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Note

The preparation of stable glass capillary columns coated with Carbowax 20M

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The rapidly increasing use of wall-coated glass capillary columns in the analysis of labile compounds of biological origin has, in recent years, stimulated much work aimed at improving the methods of producing stable films of various stationary phases on borosilicate glass surfaces. Non-polar phases of the liquid paraffin and polydimethylsiloxane type, which exhibit low contact angles, spread efficiently on high-energy glass surfaces; methods of preparing non-polar columns of high resolving power and excellent long-term stability have been described for the analysis of small amounts of labile high-boiling substances, *e.g.*, steroids[1]. More polar phases do not give stable films on untreated glass surfaces, and some modification of the surface is necessary to increase its specific surface area and hence to lower the contact angle of the wetting liquid. Novotný and Zlatkis[2] have reviewed the various methods which have been devised to produce suitable surfaces for coating. The most successful of these, *viz.*, carbonization of the inner capillary wall[3] and gas phase etching[4,5], have allowed the preparation of good columns from a number of phases of moderate polarity.

Much less success has been achieved so far in preparing stable films of phases of high polarity such as the versatile general purpose polyglycol, Carbowax 20M. In a recent paper[6], Novotný and Grohmann, elaborating an earlier postulate[2] that chemical similarities between the surface and the liquid should greatly enhance film stability, have described the use of a new reagent for silylating the free silanol groups on glass surfaces by means of which a bonded monolayer is produced. The latter also possesses reactive benzyl chloride terminal groups which may be modified chemically as desired to produce hydroxy, ester, or cyano groups, on which appropriate phases may be deposited. The authors reported very promising preliminary results for a number of polar phases.

An alternative method of producing a chemically compatible surface, on which to coat a polar phase like Carbowax 20M, stemmed from an interesting discovery by Aue *et al.*[7]. These workers found that when Carbowax 20M was coated on a diatomaceous earth support, such as Chromosorb W, heat treated at 280°, and the packing exhaustively extracted with boiling methanol to remove the phase, a highly efficient well-deactivated packing with very low bleed characteristics was produced. This material was considered to have a non-extractable, permanently bonded layer (nominally monomolecular) of Carbowax 20M in contact with the support surface. The layer was regarded as a "stretched-out" long polymer chain exhibiting optimal physical bonding between the silicic surface and the polymer, by means of hydrogen

and various types of Van der Waals bonds. While some form of chemical bond, *e.g.* condensation between surface silanol groups and terminal hydroxyl groups of the polymer, cannot be entirely ruled out for Carbowax 20M, such bonds are not expected to withstand the vigorous extraction procedure with boiling methanol.

Although glass surfaces have a very much smaller specific surface area on which to deposit an organic liquid than have diatomite supports, they resemble the latter (especially after treatment with concentrated acids) in possessing a large number of free silanol groups. The possibility of modifying glass surfaces by heat treatment with Carbowax 20 M so as to improve their subsequent coating properties for this liquid seemed worthy of examination. This note describes the preparation and some properties of stable Carbowax 20M wall-coated glass capillaries using such an approach.

EXPERIMENTAL

Glass capillaries (0.5 mm I.D.) were drawn from Pyrex tubing (7 mm O.D., 4 mm I.D.), which had been thoroughly cleaned by washing successively with 10% Decon 90 (Decon Labs. Ltd, Portslade, Brighton, Great Britain) detergent, distilled water, and acetone. A 20-m capillary was filled with concentrated (10 *N*) HCl and let stand for 24 h. After removal of the acid, the column was washed with distilled water followed by dry acetone. A 2% w/v solution of Carbowax 20M in dichloromethane (5 ml) was then passed through the column, and the column was subsequently dried in a flow of nitrogen. While still full of nitrogen, the ends were sealed off in a microburner flame and the column was placed in an oven at 280° for 16 h. After this treatment, the coating was removed by washing the column successively with dichloromethane (15 ml) and methanol (10 ml). It was then coated with a solution of Carbowax 20M (5 mg/ml) in dichloromethane according to the static method of Verzele *et al.*[8,9].

Analyses were carried out using a Pye 104 temperature-programmed gas chromatograph equipped with a flame ionisation detector. Column connections were made by means of thin-wall polytetrafluoroethylene (PTFE) tubing via a 21-gauge hypodermic needle sealed into a low volume (6 mm O.D., 1 mm I.D.) glass injection block by means of epoxy resin. The use of a sample splitter was avoided in the evaluation experiments by injecting vapour samples of the test substances with a 1 μl hypodermic syringe.

Columns prepared by the method described gave excellent performances in respect of both separating power and long-term stability of the polymer film during temperature programming. A typical plot of plate height *versus* gas velocity for 2-undecanone ($k = 4.3$) at 120° on a 20 m column is shown in Fig. 1. The minimum plate height was approximately 0.7 mm, *i.e.*, 1430 plates per metre. The plot is relatively flat even using nitrogen as the carrier gas. The efficiency of this column has remained substantially the same after nine months of extensive use, with frequent programming up to 190°. This may be seen in Fig. 2 which shows a recent separation of a mixture of low-boiling aliphatic alcohols containing a number of compounds which are normally rather difficult to separate on Carbowax 20M. The baseline separation of methanol and ethanol, as well as the partial resolution of isopropanol from ethanol, is especially noteworthy, since it was achieved on a relatively short

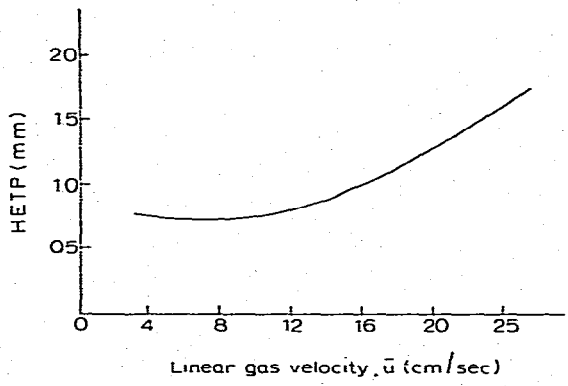

Fig. 1. Efficiency plot for Carbowax 20M coated glass capillary (20 m × 0.5 mm I.D.): k = 4.3 (2-undecanone); temperature, 120°.

column with substances having low capacity ratios (k), for which much longer capillaries are normally required. The resolution of these three compounds is superior to that reported for a 46 m × 0.25 mm copper capillary coated with Carbowax 1540 (ref. 10), a phase with separating characteristics similar to Carbowax 20M, but which affords better resolution for lower-boiling substances; the resolution shown in Fig. 2 is in fact similar to that obtained on a 15 m × 0.5 mm SCOT column coated with Carbowax 1540 (ref. 10).

While the static method of coating undoubtedly produces better columns, the process is rather slow, usually taking a number of days to complete. Columns of

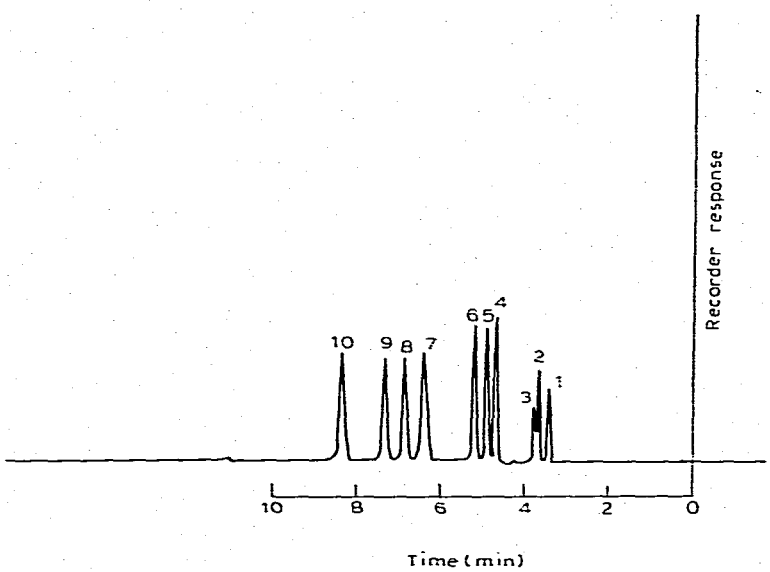

Fig. 2. Separation of low-boiling aliphatic alcohols on an "aged" Carbowax 20M capillary column (20 m × 0.5 mm I.D.); temperature, 65°; nitrogen flow-rate, 2 ml/min. Peak identity: (1) methanol, (2) ethanol, (3) isopropanol, (4) *tert.*-amyl alcohol, (5) *n*-propanol, (6) *sec.*-butanol, (7) isobutanol, (8) 3-pentanol, (9) 2-pentanol, (10) *n*-butanol.

somewhat lower (though still quite good) performance may be obtained in less than a day by the conventional dynamic (plug) method of coating[11].

Although no attempt has been made to study the nature of the glass wall after heat treatment with Carbowax 20M, there is some evidence to indicate that it had undergone a change somewhat similar to that observed for the heat-treated diatomite support. It has been pointed out[6] that for chemically treated glass the temperature dependence of *surface* critical surface tension (ψ_c) and of *liquid* surface tension (ψ) are comparable only if the surface and liquid are chemically similar. The long term stability of the coated column, especially under temperature-programmed conditions, would seem to indicate a close similarity between surface and liquid, a decrease in ψ_c with increasing temperature being matched by a corresponding decrease in ψ for the liquid. It was also observed that when an acid-treated glass column was coated with a thin film of Carbowax 20M and evaluated before the heat treatment, small quantities of injected alcohols produced peaks with considerable tailing. Evaluation of the column directly after heating indicated not only improved resolution but also total absence of tailing for the alcohols. Finally, examination by microscope of the film in an aged column showed it to be composed of large numbers of tiny, evenly spaced droplets, but with no signs of aggregation into larger pools, an effect usually observed when a coated film is beginning to break up.

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