

Separation of Heat Stable Amine Salts in Methyldiethanolamine (MDEA) Solutions Using High-Pressure IC

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Key Words

Petrochemical, Dionex IonPac AS11-HC-4 μ m, HPIC, heat stable salts, amine wastewater, methyldiethanolamine, MDEA, Dionex ICS-5000⁺, HPIC

Goal

Demonstrate high efficiency separations of heat stable salts in amine solutions using 4 μ m anion-exchange separation columns on a high pressure ion chromatography system.

Introduction

Crude natural gas (methane) must be chemically processed to remove impurities before the gas can be sold as a pure product. Some natural gas wells may contain high concentrations of carbon dioxide (CO₂) and hydrogen sulfide (H₂S), the later known as “sour gas” because of the mercaptan odor.^{1,2} The high sulfide content and acidity from dissolved carbon dioxide causes corrosion of metal pipes and acid rain, making sour gas undesirable as a commercial product. Therefore, sour gas is typically treated with amine (amine rich) solutions (e.g., ethanolamine, methanolamine, and methyldiethanolamine) to absorb hydrogen sulfide and carbon dioxide.^{1,2} The resulting pure natural gas, defined as containing < 5.7 mg/m³ hydrogen sulfide, is called “sweet” gas by the industry.¹ The amine processing solutions (amine lean) are stripped and regenerated to remove the sulfur compounds as elemental sulfur. However, the amine solutions also extract other contaminants which form salts of organic acids and sulfur species, such as oxalic acid, propanoic acid, formic acid, acetic acid, thiosulfate, and thiocyanate.² These respective anions are collectively termed “heat stable amine salts” because the salts are not removed by the amine stripping process. Furthermore, the high salt content in the amine solution increases the solution viscosity, reduces acid-absorbing capacity and increases corrosion-induced maintenance costs. These amine waste solutions must also be characterized to comply with discharge permits.

The latest advancement in ion chromatography (IC) instrumentation, the high-pressure Thermo Scientific™ Dionex™ ICS-5000⁺ HPIC™ system, can operate continuously at 5000 psi for both analytical and capillary scale formats. The Dionex ICS-5000⁺ HPIC system can therefore exploit the high-efficiency separations offered by smaller particle size separation columns. When combined with the advantages and ease-of-use of a Reagent-Free™ IC (RFIC™) system, this system permits excellent enhanced resolution of closely eluting peaks with excellent reproducibility, thereby yielding greater quantification accuracy and consistently reliable results.

In this study, we determined the anions in mixtures of both common inorganic anions and heat stable amine salts (fluoride, chloride, nitrate, nitrite, bromide, sulfate, phosphate, acetate, formate, propionate, sulfite, thiosulfate, thiocyanate) added to methyldiethanolamine solutions. The anions were separated by anion-exchange chromatography using a Thermo Scientific™ Dionex™ IonPac™ AS11-HC-4 μ m (2 × 250 mm) high-efficiency guard column and detected using suppressed conductivity. This column is optimized for high-efficiency separations of organic acids and is well suited for this application.

Table 1. Consumables list.

Product name	Type	Dionex Part Number
Dionex EGC 500 KOH	Anion Eluent Generator cartridge*	075778
Dionex CR-ATC 500	Anion electrolytic trap column*	075550
Dionex IonPac AG11-HC-4 μ m	Anion guard column*	078036
Dionex IonPac AS11-HC-4 μ m	Anion separation column*	078035
Dionex ASRS 300	Anion suppressor	064555
Dionex HP Degas Module	Degas module*	075522
Dionex HP fittings (blue)	Bolts / Ferrules*	074449 / 074373

* high pressure

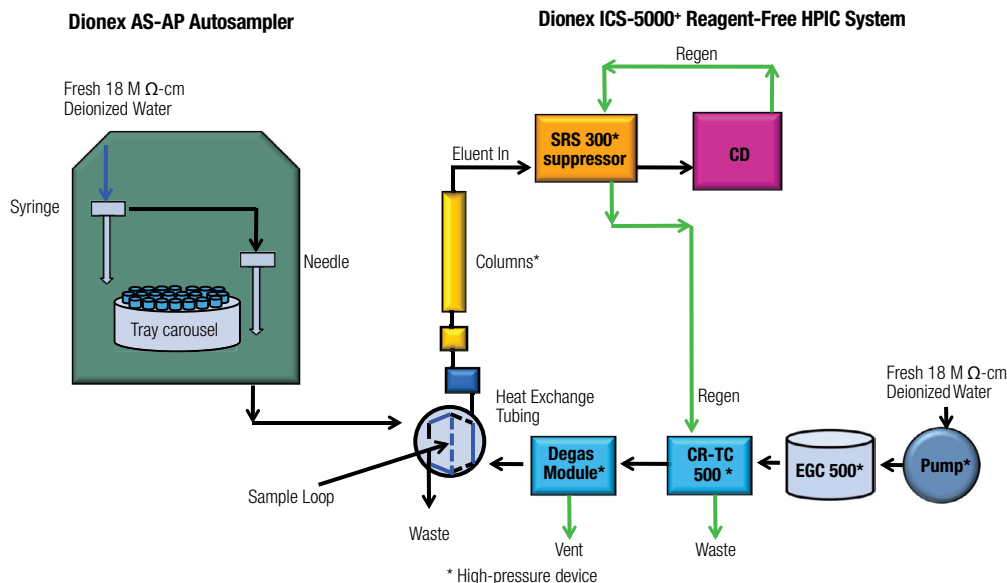


Figure 1. Flow diagram for the high-pressure, Reagent-Free Dionex ICS-5000+ HPIC system.

Equipment

Dionex ICS-5000+ HPIC system

- SP/DP Pump module
- EG Eluent Generator module with high pressure degas module
- DC Detector/Chromatography module
- Dionex AS-AP Autosampler
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software ver. 6.8 or 7.1.

Reagents and Standards

18 MΩ-cm degassed deionized water

ACS Grade reagents, Fisher Scientific

Samples

Synthetic mixtures of heat stable salts added to deionized water, and 10, 20, 30, 50 wt% MDEA

Conditions

Columns:	Dionex IonPac AG11-HC-4μm (2 × 50 mm) AS11-HC-4μm (2 × 250 mm)
Eluent Source:	Thermo Scientific Dionex EGC 500 KOH Eluent Generator Cartridge Thermo Scientific Dionex CR-ATC 500 Continuously Regenerated Cation Trap Column
Gradient:	1 mM from -10 to 8 min, 1–30 mM from 8 to 28 min, 30–72 mM from 28 to 38 min, (72–100 mM from 38 to 60 min for elution of thiocyanate)
Flow Rate:	0.38 mL/min
Column Temp.:	30 °C
Inj. Volume:	25 μL
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating Suppressor™, recycle mode, 68 mA
Background Conductance:	0.2–0.5 μS
Noise:	2–3 nS
System backpressure:	3200–3600 psi

Standard and Sample Preparation

Prepare individual stock solutions and a combined spiking solution of propionate, acetate, bromide, formate, chloride, nitrate, nitrite, sulfate, oxalate, carbonate, thiocyanate, thiosulfate, and sulfite by mixing the appropriate amounts with DI water to achieve the concentrations in Figure 2. Prepare 10, 20, 30, 40, and 50 wt% MDEA solutions spiked with the above anions in deionized water. The standards containing sulfite must be prepared daily. Calibration standards were prepared by diluting the stock standards appropriately.

Tip: It is important to use 18 MΩ-cm resistivity, deionized water for standards, eluent, and autosampler flush solution. It is recommended to degas the deionized water intended for eluent in anion determinations. (An appropriate degassing method is vacuum filtration.) Using deionized water with resistivity less than 18 MΩ-cm can reduce sensitivity, introduce contamination, and affect calibration, thereby resulting in inaccurate quantification. Results can vary and contamination introduced from samples can affect the chromatography

Instrument Setup and Installation

Tip: To achieve the best chromatography with high pressure IC, it is important to use high pressure connectors and ferrules (see Table 1) for all connections prior to the suppressor. The high pressure Dionex ICS-5000+ HPIC Reagent-Free system is designed to operate up to 5000 psi. To setup this application, plumb the consumables and modules of the Dionex ICS-5000+ HPIC system, according to Figure 1.

Install and hydrate the Dionex EGC 500 KOH cartridge, Dionex CR-ATC 500, and 2 mm Dionex ASRS 300 suppressor according to the product manual instructions. Complete the installation according to flow diagram. Use high-pressure connectors and ferrules (blue) for all of the fittings from the pump to prior to the suppressor. Standard pressure fittings can be used for the suppressor and detector connections. Detailed instructions are described in Technical Note (TN) 129, the product manuals, and the instrument installation and operator's manuals.^{3–6}

Results and Discussion

Determinations of heat stable amine salts is needed to monitor the efficiency of the amine processing of the sour natural gas. To resolve these peaks, a high-capacity, high-efficiency Dionex AS11-HC-4 μ m anion-exchange column is used.

Figure 2 compares the separations of the 14 heat stable amine salts in deionized water, 10% and 30% MDEA with excellent recoveries from 95 to 100% as compared to the deionized water. Recoveries are reduced to ~80% when spiked into the 50% MDEA (not shown here). All peaks elute within 35 min from the column with large separations between peaks 4 and 5 and between peaks 12 and 13.

Column: Dionex IonPac AG11-HC-4 μ m, AS11-HC-4 μ m, 2 \times 250 mm
 Eluent Source: Dionex, EGC 500 KOH
 Gradient: Potassium hydroxide 1 mM from -10 to 8 min,
 1–30 mM from 8 to 28 min
 3–72 mM from 28 to 38 min
 Flow Rate: 0.38 mL/min
 Inj. Volume: 25 μ L
 Column Temp.: 30 $^{\circ}$ C
 Detection: Suppressed conductivity Dionex ASRS 300, 2 mm,
 recycle mode
 Samples: Heat stable salts in A: Water; B: 10% MDEA*; C: 30% MDEA*
 IC System: High-pressure Dionex ICS-5000* HPIC

Peaks:	1. Fluoride	2 mg/L	8. Nitrate	100
	2. Acetate	10	9. Carbonate	50
	3. Propionate	10	10. Sulfite	100
	4. Formate	10	11. Sulfate	100
	5. Chloride	100	12. Oxalate	20
	6. Nitrite	10	13. Phosphate	20
	7. Bromide	10	14. Thiosulfate	10

* Methyl-diethanolamine

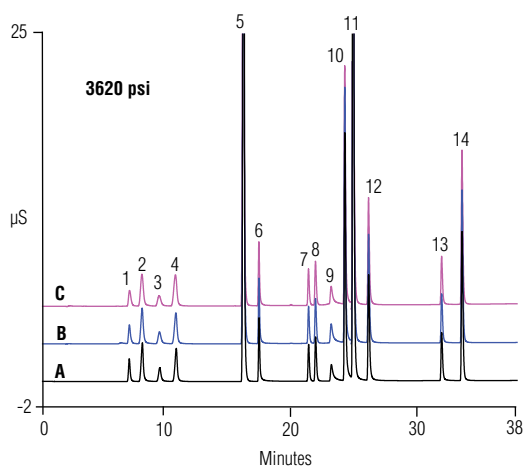


Figure 2. Separations of heat stable salts in MDEA using a shallow gradient and high-pressure IC.

Figure 3 shows the separation of thiocyanate and 14 anions spiked into 30% MDEA solution. The gradient was increased at 38 min to elute thiocyanate from the column within 50 min. A step change could also be used to reduce the run time. The peaks in both chromatograms show very high efficiency which is characteristic of this 4 μ m particle size column. The system pressure is 3620 psi which is only possible with RFIC technology when using a high-pressure IC system, such as the Dionex ICS-5000* HPIC system.

Column: Dionex IonPac AG11-HC-4 μ m, AS11-HC-4 μ m, 2 \times 250 mm
 Eluent Source: Dionex, EGC 500 KOH
 Gradient: Potassium hydroxide 1 mM from -10 to 8 min,
 1–30 mM from 8 to 28 min
 3–72 mM from 28 to 38 min
 Flow Rate: 0.38 mL/min
 Inj. Volume: 25 μ L
 Column Temp.: 30 $^{\circ}$ C
 Detection: Suppressed conductivity Dionex ASRS 300, 2 mm,
 recycle mode
 Samples: Heat stable salts in 30% MDEA*
 IC System: High-pressure Dionex ICS-5000* HPIC

Peaks:	1. Fluoride	2 mg/L	8. Nitrate	100
	2. Acetate	10	9. Carbonate	50
	3. Propionate	10	10. Sulfite	100
	4. Formate	10	11. Sulfate	100
	5. Chloride	100	12. Oxalate	20
	6. Nitrite	10	13. Phosphate	20
	7. Bromide	10	14. Thiosulfate	10
			15. Thiocyanate	10

* Methyl-diethanolamine

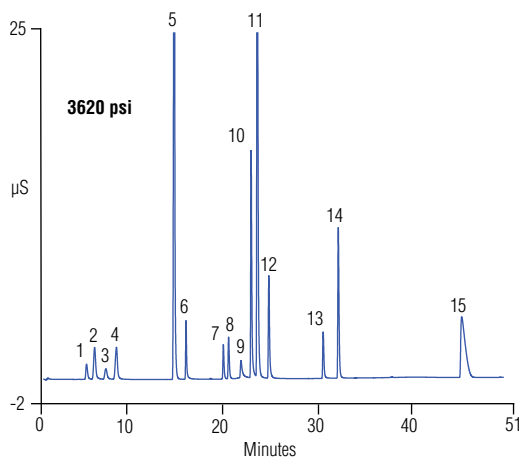


Figure 3. Separation of heat stable salts in 30% MDEA using a shallow gradient and high-pressure IC.

Conclusion

This technical note demonstrates the high-resolution, high-efficiency separations possible using a Dionex IonPac AS11-HC-4 μ m and a high-pressure Reagent-Free IC system, such as the Dionex ICS-5000⁺ HPIC system. The Dionex ICS-5000⁺ HPIC system permits continuous operations up to 5000 psi to deliver high-resolution separations across all column formats including standard bore, microbore, and capillary scale.

Additional information on inorganic anion determinations in environmental and industrial wastewater samples using standard bore and microbore IC are reviewed in application update AU 138, and application notes AN 135 and AN 138.⁷⁻⁹

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