

Determinations of Heat Stable Amine Salts and Amines in Amine Scrubbing Solutions Using Suppressed Conductivity and Charge Detection

*Terri Christison, Monika Verma, Pranathi Perati, Linda Lopez
Thermo Fisher Scientific, Sunnyvale, CA, USA*



Overview

- Heat stable amine (HSA) salts, such as organic acids, inorganic anions, and sulfur based salts, in amine scrubber solutions were separated by anion-exchange on a 4 μm particle high-efficiency capillary column.
- This method utilizes two different but complementary detectors, suppressed conductivity and charge detection. Charge detection provides higher relative responses for multi-charged anions, such as found in heat stable amine salt solutions, than chloride and sulfate.
- Using these two detectors with different responses were used to confirm peak purity and the presence of co-eluting peaks, thereby improving reporting accuracy.

Introduction

Sour crude natural gas (methane) is typically treated with amine rich scrubber solutions to neutralize carbon dioxide and remove hydrogen sulfide gas impurities before it can be sold as a pure natural gas product.^{1,2} When the neutralizing capacity is deemed inefficient, the amine solutions are regenerated and stripped of elemental sulfur. Dissolved salts (heat stable amine salts) remain, building up over time resulting in higher maintenance costs, and higher incidents of corrosion.^{2,3} Analysis of both the amine concentrations and the heat stable amine salts are needed to ensure a pure product and an efficient scrubbing process.

The Thermo Scientific™ Dionex™ QD Charge Detector promotes complete dissociation of many weakly dissociated compounds as a result, the charge responses of singly-charged, doubly-charged, and triply-charged ions are proportionally higher than conductivity. CD and QD detector provided different responses were used to confirm peak identity and the presence of unknown co-eluting peaks.

Methods

Samples / Sample Preparation

Sour gas amine samples were diluted 100-fold with deionized water. Some amine samples were treated with Thermo Scientific™ Dionex™ OnGuard™ II RP and Dionex OnGuard II Na cartridges to remove interfering cations and organic compounds.

Instrumentation

Thermo Scientific™ Dionex™ ICS-5000+ HPIC™ Ion Chromatography dual capillary system.

- DP Dual Pump, EG Eluent Generator, DC Detector Chromatography, and Thermo Scientific™ Dionex™ IC Cube™ modules
- Thermo Scientific Dionex Detectors: CD Conductivity Detector, QD Charge Detector with Thermo Scientific Dionex QDC 300 Cell
- Autosampler: Thermo Scientific Dionex AS-AP Autosampler

Data Analysis:

Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System

Conditions:

Columns: Thermo Scientific™ Dionex™ IonPac™ AG11HC-4µm,
Dionex IonPac AS11HC-4µm, 0.4 × 250 mm

Eluent Source: Thermo Scientific Dionex EGC KOH cartridge, capillary

Gradient: 1 mM KOH (-7–8 min), 1–30 mM (8–28 min), 30–85 mM
(28–38 min), 85 mM (38–45 min)

Flow Rate: 0.015 mL/min

Column Temp.: 30 °C

Inj. Volume: 0.4 µL

Detection: A: Suppressed conductivity, Thermo Scientific™ Dionex™
ACES™ 300 Anion Capillary Electrolytic Suppressor, recycle
mode; 13 mA
B: Charge detection, Dionex QDC 300 cell, 6 V

FIGURE 1. Flow diagram for the IC system using CD and QD detectors.

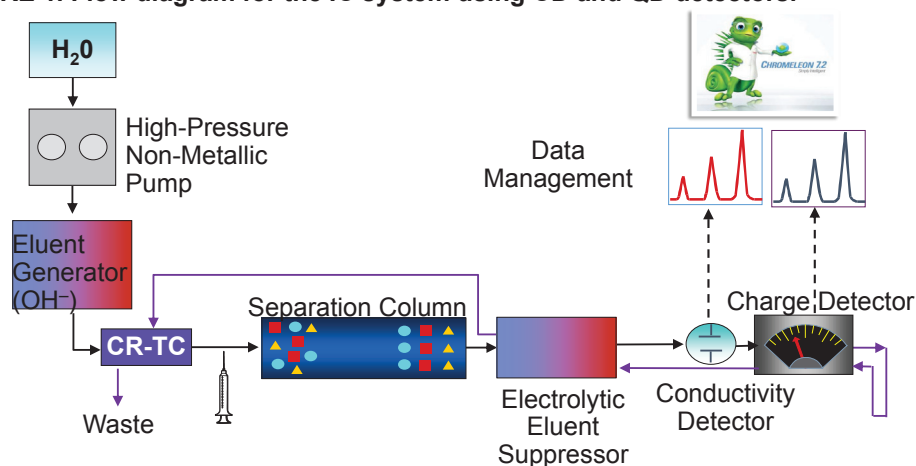
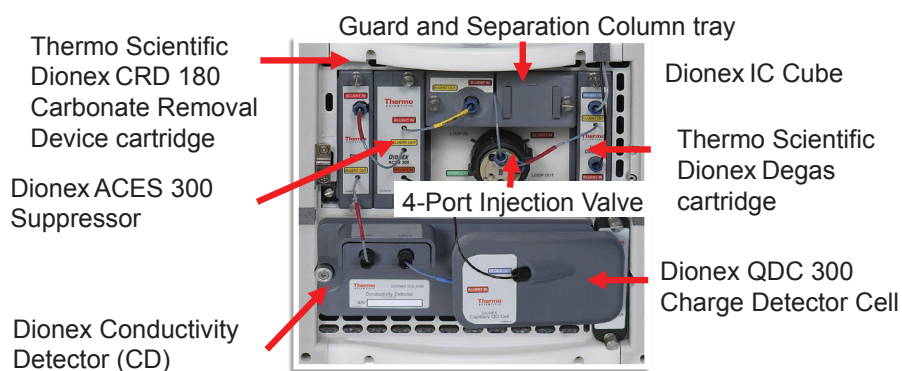


Figure 2 shows the Dionex IC Cube module and Dionex QDC 300 Charge Detector cell. The Dionex IC Cube is designed to minimize the flow path needed for a capillary flow rate system by containing the columns and consumables in close proximity.

FIGURE 2. Dionex IC Cube with capillary modules

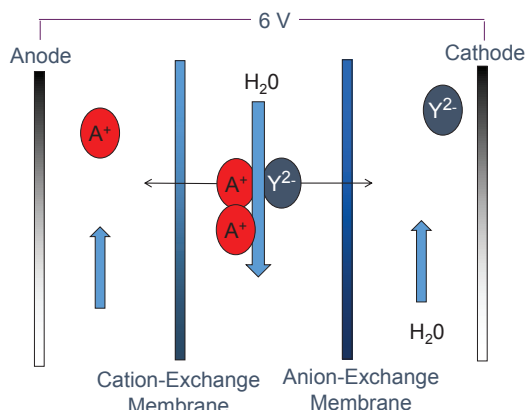


Results

Charge Detection

The Dionex QD Charge Detector promotes complete dissociation of many weakly dissociated compounds by drawing a current at a fixed potential (Figure 3). As a result, the charge responses of singly-charged, doubly-charged, and triply-charged ions are proportionally higher than conductivity.

FIGURE 3. Mechanism of QD Charged Detector



Figures 4–5 demonstrate how the different peak responses by the CD and QD can be used for improved data analysis.

Figure 4 shows an example where the peaks have with the same response by CD detection (R1) which could be either C1 or C2 concentrations; but with QD detection (R3 and R4) clearly defines the concentrations.

Figure 5 illustrates another example where QD detection (R4) correspond to both C1 and C2 concentrations but is clarified by CD detection where R1 and R2 confirm C2 concentration.

FIGURE 4. Using CD and QD detection for peak analysis.

Example 1: QD confirmation.

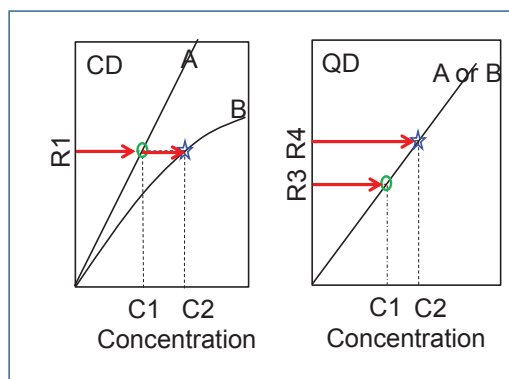


FIGURE 5. Using CD and QD detection for peak analysis.

Example 2: CD confirmation.

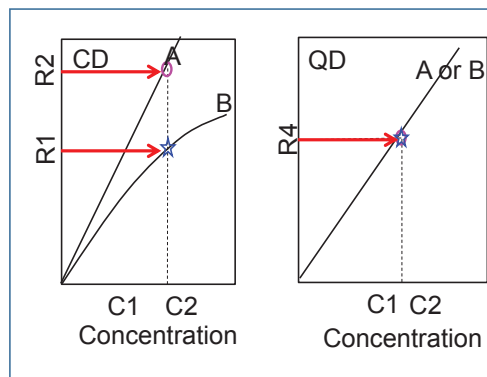
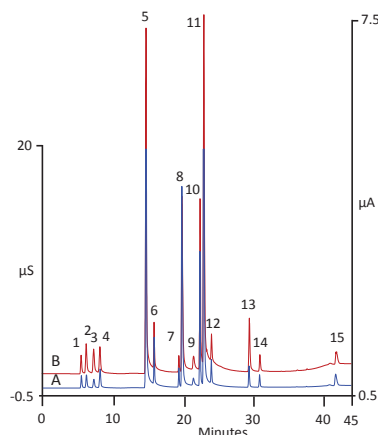


Figure 6 shows the separation of a standard containing 15 inorganic anions, organic acids, and sulfur-based anions typically found as heat stable amine salts. QD responses were normalized to the nitrite peak. Peak 10 which is doubly charged and Peaks 13 and 14 which are triply charged have higher QD response than strongly ionized singly charged nitrite. Thiocyanate is a singly charged ion which had a comparable relative response when normalized to nitrite.

FIGURE 6. Separation of mixed standard using CD and QD detection



Columns: Dionex IonPac AS11-HC-4μm with guard Capillary (0.4 × 50 mm, 0.4 × 250 mm)
 Eluent Source: Dionex, EGC-KOH (Capillary) cartridge
 Gradient: Potassium hydroxide
 1 mM (~7–8 min), 1–30 mM (8–28 min),
 30–85 mM (28–38 min),
 85 mM (38–45 min)
 Flow Rate: 0.015 mL/min
 Inj. Volume: 0.4 μL
 Column Temp.: 30 °C
 Detection: A: Suppressed conductivity,
 Dionex ACES 300 suppressor, recycle
 mode
 B: Dionex QD Charge Detection, 6 V
 Sample Prep.:

Peaks:
 1. Fluoride 0.4 mg/L 9. Carbonate 10 mg/L
 2. Acetate 2.0 10. Sulfite 20
 3. Propionate 2.0 11. Sulfate* 20
 4. Formate 2.0 12. Oxalate 4
 5. Chloride* 20 13. Phosphate 4
 6. Nitrite 2.0 14. Thiosulfate 2
 7. Bromide 2.0 15. Thiocyanate 2
 8. Nitrate 20

* CD response for chloride and sulfate was truncated at 20 μS. QD chromatogram was normalized at the nitrite peak.

Figures 7–9 show the determination of heat stable amine salts (HSA) in amine neutralizing samples. Prior to injection, the diluted scrubber sample in Figures 7 and 8 was pretreated with Dionex OnGuard RP and Dionex OnGuard Na to remove organic compounds and cation contaminants that were affecting the chromatography. These Dionex sample preparation cartridges are designed to remove select contaminants without introducing IC-detectable ionic contaminants. In Figure 7, the chloride peak in the QD chromatogram was normalized to the same peak in the CD chromatogram for easier comparison. In Figure 8, an expanded QD chromatogram reveals additional peaks (in boxes) not noticeable by CD, thereby providing additional information and peak purity.

FIGURE 7–8: Anion determinations in 100-fold diluted amine scrubber solution.

FIGURE 7: CD versus QD

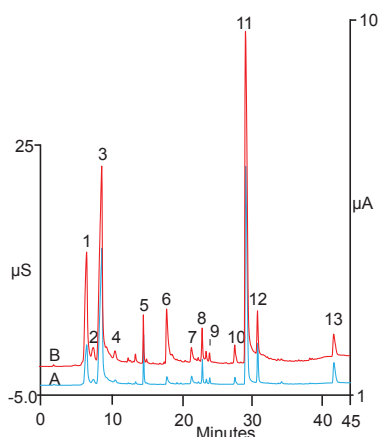


FIGURE 8: Expanded scale of QD detection. Additional peaks are revealed.

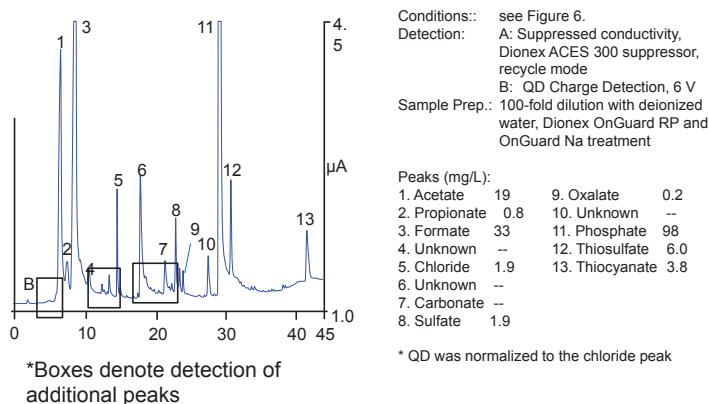
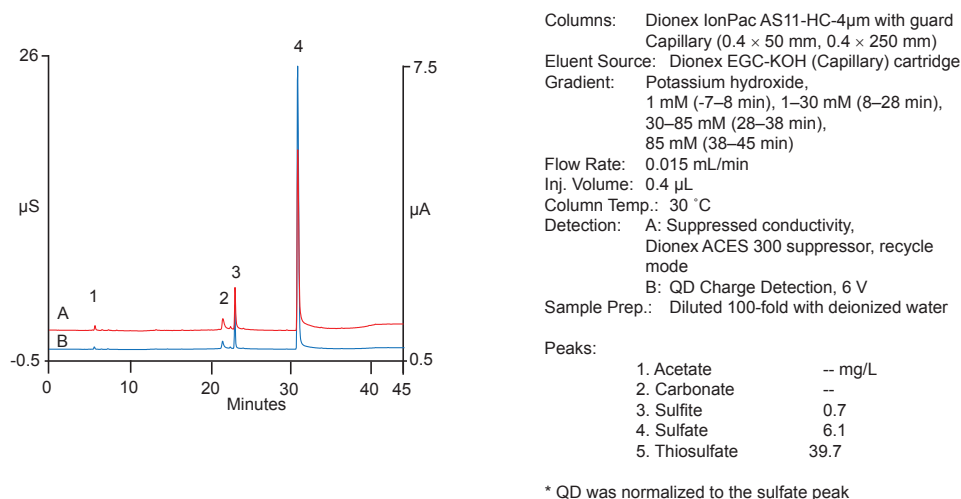


Figure 9 show the CD and QD chromatograms of an amine solution with less HSA contamination, sampled at an overhead actuator.

FIGURE 9. 100-fold Dilution of an amine solution from an overhead actuator.



Conclusion

- Heat stable amine salts are challenging samples for analysis with many sulfur species, organic acids and high concentrations of inorganic anions.
- Here we demonstrated an IC method needed by the gas industry to analyze heat stable amine salts in amines samples.
- This method has high efficiency separations made possible on a 4 μm particle capillary-size Dionex IonPac AS11-HC-4 μm column and facilitated by a high-pressure (HPIC) capillary IC system.
- Using different detectors, such as the CD conductivity detector and the QD charge detector provide advantages in improved peak identification and peak detection which result in improved reporting accuracy and information.

References

1. Natural Gas.org Home Page. <http://naturalgas.org/> (accessed April 17, 2014).
2. Rooney, P.C.; Bacon, T.R.; DuPart, M.S. Effect of Heat Stable Salts on MDEA Corrosivity, Parts 1 and 2. *Hydrocarbon Processing*, **1996**, *Mar*, **95–103**; **1997**, *Apr*, **65–71**.
3. Thermo Fisher Scientific Technical Note 122: Separation of Heat Stable Amine Salts in Methyldiethanolamine (MDEA) Solutions. Thermo Scientific P/N TN70192_E, Sunnyvale, CA, 2013. [Online] <http://www.thermoscientific.com/content/dam/tfs/ATG/CMD/CMD%20Documents/Application%20&%20Technical%20Notes/Chromatography/Ion%20Chromatography/IC%20and%20RFIC%20Systems/TN-122-Separation-Heat-Stable-Amine-Salts-Methyldiethanolamine-Solutions-TN70192-E.pdf> (accessed April 17, 2014).

www.thermoscientific.com

©2014 Thermo Fisher Scientific Inc. All rights reserved. ISO is a trademark of the International Standards Organization. All other trademarks are the property of Thermo Fisher Scientific Inc. and its subsidiaries. This information is presented as an example of the capabilities of Thermo Fisher Scientific Inc. products. It is not intended to encourage use of these products in any manners that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.



Thermo Fisher Scientific, Sunnyvale, CA
USA is ISO 9001:2008 Certified.

Africa +43 1 333 50 34 0
Australia +61 3 9757 4300
Austria +43 810 282 206
Belgium +32 53 73 42 41
Brazil +55 11 3731 5140
Canada +1 800 530 8447
China 800 810 5118 (free call domestic)
400 650 5118

Denmark +45 70 23 62 60
Europe-Other +43 1 333 50 34 0
Finland +358 9 3291 0200
France +33 1 60 92 48 00
Germany +49 6103 408 1014
India +91 22 6742 9494
Italy +39 02 950 591

Japan +81 6 6885 1213
Korea +82 2 3420 8600
Latin America +1 561 688 8700
Middle East +43 1 333 50 34 0
Netherlands +31 76 579 55 55
New Zealand +64 9 980 6700
Norway +46 8 556 468 00

Russia/CIS +43 1 333 50 34 0
Singapore +65 6289 1190
Sweden +46 8 556 468 00
Switzerland +41 61 716 77 00
Taiwan +886 2 8751 6655
UK/Ireland +44 1442 233555
USA +1 800 532 4752

Thermo
SCIENTIFIC

A Thermo Fisher Scientific Brand