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Note

Preparation of stable glass capillary columns with polar stationary phases

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Capillary columns have made gas chromatography the most useful tool available for the analysis of complex mixtures. The advantages of faster analysis at lower temperatures with improved resolution are well known; equally well known are the disadvantages[1].

Since many compounds are decomposed by or absorbed on metal surfaces, an all-glass system is the most logical choice from available materials for analysing mixtures that may contain compounds of limited stability[2]. The main problem encountered in the preparation of efficient glass capillary columns is obtaining an even, stable coat of stationary phase throughout the glass capillary. This can be done with such non-polar phases as squalane and Apiezon[2–4], but most commonly used stationary phases do not "wet" an untreated glass surface and therefore condense in tiny droplets rather than spread into a uniform layer[2,5]. This reduces the column efficiency often to a point at which capillary column gas chromatography is no longer advantageous.

Several methods for treating the glass surface to overcome these difficulties have been presented[2]. These include treating the surface initially with a layer of carbon[4,6] or an organic film[6,7], changing the contact angle of the surface by chemical corrosion[5,8–13], forming functionally orientated organic monolayers on the surface[6,11,14] or chemically modifying the reactive surface[6,11–13,15,16]. While satisfactory columns have been prepared by these methods, the procedures are often tedious and the possibility of obtaining two identical columns is remote.

Recently, another method of treating the surface of glass capillary tubing was proposed by German and Horning[17]; they prepared an efficient SE-30 column (30 m × 0.3 mm) and suggested that longer columns with other phases should be possible. However, we encountered several difficulties when we attempted to adapt their method to the preparation of capillaries (150 m × 0.5 mm) coated with phases having a wide range of polarities. We were able to prepare such capillaries, nevertheless, by using the modified procedure described here.

EXPERIMENTAL

Glass capillary columns (0.5 mm × 150 m) were drawn with a Hupe and Busch apparatus (Karlsruhe, G.F.R.) and placed on a Plexiglas even-spaced vertical

support rack similar to that previously described for the optimized dynamic coating method[18]. A 20-ml reservoir was connected to the top of the column with heat-shrink PTFE tubing. Successive plugs of hexane, chloroform, acetone, water, concentrated nitric acid, water, concentrated ammonia, water, methanol and acetone were forced through the column under pressure (20–40 p.s.i.) of nitrogen. The column was then thoroughly dried with nitrogen, treated with 10-ml plugs of toluene, 5% dichlorodimethylsilane solution in toluene and toluene, and again dried with nitrogen.

At this point, an additional 10 to 20 m of capillary tubing was connected to the end of the column with heat-shrink PTFE tubing. Since, under constant pressure, the velocity of the coating plug increases as the solution leaves the column, this trailing tubing was necessary to maintain a reasonably constant flow and thus give an even coating of stationary phase throughout the entire length of the column.

The column coating was accomplished in two stages. A solution of 40 mg of a surface-active material, Igepol CO-880 (ref. 19) in 10 ml of carbon tetrachloride was added to 200 mg of Silanox 101 (silanized silica, particle diameter 6–10 μm; Cabot Corporation, Boston, Mass., U.S.A.), and a stable suspension of the Silanox was prepared by placing the mixture in an ultrasonic bath for several minutes[20]. (To avoid possible blocking of the column, care must be exercised to ensure that suspension is completely formed, *i.e.*, there must be no visible particles or cloudiness in the mixture.) Igepol served two purposes: to assist in elimination of possible secondary adsorption effects[19,21], and to provide a light film to hold the Silanox particles to the glass surface. Immediately after a plug of carbon tetrachloride, the suspension was passed through the column under pressure (10–20 p.s.i.) of nitrogen; the column was then dried in a stream of nitrogen.

A 3% solution of the stationary phase in 10 ml of an appropriate solvent (carbon tetrachloride, chloroform, toluene and acetone have been successfully used) was then forced through the column under pressure (10 p.s.i.) of nitrogen. This allows the stationary phase solution to be prepared with the recommended solvents and eliminates solubility problems that might occur in the solvents necessary for suspension of Silanox. The column is finally thoroughly dried with nitrogen and mounted permanently in a steel-mesh cage for conditioning and use. Permanent connections from the column to the outside of the cage were made by means of glass-lined stainless-steel tubing and heat-shrink PTFE connections.

DISCUSSION

The columns prepared by this method were coated with phases chosen from the list of twelve preferred by Leary and his co-workers[22]; so far, nine columns from this list have been prepared. They appear to be stable and, in fact, seem to improve with use. Calculations of the numbers of theoretical plates have yielded values to several hundred thousand. For example, a GE XE-60 column yielded a total of 437,000 theoretical plates, and a conservative measurement of the effective number of theoretical plates was 165,000. However, the calculated number of theoretical plates may not be a true indication of the efficiency of a column, as many factors (*e.g.*, size of injection, time of residence of the test compound in the column and the dead volume of the system) significantly influence such calculations. The true efficiency can only be evaluated through practical use, and we have found these

columns to be extremely useful in our work on the analysis of complex natural flavour extracts.

The method is not difficult to follow and, with reasonable care, a stable and efficient column can be ready for use in one week.

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