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GAS CHROMATOGRAPHIC DETECTION OF DIETHANOLAMINE AND ITS DEGRADATION PRODUCTS

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SUMMARY

A gas chromatographic technique was developed for the analysis of aqueous diethanolamine solutions and their degradation products. The technique consisted of removing water by air stripping, silylating the residue with N,O-bis-(trimethylsilyl) acetamide and separating the silylation products with an OV-17–Chromosorb W HP column followed by a hydrogen flame ionization detector. Nitrogen was used as the carrier gas and the column was operated at 142 or 174°.

The technique was successfully applied to the analysis of amine solutions degraded at elevated pressures and temperatures under laboratory as well as industrial conditions. Numerous degradation compounds were detected but their chemical structures remain to be determined.

INTRODUCTION

Aqueous diethanolamine (DEA) solutions are widely used in the oil and gas industries for the absorption of carbon dioxide and hydrogen sulphide from mixtures of light hydrocarbons. The amine solutions are regenerated by steam stripping before recycling to the absorber. Although the principal reactions governing absorption and desorption are:

$$(HO\text{–}CH_2\text{–}CH_2)_2NH + H_2S \leftrightharpoons [(HO\text{–}CH_2\text{–}CH_2)_2NH_2]\,HS \quad (1)$$

$$2(HO\text{–}CH_2\text{–}CH_2)_2NH + H_2S \leftrightharpoons [(HO\text{–}CH_2\text{–}CH_2)_2NH_2]_2\,S \quad (2)$$

$$(HO\text{–}CH_2\text{–}CH_2)_2NH + CO_2 + H_2O \leftrightharpoons [(HO\text{–}CH_2\text{–}CH_2)_2NH_2]\,HCO_3 \quad (3)$$

$$2(HO\text{–}CH_2\text{–}CH_2)_2NH + CO_2 + H_2O \leftrightharpoons [(HO\text{–}CH_2\text{–}CH_2)_2NH_2]_2\,CO_3 \quad (4)$$

certain side reactions occur as well. These side reactions are undesirable because they result in a loss of valuable amine and give rise to degradation products, some of

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which are highly corrosive*. Polderman and Steele[1], Hakka *et al.*[2] and Smith and Younger[3,4] suggested that the compounds listed in Table I may result from DEA degradation.

Due to its industrial significance we initiated a systematic study on DEA degradation and found that reliable techniques had not been reported for the detection of DEA and its degradation products in aqueous solutions. The analysis is difficult because DEA and its degradation products have fairly low vapour pressures, decompose at elevated temperatures, are highly polar and occur, under industrial conditions, in dilute aqueous solutions.

Although other methods were considered[5], we decided to develop a gas chromatographic technique. Brydia and Persinger[5] had shown that ethanolamines can be analyzed chromatographically after stabilization with trifluoroacetyl anhydride (TFA), which attacks the amino and hydroxyl groups. However, TFA also reacts with water and the resulting trifluoroacetic acid causes severe tailing in the chromatograms. Piekos *et al.*[7] suggested that this problem could be minimized by using N,O-bis-(trimethylsilyl (TMS))acetamide (BSA) as the stabilizer. This compound also reacts with amino and hydroxyl groups as shown in the following example:

$$(HO{-}CH_2{-}CH_2)_2N{-}H + 3CH_3{-}C\begin{matrix}O{-}Si(CH_3)_3\\ \diagdown\\ \diagup\\ N{-}Si(CH_3)_3\end{matrix} \rightarrow$$

(DEA) (BSA)

$$((CH_3)_3{-}Si{-}O{-}CH_2{-}CH_2)_2N{-}Si(CH_3)_3 + 3CH_3{-}C\begin{matrix}O\\ \diagdown\\ \diagup\\ NH{-}Si(CH_3)_3\end{matrix} \qquad (5)$$

(DEA–TMS Derivative) (MSA)

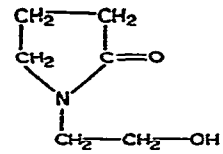
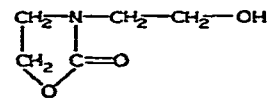
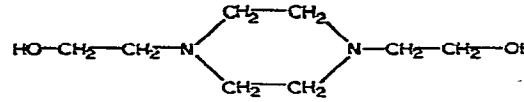
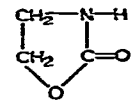
where the abbreviation MSA denotes N-trimethylsilylacetamide. Water concentrations up to 5% could be tolerated without interfering with the performance of a 150 × 4 mm I.D. glass column packed with 100–120 mesh Diatomite CQ coated with 3% OV-1. Argon on nitrogen were used as the carrier gas.

Since the water content of amine solutions used industrially ranges from about 70 to 90%, the method of Piekos *et al.*[7] is not directly applicable. Removing the water causes the precipitation of some degradation compounds. A solvent therefore had to be found, which not only dissolves the DEA and its degradation products, but also does not interfere with silylation. Choy[5] examined the following solvents: acetonitrile (CH_3CN); dimethyl sulfoxide ($(CH_3)_2SO_2$); tetrahydrofuran ($CH_2(CH_2)_2CH_2O$); pyridine (C_5H_5N); chloroform ($CHCl_3$); furan (C_4H_4O); dimethyl formamide ($HCON(CH_3)_2$). The last compound was found to be most suitable since it satisfied the aforementioned criteria for solvents, was fairly inexpensive and non-hazardous.

* The direct and indirect coasts can exceed US $ 100,000 in large gas plants.

TABLE I

POSSIBLE DEGRADATION PRODUCTS OF ETHANOL AMINES

Compound	*Structural formula*	*Mol. weight*
Hydroxyethyl imidazolidone (HEI)		113
3-(2-Hydroxyethyl)-2-oxazolidinone (MEOD)		131
N,N-Bis-(2hydroxyethyl)-piperazine (HEP)		174
N,N,N-Tris-(2-hydroxyethyl)-ethylenediamine (THEED)	$(HO{-}CH_2{-}CH_2)_2{-}N{-}CH_2{-}CH_2{-}\underset{\displaystyle H}{\underset{\vert}{N}}{-}CH_2{-}CH_2{-}OH$	236
N-Methyldiethanolamine (MDEA)	$(HO{-}CH_2{-}CH_2){-}N{-}CH_3$	119
Oxazolidone (OZD)		87
Aminoethylethanolamine	$NH_2{-}CH_2{-}CH_2{-}\underset{\displaystyle H}{\underset{\vert}{N}}{-}CH_2{-}CH_2{-}OH$	104

EXPERIMENTAL

Apparatus and operating conditions

A Varian Aerograph (Series 1440) gas chromatograph equipped with a hydrogen flame ionization detector was used. The following operating conditions were found to be optimal: injection port temperature = 195°; column temperature = 142°; detector temperature = 220°; nitrogen carrier gas flow-rate = 20 ml/min; air flow-rate = 350 ml/min; hydrogen flow-rate = 35 ml/min.

The chromatographic column was made of 316 stainless steel, 6 ft. × 1/8 in. O.D. (1830 × 0.32 mm O.D.). The column was packed with 80–100 mesh Chromosorb W HP coated with 8% OV-17. The packed column was obtained from Western Chromatographic Supplies, New Westminster, Canada.

Samples (0.3 μl) were injected into the gas chromatograph through a silicon

rubber septum using a 2-μl, Series D, Pressure-Lok, liquid syringe manufacturated by Precision Sampling, Baton Rouge, La., U.S.A.

Solvent and internal standard

Analytical grade dimethyl formamide (DMF) was supplied by Caledon Labs., Georgetown, Canada. Decanolic acid (DECA) was used as an internal standard and obtained from Matheson, Coleman and Bell, Norwood, Ohio, U.S.A.

Drying and redissolution of sample

Exactly 1-ml samples were withdrawn from the reactor, in which the DEA–CO_2–H_2S degradation reactions occurred, and transferred into a 50-ml erlenmeyer flask located in a sand bath whose temperature was set to 80°. A small stream of bone-dry air was passed over the sample for about 40 min to evaporate the water and desorb CO_2 and H_2S. To remove the last trace of water, a few milliliters of methyl chloride were added to the DEA residue and the evaporation repeated to ensure the complete azeotropic removal of water[8].

Exactly 2 ml of DMF solution spiked with $1.49 \cdot 10^{-4}$ mole of DECA were then added and the sample was diluted to 25 ml with pure DMF.

Silylation reaction

Exactly 4 ml of the above solution were transferred to 12-ml sampling bottle equipped with a PTFE-lined screw cap. A large excess of 2 ml BSA ($8.31 \cdot 10^{-3}$ mole) was then added to the sampling bottle and the cap firmly closed. Oil resistant adhesive tape was wrapped around the cap to ensure a perfect seal. The bottle was well shaken and immersed in a 60° oil bath for 1 h, which is sufficient to complete the silylation reaction. (More prolonged silylation at 70° led to identical results.)

After the silylation was complete, the sampling bottle was removed from the oil bath and the PTFE lining of the cap replaced by a silicon rubber stopper to permit syringe withdrawal of samples. The previous procedure was designed to minimize the contact between the sample and atmospheric moisture. Finally, 3-μl sample volumes were injected into the gas chromatograph set to the aforementioned conditions.

Maintenance

The chromatograph column required periodic conditioning. This was done by injecting about 20 μl of Silyl 8 (supplied by Pierce, Rockford, Ill., U.S.A.) until baseline drift was eliminated. In analyzing trimethylsilyl derivatives, SiO_2 deposits tend to accumulate slowly in the flame ionization detector. Bleeding of the silicone column phases also results in SiO_2 formation. These deposits can be removed by injecting 10 to 35 μl of Freon 113 into the chromatograph with the equipment operating and a column temperature of 150°. The Freon eluted within a few seconds and, as it burnt in the hydrogen flame, formed HF which removed any deposits from the detector.

RESULTS AND DISCUSSION

Fig. 1 shows a typical chromatogram obtained with a mixture produced by combining N-methyldiethanolamine (MDEA), monoethanolamine (MEA), DEA,

oxazolidone (OZD), decanolic acid (DECA), triethanolamine (TEA) and N,N-Bis-(2-hydroxyethyl)-piperazine (HEP). Each compound gives a fairly sharp peak with little tailing. Smaller peaks are probably due to partially silylated compounds and impurities. The separation between MEA and DEA is not complete but this was unimportant in the present degradation experiments since mixtures of amines were not used. The separation could probably be improved by adjusting the carrier gas flow-rate and/or by temperature programming. The peak areas were shown to be linear functions of the amounts of mixture components and this greatly facilitated the calibration of the chromatograph.

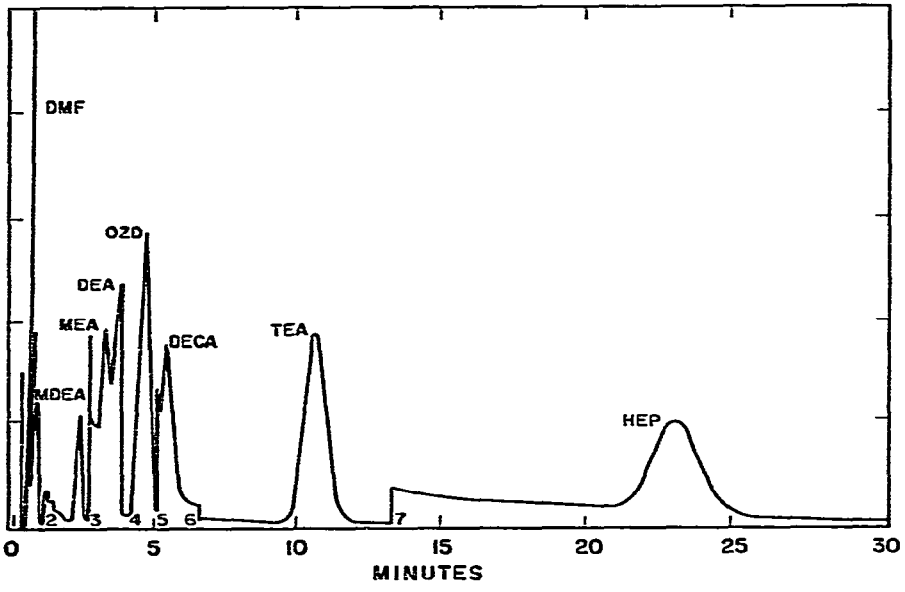


Fig. 1. Chromatogram of ethanolamines and some previously reported degradation products. (Sensitivity: (1) $512 \cdot 10^{-10}$ A f.s.; (2) $125 \cdot 10^{-11}$ A f.s.; (3) $8 \cdot 10^{-11}$ A f.s.; (4) $128 \cdot 10^{-11}$ A f.s.; (5) $16 \cdot 10^{-11}$ A f.s.; (6) $32 \cdot 10^{-11}$ A f.s.; (7) $4 \cdot 10^{-11}$ A f.s.).

The reproducibility of DEA measurements fell within $\pm$ 4% and the lower limit of measuring DEA was about $1.44 \cdot 10^{-6}$ moles; this corresponds to a DEA concentration of approximately $1.4 \cdot 10^{-2}$%. DEA peaks could however be detected at even lower concentrations. The corresponding values for HEP were: reproducibility $\pm$ 7%; lower limit for concentration measurement *ca.* $6.25 \cdot 10^{-7}$ mole/ml.

Fig. 2 shows the chromatogram for a 30% DEA solution which had been in contact with pure CO_2 at a pressure of 4234 kPa and temperature of 185° for 4 h. The five peaks labelled HEP, T, X, Y and Z are attributable to DEA degradation products. Compound T has the same elution time as triethanolamine but it may, in fact, be a different substance. Compounds X, Y and Z are also present in the parent DEA solution, but their concentrations increase rapidly as the DEA degrades. Identification of these compounds has proven to be quite difficult and is the subject of ongoing investigations.

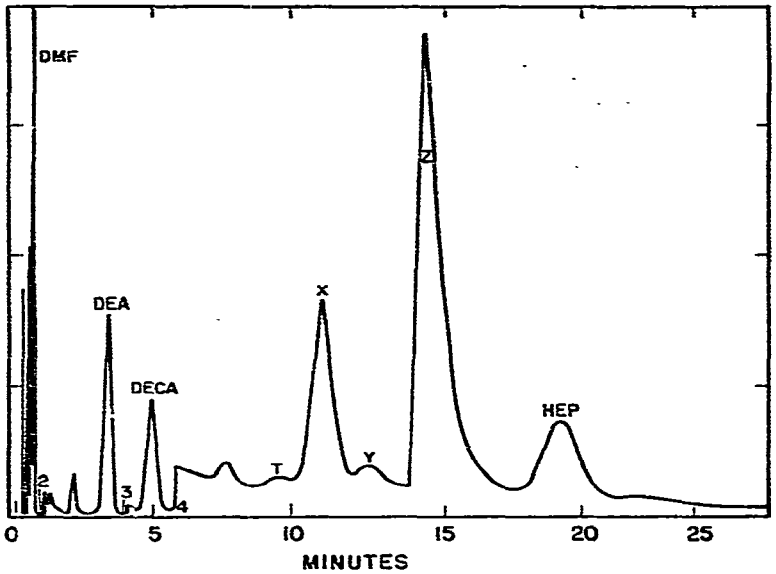


Fig. 2. Typical chromatogram of a partially degraded DEA sample. (Sensitivity: (1) $512 \cdot 10^{-10}$ A f.s.; (2) $16 \cdot 10^{-10}$ A f.s.; (3) $32 \cdot 10^{-11}$ A f.s.; (4) $32 \cdot 10^{-12}$ A f.s.).

Since all degradation products were present at low concentrations, the chromatograph had to be set to very high sensitivities ($32 \cdot 10^{-12}$ A f.s. or less). At such sensitivities minor contaminants and line voltage fluctuations can introduce disturbances and distort the peaks. Baseline drift may also be encountered. These problems can, however, be largely overcome by using a triangulation technique as suggested by McNair and Bonelli[9].

A typical chromatogram of a partially degraded DEA sample from an industrial source is shown in Fig. 3. A total of 36 industrial samples was analyzed using the present technique and no difficulties were encountered provided the samples did not contain precipitates. The general similarity of Figs. 2 and 3 is apparent even though the concentrations of the various compounds are somewhat different. In general, it may however be concluded that DEA degradation under laboratory conditions resembles industrial degradation. In some industrial facilities the DEA solution is passed through activated carbon filters, but no significant reduction in the concentrations of degradation products was noted compared with plants which did not have such filters.

An attempt was also made to detect degradation products with molecular weights higher than HEP. Using the same solution as for Fig. 3, but operating the chromatographic column at 174° gave the chromatogram shown in Fig. 4. Several compounds with long elution times are noted; their identities are unknown, but some of them may correspond to the substances listed in Table I. Degradation in the chromatographic column did not occur as could be demonstrated by injecting the silyl derivatives of pure DEA.

Although the identity and absolute concentrations of most degradation compounds remains unknown, the present chromatographic technique has considerable industrial merit. Since the technique is capable of detecting DEA and its degrada-

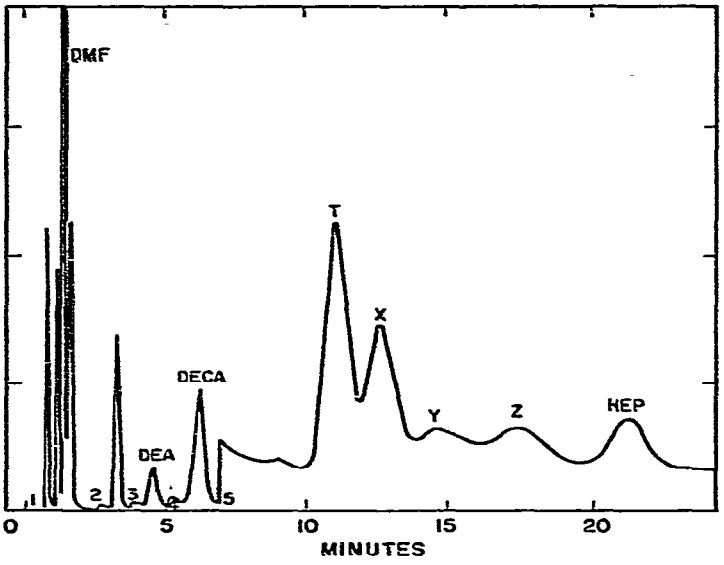


Fig. 3. Typical chromatogram of a partially degraded DEA sample from an industrial source. (Sensitivity: (1) $512 \cdot 10^{-10}$ A f.s.; (2) $32 \cdot 10^{-10}$ A f.s.; (3) $8 \cdot 10^{-10}$ A f.s.; (4) $32 \cdot 10^{-11}$ A f.s.; (5) $32 \cdot 10^{-12}$ A f.s.).

tion compounds quantitatively, it can be used to monitor the quality of DEA solutions. When significant degradation starts to occur, it may be related to plant operating conditions (temperature, pressure, gas quality, solution strength, pH, etc.) and

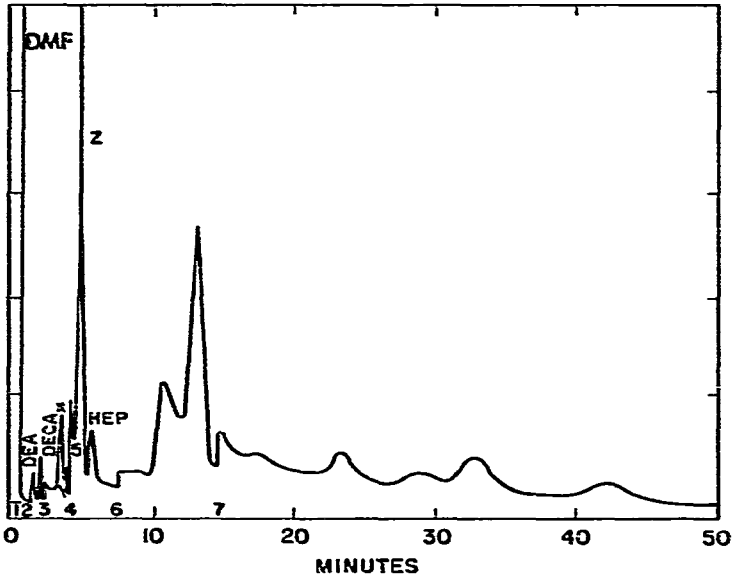


Fig. 4. Typical high-temperature chromatogram of a partially degraded DEA sample. (Sensitivity: (1) $512 \cdot 10^{-10}$ A f.s.; (2) $16 \cdot 10^{-10}$ A f.s.; (3) $32 \cdot 10^{-11}$ A f.s.; (4) $64 \cdot 10^{-12}$ A f.s.; (5) $128 \cdot 10^{-12}$ A f.s.; (6) $64 \cdot 10^{-12}$ A f.s.; (7) $32 \cdot 10^{-12}$ A f.s. Column temperature 174°).

corrective action can be taken. Furthermore, the technique can be used to monitor the performance of DEA purification systems, such as activated carbon filters. Consequently, the technique should help to improve the performance of industrial amine plants.

CONCLUSION

A chromatographic technique has been developed for measuring the concentrations of ethanolamines and products formed in the degradation of diethanolamine. The technique is based on stabilizing the compounds with BSA, a silylation agent, and is suitable for monitoring the quality of amine solutions under industrial conditions.

ACKNOWLEDGEMENT

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