ThermoFisher
SCIENTIFIC

Ion chromatography

Determination of trace organic acids and inorganic anions in boric acid-treated power plant waters using an automated reagent-free ion chromatography system

Authors
Jingli Hu and Jeffrey Rohrer

Thermo Fisher Scientific, Sunnyvale, CA

Keywords
Dionex ICS-6000 HPIC system, Dionex IonPac AS28-Fast-4μm column, trace analysis, ADRS 600 suppressor

Goal
To update Dionex AN185 with a Thermo Scientific™ Dionex™ IonPac™ AS28-Fast-4μm column, Dionex ICS-6000 instrument, and updated consumables

Introduction
For nuclear power plants using a pressurized water reactor (PWR), the primary coolant includes boric acid as a water-soluble neutron absorber to control the nuclear reaction.[1] Boron concentrations at the beginning of the fuel cycle may be as high as 2,500 mg/L (ppm), corresponding to 1.4% boric acid. At the high temperature and pressure in the PWR, this boric acid concentration can form crud that deposits metal oxides on the fuel rods. To prevent crud buildup, lithium hydroxide is added to increase the $pH_{300 °C}$ to 6.9 or higher. However, trace anionic impurities at low- or sub-μg/L concentrations from the water source, or materials such as ion-exchange polisher resins, can serve as catalysts for corrosion. The determination of sub-μg/L anionic contaminants, such as chloride and sulfate, in boric acid-treated waters is critical for nuclear power plants to minimize or inhibit corrosion and thereby reduce the associated maintenance costs.

Ion chromatography (IC) is an indispensable technique for the determination of trace concentrations of ionic impurities found in power plant waters. Dionex AN185 describes an automated RFIC method for the determination of trace anions in borated waters.[2] After lithium removal with a Thermo Scientific™ Dionex™ CR-CTC II Continuously Regenerated Cation Trap Column the sample is concentrated before separating the anions using a Thermo Scientific™ Dionex™ IonPac™ AS15 column set and an electrolytically generated potassium hydroxide gradient.

thermo scientific

This work updates AN185 with a Dionex IonPac AS28-Fast-4µm column for improved peak efficiencies and resolution, the IC instrument, and consumables. The calibration ranges, detection limits, precision, and accuracy of this method for determining trace anionic impurities in borated samples are described.

Experimental

Equipment

- Thermo Scientific™ Dionex™ ICS-6000 HPIC system including:

  - Dionex ICS-6000 DP Pump module

  - Dionex ICS-6000 DC Detector/Chromatography module with Conductivity Detector

  - Dionex ICS-6000 EG Eluent Generator module

- Automation Manager with one 10-port high-pressure valve and one three-port low-pressure valve* (P/N 075951)

- Thermo Scientific™ Dionex™ AS-HV High Volume autosampler with internal peristaltic pump (P/N 064051)

- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) Software, version 7.2.9

Consumables

- Thermo Scientific™ Dionex™ EGC 500 KOH Cartridge (P/N 075778)

- Thermo Scientific™ Dionex™ CR-ATC 600 Continuously Regenerated Anion Trap Column (P/N 088662)

- Thermo Scientific™ Dionex™ ADRS 600 Anion Dynamically Regenerated Suppressor, 2 mm (P/N 088667)

- Thermo Scientific™ Dionex™ IonPac™ ATC-HC 500 Anion Trap Column 9 × 75 mm (P/N 075978)

- Thermo Scientific™ Dionex™ CR-CTC III Continuously Regenerated Cation Trap Column (P/N 104-60001)

- Fisherbrand™ Narrow-mouth field sample bottles, high-density polyethylene (HDPE), 125 mL, 250 mL sizes for storage of standards and samples (Fisher Scientific P/N 02-895A, B)

- Thermo Scientific™ Nunclon™ 250 mL tissue culture sample flasks (P/N 064053, pkg. of 50)

- Caps and septa for sample flasks (P/N 064235, pkg. of 50)

- Santoprene® internal peristaltic pump rinse tubing for the Dionex AS-HV autosampler, one extra (2.06 mm or 0.08 in i.d., Dionex P/N 064521)

- Santoprene internal peristaltic pump sample tubing for the Dionex AS-HV autosampler, one extra (0.64 mm or 0.03 in i.d., Dionex P/N 064825)

Reagents and standards

- Deionized (DI) water, Type 1 reagent grade, 18 MΩ·cm resistivity or better

- Sodium and potassium salts, A.C.S. reagent grade or better, for preparing anions standards

Samples

- Boric acid (Fisher Scientific P/N A73-500)

- Lithium hydroxide, monohydrate (JT Baker P/N P406-04)

Chromatographic conditions

Analytical: System 1	
Columns	Dionex IonPac AG28-Fast-4µm guard column, 2 × 30 mm (P/N 088750)
	Dionex IonPac AS28-Fast-4µm analytical column, 2 × 150 mm (P/N 088749)
Eluent	7 mM KOH from 0 to 6 min, 7–20 mM KOH from 6 to 8 min, 20–72 mM from 8 to 11 min, 72 mM from 11 to 25 min
Eluent source	Dionex EGC 500 KOH cartridge with CR-ATC 600
Flow rate	0.3 mL/min
Standard injection volume	10 µL
Sample injection volume	2 mL
Column temperature	30 °C
Concentrator	Thermo Scientific™ Dionex™ IonPac™ UTAC-ULP2 (P/N 079918)
CRD	Thermo Scientific™ Dionex™ CRD 200, 2 mm (P/N 062986)
Detection	Suppressed conductivity
Suppressor	Dionex ADRS 600 (2 mm) Suppressor, recycled water mode, 54 mA current
Detection/Suppressor compartment	30 °C
Cell temperature	35 °C
Background conductance	<0.5 µS/cm
System backpressure	~3,300 psi (100 psi = 689.5 kPa)
Noise	<1 nS/cm
Run time	25 min + time for AS-HV to load sample (10–15 min)

* Note: only the 10-port high-pressure valve is used for this application

Sample preparation: System 2

Trap columns	Dionex IonPac ATC-HC 500 anion trap column for DI water carrier solution
	Dionex CR-CTC III, removal of lithium from sample
Carrier	Degassed deionized water
Flow rate	2 mL/min
Matrix elimination volume	10 mL
System backpressure	~1,600 psi

Dionex AS-HV autosampler

Peristaltic pump flow rate	1.3 mL/min
Load volumes (entered in Chromeleon CDS sequence)	1 mL (for 10 µL standard injection) 5 mL (for 2 mL sample injection)
Carrier	Degassed deionized water
Rinse volume	5 mL
Sample load mode	Pull
Preparation time	10 min (standard injection) 13 min (sample injection)

Precautions

When determining trace concentrations of ionic contaminants, extreme caution should be followed during the entire process to eliminate or at least minimize contamination. In particular, organic acids can easily be adsorbed through the atmosphere and can degrade more rapidly over time than common inorganic anions. Be sure that the DI water used for preparing eluent and standards, rinsing the containers, and the rinse solution for the Dionex AS-HV autosampler is free of measurable ionic impurities. It is also important that the Dionex AS-HV autosampler is installed in the "pull" mode and that no restrictions for the flow of liquid from it to the 10-port valve are present. If abnormal peak broadening or peak splitting is observed, particularly for early eluting peaks (i.e., fluoride, glycolate, acetate, formate), replace the Dionex IonPac UTAC-ULP2 concentrator. When replacing the concentrator, confirm that the response from the calibration standards has not changed by injecting a quality control standard. For more general precautions for trace analysis, see Technical Note 73982.[3]

System preparation and setup

Figure 1 shows a schematic diagram of the system configuration. To configure System 1:

1. Install a Dionex EGC 500 KOH cartridge, Dionex CR-ATC 600, and Dionex EGC degasser by following the Dionex ICS-6000 HPIC installation and operator's manual.[4]

2. Install a Dionex IonPac AS28-Fast-4µm column set in the lower compartment of the DC using red PEEK (0.005" i.d.) tubing between connections.

3. Install a 5 × 23 mm Dionex IonPac UTAC-ULP2 concentrator in place of sample loop on valve #1 (6-port injection valve on DC) using red PEEK tubing. The direction of sample loading should be opposite of the analytical flow.

4. Hydrate and install a Dionex ADRS 600 suppressor and a Dionex CRD 200 carbonate removal device according to the instructions in the product manuals. To minimize the interference of carbonate and therefore, improve the quantitation of sulfate, it is critical to use a carbonate removal device (CRD) for this application.
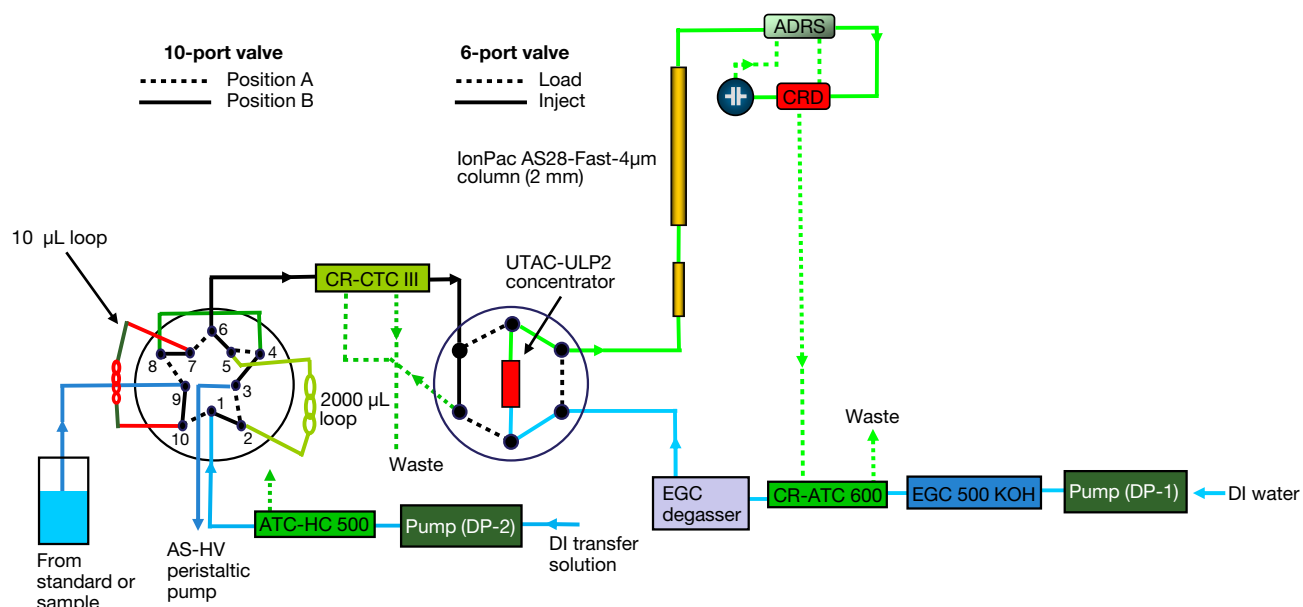

Figure 1. System configuration

The internal peristaltic pump of the Dionex AS-HV autosampler is used in this application update to rinse the PEEK needle and sample lines and to load the sample. To install and configure the autosampler:

1. Connect the peristaltic pump rinse lines to the fixed rinse reservoir and 4 L external rinse reservoir.

2. Install the sampling line in the pull mode.

3. Adjust the flow rate of the peristaltic pump by turning the rinse speed knob until a flow rate of ~1.3–1.8 mL/min is achieved. Periodically verify the flow rate of the peristaltic pump as this can change with time.

4. Connect one end of a separate piece (~185 cm) of green PEEK tubing to the PEEK needle on the autosampler and the other to port #9 on the 10-port valve. Be sure the tubing is anchored appropriately according to the Dionex AS-HV autosampler operator's manual to avoid interference with the sampling arm movement.

To configure System 2:

1. Hydrate the Dionex CR-CTC III device, which is used for removal of lithium in the simulated matrices to achieve better separation for early eluting peaks such as fluoride and formate.

2. Connect the outlet of the System 2 pump to the inlet of the Dionex IonPac ATC-HC 500 anion trap column.

3. Install the Thermo Scientific™ Dionex™ ICS-6000 AM Automation Manager tray in the upper compartment of the Dionex DC Detector/Chromatography Compartment. The 10-port high-pressure valve is used for this application. Chromeleon CDS is used to control the high-pressure valve. For automated control, commands for valve control can be included in a Chromeleon CDS instrument method. To add AM valve control commands to an instrument method, use the Script Editor.

4. Use a minimum length of black PEEK tubing (0.010" i.d.) from port #6 on the 10-port valve to Eluent In of the Dionex CR-CTC III device and from the Dionex CR-CTC III device to the six-port injection valve to minimize dead volume.

5. Connect the Dionex CR-CTC III device to CR-TC2 power on the EG module.

6. Install the connections for the 10-port valve:

   a) Connect ports #4 and #8 with green PEEK tubing (0.030" i.d.). The length should be kept to a minimum to reduce the void volume and comply with the pressure restrictions for the Dionex AS-HV autosampler.

   b) Install a 10 µL sample loop on ports #7 and #10.

   c) Prepare a 2 mL sample loop from green PEEK tubing by measuring approximately 173 in (4.4 meters). Verify the volume of the loop by determining the difference in weight between the empty sample loop and the sample loop filled with DI water. Precise volumes of the large and small loops are required to produce accurate calculations of standard concentrations used for calibration.

   d) Make sure the pressure for System 2 is between 1,500 and 2,000 psi when operating at 2 mL/min.

7. Install a Dionex EGC 500 KOH cartridge on System 2. This installation will enable the Dionex CR-CTC III device to be powered on. It is not necessary to condition this cartridge at this time.

Chromeleon CDS programs

This application update requires the use of at least three separate Chromeleon CDS (CM) programs (see Appendix A). A CM program using the small loop is used to calibrate the system with standards containing common inorganic anions and small organic acids (Table A1). When the 10-port valve is switched to position B, the Dionex AS-HV autosampler loads the 10 µL loop while the six-port valve remains in the inject position. For the analysis of each standard, a 1 mL volume is used in the "injection volume" column in the CM sequence. After the Dionex AS-HV autosampler has completed loading the standard, the 10-port valve switches to position A and the six-port valve is switched to the load position. Deionized water from pump 2 is used to transfer the standard from the 10-port valve to the concentrator on the six-port valve. The time required to transfer the standard to the concentrator will depend on the void volume between the two valves and the flow rate of pump 2. In this application update, a volume of 300 µL (0.15 min at 2 mL/min) was used. In addition, a matrix rinse volume of 10 mL was used for all standards to duplicate the procedure used for the sample analyses and therefore minimize any influence from analytes that may appear in the blank.

To analyze boric acid-containing samples, a second CM program was developed using the 2 mL large loop on the 10-port valve (Table A2). When the 10-port valve is switched to position A, the Dionex AS-HV autosampler loads the 2 mL loop while the six-port valve remains in the inject position. For the analysis of samples, a 5 mL volume is used in the "injection volume" column in the CM sequence. After the 2 mL loop is completely flushed with the sample, the 10-port valve is switched to position B and the six-port valve is switched to the load position. Deionized water from pump 2 transfers the sample from the 10-port valve to the concentrator. The time required to transfer the sample to the concentrator depends on the size of the loop (2 mL in this application), the void volume between the two valves, and the flow rate of pump 2.

In this application update, a volume of 2.3 mL (1.15 min at 2 mL/min) was used for all sample analyses. To remove most of the boric acid from the concentrator prior to injection, a matrix rinse volume of 10 mL was used.

An additional benefit of this application is the ability to spike samples online using prepared calibration standards. A third CM program was developed to load a 2 mL sample on the concentrator, as previously described, and then add 10 µL of a standard to the 2 mL sample on the concentrator column (Table A3). Multiple CM programs may be developed for this purpose depending on the number of standards used to spike the sample online and their relative positions in the Dionex AS-HV autosampler tray. The CM program required the inclusion of a series of steps:

1. Load 2 mL of sample onto the 10-port valve.

2. Transfer the sample to the concentrator.

3. Turn off the System 2 components, such as the pump and Dionex CR-CTC III device, to eliminate additional DI water entering the concentrator.

4. Rinse the PEEK needle on the Dionex AS-HV autosampler with DI water. 5. Load the standard on the 10 µL loop.

6. Turn the System 2 components on.

7. Transfer the standard to the concentrator.

8. Rinse the concentrator with 10 mL of DI water. This procedure eliminates potential contamination and errors associated with spiking samples offline to determine the method's accuracy.

Preparation of solutions and reagents
Common anions stock standard solutions
Stock standard solutions (1,000 mg/L) can be prepared by dissolving the appropriate amounts of the required analytes in 100 mL of DI water according to Table 1.

Mixed calibration intermediate stock standard solution
Add 50 mL of sulfate stock standard solution (1,000 mg/L) and 5 mL of other anions stock standard (1,000 mg/L) to a 250 mL presoaked/rinsed tissue culture flask and bring to volume with DI water.

Working standard solution
Prepare working standards in the low-µg/L to mg/L range by adding the appropriate volumes to a 250 mL rinsed/presoaked tissue culture flask, as shown in Table 2.

Table 1. Masses of compounds used to prepare 100 mL of 1,000 mg/L ion standards

Analyte	Compound	Amount (mg)
Fluoride	Sodium fluoride (NaF)	221.0
Glycolate	Sodium glycolate ($NaC_2H_3O_3$)	130.6
Acetate	Sodium acetate ($NaC_2H_3O_2$)	138.9
Formate	Sodium formate ($NaCO_2H$)	151.0
Chloride	Sodium chloride (NaCl)	164.9
Nitrite	Sodium nitrite ($NaNO_2$)	150.0
Sulfate	Sodium sulfate (Na_2SO_4)	147.9
Bromide	Sodium bromide (NaBr)	128.8
Nitrate	Sodium nitrate ($NaNO_3$)	137.1
Phosphate	Potassium phosphate, monobasic (KH_2PO_4)	143.3

Table 2. Calibration standards preparation

Calibration level	Anions except sulfate (mg/L)	Sulfate (mg/L)	Intermediate stock (mL)	DI H_2O (mL)
1	0.02	0.2	0.25	249.75
2	0.04	0.4	0.5	249.5
3	0.1	1	1.25	248.75
4	0.2	2	2.5	247.5
5	0.5	5	6.25	243.75
6	1	10	12.5	237.5
7	2	20	25	225
8	3	30	37.5	212.5
9	4	40	50	200

Sample preparation
Prepare a 1,000 mg/L lithium stock solution by adding 1.511 g lithium hydroxide monohydrate to a 250 mL presoaked/rinsed tissue culture flask and add DI water to a solution weight of 250 g. Store this solution at 4 °C. Simulated boric acid/lithium hydroxide sample matrix solutions are prepared by adding appropriate amounts of boric acid solid and lithium hydroxide stock solutions to presoaked/rinsed tissue culture flasks and adding DI water to a solution weight of 250 g. Recovery studies use three boron–lithium concentrations: 1,000 mg/L boron with 2.0 mg/L lithium, 2,000 mg/L boron with 4.0 mg/L lithium, and 2,500 mg/L boron with 5.0 mg/L lithium.

Table 3 shows the weights of boric acid and 1,000 mg/L lithium stock solution used to prepare the matrices.

Table 3. Amounts of boric acid and lithium hydroxide used to prepare 250 g of surrogate matrices

Matrix composition (mg/L)	Mass boric acid (g)	Mass lithium hydroxide solution* (g)
1,000 B + 2.0 Li	1.4305	0.5
2,000 B + 4.0 Li	2.8610	1
2,500 B + 5.0 Li	3.5763	1.25

* 1,000 mg/L lithium stock solution

Results and discussion
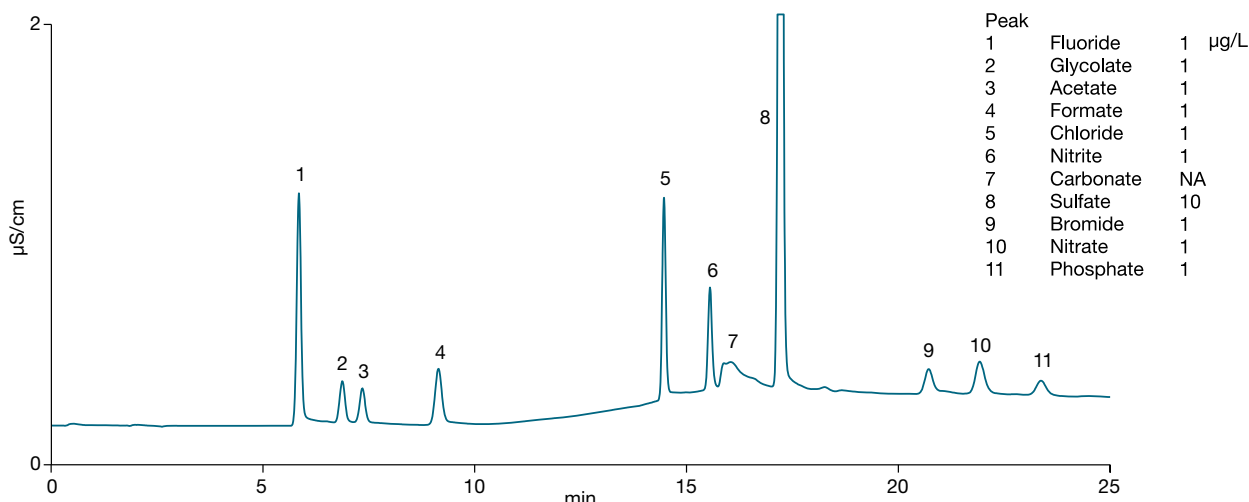
Separation

The Dionex IonPac AS28-Fast-4µm analytical column in combination with the Dionex AG28-Fast-4µm guard column is designed for the trace analysis of inorganic anions and monovalent organic acids. The selectivity of the Dionex IonPac AS28-Fast-4µm guard plus analytical column set has been designed to retain fluoride well out of the water dip and to separate common anions and low molecular weight organic acids encountered in high purity water matrices using electrolytically generated KOH gradient chromatography.

The Dionex IonPac AS28-Fast-4µm column is a high resolution, high-capacity anion exchange column with selectivity and capacity similar to the Dionex IonPac AS15 column. The high resolution provides better peak identification, and the high capacity allows injection of more concentrated samples without overloading the column.[5]

Figure 2 shows a separation of target anions in DI water using a Dionex IonPac AS28-Fast-4µm column set. All analytes were well separated within 25 min, and fluoride is well resolved from the water dip, which can be seen as a minute negative peak at the beginning of the chromatograms. Figure 3 shows a system blank chromatogram with and without injections. Trace concentrations of formate and chloride were detected in the system blank. However, the concentration was consistent during the experiments and therefore does not significantly impact the quantification of target anions.

Peak			
1	Fluoride	1	µg/L
2	Glycolate	1	
3	Acetate	1	
4	Formate	1	
5	Chloride	1	
6	Nitrite	1	
7	Carbonate	NA	
8	Sulfate	10	
9	Bromide	1	
10	Nitrate	1	
11	Phosphate	1	

Figure 2. Separation of small organic acids and common inorganic anions using a Dionex IonPac AS28-Fast-4µm column

Peak	ppm	A	B	
1	Formate	<0.1	<0.1	µg/L
2	Chloride	<0.1	<0.1	
3	Carbonate	NA	NA	
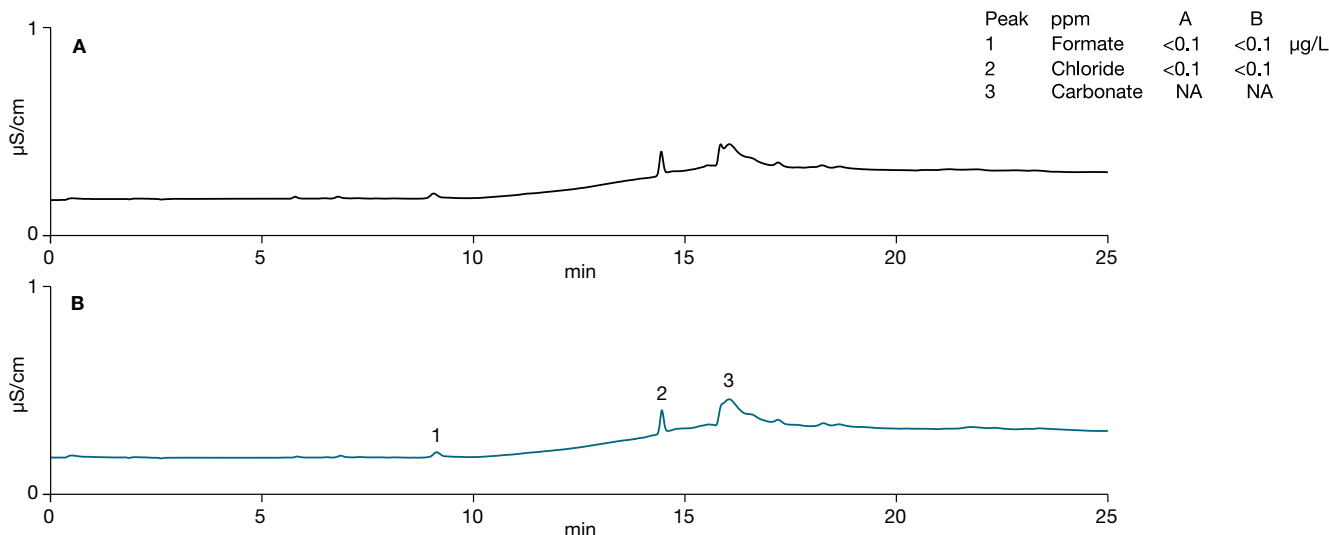
Figure 3. Comparison of representative blank chromatograms. A) System blank, B) DI water matrix blank.

Limit of detection (LOD)

The determination of LOD was based on the signal-to-noise (S/N) ratio. Determination of the S/N ratio is performed by comparing the measured signal from a standard with a low concentration of analyte with those of a blank and establishing the minimum concentration at which the analyte can be reliably detected. A S/N=3 is used for estimating LOD, and a S/N=10 is used for estimating the quantification limit (LOQ).[6] In this study, the baseline noise was first determined by measuring the peak-to-peak noise in a representative 1-min segment of the baseline where no peaks elute but close to the peak of interest. The signal was determined from the height difference of anion standard (2–40 µg/L) and DI H_2O injections.

Calibration curves for target anions were prepared by dilution of intermediate stock solutions in DI water. Table 4 summarizes calibration data, LOD, and LOQ estimates. The coefficients of determination for all target analytes were 0.999 or greater using linear fitting.

Sample analysis

Low molecular weight organic acids and mono- and divalent inorganic anions commonly encountered in the chemical, semiconductor, and power generation industries can be determined in a single sample injection on the Dionex IonPac AS28-Fast-4µm column.

The method performance was evaluated by analyzing synthetic boric acid treated water containing up to 2,500 mg/L boron as boric acid with up to 5.0 mg/L lithium as lithium hydroxide. Figure 4 demonstrates the applicability of the method for determining trace anions in 1,000 mg/L boron-containing 2 mg/L lithium. The large borate matrix peak begins to elute from the column at 9.5 min and returns to baseline well before chloride elutes. In AN185, the initial elution of borate interferes with formate and, therefore, quantitation was not possible. In this application, formate is well separated from borate and can be quantified accurately.

Table 4. Calibrations and LOD

Analyte	Range (µg/L)	Calibration type	Coefficient of determination (r^2)	LOD (µg/L)	LOQ (µg/L)
Fluoride	0.1–20	External, Linear	0.9996	0.006	0.021
Glycolate	0.1–10	External, Linear	0.9998	0.018	0.060
Acetate	0.2–20	External, Linear	0.9997	0.048	0.161
Formate	0.1–20	External, Linear	0.9996	0.012	0.041
Chloride	0.1–20	External, Linear	0.9999	0.007	0.024
Nitrite	0.1–20	External, Linear	0.9996	0.012	0.041
Sulfate	1–200	External, Linear	0.9998	0.010	0.034
Bromide	0.2–20	External, Linear	0.9997	0.035	0.117
Nitrate	0.2–20	External, Linear	0.9997	0.040	0.133
Phosphate	0.2–20	External, Linear	0.9995	0.054	0.182

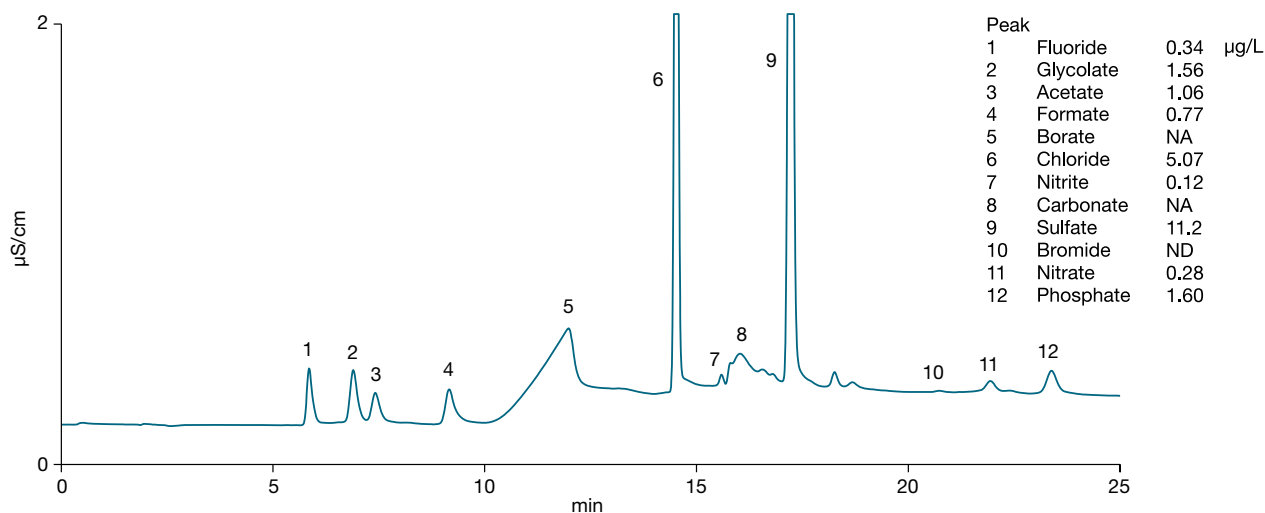| Peak			
1	Fluoride	0.34	µg/L
2	Glycolate	1.56	
3	Acetate	1.06	
4	Formate	0.77	
5	Borate	NA	
6	Chloride	5.07	
7	Nitrite	0.12	
8	Carbonate	NA	
9	Sulfate	11.2	
10	Bromide	ND	
11	Nitrate	0.28	
12	Phosphate	1.60	

Figure 4. Determination of trace anions in boric acid-treated water (1,000 mg/L boron + 2.0 mg/L lithium)

Table 5 summarizes the results for the target anions found in the simulated borated water samples. The primary components in the samples analyzed in this study consisted of chloride and sulfate with concentrations in the range of 5–13 µg/L and 11–29 µg/L, respectively.

Method accuracy and precision

Method accuracy was evaluated by determining the recoveries of the target analytes spiked into the synthetic sample matrices at concentrations ranging from 1,000 mg/L boron + 2.0 mg/L lithium to 2,500 mg/L boron + 5.0 mg/L lithium. The Dionex ICS-6000 Automation Manager combined with the large volume Dionex AS-HV autosampler permitted the samples to be spiked in situ using calibration standards, which prevented contamination from sample handling. Figure 5 compares an unspiked sample containing 2,500 mg/L boron and 5 mg/L lithium to the same

sample spiked in situ with the level 7 calibration standard. All peaks were resolved, and no significant increase of the borate peak was observed, relative to Figure 4, despite the increase in concentration. Table 5 summarizes the analyte recoveries for the samples investigated in this application update. In general, the analyte recoveries were in the range of 90–110%. The recoveries were independent of the boron concentration, indicating that the method performed well for the determination of low anion concentrations in the samples investigated in this study.

Retention time and peak area precisions were evaluated by spiking level 7 calibration standard for the target anions into a simulated matrix of 2,500 mg/L boron plus 5 mg/L lithium. Data collected from three consecutive runs yielded the precisions of retention time <0.1% and of peak area <3% for all target analytes (Table 6).

Table 5. Recoveries of anions spiked into simulated borated matrix

Sample	1,000 mg/L boron + 2.0 mg/L lithium			2000 mg/L boron + 4.0 mg/L lithium			2500 mg/L boron + 5.0 mg/L lithium		
	Amount found (µg/L)	Amount added (µg/L)	Recovery (%)	Amount found (µg/L)	Amount added (µg/L)	Recovery (%)	Amount found (µg/L)	Amount added (µg/L)	Recovery (%)
Fluoride	0.34	2.5	102	0.66	5	107	0.83	10	108
Glycolate	1.56	2.5	96.1	3.36	5	101	4.90	10	100
Acetate	1.06	2.5	96.5	2.44	5	106	3.22	10	105
Formate	0.77	2.5	90.5	1.25	5	98.2	1.59	10	101
Chloride	5.07	2.5	109	10.4	5	106	13.1	10	105
Nitrite	0.12	2.5	92.6	0.23	5	98.1	0.26	10	100
Sulfate	11.24	25	100	22.9	50	101	29.0	100	102
Bromide	0.00	2.5	92.1	0.00	5	91.4	0.00	10	96.4
Nitrate	0.28	2.5	109	0.58	5	95.2	0.69	10	98.1
Phosphate	1.60	2.5	92.8	2.97	5	102	3.99	10	105

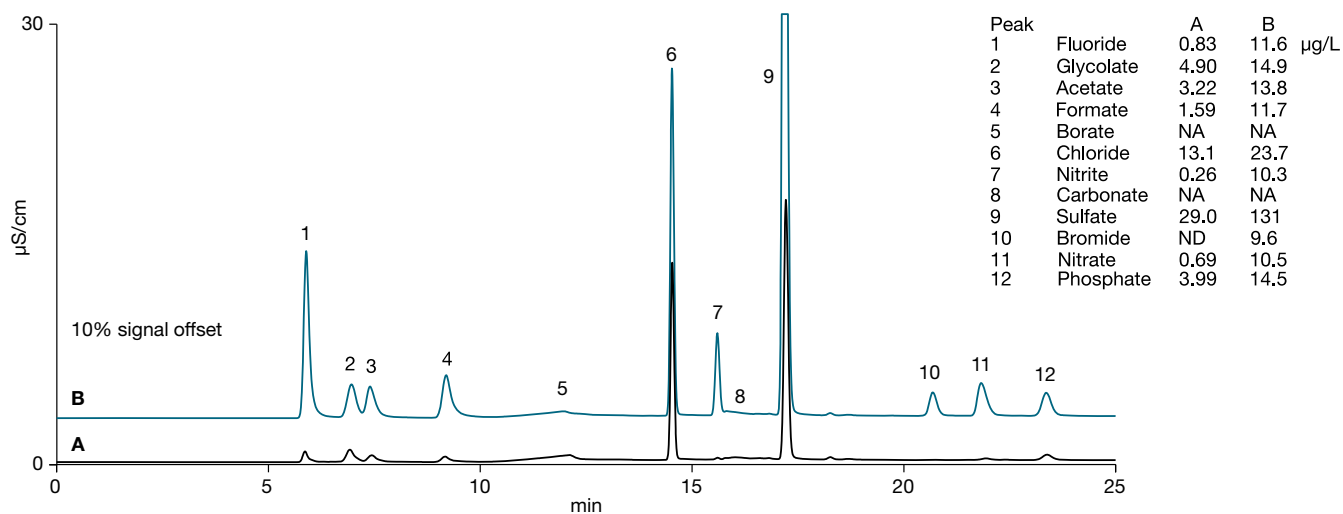| Peak		A	B	
1	Fluoride	0.83	11.6	µg/L
2	Glycolate	4.90	14.9	
3	Acetate	3.22	13.8	
4	Formate	1.59	11.7	
5	Borate	NA	NA	
6	Chloride	13.1	23.7	
7	Nitrite	0.26	10.3	
8	Carbonate	NA	NA	
9	Sulfate	29.0	131	
10	Bromide	ND	9.6	
11	Nitrate	0.69	10.5	
12	Phosphate	3.99	14.5	

Figure 5. Chromatograms of A) borated water (2,500 mg/L boron + 5.0 mg/L lithium), and B) borated water spiked with trace anions

Table 6. Retention time and peak area precisions

Component	Retention time (RSD)	CD peak area (RSD)
Fluoride	0.09	0.29
Glycolate	0.07	1.30
Acetate	0.08	2.93
Formate	0.06	1.28
Chloride	0.04	0.03
Nitrite	0.02	1.4
Sulfate	0.05	0.09
Bromide	0.02	0.5
Nitrate	0.02	0.18
Phosphate	0.04	0.25

Conclusion

This application updated AN185 with a Dionex IonPac AS28-Fast-4μm column, Dionex ICS-6000 instrument, Dionex CR-CTC III device, Dionex ADRS 600 suppressor, and Dionex IonPac UTAC-ULP2 concentrator column. The Dionex IonPac AS28-Fast-4μm column provides a faster and better separation of the target inorganic anions and low molecular weight organic acids, such as glycolate, acetate, and formate. The use of an electrolytically generated potassium hydroxide eluent eliminates the problems associated with the manual preparation of hydroxide eluents and, therefore, further increases ease-of-use and method automation. This method demonstrated good linearity, sub-μg/L detection limits, and good precision and accuracy for the target anions.

References

1. Nordmann, F. In Aspects of Chemistry in French Nuclear Power Plants, *Proceedings of the 14th International Conference on the Properties of Water and Steam*, Kyoto, Japan, **2004**, 521–530.

2. Thermo Scientific Application Note 185: Determination of Trace Organic Acids and Inorganic Anions in Boric Acid-Treated Power Plant Waters Using an Automated Reagent-Free Ion Chromatography System. https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/AN-185-IC-Organic-Acids-Inorganic-Anions-Boric-Power-Plant-Water-LPN1996-EN.pdf

3. Thermo Scientific Technical Note 73982: Techniques for successful trace anion and trace cation determinations in high purity waters. https://appslab.thermofisher.com/App/4546/tn73982-trace-techniques

4. Thermo Scientific Dionex ICS-6000+ Ion Chromatography System Operator's Manual, December **2018**. https://assets.thermofisher.com/TFS-Assets/CMD/manuals/man-22181-97002-ics-6000-man2218197002-en.pdf

5. Thermo Scientific Dionex IonPac AS28-Fast-4μm column manual. https://assets.thermofisher.com/TFS-Assets/CMD/manuals/Man-065675-IC-IonPac-AS28-4um-Man065675-EN.pdf

6. ICH Guideline Q2B, *Validation of Analytical Procedures*, Methodology (CPMP/ICH/281/95), Geneva, Switzerland, November **1996**.

Appendix A. Chromeleon CDS programs

Table A1. Small loop program for standards

Time (min)	Chromeleon CDS command	Comments
-10.150	EluentGenerator.EGC_1.Concentration 7.00 [mM]	Equilibrate column and concentrator for approximately 5 min.
	EluentGenerator.EGC_2.CR_TCOperatingMode Sample_Preparation	Choose "Sample_Preparation" from the three options: RFIC Sample_Preparation Water_Purification
	EluentGenerator.EGC_2.CR_TC	On
	DC.InjectValve_1.InjectPosition	
	DC.AM_HP1.A	
-5.210	DC.AM_HP1.B	Switches 10 μL loop on the 10-port valve in line with Dionex AS-HV autosampler.
-5.200	Sampler.Inject Sampler.Position = R0 Sampler.GotoPosition	Dionex AS-HV autosampler loads standard on 10 μL loop.
-5.150	DC.AM_HP1.A DC.InjectValve_1.LoadPosition	DI water from DP2 transfers standard from 10 μL loop to concentrator and rinses matrix from concentrator with 10 mL DI water.
0.000	DC.InjectValve_1.InjectPosition	Standard is injected on the analytical column.
	CDet1.CD_1.AcqOn CDet1.CD_1_Total.AcqOn	Start data acquisition.
6.000	EluentGenerator.EGC_1.Concentration 7.00 [mM]	Start KOH gradient.
8.000	EluentGenerator.EGC_1.Concentration 20.00 [mM]	

Table A1 (continued). Small loop program for standards

Time (min)	Chromeleon CDS command	Comments
11.000	EluentGenerator.EGC_1.Concentration 72.00 [mM]	End KOH gradient.
25.000	EluentGenerator.EGC_1.Concentration 72.00 [mM]	
	CDet1.CD_1.AcqOff CDet1.CD_1_Total.AcqOff	End data acquisition.
	DC.Column_TC.ReleaseExclusiveAccess DC.Compartment_TC.ReleaseExclusiveAccess End	

Table A2. Large loop program for samples

Time (min)	Chromeleon CDS command	Comments
-11.150	EluentGenerator.EGC_1.Concentration 7.00 [mM]	Equilibrate column and concentrator for approximately 5 min.
	EluentGenerator.EGC_2.CR_TCOperatingMode Sample_Preparation	Choose "Sample_Preparation" from the three options: RFIC Sample_Preparation Water_Purification
	EluentGenerator.EGC_2.CR_TC	On
	DC.InjectValve_1.InjectPosition	
	DC.AM_HP1.B	
-6.210	DC.AM_HP1.A	Switches 2 mL loop on the 10-port valve in line with Dionex AS-HV autosampler.
-6.200	Sampler.Inject Sampler.Position = R0 Sampler.GotoPosition	Dionex AS-HV autosampler loads sample on 2 mL loop.
-6.150	DC.AM_HP1.B DC.InjectValve_1.LoadPosition	DI water from DP2 transfers sample from 2 mL loop to concentrator and rinses matrix from concentrator with 10 mL DI water.
0.000	DC.InjectValve_1.InjectPosition	Sample is injected on the analytical column.
	CDet1.CD_1.AcqOn CDet1.CD_1_Total.AcqOn	Start data acquisition.
6.000	EluentGenerator.EGC_1.Concentration 7.00 [mM]	Start KOH gradient.
8.000	EluentGenerator.EGC_1.Concentration 20.00 [mM]	
11.000	EluentGenerator.EGC_1.Concentration 72.00 [mM]	End KOH gradient.
25.000	EluentGenerator.EGC_1.Concentration 72.00 [mM]	
	CDet1.CD_1.AcqOff CDet1.CD_1_Total.AcqOff	End data acquisition.
	DC.Column_TC.ReleaseExclusiveAccess DC.Compartment_TC.ReleaseExclusiveAccess End	

Table A3. Program for spiking samples in line with a calibration standard

Time (min)	Chromeleon CDS command		Comments
-11.350	EluentGenerator.EGC_1.Concentration 7.00 [mM]		Equilibrate column and concentrator for approximately 5 min.
	EluentGenerator.EGC_2.CR_TCOperatingMode Sample_Preparation		Choose "Sample_Preparation" from the three options: RFIC Sample_Preparation Water_Purification
	EluentGenerator.EGC_2.CR_TC		On
	DC.InjectValve_1.InjectPosition		
	DC.AM_HP1.B		
-6.600	DC.AM_HP1.A		Switches 2 mL loop on the 10-port valve in line with Dionex AS-HV autosampler.
-6.550	Sampler.Inject Sampler.Position = R0 Sampler.GotoPosition		Dionex AS-HV autosampler loads sample on 2 mL loop.
-6.450	DC.AM_HP1.B DC.InjectValve_1.LoadPosition		DI water from DP2 transfers sample from 2 mL loop to concentrator and rinses matrix from concentrator with 10 mL DI water.
-5.300	EluentGenerator.EGC_2.CR_TC	Off	
	DP.Pump_2.Motor	Off	
	Sampler.Inject	Position = R22 Volume = 2.00	Dionex AS-HV autosampler rinses needle with DI water then loads standard from position R22. This position represents the location of the calibration standard (in the Dionex AS-HV autosampler tray) used to spike the sample. This should be changed depending on the exact location of the standard in the tray.
-5.200	Sampler.Position Sampler.GotoPosition DP.Pump_2.Motor	R0 On	
-5.100	EluentGenerator.EGC_2.CR_TC	On	
-5.000	DC.AM_HP1.A		DI water from DP2 transfers standard from 10 µL loop to concentrator.
0.000	DC.InjectValve_1.InjectPosition		Standard is injected on the analytical column.
	CDet1.CD_1.AcqOn CDet1.CD_1_Total.AcqOn		Start data acquisition.
6.000	EluentGenerator.EGC_1.Concentration 7.00 [mM]		Start KOH gradient.
8.000	EluentGenerator.EGC_1.Concentration 20.00 [mM]		
11.000	EluentGenerator.EGC_1.Concentration 72.00 [mM]		End KOH gradient.
25.000	EluentGenerator.EGC_1.Concentration 72.00 [mM]		
	CDet1.CD_1.AcqOff CDet1.CD_1_Total.AcqOff		End data acquisition.
	DC.Column_TC.ReleaseExclusiveAccess DC.Compartment_TC.ReleaseExclusiveAccess End		

Learn more at **thermofisher.com/IC**

thermo scientific