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Short Communication

Application of a fused-silica column to the determination of very volatile amines by gas–solid chromatography

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Abstract

This paper reports the application of a PoraPLOT fused-silica column (PoraPLOT Amines) to the determination of very volatile amines such as monomethylamine, dimethylamine, trimethylamine and monoethylamine in aqueous, methanolic and pentane solutions. The column is also able to separate amines between C_1 and C_6 by using a temperature programme. A method for the trace determination of low-boiling amines using flame ionization detection and ammonia using an electrolytic conductivity detector for capillary GC is described. Examples of the determination of the purity of amines in the amine industry are given.

1. Introduction

The determination of volatile and very volatile amines by gas chromatography was exclusively done in the past using packed or micro-packed columns. Very volatile aliphatic amines such as mono-, di- and trimethylamine and monoethylamine have very low solubility in the usual liquid phases. Therefore, adsorption chromatography with partly deactivated sorbents is mostly preferred. Because of their high polarity and the strong basicity, aliphatic amines cause support effects (tailing) and a low separation efficiency results. Especially in the trace range and in the analysis of aqueous solutions quantitative determination is difficult. Moreover, well deactivated tubing material is important.

Di Corcia *et al.* [1] used 0.5% polyethyleneimine 40M + 0.3% KOH on graphitized carbon black (GCB A; Supelco, Bellafonte, PA, USA) in a 1.8-m packed column. The peak sequence was monomethylamine (MMA), dimethylamine (DMA), trimethylamine (TMA) and monoethylamine (MEA). Although there was good peak symmetry, the resolution was not complete.

Hollis [2] applied 10% tetraethylenepentamine (TEP) and 10% polyethyleneimine on Chromosorb 102. With a 1.8-m stainless-steel column, the separation of MMA and DMA was fairly good, but chromatograms for TMA and MEA were not shown.

Sze *et al.* [3] reported separations on a 2.7-m column packed with 15% diglycerol + 5% tetraethylenepentamine on Chromosorb W. The interesting peak sequence was TMA, DMA and MMA. We have found the same elution order with polyethyleneimine on a fused-silica column

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but with very small k' values. It seems to be a complexation reaction of the aliphatic amines with an amino-containing stationary phase. The same workers could not fully separate TMA, NH_3, DMA and MMA in this sequence on a 4.5-m column packed with 5% tetrahydroxyethylethylenediamine.

Onuska [4], Dalene *et al.* [5] and Audunsson and Mathiasson [6] used columns packed with 28% Pennwalt 223 + 4% KOH on Gas-Chrom R for the determination of free amines with different detectors. Dunn *et al.* [7] compared the qualitative separation and the quantitative results in the trace range on ten different packed columns. They could not separate DMA from TMA and there was severe tailing on these phases.

With respect to the quantitative results, a number of papers have reported relatively successful determinations of very volatile amines on Chromosorb 102 or 103 [8–11], deactivated with either KOH or trimethylchlorosilane. The determination of DMA in air with Chromosorb 103 was carried out by Böhm *et al.* [12] under constant deactivation with some ammonia in the carrier gas.

A very inert support material for the separation of highly polar compounds is Carbopack B (Supelco) [13–16]. Carbopack B deactivated with 4% Carbowax 20M + 0.8% KOH in a 2-m packed column (glass or nickel) gave a nearly complete separation of MMA, DMA, MEA and TMA, but MEA eluted before TMA.

The work reported here was stimulated by the need to analyse, *e.g.*, pure aqueous amine solutions in industry and trace amines in medicine, the pharmaceutical industry, biology, food research and in the environment using modern fused-silica columns with high separation power and sensitivity and short analysis times.

2. Experimental

Porous layer open-tubular (PLOT) columns were introduced in the early days of capillary GC [17,18]. New coating techniques have made it possible also to coat a porous polymer on the inner wall of a fused-silica capillary column. This results in a highly efficient column that can be used for specific separations, especially those in which the liquid stationary phases do not provide sufficient retention such as with very volatile amines [19,20].

We have deactivated these PoraPLOT Q columns (Chrompack, Middelburg, Netherlands) by a proprietary technique in order to obtain gas–solid columns with higher retention and resolution for the very volatile amines above ambient separation temperatures and with satisfactory tailing-free peaks (PoraPLOT Amines, Chrompack). This is of special importance for the extremely high basicity and polarity of these compounds.

Table 1 gives the dissociation constants and dipole moments of different low-boiling amines in comparison with ammonia and water.

The amines MMA, DMA, TMA and MEA were obtained from Leuna Werke (Leuna, Germany).

All GC measurements were conducted on a CP 9001 gas chromatograph (Chrompack). Split injection was used and flame ionization detection (FID) and, in one case, electrolytic conductivity detection (ELCD) (with an instrument from Fraunhofer-Institut für Lebensmitteltechnologie und Verpackung, Munich, Germany) were applied.

The concentration of the normally used aque-

Table 1
Dissociation constants and dipole moments of very volatile amines compared with ammonia and water

Compound	Temperature (°C)	Dissociation constant in H_2O		Dipole moment (D)
		pK_a	K_a	
CH_3NH_2	25	10.657	$2.70 \cdot 10^{-11}$	1.31
$(CH_3)_2NH$	25	10.732	$1.85 \cdot 10^{-11}$	1.03
$(CH_3)_3N$	25	9.81	$1.55 \cdot 10^{-10}$	0.61
$C_2H_5NH_2$	20	10.81	$1.56 \cdot 10^{-11}$	1.22
$(C_2H_5)_2NH$	40	10.489	$3.24 \cdot 10^{-11}$	0.92
$C_3H_7NH_2$	20	10.708	$1.96 \cdot 10^{-11}$	1.17
NH_3	20	9.23	$5.89 \cdot 10^{-10}$	1.47
H_2O	20	14.167	$6.81 \cdot 10^{-15}$	1.85

ous test solution was in *ca.* 0.5 μg/μl, the absolute amount of sampling at a splitting ratio 1:100 being *ca.* 5 ng per amine. In all other instances the total amount is given in the figure captions.

The optimum working conditions for a PoraPLOT Amines column of dimensions 25 m × 0.32 mm I.D. and with a layer thickness $d_f = 10$ μm were as follows: sample size, 0.5–1 μl of solution; splitting ratio, 1:50 to 1:100; injector temperature, 200°C; detector temperature, 250°C; oven temperature, 130°C; GC sensitivity, 1×10^{-11} AUFS; carrier gas, hydrogen (45 kPa); and linear gas velocity, $u_{opt} = 27$ cm/s.

After each chromatographic run it is recommended to heat the column rapidly to 220°C using a temperature programme, *viz.*, 130°C (held for 10–15 min), increased at 20°C/min to 220°C (held for 15 min), for reactivation of the adsorbent. The maximum allowable operating temperature is 250°C.

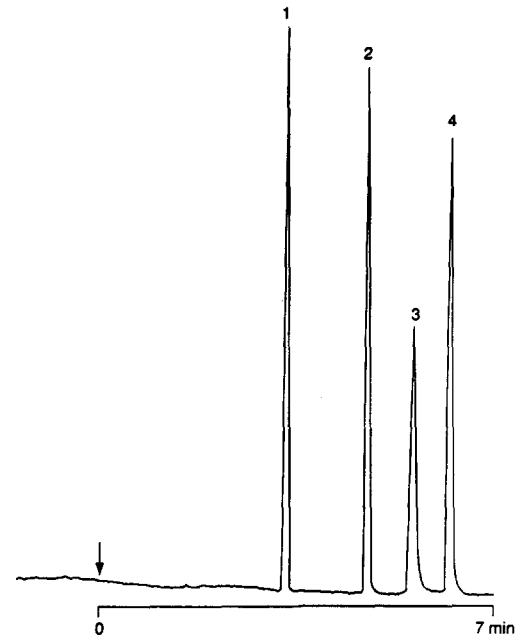

Fig. 1. Separation of very volatile amines. Column, 25 m × 0.32 mm I.D. PoraPLOT Amines; oven temperature, 130°C; detection, FID. Peaks: 1 = monomethylamine; 2 = dimethylamine; 3 = trimethylamine; 4 = monoethylamine in aqueous solution.

3. Results and discussion

Fig. 1 shows a typical chromatogram with high resolution of the four very volatile amines MMA, DMA, TMA and MEA in aqueous solution. The peaks have a very good shape except for TMA, which is the most basic amine, comparable to ammonia (see Table 1).

Evaluation of the capacity factors between 369.0 and 393.7 K shows a typical behaviour of an adsorption column. This is illustrated in Fig. 2 by a plot of k' *versus* $1/T$.

Repetitive measurements of the separation factors α for MMA–DMA and DMA–TMA demonstrated the reproducibility of the selectivity for the different columns (Table 2).

Generally, a newly developed column has to be checked for quantitative trace analysis with respect to the linear range. Especially for the compounds considered here it is necessary to verify this down to detection limit. The results are illustrated in Fig. 3, which shows a linear range between 0.5 and 20 ng of amines.

Another qualitative observation was the fact that the prolonged use of calibration mixtures of aqueous amine solutions generates double peaks on the chromatogram. This seems to be caused by chemical reactions (decomposition) due to sunlight and ambient temperature. It is therefore possible to conclude that only freshly prepared

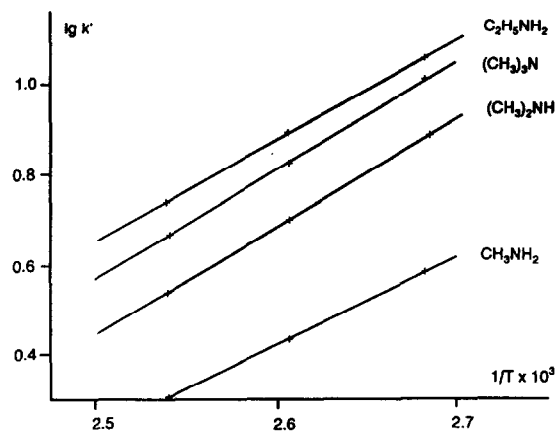

Fig. 2. Plots of capacity factors k' *versus* $1/T$ for very volatile amines.

Table 2
Column-to-column reproducibility with respect to selectivity

Column No.	α	
	MMA–DMA	DMA–TMA
462 117	1.76	1.20
462 257	1.76	1.22
462 364	1.72	1.20
462 452	1.76	1.21
462 521	1.80	1.25
462 637	1.75	1.20
462 721	1.75	1.20
Mean	1.76	1.21
Standard deviation	0.02	0.02

mixtures should be used or that they should be stored dark and cool.

Estel [21] used capillary column GC–ELCD to determine traces of ammonia in aqueous amine mixtures using a PoraPLOT Amines column. Fig. 4 shows the excellent separation and peak symmetry for ammonia and the amines in the nanogram range and high selectivity of ELCD.

Ewender and Piringer [22,23] analysed a pentane extract of C_1–C_6 amines using a PoraPLOT Amines column. The amine concentration was 80 ppm for each peak in pentane. The temperature-programmed separation is shown in Fig. 5. The use of methanol as a solvent for very volatile amines gave results comparable to those obtained with aqueous solution, but a methanol peak failed to appear.

For checking and controlling the production process in the amine industry, we used PoraPLOT Amines columns at higher linear gas velocities. It is possible to analyse pure aqueous

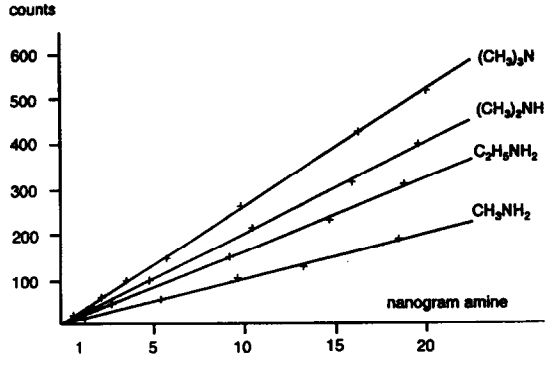

Fig. 3. Linearity of detection for very volatile amines.

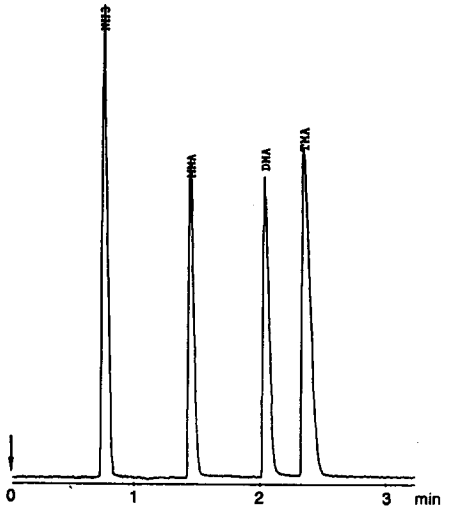

Fig. 4. Separation of ammonia, monomethylamine (MMA), dimethylamine (DMA) and trimethylamine (TMA) in aqueous solution. Column and oven temperature as in Fig. 1. Electrolytic conductivity detection (ELCD) according to Estel [21].

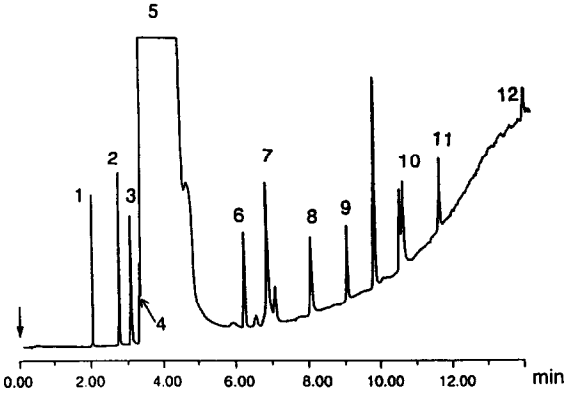

Fig. 5. Separation of C_1–C_6 amines in a pentane extract according to Ewender and Piringer [22,23]. Column and detector as in Fig. 1. Oven temperature programme, 140°C (held for 2 min), increased at 10°C/min to 250°C (held for 3 min); carrier gas, hydrogen (95 kPa). Peaks: 1 = monomethylamine; 2 = dimethylamine; 3 = trimethylamine; 4 = monoethylamine; 5 = pentane, 6 = 1-propylamine; 7 = diethylamine and *tert.*-butylamine; 8 = 2-butylamine; 9 = 1-butylamine; 10 = 2- and 3-pentylamine; 11 = *n*-pentylamine; 12 = 1-hexylamine. Concentration: 80 ppm per amine.

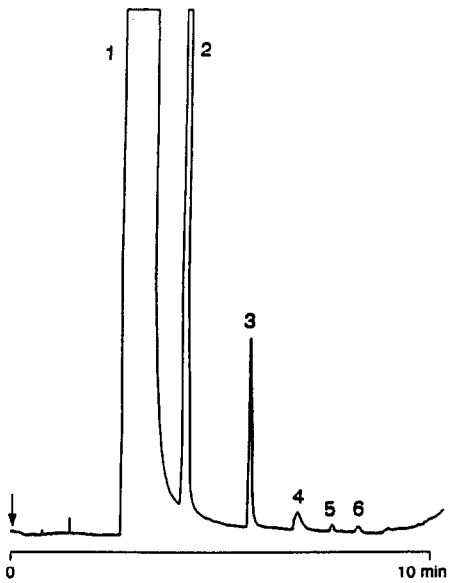

Fig. 6. Separation of impurities in technical-grade monomethylamine in aqueous solution. Column and detector as in Fig. 1. Oven temperature programme, 110°C (held for 8 min), increased at 15°C/min to 200°C (held for 10 min); carrier gas, hydrogen (100 kPa); $u = 56$ cm/s. Peaks: 1 = MMA; 2 = unknown; 3 = DMA; 4 = TMA; 5 = MEA; 6 = unknown.

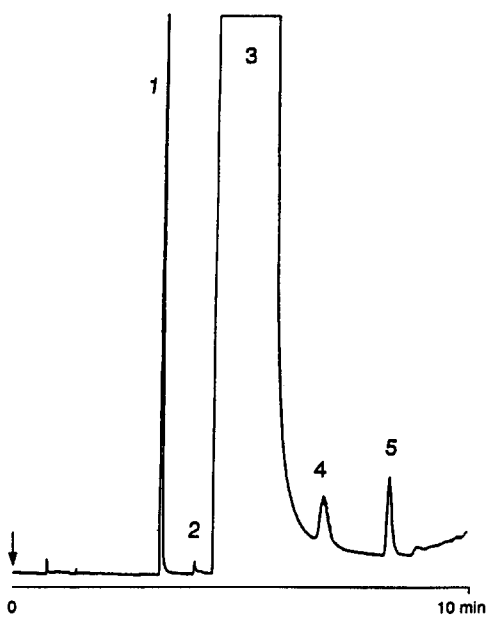

Fig. 7. Separation of impurities in technical-grade dimethylamine in aqueous solution. Conditions as in Fig. 6. Peaks: 1 = MMA; 2 = unknown; 3 = DMA; 4 = TMA; 5 = MEA.

solutions such as MMA (Fig. 6) and DMA (Fig. 7) within 10 min at $u = 56$ cm/s and a hydrogen inlet pressure of 100 kPa. The two chromatograms demonstrate the possible complete separation of the relevant trace amines. Such PoraPLOT Amines columns operated round the clock for 6 months, before the separation power decreased owing to sample impurities.

If it is necessary to determine very volatile amines by using wide-bore columns (0.53 I.D., length 25 or 50 m) with a layer thickness of $d_f = 20$ μm, such columns are also available. Wide-bore PoraPLOT Amines columns have a similarly good separation efficiency owing to the greater layer thickness.

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