Determination of Organic Acids and Inorganic Anions in Lithium-Containing Boric Acid-Treated Nuclear Power Plant Waters

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 2500 mg/L (ppm), corresponding to 1.4 percent 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 (ppb) concentrations from the water source (or materials such as ion-exchange polisher resins) can serve as catalysts for corrosion.

Two approaches highlight the advantages of electrolytic eluent generation-based systems for trace anion determination in borated waters. In Dionex AN 166, samples are introduced by a high-volume direct-injection technique and anions are separated using a precisely controlled tetraborate eluent generated from the addition of electrolytically produced potassium hydroxide gradient to boric acid eluent.[2] Simulated boric acid-treated power plant waters in AN 166 did not include lithium addition. If sample is taken after the cation polishing system in the PWR, the need for lithium removal is minimized. An alternate approach described in Dionex AN 185

concentrates the sample after removing lithium and separates anions with an electrolytically generated potassium hydroxide gradient.[3]

The experimental approach shown in this work combines the direct injection, electrolytically generated tetraborate eluent approach to analyze lithium-containing borated waters for fluoride, formate, chloride, and sulfate with the addition of a continuously regenerated cation trap column (CR-CTC II) to remove lithium and other cations from the sample. This approach uses a single-pump ion chromatography system without a concentrator column to determine single-digit µg/L sensitivities of the targeted analytes.

EQUIPMENT

Dionex ICS-2100 Ion Chromatography System including:

Single isocratic pump

Vacuum degasser

Eluent generator

High pressure 6-port injector

Column heater enclosure

Conductivity cell detector

Chromatography consumables:

IonPac® ATC-HC anion trap column, borate form (P/N 064755)

EluGen II EGC II KOH cartridge (P/N 058900)

IonPac AG22 guard column, 2 × 50 mm (P/N 064135)

IonPac AS22 analytical column, 2 × 250 mm
(P/N 064137)
Anion Self-Regenerating Suppressor (ASRS®) 300,
2 mm (P/N 064555)
CR-CTC II trap column (P/N 066262) with
CR-TC Extension Power Cable (P/N 060460)

AS Autosampler with 10 mL vial tray:
10 mL Polystyrene vials/septa/caps kit (P/N 055058)
5 mL Sample syringe (P/N 053915)

Suppression external water kit (P/N 038018)

Chromeleon® Chromatography Data System (CDS)
Version 6.8 or 7 software

250 mL Polystyrene tissue culture flask with caps
(P/N 064235) for sample/standard preparation

Green PEEK™ tubing (P/N 052305), 0.030 in. (0.75 mm)
to make a 1000 µL sample loop

Helium or nitrogen, 4.5-grade (99.995%) or better,
<5 ppm oxygen (Praxair)

Filter unit, 0.2 µm nylon (Nalgene® 90 mm Media-Plus,
Nalge Nunc International P/N 164-0020) or
equivalent nylon filter

Polypropylene Straight-Sided Jar (Nalge Nunc
International P/N 2118-0032) or equivalent for
soaking autosampler vials, caps, and septa

Vacuum pump (Gast Manufacturing Corp.
P/N DOA-P104-AA) or equivalent for
degassing eluents

REAGENTS, STANDARDS, AND SAMPLES

Deionized water, 18 MΩ-cm resistance or higher

Boric acid, ACS reagent-grade (JT Baker P/N 0084)
or better

Lithium hydroxide, monohydrate, ACS reagent-grade
(JT Baker P/N P406)

Fluoride standard, 1000 mg/L (Dionex P/N 37158)

Chloride standard, 1000 mg/L (Dionex P/N 037159 or
Ultra Scientific P/N ICC-002)

Sulfate standard, 1000 mg/L (Dionex P/N 037160 or
Ultra Scientific P/N ICC-006)

Sodium acetate, anhydrous, ACS reagent-grade
(JT Baker P/N 3470)

Sodium formate, ACS Certified (Fisher P/N S648)

CONDITIONS

Columns: IonPac AG22 Guard column,
                  2 × 50 mm (P/N 064135)

                  IonPac AS22 Analytical column,
                  2 × 250 mm (P/N 064137)

Temperature: 35 °C
Flow Rate: 0.38 mL/min
Eluent: 200 mM Boric acid titrated with
                  KOH from EGC II KOH

Gradient:

Time (min)	KOH Conc. (mM)	Comments
-1.0	14	Re-Equilibration
0	14	Inject*
9.9	14	Start Gradient
10.0	90	End Gradient
24.9	90	Start Re-Equilibration Gradient
25.0	14	End Re-Equilibration Gradient

*Aspirate sample at speed 2, deliver sample at speed 1.

Injection Volume: 1000 µL (Full loop)
Detection: Suppressed conductivity
Suppressor: ASRS 300, 2 mm (P/N 064555),
                  external water mode (1.5 to 2 mL/min)

Suppressor
Current: 85 mA

Expected Background
  Conductivity: 7 to 8 µS (14 mM Potassium
                  hydroxide, 200 mM boric acid)
  Noise: <5 nS/min peak-to-peak

System
Backpressure: 16.6 to 18.0 MPa (2400 to 2600 psi)

PREPARATION OF SOLUTIONS AND REAGENTS

Best Practices for Cleaning Solution/Reagent Containers

It is essential to use high-quality water of high
resistivity (18 MΩ-cm) containing as little dissolved
carbon dioxide, ionic impurities, organics, microorganisms,
and particulate matter larger than 0.2 µm as possible.
Prior sparging and filtration through 0.2 µm porosity
nylon filter under vacuum is recommended to remove
particulates and reduce dissolved air. Keep the eluent
solution blanketed under 34 to 55 kPa (5 to 8 psi) of
helium or nitrogen at all times to reduce contamination
from carbon dioxide gas and other contaminants.

Do not use glass containers. High-quality polystyrene and polypropylene vessels must be rinsed at least three times with filtered deionized water, soaked overnight, and rinsed again before use. Autosampler vials, caps, and septa must be rinsed, soaked overnight, and rinsed again before use. Avoid contact with the inside surface of all eluent and reagent containers. Handle containers with vinyl or nitrile disposable gloves that have been rinsed with deionized water and air dried.

Boric Acid Eluent

Weigh 12.36 g boric acid into the bottom of a rinsed, presoaked 1 L Nalgene polystyrene filter unit. Dissolve the boric acid in approximately 500 g deionized water. Add additional water to produce a solution weight of 1000 g. Filter and degas this solution through a second Nalgene polystyrene filter unit (reserve these units exclusively for boric acid eluent preparation). If using a 2 L eluent bottle, repeat this procedure. Highly accurate boric acid eluent concentrations are not necessary because boric acid is always in molar excess when titrated with electrolytically generated KOH.

Anion Stock Standards

Use purchased 1000 mg/L fluoride, chloride, and sulfate stock solutions for subsequent dilutions. Prepare individual 1000 mg/L formate and acetate stock solutions by adding 0.3776 g sodium formate and 0.3473 g sodium acetate to presoaked and rinsed 250 mL polypropylene bottles. Add deionized water to produce a solution weight of 250 g and make all dilutions gravimetrically to ensure high accuracy. Store stock solutions at 4 °C.

Prepare intermediate mixed-anion standards in the low-mg/L range by adding appropriate weights of stock solutions to a 250 mL presoaked/rinsed tissue culture flask and then add deionized water to the appropriate solution weight. These mixed-anion standards may be stored at 4 °C for up to 1 week.

Sample Preparation

Prepare 1000 mg/L lithium stock solution by adding 1.511 g lithium hydroxide monohydrate to a 250 mL presoaked/rinsed tissue culture flask and add deionized 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 boric acid solid and lithium hydroxide stock solutions to presoaked/rinsed tissue culture flasks and adding deionized water to a solution weight of 250 g. Recovery studies use three boron–lithium concentrations— 1000 mg/L boron with 2.0 mg/L lithium,

Table 1. 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 Soln.* (g)
1000 B + 2.0 Li	1.4305	0.5000
2000 B + 4.0 Li	2.8610	1.0000
2500 B + 5.0 Li	3.5763	1.2500

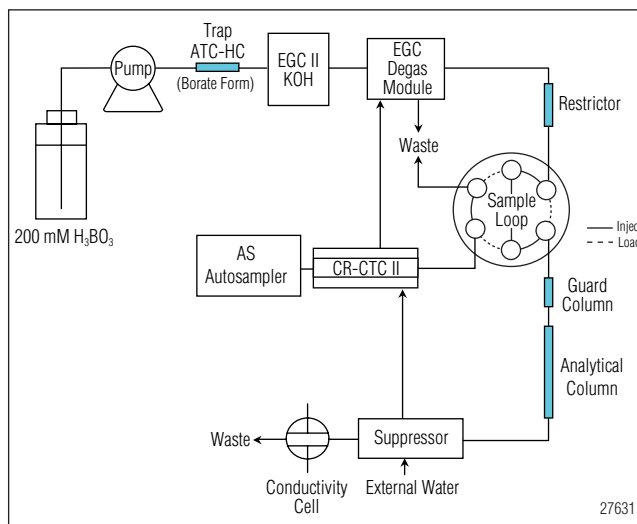*1000 mg/L lithium stock solution

Figure 1. System configuration for direct injection of borated waters containing lithium.

2000 mg/L boron with 4.0 mg/L lithium, and 2500 mg/L boron with 5.0 mg/L lithium—whereas the precision study uses only the 2000 mg/L boron with 4 mg/L lithium simulated matrix. Table 1 shows the weights of boric acid and 1000 mg/L lithium stock solution used to prepare the matrices.

System Preparation and Setup

Figure 1 illustrates the system configuration for this work. Refer to the System Preparation and Setup section of AN 166 for details of system setup with the following changes and additions:

- Because the ATC-HC is already in the borated form (P/N 064755), rinsing with 100 mM tetraborate is unnecessary. After installing the ATC-HC between the pump and EGC, rinse with boric acid eluent at 2 mL/min for at least 20 min. The ATC-HC should be periodically regenerated when any significant increase in the background conductivity beyond 10 µS is observed, indicating that the ATC-HC has exceeded its capacity to trap anionic contaminants.

- The presence of the CR-CTC II column plumbed between the AS transfer line and the sample inlet line of the injection valve generates backpressure on the needle seal assembly that may exceed the 690 kPa (100 psi) specification during sample delivery. To avoid this pressure limitation, it is recommended that a 5 mL syringe be installed in the sample tower but configured on the AS as a 10 mL syringe. When the syringe dispense speed setting of 1 (slowest dispense speed) is selected, backpressure exceeding 100 psi at the needle seal assembly will be avoided.
- Configuring a 10 mL syringe while installing a 5 mL syringe requires that the sample volume number in the sequence be doubled. Using a 1000 µL sample loop, it is recommended that a value of 4000 µL be used in the Volume column of the sequence and as the Flush volume in the Program (Instrument Method) file.
- Other autosamplers,such as the AS-DV, that will satisfactorily deliver sample with backpressure created by the CR-CTC II column in-line are acceptable.
- To avoid permanent damage, do not leave power on to the CR-CTC II column with no flow through the eluent channel. In the Program (Instrument Method) file, turn on the CR-CTC II column power immediately before the Load command and turn off the power after the Wait/InjectState command.
- It is highly recommended that a deionized water reservoir be connected to the rear seal wash of pumping systems that have this option. Small leaks of boric acid eluent can compromise the rear seal when liquid from the leak evaporates.

RESULTS AND DISCUSSION

Separation

Figure 2 shows separation of target anions plus acetate in deionized water using the 2 mm i.d. IonPac AS22 column set. The IonPac AS22 column was chosen for its high capacity, which is reflected in the higher KOH concentration needed for analyte elution, compared to the IonPac AS14 column set used in AN 166. The tetraborate eluent was generated by the reaction of boric acid with electrolytically generated potassium hydroxide according to the following equation:
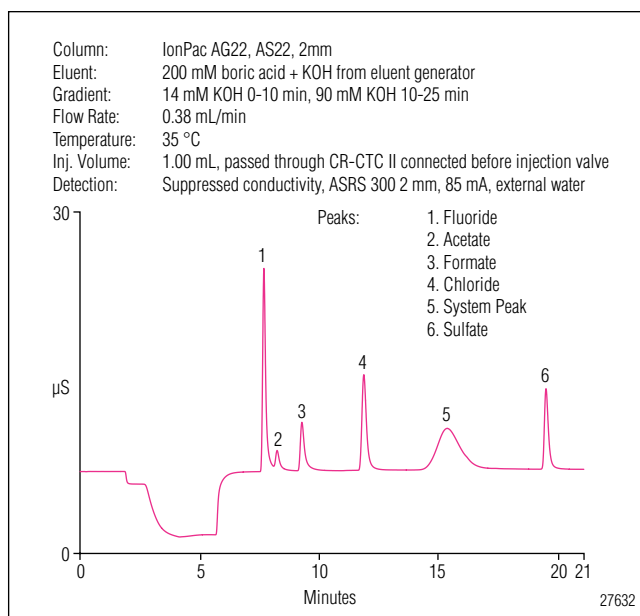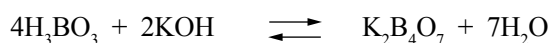
$$4H_3BO_3 \; + \; 2KOH \; \rightleftarrows \; K_2B_4O_7 \; + \; 7H_2O$$

Column: IonPac AG22, AS22, 2mm
Eluent: 200 mM boric acid + KOH from eluent generator
Gradient: 14 mM KOH 0-10 min, 90 mM KOH 10-25 min
Flow Rate: 0.38 mL/min
Temperature: 35 °C
Inj. Volume: 1.00 mL, passed through CR-CTC II connected before injection valve
Detection: Suppressed conductivity, ASRS 300 2 mm, 85 mA, external water

Peaks:
1. Fluoride
2. Acetate
3. Formate
4. Chloride
5. System Peak
6. Sulfate

Figure 2. 100 µg/L target anion standard plus acetate in deionized water.

With the KOH eluent program described in the Conditions section, the tetraborate gradient started at 7 mM and stepped to 45 mM at 10 min. The 200 mM boric acid was always in molar excess. All analytes were well separated, which allows the analyst to distinguish the presence of fluoride from acetate usually present at trace levels in water. The fluoride peak was well resolved from the large system void corresponding to the time required for the 1 mL sample to pass through the chromatographic system. A system peak that eluted from 14 to 17 min was the result of the steep increase of tetraborate eluent concentration at 10 min. The system peak significantly decreased when a shallower gradient was applied. However, if a shallower gradient is used, the retention times of strongly retained anions such as sulfate will increase significantly.

Method Performance

Figure 3 compares chromatograms from representative blanks: A) system blank, B) deionized water matrix blank, and C) 2000 mg/L boron plus 4 mg/L lithium surrogate matrix blank. Data for the system blank were collected without performing an injection (neither loading water nor switching the 6-port injection valve) by selecting Blank as the Sample Type in the Chromeleon software sequence. The only observable features in the system blank were the system peak and a small baseline decrease at the tailing edge where sulfate elutes. This baseline disturbance decreased with increasing number of system blanks, minimizing at 5 to 15 nS in the current study. Sub-µg/L amounts of fluoride, formate, and chloride were detected in the deionized water matrix blank (Figure 3B). Carbonate eluted before chloride and appeared as a broad peak.

The CR-CTC II column may contribute to measured chloride in blank injections. Flushing the sample line with more than 100 mL deionized water decreased the amounts observed in blanks to 0.5 µg/L chloride or less. Results from the simulated boric acid/lithium hydroxide sample matrix (Figure 3C) showed measurable amounts of sulfate (2.0 µg/L), fluoride (1.2 µg/L), and chloride (0.4 µg/L) contributed from the boric acid/lithium matrix compounds.

Adding the CR-CTC II column in the sample transfer line did not significantly change retention times or peak areas of target anions spiked into 2000 mg/L boron/4 mg/L lithium matrix (data not shown). Retention time differences were 1% or less, whereas peak areas differed by 5% or less (except for the chloride contamination contributed by the CR-CTC II column). Fluoride peak areas were 2% less without the CR-CTC II column. Results for simulated samples may differ from those generated from nuclear power plant samples.

Calibration curves for target anions were prepared by dilution of intermediate stock solutions in deionized water. Table 2 summarizes calibration data and method detection limit (MDL) estimates. The correlation coefficients for all target analytes were 0.999 or greater. MDLs, calculated based on 3× the signal-to-noise ratio (S/N), were consistent for fluoride and chloride with the results presented in AN 166. In this application, the quantification lower limits are dictated by chromatographic system and water purity (as shown in Figure 3B). Anionic impurities from added matrix reagents and PWR system components constitute the sample (i.e., Figure 3C) in the analyst's environment.
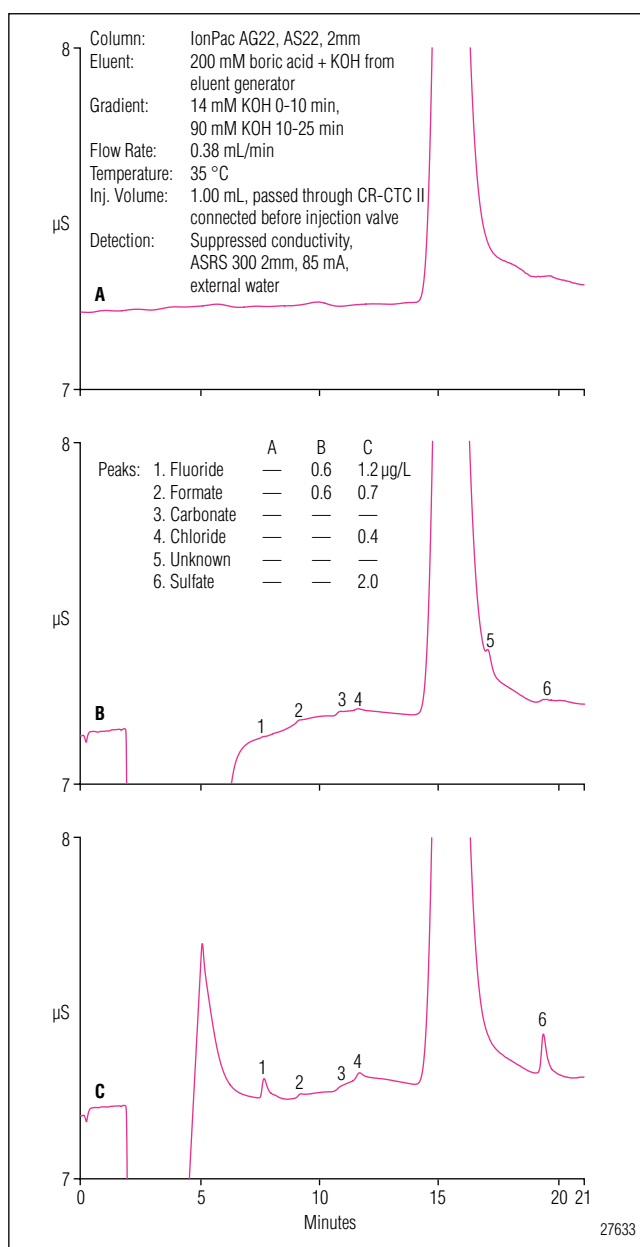

Figure 3. Comparison of representative blank chromatograms: A) system blank, B) deionized water matrix blank, and C) 2000 mg/L B plus 4.0 mg/L Li surrogate matrix blank.

Table 2. Calibration Data and Estimated Method Detection Limits for Trace Anions in Deionized Water				
Analyte	**Range (µg/L)**	**Correlation Coefficient (r²)**	**RSD**	**MDLᵃ (µg/L)**
Fluoride	1.0–26.6	0.9990	3.39	0.015
Formate	1.0–27.7	0.9990	3.43	0.056
Chloride	1.1–28.4	0.9997	1.96	0.022
Sulfate	2.5–67.0	0.9993	2.80	0.28

ᵃ Calculated from 3× S/N

Retention time and peak area precisions were evaluated by spiking intermediate stock solutions for the target anions in a simulated matrix of 2000 mg/L boron plus 4.0 mg/L lithium. A representative chromatogram from the spiked simulated matrix is shown in Figure 4. Data collected from 17 consecutive runs over 12 h yielded retention time and peak area precisions < 0.1% and < 3% for all target analytes (Table 3).

Method accuracy was evaluated by determining recovery of the target analytes spiked into three simulated matrices. Table 4 summarizes quantitative results for the target analytes in both spiked and unspiked surrogate matrix blanks. After appropriate matrix blank corrections, recoveries for fluoride, formate, chloride, and sulfate were in the range of 78 to 107%.

CONCLUSION

The large-volume, direct injection approach for the determination of selected organic acids and inorganic anions in borated waters has been extended to include lithium-containing matrices. The method uses a CR-CTC II device to remove mg/L lithium levels in the simulated matrices and a high-capacity 2 mm IonPac AS22 column set to separate the anions after a 1 mL sample injection. With attention to careful sample and system handling, low-µg/L concentrations of fluoride, formate, chloride, and sulfate can be determined with good linearity, precision, and accuracy.


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Column:        IonPac AG22, AS22, 2mm
Eluent:        200 mM boric acid + KOH from eluent generator
Gradient:      14 mM KOH 0-10 min, 90 mM KOH 10-25 min
Flow Rate:     0.38 mL/min
Temperature:   35 °C
Inj. Volume:   1.00 mL, passed through CR-CTC II connected before injection valve
Detection:     Suppressed conductivity, ASRS 300 2mm, 85 mA, external water
Peaks: 1. Fluoride    10.2 µg/L
       2. Formate      9.8
       3. Carbonate    —
       4. Chloride    11.3
       5. Sulfate     24.3
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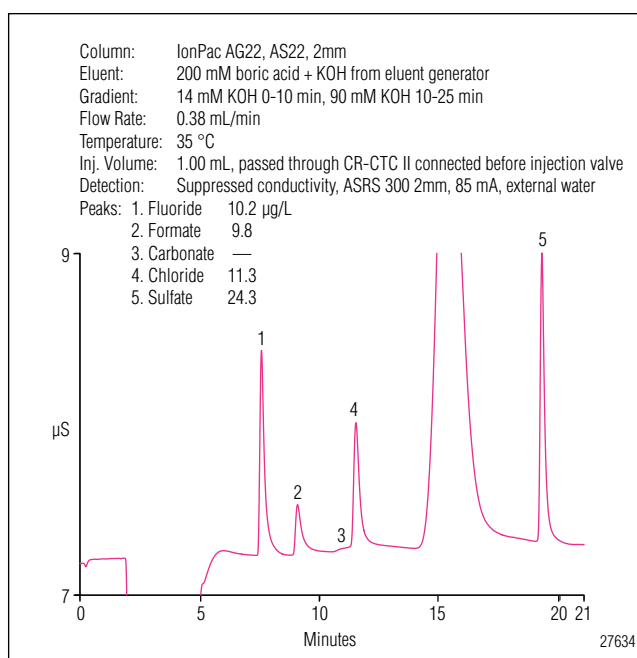
Figure 4. Typical chromatogram of trace anions spiked into 2000 mg/L boron plus 4 mg/L lithium surrogate matrix.

Table 3. Retention Time and Peak Area Precisions for Anions in Simulated Borated Matrix[a,b]

Analyte	Amount Found (µg/L)	Retention Time RSD	Peak Area RSD
Fluoride	9.3	0.06	0.30
Formate	8.9	0.06	0.95
Chloride	10.2	0.09	1.29
Sulfate	26.0	0.08	1.47

[a] Matrix = 2000 mg/L boron + 4.0 mg/L lithium

[b] n = 17 injections over 12 h

Table 4. Average Recoveries of Anions Spiked into Simulated Borated Matrix[a]

Analyte	1000 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 in Matrix Blank (µg/L ± SD)	Amount Added (µg/L)	Average Recovery (%)	Amount in Matrix Blank (µg/L ± SD)	Amount Added (µg/L)	Average Recovery (%)	Amount in Matrix Blank (µg/L ± SD)	Amount Added (µg/L)	Average Recovery (%)
Fluoride	0.92 ± 0.02	3.74	85.7	1.17 ± 0.01	9.55	93.7	1.32 ± 0.01	32.0	98.6
Formate	0.68 ± 0.02	3.90	78.3	0.70 ± 0.04	9.96	91.9	0.75 ± 0.04	33.4	97.3
Chloride	0.22 ± 0.03	3.99	107.4	0.36 ± 0.03	10.2	106.1	0.53 ± 0.06	34.2	102.6
Sulfate	0.93 ± 0.04	9.42	86.0	1.92 ± 0.07	24.0	92.3	2.06 ± 0.22	80.7	96.4

[a] n = 8 injections

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. Dionex Corporation, *Application of Eluent Generation for Trace Anion Analysis of Borated Waters*. Application Note 166, LPN 1654, 2004, Sunnyvale, CA.

3. Dionex Corporation, *Determination of Trace Organic Acids and Inorganic Anions in Boric Acid-Treated Power Plant Waters Using an Automated Reagent-Free Ion Chromatography System*. Application Note 185, LPN 1996, 2008, Sunnyvale, CA.

SUPPLIERS

Gast Manufacturing Corp., 2550 Meadowbrook Road, Benton Harbor, MI 49022, U.S.A. Tel: 269-926-6171. www.gastmfg.com

Nalge Nunc International, 75 Panorama Creek Drive, Rochester, NY 14625, U.S.A. Tel: 800-625-4327. www.nalgenunc.com

Praxair, 39 Old Ridgebury Road, Danbury, CT 06810-5113, U.S.A. Tel: 877-772-9247. www.praxair.com

Sigma-Aldrich Chemical Company, P.O. Box 14508, St. Louis, MO 63178, U.S.A. Tel: 800-325-3010. www.sigma.sial.com

Thermo Fisher Scientific, 4500 Turnberry Drive, Hanover Park, IL 60133, U.S.A. Tel: 800-766-7000. www.fishersci.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380, U.S.A. Tel: 800-932-5000. www.vwr.com

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