

Quantification of Polyphosphonates and Scale Inhibitors in High Ionic Strength Matrix Effluents Using IC-MS/MS

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Key Words

- TSQ Quantum Access
- SRM
- Ion chromatography
- Water analysis

Introduction

Scale deposits and corrosion formation in aqueous industrial cooling systems reduce the efficiency of heat transfer and can lead to equipment failure and increased operating costs. The addition of scale and corrosion inhibitors to cooling tower water streams helps to minimize corrosion formation by allowing dissolved minerals to remain soluble in water instead of depositing as scale. In turn, these additives permit the repeated cycling of water in cooling systems.

Before scale and corrosion inhibitors were commonly used, all cooling systems were “once-through” systems. Copious amounts of water were removed from lakes and streams by the cooling systems, greatly stressing aquatic life and negatively affecting the environment. By adding polyphosphonate compounds, such as HEDP (1-hydroxy ethylidene-1, 1-diphosphonic acid) and PBTC (2-phosphonobutane-1,2,4-tricarboxylic acid), to cooling water, corrosion and scale are minimized so that the cooling water can be cycled repeatedly through the system before it is released back into the environment.

When the cooling water is released back to the lake or stream, it must meet the standards of the United States Environmental Protection Agency (US EPA) Clean Water Act (CWA). Section 316(b) requires industrial plants to employ the best technology available to protect fish and aquatic life.¹ With the increased use of scale and corrosion inhibitors, polyphosphonates are now an emerging environmental contaminant and few quantitation methods exist. The ion chromatography – mass spectrometry (IC-MS/MS) technique described here provides robust quantitation in less than 20 minutes for five common scale and corrosion inhibitors in cooling water effluents – ATMP (amino trimethylene phosphonic acid), HEDP, PBTC, HPMA (hydrolyzed polymaleic anhydride), and PSO (a proprietary phosphinosuccinic oligomer)²⁻⁴.

Goal

To develop a robust IC-MS/MS method for the quantitation of scale and corrosion inhibitors in a high anionic matrix.

Experimental Conditions

Ion Chromatography

IC analysis was performed on a Dionex ICS 3000 ion chromatography system (Dionex Corporation, Sunnyvale, CA). The polyphosphonate and scale inhibitor samples were directly injected and no sample pre-treatment was required. The IC conditions were as follows:

Column set: IonPac® AG21 (2.1 × 50 mm) / AS21 (2.1 × 250 mm); guard and separator columns (Dionex)

Suppressor: ASRS® 300, 2 mm; operated at 38 mA (Dionex)

Column temperature: 30 °C

Injection volume: 100 µL

Mobile phase: Potassium hydroxide, electrolytically generated with an EGC-KOH cartridge

Gradient: 0–7 min: 20 mM KOH

7–12 min: 20–60 mM KOH

12–17 min: 60 mM KOH

17.1 min: 20 mM KOH

Flow rate: 300 µL/min

Eluent generation technology allows automatic in-situ production of high-purity IC eluent (Figure 1). The pump delivers water to an eluent generator cartridge (EGC) that converts the water into a selected concentration of potassium hydroxide eluent using electrolysis. After separation on the column, the eluent enters the ASRS suppressor, which produces hydronium ions to exchange with potassium in the eluent and neutralizes the hydroxide. This makes the mobile phase compatible with an atmospheric ionization source as featured on LC-MS and LC-MS/MS systems.

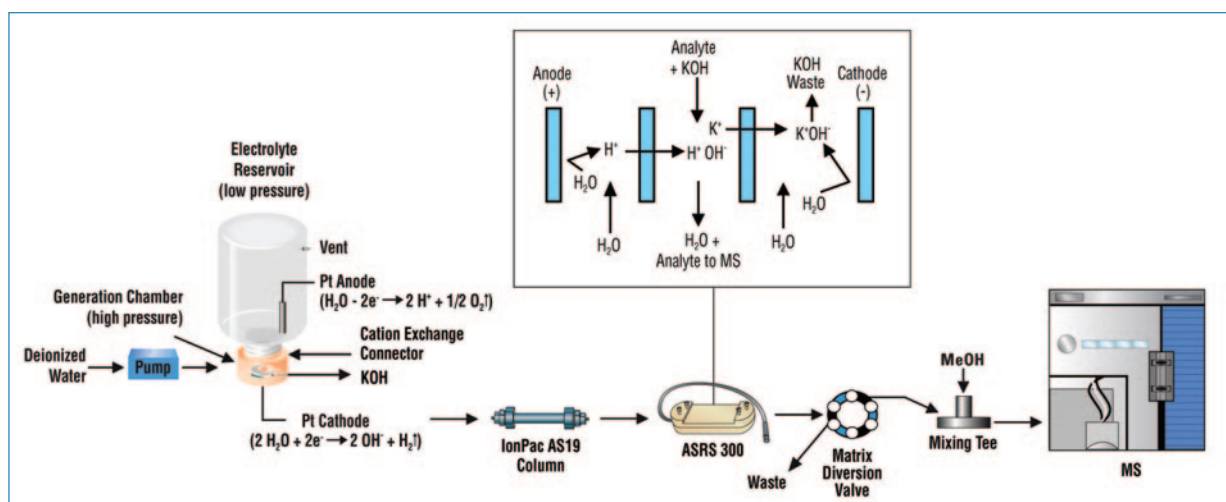


Figure 1. The flow schematic for an IC-MS application shows how an eluent generator cartridge produces potassium hydroxide. The eluent then passes through a suppressor, making it compatible with a mass spectrometer.

Mass Spectrometry

MS analysis was carried out on a Thermo Scientific TSQ Quantum Access triple stage quadrupole mass spectrometer with an electrospray ionization (ESI) source. The MS conditions were as follows:

Ion source polarity:	Negative ion mode
Spray voltage:	4000 V
Sheath gas pressure:	40 arbitrary units
Ion sweep gas pressure:	1 arbitrary unit
Auxiliary gas pressure:	2 arbitrary units
Capillary temperature:	300 °C
Collision gas pressure:	1.2 bar
Skimmer offset:	0 V
Detection mode:	Selective reaction monitoring (SRM); see Table 1 for details.

The cooling water matrix ions eluted prior to the analytes; therefore, the first 7.5 minutes of elution were diverted from the mass spectrometer to decrease source fouling. While the eluent was diverted, a make up flow of methanol was supplied to the mass spectrometer.

Table 1. SRM conditions

Name	SRM Transitions	Collision Energy (V)	Scan Width (Da)	Scan Time (s)	Tube Lens (V)
HEDP	204.580 → 168.860	16	0.01	0.5	49
	204.580 → 186.855	13			
PBTC	268.910 → 188.925	20	0.01	0.5	45
	268.910 → 206.911	16			
ATMP	297.770 → 197.896	26	0.01	0.5	54
	297.770 → 215.870	20			
PSO*	296.850 → 118.749	27	0.01	0.5	34
	296.850 → 146.832	19			
HPMA	337.490 → 318.829	16	0.01	0.5	60
	318.960 → 230.997	13			

*PSO is a proprietary molecule. For this oligomer, m/z 296.85 was found to be a consistent marker ion.

Results and Discussion

Calibration curves generated on the TSQ Quantum Access™ mass spectrometer show excellent linearity using only external quantitative measurements with no internal standard correction. The detection range for all compounds was 5-5000 ppb (Figure 2 and Table 2).

The method detection limit (MDL) in matrix was calculated by seven replicate injections of 100 ppb in a simulated matrix of fluoride (20 ppm), chloride (30 ppm), nitrate (100 ppm), phosphate (150 ppm), and sulfate (150 ppm). Using the equation $MDL = t_{99\%} \times S_{(n-1)}$, where t equals the Student's t test at 99% confidence intervals ($t_{99\%, (6)} = 3.143$) and S is the standard deviation, the MDLs for all compounds were calculated (Table 2). Figure 3 shows the response of the analytes spiked in the simulated matrix. The recoveries of all of the compounds were within 15% of the 100 ppb spike. The reproducibility of all the matrix-spiked samples was within 5%, without internal standard correction.

Table 2. Linearity and calculated detection limits of the analytes

Compound	R ²	MDL in matrix (ppb)
HEDP	0.9979	8.3
PBTC	0.9975	3.7
ATMP	0.9998	16.5
HPMA	0.9985	16.5
PSO	0.9965	8.8

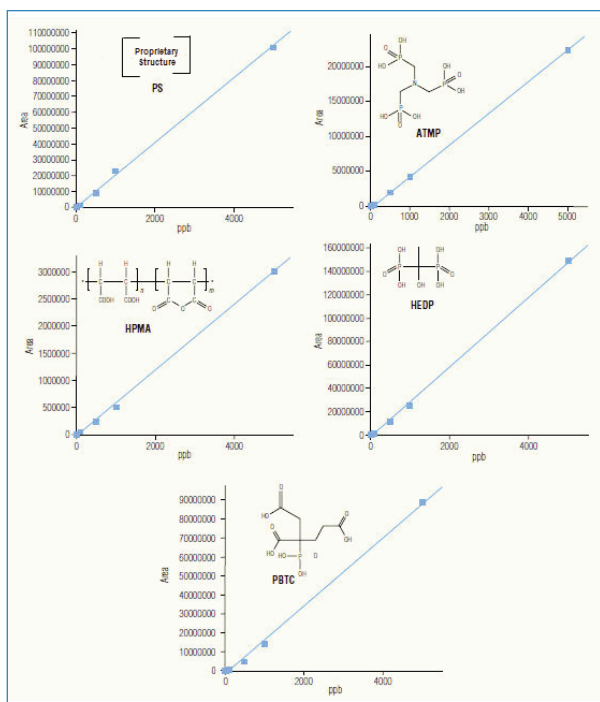


Figure 2. Calibration curves from 5 ppb to 5000 ppb for the analytes of interest, determined by linear regression analysis with equal weighting of the data.

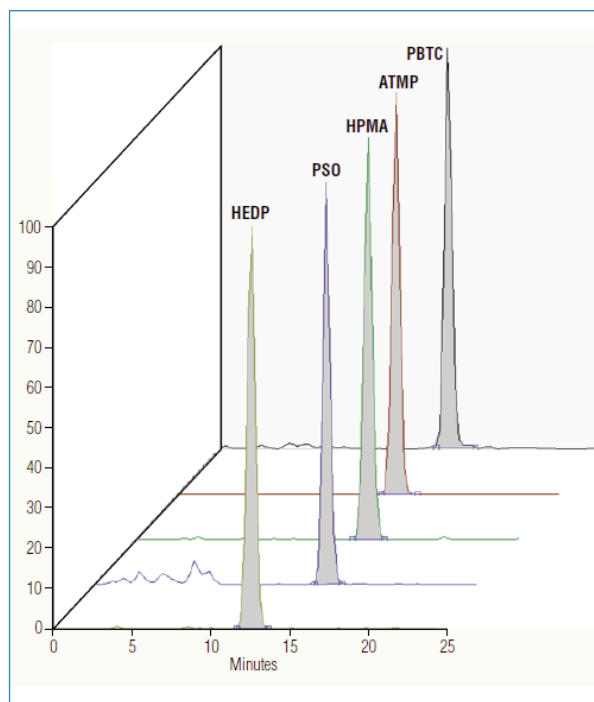


Figure 3. The response of 100 ppb analytes spiked into a high ionic strength matrix. The analytes showed excellent recoveries (within 15% of the 100 ppb spike) when spiked into the matrix.

Water treatment chemistry is a specialized field that often uses proprietary technology. As such, it is difficult to evaluate methods to reduce the environmental impact from the operation of cooling water systems. The method described here can detect the scale and corrosion inhibitors at sub-part-per-billion levels, although most cooling streams have part-per-million levels of scale and corrosion inhibitors. Any adverse matrices are diluted when the sample is diluted into the calibration range of 5-5000 ppb.

Compounds such as PSO and HPMA are proprietary blends with many components. When issued, they are sold in controlled, blended formulations. In the sample we received, one main marker and its transitions were examined. These marker ions, of m/z 297 and m/z 337, respectively for PSO and HMPA, showed excellent linearity over the quantitation range (Table 2).

Conclusion

The addition of scale and corrosion inhibitors to the water stream in industrial cooling systems reduces corrosion and allows repeat water cycling. While there is no current EPA guideline for the amount of corrosion and scale inhibitors released into the environment, interest in the quantification of these products in released water has increased. The minimum detection level established by this method shows that low-level quantitation of scale and corrosion inhibitors is possible, even in a high concentration of laboratory-simulated matrix.

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