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Gas chromatographic analysis of alkanolamine solutions using capillary and packed columns

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ABSTRACT

The detailed analysis of amine solutions used in natural gas treatment is usually based on gas chromatographic (GC) methods which utilize columns packed with Tenax GC or TA, a porous polymer based on 2,6-diphenyl-*p*-phenylene oxide. This technique has the advantages of the ability to separate the various compounds in solution, minimum sample preparation and short analysis times. Advances in chromatography have shown the general superiority of capillary columns for the analysis of complex solutions. Unfortunately, Tenax is available only in packed columns. This paper presents the results of GC analyses of fresh and partially degraded alkanolamine solutions in which the Tenax column was replaced with a polyethylene glycol-based fused-silica, wide-bore capillary column (15 m × 0.53 mm I.D., 1.0-μm film thickness). It was found that the capillary column provides better peak shape, requires significantly less sample size, maintains higher sensitivity and offers a faster and more efficient separation than the Tenax packed columns.

INTRODUCTION

Alkanolamines are commonly used to remove impurities such as CO_2, H_2S, COS and CS_2 from natural, refinery and other industrial gases in reversible absorption–desorption processes. However, irreversible or degradation reactions sometimes occur, resulting in the formation of undesirable degradation compounds. As the degradation compounds build up in solution, the concentration of the functional amines is reduced, thus limiting the absorption capacity of the process. The degradation compounds may also contribute to other problems such as corrosion [1–3], foaming [4–6] and fouling [7]. Therefore, routine analyses of plant solutions are conducted to determine the state of the plant solution and to take remedial actions for ensuring the desired plant efficiency.

Early attempts to analyse partially degraded amine solutions used methods such as potentiometric titration [8], acid titration and Kjedahl total nitrogen determination [4,9], fractional distillation and crystallization [10]. These methods were generally unsuccessful owing to a lack of reproducibility, inability to separate degradation compounds, decomposition of amines and degradation compounds at elevated temperatures and long analysis times. Derivatization has been tried as a means of making the amines more volatile, less polar and consequently more amenable to gas chromatographic (GC) analysis [11–13]. Although fairly successful, GC analysis of derivatized degraded amine solutions suffers some drawbacks which were outlined by Saha *et al.* [14]. As a result, the latter group developed a direct GC technique using a column packed with Tenax GC, a porous polymer based on 2,6-diphenyl-phenylene oxide developed by Van Wijk [15]. This column successfully separated a mixture of monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) in about 8 min. The use of the Tenax GC column was subsequently extended to the analysis of partially de-

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graded alkanolamine solutions and the detailed analytical conditions have been reported [16–18]. Other studies involving the analysis of fresh and partially degraded alkanolamine solutions using Tenax columns in combination with other columns [19,20] have also been reported. Recently, Tenax TA has replaced Tenax GC. The former is claimed to offer better tolerance to impurities, thereby limiting the number of minute peaks on the chromatogram.

Advances in GC have shown the general superiority of capillary columns for the analysis of complex solutions. Unfortunately, Tenax is available only in packed columns. This paper presents comparisons between polar capillary, semi-polar capillary and packed columns. The results show that the polar polyethylene glycol-based, wide-bore, fused-silica, bonded-phase capillary column performs better than the semi-polar capillary or the Tenax packed column in the analysis of fresh and partially degraded alkanolamine solutions.

EXPERIMENTAL

GC adaptation

A Hewlett-Packard HP 5830A gas chromatograph which is configured for packed columns was adapted for capillary columns by installing appropriate adaptors in the injection and detector ports. The adaptors consisted of a glass injection port liner and connectors which converted the 1/4- and 1/8-in. (1 in. = 2.54 cm) injection and detector ports respectively, to the dimensions of the capillary column. They also provided a means of adding make-up carrier gas.

Chromatographic columns

Analyses of fresh and degraded alkanolamine solutions were performed by using the following four columns under the conditions listed in Table I:

(1) Tenax TA packed column (9 ft. × 1/8 in. I.D.; 1 ft. = 30.48 cm); purchased from Supelco, Oakville, Canada);

(2) Supelcowax 10, a polyethylene glycol-based, fused-silica, cross-linked, bonded-phase capillary column (15 m × 0.53 mm I.D., 1.0-μm film thickness; purchased from Supelco);

(3) DB-Wax, a polyethylene glycol-based, fused-silica, cross-linked, bonded-phase capillary column (15 m × 0.53 mm I.D., 1.0-μm film thickness; purchased from Chromatographic Specialities, Brockville, Canada).

(4) HP-17, a 50% phenyl methyl-polysiloxane-based, cross-linked capillary column (10 m × 0.53 mm I.D., 2.0-μm film thickness; purchased from Hewlett-Packard, Avondale, PA, USA).

Detector sensitivity

Owing to their small diameters, capillary columns are characterized by low carrier gas flow-rates

TABLE I

OPERATING CONDITIONS FOR GC ANALYSIS

Parameter	Tenax TA	Supelcowax 10	DB-Wax	HP-17
Injection temperature (°C)	300	280	300	300
Detector (flame ionization) temperature (°C)	300	280	300	300
Oven temperature programme:				
Initial (°C)	150	125	125	125
Isothermal (min)	0.5	0.5	0.5	0.5
Rate (°C/min)	8.0	8.0	8.0	8.0
Final (°C)	300	275	230	280
Maximum (°C)*	350	280	230	280
Sample size (μl)	1.0	0.2	0.2	0.2
Nitrogen flow-rate:				
Column (ml/min)	23.0	8.0	8.0	8.0
Make-up (ml/min)	0.0	30.0	30.0	30.0

* Maximum temperature for column conditioning.

(< 10 ml/min), which increase the number of separation units per unit column length, and hence the separation efficiency, compared with packed columns. For flame ionization detectors at high sensitivity, the nitrogen, hydrogen and air flow-rate ratios are *ca.* 1:1:30. Thus, at typical air flow-rates of 300 ml/min, a nitrogen flow-rate of about 30 ml/min is required. To achieve this, it is necessary to add 25–30 ml/min of nitrogen (carrier gas) as make-up to the carrier flow leaving the capillary column.

Column conditioning

Prior to use, the capillary columns were conditioned by temperature-programmed heating at 2°C/min in the GC oven while maintaining a constant carrier gas flow-rate of *ca.* 10 ml/min, for about 16 h. For factory-preconditioned columns, only a short cure of 2–3 h was necessary. To avoid damage to the active material in the column, the highest temperature used during conditioning did not exceed the maximum temperature listed for the column (see Table I).

Amine solutions

Analyses were conducted on mixtures of alkanolamines and samples of partially degraded alkanolamine solutions obtained from the laboratory and a gas plant. The alkanolamines numbered 1–9 in Table II and those in Table III are commercially available, and were purchased from Aldrich (Milwaukee, WI, USA). Others such as hydroxyethyloxazolidone (HEOD), hydroxyethylimidazolidone (HEI), tris(hydroxyethyl)ethylenediamine (THEED) and bis(hydroxyethyl)imidazolidone (BHEI), were synthesized following previously described procedures [18]. Some of the mixtures used were prepared by adding known masses of alkanolamines to volumetric flasks and diluting to volume. When the primary objective was to demonstrate the abilities of the columns to separate the amines, the individual concentrations of the amines were not determined.

RESULTS AND DISCUSSION

The performances of the aforementioned columns can be compared in terms of retention time, peak shape, sensitivity limit, sample size, elution order, reproducibility, durability, calibration and cost.

Retention time

The retention times in Table II show that the capillary columns elute the compounds faster than the Tenax column. The differences in retention times range from 2.5 to over 10 min. Although the shorter

TABLE II

RETENTION TIMES OF ALKANOLAMINES IN VARIOUS COLUMNS USING THE OPERATING CONDITIONS IN TABLE I

Peak No.	Compound	Retention time (min)[a]			
		Tenax TA	Supelcowax 10	DB-Wax	HP-17
1	Monoethanolamine (MEA)	3.69	1.09	1.18	0.32
2	Aminomethylpropanol (AMP)	5.13	1.15	1.31	0.37
3	Diglycolamine (DGA)	8.78	3.09	3.73	0.98
4	Hydroxyethylpiperizine (HEP)	12.82	4.97	5.68	2.46
5	Methyldiethanolamine (MDEA)	10.53	5.02	5.76	1.56
6	Diisopropanolamine (DIPA)	11.27	5.24	5.97	2.00
7	Diethanolamine (DEA)	10.83	6.77	7.54	1.94
8	Bis(hydroxyethyl)piperazine (BHEP)	16.86	10.76	11.49	6.14
9	Bis(hydroxyethyl)ethylenediamine (BHEED)	16.04	11.71	12.63	5.65
10	Hydroxyethyloxazolidone (HEOD)	17.78	13.92	14.83	7.17
11	Hydroxyethylimidazolidone (HEI)	19.34	15.34	18.59	8.43
12	Tris(hydroxyethyl)ethylenediamine (THEED)	21.00	17.00	24.39	10.02
13	Bis(hydroxyethyl)imidazolidone (BHEI)	22.94	18.20	30.68	11.42

[a] Retention times may vary by up to 5%, depending on the age of the column and the concentrations of the compounds.

and less polar HP-17 column was able to elute the compounds faster than the polyethylene glycol columns, column bleeding commenced at about 200°C and was very significant above 240°C. This caused poor separation of the degradation compounds with high boiling points. The greater film thickness in the HP-17 column may have contributed to the significant bleeding observed. More generally, it appears that successful analysis of partially degraded alkanolamine solutions requires highly polar columns. It is also noted that for the non-volatile degradation compounds, the retention times in the DB-Wax column are greater than those in the Supelcowax 10 and Tenax TA columns. The reason for this is the lower temperature limit of the DB-Wax column (230°C) as opposed to 280°C and 350°C for the Supelcowax 10 and Tenax TA columns, respectively. The higher temperature limit of the Supelcowax 10 column may be due to a different bonding procedure used for the DB-Wax column. This property, plus the fact that both columns contain the same active material and cost approximately the same, make the former a more suitable choice for the analysis of partially degraded alkanolamine solutions. Further comparisons of column performances were therefore limited to the Tenax TA packed column and the Supelcowax 10 capillary column.

Peak shape

Figs. 1–6 show three sets of typical chromatograms of aqueous alkanolamine mixtures obtained using the Tenax TA and Supelcowax 10 columns. In both instances, the capillary column produced sharper peaks and better baseline separation. Lower temperature programming may eliminate the peak shouldering observed with the Tenax column, but will require longer analysis times. As will be shown later, the degree of shouldering observed does not seem to affect the reproducibility.

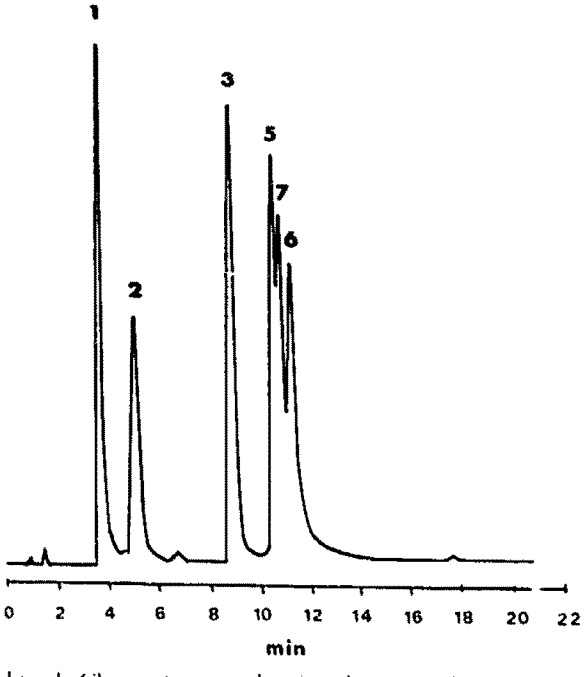

Fig. 1. Chromatogram showing the separation of a mixture of alkanolamines using the Tenax TA packed column. Peak numbers as in Table II.

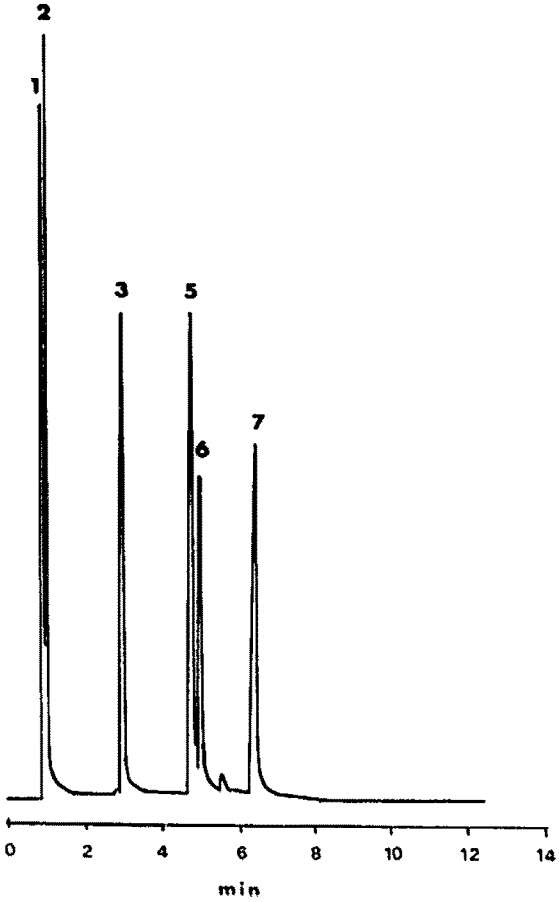

Fig. 2. Chromatogram showing the separation of a mixture of alkanolamines using the Supelcowax 10 capillary column. Peak numbers as in Table II.

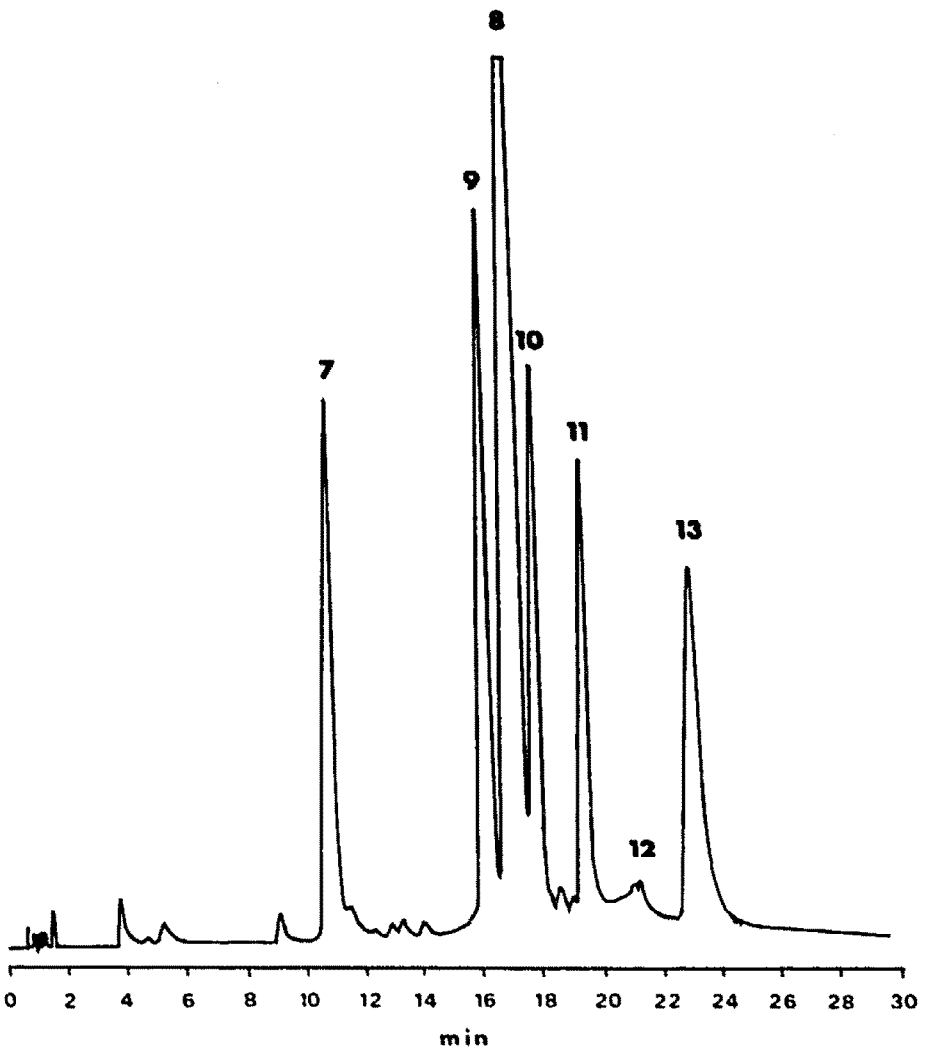

Fig. 3. Chromatogram showing the separation of a mixture of DEA and degradation compounds using the Tenax TA packed column. Peak numbers as in Table II.

Sample size

Capillary columns generally require smaller samples than packed columns. In the present instance, 0.2-μl samples were injected into the capillary columns as opposed to the 1 μl typically used for the Tenax TA column; no decrease in of sensitivity resulted. A further advantage of the Supelcowax 10 column is its ability to handle larger sample volumes typical of packed columns, while still maintaining the high separation efficiency of capillary columns (see Figs. 7 and 8). The syringe used for sample injection was fitted with a Chaney adapter that ensured reproducible sample volumes in all instances.

Sensitivity limits

To establish the sensitivity limits, and aqueous solution containing nine alkanolamines at concentrations ranging from 0.01 to 0.05 mol/l (see Table VI) was analysed with the Tenax TA and Supelcowax 10 columns. As shown in Figs. 7 and 8, the Tenax column did not produce peaks for MEA and BHEED whereas the Supelcowax 10 column only failed to separate the latter. Further, the Supelcowax 10 column separated the remaining eight compounds, unlike the Tenax TA column, which could not separate DEA from MDEA or BHEP from HEOD. As degradation compounds usually occur

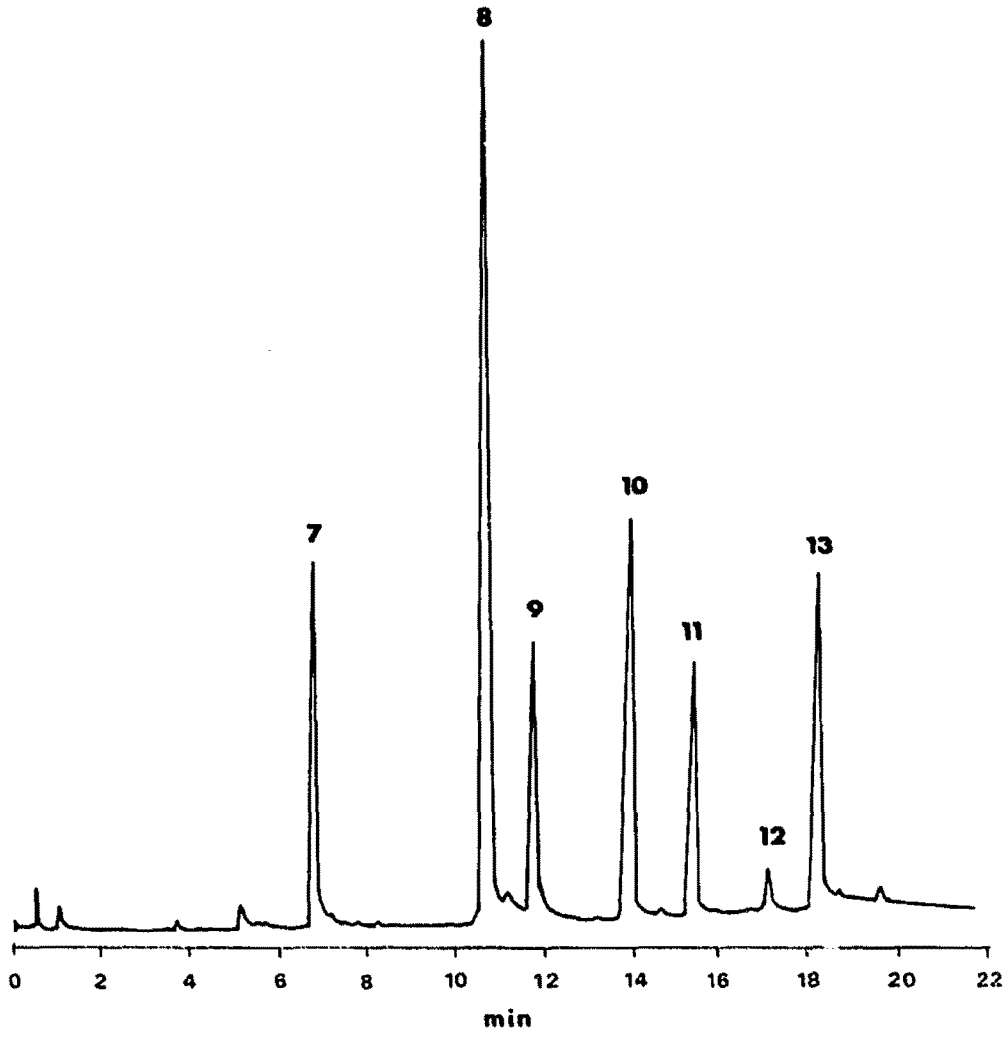

Fig. 4. Chromatogram showing the separation of a mixture of DEA and degradation compounds using the Supelcowax 10 capillary column. Peak numbers as in Table II.

in low concentrations, the higher sensitivity exhibited by the Supelcowax 10 column is a significant advantage over the Tenax TA column. The ability to separate DEA from MDEA also makes the Supelcowax 10 column better suited for detailed analyses of blended solutions of MDEA and DEA. The inability of the Tenax column to separate as efficiently as the Supelcowax 10 column may be due to a net loss of sample, which probably arises from column adsorption.

It is noteworthy that all the peaks eluted had corresponding integrated areas which indicated that these compounds can be determiend at the reported levels by using the appropriate calibration graphs. The regression equations for the present calibration graphs are not provided because they vary from one laboratory to another and depend on factors such as age of column and mode of sample injection. However, the calibration method used in this work is described later.

Elution order

The retention times listed in Table II indicate that the order of elution with the Tenax TA column differs from that with the capillary columns. To highlight this difference, the retention times of mono-

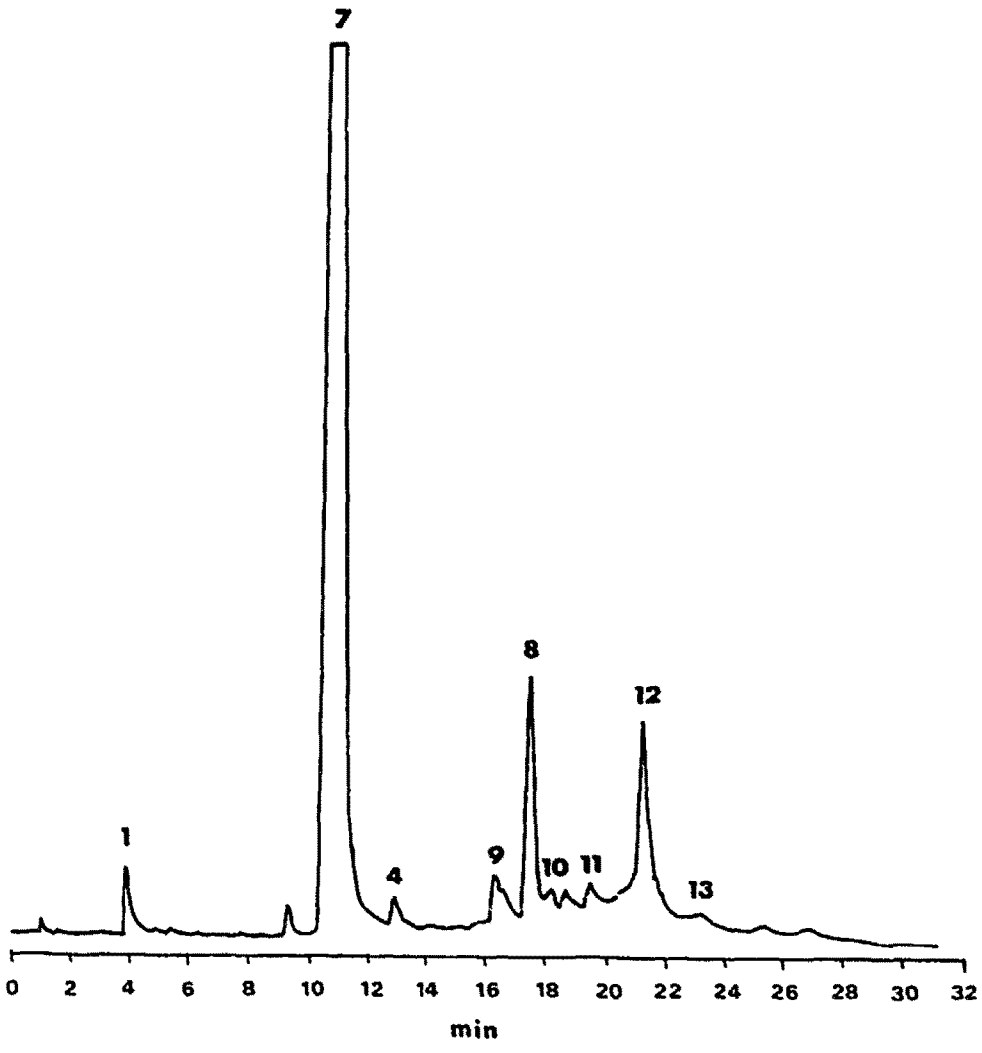

Fig. 5. Chromatogram showing the separation of an industrial DEA solution using the Tenax TA packed column. Peak numbers as in Table II.

ethanolamine, diethanolamine and their alkyl derivatives using Supelcowax 10 and Tenax columns were individually determined using the pure compounds, and are listed in Table III together with pertinent physical properties. For the Supelcowax 10 column the elution order appears to be based on boiling point, which, in turn, is influenced by the degree of hydrogen bonding of the compounds. Thus, the alkyl derivatives with higher relative molecular masses but lower boiling points are eluted before the base compounds. Conversely, the Tenax TA column shows an elution order based more on relative molecular mass than boiling point. The degree of column adsorption may also have influenced the elution order. As the capillary column contained a thin film of active material, few or no adsorption problems arose. In contrast, the mode of separation in the Tenax column is based on adsorption on the porous polymer followed by diffusion into the carrier stream. The rate of the latter determines the retention time and is influenced by molecular size, boiling point and the strength of the adsorption between the compound and the column material. The absence of significant adsorption in the Supelcowax 10 column may also be responsible for its higher sensitivity over the Tenax TA column.

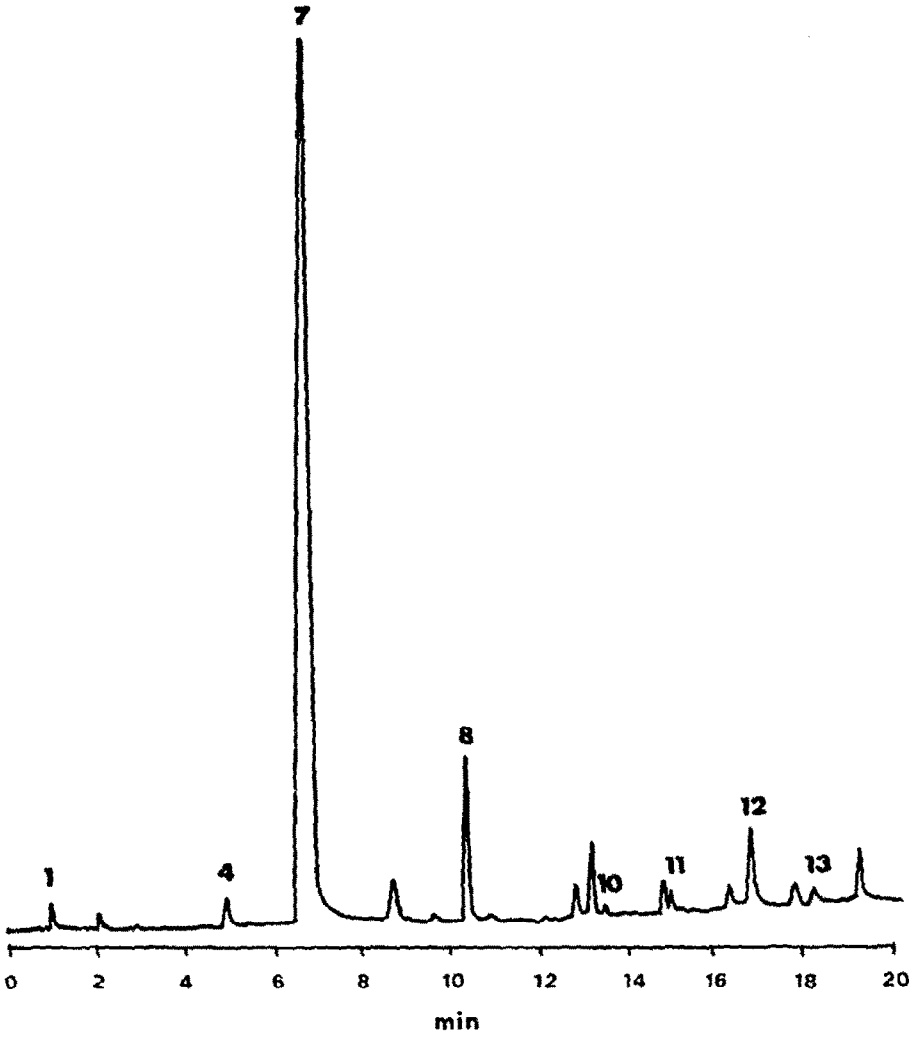

Fig. 6. Chromatogram showing the separation of an industrial DEA solution using the Supelcowax 10 capillary column. Peak numbers as in Table II.

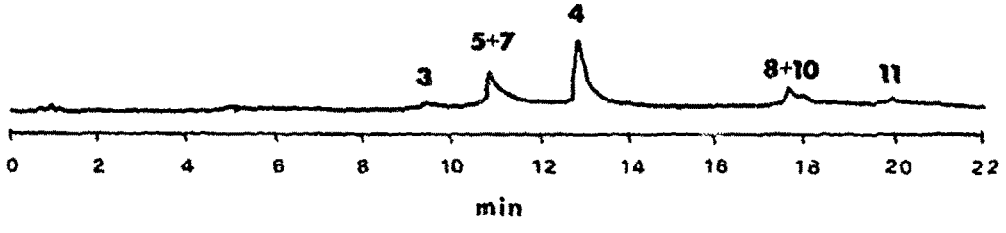

Fig. 7. Chromatogram showing the separation of 0.01–0.05 mol/l of alkanolamines using the Tenax TA column. Sample volume = 1 μl. Peak numbers as in Table II.

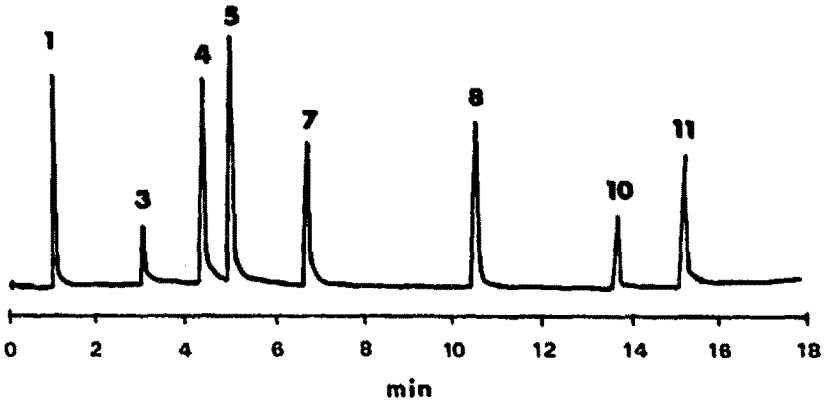

Fig. 8. Chromatogram showing the separation of 0.01–0.05 mol/l of alkanolamines using the Supelcowax 10 capillary column. Sample volume = 1 μl. Peak numbers as in Table II.

Reproducibility

In order to compare the reproducibility of analysis, three solutions were analysed using both columns. Solution 1 was arbitrarily mixed without particular attention to the concentrations of the alkanolamines. Solution 3 was a 1:4 dilution of solution 2. The standard deviation for each compound was determined from the concentration values obtained in four consecutive analyses performed on the same mixture. The only exception was solution 1, where the standard deviations were based on the integrated peak areas. Typical chromatograms for solutions 1 and 3 are shown in Figs. 3 and 4 and Figs. 7 and 8, respectively. The results in Tables IV–VI indicate that at high concentrations (Table IV) the reproducibilities of analyses with the Tenax and Supelcowax 10 columns are comparable, except for the ethylenediamines (BHEED and THEED), where the Supelcowax 10 column was superior. At lower concentrations (Tables V and VI), the degradation compounds (HEP, BHEED, BHEP, HEOD and HEI) showed better reprodubility with the Supelcowax 10 than the Tenax column. The Supelcowax 10 column is thus more reliable for the determination of low concentrations of degradation compounds.

Durability

Laboratory experience has shown that the Tenax column could be used for extended analyses over 4–6 months without any appreciable change in re-

TABLE III

ELUTION ORDER WITH SUPELCOWAX 10 AND TENAX TA COLUMNS USING THE OPERATING CONDITIONS IN TABLE I

Compound	M_r	Density (g/cm^3)	B.p. (°C)	Elution order	
				Supelcowax 10	Tenax TA
Monoethanolamine	61	1.012	70	4	1
Methylaminoethanol	75	0.935	159	2	2
Dimethylaminoethanol	89	0.887	139	1	3
Ethylaminoethanol	89	0.914	169–170	3	4
Diethanolamine	105	1.097	217/150 mmHg[a]	7	6
Methyldiethanolamine	119	1.038	246–248	5	5
Ethyldiethanolamine	133	1.014	246–252	6	7

[a] 1 mmHg = 133.322 Pa.

TABLE IV

REPRODUCIBILITY OF ANALYSIS BASED ON STANDARD DEVIATIONS (SOLUTION 1) (n = 4)

Compound	Deviation (%)[a]	
	Tenax TA	Supelcowax 10
DEA	5.19	6.25
BHEED	11.33	4.95
BHEP	1.09	2.78
HEOD	5.62	3.75
HEI	3.42	4.90
THEED	20.94	7.10
BHEI	6.83	5.10

[a] Deviation (%) = 100 (standard deviation/mean area).

tention times and separation efficiency [16–18]. Judging from the reproducibility of retention times and separation efficiency within the 2 months duration of its use, the Supelcowax 10 column appears to be as durable as the Tenax TA column. However, a more objective assessment of durability will require subjecting both columns to analyses of the same solutions over the same length of time and observing the changes in retention times and separation efficiency. It should be noted that the Supelcowax 10 column is fragile and can easily be inactivated through oxidation of the polyethylene glycol film. To prevent this occurrence, the column ends should be flame sealed when in storage or a constant flow of carrier gas must be maintained whenever the column is installed in the GC system.

TABLE V

REPRODUCIBILITY OF ANALYSIS BASED ON STANDARD DEVIATIONS (SOLUTION 2) (n = 4)

Compound	Concentration (mol/l)	Standard deviation (mol/l)	
		Tenax TA	Supelcowax 10
MEA	0.206	0.008	0.014
DGA	0.128	0.007	0.015
HEP	0.116	0.010	0.005
MDEA	0.111	0.015	0.005
DEA	0.148	0.009	0.009
BHEED	0.072	0.008	0.005
BHEP	0.057	0.003	0.002
HEOD	0.066	0.006	0.002
HEI	0.130	0.017	0.006

TABLE VI

REPRODUCIBILITY OF ANALYSIS BASED ON STANDARD DEVIATIONS (SOLUTION 3) (n = 4)

Compound	Concentration (mol/l)	Standard deviation (mol/l)	
		Tenax TA	Supelcowax 10
MEA	0.052	Not detected	0.013
DGA	0.032	0.016	0.013
HEP	0.029	0.002	0.003
MDEA	0.028	0.016[a]	0.001
DEA	0.037		0.004
BHEED	0.018	Not detected	Not detected
BHEP	0.014	0.007[b]	0.001
HEOD	0.017		0.002
HEI	0.033	0.011	0.004

[a] Value reported is for MDEA and DEA eluted as one peak.
[b] Value reported is for BHEP and HEOD eluted as one peak.

Calibration

The Supelcowax 10 column can be used for quantitative analysis just like the Tenax column. This involves the preparation of calibration graphs obtained from plots of peak area *versus* concentration for standard solutions. The calibration graphs are subsequently used to determine the concentrations corresponding to the peak areas resulting from the analysis of partially degraded alkanolamine solutions generated in the laboratory and industrially. Such graphs prepared with the Supelcowax 10 column for 0–3.2 *M* MEA, 0–5 *M* DEA and MDEA and 0–0.5 *M* degradation compounds such as HEOD, BHEP and HEI were linear.

Cost

The 15-m Supelcowax 10 capillary column is about 2.5 times more expensive than the 2.7-m Tenax TA column. The conversion kit necessary to use the capillary column in a GC system configured for packed columns is an additional cost. However, as the conversion kit makes it possible to carry out both capillary and packed column analyses, this advantage far outweighs the initial cost of the conversion kit. Further, the superior analyses offered by the capillary column should compensate for its higher cost.

The durability of the Supelcowax 10 column under extended analysis still needs to be firmly established. This may, in the long run, have a bearing on cost comparisons.

CONCLUSIONS

It has been shown that Supelcowax 10, a capillary column lined with polyethylene glycol, can be used in place of a Tenax packed column for the GC analysis of fresh and partially degraded alkanolamine solutions. The analytical conditions that permit good resolution of mixtures of amines have been established, although a lower initial temperature and/or temperature programme may suffice when analysing close-boiling amines. The capillary column provides better peak shape, maintains higher sensitivity, requires less samples and offers a faster and more efficient separation than the Tenax packed column. The higher sensitivity combined with the generally better reproducibility of analysis make the Supelcowax 10 capillary column more reliable than the Tenax column in the determination of low concentrations of degradation compounds. This work thus extends the use of capillary columns to the GC analysis of fresh and partially degraded alkanolamine solutions encountered in the clean-up of natural, refinery and other industrial gases.

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