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Separation of Polyfunctional Amines by Gas Chromatography

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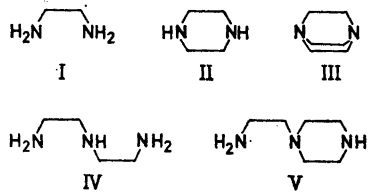
Separation by gas-liquid chromatography of triethylenediamine (III) and diethylenetriamine (IV) in the presence of ethylenediamine (I), piperazine (II), and 1-(2-aminoethyl)-piperazine (V) was accomplished by treatment of the solid support with potassium hydroxide before the application of the stationary phase. Without this alkali-treatment, no separation was obtained between triethylenediamine (III) and diethylenetriamine (IV).

The separation by gas-liquid chromatography of strongly polar substances such as polyfunctional aliphatic amines is entailed with certain difficulties. This class of compounds shows a strong tendency to adsorb on conventional solid supports.[1] As a result, severe tailing or incomplete separation is often observed in the analysis of amine mixtures by gas-liquid chromatography. When two components in a mixture differ widely in adsorbability, there exists a risk of simultaneous elution, even if the difference in boiling point is supposed to be sufficiently great. As will be shown below, the single peak thus obtained need not necessarily become skew or otherwise reveal its complex nature.



In connection with studies on the reactions of di- and polyfunctional amines carried out in this laboratory, it was necessary to analyse triethylenediamine (III) (1,4-diazabicyclo[2.2.2.]octane) in the presence of aliphatic and heterocyclic amines, such as ethylenediamine (I), piperazine (II), 1-(2-aminoethyl) piperazine (V), and diethylenetriamine (IV) (2,2′-diaminodiethylamine). Table 1 shows the molecular weights and boiling points of the substances in question.

Table 1. Components of the mixture to be separated.

Substance	B.p. °C	Molecular weight
Ethylenediamine	117	60.1
Piperazine	146	86.1
Triethylenediamine	174	112.2
Diethylenetriamine	207	103.2
Aminoethylpiperazine	222	129.2

Inspection of the boiling points suggests that a good separation between the compounds might be obtained on a nonpolar stationary phase. In the absence of diethylenetriamine (IV), sufficient separation indeed was achieved at 150°C with 20 % silicone oil as a liquid phase on Chromosorb W. However, the presence of diethylenetriamine (IV) in the mixture made the determination of triethylenediamine (III) impossible, as these two substances were eluted simultaneously. The same effect was found also with a fluorine-containing polymer support, although this type of substrate is known [2] to reduce adsorp-

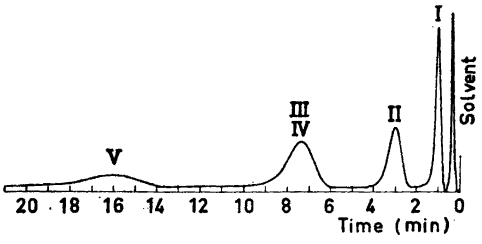


Fig. 1. Separation of the amine mixture on a fluorine-containing support. Column: 10 % silicone oil on Fluoropak 80. Temperature 150°C. Helium flow 71 ml/min.

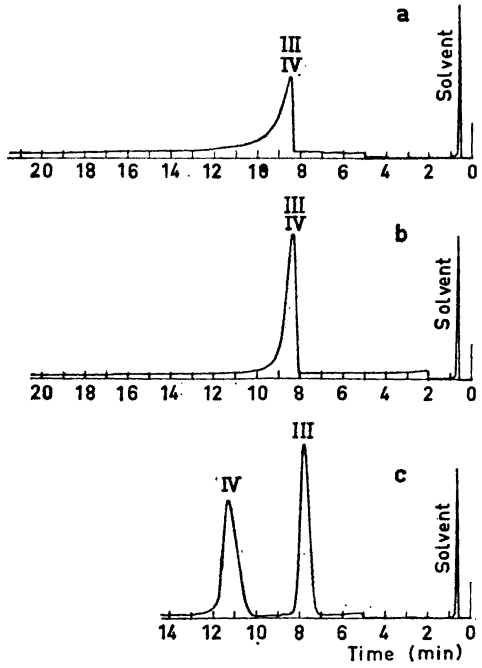


Fig. 2. Modification of the solid support. Columns: 8 % Hallcomid M-18 and 2 % silicone oil on a) Chromosorb W, b) HMDS-treated Chromosorb W, c) KOH-treated Chromosorb W. Temperature 130°C. Helium flow: a) 70, b) 71, c) 71 ml/min.

tion effects given by polar substances on conventional diatomaceous earth supports (Fig. 1).

Variation of temperature, gas flow and amount of the liquid phase did not improve the separation between the two substances. It was therefore necessary to try other techniques in order to reduce the strong adsorption.

Various methods are reported to reduce the adsorption tendency of polar substances. Sze *et al.*[3] used tetrahydroxyethylethylenediamine and tetraethylenepentamine as tail reducers in the separation of methylamines and ammonia. Treatment of the solid support with hexamethyldisilazane (HMDS) strongly reduced the adsorption of acetone.[4] The use of a support treated with alkali hydroxide was suggested by Decora and Dineen,[5] and this technique has been successfully applied to the separation of amines by Smith and Radford [1] and others.[6-8]

RESULTS AND DISCUSSION

Of the methods available, only the treatment of the solid support with potassium hydroxide improved the separation between triethylenediamine (III) and diethylenetriamine (IV). The chromatograms shown in Fig. 2 were taken with a mixture of the two amines in an ethanol solution. The same temperature, carrier gas flow and stationary phase was used. The latter was a mixture of silicone oil and Hallcomid M-18 (*cf.* below).

When this stationary phase was applied on untreated Chromosorb W, no separation was obtained between the two substances. Nor did treatment of the solid support with hexamethyldisilazane affect the separation, although the tailing was somewhat reduced. However, complete separation was obtained

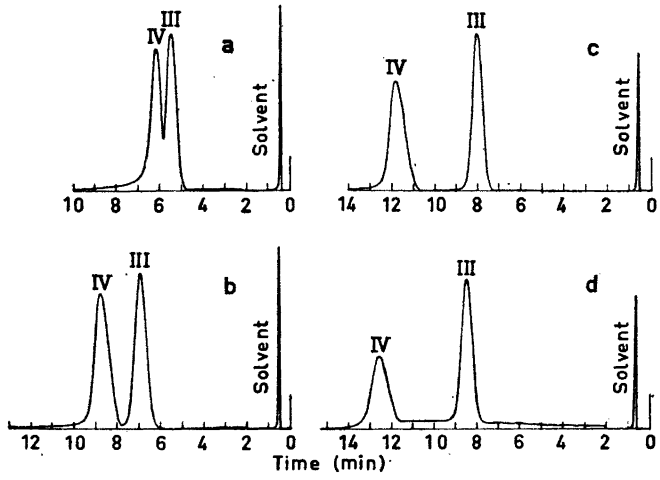


Fig. 3. Effect of the stationary phase. Columns: a) 10 % silicone oil, b) 8 % silicone oil and 2 % Hallcomid M-18, c) 2 % silicone oil and 8 % Hallcomid M-18, d) 10 % Hallcomid M-18 on HMDS- and KOH-treated Chromosorb W. Temperature 130°C. Helium flow: a) 70, b) 70, c) 69, d) 69 ml/min.

when the solid support was impregnated with 3 % potassium hydroxide before the application of the stationary phase.

The choice of stationary phase is also of great importance for the gas chromatographic separation of the two amines. As is evident from Fig. 3, the resolution obtained with silicone oil on the modified solid support is still insufficient. On the other hand, the use of Hallcomid M-18 (N,N-dimethylstearamide) gave a chromatogram with well-separated peaks, but this column material suffered from the drawback of severe tailing. As a compromise, a mixture of the two materials resulted in a stationary phase with sufficient resolution ability and moderate tailing. However, the thermal stability of this material is not satisfactory. As a result of excessive bleeding, poor baseline stability was observed at temperatures above 160°C. The limited thermal stability strongly restricts the column's utilisation for the separation of mixtures containing high-boiling components.

Highmolecular polyethylene glycol (Carbowax 20 M) was found to be a more suitable stationary phase in this respect. This material can be used to 250°C without noticeable bleeding.[9] A combination of this stationary phase with the alkali-modified and HMDS-treated solid support gave a column material with practically ideal properties. Fig. 4 shows the excellent separation between triethylenediamine and diethylenetriamine obtained at 130°C with this column packing. An isothermal run of the five amines in an ethanol solution is shown in Fig. 5. The relative retention values at 150°C are given in Table 2. Quanti-

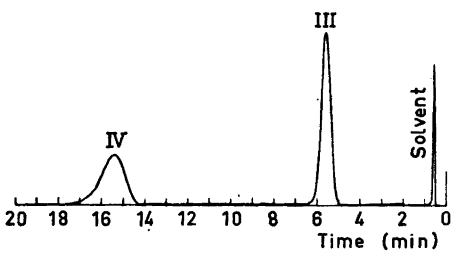


Fig. 4. Separation of triethylenediamine (III) and diethylenetriamine (IV). Column: 10 % Carbowax 20 M on HMDS- and KOH-treated Chromosorb W. Temperature 130°C. Helium flow 70 ml/min.

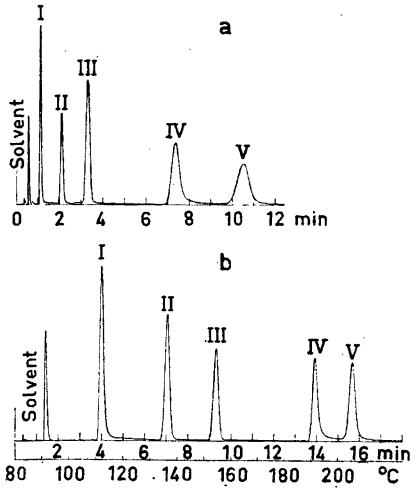


Fig. 5. Separation of ethylenediamine (I), piperazine (II), triethylenediamine (III), diethylenetriamine (IV), and aminoethylpiperazine (V). Column: 10 % Carbowax 20 M on HMDS- and KOH-treated Chromosorb W. Temperature: a) 150°C (isothermal), b) 80—200°C (linear temperature programming 8°C/min). Helium flow 70 ml/min.

Table 2. Relative retention values at 150°C.

Substance	Relative retention
Ethylenediamine	0.42
Piperazine	1.00
Triethylenediamine	1.69
Diethylenetriamine	4.01
Aminoethylpiperazine	5.78

tative analysis of the triethylenediamine content is now possible, using any conventional calibration technique. For comparison, the effect of linear temperature programming from 80°C to 200°C during the first 15 min is also shown in Fig. 5.

A column with 10 % Carbowax 20 M on HMDS-treated Chromosorb W, impregnated with 3 % potassium hydroxide has been in regular use for amine separations in this laboratory for more than one year without any complications. No special precautions to protect the packing material from atmospheric carbon dioxide and moisture have been taken. Regular rinsing of the preheater section and gas lines of the chromatograph is recommended, in order to avoid any repeater effect [10] due to carbon deposits. The column is not ideal for amine mixtures containing water, as the water is eluted only slowly with immense tailing. However, this complication does not seem to exclude its utilisation in water-containing systems.[7] Anyhow, the use of a flame ionisation detector will overcome this difficulty in analytical separations.

EXPERIMENTAL

Instruments. Except for the chromatograms given in Fig. 5, all separations were carried out with a Perkin Elmer Model F 6 Fractometer with a thermal conductivity detector. The separations in Fig. 5 were carried out with a Beckman Gas Chromatograph GC-2A, equipped with a ThermotraC temperature programmer and a thermal conductivity detector.

Materials. Amine samples of highest commercially available purity were distilled or sublimed before use. Silicone oil (Merck), Carbowax 20 M and Hallcomid M-18 (C. P. Hall Company of Illinois) were used as delivered. Untreated and HMDS-treated Chromosorb W (Johns-Manville Products) and Fluoropak 80 (Applied Science Laboratories) were used as solid supports.

Columns. The columns were made of aluminum tubing of 4 mm internal diameter and 2 m length. Treatment of the solid supports with 3 % potassium hydroxide was carried out with the method given by Smith and Radford.[1] Solid supports were sieved to 28—48 mesh before the application of the stationary phase, except in the case of Fluoropak 80, which was used as delivered. The stationary phase (10 parts) was applied in methylene chloride solution on to the solid support (90 parts). The solvent was evaporated and the dry material was evenly packed in the column. The columns were conditioned with helium for 2 h at the separation temperature before use. When temperature programming was applied, the conditioning temperature was 200°C.

Procedure. Equal amounts of the amines were dissolved in absolute ethanol and 2.0 μl of the solution was injected. Helium was used as carrier gas in all separations. The relative retention values in Table 2 refer to the position of the piperazine peak. They are measured from the air peak.

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REFERENCES

1. Smith, E. D. and Radford, R. D. *Anal. Chem.* **33** (1961) 1160.
2. Fowler, L. (Ed.) *Gas Chromatography*, Academic Press, New York 1963, p. 79.
3. Sze, Y. L., Borke, M. L. and Ottenstein, D. M. *Anal. Chem.* **35** (1963) 240.
4. Bohemen, J., Langer, S. H., Perrett, R. H. and Purnell, J. H. *J. Chem. Soc.* **1960** 2444.
5. Noebels, H. J., Wall, R. F. and Brenner, N. (Eds.) *Gas Chromatography*, Academic Press, New York 1961, p. 33.
6. Cincotta, J. J. and Feinland, R. *Anal. Chem.* **34** (1962) 774.
7. Arad, Y., Levy, M. and Vofsi, D. *J. Chromatog.* **13** (1964) 565.
8. O'Donnell, J. F. and Mann, C. K. *Anal. Chem.* **36** (1964) 2097.
9. Dal Nogare, S. and Juvet, Jr., R. S. *Gas-Liquid Chromatography*, Interscience Publishers, New York 1962, p. 121.
10. Smith, E. D. and Gosnell, A. B. *Anal. Chem.* **34** (1962) 646.

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