Journal of Chromatography, 101 (1974) 271–279
© Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 7776

PREPARATION AND PROPERTIES OF POROUS LAYER OPEN TUBULAR BOROSILICATE AND SODA-GLASS COLUMNS POSSESSING A PERMANENTLY FIXED SUPPORT LAYER

D. A. CRONIN*
Procter Department of Food and Leather Science, The University of Leeds, Leeds (Great Britain)

(Received June 17th, 1974)

SUMMARY

A new method of preparing glass porous layer open tubular columns is described. The columns are drawn from lengths of glass tubing the inner surfaces of which are previously coated with a thin even layer of a finely divided support made from a mixture of powdered Celite 545 and powdered glass. The final columns, which possess a uniform corrugated layer of support firmly fixed to the capillary wall, have high permeabilities and may be readily coated with polar and non-polar liquid phases. The properties of a number of columns prepared from both borosilicate and soda-glass and coated with the polar Carbowax 20M and the non-polar methyl silicone elastomer are compared, and the excellent properties of the soda-glass columns for the analysis of polar compounds are discussed in some detail.

INTRODUCTION

The preparation of metal porous layer open tubular (PLOT) columns by a static coating procedure was first described by Halász and Horvath[1]. The special properties of these columns and their advantages over conventional packed and wall-coated open tubular columns for many applications were subsequently elaborated by Ettre *et al.* in a number of papers[2–5]. While commercially available columns of this type have been in use for a number of years, their relatively high cost as well as difficulties in their preparation has led a number of workers to develop simpler methods for preparing both glass[6] and metal[7,8] PLOT columns using a suspension of a finely divided support mixed with the liquid phase in a suitable solvent. Yet another recent development in this area is the use of Silanox 101[9,10], a new support material consisting of hydrophobic silanized silica particles (6–10 μm) which readily form stable suspensions in many solvents, and would seem to possess almost ideal properties for dispersing organic liquids as stable films on glass or metal surfaces.

A somewhat different type of glass PLOT column which has a relatively thick layer of a diatomite support fused to the wall of the capillary by means of lithium chloride as a binding agent was developed by Grant[11]. We have described the preparation of modified columns of this type using finely powdered glass instead of lithium

---

* Present address: Department of Agricultural Chemistry, Faculty of Agriculture, University College Dublin, Glasvenin, Dublin, Eire.

chloride as the binder[12]. The method of preparation involves the drawing of the capillary column from a tube packed with a mixture of the support and finely powdered borosilicate glass. The capillary is drawn over a narrow tungsten wire, one end of which is inserted through the packing into the drawing furnace while the other end is anchored to a fixed support. The resulting columns have the support fused to the wall of the tube and an annular space through the tube centre, which gives the columns good permeabilities to gases. Columns of this type have been in use in these laboratories for a number of years and, when coated with phases of high and medium polarity, have proved very useful for the analysis of complex mixtures, particularly those of volatile flavour compounds isolated from various foodstuffs.

However, considerable difficulty was encountered when such mixtures were subjected to analysis on columns coated with non-polar phases, for example, Apiezon L or silicone elastomer. Polar compounds, such as alcohols, gave very severe tailing which could not be eliminated by silanization of the columns. The deposition of a layer of tungsten oxides on the inner surface of the support appeared to be a major cause of the adsorption effects. By washing the column successively with concentrated hydrochloric acid, water, and acetone, followed by silanization, much improved peak shapes were obtained for polar compounds, especially if a small quantity of an antitailing agent, such as Atpet 80, had been included in the coating solution. However, the procedure is both long and tedious and cannot be applied to columns prepared with lithium chloride as a binder. We have experienced similar, and in some cases worse, behaviour of polar compounds on a number of commercial PLOT columns coated with the methyl silicone OV-1, which was only slightly improved by silanization; the effect is probably caused by adsorption onto the very finely divided diatomite used for the preparation of the columns. A recently acquired batch of Silanox 101, which produced very promising columns with Carbowax 20M, has unexpectedly yielded apolar PLOT columns showing severe tailing properties with alcohols. This behaviour is receiving further study.

In the present paper a method is described for preparing glass PLOT columns of high permeability which have a thin layer of diatomite support fused to the inner wall of the tube. Tungsten wire is not used. The columns are drawn from lengths of glass tubing the internal surfaces of which are previously coated with an even thin layer of a support material. The latter is made by grinding to a very fine paste Celite 545 mixed with glass powder, in a suitable organic liquid. The final capillaries can be readily coated with both polar and non-polar phases and give superior performances to those prepared using the tungsten wire method. The properties of PLOT columns prepared from both Pyrex and soda-glass are described, and the marked superiority of the latter in respect of much lower activities towards polar compounds is discussed in some detail.

EXPERIMENTAL

Preparation of PLOT columns

Pyrex columns. Acid-washed Celite 545 of optional mesh size (10 g) is mixed in a mortar with an equal weight of powdered Pyrex (Type B-37, Glass Tubes and Components, Lemington, Newcastle-upon-Tyne, Great Britain) glass. This material is similar in composition to ordinary Pyrex but has a softening point 60° lower. The mixture is then reduced to a very fine powder by prolonged grinding with a pestle. The powder is wetted with distilled butan-2-ol to produce a thick slurry, which is further ground for several minutes to produce a very fine creamy paste. A glass tube (20 cm × 10 mm I.D.) sealed at one end is filled to about two-thirds of its volume with the paste, the thickness of which is then adjusted to satisfy the final coating requirements as follows: approximately 0.1 ml of butan-2-ol is added to the paste, and the tube is stoppered tightly with a cork and thoroughly shaken. After settling in a vertical position has taken place, a thin even unbroken film of the paste should remain deposited on the wall of the upper portion of the tube. The aim is to produce the thinnest film possible which does not break up on standing, so the above procedure may need to be repeated with the addition of a further small quantity of solvent. Visual examination of the film will readily indicate whether the paste has been over-diluted; if this happens, it is necessary to remove some of the solvent under vacuum to thicken the paste, and then to proceed as before until the correct consistency is obtained. Problems of over-dilution can normally be avoided after some practice at preparing pastes by the method described. The tube containing the paste is stoppered tightly to prevent evaporation of the solvent until a column is to be prepared.

Columns were prepared from 1-m lengths of medium-wall Pyrex tubing (7 mm O.D. × 4 mm I.D. and 6 mm O.D. × 3 mm I.D.), which were thoroughly cleaned with detergent and distilled water before use. The tubes were rinsed with butan-2-ol just prior to coating, which was carried out in the following manner. The tube containing the paste was thoroughly shaken, clamped in a vertical position and the stopper removed. The length of tubing to be coated was then inserted into the paste to touch the bottom of the container. A gentle vacuum was applied at the top of the tube and the slurry drawn slowly up the tube to within about 2 cm of the top. The vacuum was released and the slurry allowed to drain back into the container. This procedure may need to be repeated once or twice until a perfectly even film of the paste remains deposited on the inner wall of the tube over its length. The tube was then gently raised clear of the slurry and allowed to drain into the container for a few minutes, after which the latter was stoppered for subsequent use. The coated tube was allowed to partially dry overnight in a vertical position with protection from knocks and vibration which could cause the wet film to break up. The layer was dried by passing nitrogen through the tube at 30 ml/min for 3–4 h. When dry, the layer was remarkably stable and PLOT columns having internal diameters of 0.5 mm and 0.38 mm were then drawn using a machine for drawing and coiling capillaries based on the original design of Desty[13].

Soda-glass PLOT columns. The procedure used was exactly the same as that described for the Pyrex columns, except that finely powdered soda-glass was mixed with the Celite 545 to form a suitable paste, which was then deposited as a thin layer on soda-glass tubing (7 mm O.D. × 5.5 mm I.D.) to give PLOT columns having an internal diameter of 0.625 mm.

Deactivation and coating of columns

The columns were silanized before coating by filling with a 10% v/v solution of dimethyldichlorosilane (DMCS) in pentane from an all-glass pressure reservoir; the filled columns were allowed to stand overnight. After removal of the DMCS solution the columns were washed with anhydrous acetone and finally dried under a flow of nitrogen. An additional vapour-phase silanization was applied to some of the Pyrex columns by passing nitrogen saturated with hexamethyldisilazane (HMDS) vapour through the columns at 180° for 24 h.

The columns were coated by filling under a pressure of nitrogen with a solution of the liquid phase in a suitable solvent at a flow-rate of 10–20 cm/s. The solution was then ejected at the same pressure, a constant flow being maintained throughout by means of a 5-m length of "buffer" column connected to the end of the column being coated. The gas flow was continued until the column was completely dry. A number of Pyrex and soda-glass PLOT columns were coated with Carbowax 20M dissolved in dichloromethane and others with silicone elastomer, SE-30, in the same solvent.

The columns were tested in a Pye Model 104 temperature-programmed chromatograph equipped with a flame ionization detector (FID) and a heated injection head. Connection between the column and detector and between the column and a low-volume capillary glass injection block was made using thin-wall polytetrafluoroethylene (PTFE) tubing as described previously[14]. Columns were conditioned by programming from 60° at 1°/min to 200° and 220° for Carbowax 20M and SE-30, respectively, and the columns held at the maximum temperature for 2–3 h. The carrier gas was helium. Samples were injected without splitting using a 0–1 μl hypodermic syringe.

RESULTS AND DISCUSSION

The deposition of a thin, even layer of Celite–glass coating on the wall of the original tube is the most important factor in the preparation of the PLOT capillaries. A range of the more common polar and non-polar solvents, such as ethanol, chloroform and toluene were initially evaluated for the preparation of the new film of coatings. All were unsatisfactory either because of their volatility or because of their failure to produce a stable layer on the wall of the tubes. The butan-2-ol (b.p. 98.5–100°) performed the required function very effectively, both in producing a layer of excellent uniformity and in being sufficiently volatile to allow rapid drying of the coated tubes with a purge of nitrogen gas. The new PLOT capillaries possess a uniform, somewhat corrugated, layer of support firmly fused to the wall of the capillary. The layers show a high degree of physical stability and are not disturbed or displaced by repeated coating and stripping of the columns with solvents. The columns have a relatively large internal empty volume and, as a consequence, have excellent permeabilities. The permeability constants (uncorrected) for a number of columns are listed in Table I, and compare favourably with the theoretical permeability of 780×10^{-7} cm^2 for an empty capillary of 0.5 mm diameter. Values for the permeabilities were calculated from the definition:

$$\text{permeability} = \frac{\bar{u}\,\eta L\,\varepsilon_0}{\Delta p}$$

where

$\bar{u}$ = average linear gas velocity (cm/s)
η = viscosity of the carrier gas at the column temperature (poise)
Δp = pressure drop along the column (dynes/cm^2)

TABLE I

CHARACTERISTICS OF SOME TYPICAL PLOT COLUMNS

	Column no.				
	1	*2*	*3*	*4*	*5*
Type of glass	Pyrex	Pyrex	Soda	Soda	Soda
Length, m	15.2	35.6	15.9	16	16.75
Tubing I.D., mm	0.38	0.5	0.635	0.635	0.635
Column volume, ml	—	7.0	5.04	5.05	5.32
Liquid phase	Carbowax 20M	SE-30	Carbowax 20M	Carbowax 20M	SE-30
Concentration of coating solution, % (w/v)	1.0	1.5	2.0	4.0	2.0
Amount of phase deposited	—	46 mg (0.046 ml)	32.4 mg (0.032 ml)	—	46 mg (0.046 ml)
Phase ratio, β	—	152	156	—	115
HETP minimum, mm	0.85	1.0	1.25	1.55	1.3
k value*	3.85	4.5	4.03	7.7	4.6
Permeability, $\times 10^{-7}$ cm^2	147	280	645	—	640

* For 2-undecanone at 120°.

L = length of column (cm)

ε_0 = external porosity (taken as unity)*

Columns having a stable layer of support could also be prepared by depositing a somewhat thicker layer of paste on the original tube, or by reducing the amount of glass in the paste to about 30% by weight. However, such columns did not show significantly improved performances over those already described and, since their permeabilities were substantially lower, especially for columns less than 0.5 mm in diameter, further studies on these columns were discontinued.

The characteristics of a number of representative columns are shown in Table I. The amount of liquid phase deposited on Columns 2, 3, and 5, from which the β values were calculated, were determined in replicate coating experiments in which the buffer column was omitted. The excess of solution emerging from a column was collected and the residue weighed after removal of the solvent under vacuum. The difference between this weight and the quantity of phase in the original volume of coating solution represented the amount deposited. The phase ratio (β_2) obtained in this way for Column 3 was within 3% of the value obtained indirectly from the relationship:

$$k_1 \beta_1 = k_2 \beta_2$$

β_1 = phase ratio calculated for a 0.5 mm open tubular glass capillary column coated with a known amount of Carbowax 20M by the static method of Bouche and Verzele[15].

k_1 and k_2 = capacity ratios for 2-undecanone at 120° on the wall-coated and PLOT Column 2, respectively.

---

* ε_0 is not easily determined for columns of the present type, but is expected to be only slightly less than unity.

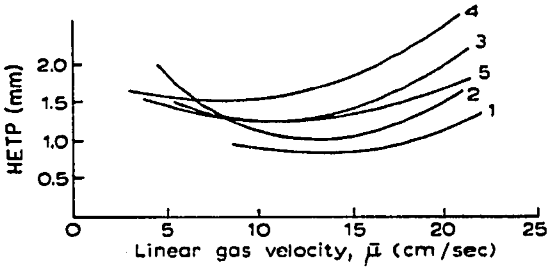

Fig. 1. Relationship between carrier gas velocity and HETP for Columns 1–5 measured for 2-undecanone at 120°.

The shapes of the HETP *versus* gas velocity curves are shown in Fig. 1. With the exception of Column 4, the ketone used had a k value of around 4 on the various columns. The plots are relatively flat with the plate height minima occurring close to the normal working range for columns of this type, *viz.* 10–15 cm/s. The increase in the minimum HETP from a little below 1 mm to about 1.3 mm for similar k values with increase in column diameter follows the pattern expected from theory. The increase in the plate height minima with increased liquid-phase loadings and its occurrence at somewhat lower values of $\bar{\mu}$, which is qualitatively in accordance with the predictions of the Golay equation[16], may be seen by comparing Columns 3 and 4, where the minimum HETP is raised from 1.25 to 1.55 mm.

The coating solutions used for Columns 2, 3, and 5 produce columns with intermediate loadings of liquid phases, and while both the β values and the minimum plate heights are somewhat higher than for the best statically coated conventional PLOT columns, these loadings represent a reasonable compromise between efficiency, sample capacity, and analysis time for compounds of intermediate boiling point. Columns with widely differing capacity ratios may be readily prepared to accommodate specific applications by simply varying the concentrations of the coating solutions. It has been shown previously[11,12] that PLOT columns made by the tungsten wire method can be prepared to specified capacity ratios on account on the linear relationship between capacity ratio and concentration of the coating solutions. The present columns give a similar relationship.

A measure of the sample capacity of a column may be obtained empirically by observing how the resolution between two peaks having close relative retentions (α) is affected by increasing the size of sample injected. Although Column 4 has a fairly high minimum HETP, it affords baseline separation for the methanol/ethanol pair ($\alpha = 1.15$), a normally difficult separation on narrow bore columns because of the relatively low capacity ratios ($k = 0.75$ for methanol). The effect on resolution upon injecting increasing amounts of a mixture of equal volumes of the two alcohols is shown in Fig. 2. The column can be seen to accept up to 0.4 μl of the mixture before the resolution begins to deteriorate, and even at 1 μl the peaks are still resolved. Sample capacity depends on many factors such as column length and diameter, liquid-phase loading, and capacity ratio, and can vary widely for different PLOT columns. Moderately long (60–70 m) PLOT columns which are most useful for the analysis of flavour volatiles have been found, even when coated with low loadings of liquid phases, to withstand repeated injections of as much as 1–2 μl of dilute solutions of compounds in diethyl ether or pentane without suffering any permanent damage.

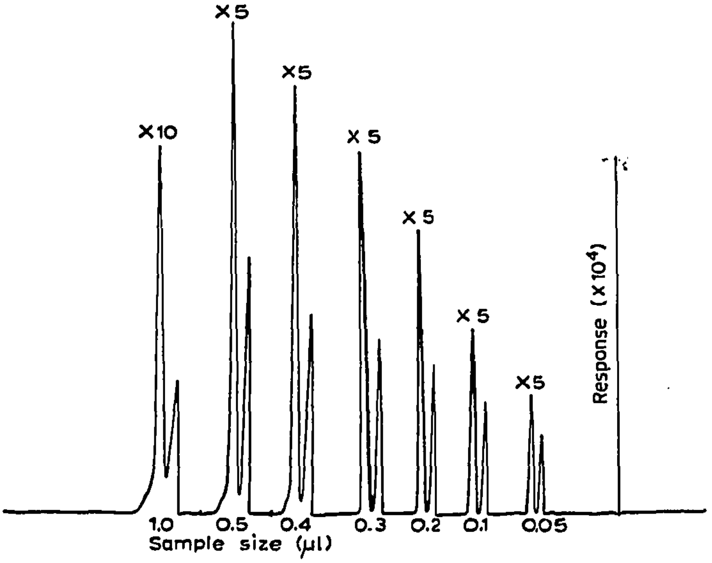

Fig. 2. Effect of sample size on the resolution of methanol and ethanol on Column 4. Temperature 70°; flow-rate 2 ml/min; chart speed 0.5 cm/min.

This represents a useful advantage over conventional wall-coated capillaries, where the liquid film on the wall is much more easily disturbed by large sample charges. The presence of the adsorbent surface on the walls of the PLOT columns also significantly reduces the liquid-phase bleed at high temperatures by comparison with wall-coated columns, a particularly useful property in combined gas chromatographic–mass spectrometric (GC–MS) applications.

An important aim of the present work was to produce columns which were satisfactory for the analysis of highly polar compounds on account of their low residual adsorption activities, especially when non-polar phases were used. In general, there was little difference in this respect between Pyrex and soda-glass columns coated with Carbowax 20M. Perfectly symmetrical peaks were obtained from small amounts of aliphatic alcohols on both types of column. There is evidence that the lack of residual adsorption activity displayed by both silanized and unsilanized Carbowax 20M PLOT columns is due to the operation of an effect recently reported by Aue *et al.*[17]. These workers showed that when diatomite supports were treated with Carbowax 20M at high temperatures and subsequently subjected to exhaustive extraction with solvents, a highly deactivated support was obtained which possessed a nominally monomolecular layer of polymer bonded to the surface of the support. PLOT columns which had received a first coating with Carbowax 20M and had been used for a period at around 200° were found, after removal of the phase by repeated washing with chloroform and methanol, to give small residual k values for selected compounds, which indicated that only about 95% of the phase had been removed. The stripped Pyrex PLOT columns displayed significantly improved peak shapes for polar compounds over those obtained on the columns before the first coating. In addition, PLOT columns of the present type as well as those prepared by the tungsten wire method have consistently shown an improvement in efficiency on receiving a second coating of the liquid phase after removal of the first.

Turning now to apolar PLOT columns, there is little difference between Pyrex and soda-glass when compounds of moderate polarity, such as aldehydes, ketones and esters, are analysed. When coated with silicone elastomer, SE-30, both types give comparable efficiencies and excellent peak shapes. However, for polar compounds the difference is striking and is illustrated by a number of examples. The separation of the C_1–C_4 *n*-alkanols on Columns 2 and 5 is shown in Fig. 3a and b. Baseline separation of the methanol-ethanol pair as well as excellent peak symmetry for all the compounds is achieved on the soda-glass column, while on the Pyrex column methanol and ethanol are almost totally lost and the other alcohols tail badly. Additional vapour-phase silanization of the coated column with HMDS at 180° produced only a marginal improvement in its behaviour towards alcohols. By recoating the column with a 1.5% (w/v) solution of silicone elastomer SE-30 containing 0.075% (w/v) of the surfactant Atpet 80, its performance was improved to some extent, as indicated by Fig. 3c.

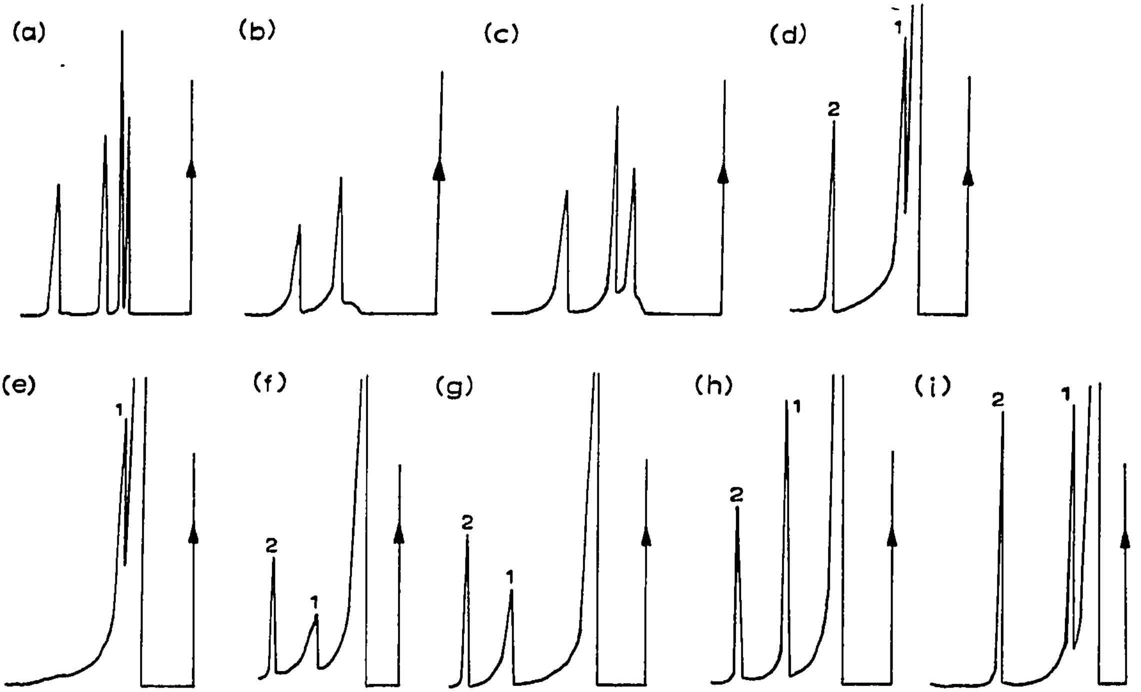

Fig. 3. (a), (b), (c) Analysis of C_1–C_4 *n*-alkanols on Column 5 (SE-30), Column 2 (SE-30), and Column 2 (SE-30 + Atpet 80), respectively. Temperature, 45°; sample, 0.02 μl; chart speed 0.5 cm/min throughout. (d), (e) Analysis of pyridine (1) and aniline (2) on Column 5 (SE-30) and Column 2 (SE-30 + Atpet 80), respectively. Temperature, 90°; sample, 0.2 μl of 0.1% (v/v) solution in diethyl ether. (f), (g), (h) Analysis of *m*-cresol (1) with dodecane (2) on Column 5 (SE-30), Column 2 (SE-30), and Column 2 (SE-30 + Atpet 80), respectively. Temperature, 120°; sample, 0.2 μl of a 0.1% (v/v) solution in diethyl ether. (i) Analysis of 0.1% (v/v) *m*-cresol (2) with heptadecane (1) on Column 3. Temperature, 180°; sample, 0.2 μl.

The performance of Column 5 for basic compounds is also much better than Column 2 (with Atpet 80), as can be seen in Fig. 3d and e. The aniline peak which is perfectly symmetrical on the soda-glass column is not even eluted from the Pyrex column.

Acidic compounds would not be expected to behave well on the somewhat basic soda-glass column, as is shown by the tailing of *m*-cresol in Fig. 3f. However, even here the performance is comparable to that obtained on Column 2 (Fig. 3g), although with added Atpet 80 the latter gives much better recovery with only slight tailing for the phenol (Fig. 3h). It is interesting to note that *m*-cresol is eluted from the Carbowax 20M soda-glass column with complete absence of tailing (Fig. 3i). In all of the above experiments Column 5 received no treatment other than the initial silanization with DMCS.

The reasons for the differences in residual adsorption activity between the two types of PLOT column are not certain, but are most unlikely to arise from the presence of free silanol groups —a well-known cause of tailing— since both types received a similar silanization treatment. A more probable cause is the large boron (B_2O_3) content of the borosilicate powder used in the Pyrex PLOT capillaries which is not present in the soda-glass. Indeed, the observed behaviour is similar to that reported in recent experiments[18] with wall-coated capillaries, where it was shown that previously etched wall-coated borosilicate columns were difficult to deactivate completely, while soda-glass columns etched with dry HCl and then coated with semi-polar silicone phases could be used without further treatment for the analysis of sensitive steroids[19].

On the basis of the excellent results obtained so far it is hoped that further evaluation of soda-glass PLOT columns prepared as described in this paper will show them to be useful columns for the analysis of sensitive high-boiling compounds derived from natural products.

ACKNOWLEDGEMENT

The author gratefully acknowledges generous financial support from the Science Research Council.

REFERENCES

1 I. Halász and C. Horvath, *Anal. Chem.*, 35 (1963) 499.
2 L. S. Ettre, J. E. Purcell and S. D. Norem, *J. Chromatogr. Sci.*, 3 (1965) 181.
3 J. E. Purcell and L. S. Ettre, *J. Chromatogr. Sci.*, 4 (1966) 23.
4 L. S. Ettre, J. E. Purcell and K. Billeb, *J. Chromatogr.*, 24 (1966) 335.
5 L. S. Ettre, J. E. Purcell and K. Billeb, *Separ. Sci.*, 1 (1966) 777.
6 R. Kaiser, *Chromatographia*, 1–2 (1968) 34.
7 J. G. Nikelly, *Anal. Chem.*, 44 (1972) 623, 625.
8 J. G. Nikelly, *Anal. Chem.*, 45 (1973) 2280.
9 M. Blumer, *Anal. Chem.*, 45 (1973) 980.
10 A. L. German, C. D. Pfaffenberger, J-P. Thenot, M. G. Horning and E. C. Horning, *Anal. Chem.*, 45 (1973) 930.
11 D. W. Grant, *J. Gas Chromatogr.*, 6 (1968) 18.
12 D. A. Cronin, *J. Chromatogr.*, 48 (1970) 406.
13 D. H. Desty, J. N. Haresnape and B. H. Whyman, *Anal. Chem.*, 32 (1960) 302.
14 D. A. Cronin, *J. Chromatogr.*, 64 (1972) 25.
15 J. Bouche and M. Verzele, *J. Gas Chromatogr.*, 6 (1968) 501.
16 M. J. E. Golay in D. H. Desty (Editor), *Gas Chromatography 1958*, Butterworths, London, 1958, pp. 36–55.
17 W. A. Aue, C. R. Hastings and S. Kapila, *J. Chromatogr.*, 77 (1973) 299.
18 G. A. F. M. Rutten and J. A. Luyten, *J. Chromatogr.*, 74 (1972) 177.
19 G. Alexander and G. A. F. M. Rutten, *Chromatographia*, 6 (1973) 231.