

# Determination of Trace Anions in Nuclear Power Plant Secondary Feed Water Containing Polyacrylic Acid

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## Key Words

Ion Chromatography, Dionex IonPac AS15 Column, Dionex IonPac UTAC-ULP2 Column, Preconcentration

## Goal

To develop an IC method to determine trace concentrations of fluoride, chloride, and sulfate in NPP secondary feed water that contains PAA

## Introduction

In 2011, nuclear power plants (NPPs) provided 12.3% of the world's electricity production.<sup>1</sup> In the U.S., pressurized water reactors (PWRs) comprise approximately two-thirds of the NPPs.<sup>2</sup> The PWR consists of a primary reactor system and a secondary steam system. The chemistry of the feed water must be strictly controlled in both the primary<sup>3</sup> and secondary systems. To protect the secondary steam system from corrosion, an amine such as ethanolamine (ETA) is added to the feed water to obtain an alkaline pH,<sup>4</sup> while a volatile oxygen scavenger such as hydrazine is used to ensure a reducing environment to form protective magnetite on the surfaces of the steam generator.<sup>5</sup>

Since 2009, polyacrylic acid (PAA) has been used at several NPPs as a dispersant in the secondary system to inhibit corrosion on the boiler surfaces.<sup>6</sup> In addition to the careful selection of reagents, the determination of trace concentrations of ionic impurities—such as fluoride, chloride, and sulfate—is critical for the identification and prevention of corrosive conditions in power plant components. Ion chromatography (IC) has been an indispensable technique to separate and identify the individual ionic species at sub- to low- $\mu\text{g/L}$  concentrations in power plant water samples.<sup>7</sup>

This study describes an IC method to determine trace concentrations of fluoride, chloride, and sulfate in simulated secondary feed water samples containing ETA, hydrazine, and PAA. The sample matrix is effectively eliminated using a Thermo Scientific™ Dionex™ IonPac™ UTAC-ULP2 Ultra Trace Anion Concentrator – Ultralow Pressure Column while trapping the anions prior to separation on a Dionex IonPac AS15 column set and detection by suppressed conductivity.



## Equipment

- Thermo Scientific™ Dionex™ ICS-5000+ system,\* including:
  - SP Single Pump module
  - EG Eluent Generator module
  - DC Detector/Chromatography Compartment
  - Dionex™ AS-AP Autosampler with Sample Syringe, 5.0 mL (P/N 074308) and 8500 mL buffer line (P/N 075520)
- Thermo Scientific™ Dionex™ Potassium Hydroxide Eluent Generator Cartridge, EGC III KOH (P/N 074532)
- Thermo Scientific™ Dionex™ CR-ATC Continuously Regenerated Anion Trap Column (P/N 060477)
- Dionex IonPac UTAC-ULP2 Column (P/N 079918)
- Dionex IonPac AG15 Guard Column, 2 × 50 mm (P/N 053943)
- Dionex IonPac AS15 Analytical Column, 2 × 250 mm (P/N 053941)
- Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating Suppressor,™ 2 mm (P/N 064555)
- Vial Kit, Polystyrene with Caps and Blue Septa, 10 mL (P/N 074228)
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System software version 7.1

\*This application can also be used with a Dionex ICS-2100 system.

## Results and Discussion

In this study, a sample containing 5 mg/L ETA, 0.1 mg/L hydrazine, and 5 µg/L PAA was prepared to simulate the power plant secondary feed water. Trace fluoride, chloride, and sulfate in the simulated sample were determined on a Dionex IonPac AS15 column set using an electrolytically generated potassium hydroxide eluent. All analytes were resolved with 35 mM KOH within 20 min, demonstrating the superior selectivity of the separation column. The analytes were detected by suppressed conductivity using the Dionex ASRS 300 Anion Self-Regenerating Suppressor operated in recycle mode. An equilibrated system showed a background conductance of ~0.6 µS and an average peak-to-peak noise of 0.8–1.2 nS.

The samples were delivered by the Dionex AS-AP Autosampler onto a Dionex IonPac UTAC-ULP2 concentrator column. The matrix resilience of the concentrator column allows direct injection of samples containing PAA. The PAA is not retained on the concentrator column and goes to waste during sample loading. The removal of the PAA ensures better preservation of the analytical column and reproducibility of the analysis.

Figure 1, Chromatogram A shows a DI water blank, which demonstrates that the system is free of contamination from the target anions. Fluoride, chloride, and sulfate were all calibrated in the range of 0.1–20 µg/L with coefficients of determination ( $r^2$ ) >0.999. The calibration data, detection limits, and quantification limits are summarized in Table 1.

Figure 1, Chromatogram B shows a typical standard of 0.5 µg/L each of fluoride, chloride, and sulfate in DI water. To validate this method, the simulated PAA-containing water sample was spiked with three concentration levels of fluoride, chloride, and sulfate. The recoveries for the three anions were in the range of 92.3–101% (Table 1).

Figure 1, Chromatogram C shows the simulated PAA-containing water sample.

Method performance was demonstrated with the simulated sample that was spiked with 2 µg/L each of fluoride, chloride, and sulfate (Figure 1, Chromatogram D).

Columns: Dionex IonPac AG15 and AS15 set, 2 mm  
 Eluent Source: Dionex EGC III KOH with Dionex CR-ATC  
 Eluent: 35 mM KOH  
 Flow Rate: 0.25 mL/min  
 Inj. Volume: 1 mL  
 Temperature: 30 °C  
 Detection: Suppressed Conductivity, Dionex ASRS 300 Suppressor, 2 mm, 22 mA, recycle mode

Peaks:	A	B	C*	D
1. Fluoride	—	0.5	0.005	2.0 µg/L
2. Glycolate	—	—	—	—
3. Acetate	—	—	—	—
4. Formate	—	—	—	—
5. Chloride	—	0.5	—	2.0
6. Carbonate	—	—	—	—
7. Sulfate	—	0.5	0.015	2.0

\*Estimate

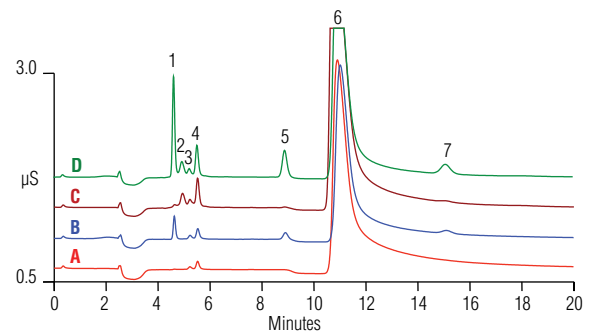


Figure 1. Chromatograms of A) a water blank; B) 0.5 µg/L fluoride, 0.5 µg/L chloride, and 0.5 µg/L sulfate in DI water; C) simulated PAA water; and D) simulated PAA water spiked with 2 µg/L fluoride, 2 µg/L chloride, and 2 µg/L sulfate.

Table 1. Calibration, detection limits, quantification limits, and recoveries of fluoride, chloride, and sulfate in simulated PAA water.

Anion	Calibration Range (µg/L)	Coefficient of Determination ( $r^2$ ) <sup>a</sup>	LOD (ng/L) <sup>b</sup>	LOQ (µg/L) <sup>c</sup>	Recovery <sup>d</sup> in Simulated PWR Secondary Feed Water				
					Unspiked Amount (ng/L)	Amount Added (µg/L)	Total Found (µg/L)	Peak Area RSD	Recovery (%)
Fluoride	0.1–20	1.000	3.8	0.012	5.0	1.00	1.01	0.99	96.4
						2.00	1.97	1.18	96.3
						4.00	4.00	0.24	98.7
Chloride	0.1–20	0.9997	5.0	0.017	—	1.00	0.923	1.49	92.3
						2.00	1.84	1.08	92.4
						4.00	3.87	2.64	96.7
Sulfate	0.1–20	0.9989	15	0.050	15	1.00	0.939	2.53	92.4
						2.00	2.04	2.21	101
						4.00	3.97	0.45	99.0

<sup>a</sup> Linear fit

<sup>b</sup> Limit of detection (LOD) = three × signal-to-noise ratio (S/N)

<sup>c</sup> Limit of quantification (LOQ) = 10 × S/N

<sup>d</sup> n = three injections

Figures 2A and 2B show the retention times and peak areas, respectively, of 69 successive injections of the spiked simulated sample. The results indicate that the method is robust.

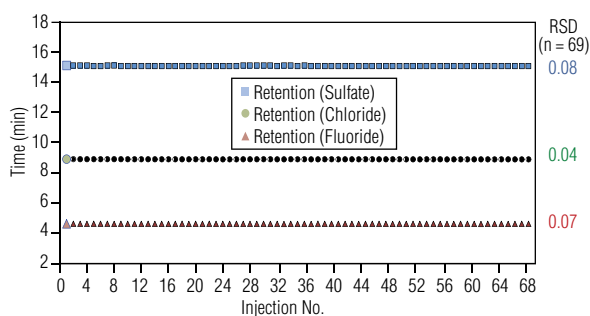


Figure 2A. Retention time reproducibility of fluoride, chloride, and sulfate in simulated PAA water spiked with 2 µg/L fluoride, 2 µg/L chloride, and 2 µg/L sulfate.

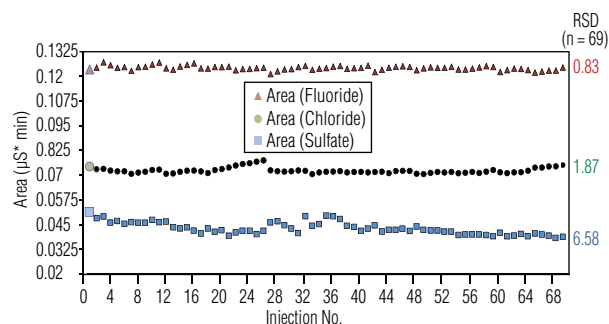


Figure 2B. Peak area reproducibility of fluoride, chloride, and sulfate in simulated PAA water spiked with 2 µg/L fluoride, 2 µg/L chloride, and 2 µg/L sulfate.

## Conclusion

This study describes the determination of low concentrations (<1 µg/L) of fluoride, chloride, and sulfate in simulated PWR feed water that contains PAA. The method demonstrated efficient trapping of the target anions on the Dionex IonPac UTAC-ULP2 concentrator column, while the sample cations (i.e., ETA and hydrazine) and PAA were diverted to waste. The anions were separated within 20 min on a Dionex IonPac AS15 column set using isocratic elution with electrolytically generated potassium hydroxide. Excellent retention time and peak area reproducibilities were demonstrated from 69 consecutive injections of a spiked simulated sample.

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