



Fast separation of heat stable salts

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Keywords

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Goal

To analyze various amine scrubbing solutions for the presence of heat stable salts

Introduction

Hydrogen sulfide (H_2S) and carbon dioxide (CO_2) are often found in natural gas streams. These gases are removed using amine-rich solutions (e.g., monoethanolamine (MEA), diethanolamine (DEA), methanolamine, and methyldiethanolamine (MDEA)) before they can be transported or used. However, amine solutions also extract other contaminants during this process, which is also known as the amine sweetening process. The contaminants in the acid gas removal processes are called heat stable salts (HSS). HSS are formed as a result of an irreversible reaction of the amine with certain acidic components present in process gases/liquids. Their strong chemical bonding with the amine molecule forms a salt that cannot be regenerated by the addition of heat. This results in a slow buildup of the HSS in the amine circulation loop. The increased HSS levels lead to several problems in an amine gas treating plant. Two major problems are corrosion and the resulting operation problems, resulting in unscheduled outages.¹ Corrosion leads to high repair and maintenance costs, potential environmental consequences, and lost production.² Thus, it is important to monitor HSS in amine solutions so appropriate action can be taken to control them.

Ion chromatography (IC) has been used to determine the presence of HSS in amine solutions.³⁻⁵ In this application note, a Thermo Scientific™ Dionex™ IonPac™ AS25A column was used to analyze various refinery samples for the presence of common inorganic anions as well as heat stable amine salt anions, including fluoride, chloride, nitrate, nitrite, bromide, sulfate, phosphate, acetate, formate, propionate, butyrate, sulfite, thiosulfate, and thiocyanate. The Dionex IonPac AS25A column has similar performance to the Dionex IonPac AS25 column, with the main difference being the separation of bromide and nitrate. The Dionex IonPac AS25A column is optimized to separate bromide and nitrate, which cannot be baseline resolved on a Dionex IonPac AS25 column. The Dionex IonPac AS25A column is a high-capacity, hydroxide-selective anion-exchange column ideally suited for determination of sulfur species in wastewater effluents from the chemical and petroleum industries.⁶ Here various refinery solutions were analyzed for the above listed anions. In addition, thiosulfate and thiocyanate concentrations were determined in these samples.

Experimental

Equipment

Thermo Scientific™ Dionex™ ICS-5000+ HPIC system* including:

- Thermo Scientific™ Dionex™ ICS-5000+ SP/DP Pump module
- Thermo Scientific™ Dionex™ ICS-5000+ EG Eluent Generator module with high-pressure degas module
- Thermo Scientific™ Dionex™ ICS-5000+ DC Detector/Chromatography module
- Thermo Scientific™ Dionex™ AS-AP Autosampler
- Thermo Scientific™ Dionex™ EGC III KOH Potassium Hydroxide Eluent Generator Cartridge (P/N 074532)
- Thermo Scientific™ Dionex™ CR-ATC Continuously Regenerated Anion Trap Column (P/N 060477)
- Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor (2 mm) (P/N 082541)
- Thermo Scientific™ Chromeleon™ Chromatography Data System, Version 7.1
- Thermo Scientific™ Dionex™ Vial Kit, 10 mL Polystyrene with Caps and Blue Septa (P/N 074228)

*The technique in this application note can be adapted for any Thermo Scientific™ Dionex™ IC system.

Reagents and standards

- Deionized (DI) water, Type I reagent grade, 18 MΩ·cm resistance or better
- Thermo Scientific™ Dionex™ Fluoride standard (1000 mg/L), 100 mL (P/N 037158)
- Thermo Scientific™ Dionex™ Chloride standard (1000 mg/L), 100 mL (P/N 037159)
- Thermo Scientific™ Dionex™ Sulfate standard (1000 mg/L), 100 mL (P/N 037160)
- Acetic acid, glacial (Certified ACS Plus), Fisher BioReagents™ (Fisher Scientific™ P/N BP 2401-500)
- Sodium formate (Crystalline/Certified ACS), Fisher Scientific (P/N S648)
- Sodium nitrite (Crystalline/Certified ACS), Fisher Scientific (P/N S347)
- Sodium bromide, Sigma-Aldrich® (P/N 229981)
- Sodium nitrate, EMD Millipore® (P/N SX0655)
- Oxalic acid dihydrate (Crystalline/Certified ACS), Fisher Chemical™ (Fisher Scientific, P/N A219-250)
- Sodium thiosulfate, Sigma-Aldrich (P/N S7062)
- Sodium phosphate, monobasic, Sigma-Aldrich (P/N S8282)
- Sodium thiocyanate, Sigma-Aldrich (P/N S7757)

Preparation of solutions and reagents

Use the 1000 mg/L anion standards for fluoride, chloride, and sulfate.

To prepare 1000 mg/L stock solutions of the other 10 inorganic and organic acid anions, use the compounds and masses listed in Table 1. To prepare a standard mixture, mix appropriate volumes of the 1000 mg/L stock solutions.

Table 1. Amounts of compounds used to prepare 100 mL of 1000 mg/L stock solutions

Anion	Compound	Mass (mg)
Acetate	Acetic acid	100
Formate	Sodium formate	151.11
Nitrite	Sodium nitrite	149.96
Bromide	Sodium bromide	128.77
Nitrate	Sodium nitrate	137.08
Oxalate	Oxalic acid dihydrate	140.03
Iodide	Potassium iodide	131.75
Thiosulfate	Sodium thiosulfate	120.51
Phosphate	Sodium phosphate, monobasic	126.33
Thiocyanate	Sodium thiocyanate	139.58

Conditions

System:	Dionex ICS-5000+ HPIC system	
Columns:	Dionex IonPac AS25A, Analytical, 2 × 250 mm (P/N SP6970) Dionex IonPac AG25A, Guard, 2 × 50 mm (P/N SP6971)	
Eluent:	KOH	
Flow Rate:	0.25 mL/min	
Eluent Generation:	EGC III KOH	
Isocratic:	36 mM KOH	
Gradient:	0 to 12 min	20–43 mM KOH
	12 to 25 min	43–70 mM KOH
	25 to 30 min	20 mM KOH
Column Temp.:	30 °C	
Injection Volume:	2.5 µL	
Injection Mode:	Push Full	
Compartment Temp.:	15 °C	
Detection:	Suppressed conductivity with Dionex AERS 500 Electrolytically Regenerated Suppressor, recycle mode	
Suppressor Current (for isocratic run):	23 mA	
Suppressor Current (for gradient run):	44 mA	
System Backpressure:	~2350 psi	
Background Conductance:	~0.1–0.2 µS/cm	
Noise:	4–5 nS/min, peak-to-peak	
Run Time:	30 min	

Results and discussion

Separation

Figure 1 shows an isocratic separation of a 14 heat stable amine salts standard. All peaks elute within 40 min with significant time gaps between peaks 10 and 11 and peaks 11 and 12. To shorten the run time, a gradient method was developed starting with 20 mM KOH and increasing to 43 mM from 0 to 12 min

and then increasing to 70 mM from 12 to 25 min. All 14 anions eluted within 30 min (Figure 2) with good separation except for the fluoride and acetate peaks, which separated with a resolution factor of 1.36. We also tried to separate propionate and butyrate in this standard mixture and found that with these conditions, propionate coeluted with acetate and butyrate eluted between acetate and formate.

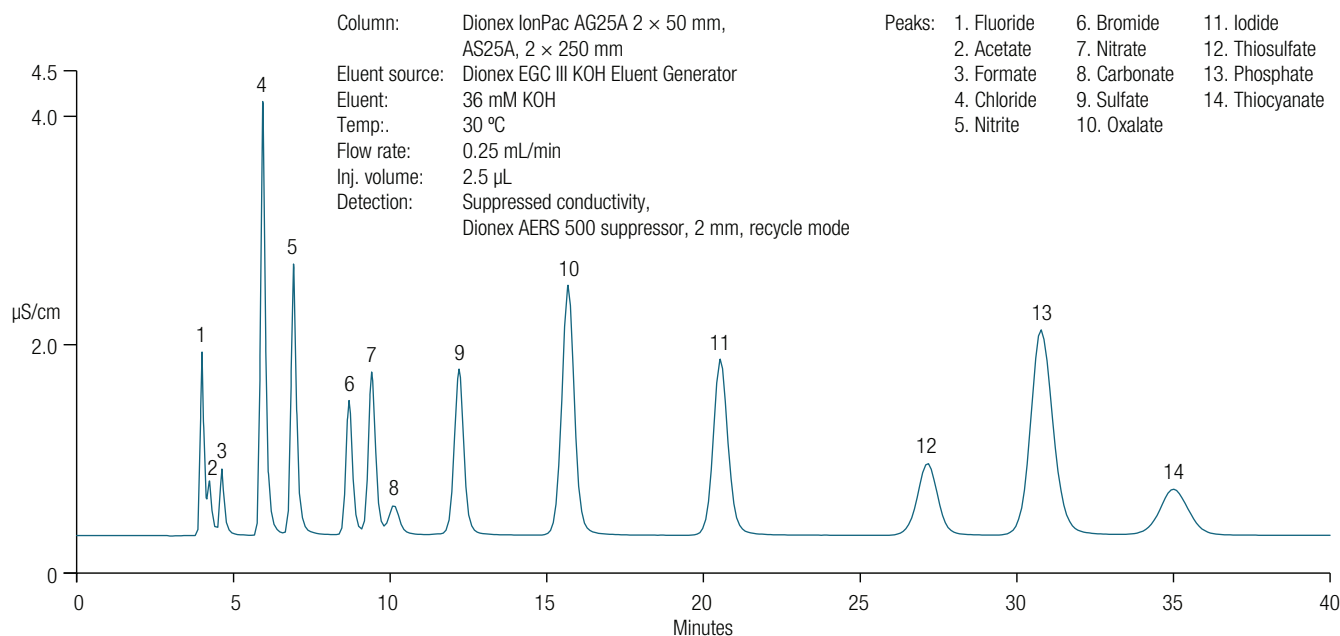


Figure 1. Isocratic separation of 14 anions

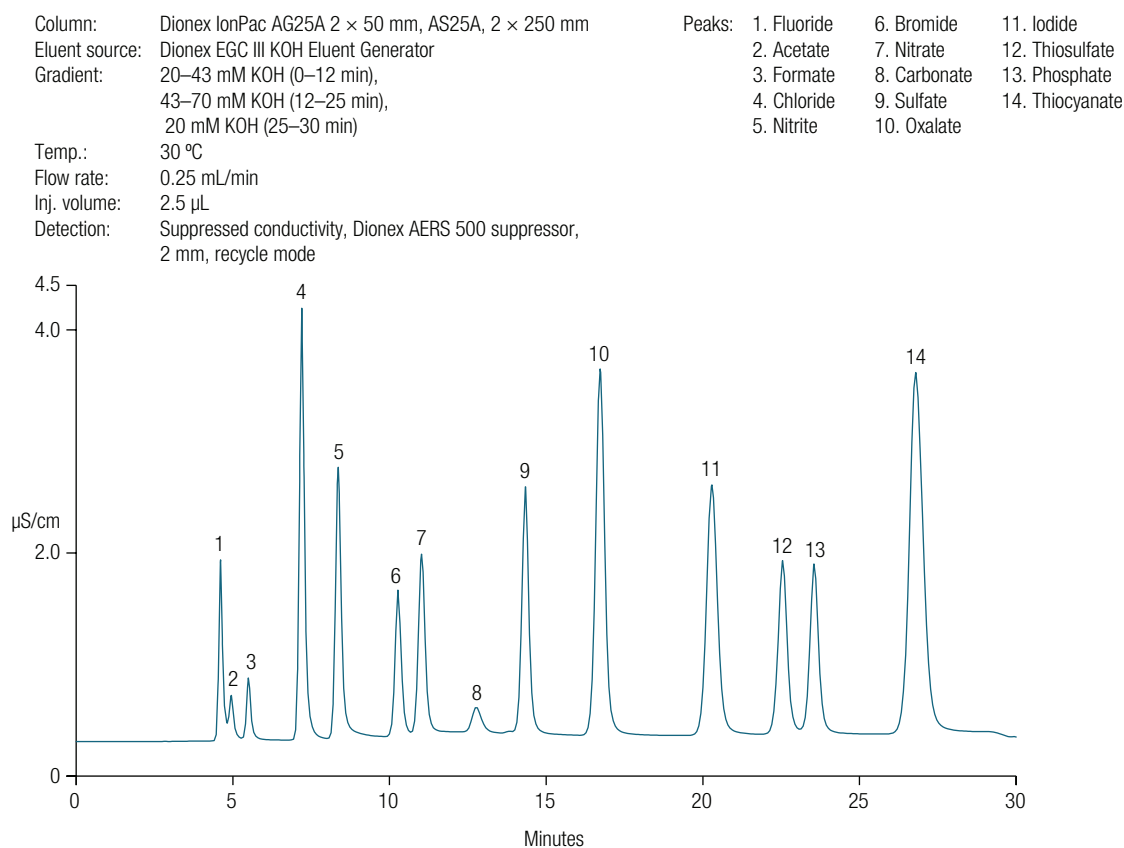


Figure 2. Gradient separation of 14 anions

Sample analysis

Table 2 lists samples along with the dilution factors used in their analyses. All samples tested here were provided by our customers in the petrochemical industry. These samples are collected from different parts/steps in the refining process (such as scrubbing stream, overhead

Table 2. List of refinery samples used in this study

#	Refinery Sample	Dilution Factor
1	RS#1	1:500
2	RS#2	1:200
3	RS#3	1:500
4	RS#4	1:500
5	RS#5	1:200
6	RS#6	1:1000
7	RS#7	1:500
8	RS#8	1:1000
9	RS#9	1:1000

accumulator, boiler, etc.). Figure 3 shows chromatograms of refinery samples RS#1 and RS#2 along with a 14-anion standard mix. Both samples contain acetate, formate, chloride, nitrite, carbonate, sulfate, and oxalate. Figure 4 displays the chromatograms of refinery samples RS#3 and RS#4. RS#3 has mainly sulfate and thiosulfate, while RS#4 is a cleaner sample with very small amounts of acetate, chloride, nitrite, sulfate, and thiosulfate. Similarly, the refinery samples RS#5 and RS#6 (Figure 5) are cleaner samples than the RS#3 sample. Both have small amounts of chloride and sulfate. Figure 6 shows the chromatogram of refinery samples RS#7, RS#8, and RS#9. All three contain large amounts of thiocyanate compared to other samples tested in this study. They are from amine scrubbing solutions used in the refinery to remove H₂S from gases and light hydrocarbon streams. Thiocyanate is formed by the reaction of H₂S gas with HCN (present in small amounts in scrubbing streams). Table 3 summarizes the analysis of the nine refinery samples.

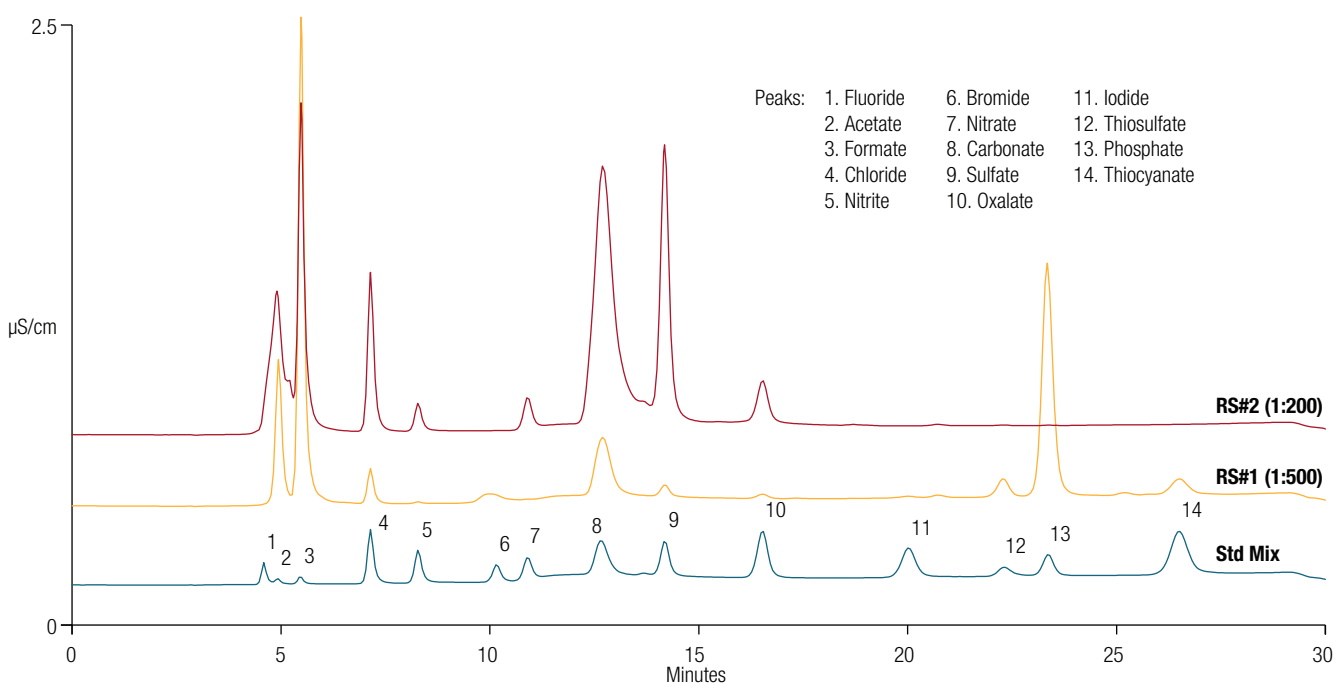


Figure 3. Chromatograms of Refinery Samples RS#1 and RS#2, and a 14 anion standard mix

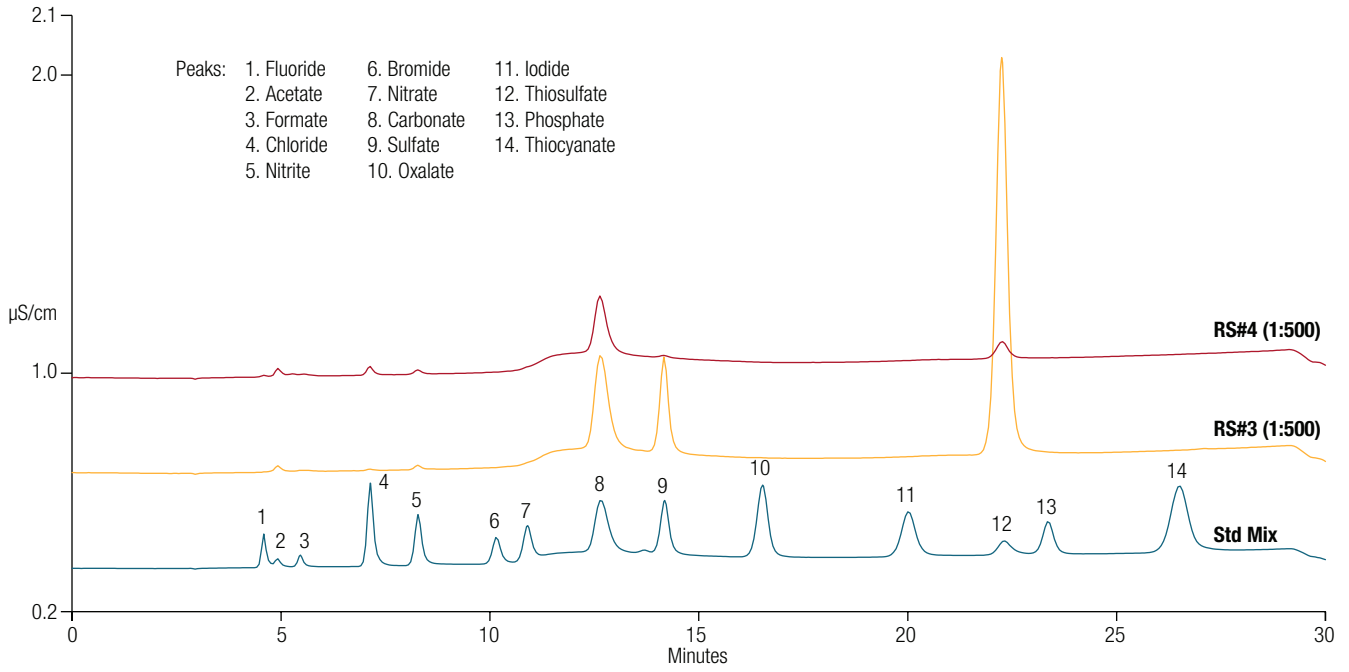


Figure 4. Chromatograms of Refinery Samples RS#3 and RS#4, and a 14 anion standard mix

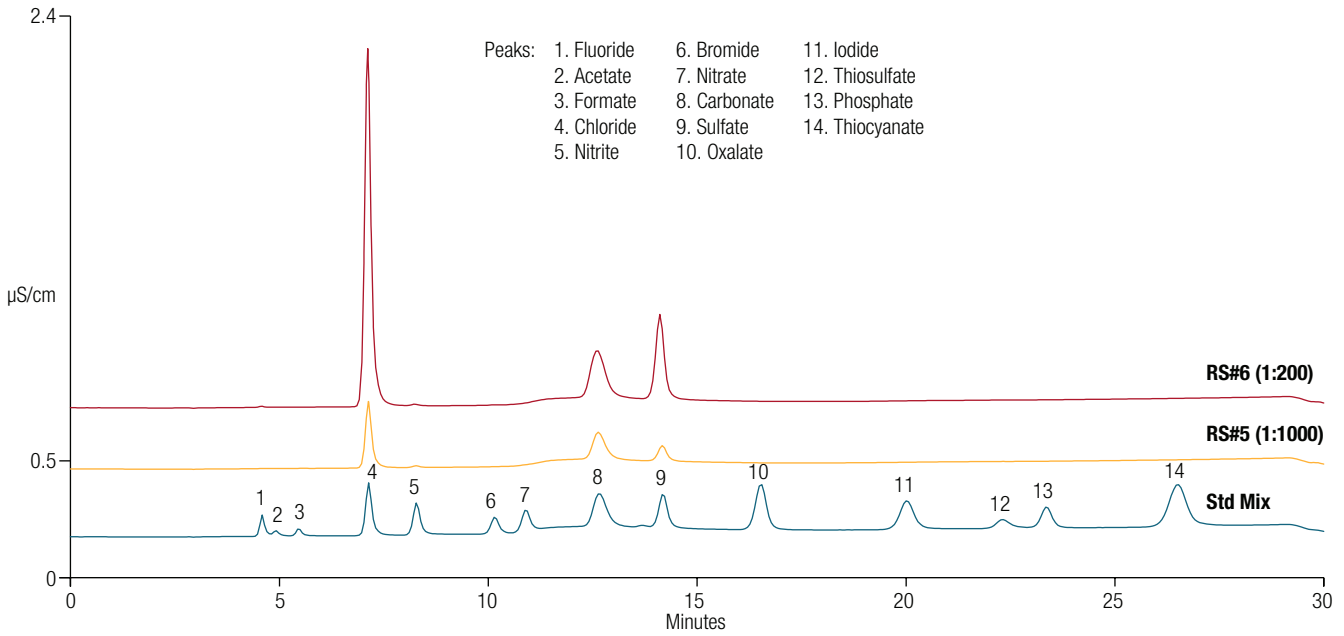


Figure 5. Chromatograms of Refinery Samples RS#5 and RS#6, and a 14 anion standard mix

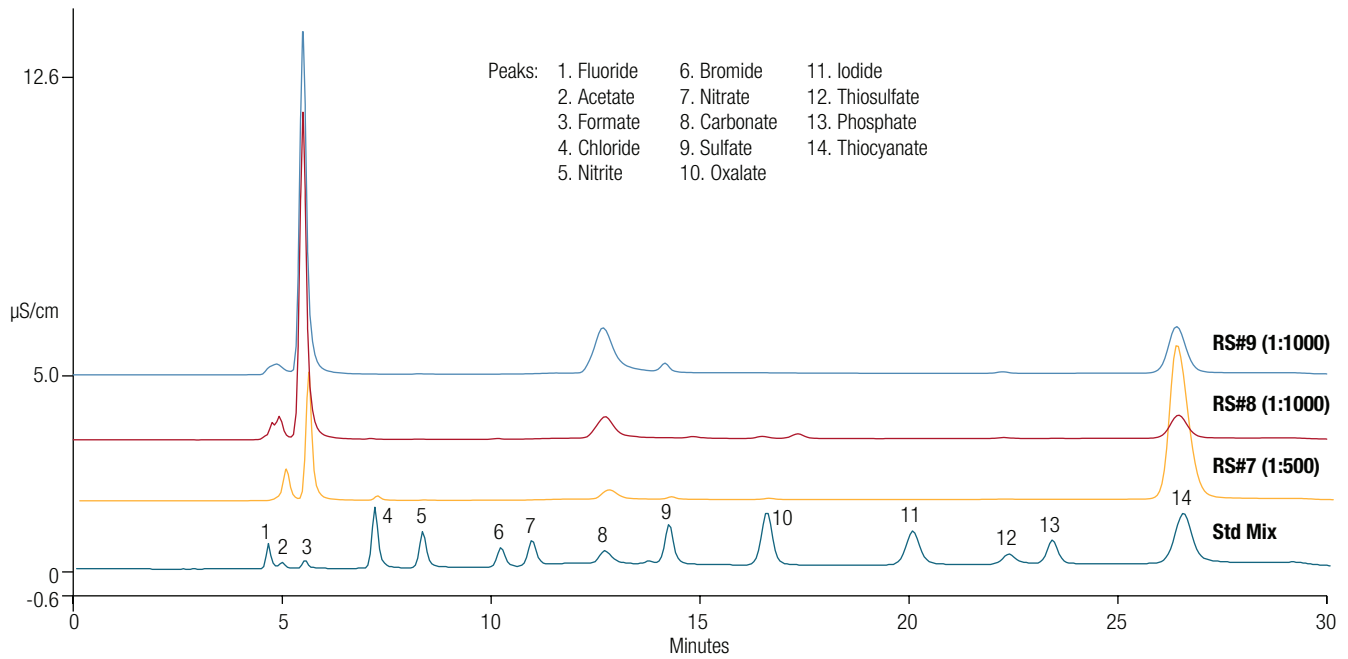


Figure 6. Chromatograms of Refinery Samples RS#7, RS#8, and RS#9, and a 14 anion standard mix

Table 3. Anions identified in refinery samples

Peak No.	Refinery Sample	RS#1	RS#2	RS#3	RS#4	RS#5	RS#6	RS#7	RS#8	RS#9
1	Fluoride								✓	
2	Acetate	✓	✓	✓	✓			✓	✓	✓
3	Formate	✓	✓					✓	✓	✓
4	Chloride	✓	✓	✓	✓	✓	✓	✓	✓	
5	Nitrite	✓	✓	✓	✓	✓	✓			
6	Bromide									
7	Nitrate		✓							
8	Carbonate	✓	✓	✓	✓	✓	✓	✓	✓	✓
9	Sulfate	✓	✓	✓	✓	✓	✓	✓		✓
10	Oxalate	✓	✓					✓	✓	
11	Iodide	✓								
12	Thiosulfate	✓	✓	✓	✓				✓	✓
13	Phosphate	✓								
14	Thiocyanate	✓						✓	✓	✓

Calibration and quantification

Calibration standards for thiosulfate and thiocyanate anions were prepared in DI water. Table 4 summarizes the calibration data obtained by injecting calibration standards between 0.10–10 mg/L and 0.20–20 mg/L for thiosulfate and thiocyanate, respectively. The calibration curves for these two anions are shown in Figure 7.

The coefficient of determination (r^2) for each is greater than 0.999. Over the course of the analysis, the relative standard deviations of the retention times of all 14 anion peaks ($n = 6$) ranged from 0.02% to 0.05%.

To determine the LOD and LOQ, the baseline noise was first determined by measuring the peak-to-peak noise in a representative one-minute segment of the baseline where no peaks elute, close to the peak of interest. The signal was determined from the average peak height of three injections of 0.1 mg/L thiosulfate and thiocyanate standard. The LOD and LOQ were determined by 3 \times and 10 \times S/N, respectively, of a 0.1 mg/L standard. The estimated LODs and LOQs are summarized in Table 4.

Sample recovery

Method accuracy was evaluated by measuring recoveries of anion standards containing 14 anions spiked at two levels into refinery samples. The recovery percentages were calculated for thiosulfate and thiocyanate according to the formula given below:

$$\text{Recovery \%} = \frac{C_{\text{spiked sample}} - C_{\text{unspiked sample}}}{C_{\text{analyte added}}} * 100$$

Figures 8 and 9 show the representative chromatograms of unspiked and spiked refinery samples RS#1 and RS#2, respectively. Table 5 summarizes the recovery percentages of thiosulfate and thiocyanate in all samples. The recovery percentages for thiosulfate and thiocyanate at two spiked levels in all the sample matrices are in the range of 85.7% to 104% and 83.4% to 91.2%, respectively.

Table 4. Results for calibration, LOD, and LOQ for thiosulfate and thiocyanate

Anion	Range (mg/L)	Calibration Type	Coefficient of Determination (r^2)	LOD (mg/L)	LOQ (mg/L)
Thiosulfate	0.10–10	Linear	0.99952	0.018	0.061
Thiocyanate	0.20–20	Linear	0.99932	0.016	0.053

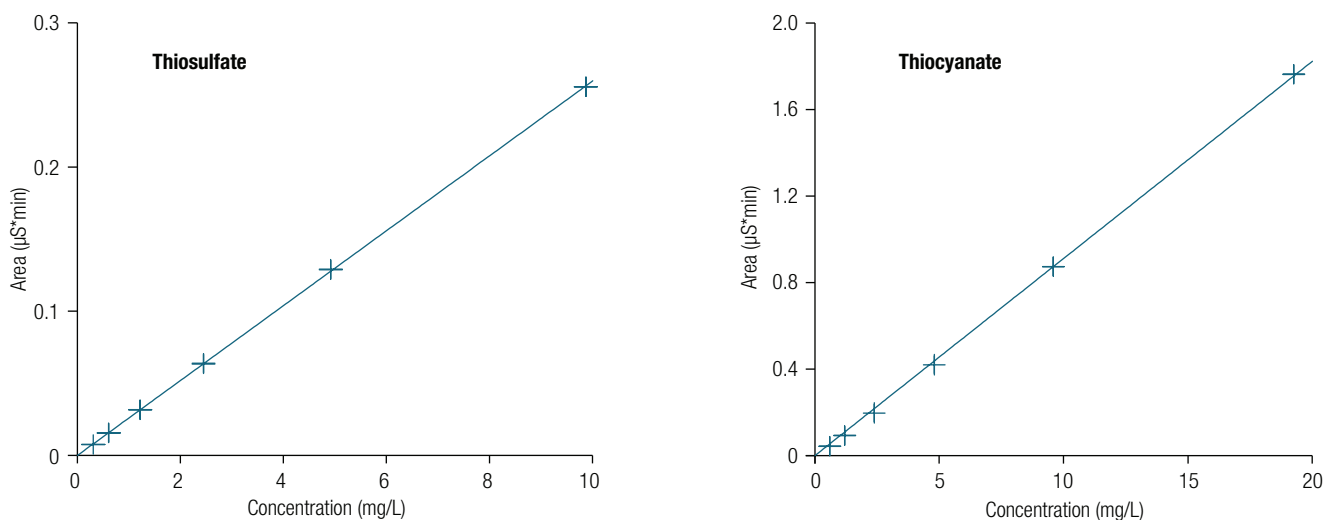


Figure 7. Thiosulfate and thiocyanate calibration curves

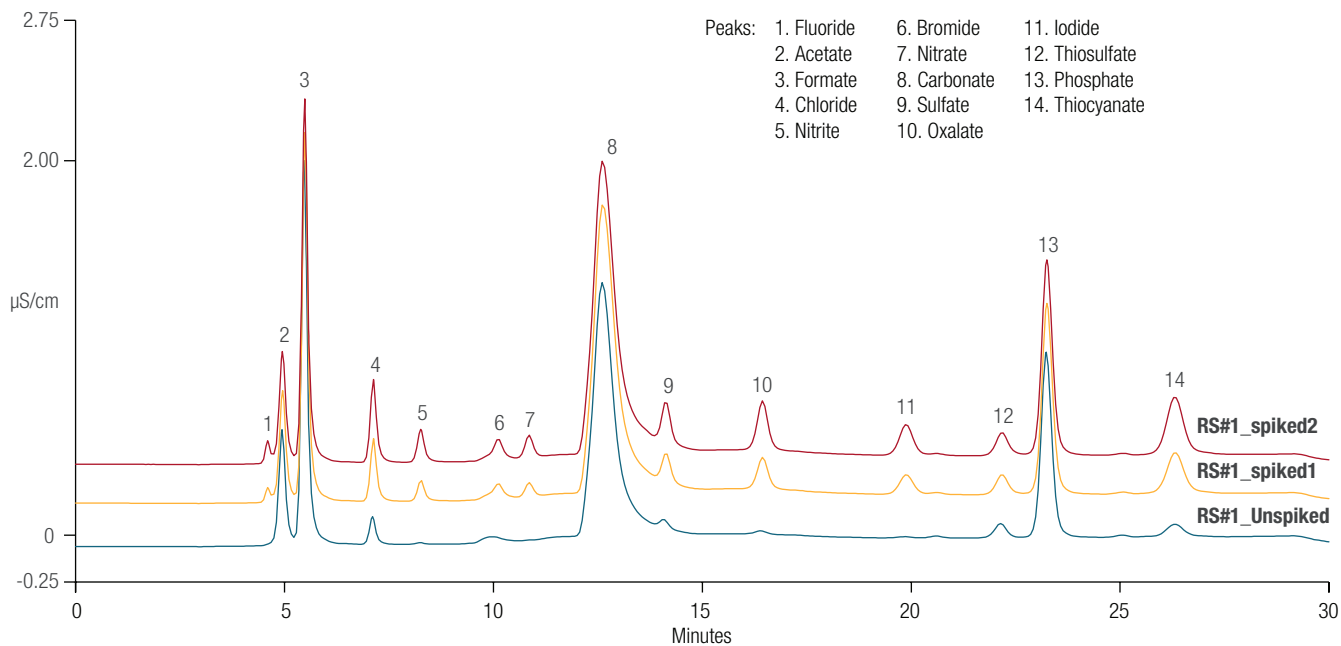


Figure 8. Chromatograms of unspiked and spiked RS#1 at two levels

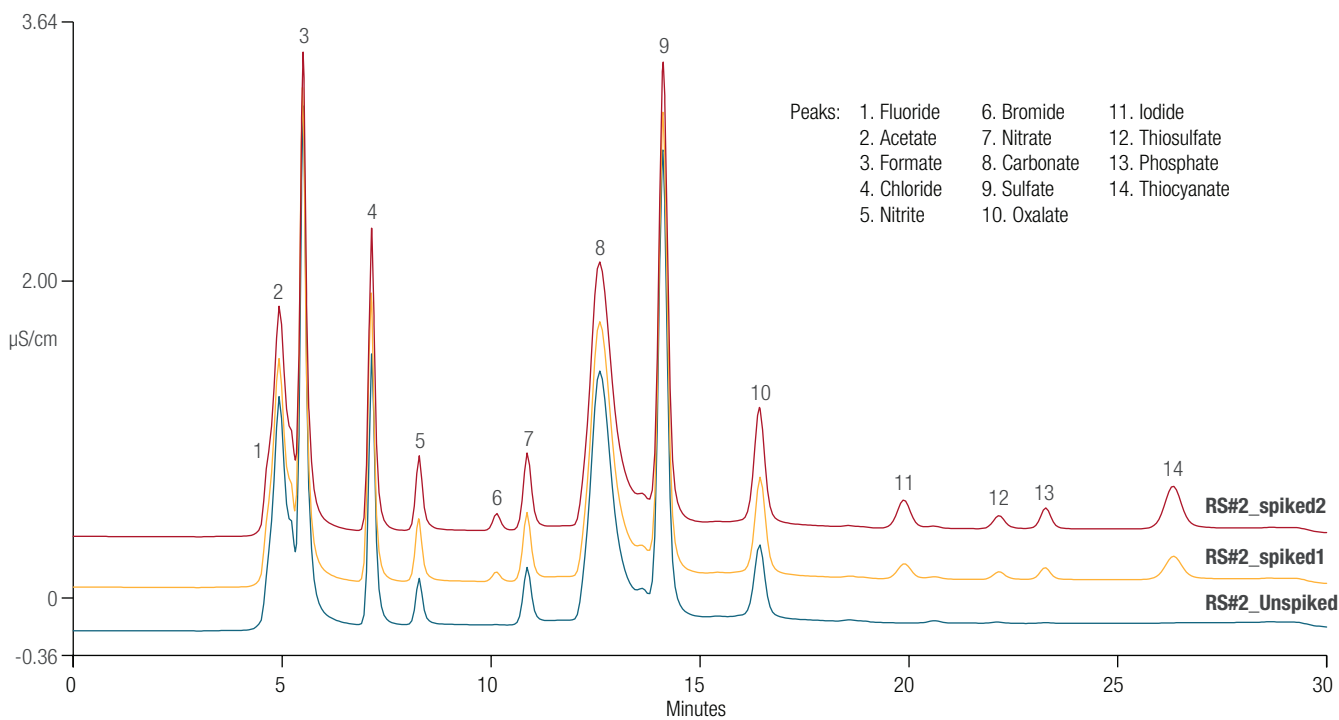


Figure 9. Chromatograms of unspiked and spiked RS#2 at two levels

Table 5. Recovery of thiosulfate and thiocyanate in various refinery samples

Sample Found (mg/L)		Thiosulfate			
		Spiked level 1		Spiked level 2	
		Added (mg/L)	Recovery (%)	Added (mg/L)	Recovery (%)
RS#1	0.85	0.49	92.9	0.76	89.9
RS#2	0.08	0.49	99.3	0.87	104
RS#3	8.02	0.45	92.3	0.80	85.9
RS#4	0.29	0.48	94.6	0.81	91.0
RS#5	0.00	0.49	85.7	0.81	86.8

Sample Found (mg/L)		Thiocyanate			
		Spiked level 1		Spiked level 2	
		Added (mg/L)	Recovery (%)	Added (mg/L)	Recovery (%)
RS#1	0.31	0.96	89.8	1.49	90.0
RS#2	0.00	0.96	83.4	1.69	85.2
RS#3	0.00	0.88	83.7	1.56	91.2
RS#4	0.00	0.94	83.4	1.58	86.2
RS#5	0.00	0.96	83.8	1.58	85.6

Conclusion

Using the Dionex IonPac AS25A column, a fast gradient method was successfully developed and validated for the analysis of industrial amine scrubbing samples for 14 heat stable salts. This column allows the separation of all 14 anions within 30 min. The method showed good precision and accuracy with a recovery range of 83–105% for thiosulfate and thiocyanate in the samples tested.

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