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## Determination of anions in amine solutions for sour gas treatment

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### Abstract

In sour gas treatment, various amine solutions are used to remove the acidic components  $H_2S$  and  $CO_2$ . These components are absorbed by the amine solution and stripped during amine regeneration. Other anions (contaminants) tie up the amine by forming heat-stable salts (HSS) which cannot be regenerated. HSS also can be formed from amine degradation by-products, i.e., organic acids. Hence the acid gas-carrying capacity of the amine will be reduced. HSS also can promote corrosion and cause foaming problems. Therefore, the determination of anions in amine solutions is very important. Using the analytical columns IonPac AS9-SC and AS10, it is possible to determine all anions of interest by ion chromatography.

### 1. Introduction

Natural gas often contains high concentrations of  $H_2S$  or/and  $CO_2$  (the highest concentrations in natural gas from Austria are 2.2 vol.-%  $H_2S$  and 16 vol.-%  $CO_2$ ). This gas is called "sour gas" and is very corrosive, so it is necessary to remove the acidic components before feeding the gas in pipelines.

One possibility is gas washing with amine solutions. Most plants use diethanolamine (DEA), monoethanolamine (MEA) or methyl-diethanolamine (MDEA) for the absorption of the acidic gases. The amine solution is continuously regenerated by stripping  $H_2S$  and  $CO_2$ . Other anions which are either fed to the amine solution by contamination (e.g., chloride and nitrate) or formed in the treating units as amine degradation by-products (i.e., organic acids) tie up the amine by forming heat-stable salts (HSS)

which cannot be regenerated. Anions observed in HSS originate from a variety of sources [1] and are listed in Table 1. To reduce problems during sour gas treatment, HSS should be minimized and should not exceed 10% of the total amine concentration [1,2]. When the concentration of any of these HSS exceeds 500 ppm, problems can be expected in the treatment unit [3]. They inactivate a portion of the basic amine and increase the rate of corrosion in the unit, resulting in higher levels of iron sulfide in the system, which subsequently causes foaming problems [3].

In our sour gas treatment plant, MDEA is used as a scrubbing solution for sour gas washing. For diagnosing corrosion and foaming problems it is useful to analyse the amine solution at several locations: the "rich" MDEA (fully charged with  $H_2S$  and  $CO_2$ ) from the contactor, the "semi-lean" MDEA (partially regenerated) and the "lean" MDEA (regenerated amine, containing only small amounts of  $H_2S$  and  $CO_2$ )

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Table 1  
Common sources of the anions of HSS (heat-stable salts)

Anion	Source
Chloride	Make-up water Brine with inlet gas Well treatment chemicals with inlet gas
Nitrate, nitrite	Make-up water Corrosion inhibitors
Sulfate, sulfite, thiosulfate	Sulfur species oxidation products Component in gas
Formate, oxalate, acetate	Acid in the feed gas O <sub>2</sub> degradation Thermal degradation
Thiocyanate	Reaction product of H <sub>2</sub> S and CN
Phosphate	Corrosion inhibitors Phosphoric acid activated carbon Cotton filters
Fluoride	Well treatment chemicals with inlet gas

before and after the carbon filter, and the amine before and after the mechanical filter [4].

Analytical procedures used for monitoring MDEA quality are based on different methods [5]. Recommended are, e.g., the determination of pH, MDEA concentration, foaming tendency, foam stability, liquid hydrocarbons, suspended solids, iron, chloride, HSS and acid gas loading [2]. For the determination of carboxylic acids no useful method was available in our laboratory. Ion chromatography seemed to be an appropriate method for the determination of inorganic and organic anions in amine solutions.

## 2. Experimental

Several different eluents were tested in combination with the IonPac AS9-SC (Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>-NaHCO<sub>3</sub> mixtures) and AS10 (NaOH and Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) analytical columns for anion separation in amine solutions. These experiments resulted in three useful methods for the determination of all anions of interest.

### 2.1. Instrumentation

The equipment used was a DX-300 gradient ion chromatography system (Dionex, Sunnyvale, CA, USA). The separated components were detected by a pulsed electrochemical detector (PED) used in the conductivity mode (10 μS range). An AMMS-II micro-membrane suppressor system was used for chemical suppression. The AMMS II was continuously regenerated with 12.5 mM sulfuric acid at a flow rate of 4–6 ml/min. Integration was performed with an HP 3396A integrator (Hewlett-Packard) and CLAS/2000 (Chromatography Laboratory Automation Software; Perkin-Elmer). The columns used for separation were AS9-SC and AS10 (250 × 4 mm I.D.) separation columns and AG9-SC and AG10 (50 × 4 mm I.D.) guard columns.

### 2.2. Reagents

All reagents were of analytical-reagent grade (Merck, Darmstadt, Germany; sodium hydroxide, 50% solution from J.T. Baker, Deventer, Netherlands). Deionized water (18 MΩ) ob-

tained from a Milli-Q water purification system (Millipore) was employed throughout.

### 2.3. Calibration standards

Stock standard solutions were prepared for each anion separately by dissolving salts in deionized water. Anion standard mixtures for calibration were prepared every week from the stock standard solutions. Evaluation was done by constructing calibration graphs up to concentrations of 2 ppm for fluoride, 10 ppm for inorganic anions and oxalate and 40 ppm for small carboxylic acids.

### 2.4. Ion chromatographic conditions

The injection volume was 25  $\mu$ l. Specific conditions for the three methods are given in Table 2.

### 2.5. Sample preparation

All samples were filtered and diluted with deionized water so that the analyte concentrations were within the calibration range. Before injection, the diluted samples were filtered through 0.45- $\mu$ m nylon filters. For the determination of carboxylic acids and sulfur species, the samples were diluted as short as possible before injection to prevent increases in concentration of these analytes owing to oxidation processes.

## 3. Results and discussion

The determination of anions in amine solutions by IC cannot be performed without analytical problems. In particular, the analysis of "rich" amine samples is subject to interferences between carbonate and early-eluting anions (using method 2 or 3). In addition to the absorbed  $H_2S$  and  $CO_2$ , the amine solutions analysed contained chloride, nitrate, orthophosphate, sulfur oxidation products (sulfite, sulfate, thiosulfate), oxalate and small carboxylic acids (formate, acetate, propionate).

Method 1 was used for separation and determination of fluoride, acetate, propionate, butyrate and formate using the IonPac AS10 column with 3.5 mM  $Na_2B_4O_7$  as eluent. The presence of other anions in the amine solutions that could not be eluted with this eluent (or very late) requires a column purge step after 20 min of elution (5 min of elution with 70 mM  $Na_2B_4O_7$ ). Samples were diluted 1:20 with deionized water.

Fig. 1 shows the chromatograms of a "semi-lean" MDEA and the corresponding standard anion solution containing 1.9 ppm of fluoride, 10.5 ppm of acetate, 10.1 ppm of propionate, 9.5 ppm of butyrate and 7.8 ppm of formate.

Method 2 was used for determination of nitrate, phosphate, sulfate, oxalate, thiocyanate and thiosulfate. Separation was performed on an IonPac AS9-SC column with 1.8 mM  $Na_2CO_3$ –1.7 mM  $NaHCO_3$  as eluent [6].

In "lean" MDEA samples, chloride and nitrite can also be determined. In "semi-lean" and

Table 2  
Specific conditions for the three methods

Parameter	Method 1	Method 2	Method 3
Analytical column	AS10	AS9-SC	AS10
Guard column	AG10	AG9-SC	AG10
Anion trap column			ATC-1
Eluent	3.5 mM $Na_2B_4O_7$	1.8 mM $Na_2CO_3$ – 1.7 mM $NaHCO_3$	100 mM NaOH
Eluent flow-rate (ml/min)	1	2	1
Background conductivity ( $\mu$ S)	2–4	14–16	4–7
System pressure (p.s.i.)	2300–2500	1300–1400	2500–2600

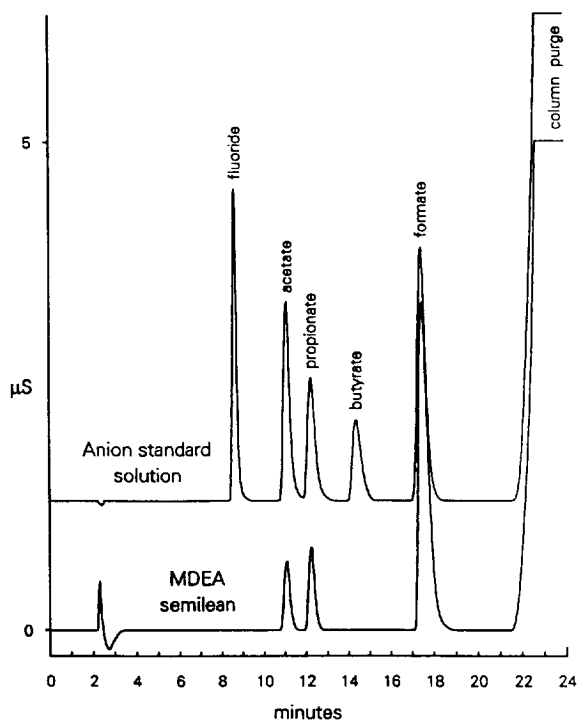


Fig. 1. Separation of anions in MDEA with IonPac AS10 + AG10 columns with 3.5 mM  $\text{Na}_2\text{B}_4\text{O}_7$  as eluent (method 1).

“rich” MDEA, carbonate interferes with these early-eluting ions. Quantification is possible but time consuming. Samples were diluted 1:10 or 1:20 with deionized water; for the determination of phosphate it was necessary to dilute the sample 1:5 because of its small content. Weak points of the method are the rapid loss of capacity (decrease in retention times with time) and the pH sensitivity of the column (application in the pH range 2–11 only; the pH of amine solutions is up to 11.5).

Fig. 2 shows the chromatograms of a “semi-lean” MDEA and an anion standard solution containing 1.9 ppm of fluoride, 3.2 ppm of chloride, 3.5 ppm of nitrite, 5.1 ppm of bromide, 3.7 ppm of nitrate, 3.5 ppm of orthophosphate, 4.2 ppm of sulfate, 10.0 ppm of iodide, 6.6 ppm of oxalate, 9.9 ppm of thiocyanate and 5.2 ppm of thiosulfate.

Method 3 was used in our laboratory when the determination of chloride could not be performed with method 2 because of carbonate

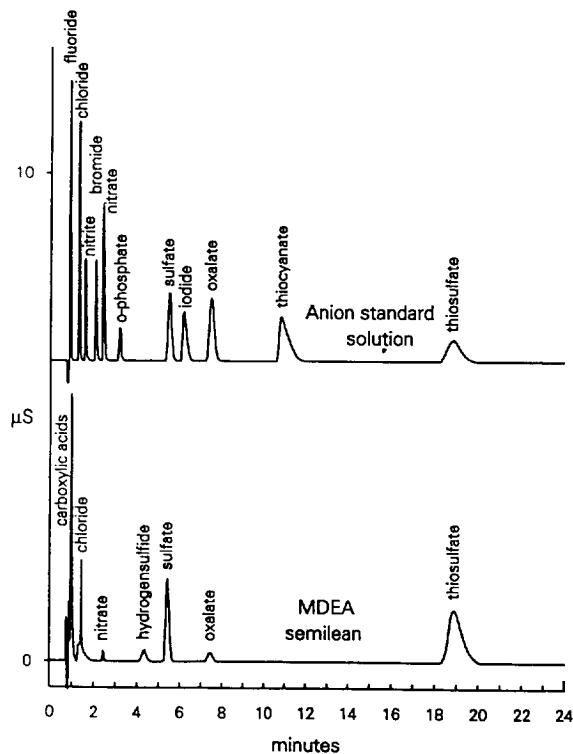


Fig. 2. Separation of anions in MDEA with IonPac AS9-SC + AG9-SC columns with 1.8 mM  $\text{Na}_2\text{CO}_3$ –1.7 mM  $\text{NaHCO}_3$  as eluent (method 2).

interferences (peak overlap). Other anions could also be determined, as shown in Fig. 3. Separation was performed with an IonPac AS10 column with 100 mM NaOH as eluent [7]. The eluent was purified with an anion trap column (ATC-1) for carbonate removal.

With new columns a good separation of hydrogensulfide–chloride and nitrite–sulfate ion pairs is possible. Using aged columns, incomplete resolution of these pairs of ions may occur. Determination of fluoride and small carboxylic acids is not useful because of incomplete resolution (fluoride–acetate) and co-elution (acetate–propionate). Hydrogensulfide should be eliminated by precipitation as cadmium sulfide or by oxidation with  $\text{H}_2\text{O}_2$  to avoid problems in the determination of chloride. Another disadvantage of this method is the very late elution of thiosulfate (about 50 min). When the determination of chloride alone is necessary, a column purge step

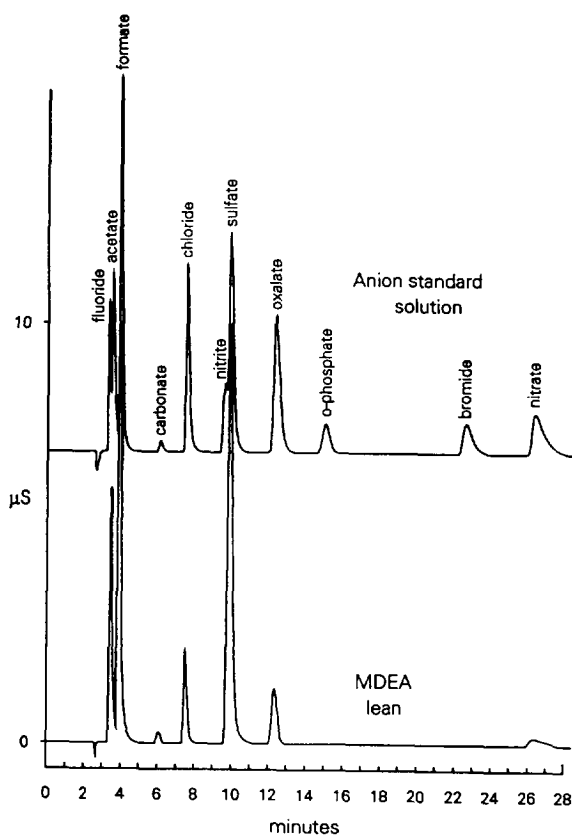


Fig. 3. Separation of anions in MDEA with IonPac AS10 + AG10 columns with 100 mM NaOH as eluent (method 3).

after 10 min would be efficient for shortening the analysis time.

#### 4. Conclusions

Methods 1 and 2 are applicable for the determination of anions in MDEA with sufficient

sensitivity. Method 3 must be further optimized (e.g., by incorporating a column purge step). For routine control it is not necessary to check all the anionic components in the amine solutions. The determination of the small carboxylic acids (method 1) and oxalate (method 2), as an indicator of the presence of HSS, of orthophosphate (method 2), which is eluted as a contaminant from filter materials, and chloride (method 3), which shows the influence of formation water, is useful.

#### References

- [1] M.S. DuPart, T.R. Bacon and D.J. Edwards, *Hydrocarbon Process.*, May (1993), 89–94.
- [2] S.A. von Phul and C.D. Houston, presented at the 72nd Annual GPA Convention, 15–17 March 1993, San Antonio, Texas.
- [3] D. Tunnell, *Petrochem. Gas Processing, HTI Q.*, Autumn (1994), 119–122.
- [4] C.R. Pauley, *Chem. Eng. Prog.*, July (1991), 33–38.
- [5] *Analysenvorschrift für das aktivierte MDEA-Verfahren der Fa. BASF*, 6th Revision, BASF, Ludwigshafen, 1990.
- [6] *Installation Instructions and Troubleshooting Guide for the IonPac AG9-SC Guard Column and the IonPac AS9-SC Analytical Column*, Dionex, Sunnyvale, CA, 1992.
- [7] *Installation Instructions and Troubleshooting Guide for the IonPac AG10 Guard Column and the IonPac AS10 Analytical Column*, Dionex, Sunnyvale, CA, 1991.