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GAS CHROMATOGRAPHIC SEPARATION OF ALIPHATIC DIAMINES

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SUMMARY

The separation of aliphatic diamines by gas-liquid chromatography using a polar and a non-polar stationary phase is described and the results are compared with those obtained using aromatic polymer beads treated with polyethylene imine. For a homologous series of diamines, Apiezon L on alkaline-washed Celite is found to be the most satisfactory material, while for diamines with similar boiling points, the polar phase Carbowax 20M is most efficient.

The different behaviour of the column materials is discussed in terms of hydrogen-bonding and other intermolecular forces between the amine and the liquid phase.

INTRODUCTION

The determination of aliphatic polyfunctional amines by gas chromatography generally involves the use of gas-liquid columns. The support is usually a diatomaceous earth, pretreated with alkali¹⁻⁴ or with a silane^{3,4}, to reduce active sites which cause tailing. Other solid supports used are fluorinated polymers, such as Teflon^{4,5}, but use of these does not eliminate tailing. Liquid phases used include, in increasing order of polarity, Apiezon L^{1,6,7} and M⁸, silicone oils^{1,4,6,8,9}, N,N-dimethylstearamide⁴ and Carbowax 20M^{1,3,4}.

This paper describes the use of aromatic polymers to separate mixtures of diamines and the results are discussed and compared with those obtained with a non-polar and a polar liquid phase.

EXPERIMENTAL

Operating conditions of the gas chromatograph

These have been described previously^{10,11}.

Materials

The packing materials used were PAR-I, 80-120 mesh (Hewlett-Packard),

Celite, 100–120 mesh (W. G. Pye and Co. Ltd.), polyethylene imine (supplied by Kodak Ltd. as Montrek 18), Carbowax 20M (Union Carbide Ltd.), and Apiezon L (Apiezon Products Ltd.).

The amines used were all commercially available.

Column preparation

The preparation of the packing materials has been described in detail^{10,11}. The following were used:

- (1) PAR-I + PEI 10% w/w (a); PAR-I + PEI 20% w/w (b);
- (2) Celite (5% w/w KOH) + Apiezon L 20% w/w;
- (3) Celite (5% w/w KOH) + Carbowax 20M 20% w/w.

RESULTS AND DISCUSSION

The separation of diamines by gas chromatography on aromatic polymer beads is severely affected by peak tailing. However, as with monofunctional amines^{10,12}, treatment of the polymer with 5% PEI improves the symmetry of the peaks considerably, and the peaks are further improved using a higher concentration of PEI and temperatures above 150°. The corresponding elution of diamines using gas-liquid columns on Celite pre-treated with potassium hydroxide is not hindered by peak-tailing, particularly at temperatures above 90°.

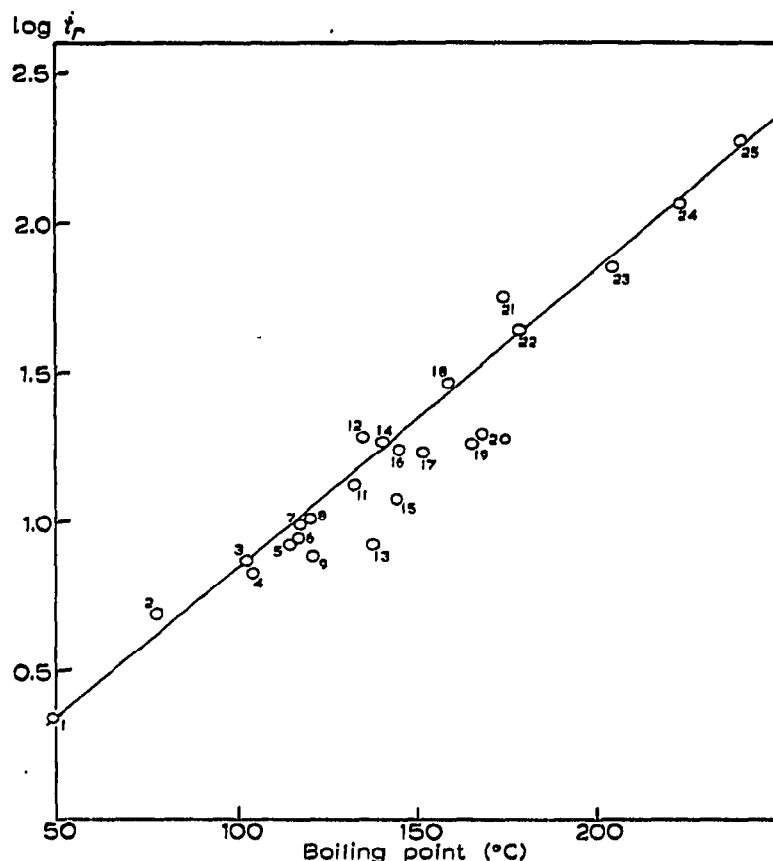


Fig. 1. Plot of $\log t_r$ vs. boiling point for aliphatic mono- and diamines. Column 1b: PAR-1 + PEI 20% w/w at 160°. For numbering of the amines, see Table I.

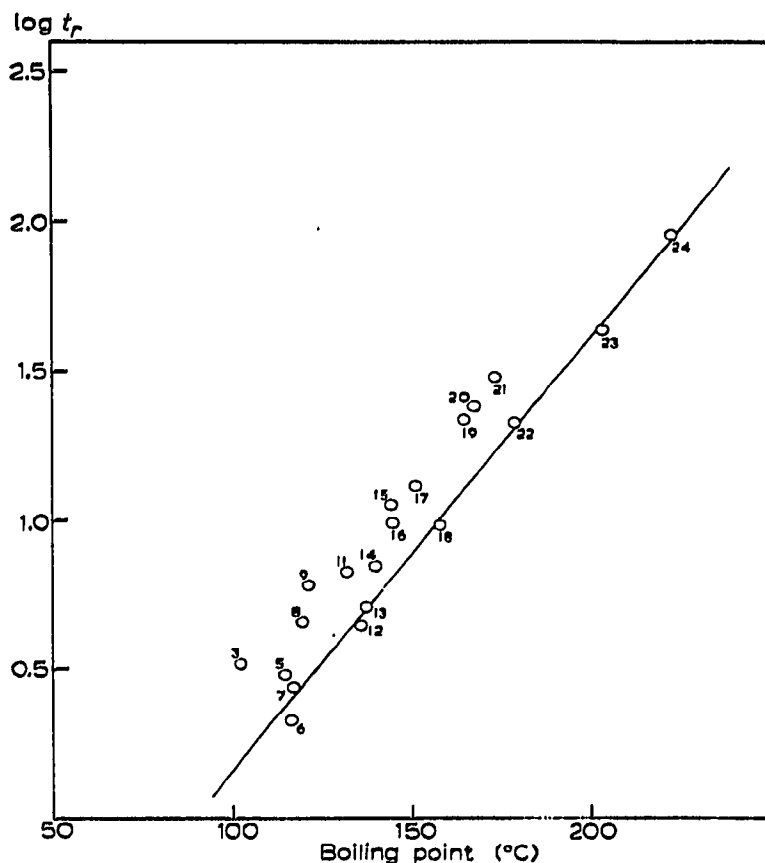


Fig. 2. Plot of $\log t_r$ vs. boiling point for aliphatic mono- and diamines. Column 2: alkaline-washed Celite + Apiezon L 20% w/w at 100°.

Comparison of the log adjusted retention time ($\log t_r$) vs. boiling point plots shows that irrespective of the column material, there is a linear relationship between the retention time of a primary diamine ($\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$) and its boiling point (Table I, Figs. 1-3). For the primary diamines there is also a linear relationship between $\log t_r$ and the number of carbon atoms (Table I).

The $\log t_r$ vs. boiling point plots also show that for the gas-liquid columns, the gradient for the non-polar Apiezon L is greater than that for the polar Carbowax 20M (a result noted already for monofunctional amines²²). The slopes of the corresponding plots for PAR-I coated with PEI are less than those for the gas-liquid columns, and decrease with increased loading of PEI. Thus although all the columns will separate mixtures of the primary straight-chain diamines, Apiezon L does this most effectively (Table I).

It is clear that although the points on the $\log t_r$ vs. boiling point plots for the primary α,ω -diamines lie on a straight line, those from isomeric amines often deviate from these lines. The extent of the deviation depends on the structure of the diamine and on the nature of the column. Thus substitution on either the alkyl carbon chain or the nitrogen atom can give rise to these deviations, and the greater the degree of substitution the greater is the difference of the retention time of the amine from that expected from the line for primary amines. Similar observations have been made for

TABLE I

ADJUSTED RETENTION TIMES (MIN) FOR ALIPHATIC MONO- AND DIAMINES

No. Amine ^a	Columns				
	(1a) PAR-1 + PEI 10% w/w 160'	(1b) PAR-1 + PEI 20% w/w 160°	(2) Celite (5% w/w KOH) + Apiezon L 20% w/w 100°	(3) Celite (5% w/w KOH) + Carbowax 20 M 20% w/w 100°	
1	<i>n</i> -Propylamine	1.9	2.2	—	0.9
2	<i>n</i> -Butylamine	3.4	4.9	—	1.6
3	<i>N,N</i> -Dimethyldiaminoethane ¹³	6.6	7.4	3.3	3.0
4	<i>n</i> -Pentylamine	5.9	6.7	—	2.4
5	<i>N</i> -Methyldiaminoethane	7.7	8.5	3.0	6.1
6	Diaminoethane	6.5	8.8	2.1	6.2
7	1,2-Diaminopropane	7.5	9.8	2.7	6.2
8	<i>N,N'</i> -Dimethyldiaminoethane	8.5	10.1	4.5	4.3
9	<i>N,N,N',N'</i> -Tetramethyldiaminoethane ¹⁴	6.0	7.6	6.0	2.6
10	<i>n</i> -Hexylamine	10.0	—	—	2.9
11	<i>N,N</i> -Dimethyl-1,3-diaminopropane ¹³	11.9	13.3	6.7	6.1
12	1,3-Diaminopropane	12.5	19.3	4.4	11.5
13	<i>N,N,N'</i> -Trimethyldiaminoethane ¹⁵	6.6	8.3	5.1	2.6
14	<i>N</i> -Methyl-1,3-diaminopropane ^{16,17}	14.7	18.5	7.0	10.2
15	<i>N,N,N',N'</i> -Tetramethyl-1,3-diamino- propane	12.0	12.0	11.5	3.4
16	<i>N,N'</i> -Dimethyl-1,3-diaminopropane ¹⁸	15.2	17.7	9.7	8.7
17	<i>N,N'</i> -Diethyldiaminoethane ¹⁸	15.1	17.0	13.0	7.3
18	1,4-Diaminobutane	21.6	29.3	9.6	22.6
19	<i>N,N,N',N'</i> -Tetramethyl-1,3-diamino- butane ¹⁹	17.6	18.5	21.9	5.8
20	<i>N,N,N',N'</i> -Tetramethyl-1,4-diamino- butane	18.8	19.6	24.1	11.8
21	Triethylenediamine ⁴	45.5	57.4	30.5	28.7
22	1,5-Diaminopentane	36.3	44.5	21.3	43.5
23	1,6-Diaminohexane	59.3	72.3	42.8	75.5
24	1,7-Diaminoheptane	97.6	117.3	90.0	132.5
25	1,8-Diaminooctane	159.1	189.5	—	—

^a For boiling points, see refs. 20 and 21, except where indicated.

the elution of monofunctional amines on aromatic polymer beads coated with PEI^{10,12} and of alcohols, ethers and diols¹¹ on PEG 1500 on Celite or PAR-I.

The cause of these deviations becomes clearer when one correlates the extent of the deviations with the nature of the column. Thus, the deviations on the non-polar columns are less than on Carbowax 20M (for example *N,N,N',N'*-tetramethyl-1,3-diaminobutane and *N,N,N',N'*-tetramethyl-1,4-diaminobutane). Further, on the Apiezon L column the deviations are above the line, while they lie below the line on Carbowax 20M columns. With the polymer columns, the extent and direction of the deviations depends on the loading of PEI; at low loadings, the divergencies are small and predominantly above the line, while with high loadings, the deviations are greater and below the line. Clearly the PEI modifies the polymer beads from a non-polar solid similar in behaviour to Apiezon L, to a semi-polar material approaching Carbowax 20M.

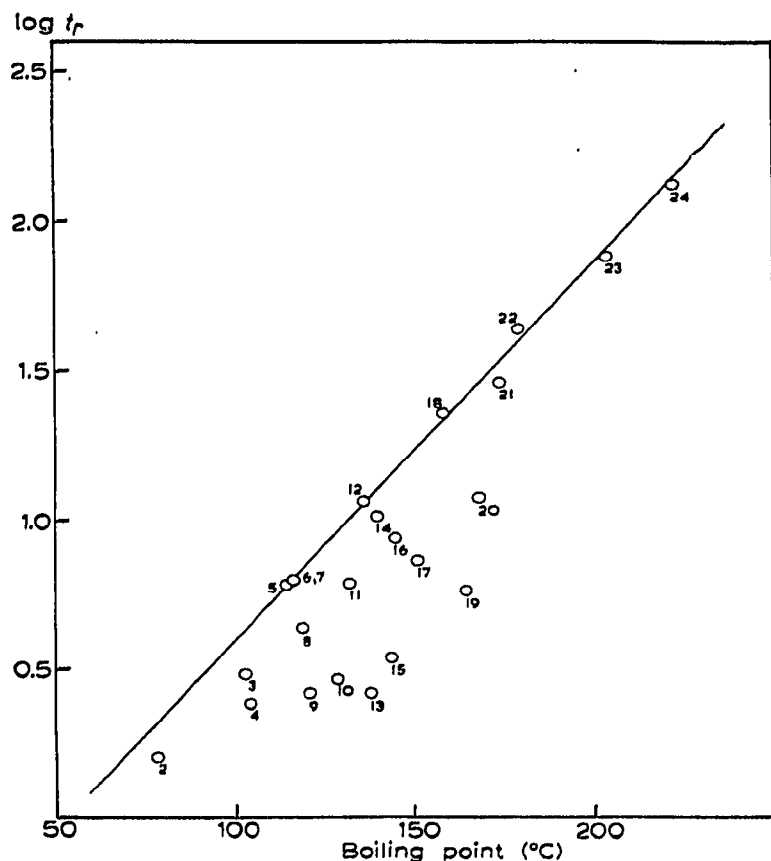


Fig. 3. Plot of $\log t_r$ vs. boiling point for aliphatic mono- and diamines. Column 3: alkaline-washed Celite + Carbowax 20 M 20% w/w at 100°.

The difference in behaviour of diamines on Carbowax 20 M columns most probably arises principally from donor-hydrogen-bonding²². Thus the more >N-H bonds in the diamine the greater the degree of donor-hydrogen-bonding and the larger the value of t_r .

Further confirmation for this explanation becomes apparent when the retention times of primary monofunctional amines are compared with those of the diamines. On the non-polar columns, the points for the monofunctional amines on the $\log t_r$ vs. boiling point plots are similar to those for the diamines. As expected, however, on the polar column there are significant differences, for example although *n*-hexylamine and 1,3-diaminopropane have similar boiling points, the monofunctional amine is eluted much more quickly than the diamine (Figs. 1 and 3).

For a completely non-polar column one might expect the points for different solutes to lie on a straight line. However, with Apiezon L, the tertiary diamines have longer retention times than the primary diamines. The explanation for this change in behaviour from the polar columns has been discussed previously for the elution of the higher secondary and tertiary amines²² on Apiezon L and has been attributed to intermolecular forces, other than hydrogen bonding, leading to a significant difference in solubility of the solutes in the liquid phase. For example, the tertiary diamines, which are the least polar, will be the most soluble in Apiezon L while the polar primary diamines will be the least soluble.

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