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GAS CHROMATOGRAPHIC TECHNIQUE FOR ANALYSING PARTIALLY DEGRADED DIETHANOLAMINE SOLUTIONS

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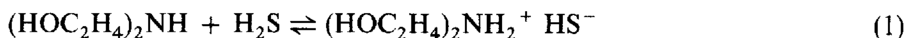
SUMMARY

A simple and reliable gas chromatographic technique is presented for the quantitative analysis of partially degraded aqueous diethanolamine solutions. The samples are injected, without preparation, into a chromatograph equipped with a 6 ft. × 1/8 in. O.D. stainless-steel column (packed with 60–80-mesh Tenax GC) and a flame-ionization detector. Nitrogen is used as the carrier gas and temperature programming is necessary. Apart from mono-, di- and triethanolamine, eleven degradation compounds could be detected and measured at concentrations as low as 0.5 wt.-% with accuracies of typically ±5%. The degradation compounds are identified and retention times are given.

INTRODUCTION

Aqueous diethanolamine (DEA) solutions are widely used in the gas processing industry for removing carbon dioxide and hydrogen sulphide from light hydrocarbons[1-3]. The process is based on the reaction of a weak base (DEA) with acid gases (hydrogen sulphide or carbon dioxide) to give water-soluble salts. The overall reactions may be summarized as follows:



$$(HOC_2H_4)_2NH + H_2S \rightleftharpoons (HOC_2H_4)_2NH_2^+ \ HS^- \quad (1)$$

$$(HOC_2H_4)_2NH + CO_2 + H_2O \rightleftharpoons (HOC_2H_4)NH_2^+ \ HCO_3^- \quad (2)$$

These reactions are reversible and the DEA is regenerated for repeated use. Unfortunately, certain side reactions may also occur which result in irreversible degradation of DEA into undesirable compounds. Degradation is undesirable because it leads to a loss of valuable DEA, fouling of the equipment with degradation products, reduction in the process efficiency and throughput and, possibly, corrosion. The direct and indirect costs resulting from degradation of DEA are, therefore, considerable to the oil and gas industry.

Owing to the industrial significance of DEA, a quantitative study of the degradation of DEA was initiated. Such a study was dependent on the availability of an

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efficient analytical procedure for detecting and measuring the concentrations of degradation compounds. Unfortunately, reliable and simple techniques had not been reported for the detection of DEA and its degradation products in aqueous solutions. The analysis is difficult to perform because DEA and its degradation products have fairly low vapour pressures, decompose at elevated temperatures, are highly polar and usually occur in dilute aqueous solutions.

Many analytical methods have been suggested[4] for DEA and its degradation compounds, *e.g.*, wet chemical techniques, infrared and ultraviolet spectroscopy and paper and thin-layer chromatography. However, they all suffer from various disadvantages such as lack of accuracy, specificity, reliability and simplicity. Therefore, in this study we concentrated on the development of gas chromatographic methods.

Brydia and Persinger[5] described a chromatographic technique for the analysis of ethanolamines. As direct gas chromatographic methods led to excessive peak tailing, they investigated derivatization with trifluoroacetic anhydride (TFA) prior to chromatographic separation. However, TFA also reacts with water and the resulting trifluoroacetic acid causes severe tailing in the chromatograms. Piekos *et al.*[6] eliminated these problems by converting the alkanolamines into trimethylsilyl derivatives by using N,O-bis(trimethylsilyl)acetamide, which reacts with both the amino and hydroxyl groups of the alkanolamines. This silylation process yielded fairly stable compounds which are more easily separated and identified by gas chromatography. Water concentrations of up to 5% could be tolerated provided that the silylating agent was used in excess.

As the water content of industrial amine solutions typically range from 65 to 90%, the method of Piekos *et al.*[6] is not directly applicable. Choy and Meisen[7] therefore modified the technique by stripping water from the degraded DEA solutions with air. The removal of water usually resulted in the precipitation of some of the degradation products. The dried sample was therefore dissolved in dimethylformamide and the resulting mixture silylated with N,O-bis(trimethylsilyl)acetamide. The silylated compounds were then separated using a 6 ft. × 1/8 in. O.D. stainless-steel column packed with 8% OV-17 on 80–100-mesh Chromosorb. A flame-ionization detector was used.

The method developed by Choy and Meisen[7], although reliable, was felt to be too time consuming for wide industrial application because of the extensive sample preparation. Further, there is the problem of incomplete silylation of some compounds; silylation of hydrogen bound to nitrogen atoms in alkanolamines is known to be difficult[8].

An attempt was therefore made to find a simple and more direct technique for analysing DEA and its degradation products. A thorough review of the literature yielded a paper by Saha *et al.*[9], who used Tenax GC to separate alkanolamines. Tenax GC is a porous polymer based on 2,6-diphenyl-*p*-phenylene oxide[10], which has a weakly interacting surface and can be used at temperatures up to 450°C. No sample preparation is required as the column is unaffected by the presence of water.

EXPERIMENTAL

A temperature-programmable gas chromatograph (Hewlett-Packard Model 5830A) equipped with a 6 ft. × 1/8 in. O.D. stainless-steel column packed with Tenax

TABLE I

ANALYTICAL EQUIPMENT AND OPERATING CONDITIONS FOR GAS CHROMATOGRAPHIC ANALYSIS

Gas chromatograph:	
Manufacturer	Hewlett-Packard
Model	5830A
Detector	H_2 flame-ionization
Chromatographic column:	
Material	Stainless steel
Dimensions	6 ft. × $\frac{1}{8}$ in. O.D.
Packing	Tenax GC, 60–80 mesh
Operating conditions:	
Carrier gas	N_2 at 25 ml/min
Injection port temperature	300°C
Detector port temperature	300°C
Column temperature	Isothermal at 150°C for 0.5 min, then increased at 8°C/min to 300°C
Syringe:	
Manufacturer	Hamilton
Model	701 (10 μl) with fixed needle and Chaney adapter
Injected sample size	1 μl

GC (purchased from Alltech, Arlington Heights, IL, U.S.A.) was used. Initial trials were performed with aqueous solutions of monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA). Using a hydrogen flame-ionization detector, nitrogen as the carrier gas and temperature programming, excellent separation was obtained. One reference[11] indicated that stainless steel causes ethanolamines to undergo catalytic degradation. No evidence of degradation within the column however, was, observed by us for any of the compounds tested.

After several initial trials, optimum conditions were found for the separation of DEA and its degradation compounds; the conditions are summarized in Table I. Temperature programming was used in order to achieve good separation of all degradation products, as these compounds varied considerably in molecular weight and polarity. A maximum temperature of 300°C was adopted to ensure that all compounds were volatilized.

Typically, 1.0-μl samples were injected directly into the column with a precision syringe fitted with a Chaney adaptor. The adaptor was used to ensure that a constant volume of sample was introduced into the column. To improve the accuracy, a needle guide was used at the injection port. This guide not only protected the fragile syringe needle, but also served as a spacer for needle penetration and lengthened the septum life.

The analysis was usually performed for 30 min in order to ensure the elution of heavy degradation compounds. After each run, the column had to be cooled, from 300 to 150°C, which took about 5 min. A complete run therefore required about 35 min.

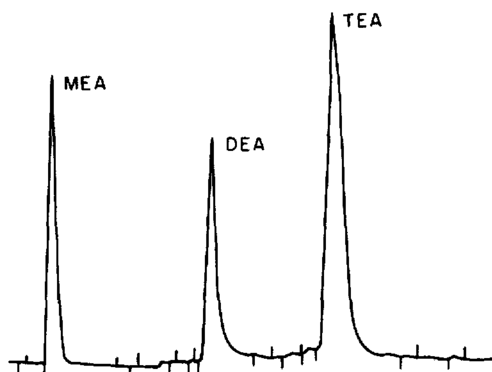

Fig. 1. Typical chromatogram for an aqueous solution of MEA, DEA and TEA.

Column performance

The column itself required no special care and was conditioned simply by passing nitrogen through it at the maximum operating temperature (300°C) for 8–10 h. The columns have a fairly long life; for example, one column was in continual use for nearly a year. However, when a column fails, it fails rapidly and becomes incapable of separating the heavy compounds.

Maintenance of the chromatographic equipment

Generally very little maintenance is required. In some instances deposits tend to build up in the injection port and must be removed. Further, deposits may accumulate on the detector jets and result in excessive noise on the chromatograms. Mechanical cleaning of the flame-ionization detector is difficult and the removal of the probes is not recommended unless absolutely necessary. A simpler method is to inject 10–30 μl of Freon 113 into the chromatograph with the equipment operating under normal conditions. Freon elutes from the column and produces hydrogen fluoride as the cleaning agent when burnt in the hydrogen flame.

As the column performance may vary somewhat, it is good practice to check the calibration after every 100 injections with standard samples. Septa should also be replaced at least every 30 injections as they tend to accumulate deposits and eventually begin to leak.

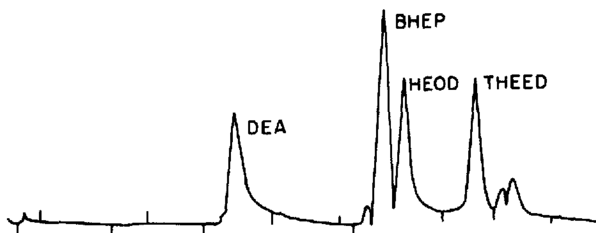

Fig. 2. Chromatogram of an aqueous DEA solution partially degraded with carbon dioxide under laboratory conditions.

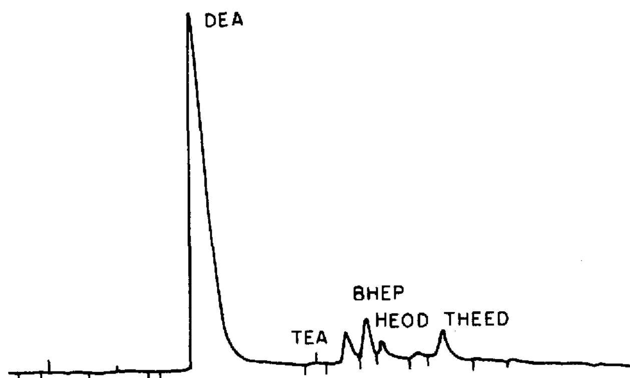

Fig. 3. Chromatogram of a partially degraded DEA solution from a gas plant in Western Canada.

RESULTS

Fig. 1 shows a typical chromatogram of a sample produced by mixing distilled water, MEA, DEA and TEA. The peaks are sharp and distinct.

From the literature it was apparent that the main degradation compounds of DEA are 3-(hydroxyethyl)-2-oxazolidone (HEOD), N,N,N-tris(hydroxyethyl)ethylenediamine (THEED) and N,N-bis(hydroxyethyl)piperazine (BHEP). Fig. 2 shows a typical chromatogram of a DEA solution degraded in the presence of carbon dioxide. As can be seen, there is good separation between DEA, HEOD, BHEP and THEED. Each compound gives a fairly sharp peak with little tailing. The smaller peaks are due to minor degradation products. Better separation especially between HEOD and BHEP, may be achieved by using a 9-ft, column. However, the longer column inevitably increases the elution times.

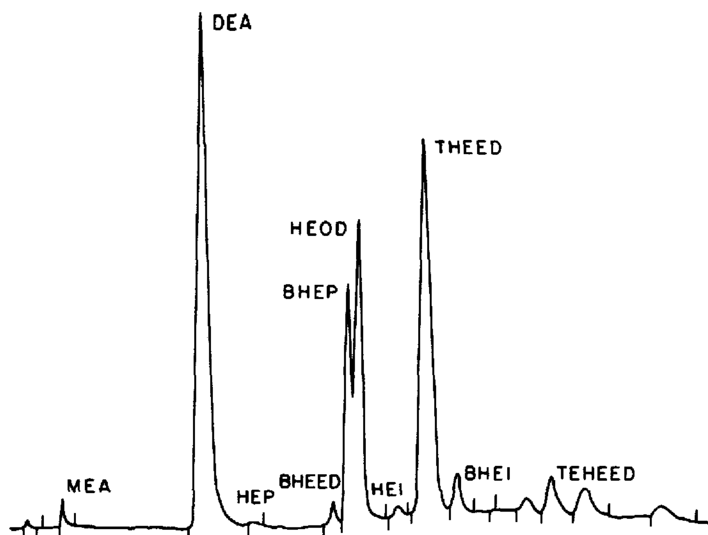

Fig. 4. Chromatogram of an aqueous DEA solution severely degraded with carbon dioxide under laboratory conditions.

TABLE II

COMPOUNDS FOUND IN DEGRADED DEA SOLUTIONS

Compound	*Structural formula*	*Typical retention time (min)*
Monoethanolamine (MEA)	$HOC_2H_4NH_2$	1.4–1.5
N-(hydroxyethyl)-ethylenimine (HEM)	$HOC_2H_4-N<(CH_2-CH_2)$ (ring)	3.1–3.5
N-(hydroxyethyl)-ethylenediamine (HEED)	$HOC_2H_4NHC_2H_4NH_2$	6.8–7.2
Diethanolamine (DEA)	$(HOC_2H_4)_2NH$	7.4–8.0
N-(Hydroxyethyl)-piperazine (HEP)	$HOC_2H_4-N<(C_2H_4)_2>NH$ (ring)	9.8–10.2
Oxazalidone (OZD)	HN–C(=O)–O–CH_2–CH_2 (ring)	10.4–10.6
Triethanolamine	$(HOC_2H_4)_3N$	12.0–12.5
N,N-Bis(hydroxyethyl)-ethylenediamine (BHEEP)	$(HOC_2H_4)_2NC_2H_4NH_2$	12.8–13.2
N,N-Bis(hydroxyethyl)-piperazine (BHEP)	$HOC_2H_4-N<(C_2H_4)_2>N-C_2H_4OH$ (ring)	13.0–13.6
3-(Hydroxyethyl)-2-oxazalidone (HEOD)	HOC_2H_4–N–C(=O)–O–CH_2–CH_2 (ring)	13.4–14.0
N-(Hydroxyethyl)-imidazalidone (HEI)	HOC_2H_4–N–C(=O)–NH–CH_2–CH_2 (ring)	15.5–16.0
N,N,N-Tris(hydroxyethyl)-ethylenediamine (THEED)	$(HOC_2H_4)_2NC_2H_4NHC_2H_4OH$	17.2–17.4
N,N-Bis(hydroxyethyl)-imidazalidone (BHEI)	HOC_2H_4–N–C(=O)–N(C_2H_4OH)–CH_2–CH_2 (ring)	18.2–18.5
N,N,N,N-Tetra(hydroxyethyl)-ethylenediamine	$(HOC_2H_4)_2NC_2H_4N(C_2H_4OH)_2$	20.4–20.6

Fig. 3 shows a typical chromatogram of a partially degraded DEA sample from an industrial source. Peaks of HEOD, BHEP and THEED are clearly evident. A peak caused by TEA is also noted. TEA is frequently present as an impurity in industrial DEA solutions. These result show that industrial samples can easily be analysed by this method.

Calibration

The peak areas were found to be linear functions of the concentration of each component, which greatly simplified the calibration of the chromatograph. "Direct calibration" rather than an internal standard was used. Calibration plots of concentration *versus* peak area were produced by simply injecting known concentrations of the various amines or degradation products and noting the peak area, which was automatically calculated by the chromatograph's computer. At least five samples were injected for each concentration and the peak area averaged.

Using this method, DEA and its known degradation products could be detected accurately at concentrations as low as 0.5 wt.-%. The reproducibility was good (typically within ±5.0% with a new column). An internal standard could be used to reduce errors arising from changes in sample injection, carrier gas flow-rate and detector sensitivity.

Identification of degradation products

As this study was undertaken to examine the degradation of DEA, it was necessary to identify the compounds causing the various peaks on the chromatogram. Some degraded DEA solutions contained up to eighteen compounds in significant concentrations (> 1 wt.-%). Using a gas chromatograph coupled to a mass spectrometer (Hewlett-Packard Model 5985B) it was possible to identify up to fourteen peaks[12] (a typical example is shown in Fig. 4). Table II lists the compounds and their retention times (based on the conditions given in Table I). Some other compounds were also detected but their concentration was very low (< 1 w.t.-%) so that their identification was neither warranted nor easily accomplished. It may be noted that this is the first time that many of these compounds have been unequivocally identified in degraded DEA solutions.

CONCLUSIONS

A gas chromatographic technique has been developed that is capable of detecting DEA and its degradation products quantitatively. It can therefore be used to monitor the quality of DEA solutions under industrial conditions. Eleven major degradation compounds have been indentified.

The advantages of the present technique are no sample preparation, the column is unaffected by water, simplicity, speed and reliability.

ACKNOWLEDGEMENT

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REFERENCES

1 K. F. Butwell, D. J. Kubek and P. W. Sigmund, *Hydrocarbon Process.*, 62 (1982) 108.
2 K. F. Butwell and C. R. Perry, *Proc. Gas Cond. Conf.*, 25(B) (1975) 1.
3 A. H. Younger, *Symposium on Sulphur Recovery from Hydrocarbon Feedstocks, Vancouver, B.C., 1973.*
4 E. T. Choy, *Masters Thesis*, University of British Columbia, 1978.
5 L. E. Brydia and H. E. Persinger, *Anal. Chem.*, 39 (1967) 1318.
6 R. Piekos, K. Kobyiczyk and J. Grzybowski, *Anal. Chem.*, 47 (1975) 1157.
7 E. T. Choy and A. Meisen, *J. Chromatogr.*, 187 (1980) 145.
8 A. de Savignac, A. Lattes and J. Carles, *J. Chromatogr.*, 7 (1962) 261.
9 N. C. Saha, S. K. Jain and R. K. Dua, *Chromatographia*, 10 (1977) 368.
10 R. van Wijk, *J. Chromatogr. Sci.*, 8 (1970) 418.
11 *Analysis of Ethanolamine, SGE Technical Publication on Glass Lined Tubing*, Scientific Glass Engineering, North Melbourne, 1978.
12 M. L. Kennard, *PhD Thesis*, University of British Columbia, 1983.