



ELSEVIER

Journal of Chromatography A, 850 (1999) 289–295

JOURNAL OF
CHROMATOGRAPHY A

Determination of amines used in the oil and gas industry (upstream section) by ion chromatography

Rainer Kadnar*

OMV-AG, Laboratory for Exploration and Production, Gerasdorferstrasse 151, A-1210 Vienna, Austria

Abstract

During production and purification of crude oil and natural gas several different amines are used as chemicals or operating materials, e.g. film forming long chain amines as corrosion inhibitors, steam volatile amines for pH correction and corrosion protection, alkanolamines as absorbents in sour gas treatment plants, etc. For analytical checks, e.g. determination of corrosion inhibitor concentration in produced media, classical chemical methods are used predominantly, because most of them can be performed in small field laboratories. Some amines, especially the small molecular aliphatic and heterocyclic amines can also be determined by ion chromatography. In our laboratory two types of separation columns (IonPac CS10 and CS12A) were available for ion chromatographic separation. The analysis of the amines in low-salt-containing water, soft water or steam condensate can be performed without problems. The presence of alkali and/or alkaline earth ions in the sample can lead to coelution with these ions, to poor peak resolution or enhanced analysis times, depending on the chromatographic conditions. This work shows some examples of ion chromatography applications for the determination of low-molecular-mass ethanolamines, morpholine and piperazine and discusses the possible interferences and troubles caused by alkali and alkaline earth ions in the matrix. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Amines; Inorganic cations; Ethanolamines

1. Introduction

Some components of crude oil or natural gas, which can cause technical problems, require the use of amines or amine-containing chemicals and operating materials during production, transport or purification.

Our laboratory work includes quality checks of the commercial available products, the determination of corrosion inhibitors in the produced liquids (hydrocarbons and water), the determination of the amine components in scrubber solutions (amine–water mixtures), the check of steam condensates for amines

(coming from inhibition and impurities) or the determination of amines in waste water samples.

Corrosion inhibitors for crude oil or gas condensates, which typically contain long chain amines, are mostly determined by colorimetric methods or by titration. These products cannot be analysed by ion-exchange chromatography.

Other inhibitors, e.g. for steam condensate systems or for the inhibition of fresh water, often contain small molecular aliphatic or cyclic amines, which can be determined by ion chromatography (IC). Aqueous alkanolamine solutions like MEA (monoethanolamine), DEA (diethanolamine) or MDEA (methyldiethanolamine) are used in sour gas treatment plants as scrubber solution to remove the acidic components H_2S and CO_2 from natural gas. In

*Fax: +43-1-404-40-995.

E-mail address: rainer.kadnar@omv.co.at (R. Kadnar)

Austrian sour gas treatment plants MDEA has been used as an absorbent for several years. The determination of MDEA and piperazine (which acts as an additive) in the scrubber solution is normally performed by non-aqueous titration. This method is easy to handle and gives reliable results in the absence of other amines.

Applications for the determination of amines and alkanolamines by IC have been known for many years [1–3]. We started our experiments with the IonPac CS10 and extended our work using also the IonPac CS12A. Our goal was to develop an alternative method for the determination of the amine concentration in the absorption solutions. A lot of technical questions and requirements from our production department made it necessary to investigate for other applications, e.g. to get a method for the determination of amines in water or waste water samples. Some results from these works are summarized below.

2. Experimental

2.1. Instrumentation

The equipment used for this work was a DX-300 gradient ion chromatographic system (Dionex, Sunnyvale, CA, USA). The separated components were detected by suppressed conductivity using pulsed electrochemical detection (PED) in the conductivity mode.

A micro membrane suppressor system CMMS-II was used for chemical suppression at the beginning of our experiments. The CMMS-II was continuously regenerated by 100 mM tetrabutylammonium hydroxide TBAOH solution at a flow-rate of 8–10 ml min⁻¹. Later, a cation self-regenerating suppressor CSRS-II was used in the autosuppression recycle mode. Integration was performed by an HP 3396A integrator (Hewlett-Packard) or by AI-450 software (Dionex).

Columns used for separation were IonPac CS10 and CS12A (250×4 mm) separator columns and IonPac CG10 and CG12A (50×4 mm) guard columns. All runs were performed using a guard and an analytical column.

2.2. Reagents

Reagents used for eluent preparation were of analytical reagent grade from Merck, Darmstadt, Germany; TBAOH solution 40% from Riedel-de-Haen, Seelze, Germany. Some of the amines used for standard preparation were only available as '99% for synthesis'. Deionized water (18 MΩ) obtained from a Milli-Q water purification system (Millipore) was employed throughout.

2.3. Calibration standards

Stock standard solutions (1 g l⁻¹) were prepared separately for each amine or commercial product by diluting with deionized water. Stock standard solutions (1 g l⁻¹) of cations were from Merck, Darmstadt, Germany. The working standard mixtures for calibration were prepared weekly from the stock standard solutions.

Evaluation was done by calibration curves.

2.4. Ion chromatographic conditions

The injection volume was 25 µl. For experiments with the CS10 column in combination with the CMMS-II, hydrochloric acid (HCl) was used as the eluent. Because it is not recommended to use hydrochloric acid with the CSRS in the autosuppression recycle mode [5], later experiments were performed with sulfuric acid (H₂SO₄) as the eluent for both analytical columns. An eluent flow-rate of 1 ml min⁻¹ was applied throughout. The background conductivity was lower than 2 µS; system pressure was 1200–1400 p.s.i. (1 p.s.i.=6894.76 Pa).

2.5. Sample preparation

All samples were filtered through 0.45 µm filters and diluted with deionized water (18 MΩ), so analyte concentrations were within the calibration range.

3. Results and discussion

The two columns CS10 and CS12A offer a lot of possibilities for the separation of alkali ions, alkaline

earth ions and amines. Depending on the application and the sample matrix, a fast isocratic run can be sufficient, or a gradient program may be necessary. We tested different eluent concentrations for separation: 15–40 mM using the CS10, and 10–25 mM using the CS12A column. The following section includes four examples of applications for the determination of amines in aqueous solutions and water samples.

Table 1 is a summary of retention times of some amines, and mono- and divalent cations, depending on the column and the eluent used for separation. The table shall demonstrate the elution sequence of the analytes.

3.1. Application 1: determination of alkanolamines in aqueous solutions and water samples

IC is a comfortable method for the determination of some ethanolamines or short chain aliphatic

amines in low salinar aqueous solutions or steam condensates. Analyzing higher salinar waters (e.g. waste waters) problems are possible. Depending on the chromatographic conditions similar retention times of alkali ions and amines can lead to coelution or poor peak resolution. The best separation can be expected using CS10 as analytical column and 15–20 mM H₂SO₄ as eluent, but we also have tested eluent concentrations up to 40 mM successfully for the determination of MDEA in amine solutions (contain no alkaline earth ions), to get shorter analysis times.

High salt contents in the samples can influence the retention time and the response factors of some components. The preparation of matrix matched calibration standard solutions is useful sometimes.

Another reason for problems may be the presence of alkaline earth metals in the sample. Under the conditions described above it needs a very long time (more than 1 h) to elute magnesium and calcium

Table 1

Retention times for cations and amines, depending on the column and the eluent concentration (H₂SO₄) when the eluent flow-rate is 1 ml min⁻¹

	Retention time (min)			
	CG10+CS10 columns		CG12A+CS12A columns	
	20 mM H ₂ SO ₄	30 mM H ₂ SO ₄	10 mM H ₂ SO ₄	20 mM H ₂ SO ₄
Li	4.8	4.0	3.8	2.9
Na	6.7	5.2	4.6	3.3
NH ₄	10.7	7.9	5.4	3.7
MEA	12.5	9.0	5.5	N.T.
K	13.0	9.4	6.8	4.6
DEA	14.4	9.1	N.T.	N.T.
Rb	17.0	11.8	8.4	5.4
TEA	17.4	12.5	N.T.	N.T.
MMEA	19.1	13.5	5.8	4.0
MDEA	20	13.1	7.0	4.7
Morpholine	36	26	8.8	N.T.
Mg	N.E.	N.E.	11.8	4.9
Mn	N.E.	N.E.	12.8	N.T.
Ca	N.E.	N.E.	14.4	5.3
Sr	N.E.	N.E.	16.8	6.0
Ba	N.E.	N.E.	24	8.1
Piperazine	N.E.	N.E.	N.E.	17.8
'N'	36.5	26	8.9	5.6
'T', component 1	12.5	9.2	5.4	3.8
'T', component 2	39	28	11.6	7.3
'D'	12.5	9.1	5.4	N.T.

N.E., not eluted; N.T., not tested.

(which are present in most natural waters or waste waters). This can cause broad spurious peaks in the following analytical runs or drifting background conductivity. If the background conductivity is not equal at the start of every run, deviations in sensitivity may be the unpleasant result, especially for MDEA (recovery of 70–80 % if background conductivity is $1.3 \mu\text{S}$ instead of $0.8 \mu\text{S}$, for example). Sensitivity loss due to irregular baseline was not equal for all amines.

To minimize analytical problems a step gradient program is useful if amines should be determined in water samples. Fig. 1 includes chromatograms from such runs where different amine/alkali standard solutions are compared. Solution 1 contained 1 ppm MEA, 10 ppm K and 2 ppm DEA. Solution 2

contained 1 ppm Li, 5 ppm NH_4 , 1 ppm Rb, 5 ppm MMEA and 50 ppm MDEA. The waste water sample contained 0.005 ppm Li, 600 ppm Na, 0.04 ppm MEA, 2.7 ppm K, 2.5 ppm DEA, 0.28 ppm NH_4 , 2.2 ppm MMEA, 88 ppm MDEA and an unquantified amount of alkaline earth ions. The high sodium concentration caused a slight shifting of the retention times of some analytes. A step gradient program was used starting with 20 mM H_2SO_4 for 25 min, followed by a column purge step (120 mM H_2SO_4 for 5 min) and an equilibration step (20 min with 20 mM H_2SO_4). So it was possible to get a constant background conductivity (approx. $0.8 \mu\text{S}$) at the start of every run and a stable baseline. The only disadvantage is the enhanced analysis time of 50 min for one run.

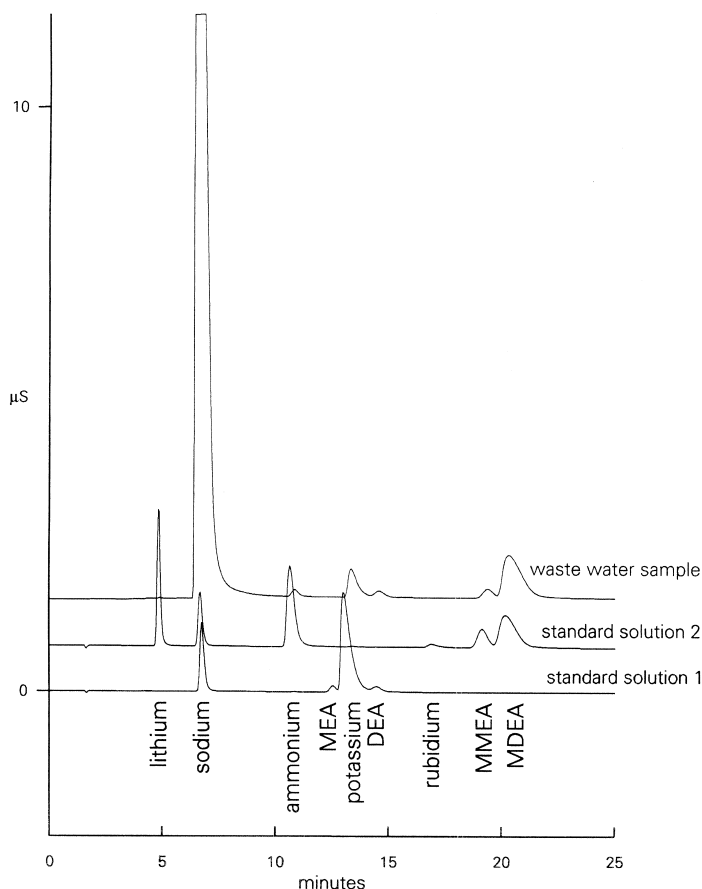


Fig. 1. Separation of ethanolamines with CS10 and 20 mM H_2SO_4 as eluent.

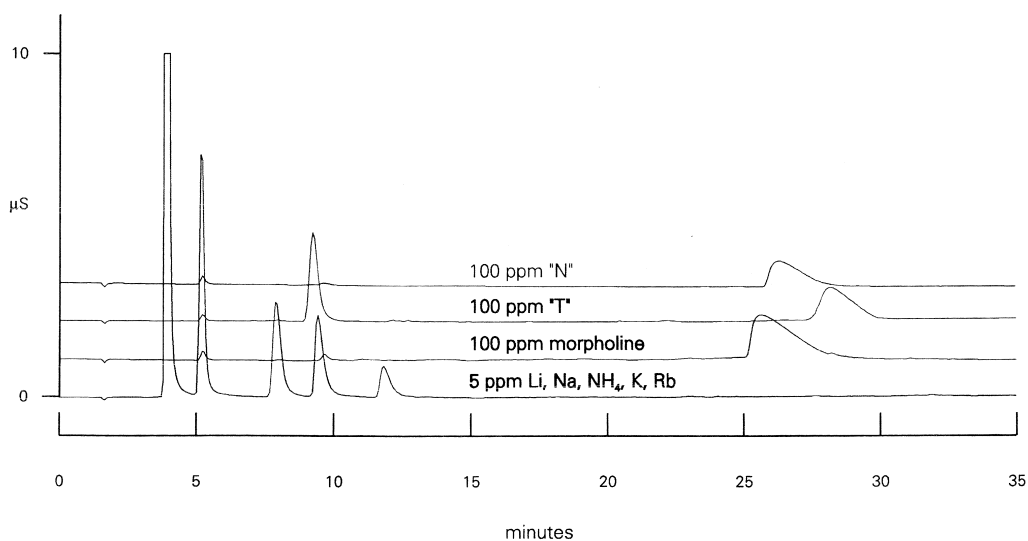


Fig. 2. Separation of steam volatile amines with CS10 and 30 mM H₂SO₄ as eluent.

3.2. Application 2: determination of steam volatile corrosion inhibitors in condensate samples

In steam condensate systems it is necessary to add steam volatile amines to protect the system against CO₂ corrosion. Chemicals like morpholine or commercial available products, which often are mixtures

of volatile amines can be used. At our sour gas treatment plants two different products have been applied in recent years: product 'N', which contains only one amine component that can be separated by IC; and product 'T', which is a combination of various volatile alkylamines and aminoalcohols, whereby two components could be separated during

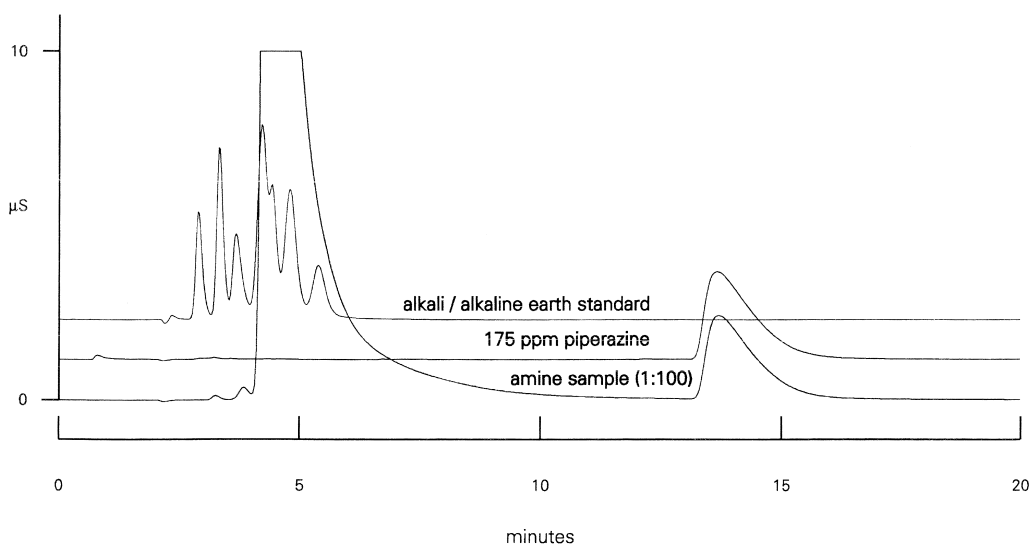


Fig. 3. Determination of piperazine in aqueous MDEA solutions with CS12A and 22 mM H₂SO₄ as eluent.

our experiments. Both columns can be used for separation, but CS10 should be preferred, because the separation of alkali and amines is better with CS10 than with CS12A. Problems caused by alkaline earth ions in these samples are not expected, because steam condensates normally contain no total hardness. Fig. 2 shows chromatograms of aqueous solutions (100 ppm) of morpholine, the products 'N' and 'T', and a 5 ppm alkali standard solution. Separation was performed with a CS10 analytical column and 30 mM H₂SO₄ as eluent.

3.3. Application 3: determination of piperazine in aqueous amine solutions

In one of our sour gas treatment plants a combination of MDEA and piperazine is used as scrubber

solution. Using the CS12A analytical column with 20–25 mM H₂SO₄ as eluent, separation of both amines is possible within 20 min, which is an acceptable analysis time. Fig. 3 shows the chromatograms of an amine sample from the sour gas treatment plant (diluted 1:100), a piperazine standard solution (175 ppm) and a cation standard solution (1 ppm Li, 5 ppm Na, NH₄, K, Mg, Ca, Sr) using 22 mM H₂SO₄ as eluent. The determined piperazine concentrations were comparable with results from non-aqueous titrations. The method is also useful to determine piperazine in water samples or MDEA in scrubber solutions. The determination of MDEA or other alkanolamines in water samples, containing alkali and alkaline earth ions cannot be performed, because all these components are eluted within a few minutes, so poor peak resolution can be expected.

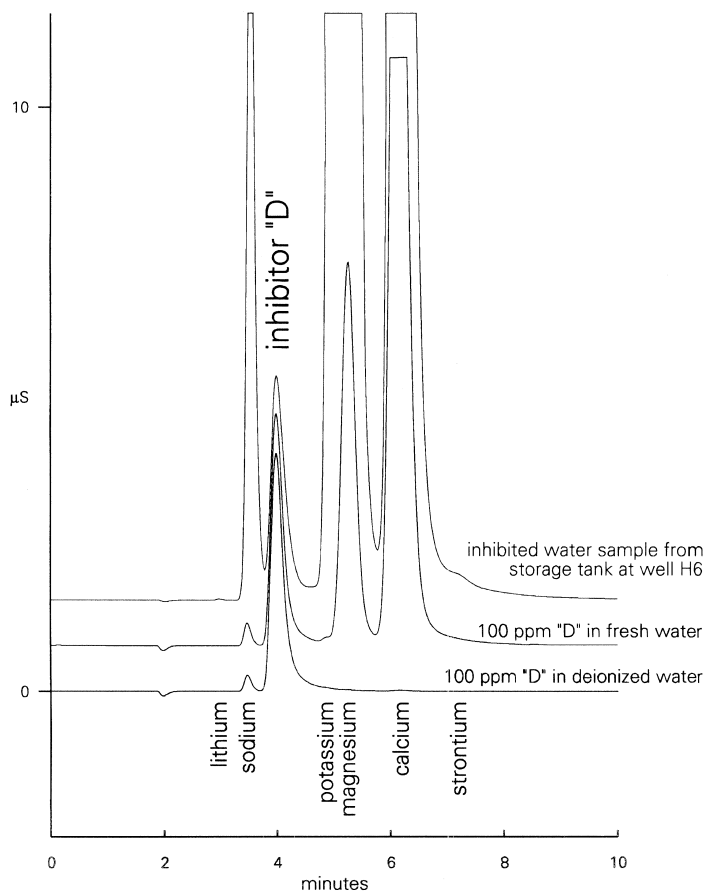


Fig. 4. Determination of inhibitor 'D' with CS12A and 16.5 mM H₂SO₄ as eluent.

3.4. Application 4: determination of an annular chamber corrosion inhibitor

Inhibitor 'D' is a commercial available, MEA containing corrosion inhibitor, predominately used to inhibit annular chamber liquids at gas wells. Another application is the inhibition of raw water which is used for cleaning or the intermediate filling of tanks during maintenance stops of gas treatment plants.

The check of the added inhibitor concentration is possible by IC when the inhibited water contains only traces of ammonium and low concentration of potassium, because both ions may disturb the determination (enhanced results caused by coelution). When the inhibitor is mixed with fresh water there are no problems to expect. We tested both columns for separation with various eluent concentrations. The examples in Fig. 4 show the chromatograms of solutions of 100 ppm 'D' in deionized water and fresh water (total hardness 8 °dH), and a sample from a storage tank at a gas well. A CS12A analytical column was used with 16.5 mM H₂SO₄ as eluent. If separation is performed using CS10 column, the presence of potassium in the sample also can cause problems. A step gradient program including a column purge step after the elution of the alkali ions is recommended to remove the remaining alkaline earth ions from the column.

4. Conclusions

The separation and determination of some amines can be performed with CS10 and CS12A as analytical column and hydrochloric acid or sulfuric acid

within acceptable analysis times isocratically. For determination of alkanolamines it is better to use CS10, but depending on the matrix it can be necessary to use a step gradient program for separation to minimize analytical problems. High salt concentrations in the sample can influence the retention behaviour and the response factors of some analytes. For the determination of piperazine the use of a CS12A analytical column is recommended.

Recently we received additional informations about other applications and columns [4,6,7]. There was no time to check this informations for applicability in our laboratory. Maybe it would be very interesting to test the IonPac CS11 or the CS14, but this has to be done in the future.

References

- [1] Installation Instructions and Troubleshooting Guide for the IonPac CG10 Guard Column and the IonPac CS10 Analytical Column, Dionex, Sunnyvale, CA, 1990.
- [2] Application Note 39: Determination of Ethanolamines in Refinery Water, Dionex, Sunnyvale, CA, 1982.
- [3] Installation Instructions and Troubleshooting Guide for the IonPac CG12A Guard Column and the IonPac CS12A Analytical Column, Dionex, Sunnyvale, CA, 1995.
- [4] Product Information for the IonPac CS14 Cation Exchange Column, Dionex, Sunnyvale, CA, 1994 (draft).
- [5] Installation Instructions and Troubleshooting Guide for the Cation Self-Regenerating Suppressor CSRS-II, Dionex, Sunnyvale, CA, 1994.
- [6] Application Update 138: Determination of Ethanolamines in Industrial Waters by Cation-Exchange Chromatography, Dionex, Sunnyvale, CA, 1998.
- [7] Dionex Solutions for Increased Productivity, Dionex, Sunnyvale, CA, 1997.