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HIGH RESOLUTION PARTITION CAPILLARY COLUMNS

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SUMMARY

Various procedures to obtain high resolution glass capillary columns are described. By roughening the glass surface either with a layer of carbon or with polymerized material, a stationary phase of any polarity can be successfully coated. Results obtained with Carbowax, trimer acid and squalane columns are reported; the separation of polar and non-polar compounds from their deuterated homologs ($C_6H_5CD_3$–$C_6H_5CHD_2$–$C_6H_5CH_2D$–C_7H_8; C_2H_6SO–C_2D_6SO) is shown.

INTRODUCTION

It has been reported[1] that high resolution partition capillary columns can be obtained if the liquid phase is uniformly distributed on the wall of glass capillaries. A number of factors affect the spreading of the stationary phase, one of the more important being the wettability of the glass wall.

If ordinary glass tubing is used for the manufacture of the glass capillary a homogeneous and uniform layer is only obtained when the stationary phase has a low surface tension; this characteristic has, so far, prevented the use of a large number of stationary phases.

To overcome this limitation and to be able to use liquids with a high surface energy two techniques have been proposed: the use of surface-active agents which can reduce the surface tension of the liquid phase; and the roughening of the walls of the capillary to decrease the contact angle between the liquid and the glass. The former technique is of limited use as the properties of the stationary phase and its working temperature range may be strongly affected by the addition of surface active agents; the latter procedure can be implemented by building up either a thin layer of carbon or of a polymeric material such as polybutadiene or polytrifluorochloroethylene on the walls of the capillary.

This procedure increases the roughness of the glass surface, eliminates the active sites of the glass and makes the spreading easier.

This work shows that by use of the above procedures columns of great efficiency with any stationary phase can be obtained; as far as polarity is concerned there is no limitation to their application. Experimental results obtained on columns prepared by various procedures are discussed.

SQUALANE COLUMNS

Squalane has a low surface tension (29.95 dynes/cm) and its coating on capillaries is quite smooth providing the walls have been thoroughly cleaned. A uniform layer is obtained by allowing an ether solution of squalane to flow through the capillary. It is easy to obtain high resolution columns of a suitable length. As an example a 200 m column has an efficiency of 250,000 theoretical plates when *n*-heptane is chromatographed and the height equivalent to a theoretical plate is less than 0.1 cm. Such columns can be successfully employed for the analysis of non-polar mixtures.

One application which is related to the high efficiency of these columns is the separation of isotopic molecules such as hydrocarbons from their deuterated homologs. Fig. 1 shows the separation of a mixture of $C_6H_5CD_3$–$C_6H_5CHD_2$–$C_6H_5CH_2D$–

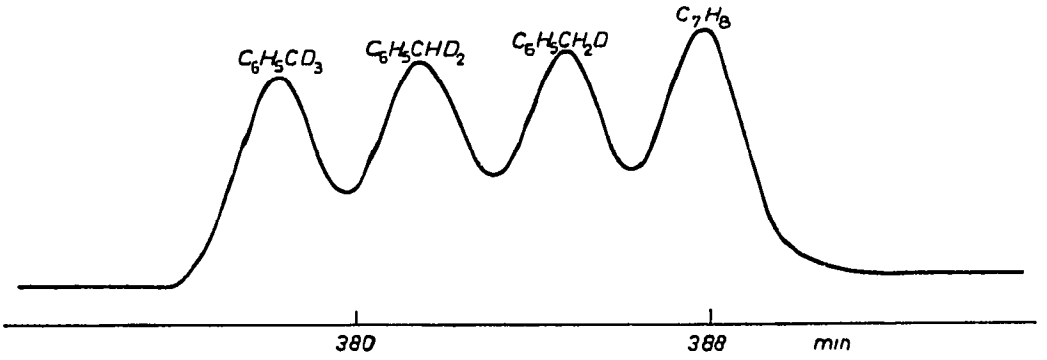

Fig. 1. Gas chromatogram of a mixture of toluene and deuterotoluenes on a 200 m squalane column. Temperature: 16°. Inlet pressure (nitrogen): 1.05 kg/cm². Flow rate: 0.57 ml/min.

C_7H_8 carried out at 16°. A reverse isotopic effect is observed; the heavier species being eluted before the lighter ones. It is worth noting that the mass difference among the various species, is about 1%.

TRIMER ACID COLUMNS

Trimer acid, a C_{54} tribasic acid with about 10% C_{36} dibasic acid, can be considered as a stationary phase of medium polarity as it has been found to be more polar than Apiezon and less polar than Emulphor or Triton X (ref. 2). This phase has a large working temperature range (60–200°) and has a number of interesting features as it yields symmetrical peaks with free acids, carbonyl compounds and alcohols.

This liquid phase does not coat the glass walls under ordinary conditions but a uniform layer of trimer acid can be obtained if the capillary is precoated with a carbon layer obtained by pyrolysis of methylene chloride. A methylene chloride–trimer acid solution is then passed through the column. A 77 m trimer acid capillary column has an efficiency of 130,000 theoretical plates using *n*-tetradecane as reference.

Being a stationary phase of medium polarity, it seems to be the most efficient fractionation medium for the analysis of complex mixtures where components with a wide range of polarity are present as, for example, in essential oils. By operating columns of this type under alternatively isothermal and programmed temperature conditions, it has been found that many natural essential oils consist of a very large

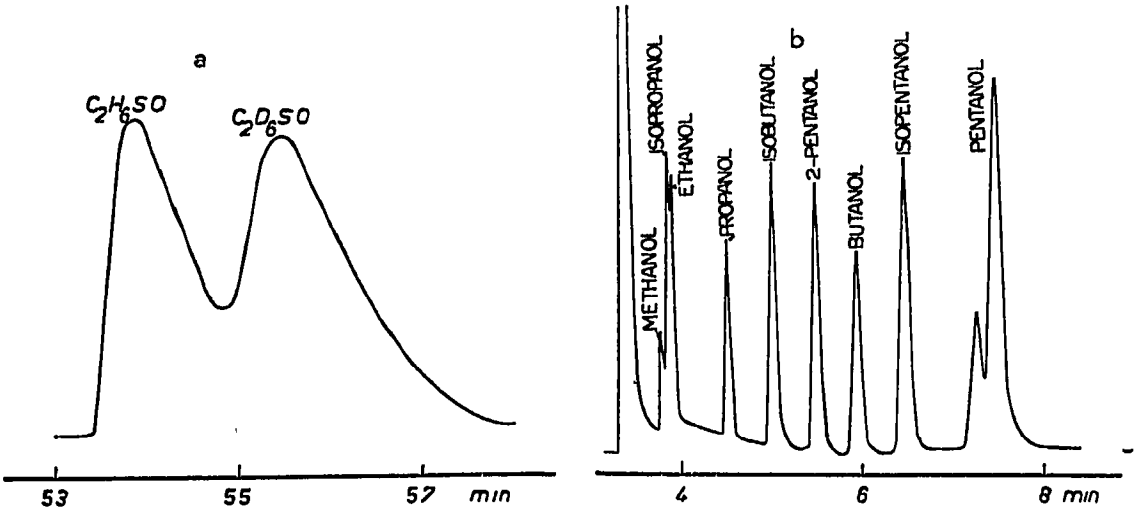

Fig. 2. (a) Separation of dimethylsulfoxide and deuterodimethylsulfoxide on a 28 m Carbowax 1540 glass capillary column. Temperature: 70°. Inlet pressure (nitrogen): 0.5 kg/cm². Flow rate: 1.0 ml/min. (b) Separation of a mixture of alcohols on a 28 m Carbowax 1540 glass capillary column. Temperature: 50°. Inlet pressure: 0.5 kg/cm². Flow rate: 1.0 ml/min.

number of components (about 250 for agrume oils and 400 for coffee oils)[3]. These columns would seem to be very useful for the study and the evaluation of essential oils and perfumes.

CARBOWAX COLUMNS

The Carbowaxes are more polar stationary phases and the preparation of uniform layers of them on the glass walls of the capillary can be realized by roughening the surface with polytrifluorochloroethylene or polybutadiene according to GROB[4]. The capillary, after being coated with polymeric material, is treated with a methanol solution of the chosen Carbowax; columns of great efficiency are obtained. The high resolution of these columns permits their use for the separation of polar isotopic molecules. As an example the separation of dimethyl sulfoxide from deuterium dimethylsulfoxide is shown in Fig. 2(a). The separation of a mixture of alcohols is shown in Fig. 2(b). In both cases Carbowax 1540 was used to coat the 28 m column. A temperature of 70° was used for the first separation and 50° for the second.

CONCLUSIONS

Glass capillary column technology has been developed and by means of the procedures described it is shown that stationary phases of any polarity can be successfully used for coating and yield columns of high efficiency. The ability to prepare high resolution glass capillary columns provided a very useful tool for the study of very complex mixtures, for isotopic separations and for separations of geometrical and positional isomers.

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