A Continuously Regenerated Polisher Column for Sample Prep Applications for the Nuclear Power Industry

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ABSTRACT

Anions in borated waters in nuclear power plants' pressurized water reactors (PWR) are typically analyzed using a sodium tetraborate eluent and IonPac® AS14 or AS4A columns. Hydroxide eluents are also used depending on the concentration of the boron in the matrix. The important parameters of the primary reactor coolant chemistry are the boric acid, lithium hydroxide, and hydrogen concentrations, and the resulting pH level. The presence of lithium causes chromatographic performance issues such as poor peak shapes and recovery of the trace anions. Due to the formation of LiF, fluoride quantitation is frequently hampered. Typically, most plants pursue a manual polishing step to convert the lithium to hydronium and this is usually done using a packed bed in an off-line format. The issue with the packed bed is limited capacity and the need to replenish the bed when exhausted.

A continuously regenerated cation trap column (CR-CTC) was introduced in ion chromatography for removing cationic impurities from the eluent. However, this column was made with a cation exchanger with sulfonic acid functionality. Exposing the sample to such a phase resulted in some cases with a higher sulfate blank and quantitating sulfate became a problem at trace level concentrations. To address the above application we designed a CR-CTC with a 17-µm macroporous vinylbenzyl/divinylbenzene copolymer which is covalently bonded with iminodiacetic acid functional groups. This CR-CTC column was used successfully for analysis of trace level of anions in a lithium boron matrix. Excellent performance was observed. The CR-CTC columns were continuously electrolytically regenerated and did not require any offline steps. In combination with the electrolytic generation of eluent and regenerant, a completely automated Reagent-Free™ IC (RFIC™) system solution was obtained. No manual sample pretreatment was required.

INTRODUCTION

- Borated water is commonly used in PWR nuclear power plants for reactivity control because boric acid is an excellent neutron absorber. It is essential to monitor the presence of ionic impurities in such borated water since even trace (low-µg/L level) corrosive ions, such as fluoride, chloride and sulfate, can make the stainless steel components in the PWR susceptible to cracking.
- Due to the presence of large amount of boric acid matrix, the measurement of ionic contaminants are currently achieved through a tetraborate gradient with IonPac AS4A/AS14 chemistry. Boric acid elutes before other anions.
  - Currently implemented with EGC using a boric acid feed solution
- When the level of boric acid is low the analysis is done using hydroxide chemistry
  - Currently implemented with EGC using a DI water feed solution

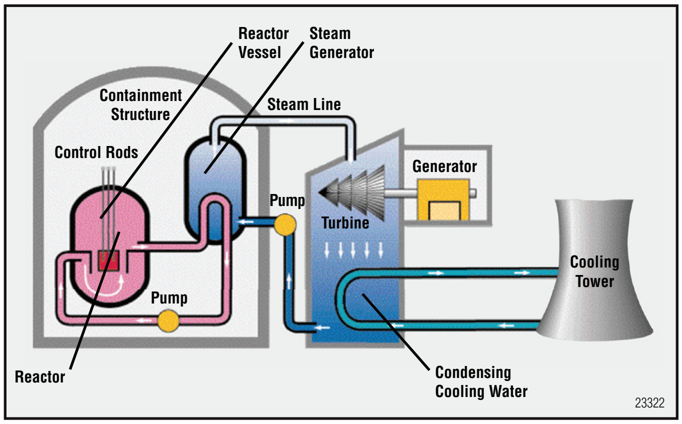

Figure 1. Pressurized water reactor.

POWER PLANT GOALS

- Minimized the metal release rate of structural materials
- Avoid selective corrosion
- Reduce deposits on heat transfer surfaces

PRIMARY REACTANT COOLANT CHEMISTRY

- Chemical variables
  - Boric acid
  - Lithium hydroxide
  - Hydronium concentration
- Boron is added to control the reaction
  - Neutron absorber
- pH control between 6.9 and 7.4 when measured at 300 °C
  - Lithium hydroxide is added to adjust the pH

ANALYTICAL NEEDS

- Trace anions
- Trace cations (Group I/II)

In a variety of matrices such as:

- Ultrapure Water (UPW)
- pH adjusted cooling waters
- Borated waters

ANION ANALYSIS IN BORATED WATERS

- Trace anions in borated waters with no major cation matrix
  - Large volume preconcentration followed by analysis
- Trace anions in borated waters with mg/L levels of lithium
  - Offline polishing of the samples to remove lithium
  - Packed bed column is used
    - ° Needs monitoring for residual capacity
    - ° Needs replacements when capacity is depleted or offline regeneration
    - ° Added processing steps and labor

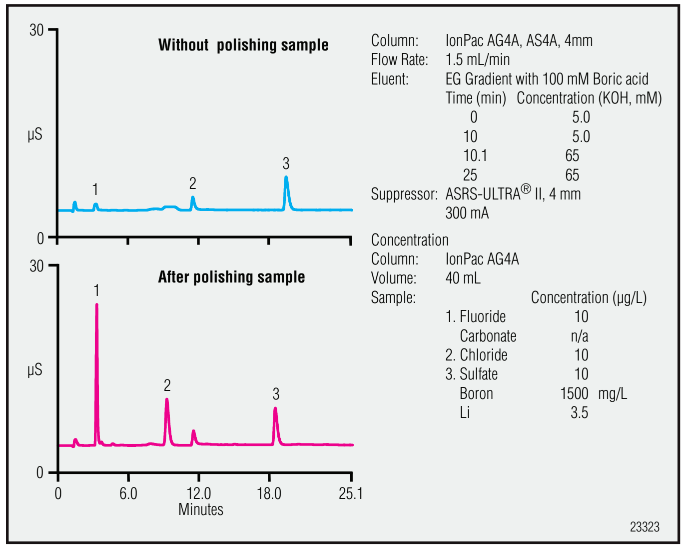

Figure 2. This example compares a simulated borated water sample consisting of trace anions and lithium. The polishing step ensured complete recovery of both response and peak shapes for all ions.

CR-CTC AS A SAMPLE PREP TOOL

- Continuously electrolytically regenerated trap column
- No down time
- No offline regeneration steps
- Labor savings
- Reliable
- Issues
  - Sulfonated substrate resin tends to leach at low levels
    - ° High sulfate blanks
    - ° Hence not suitable for sample polishing
    - ° Requires long equilibration or cleanup to reduce the blanks
- Solution
  - Design a carboxylate phase substrate resin
  - No issue with leachates
  - Ideally suited for sample polishing applications
    - ° No sulfate blanks
    - ° No cleanup was needed

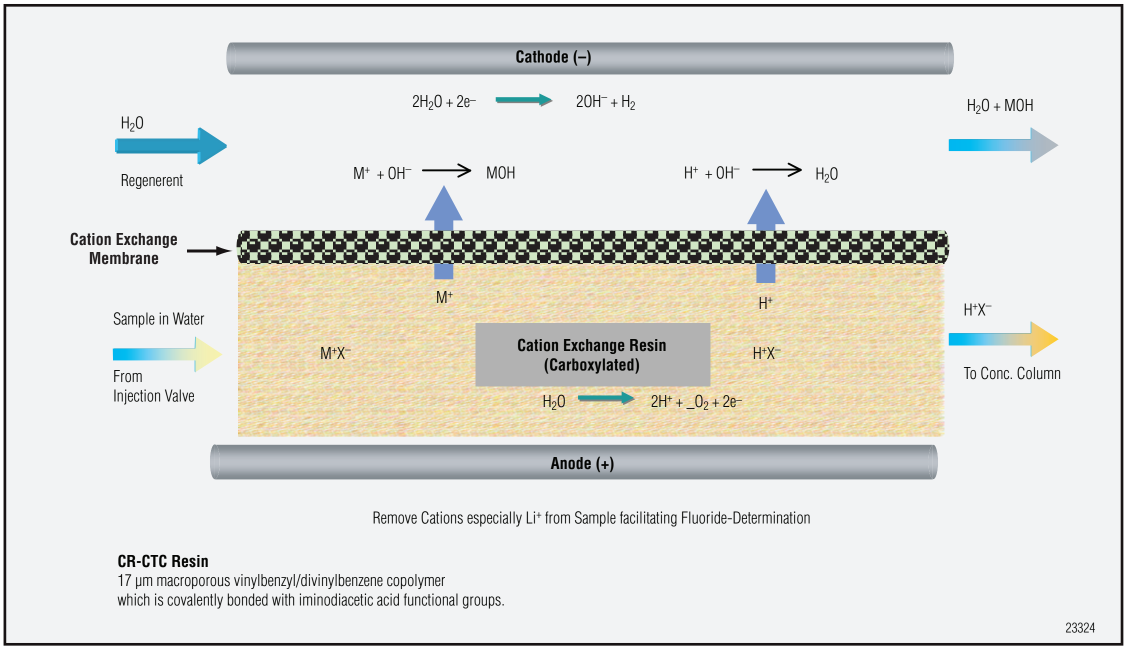

Figure 3. The operation schematic of a CR-CTC. The cations are drawn towards the cathode and migrate across the cation exchange membrane and are diverted to waste as a base. The anions in the sample are diverted out of the device in the acid form.

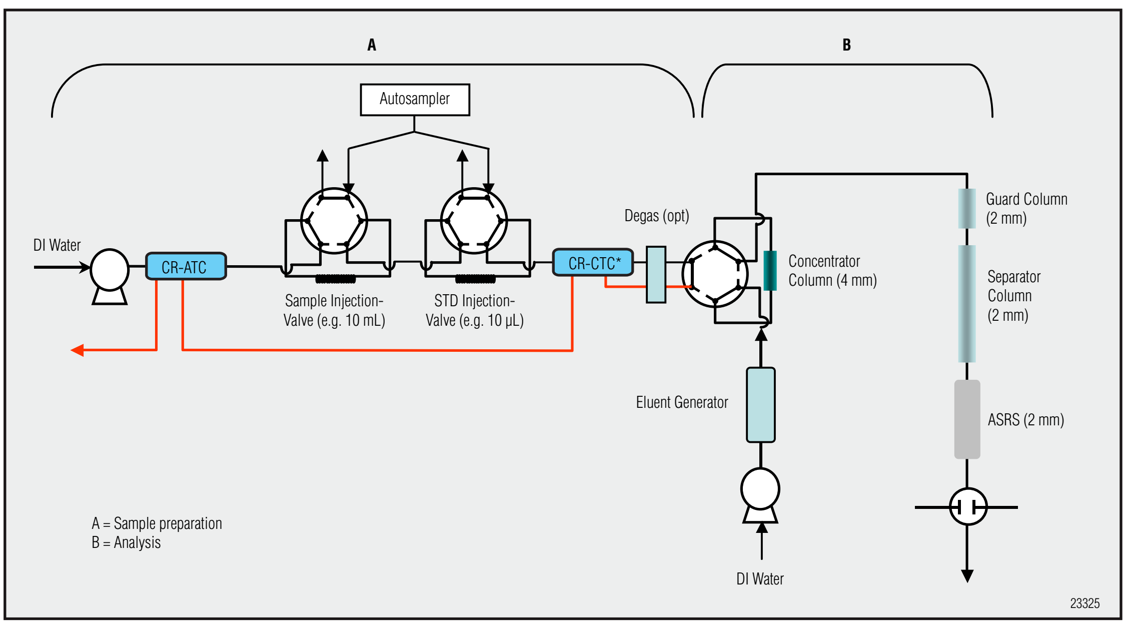

Figure 4. The instrumentation schematic is shown here. Label A depicts the sample preparation section and label B shows the analysis part. Note that the sample could be pumped directly into the CR-CTC for polishing.

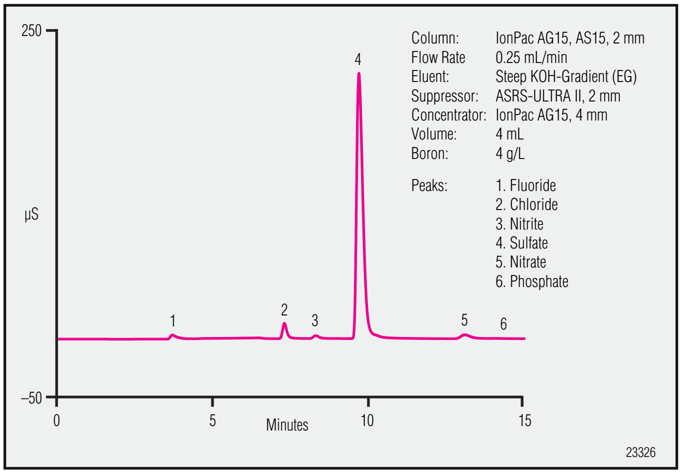

Figure 5. A simulated sample of borated water analyzed by the present method.

Table 1. Typical Calibration Characteristics

	Cal Type	Points	RSD %	Coeff. Det %	Offset	Curve
Fluoride	LOff	3	2.3275	99.9803	–0.0051	0.0004
Chloride	LOff	3	1.3602	99.9914	0.0104	0.0003
Nitrite	LOff	3	2.3430	99.9805	–0.0031	0.0002
Sulfate	LOff	3	1.6788	99.9878	0.0051	0.0002
Bromide	LOff	3	1.9399	99.9864	–0.0015	0.0001
Nitrate	LOff	3	1.5335	99.9918	–0.0030	0.0001
Phosphate	LOff	3	0.9175	99.9971	–0.0018	0.0001

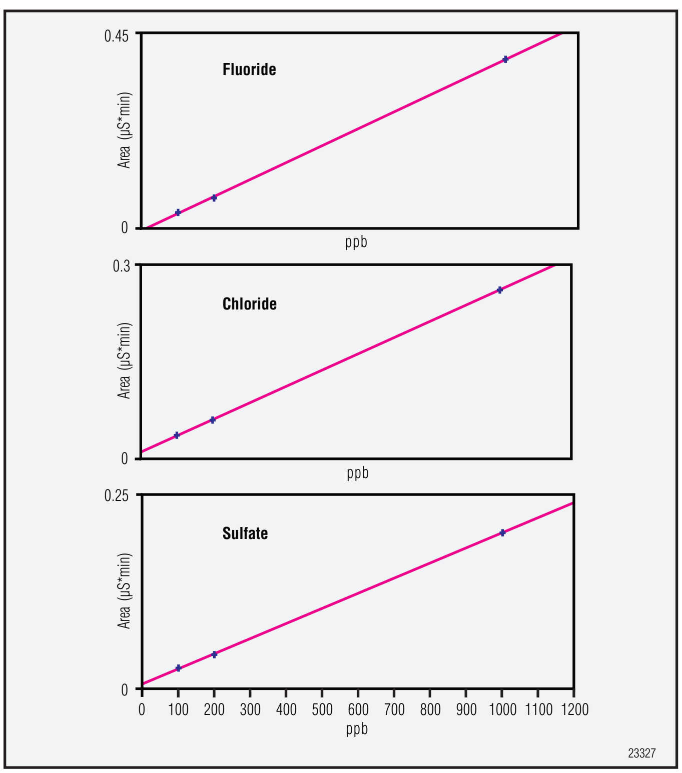

Figure 6. The calibration curve for a simulated borated water sample. Excellent linearity was observed.

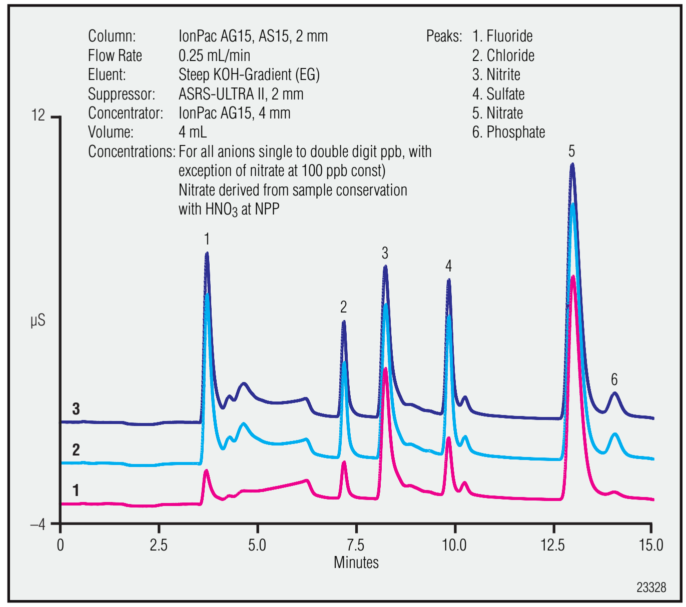

Figure 7. Overlay of three runs of different samples of borated water from a nuclear power plant that was fortified with Std-Anions. Preconcentration was achieved on a AG15 concentrator column (4 mL sample volume) and analysis was done using a 2-mm AS15 column with an RFIC system generated hydroxide gradient.

CONCLUSIONS

- A carboxylate based CR-CTC was found acceptable for polishing cations from a borated water sample
  - Continuously regenerated
  - Required no cleanup
    - Time savings
  - Sulfate blanks were eliminated
- Complete automation of the polishing step became possible
  - Using hydroxide eluents and RFIC systems, the device required only deionized water to operate
  - Using borate eluents and RFIC systems, the device required only boric acid to operate

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