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GAS CHROMATOGRAPHY OF SOME POLYAMINES ON THREE POROUS POLYMER COLUMNS*

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SUMMARY

The gas–solid chromatographic properties of some polyamines employing porous polymer bead packings are described. A review of the literature pertaining to the gas chromatography of amines in general is included and the approaches taken by other workers to problems encountered in the separation of amines are briefly discussed.

INTRODUCTION

For some time we have been interested in the gas chromatographic (GC) separation of amines[1–3]. This work has involved the quantitative and qualitative analyses of amine mixtures as well as determination of the purity of synthesized products. Recently[3] it became necessary to analyse an amine mixture containing trace amounts of water and substantial quantities of methyl cellosolve.

Gas–solid chromatography (GSC) employing porous polymer beads has been shown to be ideally suited to the separation of water from volatile organic compounds[4–6]. In addition, a polymer packing, Chromosorb 103 (Johns-Manville, Denver, Colo., U.S.A.), has been developed specifically for the GSC separation of amines. Favourable reports on its capabilities have been published[7–9], and as a result experimentation with polymer packings[3] was initiated.

The GSC behaviour of diamines on polymer column packings has been described previously[5,7–10] but to our knowledge such packings have not hitherto been used for the separation of higher polyamines as described herein.

This paper describes the separation of polyamine mixtures by GSC using three polymer bead columns and compares the results obtained with those found by other workers using different column packings. In addition, the literature pertinent to the GC separation of amines has been summarized.

EXPERIMENTAL

An F & M (Palo Alto, Calif., U.S.A.) Model 5750 research gas chromatograph equipped with a thermal conductivity detector (TC – bridge current 150 mA) was used for all of the chromatographic separations. The carrier gas (He) flow-rate was set

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at 30 ml/min, and injection port and detector temperatures were maintained at 230° and 270°, respectively. Three stainless-steel (1/8 in. O.D.) columns were prepared, *viz.* (a) Porapak Q, 80–100 mesh, 12 in.; (b) Porapak Q, 80–100 mesh, impregnated with 0.5% KOH, 12 in.; (c) Chromosorb 103, 80–100 mesh, 18 in. Temperature programming (60°/min) from 180–245° was used with all columns (except as noted in Table I).

TABLE I

CONDITIONS EMPLOYED FOR THE GSC SEPARATION OF POLYAMINE MIXTURES

Columns a, b, and c, see text.

Mixture No.	*Sample size (μl)**			*Upper temperature hold (min)*		
	a	*b*	*c*	*a*	*b*	*c*
1**	0.75	0.75	0.75	4	3	3
2	0.8	1.0	0.6	6	6	3
3	0.5	0.8	0.4	8	8	6
4	0.8	1.0	0.5	8	8	6

* Sample size was adjusted to yield the most satisfactory separation for each combination of polyamine mixture and column.

** Program limits for mixture No. 1: column a, 150–245°; column b, 170–245°; column c, 140–240°.

Four polyfunctional amine mixtures were examined: (No. 1) water, methyl cellosolve, diethylenetriamine and 1-(2-aminoethyl)piperazine; (No. 2) the heterocyclic amines piperazine, 1-(2-aminoethyl)piperazine, and triethylenediamine(1,4-diazabicyclo[2:2.2]octane); (No. 3) the aliphatic amines ethylenediamine, diethylenetriamine, triethylenetetramine, and tetraethylenepentamine; (No. 4) a combination of Nos. (2) and (3). The conditions shown in Table I are those found most satisfactory for the separation of these various polyamine mixtures.

DISCUSSION AND RESULTS

Literature review

Diatomaceous earth has long been popular as a solid support for GC but unfortunately causes various problems whenever amines are involved. The GC difficulties encountered with amines have generally been ascribed to the fact that they can act both as hydrogen-bond acceptors or donors[11]. Consequently, they may cause severe tailing[12], failure to elute[1,13], partial adsorption and subsequent "ghost" peaks[14], or differing response factors as columns age[15].

Very soon after the introduction of GC[16,17], it was found that washing[18] diatomaceous earth supports with 5% methanolic alkali (NaOH) decreased, but did not completely remove the tailing problem. In some cases[13] it has been found that even with support washing, amines still fail to elute. Soaking the support for extended periods in methanolic alkali has been reported[19] and considered to provide an improvement over simple washing. Further decreases in amine tailing have been

TABLE II

REFERENCES TO IMPREGNATION OF DIATOMACEOUS EARTH SUPPORTS WITH ALKALIS

*Percent alkali**									
1	*1.6*	*2.0*	*2.5*	*3.0*	*5*	*6*	*10*	*15*	*20*
13	13	22	13	36	1	39	13	14	13
			23		10		15		32
					11		19		
					13		40		
					41				

* NaOH or KOH.

achieved by actually impregnating the support with varying amounts of alkali (NaOH or KOH), prior to application of the stationary phase. Table II shows the different percentages of alkali used and the corresponding references.

Many of the references shown in Table II report nearly ideal peak shape for a variety of compounds, including aliphatic primary amines ranging from C_1 to C_{18}, as well as secondary, tertiary and heterocyclic polyamines. Although Table II lists a wide range of alkali percentages, Smith and Radford[13] found that the concentration of alkali was not important as long as the stoichiometric amount necessary for neutralization of the "acid sites" of the support was exceeded. The same authors[13] reported similar results after impregnation with the less basic sodium carbonate. Substitution of trisodium phosphate for potassium hydroxide has been found to give sharper peak shapes for some aliphatic amines[20]. Except for primary aliphatic amines long capillary columns[21] appear to be better than alkali impregnated packed columns for the separation of amines which are isomers by virtue of aliphatic chain branching.

Organic bases have been successfully substituted for the alkali hydroxides in the impregnation of diatomaceous earth supports. Indeed, reagents such as polyethyleneimine have been found to produce results superior to potassium hydroxide in some instances[11]. Tetrahydroxyethylethylenediamine[22,23], tetraethylenepentamine[22,23] and triethanolamine[9] have also been used as amine tail reducers. O'Donnell and Mann[23], however, found these organic reagents less effective in their work than a combination of sodium hydroxide and Dowfax 9N9.

The use of sodium metanilate (3-aminobenzene-1-sulphonate), as an impregnating agent, has recently been reported[24] for the separation of secondary aliphatic amines and pyridine bases. Continuous addition of a reagent to the carrier gas, for the purpose of neutralizing the active sites of the solid support, has been used in the GC separation of a variety of polar compounds. To this end water has been employed in the chromatography of glycols[25], alcohols[25,26], organic acids[26] and amines[26], formic acid for fatty acids[27,28] and barbiturates[29] and *n*-hexylamine for amines[30]. High stationary phase loading (up to 40%) employing organic amines, especially diethanolamine, has been used with some success in the separation of ammonia, mono-, di- and trimethylamine[31].

To avoid the necessity of impregnating the solid support, many workers

used more inert support materials. One of the earliest efforts in this direction employed sodium chloride[32]. Soon after the introduction of polymerized tetrafluoroethylene (PTFE), the material was recognized to be relatively inert[33] and as such to possess the potential of a possible solution to the problems encountered during the GC of amines. Several workers[1, 33–35] have reported successful results with this polymer, but apparently it also is not universally satisfactory. Situations such as stereoisomers[1] and certain pairs of amines[36] failing to separate, tailing[23] worse than with an alkali-treated diatomaceous earth, or irreversible adsorption[34] of minor components have occurred during its use.

After their introduction, porous polymer beads were also quickly recognized as potential packings for the GC separation of polar compounds[4,5] (water, alcohol, etc.) and are still used extensively for this purpose[8]. The early preparations failed, however, to yield suitable peaks with amines[4,5,10,37], exhibiting the familiar tailing characteristic. It has been observed that modification of the polymer beads with organic bases such as tetraethylenepentamine[4,5,37] and polyethyleneimine[4,5,10,37] can overcome this difficulty. Some of the amine tailing noted during the use of these packings has been attributed to the presence of transition metal ions in the porous beads[37]. More recently[38], the unreacted vinyl groups in some polymers have been blamed for this behaviour and have been removed by reaction with hydrogen fluoride.

We observed the retention of some amines when copper was used as the column casing. This observation was verified by chromatographing the same amines on columns which were identical except for the casing material. With stainless-steel or aluminium columns the amines eluted but failed to do so when copper tubing was used. "Ghost" peaks[14] and changing response factors[15] have been observed when copper columns were employed but these aberrations were not ascribed to the copper tubing. In other instances[19,23] no difficulties were encountered which could be attributed to the copper tubing used.

The silicone oils, Apiezons, and Carbowaxes are the most popular stationary phases for the separation of amines. As has been pointed out[36], however, the selection of the stationary phase is as important as the selection or impregnation of the solid support if the best possible results are to be obtained.

Gas chromatography

GC data for most of the amines examined here have been reported previously. These reports range from one of the compounds in relation to other materials, to the separation of five members of the group. This earlier work, however, for the most part involved diatomaceous earth supports except as indicated in Table III. Table III also lists the chemical and chromatographic (Fig. 2) characteristics of the amines involved. Fig. 1 illustrates the separation achieved during analysis of the amine mixture No. 1, containing water and methyl cellosolve. The chromatographic traces a, b and c represent the results obtained with each of the three porous polymer columns described in Experimental. Impregnation of Porapak Q with 0.5% potassium hydroxide (column b) improved the amine peak shape but not as much as the use of Chromosorb 103 (column c). Attempts to increase the amount of alkali to the concentration levels reported by other workers[9,37] (up to 10%) were unsuccessful. When the potassium hydroxide impregnation reached 1% or above,

TABLE III

GC AND CHEMICAL CHARACTERISTICS OF THE COMPONENTS OF POLYAMINE MIXTURE NO. 4

Component	*Reference**	*Mol. wt.*	*B.p.* (°C)	*Retention time (min)*		
				a	*b*	*c*
Ethylenediamine	5***,7***,8***, 14,39,36,34**	60.1	117	0.4	0.4	0.4
Piperazine	36	86.1	146	1.2	1.2	1.1
Triethylenediamine	10,36***	112.2	174	2.2	2.0	1.8
Diethylenetriamine	3***,39,36,34**	103.2	207	2.2	2.0	1.9
1-(2-Aminoethyl)piperazine	36	129.2	222	3.6	3.2	2.6
Triethylenetetramine	39,34**	146.2	266	—§§	7.2§	5.3
Tetraethylenepentamine	39,34**	189.3	340	—§§	—§§	—§§

* Diatomaceous earth support except where specified.
** PTFE support.
*** Polymer bead support.
§ Badly smeared.
§§ — = Failed to elute.

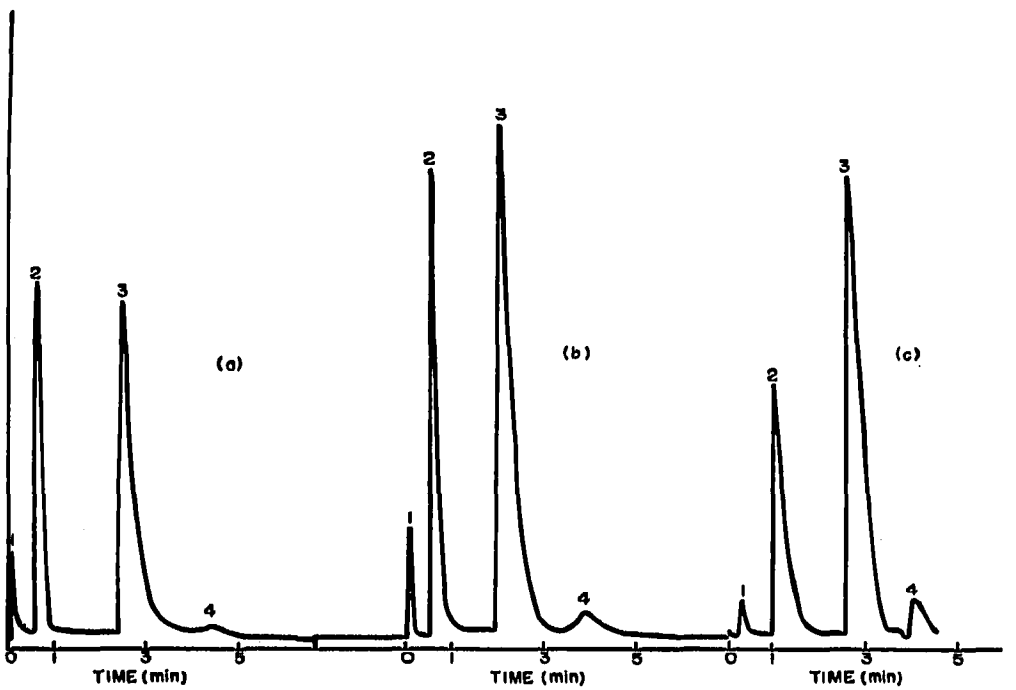

Fig. 1. Chromatograms of mixture No. 1 on the three porous polymer columns a, b, and c (*cf.* text). 1= Water; 2= methyl cellosolve; 3= diethylenetriamine; 4= 1-(2-aminoethyl)piperazine.

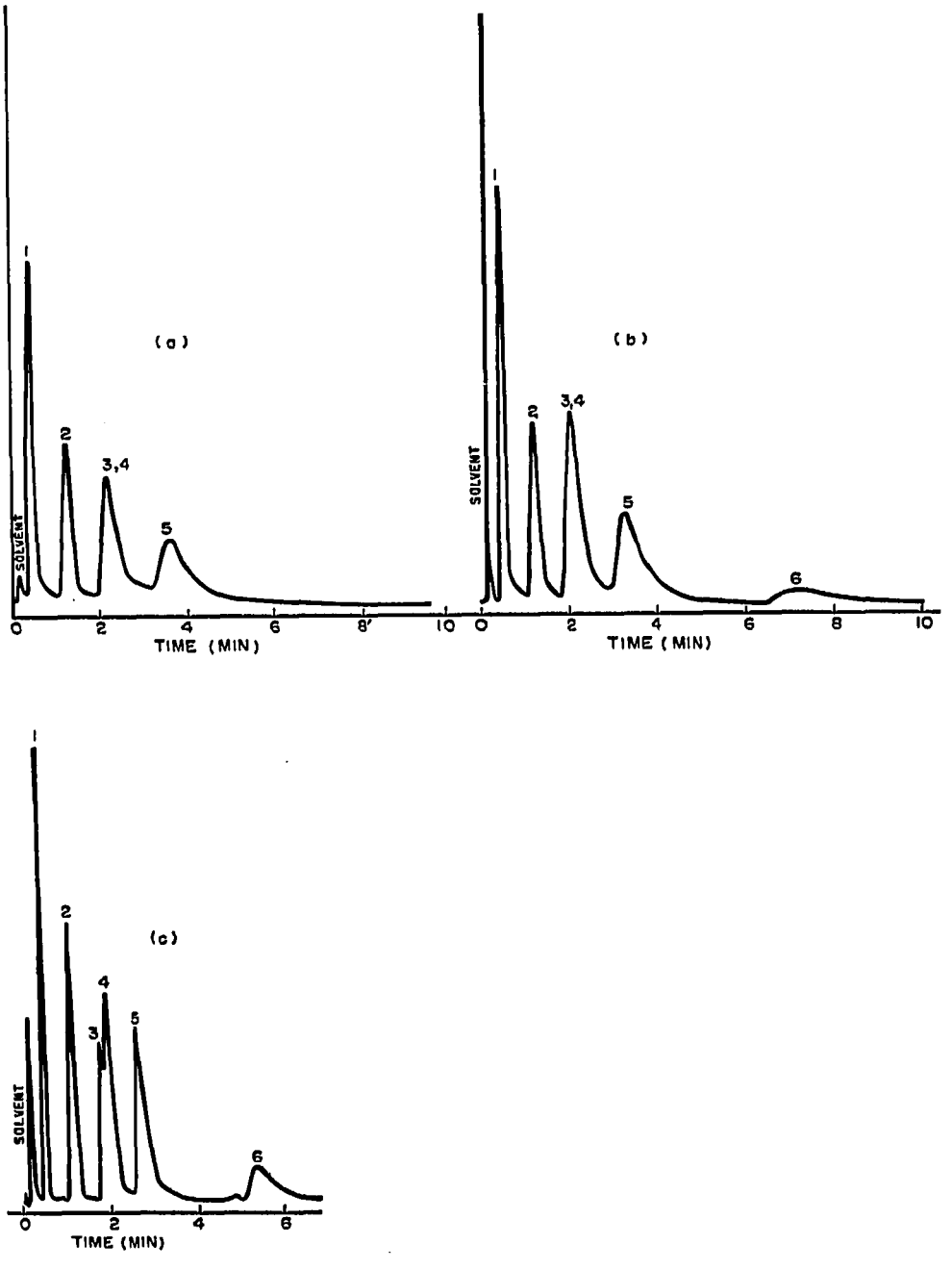

Fig. 2. Chromatograms of polyamine mixture No. 4 on the three porous polymer columns a, b, and c. 1= Ethylenediamine; 2= piperazine; 3= triethylenediamine; 4= diethylenetriamine; 5= 1-(2-aminoethyl)piperazine; 6= triethylenetetramine.

the water and methyl cellosolve either failed to separate or were so badly tailed as to make trace analysis difficult or impossible. Adding polyethyleneimine[4,5,10,37] (15%) to Porapak Q did not improve the separation or decrease the tailing sufficiently to warrant using it in our work.

A comparison of the three columns a, b, and c, with regard to their relative capabilities for the separation of the polyfunctional amines in mixture No. 4 can be made from Fig. 2. Mixtures No. 2 and No. 3 are both represented in mixture No. 4 and the separation afforded of their respective components can also be seen in Fig. 2. The chromatographic traces show a steady decrease in the amount of amine tailing from column a to b to c, and as a result a corresponding improvement in peak resolution coupled with shorter retention times (Table III). Columns a and b did not separate the two compounds diethylenetriamine and triethylenediamine, while column c indicated two peaks, but without complete resolution. Difficulty in separating these compounds has been reported earlier, although good separation and peak shape was finally realized using an alkali-treated diatomaceous earth support[36]. It should be noted, however, that the Chromosorb 103 column provided separation of all the other amines while reducing the overall analysis time to one third of that required previously[36].

Triethylenetetramine failed to elute from column a, was badly smeared on column b, but with column c, a satisfactory peak is obtained even though some tailing is evident. Tetraethylenepentamine is not shown as a peak in Fig. 2 and it should be noted that this material failed to elute from all three columns. Difficulty in eluting tetraethylenepentamine from these columns might be expected since other workers[4,5,37] have used this compound as a stationary phase on polymer bead packings. It was therefore concluded that when higher homologues of ethylenediamine are involved it may be necessary to resort to the use of alkali-treated diatomaceous earth supports[39] or Teflon[34]. For the separation of low-molecular-weight polyamines as described herein, or diamines and primary amines up to C_5 (refs. 7 and 8), however, the porous polymer packings should be considered, especially those manufactured specifically for use in the GSC of amines. Columns are easily prepared with these packings since pre-treatment of the beads or use of stationary phases is unnecessary. These packings can be conditioned more rapidly than those with stationary phases, are stable and consequently show very little "bleeding" during temperature programming. They were also found to give analytical results with excellent reproducibility during day-to-day operation. Columns packed with porous polymer beads may be shorter than those normally required for amine chromatography and care must be taken to employ the optimum column length for a specific amine separation. Long retention times, peak broadening, or failure to elute do not necessarily indicate that the packing is unsuitable, but may be due to an excessively long column.

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