system, select Add an Instrument, and enter an appropriate name (for example: Aquion_EPA300_1). Add the Dionex Aquion IC system and Dionex AS-DV Autosampler modules to this instrument configuration.

Plumbing the IC system

To plumb the Dionex Aquion IC system, first connect the pump eluent line to the eluent bottle containing DI water. Prime the pump by opening the priming knob ¼ turn and pressing the priming button. Refer to the Dionex Aquion Ion Chromatography System Operator's Manual for details.[2] Prime the pump until no bubbles are visible and water is flowing at a steady rate out of the pump waste line. Close the priming knob to finger-tight. Turn on the pump and flush the system with DI water. Install the backpressure coil (so that pump pressure is ≥ 200 psi) from Port C of the injection valve and direct it to the waste container. After flushing the system with DI water for an hour, turn off the pump and connect the pump eluent line to the bottle containing 4.5 mM sodium carbonate/1.4 mM sodium bicarbonate eluent, and prime the pump with the eluent as described above.

Conditioning suppressor and columns

Prior to installing the columns and suppressor, flush the system with the 4.5 mM sodium carbonate/ 1.4 mM sodium bicarbonate eluent for ~ 30 min. Remove the backpressure coil and install the columns. Install the columns in their proper order (i.e. guard column before analytical column), then pump eluent through the columns for about 30 min, directing the eluent exiting the column to a waste container. While the columns are being flushed with eluent, prepare the Dionex AERS 500 Carbonate Suppressor for use by hydrating the internal membrane. Follow the Quick Start Instructions received with the suppressor, which can also be found in the suppressor product manual.[3] Push 3 mL of DI water through the Eluent Out port and 5 mL of DI water through the Regen In port. Allow the suppressor to sit for 20 min to ensure complete hydration before installing it in the system. Install the black PEEK (0.010 in i.d. tubing) backpressure loop from the slotted compartment next to the CD detector (exerting an additional ~40 psi) between the CD outlet and the suppressor Regen In port. Refer to the suppressor manual for additional details.[3] Equilibrate the column using Quality Assurance Report (QAR) conditions (found with the insert in the column box and in the column manual) for 30 min and monitor the baseline until the background conductivity is between 20–23 µS/cm.

Installing the Dionex AS-DV Autosampler

Install the autosampler transfer line into Port S of the injection valve. For more information review the Thermo Scientific Dionex AS-DV Operator's Manual (Document No. 065259).[4]

Creating an instrument method

To create a new instrument method using the Chromeleon Wizard, select *Create, Instrument Method,* and select an instrument. On the Console, on the menu bar, click the arrow Next > to *Create,* and then click *Instrument Method.* Select the instrument in which the Dionex Aquion IC system and Dionex AS-DV Autosampler are configured and click Next >. For the selected instrument, wizard pages for these devices are displayed. On each wizard page, select the required parameters (Table 1) and click Next >.

Table 1. Chromatographic conditions

System:	Dionex Aquion IC system
Columns:	Dionex IonPac AS22, Analytical, 4 × 250 mm Dionex IonPac AG22, Guard, 4 × 50 mm
Eluent:	4.5 mM Na_2CO_3 / 1.4 mM $NaHCO_3$
Flow Rate:	1.2 mL/min
Column Temperature:	30 °C
Injection Volume:	10 µL
Detection:	Suppressed conductivity with Dionex AERS 500 Carbonate Anion Electrolytically Regenerated Suppressor, recycle mode
Suppresser Current:	31 mA
System Backpressure:	~1850 psi
Background Conductance:	~21–22 µS/cm
Noise:	2.8–3 nS/min peak-to-peak
Run Time:	15 min

On the AS-DV Autosampler > Preparation Options page (Figure 1) select the preferred options.

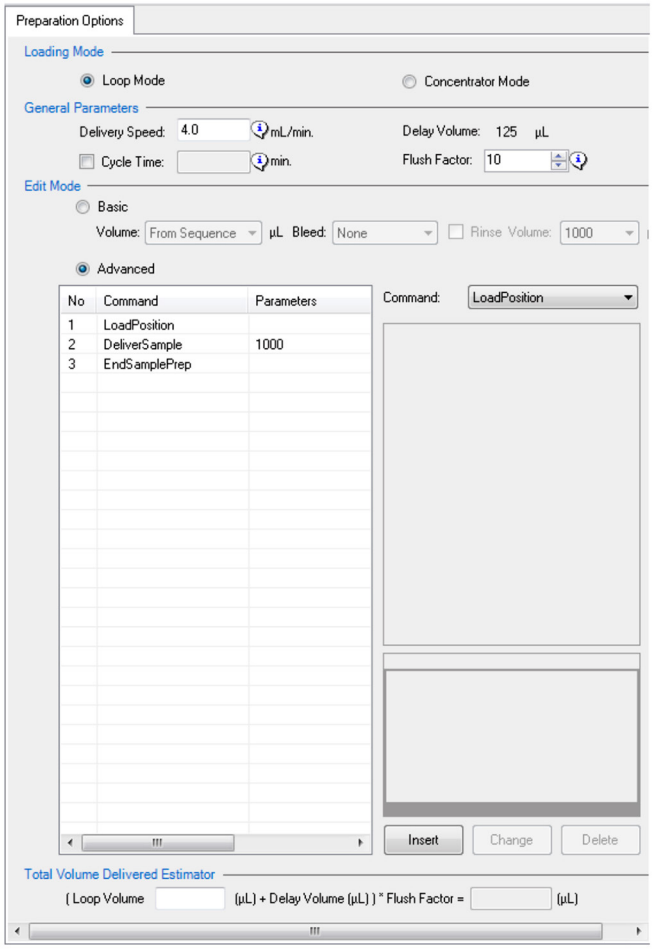

Figure 1. Sample preparation options

Under Loading Mode, select *Loop Mode* (to load a sample loop). Under General Parameters, set *Delivery Speed* at 4.0. Delivery speed determines the speed at which the sample is delivered to the sample loop. The recommended delivery speed for this set up is 4.0.

Chromeleon CDS uses the Flush Factor in the formula that determines the volume of sample delivered from the vial. The formula is shown in the Total Volume Delivered Estimator. The Flush Factor determines how much excess sample will be flushed through the sample loop. A value of 1 to 10 can be entered.

Under Edit Mode, select Advanced. This mode controls the sample delivery volume. Refer to the Dionex AS-DV Autosampler operator's manual for details.[4] The simplest way of controlling delivery volume is to deliver the specified number of microliters from the vial. For example, to take five injections from a filled 5.0 mL vial, select 1000 µL.

In the Instrument Method Script Editor, enter the command "Sampler.DeliverSample" just before the command "Sampler.EndSamplePrep" by using the drop-down window on the Command tab and entering a value of 1000 in the Value tab (Figure 2).

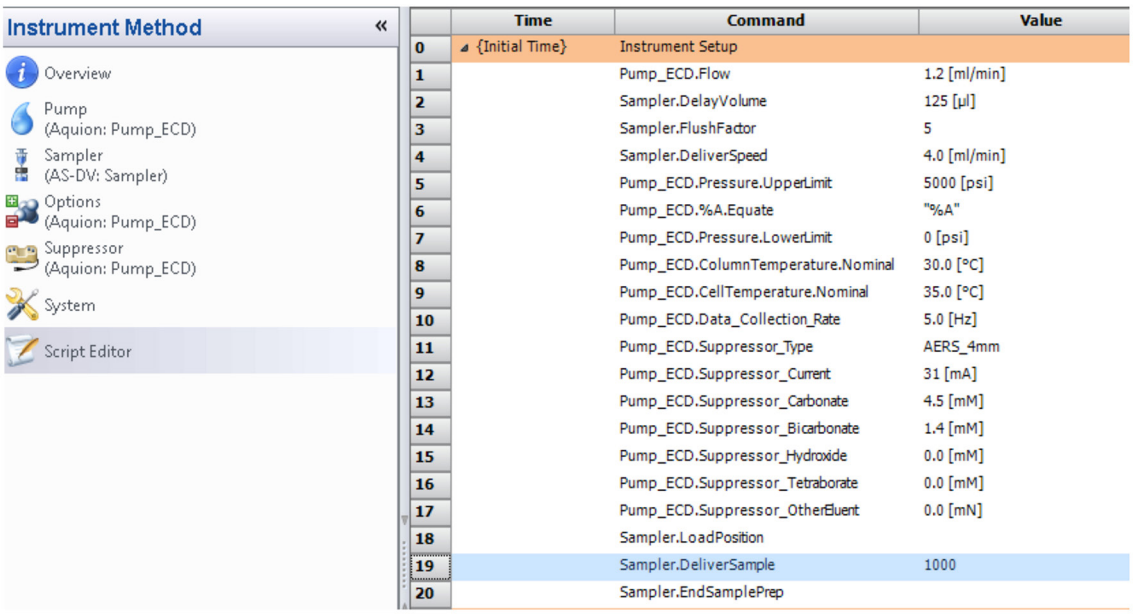

Figure 2. Script editor

Preparation of standards and samples

Preparation of stock standard solutions, 1000 mg/L

Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade potassium or sodium salts as listed below, for most analytes.

To prepare 1000 mg/L stock solutions, use the compounds and masses listed in Table 2.

Table 2. Amounts of compounds used to prepare 100 mL of 1000 mg/L stock solutions

Anion	Compound	Mass (mg)
Fluoride	Sodium fluoride	221.00
Chloride	Sodium chloride	164.90
Nitrite (NO_2^- - N)	Sodium nitrite	492.61
Bromide	Sodium bromide	128.77
Nitrate (NO_3^- - N)	Sodium nitrate	606.80
Phosphate (PO_4^{3-}- P)	Sodium phosphate, monobasic	387.41
Sulfate	Potassium sulfate	181.41

Preparation of the QAR standard mix

Add an appropriate volume (Table 3) of 1000 mg/L stock standard solution of each anion standard to a 100 mL volumetric flask and make up the volume with DI water to prepare the QAR standard mix.

Table 3. Volumes of 1000 mg/L stock standards to prepare the QAR standard mix

Anion	Concentration (mg/L)	Volume to add (mL)
Fluoride	5.0	0.500
Chloride	10.0	1.00
Nitrite	15.0	1.50
Bromide	25.0	2.50
Nitrate	25.0	2.50
Phosphate	40.0	4.00
Sulfate	30.0	3.00

Preparation of mixed anions standard solution, 100 mg/L

Add 10 mL of 1000 mg/L stock standard solution of each anion standard to a 100 mL volumetric flask and make up the volume with DI water to prepare a 100 mg/L mixed anion standard solution.

Preparation of calibration standards

Add appropriate volumes of the 100 mg/L mixed anions standard solution (Table 4) to 100 mL volumetric flasks and make up the volume with DI water to the prepare the calibration standards.

Table 4. Preparation of 100 mL calibration standards

Calibration Std	Volume of 100 mg/L Mixed Anions Std (mL)
Std 1 (0.2 mg/L)	0.200
Std 2 (0.5 mg/L)	0.500
Std 3 (1.0 mg/L)	1.00
Std 4 (2.5 mg/L)	2.50
Std 5 (5.0 mg/L)	5.00
Std 6 (10 mg/L)	10.0
Std 7 (20 mg/L)	20.0

Results and discussion

Column Quality Assurance Report (QAR)

Inject the QAR standard mix into the column set. The column will be equilibrated when three consecutive injections of this standard produce the same retention times (RTs) for all analytes. Confirm that the resulting chromatogram resembles the QAR that comes with the column. Note that the chromatogram shown in the QAR sheet is generated without the guard column; therefore, analyte RTs should be greater than those shown in the QAR. Refer to the column manual for additional details.[5] Figure 3 displays the chromatogram of the Dionex IonPac AS22 QAR standard mix.

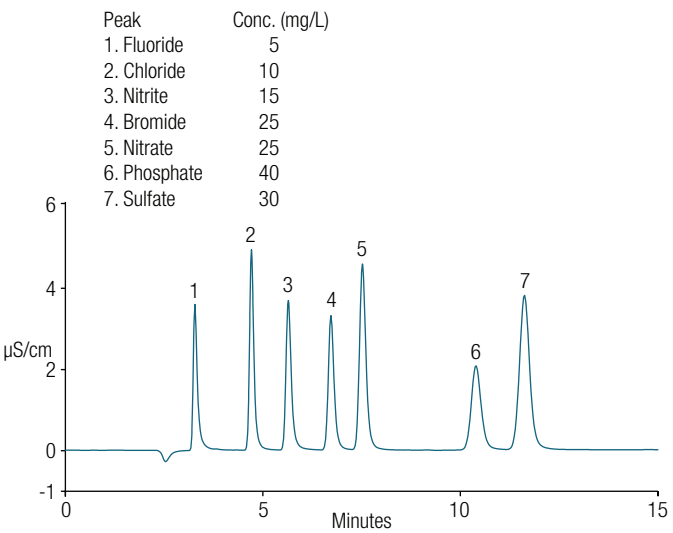

Figure 3. Chromatogram of the QAR standard mix

Calibration and quantification

Calibration standards for seven anions were prepared in DI water as described earlier. The calibration plots of peak area versus concentration were fit using linear regression functions that yielded coefficients of determination (r^2) greater than 0.9999. This was done automatically in Chromeleon CDS data processing. Table 5 summarizes the calibration data obtained by making triplicate injections of calibration standards between 0.20–20 mg/L.

Limit of detection (LOD) and limit of quantitation (LOQ)

The detection limit of an individual analytical method is the lowest amount of analyte in a sample that can be detected but not necessarily quantitated as an exact value. The quantification limit of an individual analytical method is the lowest amount of analyte in a sample that can be quantitatively determined with suitable precision and accuracy. There are several approaches for determining the detection limit. The approach taken here is based on signal-to-noise ratio (S/N). To determine the S/N, the baseline noise was first determined by measuring the peak-to-peak noise in a representative one-minute segment of the baseline where no peaks elute, but that is close to the peak of interest. We used the 8–9 min segment for all the ions. The signal was determined from the average peak height of five injections of the lowest concentration at which the analyte can be reliably detected: a 0.05 mg/L standard solution for fluoride and chloride, and a 0.1 mg/L standard solution for nitrite, bromide, nitrate, sulfate, and phosphate. The LOD and LOQ were then determined by 3x and 10x the S/N. The estimated LODs and LOQs are summarized in Table 6.

Table 5. Calibration results for seven anions

Peak	Name	Ret. Time (min)	Cal. Range (mg/L)	Cal. Type	Coeff.of Determination (r^2)
1	Fluoride	3.317	0.2–20	Lin, WithOffset	0.99997
2	Chloride	4.780	0.2–20	Lin, WithOffset	0.99995
3	Nitrite	5.733	0.2–20	Lin, WithOffset	0.99995
4	Bromide	6.843	0.2–20	Lin, WithOffset	0.99994
5	Nitrate	7.657	0.2–20	Lin, WithOffset	0.99995
6	Phosphate	10.713	0.2–20	Lin, WithOffset	0.99996
7	Sulfate	11.957	0.2–20	Lin, WithOffset	0.99999

Table 6. Calculation of S/N, LOD, and LOQ

Anion	Concentration (mg/L)	Signal (µS)	Noise (µS)	S/N	LOD (mg/L)	LOQ (mg/L)
Fluoride	0.05	0.0342	0.003	11.39	0.013	0.044
Chloride	0.05	0.0209	0.003	6.97	0.022	0.072
Nitrite	0.10	0.0232	0.003	7.72	0.031	0.065
Bromide	0.10	0.0149	0.003	4.95	0.048	0.101
Nitrate	0.10	0.0180	0.003	6.00	0.040	0.083
Phosphate	0.10	0.0079	0.003	2.62	0.092	0.191
Sulfate	0.10	0.0125	0.003	4.15	0.065	0.120

Sample analysis

Two drinking water samples (tap water and bottled water) were collected and analyzed. Figure 4 displays the chromatograms of water samples showing the separation of anions on a Dionex IonPac AS22 column set. Seven anions were identified by comparing their retention times with those of the standards. The anion concentrations in both samples were determined using the calibration curves (Table 7).

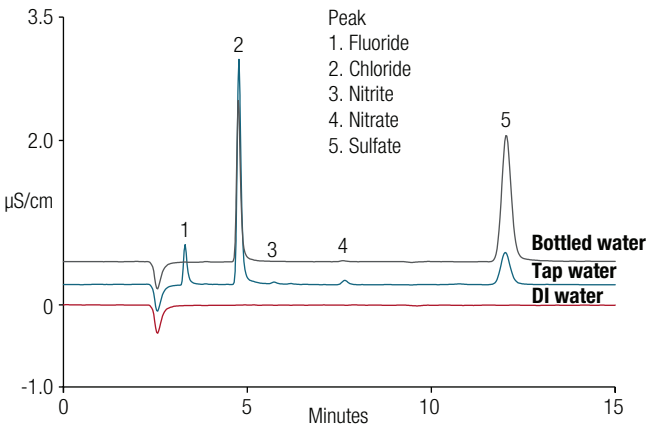

Figure 4. Chromatograms of DI water, tap water, and bottled water samples

Method accuracy

To validate the determination of anions in water samples, the samples were spiked with known amounts of standards at two levels i.e., 2.5 mg/L and 5 mg/L. Figure 5 shows the chromatograms of the native and spiked tap water sample.

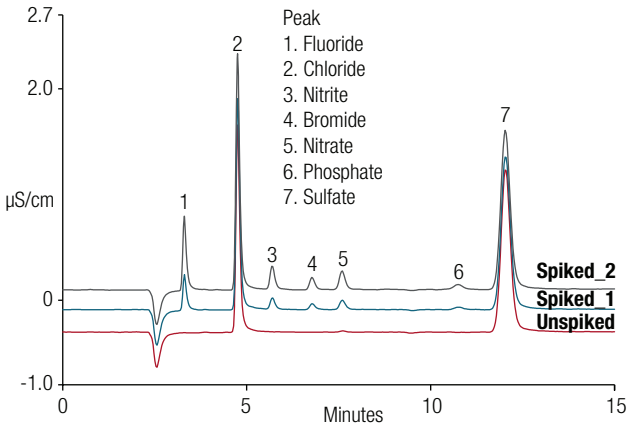

Figure 5. Chromatograms of unspiked and spiked tap water sample at two levels

Table 7. Concentrations of seven anions in two water samples

Anion	Tap Water		Bottled Water	
	mg/L	RSD (n=3)	mg/L	RSD (n=3)
Fluoride	0.73	0.09	n.d.	
Chloride	6.08	0.21	4.39	0.19
Nitrite	0.20	0.20	n.d.	
Bromide	n.d			
Nitrate	0.32	0.27	0.08	0.97
Phosphate	0.27	0.55	n.d.	
Sulfate	3.48	0.3	13.4	0.29

n.d. – not detected

The recovery percentages were calculated according to formula given below:

$$Recovery\ \% = \frac{C\ spiked\ sample - C\ analyte\ added}{C\ analyte\ added} * 100$$

Table 8 summarizes the recoveries of seven anions in the two water samples.

Conclusion

In this technical note we demonstrated that U.S. EPA Method 300.[1] (Determination of inorganic anions in drinking water by ion chromatography) could be successfully executed on a Dionex Aquion IC system. With easy system set up, seven anions were separated under isocratic conditions using a carbonate/bicarbonate eluent and a Dionex IonPac AS22 column set. Two drinking water samples were successfully analyzed for the seven common inorganic anions. The method showed good precision and accuracy for all seven anions with recoveries from 95 to 104%.

References

1. The Determination of Inorganic Anions in Drinking Water by Ion Chromatography; Method 300.1 (Revision 1); U.S. Environmental Protection Agency; Cincinnati, Ohio, 1997.
2. Thermo Scientific Dionex Aquion Ion Chromatography System Operator's Manual. Document No. 22176-97003 Revision 02, Sunnyvale, CA, June 2016. [Online] https://assets.thermofisher.com/TFS-Assets/CMD/manuals/Man-22176-97003-IC-Aquion-Man2217697003-EN.pdf (accessed July 9, 2018).
3. Thermo Scientific Dionex DRS 600 Suppressor, Dionex ERS 500e Suppressor, Dionex ERS 500 Carbonate Suppressor Product Manual, P/N 031956, Revision 13, Sunnyvale, CA, March 2018. [Online] https://assets.thermofisher.com/TFS-Assets/CMD/manuals/man-031956-dionex-suppressors-man031956-en.pdf (accessed July 9, 2018).
4. Thermo Scientific Dionex AS-DV Autosampler Operator's Manual. Document No. 065259 Revision 05 October 2012, Sunnyvale, CA, 2016. [Online] https://assets.thermofisher.com/TFS-Assets/CMD/manuals/man-065259-as-dv-autosampler-man065259-en.pdf (accessed July 9, 2018).
5. Thermo Scientific Dionex IonPacAS22 and IonPac AS22-Fast Column Product Manual. P/N 065119-08, Sunnyvale, CA, March 2013. [Online] https://assets.thermofisher.com/TFS-Assets/CMD/manuals/Man-065119-IC-IonPac-AS22-Fast-Man065119-EN.pdf (accessed July 9, 2018).

Table 8. Recoveries of seven anions in two water samples

Anion	Unspiked (mg/L)	Spike Level 1 (mg/L)	Recovery (%)	Spike Level 2 (mg/L)	Recovery (%)
Tap Water					
Fluoride	0.73	3.16	97.2	5.85	102
Chloride	6.08	8.65	103	11.2	102
Nitrite	0.20	2.77	103	5.36	103
Bromide	0.00	2.58	103	5.17	103
Nitrate	0.32	2.93	104	5.41	102
Phosphate	0.27	2.75	99.2	5.26	100
Sulfate	3.48	5.95	99.0	8.22	95
Bottled water					
Fluoride	0.00	2.55	102	5.13	103
Chloride	4.39	6.65	90.3	9.32	99
Nitrite	0.00	2.45	98.1	5.20	104
Bromide	0.00	2.62	105	5.05	101
Nitrate	0.08	2.65	103	5.08	100
Phosphate	0.00	2.62	105	5.13	103
Sulfate	13.40	15.9	99.8	18.2	95

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