Journal of Chromatography, 329 (1985) 213–230
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17 704

IMPROVED METHOD FOR THE PREPARATION OF IMMOBILISED PYRIMIDONESILICONES AS POLAR STATIONARY PHASES USED FOR THE CAPILLARY COLUMN GAS CHROMATOGRAPHIC SEPARATION OF UNDERIVATISED BARBITURATES

W. M. L. CHOW and B. CADDY*
Forensic Science Unit, University of Strathclyde, 204 George Street, Glasgow G1 1XW (U.K.)
(First received November 22nd, 1984; revised manuscript received March 5th, 1985)

SUMMARY

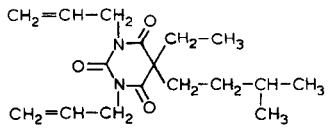
The preparation and chromatographic performance of SE-54 columns into which have been incorporated 2–100% (w/w) of a pyrimidone moiety are described. The resulting pyrimidonesilicones were rendered non-extractable by treatment with peroxide. Best performance was obtained from a column with 4% incorporation of monomer which enabled 21 out of 22 barbiturates to be resolved. For the separation of difficult barbiturate pairs, columns with 30% or 50% incorporation of the monomer are recommended and an improved method for the preparation of these columns is described.

INTRODUCTION

By far most commonly used immobilised stationary phases for capillary gas chromatography (GC) are the non-polar methylsilicones[1]. The methylphenylsilicones[2,3] and cyanosilicones[4–6] are also widely used because of their different selectivities and high thermal stability. Recently, Buijten *et al.*[7] reported the preparation of immobilised polyethylene glycol (PEG) for capillary GC which can be used up to 300°C, and Kuei *et al.*[8] reported the preparation of a crosslinkable biphenylmethylsilicones for the separation of isomeric polycyclic aromatic compounds. Still, the choice of crosslinkable polar phases for capillary GC is limited and there is a need for other selective phases to resolve mixtures tht cannot be separated on non-polar phases.

We have developed a simple method to extend the selectivity of the non-polar methylsilicones by incorporating a monomer containing a pyrimidone moiety into an SE-54 stationary phase[9]. These immobilised pyrimidonesilicones provide useful selective interactions during separation, especially for the difficult-to-separate barbiturates but the flexibility of this approach has still to be assessed. The present paper deals with the affects on the separation of barbiturates of varying the concentration of the incorporated monomer I and of changing the deactivation reagent to make it more compatible with the newly generated phases.

0021-9673/85/$03.30



I

EXPERIMENTAL

Synthesis of the monomer containing a pyrimidone moiety: 1,3-diallyl-5-ethyl-5-isoamylbarbituric acid (I)

The monomer was synthesised by di-allylation of 5-ethyl-5-isoamylbarbituric acid (May and Baker, Dagenham, U.K.) with allyl bromide according to a procedure described previously[9].

Column preparation

Glass capillaries (0.23 mm I.D. and 0.80 mm O.D.) were drawn from Pyrex glass tubes (3.5 mm I.D. and 6.0 mm O.D.) on a Carlo Erba GCDM 60 glass-drawing machine.

Cleaning of glass tubing, leaching followed by rinsing and dehydration of the drawn capillaries were carried out as described earlier[9].

A solution for static coating was prepared by first dissolving SE-54 (0.29%, Phase Sep) in pentane (AnalaR grade, BDH) and then adding from 2 to 100% (w/w) of the unsaturated barbiturate monomer (I) [2% (w/v) in methylene chloride]. Finally, 0.4–10% (w/w) dicumyl peroxide (DCUP) (2% in toluene) was added. Details are summarised in Tables I and II. Also, SE-54 columns (0.29%) were prepared without addition of the barbiturate monomer (I) so as to compare the performance between SE-54 columns and the modified columns.

TABLE I

CHARACTERISTICS OF THE COLUMNS PREPARED

*Column**	*Amount of DCUP added (%)*
SE-54	0.4
SE-54 with 2% monomer I incorporated	0.7
SE-54 with 4% monomer I incorporated	0.7
SE-54 with 10% monomer I incorporated	1
SE-54 with 20% monomer I incorporated	2
SE-54 with 30% monomer I incorporated	3
SE-54 with 50% monomer I incorporated	5
SE-54 with 100% monomer I incorporated	10

* All leached columns are 0.23 mm I.D., and are persilylated with DPTMDS.

The columns were statically coated as described earlier[9] but 2 m at both ends were kept free of coating. After static coating, the columns were flushed with dry nitrogen for 1 h and cured according to the method of Blomberg *et al.*[10], in which the capillary was sealed under vacuum and then placed in an oven at 140°C for 30

min. The oven was cooled rapidly and the column flushed with dry nitrogen at room temperature for 3 h. The ends of the columns were straightened using a Carlo Erba GESM 102-20 automatic electrical end-straightening machine under a flow of dry nitrogen. The column was conditioned at 250°C overnight and tests run. Finally, the column was washed with 5 ml methylene chloride (AnalaR grade, BDH), dried in a stream of nitrogen and re-conditioned overnight at 300°C before re-testing.

Hydrofluoric acid roughening

Some columns were roughened, prior to hydrochloric acid leaching, by hydrofluoric acid using a procedure similar to that described by Onuska *et al.*[11]. The inner surface of the capillary was filled with a freshly prepared solution of ammonium hydrogen difluoride [NH_4HF_2; 1% (w/v) in methanol; BDH], and the solution allowed to stand for 20 min. The solvent was then removed by a uniform nitrogen flow which was continued until the column became opaque. The column was then sealed and heated at 400°C for 4 h. The ends were opened in a fume hood and the column rinsed with 5 ml of methanol (AnalaR grade, BDH) and blown dry with nitrogen. The column was then submitted to leaching.

Deactivation by persilylation

Persilylation with diphenyltetramethyldisilazane (DPTMDS; Fluka, Buchs, Switzerland) was carried out as described earlier[9] employing a filling rate of 0.5 cm sec^{-1}. Persilylation with 3,3,3-trifluoropropyl(methyl)cyclosiloxane (F_3/F_4); Petrarch System, Bristol, PA, U.S.A.) was carried out according to Blomberg *et al.*[12] with a filling rate of 2 cm sec^{-1}. Persilylation with tetraphenyldimethyldisilazane (TPDMDS; Fluka) was performed according to Grob and Grob[13] with a filling rate of 1 cm sec^{-1}. Persilylation with divinyltetramethyldisilazane (DVTMDS; Fluka), DVTMDS–DPTMDS (1:1, v/v) and DVTMDS–DPTMDS (1:3, v/v) were performed according to Grob and Grob[14] with filling rates of 3 cm sec^{-1}, 1 cm sec^{-1} and 0.5 cm sec^{-1}, respectively. In all instances, the time of persilylation was 16 h. The temperatures of persilylation using different silanizing agents are summarised in Table II. After persilylation, the column was allowed to cool slowly in a closed oven for 1 h and rinsed with 2 ml of methylene chloride followed by 2 ml of methanol. Finally the capillary was rinsed with 5 ml of methylene chloride and dried in an oven at 150°C for 2 h under a slow carrier gas flow of nitrogen.

Deactivation with polyethylene glycol

Instead of deactivating the leached column wall surface by persilylation, a portion of Carbowax 20M [5% (w/v) PEG 20M in methylene chloride] was forced at a constant rate of 1 cm sec^{-1} through the column, which was emptied in the same way. After drying under nitrogen, the column was vacuum sealed and heated at 280°C for 16 h. After cooling, the column was rinsed and dried in the same way as described for the persilylated columns.

Gas chromatography

Capillary GC was performed with a standard Hewlett Packard Model 5710A GC system modified for capillary GC analysis and equipped with a flame ionisation detector (air, 240 ml/min; hydrogen, 30 ml/min). The carrier gas was nitrogen with

TABLE II

COMPARISON OF SEPARATION EFFICIENCIES (TZ) OBTAINED FROM VARIOUS METHODS OF PREPARATION OF COLUMNS

Column No.	*Length* (m)*	*Stationary phase*	*Amount of DCUP (%)*	*Hydrofluoric acid roughening*	*Deactivation agent*	*Deactivation temp. (°C)*	*TZ**,****
1	22	SE-54	0.4	–	DPTMDS	400	25.9
2	23	SE-54 + 30% monomer I	3	–	DPTMDS	400	9.0
3	17	SE-54 + 30% monomer I	3	–	F_3/F_4	400	1.3
4	10	SE-54 + 30% monomer I	3	+	DPTMDS	400	7.5
5	14	SE-54 + 30% monomer I	3	–	TPDMDS	400	1.2
6	14	SE-54 + 30% monomer I	1.5	–	DVTMDS–DPTMDS (1:3, v/v)	350	22.4
7	15	SE-54 + 30% monomer I	1.5	–	DVTMDS–DPTMDS (1:1, v/v)	350	22.7
8	15	SE-54 + 30% monomer I	1.5	–	DVTMDS	350	29.1
9	14	SE-54 + 30% monomer I	3	–	PEG 20M	280	14.4
10	12	SE-54 + 30% monomer I	3	+	PEG 20M	280	7.0
11	15	SE-54 + 100% monomer I	6	–	DVTMDS	350	9.4

* All Pyrex columns are 0.23 mm I.D.

** Conditions of Grob test mixture for all columns are: 40°C, 8°C/min (except for column 2 which is 100°C, 8°C/min).

*** Average of TZ1 between methyldecanoate (E_{10}) and methylundecanoate (E_{11}), and TZ2 between methylundecanoate (E_{11}) and methyldodecanoate (E_{12}).

injector and detector temperatures of 300°C. A split ratio of 50:1 was used. Nitrogen was used as the make-up gas (20 ml/min).

RESULTS AND DISCUSSION

The presence of two allyl groups in the synthetic barbiturate monomer (I) facilitates the cross-linking with the SE-54 matrix following treatment with peroxide[15] and the resulting pyrimidone silicones become non-extractable with solvents. Side products after curing can conveniently be removed by solvent washing.

In order to obtain a column which can resolve most of the common barbiturates including the difficult-to-separate pairs, in one temperature program run, SE-54 columns containing 2%, 4%, 10%, 20%, 30%, 50% and 100% incorporation of the barbiturate monomer (I) were prepared (Table I) and their chromatographic performance compared with a standard SE-54 column. The polarity, acidity and activity of the columns prepared were tested by the Grob test mixtures I and II[16,17] while the selectivity towards separation of barbiturates was tested with a standard barbiturate mixture.

It was found that an SE-54 column containing 2% incorporation of monomer I had roughly the same chromatographic performance as the reference SE-54 column in terms of polarity, acidity and activity (Table III) but more tailing was evident with the standard SE-54 column. Also, the selectivity towards the separation of barbiturates of the two columns was roughly the same. It can be concluded that 2% incor-

TABLE III

COLUMN EVALUATION

TZ	*Length** *(m)*	*Stationary phase*	*Amount of some components of the Grob mixtures as a percentage of the original concentration*		
			*1-Octanol (%)***	*2,6-Dimethyl-phenol (%)*	*2,6-Dimethyl-aniline (%)*
25.9	22	SE-54	60	68	82
24.9	13	SE-54 with 2% monomer I incorporated	75	69	94
19.0	15	SE-54 with 4% monomer I incorporated	62	79	90
15.5	15	SE-54 with 10% monomer I incorporated	84	100	52
13.5	23	SE-54 with 20% monomer I incorporated	83	97	51
9.0	23	SE-54 with 30% monomer I incorporated	72	100	57
8.3	21	SE-54 with 50% monomer I incorporated	87	–	–

* All Pyrex columns are 0.23 mm I.D.

** Percent of peak height that would be obtained if no adsorption occurred as determined by peak heights of hydrocarbons and methyl esters.

poration was too low a concentration to allow for change in polarity and selectivity which would assist in the separation of barbiturates.

The polarity of the columns started to increase from 4% to 50% incorporation as evidenced from the increasing retention of the polar components of the Grob test mixtures. For a column with 10% incorporation, 1-octanol eluted after undecane for the Grob mixture I and 2,6-dimethylaniline and 2-ethylhexanoic acid eluted after dodecane for the Grob mixture II as compared with the reference SE-54 column. This increase in polarity of the columns as the percentage incorporation of the barbiturate monomer (I) increased was expected. The polarities of columns having 20% and 30% incorporation of monomer I differed little. Generally, however, the elution pattern of peaks for the Grob test mixtures was different for columns having different percentages of incorporation of monomer I and consequently each column should be treated as one of different polarity.

When the acidity and activity of the columns were evaluated (Table III), it was found that the reference SE-54 column was slightly basic in character and that acidity increased as the percentage incorporation of the barbiturate monomer (I) increased. For 10% incorporation, the column had become acidic in character. Activity towards 1-octanol was low, about 60–80% of the peak height generally being obtained for the new columns compared with the standard SE-54 column.

Attempts to prepare SE-54 columns containing 100% incorporation of monomer I were at first unsuccessful because the coatings separated into visible droplets. It was concluded that, the surface tension of the resultant liquid phase was too high and the surface energy of the silylated glass too low.

It was also found that the higher the percentage incorporation of monomer I into SE-54 columns, the higher was the selectivity towards separation of the barbiturate mixture especially for the difficult-to-separate pairs such as butobarbital and butalbital, amylobarbital and nealbarbital, and brallobarbital and hexobarbital, as compared with the reference SE-54 column which failed to separate them[9]. The results are summarised in Table IV. For the SE-54 column with 4% incorporation of monomer I, complete baseline separation of brallobarbital and hexobarbital was achieved (Fig. 1). For the SE-54 column with 50% incorporation of monomer I, complete baseline separation of amylobarbital and nealbarbital (Fig. 2), and about 80% separation of butobarbital and butalbital (Fig. 3) were achieved.

When the columns were tested with a standard barbiturate mixture containing 13 common barbiturates (Fig. 4), it was found that as the percentage incorporation of monomer I into SE-54 columns increased, some components of the mixture, namely allobarbital (peak 2), nealbarbital (peak 6), brallobarbital (peak 9) and phenobarbital (peak 11), were retained to a greater extent as compared with the rest of the components. For the reference SE-54 column, peaks 5 and 6 were unresolved (Fig. 5), and peaks 6 and 7 were also unresolved for the column with 10% incorporation (Fig. 4B). Best performance was obtained for the column with 4% incorporation in which all 13 components were resolved in one temperature programme run for the first time (Fig. 4A).

Having obtained the column which gave the best performance for the separation of the standard barbiturate mixture containing 13 components (4% incorporation of monomer) it was then necessary to establish whether this same column was able to resolve most of the common barbiturates including the difficult-to-separate

TABLE IV

VARIATION OF RESOLUTION NUMBER (R)* BETWEEN AMYLOBARBITAL AND NEALBARBITAL, BUTOBARBITAL AND BUTALBITAL, AND HEXOBARBITAL AND BRALLOBARBITAL WITH SE-54 COLUMNS CONTAINING DIFFERENT PERCENTAGES OF INCORPORATION OF THE BARBITURATE MONOMER (I)

*Length*** *(m)*	*Stationary phase*	*R*		
		Amylobarbital and nealbarbital	*Butobarbital and butalbital*	*Hexobarbital and brallobarbital*
15	SE-54 with 4% monomer I incorporated	0.8	–	4.1
15	SE-54 with 10% monomer I incorporated	1.0	0.8	4.6
23	SE-54 with 20% monomer I incorporated	1.0	1.0	–
23	SE-54 with 30% monomer I incorporated	1.1	1.1	5.7
21	SE-54 with 50% monomer I incorporated	1.5	1.2	11.1

* The resolution number (R) was calculated between two components using the formula[18]

$$R = \frac{2\Delta t}{1.7\,(W_{h1} + W_{h2})}$$

where Δt = distance between the two peak maxima; W_{h1} = peak width at half height of component 1; W_{h2} = peak width at half-height of component 2.

** All Pyrex columns are 0.23 mm I.D.

pairs in one temperature programme run. The separation of 22 common barbiturates encountered in toxicological cases is shown in Fig. 6B. All components showed some resolution except brallobarbital and cyclopentobarbital (peaks 14 and 15, respectively) which eluted together. Fig. 6A shows the same test on the reference SE-54 column in which peak pairs 6 and 7, 8 and 9, 13 and 14, 20 and 21 cannot be resolved although the rest were resolved. It was found that, for the 4% incorporated column, some components of the mixture, namely allobarbital (peak 3), butalbital (peak 7), nealbarbital (peak 9), brallobarbital (peak 14), cyclopentobarbital (peak 15), ibomal (peak 16), phenobarbital (peak 18) and 5-ethyl-5-tolyl-barbital (peak 20) were retained to a greater extent as compared with the reference SE-54 column.

As mentioned above, although SE-54 columns incorporating various percentages of monomer I coated on leached, DPTMDS persilylated surface were both selective and efficient, efficiency decreased drastically from 20% incorporation onwards (Table III). In order to fully utilise the unique selectivities of SE-54 columns with high percentage of incorporation of monomer I, two approaches were tried.

In the first, the surface of the inner walls of the columns was increased by controlled treatment with hydrofluoric acid, prior to the leaching step[11]. The second approach consisted in chemical modification of the surface using different deactivating agents capable of generating surfaces more compatible with the stationary phase[13].

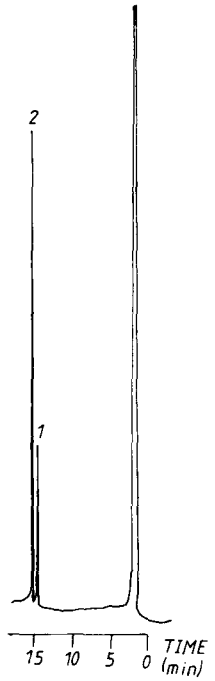


Fig. 1. Separation of hexobarbital (1) and brallobarbital (2) on an SE-54 Pyrex column with 4% monomer I incorporated, 15 m × 0.23 mm I.D. (chart speed, 120 mm/h). Chromatographed at 120°C for 2 min, programmed at 8°C/min to 230°C.

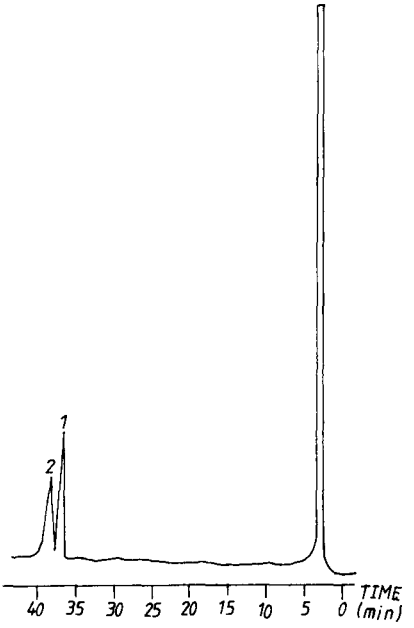


Fig. 2. Separation of amylobarbital (1) and nealbarbital (2) on an SE-54 Pyrex column with 50% monomer I incorporated, 21 m × 0.23 mm I.D. (chart speed, 120 mm/h). Chromatographed at 120°C for 2 min, programmed at 4°C/min to 230°C and held at the upper temperature for 15 min.

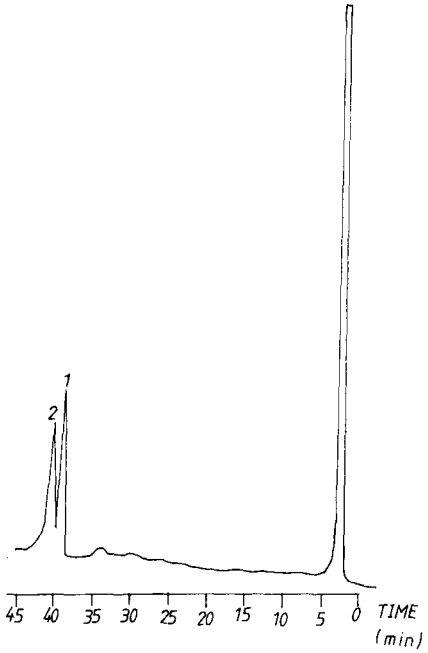
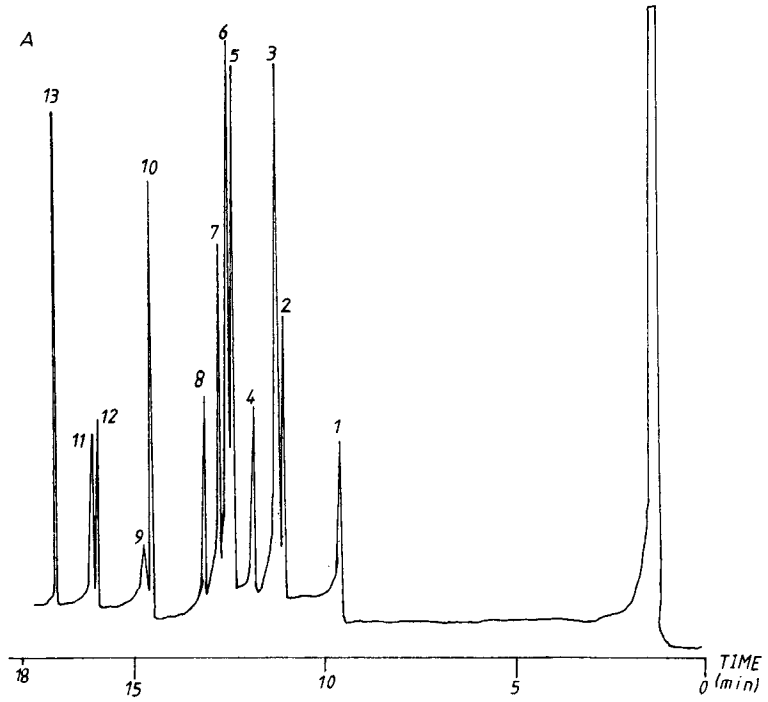


Fig. 3. Separation of butobarbital (1) and butalbital (2) on an SE-54 Pyrex column with 50% monomer I incorporated, 21 m × 0.23 mm I.D. (chart speed, 120 mm/h). Chromatographed at 120°C for 4 min, programmed at 4°C/min to 220°C and held at the upper temperature for 15 min.

The same stationary phase, *i.e.* SE-54 but with 30% incorporation of monomer I, was employed to assess the effects of the different surface pre-treatments (Table II). Very low efficiency was obtained using DPTMDS as persilylating agent [separation efficiency (TZ) = 9.0, Table II; coating efficiency (CE) = 33%, Table V]. Clearly improvements are necessary if the high efficiency of the standard SE-54 column (TZ = 25.9, Table II; CE = 88%, Table V) was to be matched.

Roughening by hydrofluoric acid increased the surface area of the inner walls of the column by forming silica whiskers[11]. Whisker walls are highly active and have to be deactivated[19]. The total surface energy of the deactivated whisker walls was increased, enabling them to "hold" stationary phases of high surface tension[19]. Surprisingly, the efficiencies of the hydrofluoric acid treated columns (columns 4 and 10, Table II) were found to be lower than the corresponding columns without hydrofluoric acid treatment (columns 2 and 9, respectively, Table II). This may be due to the difficulty in creating uniform whiskers throughout the whole inner surface of the column. As a result, a uniform coating of the stationary phase cannot be formed, leading to inefficient columns.

The wettability to the newly generated stationary phase was worse for F_3/F_4 and TPDMDS persilylated surfaces as compared with DPTMDS persilylated surface, as evidenced by a drastic decrease in TZ values (Table II). However the efficiency improved for the column deactivated with PEG 20M as compared with the DPTMDS persilylated column and TZ value increased by a factor of *ca.* 1.6 (Table II). Fur-


A
13
6
5
3
10
7
2
8
4
12
11
1
9
18
15
10
5
0
TIME
(min)

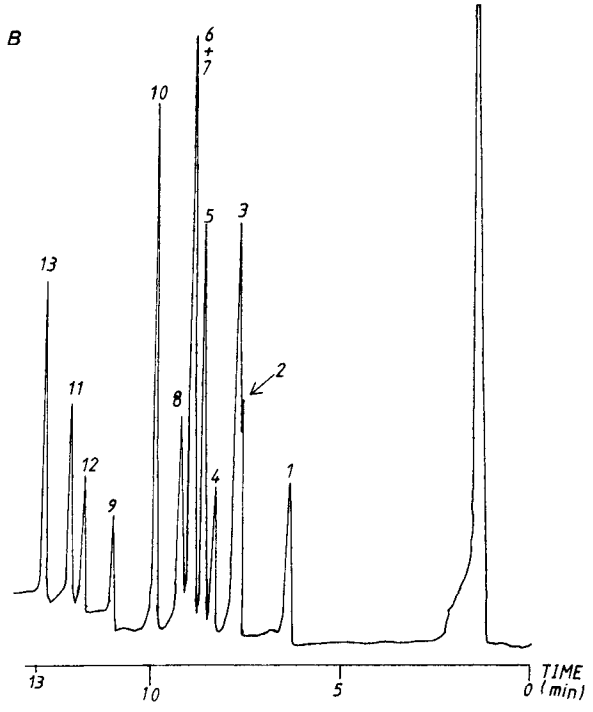

B
6
+
7
10
5
3
13
2
11
8
12
4
9
1
13
10
5
0
TIME
(min)

Fig. 4.

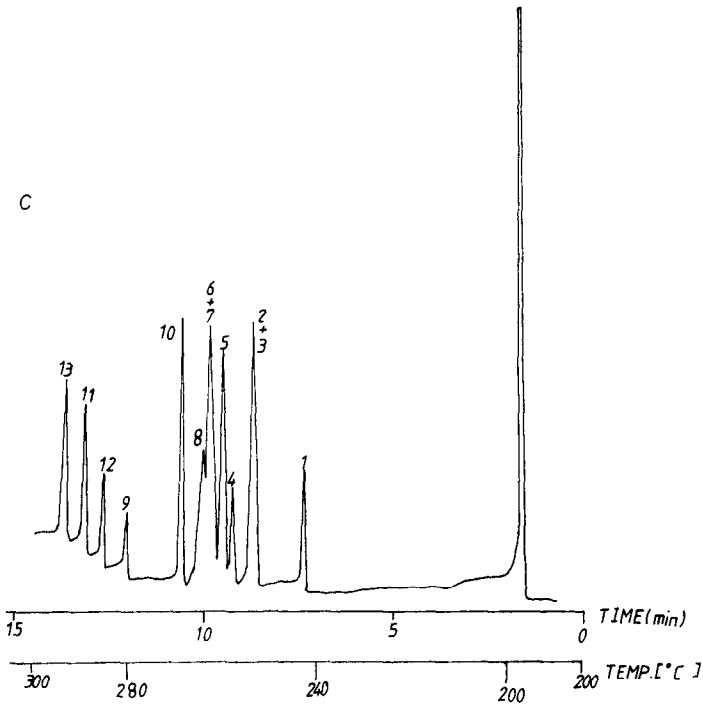


Fig. 4. Gas chromatograms of a standard barbiturate mixture (chart speed, 600 mm/h). (A) An SE-54 Pyrex column with 4% monomer I incorporated, 15 m × 0.23 mm. Chromatographed at 120°C for 2 min, programmed at 8°C/min to 250°C. (B) An SE-54 Pyrex column with 10% monomer I incorporated, 15 m × 0.23 mm. Chromatographed at 180°C for 2 min, programmed at 8°C/min to 270°C. (C) An SE-54 Pyrex column with 50% monomer I incorporated, 21 m × 0.23 mm. Chromatographed at 200°C for 2 min, programmed at 8°C/min to 300°C. Peaks: 1 = barbital, 2 = allobarbital, 3 = aprobarbital, 4 = butalbital, 5 = amylobarbital, 6 = nealbarbital, 7 = pentobarbital, 8 = vinbarbital, 9 = brallobarbital, 10 = methylphenylbarbital, 11 = phenobarbital, 12 = cyclobarbital, 13 = heptabarbital.

thermore, PEG 20M deactivated surface affected the overall polarity, leading to a more polar column. Selectivity towards the separation of barbiturates improved for the PEG 20M deactivated column (Fig. 7) as compared with the DPTMDS persilylated column (Fig. 8). On the whole the overall performance of the PEG 20M column was better than that of the DPTMDS column, the only limitation of the former being their thermal stability, PEG 20M columns having a temperature limit of 280°C. The TZ value, though improved, was still low when compared with the standard SE-54 column (Table II).

Very efficient columns were obtained from 30% incorporation of monomer I persilylated with DVTMDS, DVTMDS–DPTMDS (1:1) or DVTMDS–DPTMDS (1:3). TZ values increased by a factor of *ca.* 2.5–3.0 (Table II) and were comparable with that of the standard SE-54 column. High coating efficiencies were also obtained (Table V). They showed similar polarity with the DPTMDS column, were slightly basic in character, and showed very good tailing behaviour. The columns also showed very weak, but clearly observable, column activity, but can be used up to at least

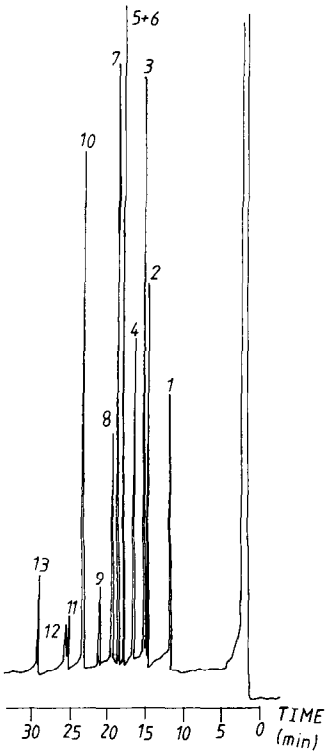


Fig. 5. Gas chromatogram of a standard barbiturate mixture on an SE-54 Pyrex column, 22 m × 0.23 mm (chart speed, 120 mm/h) chromatographed at 120°C for 2 min, programmed at 4°C/min to 220°C and held at the upper temperature for 10 min. For peak identification see Fig. 4.

300°C. The selectivity towards separation of barbiturates improved markedly and for the column persilylated with DVTMDS, all 13 barbiturates in the standard barbiturate mixture were resolved (Fig. 9), and 21 out of 22 barbiturates, which include the difficult-to-separate pairs, were resolved with an analysis time of less than 21 min (Fig. 10).

The use of DVTMDS serves two purposes. Firstly it reduces the amount of DCUP required to render columns immobilised[14]. This was evidenced by the decreasing percentage of extractability of the stationary phase with increasing percentage of DVTMDS used in conjunction with DPTMDS in persilylation (Table V). Secondly, it seems to have generated a surface compatible with the stationary phase, probably because the persilylated surface and the monomer I incorporated into the stationary phase both contain unsaturated alkene groups. This closer chemical similarity between glass wall and the stationary phase are important for homogenous film spreading to produce efficient columns[20]. This kind of speculation is supported by the observation that TZ and CE increased with increasing percentage of DVTMDS used in conjunction with DPTMDS in persilylation (Tables II and V).

Droplet formation was observed for SE-54 columns with 100% incorporation

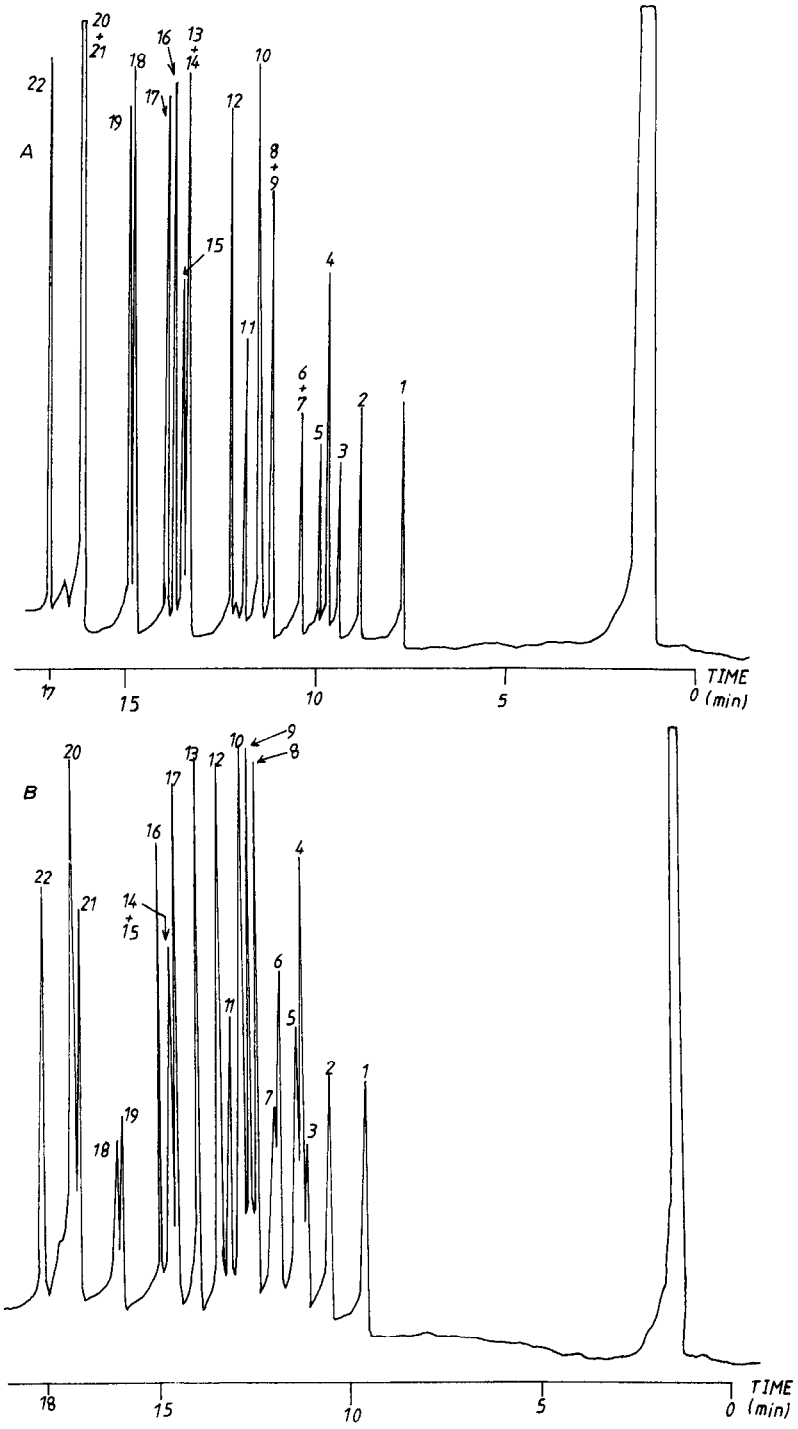


Fig. 6. Chromatograms of 22 barbiturates (chart speed, 600 mm/h; flow-rate, 16.3 cm sec^{-1}) on (A) an SE-54 Pyrex column, 15 m × 0.23 mm, chromatographed at 120°C for 2 min, programmed at 8°C/min to 240°C and held at the upper temperature for 5 min and (B) an SE-54 Pyrex column with 4% monomer I incorporated, 15 m × 0.23 mm, chromatographed as for 6A. Peaks: 1 = barbital, 2 = probarbital, 3 = allobarbital, 4 = aprobarbital, 5 = ethylcrotylbarbital, 6 = butobarbital, 7 = butalbital, 8 = amylobarbital, 9 = nealbarbital, 10 = pentobarbital, 11 = vinbarbital, 12 = quinalbarbital, 13 = hexobarbital, 14 = brallobarbital, 15 = cyclopentobarbital, 16 = ibomal, 17 = methylphenylbarbital, 18 = phenobarbital, 19 = cyclobarbital, 20 = 5-ethyl-5-*p*-tolylbarbital, 21 = heptabarbital, 22 = reposal.

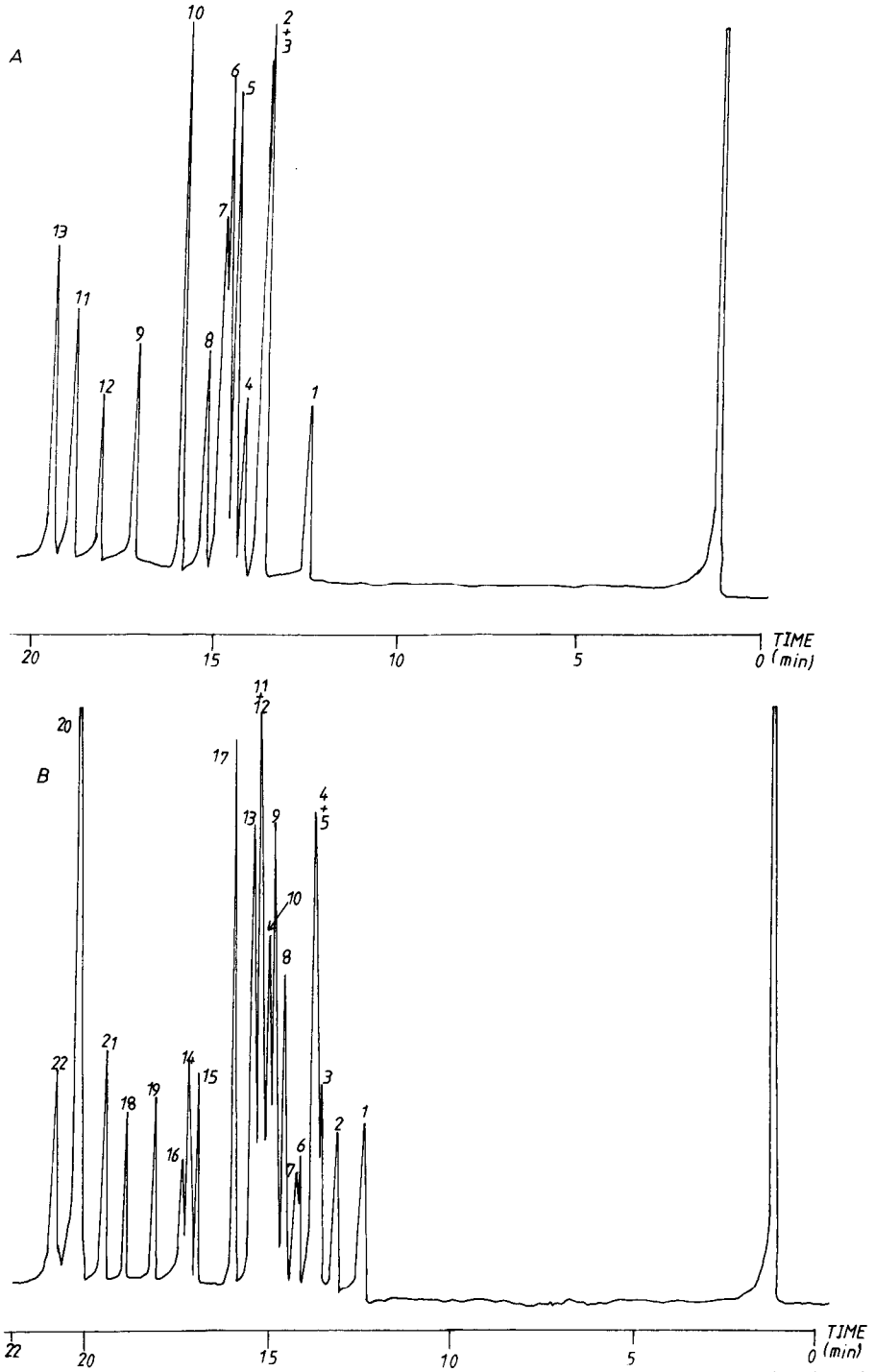


Fig. 7. Gas chromatograms of an SE-54 column with 30% monomer I on PEG 20M deactivated surface (chart speed, 600 mm/h). Peaks are numbered according to the sequence they elute on a reference SE-54 column of the same column dimensions. (A) Standard barbiturate mixture. Chromatographed at 120°C for 2 min, programmed at 8°C/min to 240°C and held at the upper temperature for 3 min. For peak identification see Fig. 4. (B) 22 Barbiturates, chromatographed as in Fig. 7A except the upper temperature was held for 5 min. For peak identification see Fig. 6.

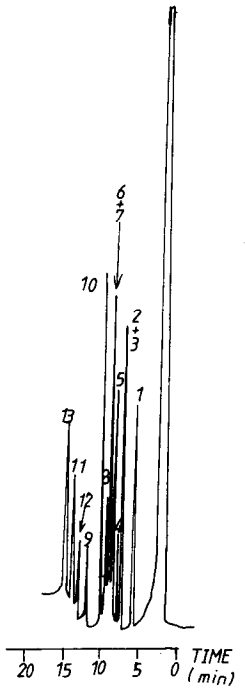


Fig. 8. Gas chromatogram of a standard barbiturate mixture on an SE-54 column with 30% monomer I on DPTMDS persilylated surface (chart speed, 120 mm/h). Chromatographed at 210°C for 2 min, programmed at 4°C/min to 260°C. For peak identification see Fig. 4.

of monomer I coated on leached, DPTMDS persilylated surface. Employing DVTMDS as persilylating agent, however, SE-54 columns with 100% incorporation of monomer I can be prepared with medium quality [TZ = 9.4; k' = 8.5; height equivalent to a theoretical plate (HETP) = 0.60; CE = 33% for C_{16} measured at 200°C] showing no droplet formation.

SE-54 columns with 30% incorporation of monomer I persilylated with DVTMDS, DVTMDS–DPTMDS (1:1) or DVTMDS–DPTMDS (1:3) can be used as a general polar phase for capillary GC because they are efficient, selective, thermally stable and showed very good tailing behaviour. They are by no means limited to the separation of underivatised barbiturates and have been successfully applied to the separation of a mixture of benzodiazepines.

CONCLUSIONS

Although SE-54 columns incorporating various proportions of monomer I coated on leached, DPTMDS persilylated surface were both selective and efficient, efficiency decreased drastically from 20% incorporation onwards. Very efficient columns were obtained for SE-54 columns with 30% incorporation of monomer I persilylated with DVTMDS, DVTMDS–DPTMDS (1:1) or DVTMDS–DPTMDS (1:3) when TZ values increased by a factor of *ca.* 2.5–3.0; such columns were comparable

TABLE V

COMPARISON OF THE CHARACTERISTICS OF SOME OF THE COLUMNS PREPARED

Column No.*	*Stationary phase*	*Amount of DCUP (%)*	*Hydrofluoric acid roughening*	*Deactivation agent*	*k' for hexadecane at 140°C*	*HETP (mm) for hexadecane at 140°C*	*CE (%)*	*Percent decrease in k' of hexadecane at 140°C after rinsing with solvent*
1	SE-54	0.4	–	DPTMDS	7.8	0.22	88	2.6
2	SE-54 + 30% monomer I	3	–	DPTMDS	20.0	0.63	33	0
6	SE-54 + 30% monomer I	1.5	–	DVTMDS–DPTMDS (1:3, v/v)	7.3	0.29	67	11
7	SE-54 + 30% monomer I	1.5	–	DVTMDS–DPTMDS (1:1, v/v)	6.2	0.28	69	7.8
8	SE-54 + 30% monomer I	1.5	–	DVTMDS	6.5	0.25	77	5.2
9	SE-54 + 30% monomer I	3	–	PEG 20M	8.6	0.38	53	n.d.**
10	SE-54 + 30% monomer I	3	+	PEG 20M	13.0	0.65	32	n.d.

* The column numbers are assigned according to Table II.

** n.d. = not determined.

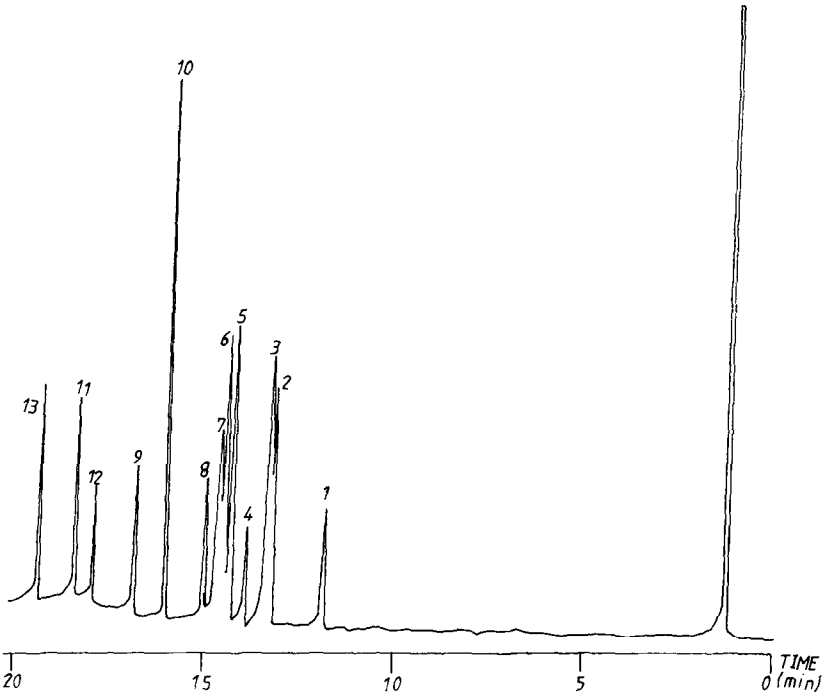


Fig. 9. Gas chromatogram of a standard barbiturate mixture on SE-54 columns incorporating 30% monomer I and deactivated with DVTMDS. Chromatographed at 120°C for 2 min, programmed at 8°C/min to 240°C and held at the upper temperature for 3 min. For peak identification see Fig. 4.

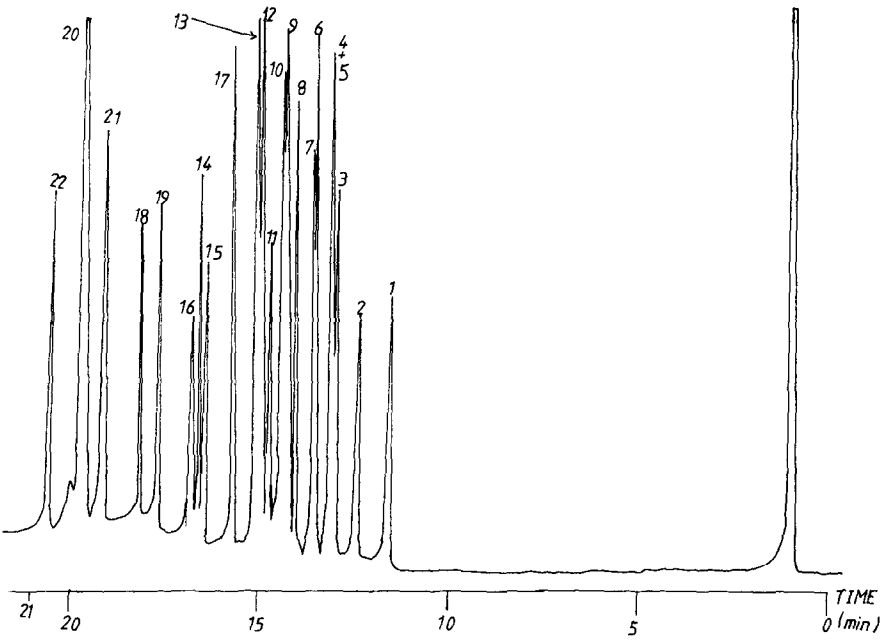


Fig. 10. Chromatograms of 22 barbiturates on SE-54 columns with 30% incorporation of monomer I deactivated with DVTMDS. Chromatographed at 120°C for 2 min, programmed at 8°C/min to 240°C, and held at the upper temperature for 5 min. For peak identification see Fig. 6.

in efficiency to a standard SE-54 column. The columns also showed marked improvement for the separation of barbiturates, very good tailing behaviour and higher thermal stability.

ACKNOWLEDGEMENTS

W.M.L.C. wishes to thank the Committee of Vice-Chancellors and Principals of the Universities of United Kingdom, and the University of Strathclyde for financial support to carry out this work, Mr. F. Drumm for excellent technical assistance and Mrs. G. Adams for secretarial help.

REFERENCES

1 P. Sandra, M. Van Roelenbosch, I. Temmerman and M. Verzele, *Chromatographia*, 16 (1982) 63.
2 M. Verzele, F. David, M. Van Roelenbosch, G. Diricks and P. Sandra, *J. Chromatogr.*, 279 (1983) 99.
3 J. S. Bradshaw, S. J. Crowley, C. W. Harper and M. L. Lee, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 89.
4 K. Markides, L. Blomberg, J. Buijten and T. Wännman, *J. Chromatogr.*, 254 (1983) 53.
5 K. Markides, L. Blomberg, J. Buijten and T. Wännman, *J. Chromatogr.*, 267 (1983) 29.
6 B. E. Richter, J. C. Kuei, L. W. Castle, B. A. Jones, J. S. Bradshaw and M. L. Lee, *Chromatographia*, 17 (1983) 570.
7 J. Buijten, L. Blomberg, K. Markides and T. Wännman, *J. Chromatogr.*, 268 (1983) 387.
8 J. C. Kuei, J. I. Shelton, L. W. Castle, R. C. Kong, B. E. Richter, J. S. Bradshaw and M. L. Lee, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 13.
9 W. M. L. Chow and B. Caddy, *J. Chromatogr.*, 318 (1985) 255.
10 L. Blomberg, J. Buijten, K. Markides and T. Wännman, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 578.
11 F. I. Onuska, M. E. Comba, T. Bistricki and R. J. Wilkinson, *J. Chromatogr.*, 142 (1977) 117.
12 L. Blomberg, K. Markides and T. Wännman, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 527.
13 K. Grob and G. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 197.
14 K. Grob and G. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 491.
15 R. C. Laible, in N. G. Gaylord and N. M. Bikales (Editors), *Encyclopedia of Polymer Science and Technology*, Vol. 1, Interscience, New York, 1964, p. 750.
16 K. Grob Jr., G. Grob and K. Grob, *J. Chromatogr.*, 156 (1978) 1.
17 K. Grob, G. Grob and K. Grob Jr., *J. Chromatogr.*, 219 (1981) 13.
18 R. R. Freeman, *High Resolution Gas Chromatography*, Hewlett-Packard Co., Avondale, PA, 1979.
19 M. Verzele, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 647.
20 M. Novotný and K. Grohmann, *J. Chromatogr.*, 84 (1973) 167.