

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

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Overview

Purpose: This work demonstrates the performance of charged aerosol detection applied to the analysis of polyacrylic acid (PAA) in boiler water.

Methods: PAA is separated from low-molecular weight components by size-exclusion chromatography and quantified by charged aerosol detection.

Results: Direct measurement of PAA in boiler water is shown at concentrations below 10 µg/L.

Introduction

Boiler scale is formed either 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.

Scale formation can be prevented through the use of inhibitors. These inhibitors, also called anti-scalants, slow the precipitation process of sparingly soluble salts by absorbing to the salt crystals forming on surfaces. Anionic scale inhibitors also have dispersive qualities. Particles of suspended salt or organic solids are surrounded by the anionic-charged scale inhibitor forming anionic particles that will repel each other, thereby preventing agglomeration and precipitation.

PAA, a widely used anti-scalant additive, has both scale inhibition and dispersion properties. It is typically used at rates of 1–1000 µg/L, depending on the load of metals in the boiler water¹. 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. Unfortunately, PAA only has a weak UV chromophore so UV absorbance detection is limited to more concentrated samples. Charged aerosol detection, a mass-sensitive approach capable of measuring any non-volatile and many semi-volatile species, shows excellent sensitivity, a wide dynamic range, and does not require a chromophore for analyte detection. The recent improvements found in the Thermo Scientific™ Dionex™ Corona™ Veo™ charged aerosol detector now allows direct measurement of PAA in boiler water at <10 µg/L.

Methods

Materials

Acetonitrile, Fisher Scientific™, Optima™ HPLC grade, Cat. No. A996

Water purified by a Millipore Milli-Q™ Advantage A-10 system.

PAA ethanolamine salt, GE Betz, OptiSpere™ PWR6600, 10% PAA solution in purified water.

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).

Liquid Chromatography

HPLC System:

Thermo Scientific™ Dionex™ UltiMate™ 3000 RS system with a Corona Veo charged aerosol detector:

Evaporator temperature: 55 °C

Data linearization: Power function = 1.20

Data collection rate: 5 Hz

Filter 5.0 sec.

Data Analysis

Thermo Scientific™ Dionex™ Chromeleon™ chromatography data software (v 6.8) was used to collect and analyze the data. The charged aerosol data was smoothed with a 2-pass 25-point Savitsky-Golay algorithm. The calibration was quadratic, with a forced zero intercept and 1/x weighting.

PAA Analysis

Column: Thermo Scientific™ Acclaim™ SEC-300
5 µm, 4.6 × 300 mm

Column temp.: 30 °C

Flow rate: 0.35 mL/min

Injection vol.: 2–100 µL

Mobile phase: 10:90 acetonitrile:water (v/v)

Sample prep.: Standards were prepared by serial dilution with water. Recovery samples were prepared by serial dilution with matrix.

Results and Discussion

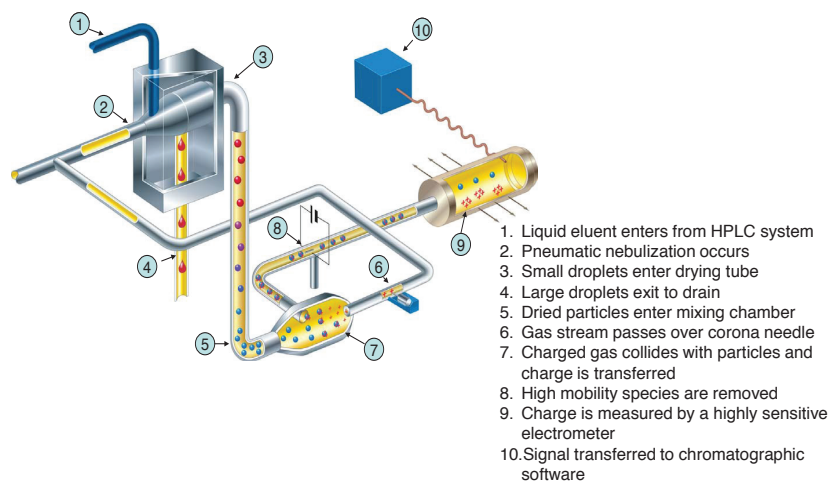
Size-Exclusion Chromatography

The Acclaim SEC-300 columns use a hydrophilic polymer with a controlled pore structure that gives a quantitative relation between molecular size and retention time for polymers up to 50,000 Da. Its intended use is for the analysis of water-soluble polymers, including PAA. The stationary phase has some residual carboxylate groups on the surface, so ordinarily a buffered mobile phase would be used to suppress electrostatic effects when determining molar mass. However, in this case, only the concentration is needed, so the buffer is omitted; this shifts the retention time near to the exclusion volume, sharpens the peak, and reduces noise in the detector. The Corona Veo detector gave better signal-to-noise performance with 10% acetonitrile added to the mobile phase; this had no significant effect on the chromatographic performance.

Charged Aerosol Detection

An evolution for charged aerosol detection, the Corona Veo detector has a new nebulizer designed for micro flow-rates, enhanced semi-volatile sensitivity, and technological advancements that improve its compatibility with mobile-phase conditions used with UHPLC. The principle of operation of charged aerosol detection is shown in Figure 1. Charged aerosol detection first nebulizes eluent from the column. Large droplets exit the detector to waste. Selected smaller droplets then enter the drying tube and form particles once the solvent is evaporated. Particles enter a reaction chamber where they collide with ionized gas formed when nitrogen is passed over a corona wire. Charge is transferred from the ionized gas to the analyte particles. Once unreacted ionized gas is removed by an ion trap, the charge on the particle is measured by a sensitive electrometer. The response of the detector is related to the mass of the analyte entering the detector by a power function. An exponent of 1.2 was found to best linearize the data.

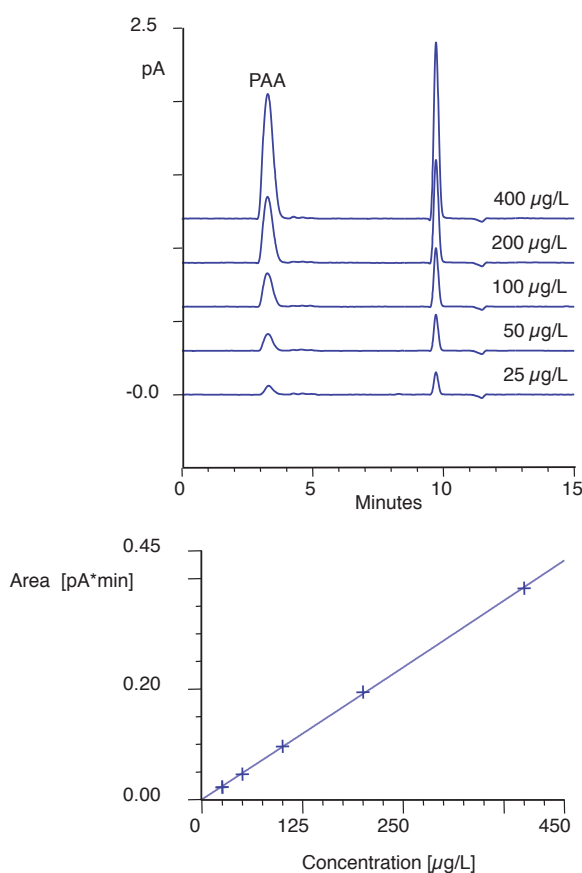
FIGURE 1. Schematic and functioning of charged aerosol detection.



Due to universal nature of charged aerosol detection and the improved sensitivity of the Corona Veo detector, care must be taken to avoid mobile phase and system contamination, and column bleed. The Acclaim SEC columns have excellent low-bleed performance. For best performance, acetonitrile should be LC/MS grade or pesticide-residue grade. Water must have 18.2 M Ω -cm conductivity and ≤ 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 these were found to reduce recovery of PAA at low ppb levels.

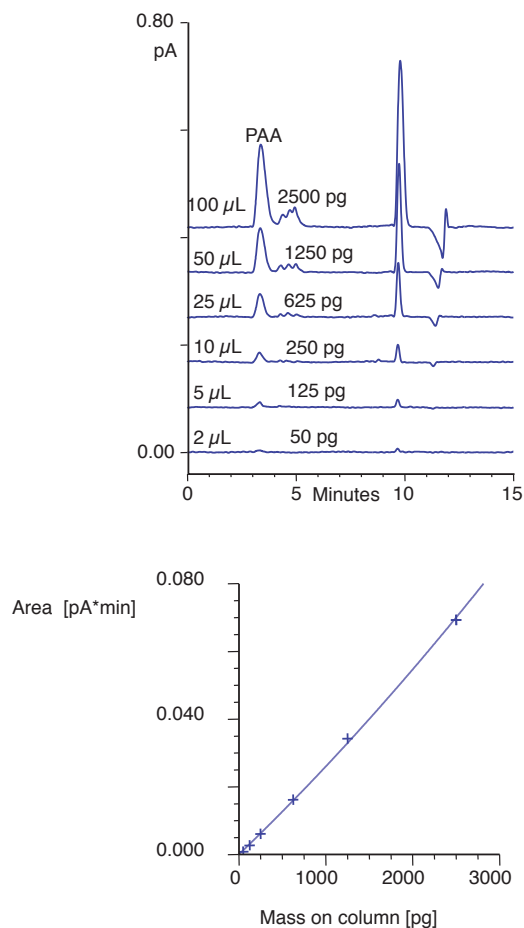
Calibration data for 25–400 $\mu\text{g/L}$ PAA is presented in Figure 2. Data showed a good fit with 3.3% RSD.

FIGURE 2. Calibration data for aqueous PAA standard (35 μL volume analyzed).



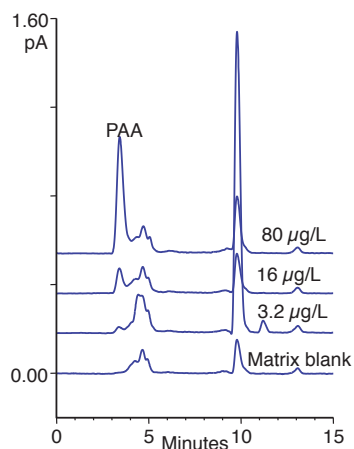
Data for limits of detection (LOD) are presented in Figure 3 and were found to be 50 pg on column ($2 \mu\text{L} \times 25 \mu\text{g/L}$), with a signal/noise of 3. Data showed a good fit with 12% RSD.

FIGURE 3. Detection limits for 25 $\mu\text{g/L}$ aqueous PAA standard (2–100 μL volume analyzed).



Data for spiked recovery are presented in Figure 4 and were found to be 59–93%. Recovery is adequate for $\geq 16 \mu\text{g/L}$, and further work will be needed to improve at the lowest levels.

FIGURE 4. Recovery of PAA added to boiler water matrix (100 μL volume analyzed).



Recovery in Matrix		
Added ($\mu\text{g/L}$)	Found ($\mu\text{g/L}$)	Recovery (%)
400	330	83
80	74	93
16	12	75
3.2	1.9	59
0	0.1	n/a

Conclusion

- Improvements found in the new Corona Veo detector make it possible to directly measure PAA to $<10 \mu\text{g/L}$ in matrix.
- The Acclaim SEC-300 column provides the resolution and low background needed for successful trace analysis of PAA.

References

1. GE Power & Water: http://www.gewater.com/pdf/Presentations_Cust/Americas/English/OptiSperserPWR6600DispersantReview_EN.ppt (accessed May 1, 2013)

Acknowledgements

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