Application Note 1058

Determination of Polyacrylic Acid in Nuclear Power Plant Pressurized Water Reactor Secondary Feed Water

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Key Words
Acclaim SEC-1000 Column, Size-Exclusion Chromatography, Corrosion Inhibition

Introduction

The cost of corrosion-related failures in nuclear power plants (NPPs) is significant, prompting extensive study of corrosion-inhibiting mechanisms for nuclear power reactor systems. In pressurized water reactors (PWRs), deposit fouling in the secondary system (steam generator) can cause undesired consequences such as heat-transfer losses, corrosion of heat-exchange tubes, and reduction in plant output.[1] Studies have shown that the addition of polyacrylic acid (PAA) polymer dispersant to the steam generator water increases the corrosion resistance of steel and promotes removal of iron-based deposits from surfaces.[2]

Since 2009, PAA has been used at several NPPs as a dispersant in the feed water to reduce the accumulation of metal oxide deposits on the secondary-side surfaces of the steam generators.[3,4] These NPPs need to accurately measure PAA to ensure that the added amount is within the plant's administrative limits. The feed water in the secondary system contains other corrosion inhibitors (e.g., ethanolamine [ETA]) to obtain an alkaline pH,[5] and a volatile oxygen scavenger (e.g., hydrazine) to form protective magnetite on the surfaces of the steam generator components.[6] To measure PAA in these samples, size-exclusion chromatography (SEC) is considered the most effective method of separating PAA from small molecules present in the secondary feed water.

Goal

To develop a simple SEC analysis method for the determination of low concentrations (<20 µg/L) of PAA in secondary feed water

Equipment

- Thermo Scientific™ Dionex™ ICS-5000+ system, including:
  - SP Single Pump
  - DC Detector/Chromatography Compartment
  - Dionex AS-AP Autosampler* with 5.0 mL sample syringe and 8.5 mL buffer line (P/N 075520)
  - ICS-Series Variable Wavelength Detector, VWD-IC, 2G**
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data system (CDS) software version 7.1

* A Dionex AS-DV Autosampler can also be used for sample delivery.

** Either the 1 Channel (P/N 069116) or 4 Channel (P/N 069117) version may be used.

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Consumables

- Vial Kit, 1.5 mL, Glass with Caps and Septa (P/N 055427)
- PEEK tubing, 0.30 in, i.d., approximately 26 in. (66 cm)

Reagents and Standards

- Deionized (DI) water, Type I Reagent Grade, 18 MΩ-cm resistance or better
- Ethanolamine, 99% (Fisher Scientific P/N AC42725)
- Hydrazine monohydrate, >99% (Fisher Scientific P/N AA1665122)
- Polyacrylic acid, 9.9% (Sigma-Aldrich® P/N 181293)

Conditions	
Columns:	Thermo Scientific™ Acclaim™ SEC-1000 Analytical, 7.8 × 300 mm (P/N 079721)
Eluent:	DI Water
Flow Rate:	1.0 mL/min
Inj. Volume:	300 µL
Temperature:	30 °C
Detection:	200 nm
System Backpressure:	~1044 psi
Noise:	~20 µAU peak-to-peak
Run Time:	15 min

Preparation of Solutions and Reagents

Best Practices for Cleaning Solution/Reagent Containers

To obtain consistent sensitivity and good reproducibility, use high-quality water (≥18 MΩ-cm resistance) to prepare all eluent solutions, standards, and sample solutions. Keep the eluent blanketed under 34.5 kPa (5 psi) of helium or nitrogen at all times to reduce carbon dioxide intrusion.

To avoid introducing contamination, do not use polymer containers. Rinse glass vessels thoroughly with DI water before use. Trace amounts of PAA can be adsorbed by polymer containers; therefore, use glass autosampler vials to reduce the possibility of inaccurate measurements.

PAA Primary Stock Solution, 1000 mg/L

Transfer 1 mL of 9.9% PAA solution into a glass 100 mL volumetric flask and dilute to volume with DI water. Store the solution at 4 °C for up to one week.

PAA Secondary Stock Solution, 1 mg/L

Transfer 0.1 mL of 1000 mg/L PAA primary stock solution into a glass 100 mL volumetric flask and dilute to volume with DI water. This solution is good only on the day of preparation.

PAA Working Standard Solutions

To prepare PAA working standards, transfer the appropriate volumes of 1 mg/L PAA secondary stock solution to separate glass 100 mL volumetric flasks and dilute to volume with DI water. Prepare the working standard solutions on the day of analysis.

Ethanolamine Stock Solution, 1000 mg/L

Transfer 0.100 mL of ethanolamine into a glass 100 mL volumetric flask and dilute to volume with DI water.

Hydrazine Primary Stock Solution, 1000 mg/L

Transfer 151 µL of hydrazine monohydrate reagent solution (1.027 g/mL density) into a glass 100 mL volumetric flask and dilute to volume with DI water.

Hydrazine Secondary Stock Solution, 100 mg/L

Transfer 10 mL of 1000 mg/L hydrazine primary stock solution to a glass 100 mL volumetric flask and dilute to volume with DI water.

Simulated Secondary Feed Water

To prepare the simulated secondary feed water matrix blank, transfer 0.5 mL 1000 mg/L ethanolamine and 0.1 mL 100 mg/L hydrazine secondary stock solution into a glass 100 mL volumetric flask and dilute to volume with DI water. Table 1 shows the volumes of PAA, ETA, and hydrazine stock solutions used to prepare the simulated secondary feed water samples in 100 mL volumetric flasks.

Table 1. Preparation of PAA, ETA, and hydrazine stock solutions in 100 mL of surrogate matrices.

Matrix Composition	Volume of 1 mg/L PAA Secondary Stock Solution (mL)	Volume of 1000 mg/L ETA Stock Solution (mL)	Volume of 100 mg/L Hydrazine Stock Solution (mL)
5 ppm ETA + 0.1 ppm Hydrazine	0	0.5	0.1
6 ppb PAA + 5 ppm ETA + 0.1 ppm Hydrazine	0.6	0.5	0.1
10 ppb PAA + 5 ppm ETA + 0.1 ppm Hydrazine	1	0.5	0.1
20 ppb PAA + 5 ppm ETA + 0.1 ppm Hydrazine	2	0.5	0.1

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. To accommodate the large sample injection volumes in this application, install a 5 mL sample syringe and an 8.5 mL buffer line assembly. Prepare a 300 µL sample loop by measuring approximately 26 in. (66 cm) of 0.030 in. i.d. PEEK tubing. Verify the volume of the loop by the following steps: first weigh the empty loop, fill the loop with DI water, then reweigh the filled loop and calculate the volume. The total sample volume must be 300 µL ±5%.

In the Instrumental Method of Chromeleon CDS software version 7.1 under the Sampler Injection Mode, set the Overfill Factor to 4.5 to ensure injection reproducibility and to avoid exceeding the capacity of the sample vials. Install the sample loop on the injection valve in the lower compartment of the DC module. Flush the syringe, buffer line, and sample transfer line extensively to minimize contamination. Refill the wash reservoir with fresh DI water at least once every two days.

Install the Acclaim SEC-1000 column (7.8 × 300 mm) in the lower compartment of the DC. Connect the column outlet and the inlet of the flow cell in the VWD compartment using 0.005 in. i.d. PEEK tubing. Keep the lengths of the connecting tubing to a minimum.

Analyze the reproducibility of at least three injections of high-purity DI water blank to ensure that the Dionex AS-AP Autosampler is properly configured and free of contamination. Figure 1, Chromatogram A shows an example of a water blank injection.

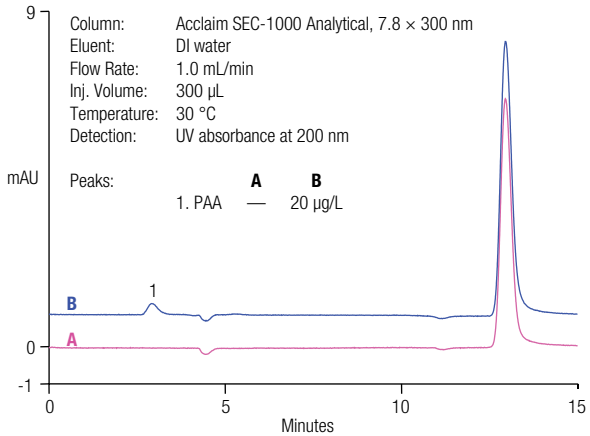

Figure 1. A) DI water blank and B) 20 µg/L PAA standard, with a 10% signal offset applied.

Results and Discussion

Separation

In SEC, the retention of analytes depends on the size of the molecules to be separated. Molecules that are larger than the pore size of the stationary phase are excluded from the pores and rapidly eluted into the void. Small molecules that enter the pores in the stationary phase have some degree of retention. The smaller the molecule, the more it is able to penetrate the stationary phase pores and thus the longer the retention time. SEC allows polymers such as PAA to be easily separated from small molecules (e.g., ETA and hydrazine) present in the secondary feed water. The Acclaim SEC-1000 column with a nominal pore size of 1000 Å is suitable for separating polymers and oligomers in the MW range of 1000 to 1,000,000 Da therefore, this column was selected for the determination of PAA.

PAA shows a maximum UV absorption ~200 nm.[7] Because most buffers and solvents will absorb at 200 nm, water was chosen as the eluent in this method to maximize the sensitivity of PAA. At neutral pH, many of the PAA side chains lose their protons and acquire negative charges on the carboxylic acid groups.[8] The Acclaim SEC-1000 column is packed with hydrophilic polymethacrylate particles, which have negative charges on the surface; therefore, PAA is repulsed from the surface and eluted from the column close to the void volume with a retention time of 2.92 min, as shown in Figure 1, Chromatogram B. Therefore, it is important to use high-quality water and ensure the system is free from contamination of polymers, which may interfere with the determination of PAA.

To achieve sufficient sensitivity for the determination of low concentrations of PAA, a 300 µL volume injection was used to develop this method. To assess the separation of PAA from the compounds typically used in the secondary feed water, a simulated sample containing 5 mg/L ETA and 0.1 mg/L hydrazine was prepared. As seen in Figure 2, no interference to PAA was observed in the simulated water matrix blank (Chromatogram A) and Chromatogram B shows the determination of 10 µg/L PAA in the simulated sample.

Linearity and Method Detection Limit

A calibration curve with six concentration levels was constructed using PAA from 5.0 to 200 µg/L prepared in DI water. The results yielded a quadratic relationship of peak area to concentration with a coefficient of determination (r^2) greater than 0.999. The method detection limits (MDLs) for PAA in DI water, simulated secondary feed water, and secondary feed water were determined from seven injections of each sample fortified with 10 µg/L PAA. The results of the calibration and MDL studies are summarized in Table 2.

Sample Analysis

A secondary feed water sample containing no PAA was provided by a NPP and used as a matrix blank to establish the validity of this method. The secondary feed water sample contained approximately 2.5 mg/L ETA and 0.075 mg/L hydrazine. In Figure 3, Chromatogram A shows the matrix blank of the secondary feed water sample and Chromatogram B shows the same sample spiked with 6 µg/L PAA. The chromatography indicates that ETA and hydrazine do not interfere with the determination of PAA.

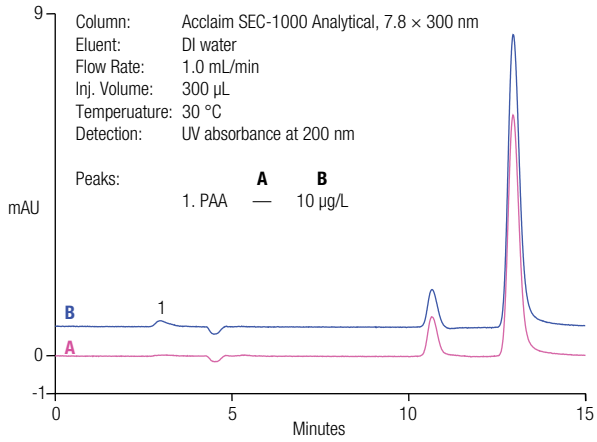

Figure 2. A) Simulated secondary feed water matrix blank and B) simulated secondary feed water spiked with 10 µg/L PAA, with a 10% signal offset applied.

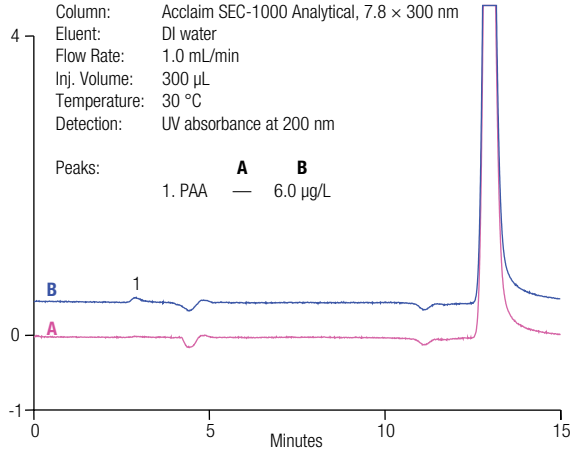

Figure 3. A) Secondary feed water matrix blank and B) secondary feed water spiked with 6 µg/L PAA, with a 10% signal offset applied.

Table 2. Calibration data and estimated MDLs of PAA.

Analyte	Range (µg/L)	Coefficient of Determination (r^2)[a]	MDL[b] in DI Water (µg/L)	MDL[b] in Simulated Secondary Feed Water[c] (µg/L)	MDL[b] in Secondary Feed Water[d] (µg/L)
PAA	5.0–200	0.9994	2.16	2.55	2.60

[a] Quadratic fit

[b] MDL = (SD) × (t_s), where (t_s) is the Student's t value for a 99% confidence level (t = 3.14 for seven replicate injections).

[c] Sample contains 5 mg/L ETA and 0.1 mg/L hydrazine.

[d] Sample contains ~2.5 mg/L ETA and 0.075–0.080 mg/L hydrazine.

Sample Accuracy and Precision

To determine the accuracy of this method, the recovery of PAA was examined in a simulated secondary feed water sample and a secondary feed water sample obtained from a nuclear power plant. The samples contained no PAA and were spiked with PAA at concentrations of 6, 10, and 20 µg/L. Three replicates of the spiked samples were analyzed and recoveries were in the range of 99.5–109% (Table 3), offering further evidence that ETA and hydrazine do not interfere with the determination of PAA. Seven replicates each of 10 µg/L PAA prepared in DI water, simulated secondary feed water, and secondary feed water were injected; the retention time and peak area precisions for all were between 0.69 and 6.63%, respectively. Figure 4 shows the overlay of seven chromatograms of secondary feed water spiked with 10 µg/L PAA. Table 4 summarizes the precision of the sample analyses. The data in Tables 3 and 4 indicate that the method is accurate and reproducible.

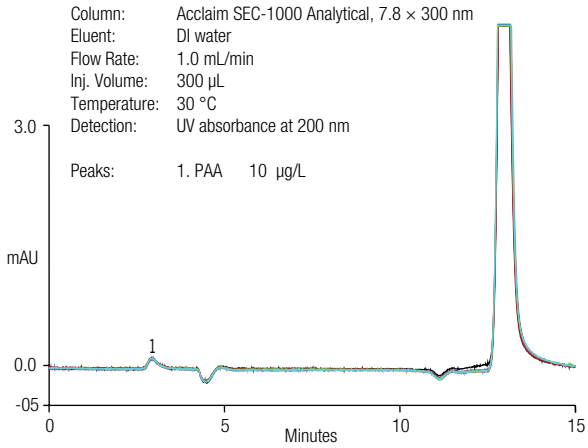

Figure 4. Overlay of seven chromatograms of secondary feed water spiked with 10 µg/L PAA.

Table 3. Recoveries of PAA in simulated secondary feed water and secondary feed water from a NPP.

Sample[a]	Amount Added (µg/L)	Total Found (µg/L)	Recovery (%)	Peak Area RSD
Simulated Secondary Feed Water[b]	6.00	6.36	106	2.87
	10.0	10.4	104	2.27
	20.0	21.0	105	3.26
Secondary Feed Water[c]	6.00	6.53	109	4.75
	10.0	9.95	99.5	4.76
	20.0	20.7	103	1.98

[a] n = three injections.
[b] Sample contains 5 mg/L ETA and 0.1 mg/L hydrazine.
[c] Sample contains ~2.5 mg/L ETA and 0.075–0.080 mg/L hydrazine.

Table 4. Retention time and peak area precisions.

Sample[a]	Retention Time RSD	Peak Area RSD
10 µg/L PAA Standard	0.52	4.79
10 µg/L PAA in Simulated Secondary Feed Water[b]	0.36	4.92
10 µg/L PAA in Secondary Feed Water[c]	0.69	6.63

[a] n = seven injections.
[b] Sample contains 5 mg/L ETA and 0.1 mg/L hydrazine.
[c] Sample contains ~2.5 mg/L ETA and 0.075–0.080 mg/L hydrazine.

Conclusion

This study demonstrates the determination of low concentrations of PAA in secondary feed water containing ETA and hydrazine. PAA is resolved from the matrix using an Acclaim SEC-1000 polymer-based size-exclusion column. Water is used as the eluent to maximize sensitivity and eliminate the need for eluent preparation. PAA is detected at 200 nm with a MDL of ~2.6 µg/L in secondary water samples. This method provides a relatively simple and economical solution for NPPs to determine PAA in secondary feed water.

References

1. Turner, C. W. *Implications of Steam Generator Fouling on the Degradation of Material and Thermal Performance*, Proceedings of the 15th International Conference on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, Colorado Springs, CO, Aug. 7–11, 2011; 2287–2299.
2. Fruzzetti, K. Effect of Polymer Dispersant on Flow-Accelerated Corrosion of Steam Generator Materials; Technical Report for Electric Power Research Institute: Washington, DC, June 2005 [Online] www.epri.com/abstracts/Pages/ProductAbstract.aspx?ProductId=000000000001012056 (accessed May 23, 2013).
3. Lepine, L.; Gilbert, R. Thermal Degradation of Polyacrylic Acid in Dilute Aqueous Solution. *Polym. Degradation and Stability* **2002**, *75* (2), 337–345.
4. Fruzzetti, K. Reducing Deposits in Steam Generators. *Nucl. Plant J.* **2009**, *27*, 42–44.
5. Keeling, D. L.; Polidoroff, C. T.; Cortese, S.; Cushner, M. C. *Ethanolamine Properties and Use for Feed Water pH Control: A Pressurized Water Reactor Case Study*, Proceedings of the 7th International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, Breckenridge, CO, Aug. 7–10, 1995; 675–685.
6. Pein, K.; Molander, A.; Sawicki, J. A.; Stutzmann, A. *Distribution of Iron Redox States for Different Hydrazine Concentrations and Potentials - A Laboratory Study*, Proceedings of the 8th International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, Amelia Island, FL, Aug. 10–14, 1997; 113–119.
7. Liu, A.; Honma, I.; Ichihara, M.; Zhou, H. Poly(acrylic Acid)-Wrapped Multi-Walled Carbon Nanotubes Composite Solubilization in Water: Definitive Spectroscopic Properties. *Nanotechnology* **2006**, *17*, 2845–2849.
8. Jorand, F.; Sergent, A. S.; Remy, P. P.; Bihannic, I.; Ghanbaja, J.; Lartiges, B.; Hanna, K.; Zegeye, A. Contribution of Anionic vs Neutral Polymers to the Formation of Green Rust 1 from γ-FeOOH Bioreduction. *Geomicrobiol. J.* **2012**, *30*, 600–615.

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