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## GLASS MICRO-BEADS TREATED WITH SODIUM DODECYLBENZENE-SULPHONATE AS A GAS CHROMATOGRAPHIC SUPPORT MATERIAL

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### SUMMARY

The layer of surfactant on glass micro-beads gives high theoretical plate numbers in gas-liquid partition chromatography and reduces considerably the activity of the glass. An optimum value of 0.4 for the ratio between the surfactant and stationary phase was found. Separations of isomeric compounds with high-efficiency packed columns by gas-liquid chromatography are described.

### INTRODUCTION

It is well known that conventional soda-lime micro-beads are poor support materials in gas-liquid partition chromatography because the liquid phase does not coat the beads uniformly, causing low column efficiencies and peak tailing with polar compounds.

Surface etching of soda-lime glass beads resulted in improved column efficiencies<sup>1,2</sup>. The use of surface-textured glass beads of an optimized glass composition<sup>3</sup> and of high-purity glass beads<sup>4,5</sup> has also been described. High-efficiency packed columns have been prepared with carbon-coated soda-lime glass beads, this support material being obtained by pyrolysis of methylene chloride on the glass surface<sup>6</sup>.

In this paper the preparation and use of soda-lime glass beads coated with a layer of sodium dodecylbenzenesulphonate (SDBS) as a gas-liquid chromatographic support material is described.

### EXPERIMENTAL

Glass beads obtained from Analabs (North Haven, Conn., U.S.A.) were sieved and the 70-90-mesh fraction was used. The beads were washed successively with water plus detergent, water alone, acetone, and diethyl ether. They were then dried by heating them in an oven at 120°. SDBS obtained from Analabs (Siponates DS-10) was used for treating the glass beads.

#### *Preparation of SDBS-coated glass beads*

A weighed amount of glass beads (30 g) was transferred into a 50-ml beaker

and 15 ml of methanol were added. A sufficient volume of a 2% aqueous solution of SDBS to give the required surfactant layer was then added, and the solvent was evaporated with hot air, stirring the glass beads. In order to eliminate water completely, the glass beads were dried in an oven at 120° and then cooled in a desiccator (trace amounts of water can be responsible for non-homogeneous deposition of the stationary phase on the glass bead surface).

## RESULTS AND DISCUSSION

The thin layer of SDBS on glass beads has good mechanical strength and does not cause significant variations of either the support surface area or the retention volumes, even when it is present in a greater proportion than the stationary phase.

The gas chromatographic behaviour of SDBS-coated glass beads was studied by packing beads loaded with different amounts of SDBS and SE-52 into 2 m × 0.35 cm I.D. glass columns and determining the plate heights at 120° for *n*-hexadecane at various linear carrier gas velocities. The values obtained are shown in Fig. 1 (curve B) and compared with the results for a column prepared in the same way with untreated glass beads (curve A).

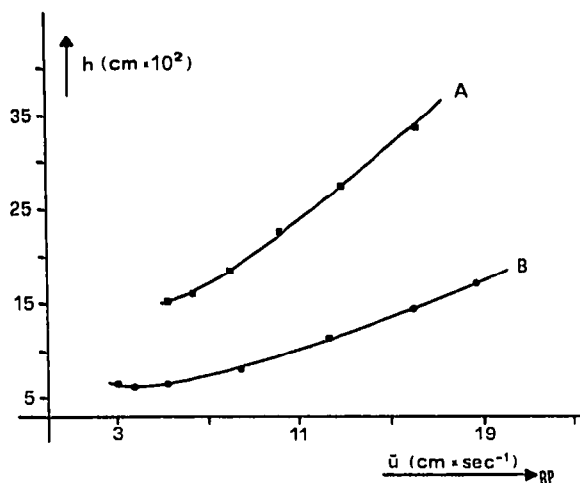


Fig. 1. Graphs of HETP ( $h$ ) versus linear carrier gas velocity ( $\bar{u}$ ) obtained for *n*-hexadecane on (A) untreated and (B) 0.05% SDBS-coated glass beads. Glass column 2 m long, 0.35 cm I.D.; packing, 70–90-mesh glass beads; stationary phase, SE-52 silicone gum, 0.1% (w/w); carrier gas, nitrogen; detector, FID; column temperature, 120°.

The optimum amount of SDBS to be added to the glass beads is not critical; it was observed that this amount increases as the amount of stationary phase is increased. Therefore, columns with different proportions of the surfactant and the stationary phase (SE-52) were prepared and the HETP<sub>min.</sub> values at 120° for *n*-hexadecane were measured. It was observed that the optimum value of the ratio between surfactant and stationary phase was about 0.4, whereas HETP<sub>min.</sub> obviously increases with the increase in the amount of stationary phase. The values of HETP<sub>min.</sub> for different proportions of SDBS and SE-52 are reported in Table I. Concentrations of

TABLE I

VARIATION OF  $HETP_{min}$  WITH THE AMOUNT OF STATIONARY PHASE AND SDBS USED TO COAT THE GLASS BEADS

Column	SDBS (% w/w)	Stationary phase (SE-52) (% w/w)	$HETP_{min}$ . ( $cm \times 10^2$ )
1	0.050	0.100	6.5
2	0.050	0.050	7.3
3	0.050	0.025	7.5
4	0.025	0.050	6.2
5	0.025	0.025	7.2
6	0.012	0.025	4.8

SDBS less than 0.012% were not used because of the difficulty in stratifying such small amounts. In addition, with concentrations of stationary phase less than 0.025%, the chromatographic process can no longer be considered to be a pure solution process.

The low values of  $HETP_{min}$  is not the only advantage of columns packed with SDBS-coated glass beads. The thin layer of surfactant is also responsible for a considerable reduction in the activity of the glass. This feature was illustrated by injecting some substances of medium polarity on to different columns. Fig. 2 shows the peak shapes obtained for benzophenone and phenanthrene obtained on columns packed with (A) untreated and (B) SDBS-coated glass beads. The peak tailing (A) is due to the adsorption on the uncovered glass surface.

Finally, the effect on column efficiency of coating SDBS-coated glass beads

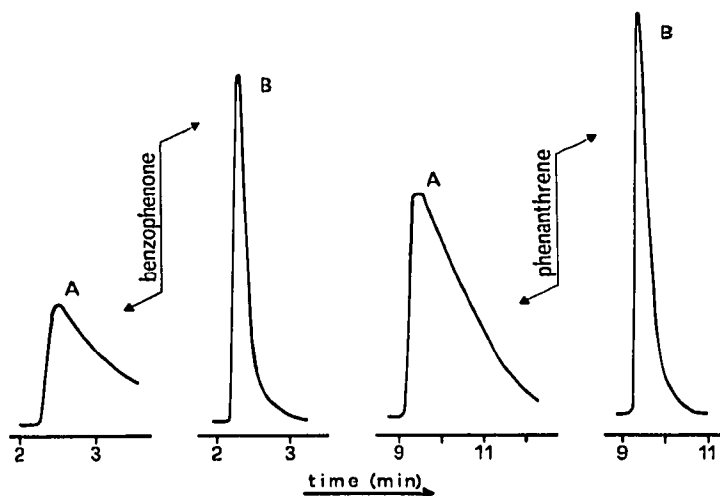


Fig. 2. Shapes of benzophenone and phenanthrene peaks obtained on (A) untreated and (B) 0.05% SDBS-coated glass beads. Glass column 2 m long, 0.35 cm I.D.; packing, 70-90-mesh glass beads; stationary phase, SE-52 silicone gum, 0.1% (w/w); carrier gas, nitrogen; detector, FID; column temperature, 150°; injector temperature, 200°; chart speeds, 1 in.·min<sup>-1</sup> for benzophenone and ½ in.·min<sup>-1</sup> for phenanthrene peaks; attenuation, ×16; sample, 1.0 μg (A) and 0.05 μg (B).

with several stationary phases of increasing polarity was studied. For this purpose, columns with the stationary phases SE-52, OV-1, OV-17, Dexsil 300, Apiezon L, PMP, FFAP and Carbowax 20M were prepared and HETP<sub>min</sub> and the maximum working temperature were measured for each column. All columns showed about the same efficiency. Maximum working temperatures lower than those obtainable on diatomaceous earth supports were found for silicone gums (SE-52, OV-1, OV-17) and particularly for Dexsil 300.

The maximum working temperature for Apiezon L was found to be 270° when it was present in concentrations from 0.10 to 0.05%. This limit could be increased to 290° when the ratio was lower than 0.05%. For example, the bleeding of a column containing 0.05% (w/w) of Apiezon L was about 10 pg·sec<sup>-1</sup> at 250°.

The low HETP<sub>min</sub> values obtainable with columns packed with SDBS-coated glass beads, coupled with positive characteristics of columns packed with glass beads such as the low  $V_{\text{liquid}}/V_{\text{gas}}$  value and the high permeability to the carrier gas, make the preparation of high-efficiency packed columns for gas-liquid chromatography very useful.

Fig. 3 shows some separations of isomeric polynuclear aromatic hydrocarbons obtained with a 12-m glass column packed with SDBS-coated glass beads and with Apiezon L as the stationary phase (see column D in Table II). An efficiency of about 18,000 theoretical plates was obtained with this column for *n*-octacosane at 250°.

Table II gives values of  $R^2 \cdot t^{-1}$  for the isomeric pairs 1,2-benzanthracene-chrysene, 4,5-benzopyrene-1,2-benzopyrene and 1,2-benzopyrene-perylene shown in Fig. 3 obtained at 250° on four different columns. The columns used were: A, a 60-m glass capillary column coated with SE-52; B, a 5-m glass column packed with silanized Chromosorb G coated with 1% (w/w) SE-52; C, a 5-m glass column packed

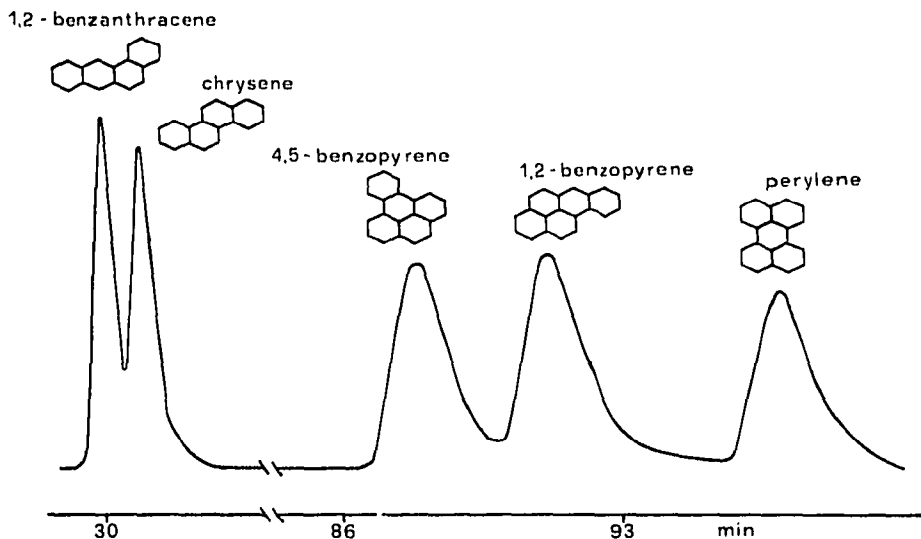


Fig. 3. Separation of isomer polynuclear aromatic hydrocarbons. Glass column 12 m long, 0.35 cm I.D.; packing, 70-90-mesh glass beads coated with 0.012% (w/w) of SDBS and 0.025% (w/w) of Apiezon L; column inlet pressure, 1.7 kg·cm<sup>-2</sup>; carrier gas, nitrogen; linear gas velocity, 5 cm·sec<sup>-1</sup>; detector, FID; column temperature, 260°; injector temperature, 300°.

TABLE II

## RESOLUTION OF ISOMERIC POLYNUCLEAR AROMATIC HYDROCARBONS ON DIFFERENT COLUMNS

The columns are specified in the text.  $R$  = Resolution;  $t$  = retention time.

Column type	$R^2 \cdot t^{-1}$		
	1,2-Benzanthracene-chrysene	4,5-Benzopyrene-1,2-benzopyrene	1,2-Benzopyrene-perylene
A	0.0372	0.0106	0.0465
B	0.0126	0.0085	0.0310
C	0.0299	0.0142	0.0433
D	0.0283	0.0150	0.0442

with 0.012% SDBS-treated glass beads coated with 0.025% Apiezon L; and D, a 12-m glass column packed as C. The high  $R^2 \cdot t^{-1}$  values obtained on columns C and D for different isomeric pairs is due either to a low HETP<sub>min.</sub> value or to the high selectivity of Apiezon L for the aromatic polynuclear compounds; in the case of the benzopyrene pair, this value is even higher than that obtained with the capillary column. About the same values were obtained with columns C and D because with the latter the resolution increases but the analysis time also increases.

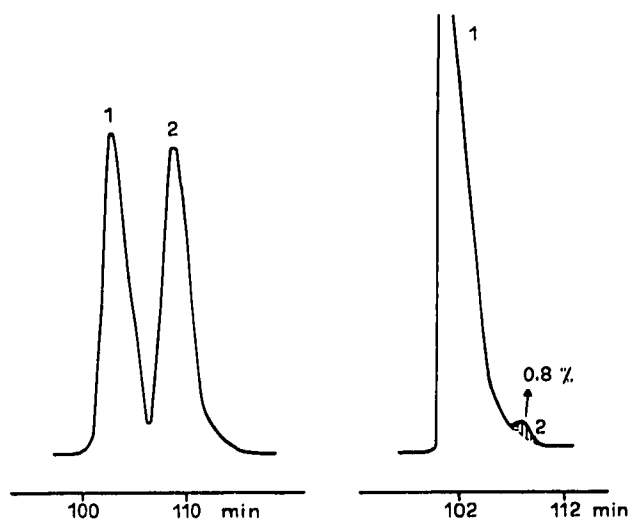


Fig. 4. Separation of oleic (1) and elaidic (2) methyl esters. Same column as in Fig. 3; column temperature, 188°; injector temperature, 230°.

Fig. 4 shows the separation of oleic and elaidic methyl esters injected in comparable and very different amounts. These separations were obtained on column D (Table II) at 188°.

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