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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

INTRODUCTION

Nuclear power plants produce nearly 20% of the electrical energy used in the U.S and nearly 36% in Europe.[1,2] These power generators must be properly maintained to supply continuous, uninterrupted electrical energy to meet consumer demands. Corrosion is a major contributor to the operation and maintenance costs associated with nuclear power plants.[3] The buildup of impurities from sub-µg/L concentrations in water used to drive steam generators and turbines can propagate stress corrosion cracking and other corrosion mechanisms. This corrosion can lead to component failures and plant shutdowns, resulting in significant loss of power generation. Hence, monitoring the presence of ionic impurities in cooling waters, boiler waters, feed waters, and steam condensate in nuclear power plants is critical.

In pressurized water reactors (PWRs) boric acid is used as a water soluble neutron absorber to control the nuclear reaction. At the beginning of the fuel cycle, the boric acid concentration is relatively high (1000–2500 ppm) and gradually decreases to 0 ppm as the fuel is spent.[4,5] Lithium hydroxide concentration is coordinated with the boric acid concentration to achieve a desired $pH_{300\,^{\circ}C}$ of 6.9 or higher, to prevent crud deposits on the fuel rods. The lithium concentration is typically in the range of 1.8–4 ppm for a corresponding boron concentration range of 1000–2000 ppm, and then is decreased as the boron concentration is reduced.[4] However, trace impurities from the reagents or the water source can accumulate over time, serving 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. Previously, the determination of anionic contaminants in borated waters has been achieved using a tetraborate eluent with an IonPac® AS4A or AS14 column.[6] However, the tetraborate gradient caused a significant increase in the baseline, which led to higher detection limits. An alternative approach prepared the tetraborate eluent in situ using electrolytically generated potassium hydroxide and a boric acid eluent.[7,8] The boric acid concentration was constant while the potassium hydroxide concentration was varied to perform a gradient elution of the target analytes by the resulting borate anions. In this configuration, the background was essentially constant during the gradient and therefore provided consistent peak area response and improved detection limits.

This Application Note describes an IC method using a 2-mm IonPac AS15 and electrolytically generated potassium hydroxide eluent for the determination of low µg/L concentrations of target organic acids and inorganic anions in simulated boric acid-treated power

plant waters. This method combines the key benefits of the ICS-3000 system's dual pump, Automation Manager, and AS-HV High-Volume Autosampler to facilitate the determination of trace anionic contaminants in borated waters. Electrolytic eluent generation saves time and labor compared to manual eluent preparation, and reduces the chance of inconsistent results between operators. Electrolytic eluent generation also decreases the risk of contamination from glassware, equipment, and adsorbed atmospheric gases.

Spiking the samples online using calibration standards decreases the chance for contamination during handling and increases reproducibility while reducing labor. The use of a continuously regenerated cation trap column (CR-CTC II) in the sample flow path removes lithium, reducing potential interference. The elimination of most of the boric acid matrix from the concentrator column prior to analysis reduces interference and prevents potential column overloading. Using deionized water treated inline with a continuously regenerated anion trap column (CR-ATC) for matrix elimination prevents contamination from the water source or adsorbed atmospheric gases.

This series of automated steps minimizes interference and contamination, providing the high sensitivity needed for trace analysis. The use of an electrolytically generated hydroxide eluent without added boric acid further decreases sources of contamination and error. The linearity, detection limits, precision, and accuracy of this method for determining trace anionic impurities in borated samples are described.

EQUIPMENT

Dionex ICS-3000 Reagent-Free™ Ion Chromatography (RFIC™) system consisting of:

- DP Dual Pump module
- EG Eluent Generator module
- DC Detector/Chromatography module (single or dual temperature zone configuration) with optional Detector Analog Relay – TTL (P/N 062201)
- Automation Manager with one 10-port high-pressure valve and one three-port low-pressure valve (P/N 079837)
- EG40 CR-TC Add-on Kit (P/N 060476)
- Two EluGen® EGC II KOH cartridges (P/N 058900)
- Two Continuously Regenerated Anion Trap Columns (CR-ATC, P/N 060477)
- Continuously Regenerated Cation Trap Column (CR-CTC II, P/N 066262)

AS-HV High Volume autosampler with internal peristaltic pump (P/N 064508)

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

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

Tissue culture filter units to supply water to AS-HV, 1000 mL (VWR P/N 28198-514)

Chromeleon® 6.8 Chromatography Management Software

Green PEEK™ tubing (P/N 044777), 0.030-in. (0.75-mm) i.d., 15-ft. (4.58-m) to construct 2-mL sample loop

Blue PEEK tubing (P/N 049714), 0.013-in. (0.325-mm) i.d., 6-in. to construct 10-µL standard loop or use a 10-µL standard loop available from Dionex (P/N 064668)

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

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

REAGENT AND STANDARDS

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

Combined Seven Anion Standard II, 100 mL (Dionex P/N 057590)

Sodium fluoride, ACS grade, 99% (JT Baker, P/N JT3688-4)

Glycolic acid, ≥98% (Sigma-Aldrich, P/N G8284)

Sodium acetate, anhydrous, ≥99% (Fluka, P/N 71179)

Sodium formate, ≥99% (Fisher Scientific, P/N S648)

Sodium chloride, 99% minimum (JT Baker Ultrapure Bioreagent, P/N JT4058-1)

Sodium nitrite, 98% minimum (JT Baker, P/N JT3780-1)

Sodium bromide, ≥99% (Sigma-Aldrich, P/N 310506)

Sodium nitrate, ≥99% (Fisher Scientific, P/N S343)

Sodium sulfate, anhydrous, 99% minimum (EM Science, P/N EM-SX0760)

Sodium phosphate, dibasic, anhydrous, 99% minimum (JT Baker, P/N JT4062)

SAMPLES

Boric acid, 99.5% minimum (JT Baker, P/N 0084)

Lithium hydroxide, monohydrate, 99.5% (Sigma-Aldrich, P/N 254274)

CONDITIONS

Analytical: System 1

Columns:	IonPac AG15, 2 × 50 mm (P/N 053943) IonPac AS15, 2 × 250 mm (P/N 053941)
Eluent:	7 mM KOH from 0–10 min, 7–40 mM KOH from 10–16 min, 40–60 mM KOH from 16–22 min, 60 mM KOH from 22–30 min*
Eluent Source:	EGC II KOH with CR-ATC
Flow Rate:	0.40 mL/min
Temperature:	30 °C (lower and upper compartment)
Standard Inj. Vol.:	10 µL
Sample Inj. Vol.:	2 mL
Matrix EliminationVol.:	10 mL
Concentrator:	IonPac UTAC-ULP1, 5 × 23 mm (P/N 063475)
CRD:	CRD 200, 2-mm (P/N 062986)
Detection:	Suppressed conductivity, ASRS® ULTRA II,** 2-mm, (P/N 061562) recycle mode, 65 mA
System Backpressure:	~2200 psi
Expected Background:	<0.8 µS
Noise:	~1-2 nS/min peak-to-peak
Run Time:	30 min

*The concentrator and columns are equilibrated for 5 min prior to each injection.

**The ASRS ULTRA II suppressor has been discontinued and replaced by the ASRS 300. The ASRS 300 will provide equivalent or improved performance for this application.

Sample Preparation: System 2

Trap Columns:	CR-ATC, trap column for DI water carrier solution CR-CTC II, removal of lithium from sample
Flow rate:	2.0 mL/min
Carrier:	degassed deionized water
Matrix Elimination:	10 mL
System Backpressure:	~1900 psi

AS-HV

Peristaltic Pump Flow rate:	1.8 mL/min
Load Volumes:	1 mL (for 10 µL standard injection), 5 mL (for 2 mL sample injection), volumes entered into Chromeleon sequence
Rinse Volume:	5 mL (Flush)
Sample Load Mode:	Pull
Prep. Time:	10 min (standard injection); 13 min (sample injection)

PREPARATION OF SOLUTIONS AND REAGENTS

Rinse Solution Reservoir for AS-HV Autosampler

Rinse the tissue culture filter unit with deionized water at least three times. Fill the unit with deionized water, cap, and soak overnight. Discard the water in the container and fill with deionized water. Connect the bottle to the rinse fluid reservoir tubing on the peristaltic pump. Replace this water at least daily.

Deionized Water for Systems 1 and 2

For System 1, rinse one 2-L eluent bottle with deionized water at least three times. Fill the bottle with fresh degassed deionized water to the 2-L mark and connect the eluent bottle to the Eluent A line of pump 1. System 2 requires at least two 2-L eluent bottles to allow continuous operation for at least 15 h. Prepare the eluent bottles by first soaking in deionized water overnight. Discard the deionized water and fill each bottle with fresh degassed, deionized water, as described for System 1. Connect the eluent bottles for System 2 in series by applying helium pressure (~3–5 psi) to the first bottle and connecting the last bottle directly to the Eluent A line of pump 2.

Mixed Inorganic Anion Stock Solution

To estimate concentrations of the target anions in the sample, compare a 10-µL injection of a 100-fold dilution of the Combined Seven Anion Standard II to a 2-mL injection of a simulated boric acid treated sample. Prepare a concentrated mixed inorganic anion stock solution at concentration ratios relative to the highest analyte concentration observed in the simulated sample (e.g., sulfate). For example, if the estimated concentration of sulfate is 25 µg/L and chloride is 5 µg/L, then the concentration of chloride in the mixed inorganic anion stock solution should be five times less than the sulfate concentration. However, due to the injection volume ratio between the sample and standard, the estimated concentrations require a multiplication factor of 200 (see the section on Working Standard Solutions). In the example shown above, 25 µg/L sulfate is equivalent to 5000 µg/L sulfate prepared in solution and 5 µg/L chloride is equivalent to 1000 µg/L chloride prepared in solution. (Note: These ratios will vary from laboratory-to-laboratory based on the purity of the boric acid and lithium hydroxide.) The mass of each compound added to a 250 mL polypropylene bottle and the final concentration of each analyte are shown in Table 1. When stored at 4 °C, this solution is stable for at least two months.

Organic Acid Stock Solution

Prepare a combined stock standard solution of 100 mg/L each of glycolate, acetate, and formate in a 250-mL rinsed/presoaked tissue culture flask. Add 0.025 g glycolic acid, 0.3473 g sodium acetate, and 0.3776 g sodium formate to the flask and bring to volume with deionized water. When stored at 4 °C, this solution is stable for at least one month.

Intermediate Mixed Inorganic Anion Solution

Prepare the intermediate inorganic anion solution by adding 5 mL of the inorganic anion stock solution to a 250-mL presoaked/rinsed tissue culture flask and bring to volume with deionized water (50-fold dilution). When stored at 4 °C, this solution is stable for at least one month.

Working Standard Solutions

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.

Precaution: The organic acids included in the calibration standards in this Application Note were found to be stable at room temperature from <12 h to 48 h. The stability of these analytes will vary significantly depending upon laboratory conditions. If the responses decrease below an acceptable level, prepare a fresh standard from the stock solutions.

The configuration described in this Application Note for calibration is similar to the Dionex AutoPrep™ system, with the exception that multiple standards are prepared instead of a single standard. Standards are injected on the concentrator using a 10 µL loop installed on the 10-port injection valve in the Automation Manager. This is essentially equivalent to injecting 2 mL of a 200-fold dilution (2000 µL/10 µL = 200) of the standard on the concentrator. Therefore, the standard concentrations calculated from the volumes used in Table 2 should be divided by 200 to determine the actual concentrations injected to produce the calibration curves. This configuration minimizes many sources of contamination that can compromise trace analysis.

Table 1. Amount of Compound Used to Prepare 250 mL of a Mixed Common Inorganic Anion Stock Solution

Anion	Compound	Mass (g)	Final Concentration (mg/L)
Fluoride	Sodium fluoride (NaF)	0.5525	1000
Chloride	Sodium chloride (NaCl)	2.060	5000
Nitrite	Sodium nitrite ($NaNO_2$)	0.1874	500
Sulfate	Sodium sulfate (Na_2SO_4)	9.240	25000
Bromide	Sodium bromide (NaBr)	0.1609	500
Nitrate	Sodium nitrate ($NaNO_3$)	0.8565	2500
Phosphate	Sodium hydrogen phosphate (Na_2HPO_4)	0.1868	500

Table 2. Preparation of Calibration Standards in 250-mL Tissue Culture Flasks

Calibration Level	Volume of Mixed Anion Stock (mL)	Volume of Intermediate Anion Stock (mL)	Volume of Organic Acid Stock (mL)
1	—	0.25	0.17
2	—	1.27	0.28
3	—	2.55	0.85
4	0.15	—	1.70
5	0.25	—	2.85

SAMPLE PREPARATION

1000 mg/L Lithium

Add 1.511 g lithium hydroxide monohydrate to a 250-mL presoaked/rinsed tissue culture flask and bring to volume with deionized water. Store this solution at 4 °C when not in use.

Simulated Boric Acid Treated Samples

A boron concentration in the range of 1000–2500 mg/L with an added lithium concentration in the range of 1.8–5.0 mg/L was analyzed in this study. To prepare a solution containing 1000 mg/L boron and 1.8 mg/L lithium, add 1.4297 g boric acid to a 250-mL rinsed/presoaked tissue culture flask and dilute to 200 mL with deionized water. Agitate the solution to fully dissolve the boric acid. Add 0.45 mL of the 1000 mg/L lithium solution to the dissolved boric acid and dilute to a final volume of 250 mL. To prepare a solution containing 2000 mg/L boron and 4 mg/L lithium, combine 2.8596 g boric acid with 1 mL of the 1000 mg/L lithium solution as described for the 1000 mg/L boron sample above. For the 2500 mg/L boric acid with 5.0 mg/L lithium sample, combine 3.574 g boric acid with 1.25 mL of 1000 mg/L lithium.

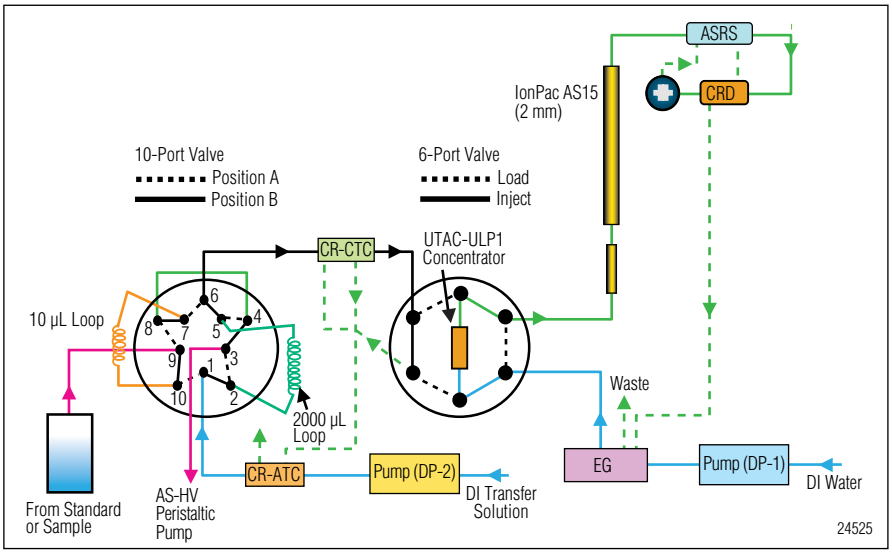

Figure 1. Schematic diagram of system configuration.

SYSTEM PREPARATION AND SETUP

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

1) Install an EGC II KOH cartridge on the System 1 channel.
2) Install backpressure tubing in place of the columns on System 1 to produce a total backpressure of ~2000–2500 psi at a flow rate of 1 mL/min.
3) Condition the cartridge by setting the KOH concentration to 50 mM at 1 mL/min for 30 min.
4) Disconnect the backpressure tubing installed in place of the column set.
5) Install a CR-ATC between the EGC II KOH cartridge and the EGC degas.
6) Hydrate the CR-ATC prior to use by following the instructions outlined in the EluGen Cartridge Quickstart Guide.[9]
7) Install 2 × 50 mm AG15 and 2 × 250 mm AS15 columns in the lower compartment of the DC using red PEEK (0.005” i.d.) tubing between connections.
8) Install 5 × 23 mm UTAC-ULP1 concentrator in place of sample loop on valve #1 using red PEEK tubing. Direction of sample loading should be opposite analytical flow.
9) Make sure 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 or trim tubing between degas assembly and injection valve to achieve recommended pressure.
10) Hydrate and install the ASRS ULTRA II suppressor and Carbonate Removal Device (CRD 200) according to the instructions in the product manuals.[10,11]
    a) Install in recycle mode using red PEEK tubing for all connections.
    b) To minimize added backpressure on suppressor, install sufficient black PEEK (0.010” i.d.) tubing on cell outlet to reach the Regen In port of the suppressor.

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

1) Connect the peristaltic pump rinse lines to the fixed rinse reservoir and 1-L external rinse reservoir (e.g., tissue culture filter unit).
    a) Install the 0.25” Nalgene waste line and the Santoprene 2.06 mm i.d. peristaltic tubing according to the instructions in Section B.3.4

in the Dionex AS-HV Operator's Manual (Document No. 065125-01).[12]

2) To install the sampling line in the pull mode (Figure B-13, AS-HV Operator's Manual), install a second piece of 0.64 mm (0.03" i.d.) Santoprene peristaltic tubing on the inside track of the peristaltic pump motor.
   a) Santoprene tubing degrades over time and should be changed periodically.
3) Connect the free end on the top of the peristaltic pump to a 2-mm PTFE waste line using a ¼-28 to 10-32 coupler.
4) To verify that the peristaltic pump is working properly, place the waste container in a visible location. Periodically check waste level to assure that solvent is flowing
5) Connect the other end (bottom part) of the 0.64 mm Santoprene tubing to green PEEK tubing (~100-cm).
6) Connect the free end of the PEEK tubing to port #3 on the 10-port valve located in the Automation Manager.
7) Adjust the flow rate of the peristaltic pump by turning the rinse speed knob until a flow rate of ~1.8 mL/min is achieved. Periodically verify the flow rate of the peristaltic pump as this can change with time.
8) Connect one end of a separate piece (~185-cm) of green PEEK tubing to the PEEK needle on the AS-HV, and the other to port #9 on the 10-port valve. Be sure the tubing is anchored appropriately according to Figure B-7 and B-8 in the AS-HV Operator's Manual to avoid interference with sampling arm movement.

To configure System 2:

1) Hydrate the CR-ATC and CR-CTC II following the instructions outlined in the Quickstart Procedure for the CR-TC Continuously Regenerated Trap Columns.[13]
2) Connect the outlet of the System 2 pump to the Eluent In port of the CR-ATC.
3) Connect a short piece (~11in.) of yellow PEEK tubing (0.003" i.d.) to Eluent Out port of CR-ATC.
4) Use a minimum length of black PEEK tubing (0.010" i.d.) from port #6 on 10-port valve to Eluent In of CR-CTC II and from the CR-CTC II to the six-port injection valve to minimize the dead volume.
5) Connect the CR-CTC II to the CR-TC add-on power supply and connect the power supply to the TTL1 connector located on the Detector Analog Relay–TTL panel on the back of the DC.

CAUTION: Be sure to turn off the power to the CR-CTC II (DC_TTL1 set to 5V) before turning off the System 2 pump. Failure to do this will result in permanent damage to the CR-CTC II.

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 pressure restrictions for the AS-HV.
   b) Install a 10-µL sample loop, prepared from blue PEEK tubing, on ports #7 and #10.
   c) Prepare a 2-mL sample loop from green PEEK tubing by measuring approximately 173 in. Verify the volume of the loop by determining the difference in weight between the empty sample loop and the sample loop filled with deionized 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 1500-2000 psi when operating at 2 mL/min.
7) Install an EGC II KOH cartridge on System 2. This installation will enable the CR-ATC to be powered on. It is not necessary to condition this cartridge at this time. When the EGC II KOH cartridge is depleted on System 1, exchange it with the cartridge that is installed on System 2.

CHROMELEON PROGRAMS

This Application Note requires the use of at least three separate Chromeleon (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. When the 10-port valve is switched to position B, the AS-HV 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 AS-HV 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 Note, 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 treated samples, a second CM program was developed using the 2 mL large loop on the 10-port valve. When the 10-port valve is switched to position A, the AS-HV 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 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 Note, 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. 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 AS-HV autosamper tray. The CM program required the inclusion of a series of steps: 1) load 2-mL sample on 10-port valve; 2) transfer the sample to the concentrator; 3) turn the System 2 components off, such as the pump, CR-ATC, and CR-CTC II, to eliminate additional DI water from entering the concentrator; 4) rinse the PEEK needle on the AS-HV with DI water; 5) load standard on 10-µL loop; 6) turn System 2 components on; 7) transfer 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.

RESULTS AND DISCUSSION

The Electric Power Research Institute (EPRI) publishes Water Chemistry Guidelines for the primary and secondary systems of PWRs. All U.S. nuclear power plants (NPPs) and many NPPs worldwide implement these PWR guidelines, which are used to minimize corrosion and radiation exposure. The EPRI guidelines specify action levels for corrosive anions, such as fluoride, chloride, and sulfate, in the low-µg/L range to control intergranular attack/stress corrosion cracking and other localized forms of corrosion.[3] For example, the presence of these aggressive anions in the secondary water can increase the risk of detrimental corrosion reactions. Their presence can be a result of the poor make-up water quality, a major leakage of ion-exchange resins, or leakage of the cooling water into the system.[14] However, each NPP has different action limits based on site-specific chemistry or pH program.[3]

IC with suppressed conductivity detection is a well established analytical technique for monitoring corrosive anions in power plant waters. The determination of target inorganic anions, such as fluoride, chloride, and sulfate, and low-molecular-mass organic acids, such as glycolate, acetate, and formate, can be completed within a reasonable run time. This Application Note demonstrates a matrix elimination and preconcentration method that can perform this determination with high precision and accuracy. The IonPac AS15 column was chosen as the separation column because it is a hydroxide-selective column specifically developed for the rapid and efficient determination of trace concentrations of inorganic anions and low molecular weight organic acids in NPP matrices. The 2-mm column format was chosen to increase mass sensitivity, thereby lowering the required sample volume and matrix rinse volume, and reducing eluent consumption and waste. To achieve the required analyte sensitivity, 2 mL of sample was preconcentrated on the UTAC-ULP1 concentrator prior to separation on the analytical column.

The hydroxide-selective AS15 column combined with an electrolytically generated potassium hydroxide eluent produces low background and baseline noise. After suppression, a hydroxide eluent has significantly lower background conductivity, lower baseline noise, and therefore lower detection limits relative to carbonate eluents. In addition, the electrolytic generation of the potassium hydroxide eliminates the difficulty encountered

when manually preparing a hydroxide eluent. The adsorption of carbon dioxide in manually prepared hydroxide eluents can result in undesirable baseline shifts and irreproducible retention times, and therefore compromise the integrity of the analytical results. To remove any residual carbonate present in the deionized water used to supply the eluent generator (EG), a continuously regenerated anion trap column (CR-ATC) was installed between the EG and the degas module. To further simplify and improve the performance of the method, a CR-ATC and CR-CTC II were used in System 2 for sample preparation. The use of continuously regenerated trap columns eliminates the need to manually regenerate the columns offline, which is tedious, time-consuming, and can result in the leaching of ionic contaminants into the system.

The hydroxide gradient conditions for the separation of the target analytes on the IonPac AS15 column were optimized using the EG. The primary consideration in developing the optimized gradient conditions was the separation of weakly retained analytes, such as fluoride, glycolate, acetate, and formate, from borate present in the simulated power plant water samples. To resolve the early eluting analytes, the potassium hydroxide concentration was maintained at 7 mM for 10 min prior to being increased to 40 mM to elute chloride and nitrite and finally to 60 mM to elute the more strongly retained anions, such as sulfate, bromide, nitrate, and phosphate. However, formate could not be resolved from borate under these conditions.

Method Performance

It is important to establish a system blank and ensure the stability of the blank analyses over a period of several days. The data for the system blank were collected without performing an injection by selecting Blank as the Sample Type in the Chromeleon sequence. This enabled the determination of any anionic contaminants present in the flow path of System 2, which includes the CR-ATC, 10-port valve, CR-CTC II, and 6-port valve. Figure 2A shows a representative system blank chromatogram obtained by concentrating 10 mL of deionized water delivered by the System 2 analytical pump. Trace concentrations of formate (<0.1 µg/L) and chloride (0.15 µg/L) were detected in the system blank. The chloride present was determined to originate from the CR-CTC II. However, the concentration was consistent during the experiments in this Application Note. In

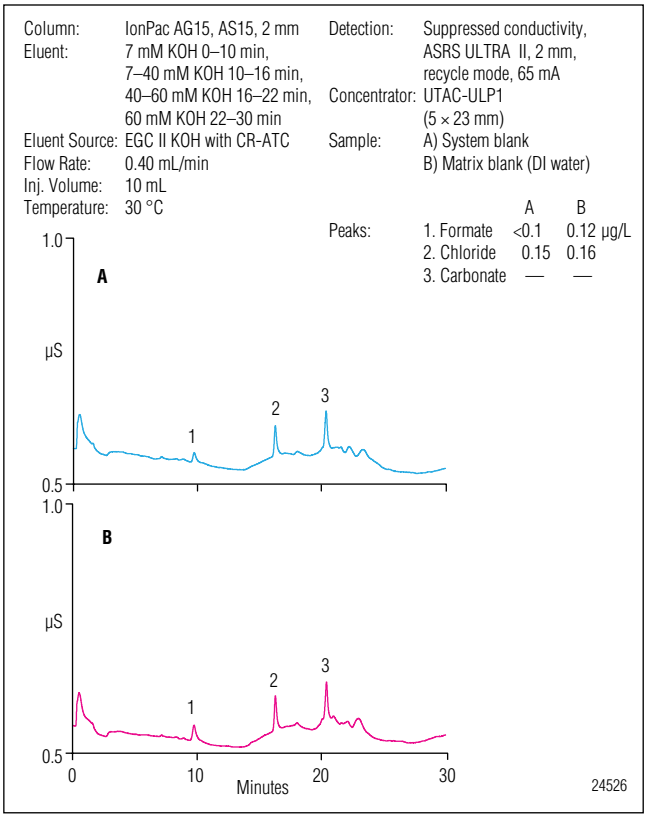

Figure 2. Comparison of representative blank chromatograms. A) System blank, B) deionized water matrix blank.

addition, the chloride concentration is generally present at a significantly higher concentration in boric acid than detected in our blank. The EPRI Secondary Water Chemistry Guidelines shows a current steam generator blowdown water chemistry specification for chloride at >5 µg/L (action level 1) to control stress corrosion cracking and other localized forms of corrosion.[3]

A deionized water blank was determined by injecting 10 µL onto the concentrator column, followed by rinsing the concentrator with 10 mL of deionized water from the System 2 analytical pump. To obtain a representative blank, the same set of containers and other components used to prepare the boric acid samples should be used for the deionized water blank. As shown in Figure 2B, trace concentrations of formate and chloride were also detected in the water blank.

Calibration curves for the target anions were prepared in deionized water from the stock standard solutions. The use of the ICS-3000 Automation Manager allowed the automatic in situ preparation of trace (sub-µg/L to µg/L) standards to minimize contamination that can occur from manually diluting standards. The range of the calibration

curves and the linearity for each target anion are shown in Table 3. The results demonstrate that the calibration curves for the target anions had good linearity with correlation coefficients (r^2) greater than 0.999. Table 3 also summarizes the method detection limits (MDLs) for the target analytes, calculated based on three times the signal-to-noise ratio (S/N).

Figure 3 shows a representative chromatogram of a standard containing the target anions in deionized water. The analyte concentrations in this standard ranged from 0.5 µg/L for nitrite, bromide, and nitrate to 25 µg/L for sulfate. This chromatogram demonstrates that fluoride is well resolved from the void volume and also resolved from the low molecular weight organic acids under the conditions specified in this Application Note.

The method performance was evaluated by analyzing synthetic boric acid treated water containing up to 2500 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 1000 mg/L boron containing 1.8 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. However, the initial elution of borate interferes with formate and therefore quantitation was not possible using the conditions described in this Application Note.

Table 3. Calibration Data and Estimated Method Detection Limits for Trace Anions in Deionized Water

Analyte	Range (µg/L)	Correlation Coefficient (r^2)	RSD	MDL[a] (µg/L)
Fluoride	0.10–5.3	0.9997	2.86	0.006
Glycolate	0.30–5.0	0.9993	3.81	0.040
Acetate	0.30–5.0	0.9998	2.17	0.034
Formate	0.30–5.0	0.9999	1.16	0.014
Chloride	0.50–26.5	0.9997	2.75	0.007
Nitrite	0.050–2.6	0.9998	2.10	0.017
Sulfate	2.5–132	0.9997	2.76	0.012
Bromide	0.050–2.6	0.9992	4.68	0.050
Nitrate	0.25–1.3	0.9998	2.14	0.033
Phosphate	0.050–2.6	0.9999	1.61	0.050

[a]Calculated from 3 × S/N

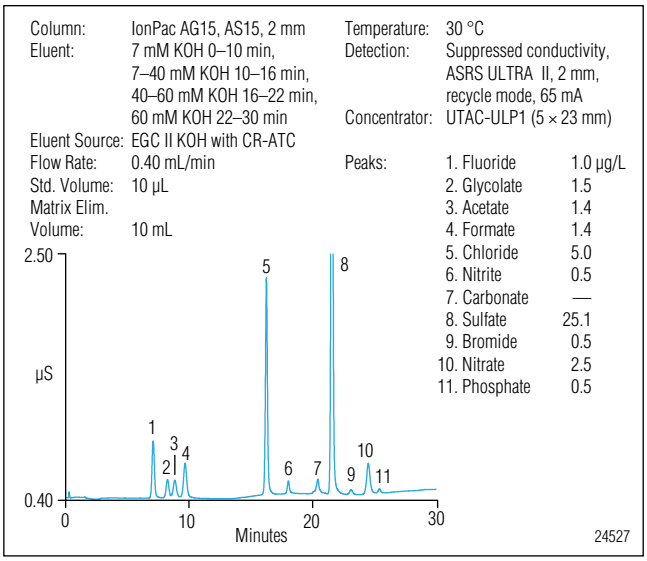

Figure 3. Separation of small organic acids and common inorganic anions using an IonPac AS15 column.

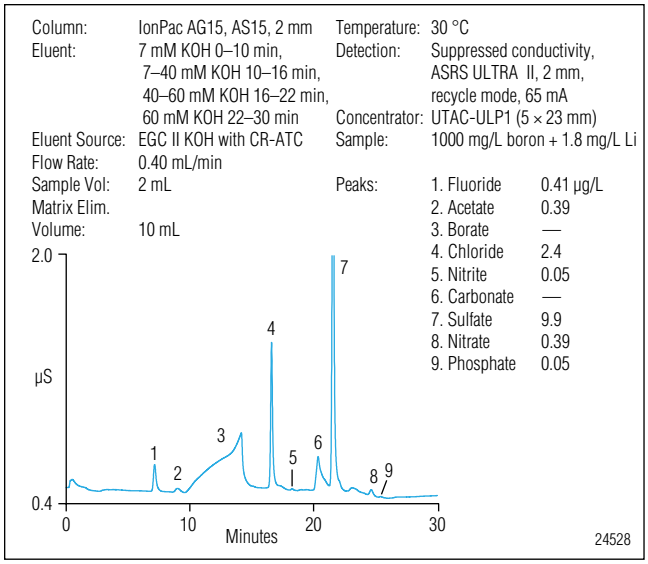

Figure 4. Determination of trace anions in boric acid-treated water using an automated RFIC method.

Increasing the matrix elimination volume did not provide significant improvement in removing the boric acid from the concentrator column. Therefore, a 10 mL matrix elimination volume was considered optimal for this method. 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. The CRD significantly enhances the method's ease-of-use by eliminating the need to degas samples offline. Table 4 summarizes the results for the target anions found in the simulated borated samples. The primary components in the samples analyzed in this study consisted of chloride and sulfate with concentrations in the range of 2–7 µg/L and 10–27 µg/L, respectively. Most of the other target anions were detected at <1 µg/L. Exposure of the sample to the atmosphere can result in an increase in acetate over time. This may have contributed to higher acetate peak area RSDs from the replicate injections relative to the other target analytes. Excluding acetate, the retention time and peak area precisions for 10 replicate injections were <0.1% and <3%, respectively, for most target anions.

Method accuracy was evaluated by determining the recoveries of the target analytes spiked into the synthetic sample matrices at concentrations ranging from 0.25–78 µg/L. The ICS 3000 Automation Manager combined with the large volume 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 2000 mg/L boron and 3.8 mg/L lithium to the same sample spiked in situ with the level 3 calibration standard. All peaks were resolved, with the

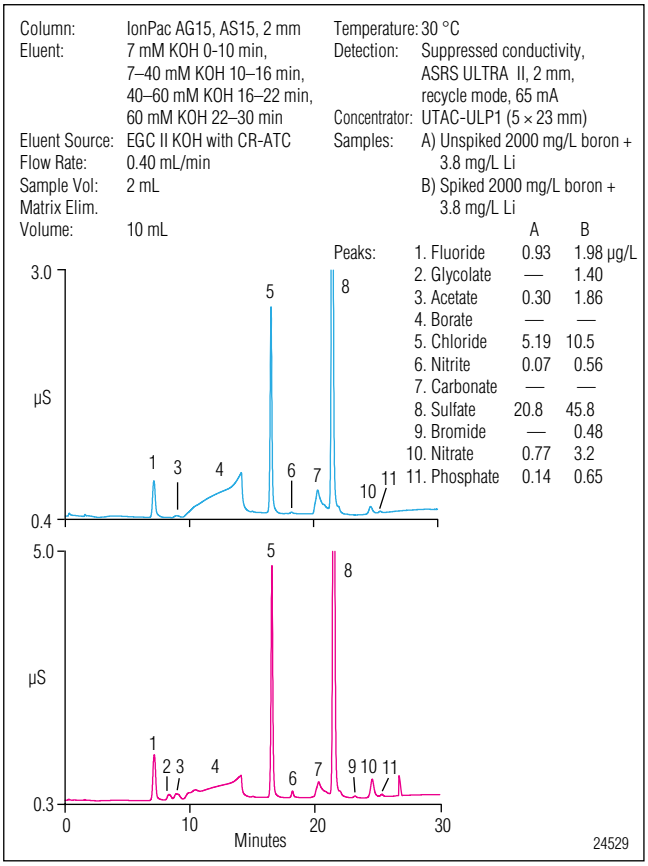

Figure 5. Chromatograms of A) borated water, and B) borated water spiked with trace anions.

Table 4. Summary of Data Obtained for Target Anions in Different Simulated Borated Waters

Analyte[a]	1000 mg/L boron + 1.8 mg/L lithium			2000 mg/L boron + 3.8 mg/L lithium			2500 mg/L boron + 5 mg/L lithium		
	Amount Found (µg/L)	Retention Time RSD	Peak Area RSD	Amount Found (µg/L)	Retention Time RSD	Peak Area RSD	Amount Found (µg/L)	Retention Time RSD	Peak Area RSD
Fluoride	0.41	0.03	1.28	0.93	0.03	0.347	1.2	0.03	0.448
Acetate	0.39	0.17	3.94	0.30	0.40	8.44	0.47	0.12	3.41
Chloride	2.4	0.02	0.70	5.2	0.02	0.207	6.6	0.01	0.609
Nitrite	0.052	0.02	7.40	0.072	0.02	3.15	0.075	0.01	1.94
Sulfate	9.9	0.01	0.76	20.8	0.02	0.836	27.2	0.02	1.66
Nitrate	0.39	0.02	2.61	0.77	0.04	0.673	0.95	0.01	1.37
Phosphate	0.055	0.04	4.19	0.14	0.02	1.37	0.17	0.02	3.14

[a]n = 10 injections

exception of formate, and no significant increase in the borate response was observed, relative to Figure 4, despite the increase in concentration. Table 5 summarizes the analyte recoveries for the samples investigated in this Application Note. In general, the analyte recoveries were in the range of 89–112%. 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.

CONCLUSION

An automated RFIC method was developed for the determination of trace anions in borated waters. This method was designed to increase automation, decrease sample handling, and improve accuracy by minimizing the potential for contamination when determining sub- to low-µg/L concentrations of target anions. The hydroxide-selective AS15 column provides a rapid and efficient 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. The ICS-3000 Automation Manager and AS-HV large volume autosampler permitted the in situ preparation of calibration standards and in situ spiking of the borated samples to reduce labor, eliminate errors, and minimize potential contamination. In addition, the use of continuously regenerated trap columns eliminates the need for offline chemical regeneration, which eliminates the potential for system contamination. This method demonstrated good linearity, sub-µg/L detection limits, and good precision and accuracy for the target anions.

PRECAUTIONS

When performing an analysis of 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 deionized water used for preparing eluent, standards, rinsing the containers, and the rinse solution for the AS-HV autosampler is free of measurable ionic impurities. It is also important that the AS-HV is installed in the "pull" mode and that no restrictions for the flow of liquid from the AS-HV to the 10-port valve are present. If abnormal peak broadening or peak splitting is observed, particularly on early eluting peaks (i.e., fluoride, glycolate, acetate, formate), replace the UTAC-ULP1 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 Application Note 166.[7]

Table 5. Average Recoveries of Target Analytes Spiked in Situ Using the Automation Manager and AS-HV Autosampler

Analyte[a]	1000 mg/L boron + 1.8 mg/L lithium		2000 mg/L boron + 3.8 mg/L lithium		2500 mg/L boron + 5 mg/L lithium	
	Amount Added[b] (µg/L)	Avg. Recovery (%)	Amount Added[c] (µg/L)	Avg. Recovery (%)	Amount Added[d] (µg/L)	Avg. Recovery (%)
Fluoride	0.50	103.4	0.98	107.2	3.14	105.6
Glycolate	0.49	93.4	1.44	96.9	2.94	93.7
Acetate	0.47	109.2	1.39	112.2	2.85	88.8
Formate	0.46	—[e]	1.36	—[e]	2.78	—[e]
Chloride	2.50	110.3	4.90	108.5	15.7	104.3
Nitrite	0.25	97.3	0.49	100.6	1.56	100.9
Sulfate	12.5	98.7	24.6	101.7	78.5	101.1
Bromide	0.25	105.3	0.48	99.7	1.54	97.4
Nitrate	1.25	95.4	2.45	100.1	7.81	101.2
Phosphate	0.25	92.7	0.49	105.1	1.55	102.0

[a]n = 5 injections.
[b]Calibration level 2.
[c]Calibration level 3.
[d]Calibration level 4.
[e]Could not be determined due to interference with borate.

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LIST OF SUPPLIERS

VWR International, 1310 Goshen Parkway, West Chester, PA, 19380, 1-800-932-5000, www.vwr.com

Sigma-Aldrich, PO Box 14508, St. Louis, MO, 63178, 1-800-325-3010, www.sigma-aldrich.com

Fisher Scientific, 2000 Park Lane Drive, Pittsburgh, PA, 15275, 1-800-766-7000, www.fishersci.com

APPENDIX A: CHROMELEON PROGRAMS

Table 6. Small Loop Program for Standards

Time (min)	Chromeleon Commands	Comments
-10.150	EGC_1.Concentration 7.00 [mM] EGC_1.Curve = 5	Equlibrate column and concentrator for approximately 5 min.
-5.210	AM_HP1.B ;Duration=0.01[a]	Switches 10-µL loop on 10-port valve inline with AS-HV.
-5.200	Inject Position = R0 GotoPosition	AS-HV loads standard on 10-µL loop.
-5.150	AM_HP1.A ;Duration=0.01[a]	DI water from DP2 transfers standard from 10-µL loop to concentrator and rinses matrix from concentrator with 10 mL DI water.
	InjectValve_1.LoadPosition ;Duration=0.01[a]	Six-port valve switches to load position.
0.000	InjectValve_1.InjectPosition ;Duration=0.01[a]	Standard is injected on the analytical column.
	CD_1.AcqOn CD_1_Total.AcqOn	Start data acquisition.
10.000	EGC_1.Concentration 7.00 [mM] EGC_1.Curve = 5	Start KOH gradient.
16.000	EGC_1.Concentration 40.00 [mM] EGC_1.Curve = 5	
22.000	EGC_1.Concentration 60.00 [mM] EGC_1.Curve = 5	End KOH gradient.
30.000	CD_1.AcqOff CD_1_Total.AcqOff	End data acquisition.
	EGC_1.Concentration = 60.00 [mM] EGC_1.Curve = 5 Compartment_TC.ReleaseExclusiveAccess Column_TC.ReleaseExclusiveAccess End	

[a]These commands were modified to REM statements and do not represent the duration that the valves were in a particular position.

Table 7. Large Loop Program for Samples		
Time (min)	**Chromeleon Commands**	**Comments**
-11.150	EGC_1.Concentration 7.00 [mM] EGC_1.Curve = 5	Equlibrate column and concentrator for approximately 5 min.
-6.210	AM_HP1.B ;Duration=0.01[a]	Switches 2-mL loop on 10-port valve inline with AS-HV.
-6.200	Inject Position = R0 GotoPosition	AS-HV loads sample on 2-mL loop.
-6.150	AM_HP1.A ;Duration=0.01[a]	DI water from DP2 transfers sample from 2-mL loop to concentrator and rinses matrix from concentrator with 10 mL DI water.
	InjectValve_1.LoadPosition ;Duration=0.01[a]	Six-port valve switches to load position.
0.000	InjectValve_1.InjectPosition ;Duration=0.01[a]	Sample is injected on the analytical column.
	CD_1.AcqOn CD_1_Total.AcqOn	Start data acquisition.
10.000	EGC_1.Concentration 7.00 [mM] EGC_1.Curve = 5	Start KOH gradient.
16.000	EGC_1.Concentration 40.00 [mM] EGC_1.Curve = 5	
22.000	EGC_1.Concentration 60.00 [mM] EGC_1.Curve = 5	End KOH gradient.
30.000	CD_1.AcqOff CD_1_Total.AcqOff	End data acquisition.
	EGC_1.Concentration = 60.00 [mM] EGC_1.Curve = 5 Compartment_TC.ReleaseExclusiveAccess Column_TC.ReleaseExclusiveAccess End	

[a]These commands were modified to REM statements and do not represent the duration that the valves were in a particular position.

Table 8. Program for Spiking Samples Inline with a Calibration Standard			
Time (min)	**Chromeleon Commands**		**Comments**
-11.350	EGC_1.Concentration EGC_1.Curve =	7.00 [mM] 5	Equlibrate column and concentrator for approximately 5 min.
-6.600	AM_HP1.B	;Duration=0.01[a]	Switches 2-mL loop on 10-port valve inline with AS-HV.
-6.550	Inject Position = GotoPosition	R0	AS-HV loads sample on 2-mL loop.
-6.450	AM_HP1.A	;Duration=0.01[a]	DI water from DP2 transfers sample from 2-mL loop to concentrator and rinses matrix from concentrator with 10 mL DI water.
	InjectValve_1.LoadPosition	;Duration=0.01[a]	Six-port valve switches to load position.
-5.300	DC_TTL_1.5v		CR-CTC II is turned to off position.
	Pump_2.Motor =	Off	DP2 is turned off.
	Inject	Position=R8 Volume=2.00	AS-HV rinses needle with DI water then loads standard from position R8.[b]
-5.200	Position = GotoPosition	R0	The AS-HV is sent back to the home position.
	Pump_2.Motor =	On	DP2 is turned on.
-5.100	DC_TTL_1.0v		CR-CTC II is turned on.[c]
	EGC_2.CR_TC =	On	CR-ATC (system 2) is turned on.
-5.000	AM_HP1.A		DI water from DP2 transfers standard from 10-µL loop to concentrator.
0.000	InjectValve_1.InjectPosition	;Duration=0.01[a]	Sample is injected on the analytical column.
	CD_1.AcqOn CD_1_Total.AcqOn		Start data acquisition.
10.000	EGC_1.Concentration EGC_1.Curve =	7.00 [mM] 5	Start KOH gradient.
16.000	EGC_1.Concentration EGC_1.Curve =	40.00 [mM] 5	
22.000	EGC_1.Concentration EGC_1.Curve =	60.00 [mM] 5	End KOH gradient.
30.000	CD_1.AcqOff CD_1_Total.AcqOff		End data acquisition.
	EGC_1.Concentration = EGC_1.Curve = Compartment_TC.ReleaseExclusiveAccess Column_TC.ReleaseExclusiveAccess End	60.00 [mM] 5	

[a]These commands were modified to REM statements and do not represent the duration that the valves were in a particular position.
[b]This position represents the location of the calibration standard (in the AS-HV tray) used to spike the sample. This should be changed depending on the exact location of the standard in the AS-HV tray.
[c]A delay time of at least 0.1 min should be used between the time the DP2 is turned on and the subsequent time the CR-ATC for System 2 is turned on to prevent the CR-ATC from being automatically turned off by the system.

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