

# Determination of trace anions in borated waters by ion chromatography using a large-volume direct injection

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## Goal

To develop a simple and robust IC method for the determination of trace fluoride, chloride, nitrate, phosphate, and sulfate in lithium-containing borated waters

## Introduction

In pressurized water reactor (PWR) power plants, boric acid is added in the reactor coolant to control the nuclear reaction in the primary reactor.<sup>1</sup> The pH of the coolant is crucial in maintaining the system because a pH lower than 6.9 (at an elevated temperature of ~300 °C) can cause accelerated corrosion of the fuel rod cladding.<sup>2</sup> Lithium hydroxide is often added to the coolant to achieve the desired pH to prevent crud buildup. In PWR plants, it is critical to measure trace levels of ionic impurities in borated water for the identification and prevention of corrosive conditions. The presence of low µg/L (ppb) concentrations of chloride and sulfate can make the stainless-steel components of a power plant, such as steam generators, boiler tubes, condenser tubes, and turbine blades,



susceptible to stress-induced corrosion cracking. Thus, corrosive ions should be minimized and continuously monitored.

Ion chromatography (IC) is the most popular technique for the determination of anions in power plant waters because it provides the required sensitivity to detect trace-level concentrations.<sup>3-7</sup> Thermo Scientific™ Dionex™ Application Note (AN) 114 describes the determination of trace anions in high-purity waters using direct injection and a two-step isocratic elution.<sup>3</sup> In AN114, the Thermo Scientific™ Dionex™ IonPac™ AS14 analytical column is used with manually prepared borate eluent to effectively

resolve the weakly retained analytes in high-purity waters. For the determination of trace anions in borated waters, three Thermo Scientific Dionex application documents, AN166<sup>4</sup>, AN185<sup>5</sup>, and AU175<sup>6</sup>, describe the use of Dionex IonPac AS14, Thermo Scientific™ Dionex™ IonPac™ AS15, and Thermo Scientific™ Dionex™ IonPac™ AS22 analytical columns, respectively, with tetraborate eluent generated by inline mixing of boric acid with electrolytically generated potassium hydroxide. Although AN185 and AU175 demonstrate the labor-saving benefit of using the electrolytically generated eluent, the borate from the samples elutes between the anions of interest, which can pose a challenge for accurate quantification. To minimize interference from the borate peak, matrix elimination is applied in AN185, although that increases method complexity.

Simulated boric acid-treated power plant waters in AN166 did not include lithium addition. Both AN185 and AU175 analyze lithium-containing borated waters. AN185 uses a potassium hydroxide eluent produced by an eluent generator and the addition of a continuously regenerated cation trap column (Thermo Scientific™ Dionex™ CR-CTC II continuously regenerated cation trap column) in the sample flow path to remove lithium and other cations from the sample. AU175 uses the same eluent approach as AN166 (i.e., titration of 50 mM boric acid online with potassium hydroxide) but with the addition of the Dionex CR-CTC-II column as in AN185. AU191<sup>7</sup> uses an approach similar to AN114; a Dionex IonPac AS14 column and manually prepared eluent are used with slightly modified elution conditions to determine fluoride, chloride, and sulfate in simulated borated waters with added lithium.

This Application Update (AU) revises AN166 using the Thermo Scientific™ Dionex™ ICS-6000 system with an eluent generator module equipped with a Thermo Scientific™ Dionex™ EGC 500 potassium hydroxide (KOH) eluent generator cartridge, and a Dionex IonPac AS14 (2 × 150 mm) column for trace-level anion analysis. The experimental approach shown in this work combines the direct injection, electrolytically generated tetraborate eluent approach to analyze lithium-containing borated waters for fluoride, chloride, nitrate, phosphate, and sulfate. The large-volume direct injection technique achieves sensitive detection at low to sub- $\mu\text{g/L}$  levels without using a concentrator column, sample loading pump, and additional valve. Similar to the results seen in AN166, the borate peak elutes early and is well resolved from the target anions, therefore obviating the need for matrix elimination.

## Experimental

### Equipment

- Dionex ICS-6000 HPIC system including:
    - Dionex ICS-6000 DP Pump module
    - Dionex ICS-6000 EG Eluent Generator module with high-pressure degasser module
    - Dionex ICS-6000 Low Temperature DC Detector/Chromatography module with two injection valves
    - CD Conductivity Detector
    - Tablet control
  - Thermo Scientific™ Dionex™ AS-AP Autosampler with Tray Temperature Control (P/N 074926)\*, sample syringe, 5 mL (P/N 074308), and buffer line, 8.5 mL (P/N 075520)
- \* The Dionex AS-AP autosampler comes with pre-installed 250  $\mu\text{L}$  sample syringe, and 1.2 mL buffer line. For trace anion analysis we use large-volume injections, thus we need 5 mL sample syringe and 8.5 mL buffer line as replacements.
- Thermo Scientific™ Dionex™ IonPac™ ATC-HC 500 borate form, Anion Trap Column, 9 × 75 mm (P/N 075979)
  - Dionex EGC 500 KOH Eluent Generator Cartridge (P/N 075778)
  - Thermo Scientific™ Dionex™ AERS 500e Anion Electrolytically Regenerated Suppressor for External Water Mode (2 mm) (P/N 302662)
  - The Thermo Scientific™ Dionex™ Suppressor External Regen Installation Kit (P/N 038018) contains all the components needed to install and operate the Dionex AERS 500e with a pressurized regenerant reservoir. The kit contains the Dionex ERS Installation Parts Kit (P/N 039055), a 25-psi regulator (P/N 038201), and a 4-liter regenerant reservoir (P/N 039164).
  - Thermo Scientific™ Dionex™ Vial Kit, 10 mL polystyrene with caps and blue septa (P/N 074228)
  - Corning™ polystyrene non-treated culture flasks (Fisher Scientific™, P/N 08-757-502) for low-level standards and samples
  - Gloves, Ansell™ Nitrilite™, nitrile cleanroom Class 5 (Fisher Scientific, P/N 19-014)
  - Berkshire™ Gamma Wipe™ 120 cleanroom wipes, polyester (Berkshire, P/N GW120ST15; Fisher Scientific, P/N 18-999-306)

- Thermo Scientific™ Nalgene™ Rapid-Flow™ filter flask containers for soaking vials, caps, septa, pipette tips, or connectors (P/N 164-0020)
- Thermo Scientific™ Nalgene™, 125 mL Sterile Nalgene High-Density Polyethylene (HDPE) Bottles (P/N N411-0125)

### Reagents and standards

- Deionized (DI) water, Type I reagent grade, 18 MΩ·cm resistance or better
- Boric acid, J. T. Baker reagent grade – Do not use lower quality boric acid for the eluent.
- Sodium borate, tetrahydrate, J. T. Baker reagent grade
- Lithium hydroxide, monohydrate, ≥98%, ACS reagent (Fisher Scientific P/N AC41332)
- 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)
- Thermo Scientific™ Dionex™ Nitrate standard 1000 mg/L, 100 mL (P/N 056497)

### Software

- Thermo Scientific™ Chromeleon™ Chromatography Data System software version 7.2

### Preparing for successful trace level (<10 µg/L) ion determinations

There are many sources of contamination that can interfere with reliable and consistent trace ion determinations. Working in a trace analysis environment requires patience, consistent work routines, and awareness of normal lab activities and items that pose contamination risks. This section discusses and reviews the importance of clean water; an isolated clean, low-particle work environment; the selection and use of laboratory gloves; the impacts of behaviors, social interactions, and personal care products on trace-level anion analysis; and tools suitable for the trace analysis work area (Table 1). For details, refer to Technical Note (TN) 112.<sup>8</sup>

### Preparation of solutions and reagents

#### 50 mM boric acid eluent

Weigh 3.09 g of boric acid. Carefully add this amount to a 1 L volumetric flask containing about 500 mL DI water. Dilute to the 1 L mark and mix thoroughly. Use a stir bar or ultrasonic bath to ensure that boric acid is completely dissolved. Filter the solution through a 0.2 µm nylon filter unit. Transfer this solution to an eluent container and vacuum degas for 5 min.

#### Standard solutions

For successful trace ion determinations, it is crucial to minimize contamination to the sample and standard containers. Here are some of the general practices on the preparation of containers followed by a discussion on preparation of standards.

#### Preparing containers

Preparing samples and standards for trace analysis requires containers that have low extractable ionic contamination and special handling techniques. Two types of containers have low ionic contamination suitable for trace analysis: non-treated polystyrene culture flasks and FEP containers. Non-treated polystyrene (Corning) culture flasks are recommended for storing samples and standards. Never use caps with liners or filters because the liners and filters typically contain mg/L concentrations of chloride and sulfate.

To prepare (clean) the flasks, turn on the 18.2 MΩ·cm DI water, rinse the flask five times with this water, fill the flask to the top (leaving as little air as possible), cap it with a cap that has been pre-rinsed five times, and let soak overnight. Repeat the same rinsing and soaking process daily for at least three days.

#### Stock anion standard solution (1000 mg/L)

Several of the analytes of interest are available as 1000 mg/L ion standard solutions from Thermo Fisher Scientific or other commercial sources. In cases where standards are not available, 1000 mg/L standards can be prepared by dissolving the appropriate amounts of the corresponding mass in 100 mL of DI water according to Table 2. We recommend making a 100 mL final volume of 1000 mg/L stock standards in 125 mL high-density polyethylene (HDPE) containers. Concentrated standards are stable for at least one month when stored at 4 °C.

**Table 1. Preparing for successful trace level ion determinations**

Item	Recommendation
DI water	Use only freshly generated 18.2 MΩ-cm deionized (DI) water.
Work environment	<ul style="list-style-type: none"> <li>a. Isolate the instrument in a low-traffic area away from heater, air conditioner, and instrument vents, and away from chemical storage and weighing areas.</li> <li>b. Wipe down all surfaces using cleanroom wipes and fresh DI water.</li> <li>c. Minimize group discussions near the work area. People can stir up and emit dust particles and aerosols of ionic contamination.</li> </ul>
Gloves	<ul style="list-style-type: none"> <li>a. Always wear fresh gloves in the trace analysis work area.</li> <li>b. Use powder-free Class 10 or Class 100 undyed nitrile cleanroom gloves (such as Ansell Nitrilite, Fisher Scientific, P/N 19-014-687, 19-014-688, 19-014-689).</li> <li>c. Touch only the glove sleeves when putting on gloves. Never touch the glove tips.</li> <li>d. Select the glove size that results in a comfortable but tight fit. The glove tips should not extend past your fingers more than a few millimeters. Oversize gloves can easily contaminate the sample containers.</li> <li>e. Discard the gloves after touching your face, hair, or extra surfaces, especially any concentrated standards, solid reagents, or paper products.</li> <li>f. Avoid touching the neck or cap of the sample container or standard container.</li> </ul>
Personal	<ul style="list-style-type: none"> <li>a. Avoid personal care products such as deodorant, powders, hair products, makeup, perfume, and lotions.</li> <li>b. Avoid talking, sneezing, laughing, and coughing near the work area to prevent the generation of airborne mists of particles containing high concentrations of chloride, sulfate, and organic acids. Note that one grain of salt in a cup of water is equivalent to ~20 mg/L chloride.</li> </ul>
Sample preparation, sample containers, and sample vials	<ul style="list-style-type: none"> <li>a. Use pipette tips only when preparing concentrated standards, such as the intermediate standard, and not for any low-level work.</li> <li>b. Before using pipette tips, soak them in fresh DI water in a pre-cleaned polystyrene flask, and handle them only with stainless steel alloy (SS 416) tweezers to further ensure cleanliness.</li> <li>c. Avoid use of any cellulose products—including lab wipes, weighing paper, and cotton swabs. These contain high concentrations of chloride and sulfate, and therefore are major sources of contamination.</li> <li>d. Use low-particle, low ionic contamination polyester wipes, such as Berkshire Gamma Wipe 120 Class 10 cleanroom wipes.</li> <li>e. Use either cleanroom adhesive tape or labels or use markers to label samples.</li> <li>f. Do not use plastic weighing dishes to handle anything related to standards and samples; instead, tare final containers and transfer materials directly from their source to the final containers.</li> <li>g. Use only polystyrene or FEP (fluorinated ethylene propylene polymer) for containers and only polystyrene for vials.</li> <li>h. Use only autosampler vial septa that have been verified to be contaminant-free, such as blue septa that come with an AS-AP 10 mL vial kit (P/N 074228) or (preferably) single-use PTFE septa.</li> </ul>

**Table 2. Amounts of compounds used to prepare 100 mL of 1000 mg/L anion standards**

Anion	Compound	Mol. wt.	Mass (g)
F <sup>-</sup>	Sodium fluoride	41.99	0.221
Cl <sup>-</sup>	Sodium chloride	58.44	0.165
SO <sub>4</sub> <sup>2-</sup>	Sodium sulfate	142.04	0.148
NO <sub>3</sub> <sup>-</sup>	Sodium nitrate	84.99	0.137
PO <sub>4</sub> <sup>3-</sup>	Potassium phosphate	136.09	0.143

**Mixed standard solution**

To prepare the mixed intermediate anion standard, turn on and leave on the DI water faucet until the standard is prepared. Follow the same rinsing process on the pre-cleaned flask by rinsing it five times with DI water. Shake out the excess water and tare the flask on a top loading balance. Fill the flask directly from the DI water faucet

with DI water to  $\sim 250 \pm 1$  g. If the water weight is  $< 249$  g, quickly put the flask under the faucet. If the flask contains  $> 251$  g, gently flick the excess water into the sink. (Turn off the DI water.) Record the weight. Using a micropipette with a disposable pipette tip, transfer 25  $\mu$ L each of the certified 1,000 mg/L fluoride, chloride, nitrate, phosphate, and sulfate standards into the flask containing the previously weighed DI water. Record the final weight, cap, gently mix, and recalculate the actual concentrations based on the volume of standard in the total weight. The density of water of 0.99707 g/mL is used for calculations. The approximate concentration of each anion is  $\sim 100$   $\mu$ g/L. This flask should only be used for this standard because it can introduce contamination in lower concentration samples and standards. Therefore, this flask should never be used to store samples or working standards unless the container is re-cleaned and verified clean by testing to  $< 10$  ng/L ion concentrations.

### 1000 mg/L lithium stock solution

Dissolve 0.6044 g lithium hydroxide monohydrate in 100 mL DI water. Store this solution in a 125 mL HDPE container.

### Simulated boric acid treated sample

To prepare a solution containing 2000 mg/L boron and 4 mg/L lithium, add 1.1438 g of boric acid solid and 0.40 mL of the 1000 mg/L lithium stock solution to a 100 mL PMP Class A volumetric flask, then dilute to a final volume of 100 mL with DI water. Store the samples in 125 mL HDPE containers at 4 °C.

### System preparation and setup

The Dionex ICS-6000 HPIC system is configured with a CD Conductivity Detector, eluent generation, and temperature control of the column oven and detector-suppressor compartment. As shown in Figure 1, connect the Dionex IonPac ATC-HC 500 borate form, anion trap column to the outlet of the gradient pump. Because the column is already in the borated form, rinsing with 100 mM tetraborate is unnecessary. After installing the column, rinse with boric acid eluent at 2 mL/min for at least 20 min. Install the Dionex EGC 500 KOH eluent generator cartridge. Condition the cartridge according to instructions in its product manual<sup>9</sup> and the Dionex ICS-6000 System Operator's Manual.<sup>10</sup> Make sure

the pressure is ~2200–2500 psi using the operating conditions described earlier to allow the degas assembly to remove electrolysis gases. If necessary, install additional backpressure tubing between the degas assembly and injection valve to achieve the recommended pressure.

Prepare the Dionex AERS 500e suppressor for use by hydrating the internal membrane. Refer to the product manual for step-by-step instructions on hydration of the 2 mm Dionex AERS 500e suppressor.<sup>11</sup> To minimize damage to the suppressor during hydration, do not add any backpressure tubing coils after the suppressor. To complete the hydration step, wait an additional 20 min without eluent flow before installing the suppressor. Connect Regen Out on the suppressor to the waste. Configure the pressurized water reservoirs to supply external water for suppressor regeneration. Use at least two 4 L bottles plumbed in tandem to ensure uninterrupted external water delivery. Fill the reservoirs with DI water and apply 5–15 psi nitrogen gas to the reservoir to deliver DI water through the regenerant channel. Ensure that the cap of the reservoir is sealed tightly. For more information on installation and operation of a Dionex AERS 500e suppressor, consult the product manual, Document No. 031956. Install and condition the guard and separation columns for 40 min (3 column volumes) using the same conditions.

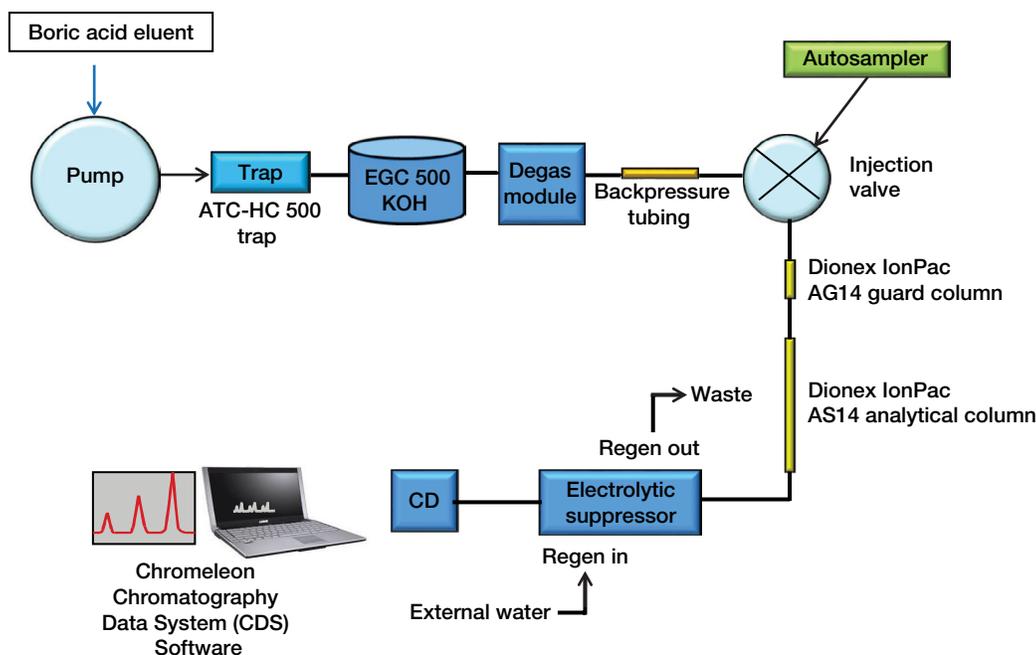


Figure 1. System configuration

Install and configure the Dionex AS-AP Autosampler in Push Mode. Follow the instructions in the Dionex AS-AP Autosampler Operator's Manual (Document No. 065361) to calibrate the sample transfer line to ensure accurate and precise sample injections. Due to the large sample injection volume in this application, a sample syringe size of 5 mL must be installed, and a buffer line assembly of 8.2 mL size is required. Make a 1000 µL sample loop by cutting a 220 cm portion of the green 0.030 in. (0.75 mm) i.d. PEEK tubing. If a different loop or tubing with a different internal diameter is desired, refer to Table 3 to calculate the length needed. The volume of a loop can be verified by measuring the weight difference between the sample loop filled with DI water and the empty loop. The inside diameter of tubing varies by as much as 20% (for example, 0.010 ± 0.002 in.)

**Table 3. Volume per unit length for various tubing internal diameters**

Material	Color	Internal diameter (in)	Internal diameter (mm)	Estimated vol. (µL/cm)
PEEK	Red	0.005	0.125	0.126
PEEK	Black	0.010	0.250	0.506
PEEK	Orange	0.020	0.500	2.022
PEEK	Green	0.030	0.750	4.550

### System operation

To start the system, turn on the pump and immediately turn on the Dionex EGC 500 eluent generator cartridge. Turn on the Dionex AERS 500e suppressor when liquid is flowing through the devices. Confirm that there are no leaks in the chromatographic pathway. Allow the system to equilibrate for 30 min and run a system blank. If properly operating, the system should display the background conductance and noise listed under Conditions (Table 4). Assess the quality of the blank by measuring the short-term noise. In a representative one-minute level portion of the chromatogram, a “peak-to-peak” measurement should be less than 5 nS/cm. It will take at least 4 h for the system to equilibrate to a stable background conductivity for trace analysis. At times there will be brief increases in conductivity that will minimize upon further operation of the system. The elements of the chromatographic instrumentation's flow path (eluent containers, injector, pump, valves, tubing, columns, suppressor, and conductivity cell) are all potential sources of trace-level contamination. Use caution when

switching from a system setup that has previously seen significant concentrations of anions. Rinse with high-purity water to reduce residual contamination. It is therefore a good practice to run a system overnight to equilibrate prior to using it the following day.

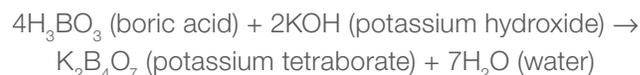
**Table 4. Chromatography conditions**

IC conditions	
System	Dionex ICS-6000
Columns	Dionex IonPac AS14, Analytical, 2 × 250 mm (P/N 046129) Dionex IonPac AG14, Guard, 2 × 50 mm (P/N 046138)
Eluent	50 mM boric acid (bottle A) titrated with potassium hydroxide from the EGC 500 KOH cartridge
Gradient	-7–0 min: 4 mM KOH with 50 mM boric acid (Equilibration step) 0–6 min: 4 mM KOH with 50 mM boric acid 6–18 min: 4–30 mM KOH with 50 mM boric acid 18–30 min: 30 mM KOH with 50 mM boric acid
Flow rate	0.38 mL/min
Injection volume	1000 µL
Column temp.	30 °C
Detection	Suppressed conductivity
Suppressor	Dionex AERS 500e (2 mm) Suppressor, external water mode, 52 mA
External water regenerant flow rate	1 mL/min
Detection/suppressor compartment temp.	20 °C
Run time	30 min
Background conductance	~2.6–2.75 µS/cm
Noise	1–1.5 nS/cm
System backpressure	~2200–2400 psi (100 psi = 0.689 MPa)

## Results and discussion

### Separation

The eluent used in this study is a mixture of potassium tetraborate and potassium hydroxide. The tetraborate eluent was made by a chemical reaction between boric acid and potassium hydroxide:



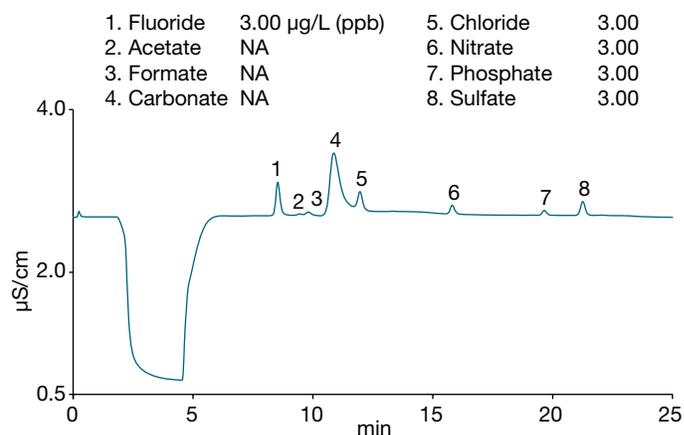
Four moles of boric acid react with two moles of potassium hydroxide to form one mole of tetraborate. The 50 mM boric acid eluent is “titrated” with the potassium hydroxide generated inline through the eluent generator. A Dionex EGC 500 KOH cartridge was used to electrolytically produce high-purity, carbonate-free KOH eluent. A high-capacity anion trap column (Dionex IonPac ATC-HC 500 borate form) was used to trap anionic contaminants in the boric acid eluent. The Dionex IonPac ATC-HC 500 borate form column is placed between the outlet of the gradient pump and the inlet of the Dionex EGC 500 KOH cartridge. Do not use a Continuously Regenerated Trap Column (CR-ATC) for this application, because it would remove anionic compounds including borate ions from the boric acid eluent. Producing tetraborate eluent by mixing boric acid and potassium hydroxide gives better eluent quality than the traditional method of dissolving potassium tetraborate in water, due to the purity of the chemicals available. By making the tetraborate eluent in line with the Dionex EGC 500 KOH cartridge, carbonate is not mixed into the solution and therefore the chromatography is improved. Figure 1 illustrates how this eluent is made online. This technique has several advantages. The eluent strength can be adjusted by the online addition of potassium hydroxide. The background is maintained at the same level during gradient runs because the boric acid concentration is held constant during the run.

The eluent program (Table 4) starts with a low eluent concentration to separate fluoride, chloride, and other weakly retained anions; then a step change to a higher concentration eluent accelerates the elution of the strongly retained anions, including phosphate and sulfate. Figure 2 shows a typical chromatogram for a five anions standard at trace levels. The typical background conductance ranges from ~2.6 to 2.75  $\mu\text{S}/\text{cm}$ . However, the background conductance gradually increases, due to exhaustion of the Dionex IonPac ATC-HC 500 borate form anion trap column. Depending on the purity of the eluent and the degree of  $\text{CO}_2$  intrusion, the Dionex IonPac ATC-HC 500 borate form anion trap column used under the suggested experimental conditions can be effective from 10 to 14 days. A background conductance  $>5 \mu\text{S}/\text{cm}$  at the higher eluent concentration is an indication that the Dionex IonPac ATC HC 500 anion trap column requires regeneration (refer to the Dionex IonPac ATC HC 500 Anion Trap Column Product Manual, Document No. 032697-09, for instruction). The separation is performed at 30 °C to provide consistent retention times during analysis.

Fluoride is well resolved from the system void and from the organic acids (acetate and formate). Sufficient resolution of chloride and sulfate from other anions is also obtained. The large peak at ~11 min is carbonate, the size of which will vary with the amount of dissolved carbon dioxide in the sample. A large direct-injection volume of 1000  $\mu\text{L}$  was used to achieve sufficient sensitivity at low analyte concentrations while keeping the method simple and robust. External water regeneration was chosen over the recycle mode to reduce baseline noise.

**Table 5. Concentrations of calibration standards**

	Level 1 ( $\mu\text{g}/\text{L}$ )	Level 2 ( $\mu\text{g}/\text{L}$ )	Level 3 ( $\mu\text{g}/\text{L}$ )	Level 4 ( $\mu\text{g}/\text{L}$ )
1. Fluoride	0.30	1.00	3.00	10.0
2. Chloride	0.30	1.00	3.00	10.0
3. Nitrate	0.30	1.00	3.00	10.0
4. Phosphate	0.30	1.00	3.00	10.0
5. Sulfate	0.30	1.00	3.00	10.0



**Figure 2. Separation of a trace anion standard**

### System and water blanks

In all trace ion applications, the system and water blanks can often compromise detection limits of the analytical method and therefore are an important parameter when assessing the method qualification. A system blank is a blank injection where no injection is made through the autosampler, but the system is operated for the whole run with the method conditions. To set a system blank injection in the Chromeleon CDS software, we put a “blank” in the “type of sample” column in the injection sequence. A representative system blank and DI water blank (injecting DI water rather than sample) for this method are shown in Figure 3.

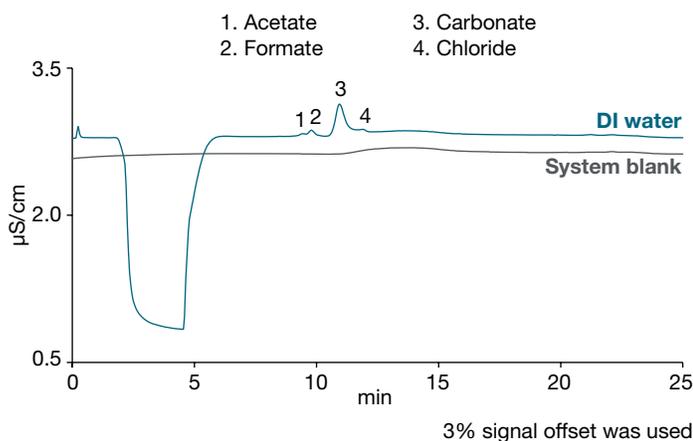


Figure 3. Chromatograms of a system blank (no injection) and a DI water injection blank

### Calibration

Calibration curves were obtained with standards prepared in DI water using the concentrations listed in Table 5. Figure 4 displays the chromatograms of four calibration standards. Calibration curves for the anions of interest were linear and had coefficients of determination ( $r^2$ ) greater than 0.99 (Table 6).

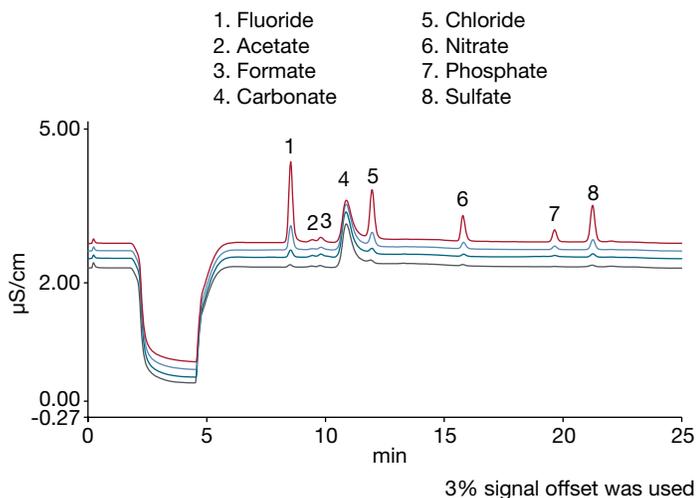


Figure 4. Chromatograms of calibration standards 1 to 4

Table 6. Calculated coefficients of determination

Analyte	Range (µg/L)	Coefficient of determination ( $r^2$ )
Fluoride	0.30–10.0	0.998
Chloride	0.30–10.0	0.997
Nitrate	0.30–10.0	0.998
Phosphate	0.30–10.0	0.997
Sulfate	0.30–10.0	0.999

### Method detection limit

Method detection limits (MDLs) were determined based on three times the signal-to-noise (S/N) ratio. Baseline noise (N) was determined by measuring the peak-to-peak noise in a representative one-minute segment of the baseline where no peaks elute, but close to the analyte peak. The signal (S) was determined from the average peak height of three injections of the lowest level standard (3–5 times the estimated MDL). Table 7 summarizes the MDLs for the target analytes. In our experiments, a standard MDL calculation method cannot be used for chloride because it was found as a contaminant in the DI water blanks (Figure 2). In such cases, if the contamination amount is more than the MDL, then the amount of contamination can be effectively considered the MDL. In other cases, the MDL is what is determined with the low concentration standard. MDLs will vary from lab to lab depending on water quality and lab environment and ultimately each lab must decide how they handle MDLs in case of low-level contamination.

Table 7. Method detection limits

Analyte	MDL (µg/L)
Fluoride	0.030
Chloride*	0.11
Nitrate	0.10
Phosphate	0.35
Sulfate	0.20

\* Found as contaminant in the DI water blanks

### Analysis of simulated borated water

This method is applicable to high-purity power plant waters containing up to 2500 mg/L boron and 10 mg/L lithium. Figure 5 shows the chromatogram of a simulated borated water sample with (containing 2000 mg/L boron plus 4 mg/L lithium) and without added lithium (containing 2000 mg/L boron). The chromatograms look the same. Fluoride may be low due to presence of lithium, thus for the highest fluoride accuracy, a Dionex CR-CTC II continuously regenerated cation trap column should be used to remove lithium from the sample as in AN185.<sup>5</sup> In AU175, 2% less fluoride was noted in the absence of the Dionex CR-CTC II column.<sup>6</sup> The large borate matrix peak that begins at 1.7 min returns to the baseline before the first analyte of interest elutes. No significant differences in peak efficiencies or retention times were observed for the peaks detected in the matrix blank compared to the standard prepared in DI water.

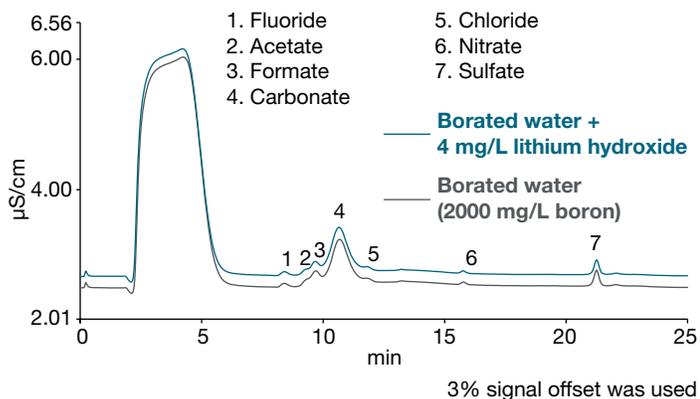


Figure 5. Chromatogram of simulated borated water with and without added lithium

### Recoveries and precision study

To validate this method, recoveries of five anions from a simulated borated water sample that contained 2000 mg/L boron plus 4.0 mg/L lithium were measured. The borated water sample was spiked at two levels, 0.3 µg/L and 1 µg/L. Figure 6 displays the chromatograms of unspiked and spiked borated water samples. Three replicates of the spiked samples were analyzed and recoveries for the five anions in the simulated borated water using two spike levels were in the range of 86% to 116% (Table 8).

Seven replicates of a simulated borated water containing 2000 mg/L boron plus 4 mg/L lithium were injected (Figure 7). The retention time and peak area precisions for standards and samples were less than or equal to 0.11% and 5%, respectively (Table 9).

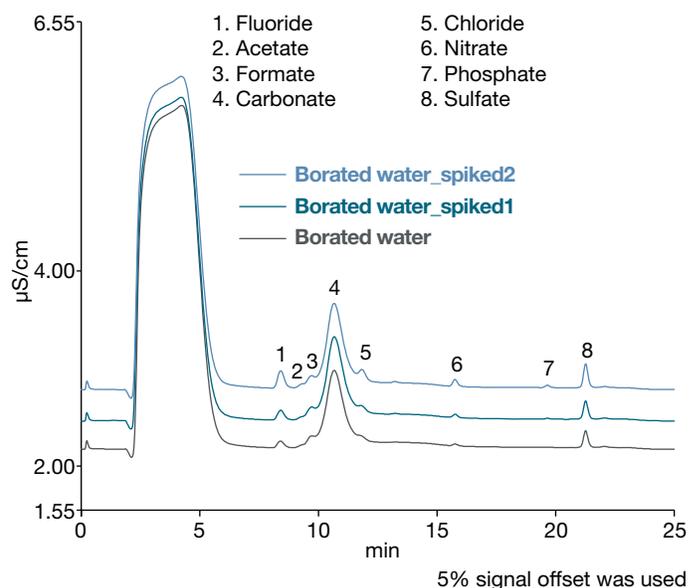


Figure 6. Chromatograms of simulated borated water along with spiked borated water at 0.3 and 1 µg/L levels

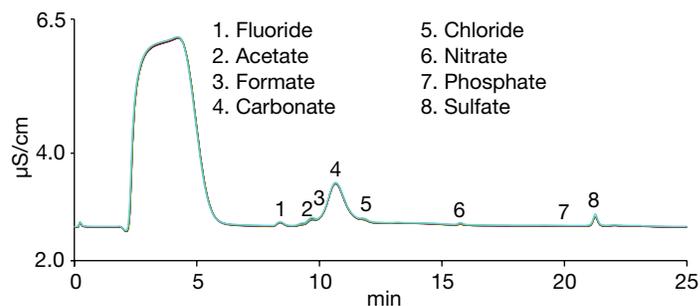


Figure 7. Overlay of seven chromatograms of simulated borated water

Table 8. Spike recovery results in simulated borated water

Analyte	Amount found (µg/L)	Spiked 1 (µg/L)	Recovered 1 (µg/L)	Recovery (%)	Spiked 2 (µg/L)	Recovered 2 (µg/L)	Recovery (%)
Fluoride	0.90	0.30	1.17	90.4	1.00	2.01	111
Chloride	0.208	0.30	0.466	86.3	1.00	1.22	101
Nitrate	0.48	0.30	0.79	104	1.00	1.64	116
Phosphate	Not detected	0.30	0.340	113	1.00	1.15	115
Sulfate	2.73	0.30	3.00	91.0	1.00	3.78	105

Table 9. Precision (RSD, n=7) of retention time (RT) and peak area of five anions

Analyte	0.3 µg/L anion std		Simulated borated water		Simulated borated water + 0.3 µg/L anion std.		Simulated borated water + 1 µg/L anion std.	
	RT	Peak area	RT	Peak area	RT	Peak area	RT	Peak area
Fluoride	0.04	3.16	0.02	1.13	0.03	1.39	0.02	0.22
Chloride	0.06	1.56	0.11	0.75	0.03	3.28	0.02	4.50
Nitrate	0.02	2.73	0.01	3.48	0.02	1.41	0.02	3.88
Phosphate	0.04	3.69	n.a	n.a	0.02	1.93	0.01	1.07
Sulfate	0.01	1.65	0.01	0.55	0.01	0.11	0.01	1.61

## Conclusion

This study demonstrates the determination of trace anions in simulated borated waters containing lithium using a borate eluent and a large-volume direct injection. This method is based on AN166 and extends the analysis of anions in high-purity water to lithium-containing borated waters. The method is validated by recovery and precision studies on simulated borated water samples. The MDLs of fluoride, chloride, nitrate, phosphate, and sulfate reported in this study are comparable to those in AN166.

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