Determination of Polyacrylic Acid in Boiler Water Using Size-Exclusion Chromatography with Charged Aerosol Detection

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Key Words

Acclaim SEC columns, size-exclusion chromatography, Corona Veo charged aerosol detector, polyacrylic acid, boiler water, power generation

Abstract

Polyacrylic acid (PAA) is widely used as an anti-scaling additive for boiler water in conventional steam generators and, more recently, in nuclear steam generators. This work demonstrates the application of Thermo Scientific™ Acclaim™ SEC columns and the Thermo Scientific™ Dionex™ Corona Veo™ charged aerosol detector to the measurement of PAA in boiler water. No sample extraction or pre-concentration is needed to attain detection limits below 10 µg/L. The linear range exceeds 200 µg/L, with a useful dynamic range exceeding 400 µg/L, and recoveries are 60–120% over the range of 3–400 µg/L in a boiler water matrix.

Introduction

Boiler scale is formed when impurities in water precipitate onto heat transfer surfaces or when suspended matter in the water settles out forming hard, adherent coatings. If unchecked, scaling causes progressive lowering of the boiler efficiency due to heat retardation as it acts as an insulator. Boiler deposits can also cause plugging leading to decreased operating efficiency, boiler damage, unscheduled boiler outages, and the need for costly cleaning procedures. Such scale-related issues are major problems for the generation of electrical power whether using conventional steam generators or nuclear power.

Polyacrylic acid, a widely used anti-scaling additive, has both scale inhibition and dispersion properties. It is typically used at concentrations of 1–1000 µg/L, depending on the load of metals in the boiler water. The amount of PAA remaining needs to be measured for both process control and for wastewater discharge. Since PAA is the only macromolecule normally present in boiler water, it can easily be resolved from other components using size-exclusion chromatography (SEC).

Size-exclusion chromatography is the dominant mode of separation for polymers. It is based on the discrimination of individual sample components in the pore volume of the packing material. Large sample molecules cannot or can only partially penetrate the pores, whereas smaller molecules can access most or all pores. Thus, large molecules elute first and smaller molecules elute later.

Acclaim SEC columns use hydrophilic polymer particles with a well controlled pore-size distribution that gives a quantitative relation between molecular size and retention time. These columns are designed for the analysis of water-soluble polymers, including PAA.

Unfortunately, PAA only has a weak UV chromophore so UV absorbance detection is limited to more concentrated samples. Charged aerosol detection (CAD), a mass-sensitive approach capable of measuring any non-volatile and many semi-volatile species, shows excellent sensitivity and a wide dynamic range and does not require a chromophore for analyte detection. The Corona Veo charged aerosol detector is an excellent choice of detector for polymers, especially ones with weak UV chromophores. Detection begins with the nebulization of the column effluent, followed by the generation of a dry aerosol and the subsequent adsorption of ionized nitrogen onto the particle surface. In a final step, this charge is then

measured by an electrometer. With full coverage of the aerosol particles, this charge is proportional to the surface area and is thus – as a first approximation – to its mass. Since this process does not depend on the chemical or spectroscopic properties of the particles, it is nearly universal for nonvolatile analytes. Compared to light-scattering detection, electrical detection provides superior detection limits.

Here we demonstrate direct analysis for polyacrylic acid using SEC separation and charged aerosol detection with detection limits below 10 µg/L, recoveries of 60–110%, and a useful dynamic range greater than 400 µg/L.

Experimental Details

Consumables	Part Number
Thermo Scientific™ Chromacol Instrument Select Kit, clear standard opening screw thread vial (8-425), black closure with white silicone/red PTFE septum	TSL
Acetonitrile, Fisher Chemical™ Optima™ LC-MS grade	A955
Deionized water	
Polyacrylic acid ethanolamine salt 10% PAA solution in purified water from a reputable supplier	
A specimen of boiler water matrix without PAA was kindly provided by a customer. The specimen was preserved by the addition of acetonitrile (10% v/v).	

Sample Preparation

PAA stock standard, 1000 µg/L, was prepared by serial dilution in water of the 10% PAA solution. Working standards at 200, 100, 50, and 25 µg/L were prepared by diluting the stock standard with water directly into the autosampler vials. The matrix recovery solutions were prepared by diluting the stock standard in preserved boiler water matrix to 400 µg/L, then serially diluting to 80, 16, and 3.2 µg/L, again directly into the autosampler vials.

Separation Conditions		Part Number
Instrumentation:	Thermo Scientific™ Dionex™ UltiMate™ 3000 Liquid Chromatography System consisting of	
	DGP-3600RS Pump	5040.0066
	TCC-3000RS Column Oven	5730.0000
	WPS-3000RS Sampler	5840.0020
	DAD-3000RS Diode-array Detector	5082.0020
	Corona Veo RS Charged Aerosol Detector	5081.9920
Columns:	Acclaim SEC-300 5 µm, 4.6 × 300 mm	079723
	Acclaim SEC-1000 7 µm, 4.6 × 300 mm	079724
Mobile phase A:	Water	
Mobile phase B:	Acetonitrile	
Isocratic 90% A,	10% B	
Flow rate:	0.35 mL/min	
Column temperature:	30 °C	
Injection details:	Variable, 2–100 µL	
Diode array detection:	UV 200 nm, data rate 1 Hz, filter 2 s	
Charged aerosol detection:	Evaporator temperature 55 °C, gas pressure 60 psi, data rate 2 Hz, filter 5 s, power function 0.80	

Data Processing

Software: Thermo Scientific™ Dionex™ Chromeleon™ 6.8 SR13 Chromatography System. The CAD data was smoothed by a two-pass 25-point Savitsky-Golay filter.

Results

The chromatographic method used a 4.6 × 300 mm Acclaim SEC-1000 column with water / acetonitrile (90:10 v/v) for the mobile phase. This permitted a direct injection of a relatively large volume (35 μL) of aqueous sample without any pre-concentration. Detection with the Corona Veo charged aerosol detector gave good linearity and satisfactory detection limits.
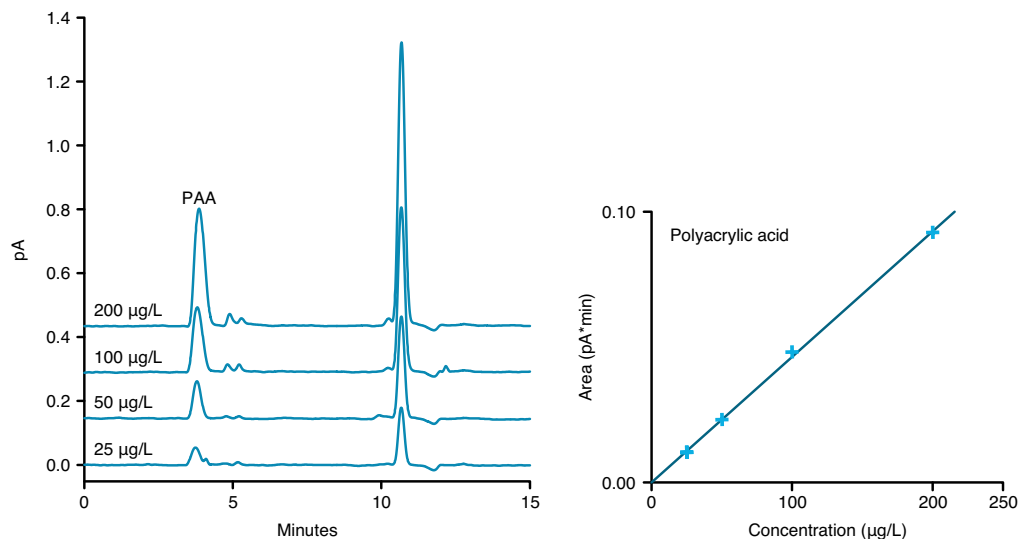

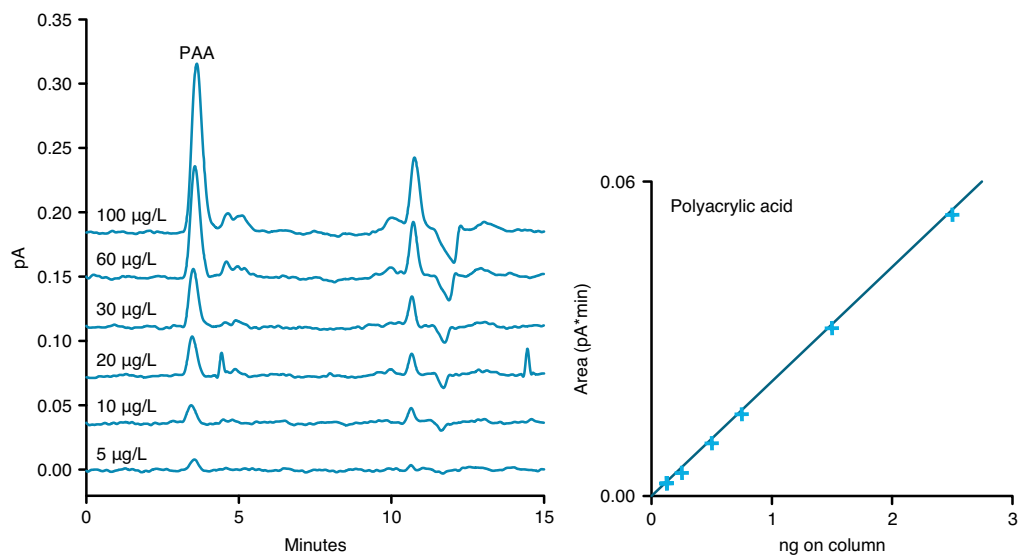Figure 1: Calibration data for PAA using Acclaim SEC-1000 column and 35 μL injection of standards in water

Figure 2: Detection limit data for PAA using Acclaim SEC-1000 column and injection volumes as indicated of a 25 μg/L standard in water
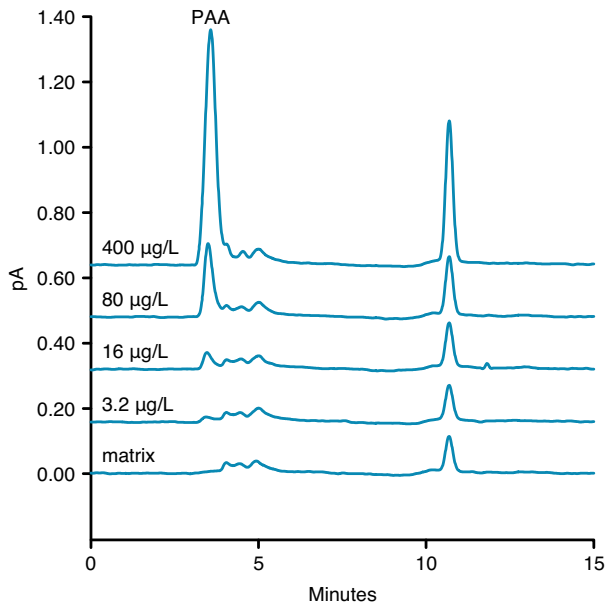
4

Figure 3: Recovery data for PAA using an Acclaim SEC-1000 column and injections of 35 µL of matrix fortified as indicated

Figures 1, 2, and 3 show typical calibration, detection limit, and recovery chromatograms using the Acclaim SEC-1000 column. Typical calibration data are presented in Table 1. Calibration was calculated using a quadratic fit forced through zero, with 1/X weighting. Calibration standards in water were 25–400 µg/L. The fit quality was good at 4%RSD for a 35 µL injection. Carryover was not observed in a blank injection following an injection of 400 µg/L PAA. Detection limit data are presented in Figure 2. The limit of detection (LOD) was found to be 125 pg on column (5 µL × 25 µg/L), with a signal-to-noise ratio of 3. Data showed an adequate fit with 6% RSD. This data also showed that large injections up to 30 µL caused no peak broadening, and up to 100 µL caused only minor broadening. Data for recoveries are presented in Figure 3 and Table 2, and were found to be 86–109%. The Acclaim SEC-1000 column showed better resolution between the PAA and the interfering peaks in the matrix and provided satisfactory recoveries.

Compound	Calibration Range (µg/L)	Coefficient of Determination	Mean Relative Error (%)
PAA on Acclaim SEC-300 column	25–400	0.996	3.3
PAA on Acclaim SEC-1000 column	25–400	0.999	3.9

Table 1: Accuracy – (Acceptance criteria: the back calculated concentrations should fall within ±15% of their nominal values at all levels except for the LLOQ where ±20% is acceptable. No two adjacent levels should be outside their criteria.)

	Acclaim SEC-300 Column		Acclaim SEC-1000 Column	
Spiking Level µg/L	Found µg/L	% Recovery	Found µg/L	% Recovery
400	330	83	358	90
80	74	93	67	84
16	12	75	14	89
3.2	1.9	59	3.5	109
Blank	0.1	n/a	0.0	n/a

Table 2: Recovery – (Calculate the recovery – acceptance criteria: method dependant, target >80% and at least as good as the competition)

Standard SEC methods for measuring molecular weight employ a buffered mobile phase, which is used to suppress electrostatic effects between an ionic polymer and the stationary phase. In this case, the buffer was omitted, which shifted the retention time near to the exclusion volume and sharpened the peak, thereby improving resolution between PAA and interferences. This also reduced baseline noise in the detector. The Corona Veo charged aerosol detector gave better signal-to-noise performance with 10% acetonitrile added to the mobile phase, which had no significant effect on the chromatographic performance.

The Corona Veo charged aerosol detector measures the electrical current carried by charge-bearing aerosol particles. The charge on a particle is limited by its surface area, so to relate the charge on a particle to its mass, a linearizing function is applied. After calibration, the detector signal is proportional to the mass of analyte delivered to the detector. In this instance the optimal linearity was obtained with a power function value of 0.80.

Due to the universal nature of charged aerosol detection and the sensitivity of the Corona Veo, care must be taken to avoid column bleed and contamination of the mobile phase or LC system. The Acclaim SEC columns have extremely low-bleed performance when properly equilibrated and conditioned. For best performance, acetonitrile should be LC/MS grade or pesticide-residue grade and water must have 18.2 MΩ-cm conductivity and $\leq$ 5 ppb total organic carbon. To minimize down-time, an HPLC dedicated for use with volatile mobile phases should be used. Washed glass sample vials are preferable to polypropylene vials as the latter were found to reduce recovery of PAA at low ppb levels.

Conclusion

- The Acclaim SEC columns provide the resolution and low background needed for successful trace analysis of polyacrylic acid.

- The Corona Veo charged aerosol detector excellent sensitivity for directly measuring polyacrylic acid to < 10 µg/L in boiler water matrix.

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