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ADSORPTION CHROMATOGRAPHY CAPILLARY COLUMNS

I. RUBIDIUM CHLORIDE

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SUMMARY

A new approach to the preparation of adsorption capillary columns for gas chromatography is described. Soda glass capillary tubing is treated with dilute ammonium hydroxide at elevated temperatures to generate a silica layer. Deactivation of this layer of silica is then achieved by coating with rubidium chloride to yield columns of controlled activity and high thermal stability. Separations of polynuclear aromatic hydrocarbons and of *n*-alkanes have been achieved on these gas-solid columns. The importance of column length and of rubidium chloride concentration is discussed.

INTRODUCTION

The potential of capillary gas chromatography has still to be fully exploited but rapid advancement awaits the development of a simple, reliable and efficient column technology. Many different materials including plastics, metals and glass have been successfully used for the preparation of capillary columns¹. Of the materials readily available for the preparation of such columns glass appears best suited to the purpose because the catalytic activity and absorptivity are low.

To achieve high separation efficiency with a capillary column a homogeneous thin film must be applied to the column wall. In recent years the importance of pre-treating the glass surface has become generally recognised²⁻⁵. Permanent spreading of a liquid over a solid surface may be achieved by two main mechanisms. A liquid film may be stabilised on a smooth surface by intermolecular forces that attract the liquid to the solid. This mechanism applies when untreated glass is coated with an apolar phase. The second stabilising factor is the so-called micro-roughness. Both factors may operate in combination⁶ but the first, *i.e.* wetting mechanism, produces higher separation efficiencies as a consequence of forming a more homogeneous

liquid film⁵. In contrast, polar liquids spread almost exclusively on roughened surfaces where the necessary degree of roughening produces a corresponding loss of film homogeneity with concomitant loss of column efficiency.

When considering their suitability for general application the surface roughening procedures may be divided into two groups. The first group produces micro-roughness on the glass surface by etching or via the growth of crystals or both. The second group introduces small particles onto the walls of the column that act in the same way as a roughened surface. Surface roughening by etching has been achieved, using gaseous HCl⁷, gaseous HF⁸, or both⁹. Particle introduction may be routinely performed for barium carbonate^{10,11} and silica¹².

Surface preparation, surface deactivation and the coating of stationary liquid phases are all part of the complicated technology of capillary column preparation. However, the disadvantages presented by the use of a liquid stationary phase may be avoided if gas-solid chromatography (GSC) is employed. Although at present the resolution offered by GSC is inferior to that of gas-liquid chromatography (GLC), the high thermal stability of these columns allows the elution of compounds with low volatility. Such compounds as dibenz[*ah*]anthracene and dibenzo[*ae*]fluoranthene (found in tobacco smoke), are difficult to chromatograph routinely and reliably on conventional GLC columns, but they are readily eluted from GSC columns. Interest in GSC has grown rapidly since Scott¹³ demonstrated that elution chromatograms may be obtained which are comparable with those obtainable by GLC. The development of GSC is related to a greater control of the homogeneity and specificity of molecular adsorbents. This has been largely achieved through advances in the synthesis of adsorbents of high chemical purity whose nature, specific surface area and degrees of porosity can be controlled by the chemical modification of their surfaces^{14,15}.

We now report the preparation of GSC columns containing a porous silica layer which has been modified by adsorption of rubidium chloride. Such columns show promise for the separation of alkanes and more especially polynuclear aromatic hydrocarbons (PAHs).

EXPERIMENTAL

General reagents

Ammonium hydroxide, sodium hydroxide, hydrochloric acid and sulphuric acid were AnalaR grade. All organic solvents were twice distilled.

Stationary phases

Carbowax 20M and SE-52 were purchased from Jones Chromatography, Llanbradach, Great Britain; OV-17 from Phase Separations, Chester, Great Britain and rubidium chloride (Specpure) from Johnson-Mathey Chemicals, Reading, Great Britain.

Standard compounds

All polynuclear aromatic compounds were purified by recrystallisation before use. The C₂₂-C₃₀ alkane mixture was a gift from ICI, Runcorn, Great Britain.

Apparatus

Either a Pye Series 104 gas chromatograph (Pye Unicam, Cambridge, Great Britain) or a Fractovap Series 2150 gas chromatograph (Carlo Erba, Milan, Italy) was used. Both instruments were equipped with flame-ionisation detectors. The Pye Series 104 instrument was specially modified for use with capillary columns by addition of a variable split inlet system (Model GISS-4BK; SGE, London, Great Britain). The septum was cooled by an airflow directed onto the upper surface of the septum cap. A considerable increase in useful septum life was achieved in this manner. Column eluates were made up to 25–30 ml min⁻¹ with nitrogen immediately prior to detection. All connections were made with graphlock ferrules (SGE).

Preparation of capillary tubing

Typically a glass capillary column was filled with NH₄OH solution (14–17%). The ends were sealed and the column heated (180°C) for 12–14 h. Capillaries were then opened and excess solution removed. Subsequent treatment was: washing with water followed by acetone and then drying in air. Columns were then heated to 190°C at 10°C min⁻¹ under a stream of nitrogen and then held at 190°C overnight.

Adsorption column coating

Prior to coating, the etched columns were activated (50°C to 360°C; 10°C min⁻¹, nitrogen purge). The appropriate RbCl solution was forced through the capillary by vacuum until the tube was completely full. The column was then left for *ca.* 5 min before excess solution was removed under vacuum and the column “dried off” under a stream of dry nitrogen. The following temperature programme and a nitrogen stream was used to condition columns: 100°C hold 1 min then 10°C min⁻¹ to 400°C hold 30 min.

RESULTS AND DISCUSSION

In this investigation the idea of salt-modified supports, so successfully applied with packed columns¹⁶, has been extended to capillary columns. It has been reported^{17,18} that glass capillaries etched with hydroxide solutions behave as adsorption columns. This treatment corrodes the soda glass and leaves a surface film which differs considerably from the original material. Such films, which consist mainly of finely dispersed silica, have a considerable adsorbing power. Thus the hydroxide etching is thought to modify the glass surface by increasing the internal surface area of the wall of the capillary and by building up a porous active layer. The thickness of the porous layer varies, according to the severity of the alkali treatment. Typically a 14–17% NH₄OH solution, maintained at 160–180°C for 12–14 h yielded an evenly etched column. Use of higher concentrations, higher temperatures or longer reaction times usually resulted in excessive reaction with consequent blocking of the column. Incidentally, the use of more dilute solutions (*ca.* 9–12%) for shorter times at lower temperatures yielded nicely etched columns which could be readily coated with phases such as SE-52 and OV-17 to give columns which are essentially a liquid-impregnated porous-layer open-tubular column (PLOT column). Typical efficiencies of *ca.* 1000 plates per metre¹⁹ were measured for this type of column.

The high degree of hydroxylation of the surface of this etched glass and its

microporous structure make this material quite unsuitable for chromatographic purposes, unless some deactivation takes place. The forces contributing to adsorption range from weak van der Waals attractions to strong chemical bonds. One of these forces may be termed hydrogen bonding. On the surface of the silica two types of hydrogen bonding may exist. First there is the silanol (Si-OH) group, which acts as a proton donor, and second there is the siloxane (-Si-O-Si-) grouping, which can act as a proton acceptor. However, the acidic hydroxyl group is much more effective in forming hydrogen bonds than the siloxane group.

Compounds which form strong hydrogen bonds display considerable "tailing" when chromatographed on active siliceous supports. It has been shown²⁰ that the elimination or reduction of adsorption may be carried out by (a) saturation of the adsorption sites with a liquid phase, (b) removal of the sites by reaction of the silanol group, (c) removal of the sites by washing with acid, or (d) coating the support with a solid material. This last possibility offers the triple advantages of permanence, thermal stability and completeness. From the different salts which could be used rubidium chloride was chosen because of the excellent results that it has given when used in packed columns¹⁶.

The exact nature of this salt-modified surface has not been established but a plausible model is one in which the original surface has been covered by one or more layers of the modifying agent. The modified surface will be of smaller surface area than the original due to a partial filling of the pores, and will be of considerably lower activity because the silanol groups are masked by the salt layer. The amount of modifier deposited on the surface of the glass is thus of fundamental importance.

The effect of variation of rubidium chloride content of column surfaces is depicted in Fig. 1. Rubidium chloride content was varied by coating columns with solutions of different concentrations. The consequence with respect to column performance was evaluated using a standard solution of PAHs (Table I). The chromatographic traces in Fig. 1a and b were obtained by injecting this mixture onto a blank column before (Fig. 1a) and after (Fig. 1b) etching with NH_4OH . The activity of the etched surface is illustrated by the long "tail" on the single peak which presumably contains all nine components together with the solvent. The traces in Fig. 1c-g were obtained from columns with increasing rubidium chloride content. At the highest concentration used (30% RbCl; Fig. 1g), all nine components present were observed and elution was complete in 6 min. The critical concentration for drastically modifying column activity appears to be between 15 and 20%, *i.e.* between Fig. 1d and e. Higher concentrations than 30% were tried but blockage of the column usually resulted. Hence a 30% solution was considered optimum for column deactivation.

Column length is of considerable importance in capillary GSC. Initially columns were prepared to a standard length (20 m). However, it soon became evident that such columns were unsuitable. Retention times for compounds were unacceptably long and, in some cases, irreversibly adsorption took place. Columns varying in length from 0.2 to 3.2 m were prepared with 30% RbCl deactivation. The results of chromatographing the PAH mixture on these columns are shown in Fig. 2. Even the shortest column (Fig. 2a; 40 cm) showed a separative capability, and a column of only 80 cm (Fig. 2b), was able to resolve eight of the nine components. Optimum column length would appear to be *ca.* 3 m (Fig. 2d and e).

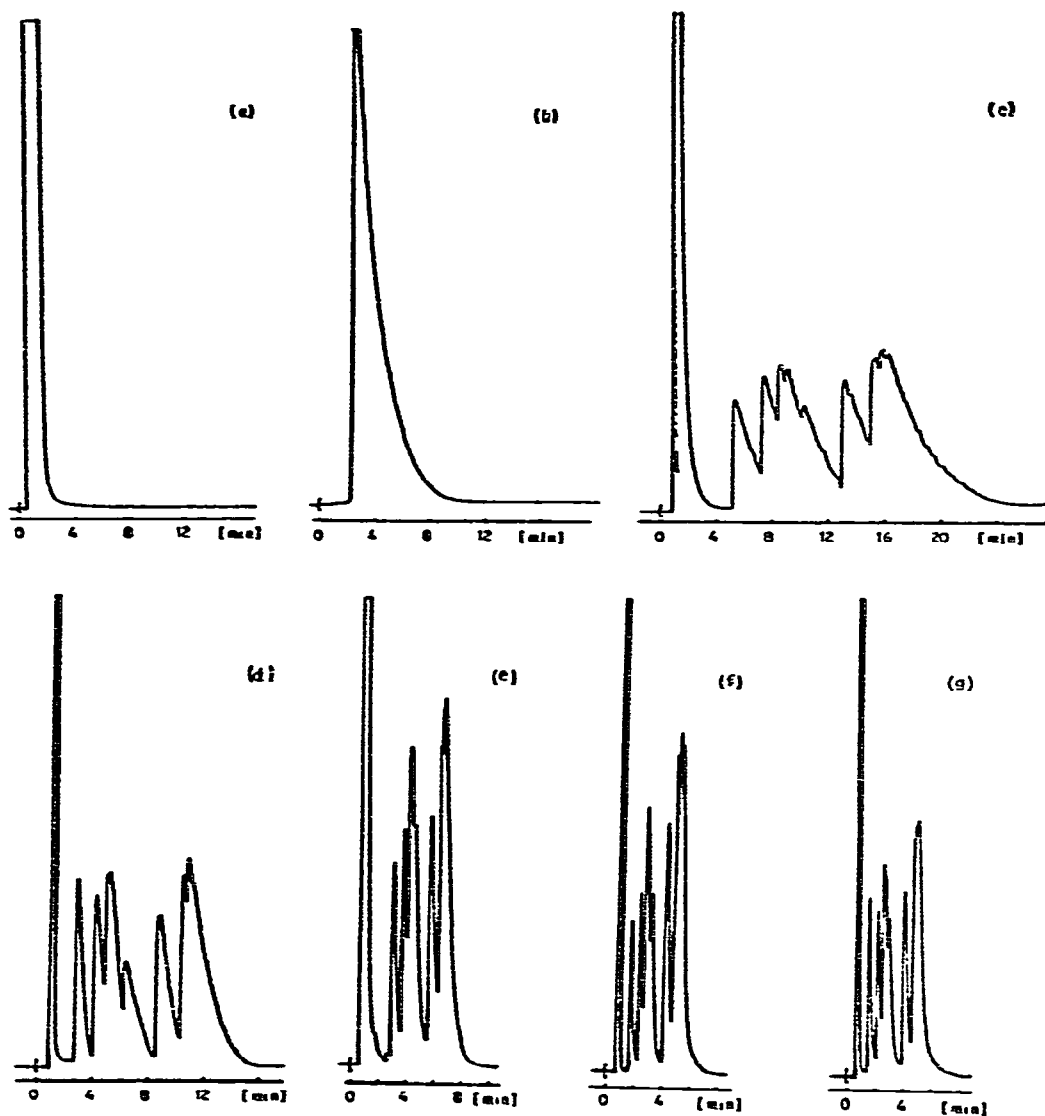


Fig. 1. Effect of rubidium chloride concentration. (a) Empty column; (b) etched column; (c) 6% RbCl; (d) 15% RbCl; (e) 20% RbCl; (f) 25% RbCl; (g) 30% RbCl. Temperature programme 80–300°C at 30°C/min⁻¹; flow-rate 8 ml min⁻¹ nitrogen.

To evaluate the performance of these columns with respect to compounds of much lower volatility a second PAH standard containing pyrene, benz[*a*]anthracene, chrysene and dibenz[*a,h*]anthracene was used (Fig. 3). Again a column of only 0.8 m (Fig. 3b; 30% RbCl deactivation) was capable of resolving the four compounds with elution being complete in *ca.* 6 min.

The versatility of this type of column was demonstrated by chromatographing a third standard mixture. This solution contained a range of *n*-alkanes present as three

TABLE I
COMPOSITION OF POLYNUCLEAR AROMATIC HYDROCARBON TEST MIXTURE

Peak no.	Compound	Concentration ($\text{ng } \mu\text{l}^{-1}$)
1	Naphthalene	85
2	1-Methylnaphthalene	76
3	Biphenyl	55
4	2,7-Dimethylnaphthalene	72
5	Acenaphthene	95
6	Phenanthrene	90
7	<i>o</i> -Terphenyl	115
8	Fluoranthene	80
9	Pyrene	80

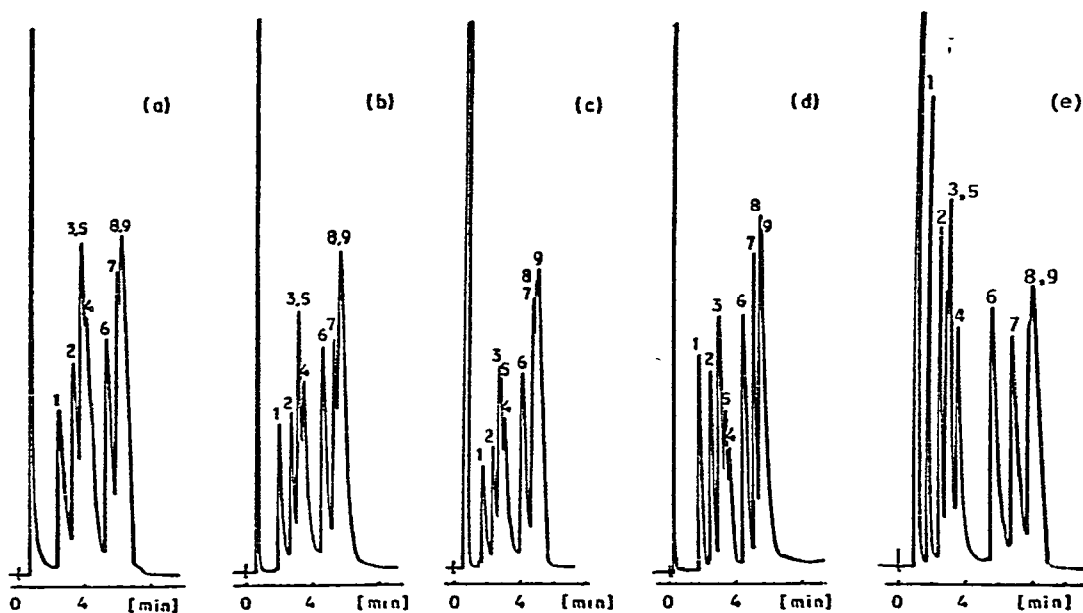


Fig. 2. Effect of column length. (a) 0.4 m; (b) 0.8 m; (c) 1.2 m; (d) 2.8 m; (e) 3.2 m. Other conditions as for Fig. 1.

groups, viz. C_{10} - C_{13} , C_{14} - C_{17} and C_{22} - C_{30} . Typical chromatograms are depicted in Fig. 4. From the chromatograms it can be seen that a minimum column length of *ca.* 1.2 m was required to give a reasonable separation for these *n*-alkanes. With shorter columns the efficiency was too low for a good separation of the heavier hydrocarbons to be achieved. The outstanding baseline stability at high temperatures clearly indicates that the analysis of high boiling compounds is possible with this type of column.

Although these are termed adsorption columns, the mechanism whereby separation of components is accomplished is clearly complex. Compounds such as polycyclic aromatic hydrocarbons, which possess delocalised π -electrons, are obvi-

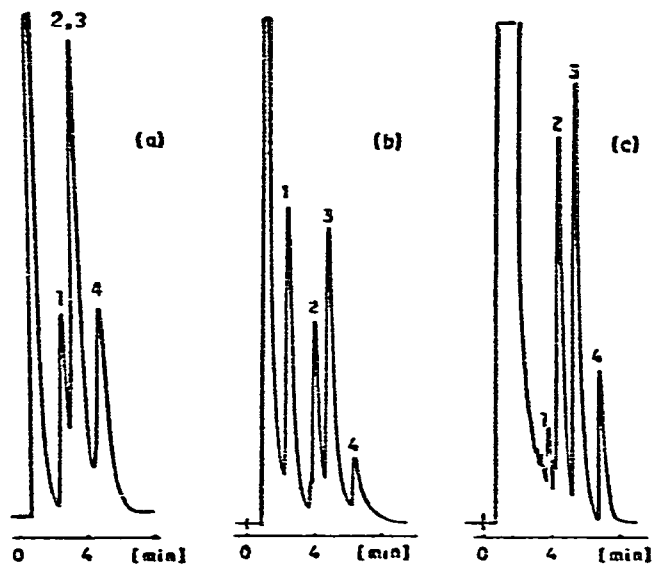


Fig. 3. Separations of high-molecular-weight polynuclear aromatic hydrocarbons on 30% RbCl adsorption columns of various lengths. (a) 0.4 m; (b) 0.8 m; (c) 1.2 m. Peak assignment: 1 = pyrene; 2 = benz[*a*]anthracene; 3 = chrysene; 4 = dibenz[*ah*]anthracene. Other conditions as for Fig. 1.

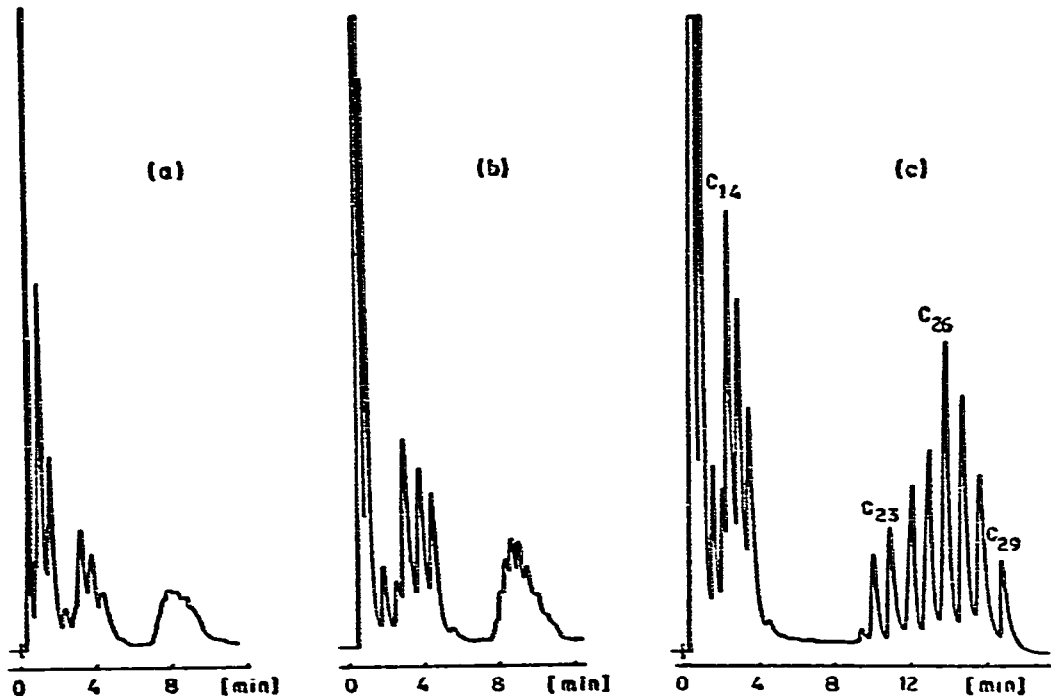


Fig. 4. Separation of a mixture of *n*-alkanes on 30% RbCl columns of different lengths. (a) 0.4 m; (b) 0.8 m; (c) 1.2 m. Other conditions as for Fig. 1.

ously capable of adsorption because of potential electronic interactions with the vacant, low-energy d-orbitals on the silicon atoms. The planar nature of these compounds presumably assists in, and helps to stabilise the bond formation. Such a mechanism is unavailable to the non-polar *n*-alkanes. In this case it seems likely that separation by virtue of a difference in boiling point is being achieved. However, some elements of separation by boiling point difference will also be utilised in the PAH separation, as elution order appears to correlate with increasing molecular weight.

CONCLUSIONS

Capillary GSC columns have been prepared in which the glass surface has been modified by deposition of rubidium chloride. Such columns show exceptional thermal stability and may be routinely used to 450°C. The rapid analysis of high boiling compounds may thus be achieved. However, column efficiencies are low in comparison with conventional GLC columns. The interesting possibility of two-dimensional chromatography, involving a tandem arrangement of GSC and conventional GLC columns thus suggests itself. Alternatively the ability of RbCl to "deactivate" a glass surface may make it a suitable alternative to Carbowax 20M for the preparation of conventional capillary GLC columns which require a high thermal stability.

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