

CHROM. 4652

THE PREPARATION OF POROUS LAYER OPEN TUBULAR COLUMNS USING POWDERED GLASS AS A BINDING AGENT

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(Received January 28th, 1970)

SUMMARY

The use of finely powdered glass as a binder when mixed with a diatomaceous earth support is described for the preparation of porous layer open tubular (PLOT) capillary columns. The method, which is based on the technique developed by GRANT for making PLOT columns using lithium chloride as a binder, produces columns with similar performance characteristics, but which show considerably less residual activity in the support material than those prepared using the inorganic salt.

INTRODUCTION

The use of porous layer open tubular (PLOT) columns for gas chromatography was first described by HALÁSZ AND HORVATH². These columns, whose characteristics are midway between conventional packed and wall-coated capillary columns, reduce the need to use a multiplicity of liquid phases in the analysis of complex mixtures, and have been the subject of a number of papers³⁻⁷. Columns of this type consist of a length of stainless steel tubing usually 16 m \times 0.5 mm I.D. and have a thin layer of powdered diatomaceous earth deposited on the inside wall. The amount of liquid phase applied is adjusted to the volatility and quantity of the sample to be analysed.

Recently GRANT¹ described the preparation and properties of a new type of glass PLOT column of high permeability, which has a moderately thick layer of support deposited on the inner wall of the capillary tube. The method of preparation requires the use of a glass capillary drawing machine and essentially involves the drawing of a capillary column from a tube packed with a mixture of the support material (*e.g.*, Celite) and some lithium chloride to act as a cementing agent. The capillary is drawn over a narrow tungsten wire, one end of which is inserted through the packing material into the drawing furnace, while the other end is anchored to the machine. In this way the support is affixed to the inner wall of the tube to give a capillary tube with a final orifice of the same diameter as the tungsten wire and a layer thickness of approximately 0.1 mm.

Gas chromatographic columns prepared in this manner have considerable analytical potential in flavour chemistry, *i.e.*, for the separation of complex mixtures of

volatile organic compounds isolated from various foodstuffs. In this type of work the use of columns made of glass instead of metal is to be preferred, since the mixtures under examination frequently contain labile high-boiling compounds, susceptible to catalytic degradation or rearrangement when in contact with hot metal surfaces. A number of PLOT columns were prepared by GRANT's method and coated with various liquid phases. Good performances under temperature-programmed conditions for mixtures of wide boiling range were obtained and lengths of up to 50 m or greater were practicable. An important advantage was the ability to prepare columns with a wide range of capacity ratios. Columns can therefore be tailor-made to specific requirements, e.g. columns with either low phase loadings for rapid analysis of high-boiling compounds or high phase loadings to accept moderately large sample charges in experiments in which emerging peaks are to be trapped.

It was observed that the presence of the lithium chloride binder appeared to produce some undesirable characteristics in the PLOT columns. Some tailing of moderately polar compounds occurred when non-polar and semi-polar phases were used at low loadings. Silylation of the support did not bring about a marked improvement in the effect. With polar phases peak symmetry was very much better, especially for alcohols, although peak widths for the latter were somewhat greater than for less polar compounds of equivalent capacity ratio (k).

Of more importance than the tailing effect was the appearance on columns of low phase loadings of slight but random variations in the retention times of some compounds which occurred with slight changes in the size of sample injected. This effect is a property of gas-solid chromatographic systems, where reproducibility of retention times is critically dependent on the use of very small sample sizes. Since inorganic salts function as efficient separating media in their own right and show high selectivity for many types of compounds^{8,9}, any interaction between the lithium chloride and the solutes could seriously limit the use of published retention data for the liquid phases used.

In this paper a method for the preparation of PLOT columns is described which involves the use of finely powdered glass as a binding agent instead of lithium chloride. The columns produced are comparable to the lithium chloride ones in respect of performance, permeability, and stability, but do not possess the adverse properties of the latter discussed above.

EXPERIMENTAL

Preparation of PLOT columns

The glass powder is prepared from a brand of pyrex (Type B-37*) glass. This material is a borosilicate glass of similar composition to ordinary pyrex, to which it can be joined, but has a softening point of 760°, which is 60° lower than the latter. Its principal use is in tungsten sealing.

Small pieces of B-37 glass are thoroughly ground in a mortar to a fine powder. Particles larger than 200 B.S. mesh are removed by sieving and discarded. The fine powder is then mixed (30% w/w) with acid- and base-washed 120-150 mesh Celite 545. Thorough mixing of the two substances is achieved by vigorous shaking.

* Supplied by: Glass Tubes and Components Ltd., Lemington, Newcastle-upon-Tyne.

A narrow tungsten wire, 0.34 mm in diameter, is fixed to a rigid support about 2 m back from the entrance to the drawing furnace of a DESTY-type¹⁰ capillary drawing machine. The length of the wire is adjusted so that it extends a distance of 15–25 mm past the exit of the drawing furnace. A small funnel is then attached to a pyrex tube, 9 mm O.D. × 3 mm I.D., which is plugged or sealed at the other end, and the wire inserted down the length of the tube almost up to the plug. The tube is filled with the glass–Celite mixture through the funnel using gentle tapping to obtain a packing density of 3 g/m. The packed tube is then laid horizontally on the feed bed of the drawing machine with the plugged end extending about 50 mm past the exit of the hot furnace. The tungsten wire is carefully pulled back until its end is just outside the entrance of the furnace. The machine which possesses a drawing ratio of 50:1 is started to produce initially a completely packed capillary tube. The tube quickly attains a constant diameter (0.5 mm) and after a short period the tungsten wire is picked up and drawn by the capillary a distance of 15–25 mm past the furnace exit. Thus, the tube and packing material are drawn over the wire to leave a final orifice of the same diameter as the tungsten wire. It is very important that the portion of the tungsten wire within the furnace is thoroughly cleaned (preferably electrolytically) before use to remove any oxide film from the surface. Such a film can occasionally cause the wire to stick to the packing impeding the movement of the capillary and resulting in a widening of the diameter of the capillary drawn.

To coat the column, it is first filled with a solution of the liquid phase in a suitable solvent under a pressure of 10–15 kg/cm² of nitrogen, depending on its length. The solution is then ejected, using initially the same pressure. As the column empties the rate of liquid flow gradually slows down, due to the formation of a number of vapour-locked liquid bubbles in the emptied portion, and it is desirable to increase the pressure somewhat to maintain the flow of liquid from the column exit reasonably constant. The pressure is maintained until all excess of solvent is removed. With low-boiling solvents, like methylene chloride and ether, the coating procedure takes 1½–2 h. The actual rate of coating and uniformity of liquid flow have, within reasonable limits, very little effect on the amount of liquid phase laid down or on the efficiency of the final PLOT column.

Testing of columns was carried out in a Pye Model 104 flame ionisation gas chromatograph, equipped with a heated injection system. A special injection block with a very low dead volume was constructed and the column connected to this by means of a short length of thin-wall narrow-bore PTFE tubing. Nitrogen carrier gas was used with operating pressures in the range of 2–5 kg/cm² for column lengths of up to 20 m.

RESULTS AND DISCUSSION

The overall performance characteristics of the PLOT columns prepared as described were quite similar to those prepared using lithium chloride as the binding agent.

The permeability constant was 136×10^{-7} cm² and was readily reproduced from column to column. This value, which is approximately the same as that reported by GRANT for PLOT columns prepared from 150–200 mesh Celite with 10% lithium chloride binder, is very much better than the values for ordinary packed and packed

capillary columns¹¹, whose specific permeability coefficients are about $1 \times 10^{-7} \text{ cm}^2$ and $6\text{--}11 \times 10^{-7} \text{ cm}^2$, respectively. It is much closer to the values for open tubular columns, which range from about $30 \times 10^{-7} \text{ cm}^2$ (0.1 mm I.D.) to $780 \times 10^{-7} \text{ cm}^2$ (0.5 mm I.D.). The stability of the layer of support on the wall was demonstrated by the permeability remaining unchanged when a 20 m length of column was uncoated and recoated with liquid phase six consecutive times.

It might be expected that the relatively large amount of glass binder used in the preparation of these columns would seriously reduce the porosity of the solid support for liquid phase by forming a thin film of glass over its surface area. This effect would be manifested in a marked deterioration in efficiency with increased loading of stationary phase and possibly with short column life at high operating temperatures due to globule formation. While there is obviously some reduction in the support porosity in this manner, the performance of the columns does not appear to be greatly affected.

The effect of liquid phase loading on column performance was measured on a 20 m column coated with Carbowax 20M, operated at 120° , and using a series of methyl ketones as test substances. The shape of the HETP *versus* gas velocity curve for 2-heptanone for a range of k values is shown in Fig. 1. The plots are qualitatively similar

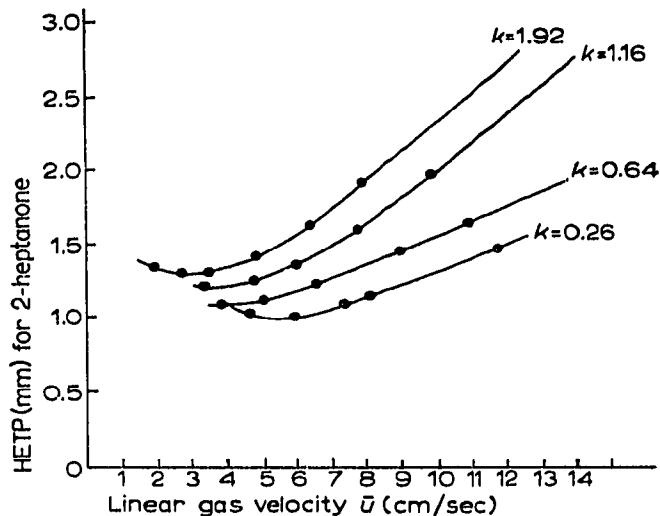


Fig. 1. Effect of liquid phase loading on column efficiency.

to those predicted by the Golay equation, the minima occurring at lower \bar{u} values and becoming sharper as k increases, and thus emphasize the need for low gas velocities when columns are prepared for high k values and loading capacity. The HETP minimum is not greatly affected by change in capacity ratio. It increases from about 1 to 1.3 mm for a sevenfold increase in k value, giving theoretical plates in the range of 18,000–14,000.

A linear relationship exists between k and the concentration of liquid phase in the coating solution, which indicates how columns can readily be prepared with specified capacity ratios. A Carbowax 20M column coated with a 4% w/v solution has shown no signs of deterioration after two months of extensive use.

A comparison of two 20 m PLOT columns, one prepared using 120–150 mesh Celite with 10% w/w lithium chloride binder and the other with B-37 glass binder is shown in Fig. 2, where the k value is plotted against the HETP for a series of n -alcohols

up to nonanol. The columns were coated with a 0.9% w/v solution of Carbowax 20M in methylene chloride and operated under the same conditions. While the HETP *versus* \bar{n} plots for 2-heptanone at 120° were almost identical for both columns, the respective k values for lithium chloride and B-37 columns being 0.54 and 0.53, the superior performance of the latter for the alcohol mixture is evident from Fig. 2.

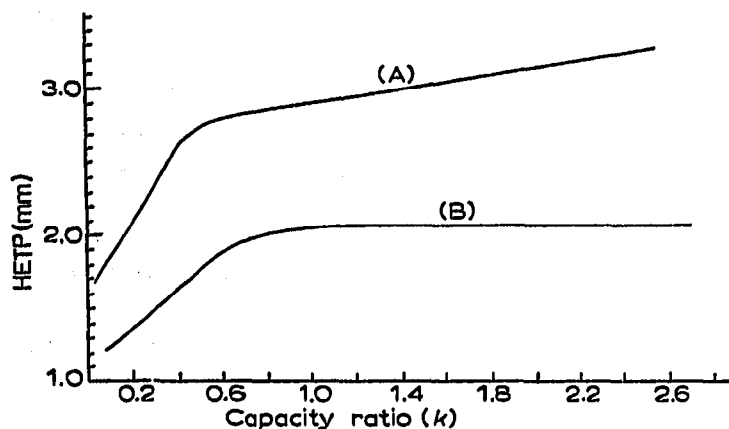


Fig. 2. Plot of k values against efficiency (HETP) for C_2-C_{10} n -alcohols on (A) 20 m lithium chloride PLOT column and (B) 20-m B-37 glass PLOT column. Temperature, 130°, \bar{n} , 7.5 cm/sec for both columns.

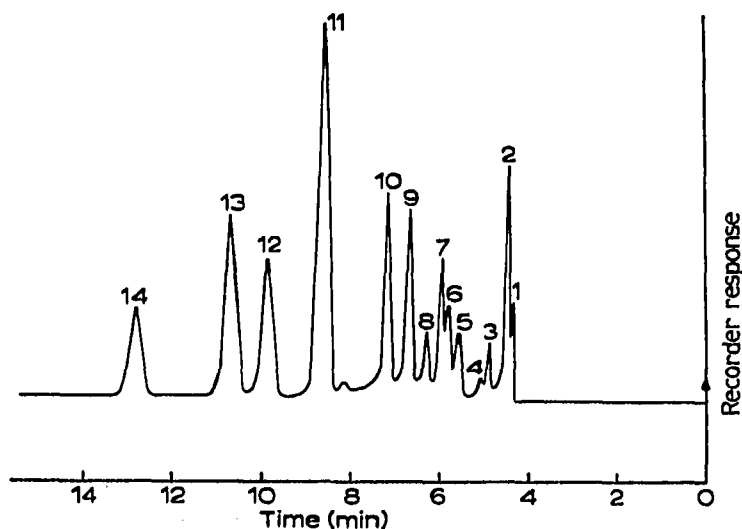


Fig. 3. Separation of aliphatic alcohols. Column, 20 m PLOT coated with Carbowax 20M. Temperature, 90°. Number of theoretical plates (n -hexanol), 9300. 1 = Methanol; 2 = ethanol; 3 = *tert.*-butanol; 4 = n -propanol; 5 = isobutanol; 6 = 3-pentanol; 7 = 2-pentanol; 8 = n -butanol; 9 = 3-buten-1-ol; 10 = 2-methylbut-3-en-2-ol; 11 = n -pentanol; 12 = 4-heptanol; 13 = isohexanol; 14 = n -hexanol.

Fig. 3 shows the separation of a mixture of aliphatic alcohols on a 20 m column coated with 0.68% w/v solution of Carbowax 20M. The complete absence of support activity is shown by the excellent shapes of the peaks. No treatment of the support apart from acid and base washing was carried out.

The PLOT columns described in this paper which have 30% by weight of B-37 glass powder in the porous layer represent the best compromise achieved to date be-

tween efficiency on the one hand and permeability on the other. The effect on these properties of using different types of glass as a binding agent as well as the effect of varying the particle size of the support material is receiving further study.

ACKNOWLEDGEMENTS

Financial support from the Science Research Council for this work is gratefully acknowledged as also are facilities for use of the capillary drawing machine of the School of Chemistry in this University.

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