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## DENSE-LAYERED C<sub>18</sub> REVERSED-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC COLUMN PACKINGS OBTAINED BY CHEMICAL BONDING OF OCTADECYLSILANE TO CONTROLLED-POROSITY GLASSES

### INFLUENCE OF ACTIVATOR

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#### SUMMARY

Controlled-porosity glasses (CPGs) are often employed as packings for gas and liquid chromatography. The characteristic feature of GPCs is the presence of boron atoms on their surface, the concentration of which can be changed easily by appropriate thermal treatment. Such glasses can be used as a support for chemically bonded phases. The surface chemical modification of the siliceous supports can be affected by the use of an activator. The present paper deals with the properties and coverage density of materials obtained by chemical bonding of monochlorodimethyl-octadecylsilane to boron-enriched CPGs in the presence of an activator.

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#### INTRODUCTION

The synthesis of reversed-phase silica for high-performance liquid chromatography (HPLC) remains an area of considerable interest from both a practical and a theoretical point of view. The reaction of surface hydroxyl groups with reactive silanol modifiers is mostly used for this purpose owing to the high stability and reproducibility of the resulting packings<sup>1</sup>.

In general there are two methods for obtaining packings with a high coverage with alkyl ligands. According to Kováts and co-workers<sup>2,3</sup>, dimethylaminodimethyl-*n*-alkylsilanes can be used as modifiers, giving packings with a coverage of up to 4.3  $\mu\text{mol m}^{-2}$ . The second method utilizes an activator (A) and a monochlorodimethyl-*n*-alkylsilane as a bonding ligand<sup>4–6</sup>.

Silica gels have been used successfully as supports for chemically bonded phases. Controlled-porosity glass (CPG) has also been used for this purpose<sup>7–9</sup>, but only very rarely as a support for bonded phases<sup>7–10</sup>. In previous work the porous glasses used were characterized by low surface areas<sup>7–10</sup>. An interesting feature of CPGs is the presence of boron atoms on their surface, and the surface boron concentration may be changed by thermal treatment<sup>11,12</sup>. It has been shown that the properties of

materials with phases chemically bonded to boron-enriched porous glass are different from those of chemically bonded sorbents based on silica gel. For example, they do not exhibit the phase transitions<sup>7</sup> that are characteristic of analogous packings made of silica gel<sup>13,14</sup>.

In this work, we studied the properties and density of coverage of materials obtained by chemical bonding of monochlorodimethyloctadecylsilane to boron-enriched glasses of controlled porosity in the presence of an activator. In previous works<sup>7-10</sup> the activator was not used for the synthesis of chemically bonded materials based on CPG. The reaction conditions used in this study were different to those previously employed<sup>5,7,9</sup>.

## EXPERIMENTAL

### *Materials and reagents*

Small CPG particles ( $d_p = 10 \mu\text{m}$ ) were fabricated according to a previously described method<sup>15</sup>. Enrichment was carried out at 893 K for 2, 20 or 70 h. The heated materials were then rehydroxylated as described elsewhere<sup>8</sup>.

For chemical modification, octadecyldimethylchlorosilane (ODMCS) (Petrarch Systems, Levittown, PA, U.S.A.), specially prepared morpholine<sup>5</sup> (Reachim, Moscow, U.S.S.R.) as an activator (A) and toluene (POCH, Gliwice, Poland) were used. The reaction was carried out in glass ampoules. The method, mechanism and conditions have been described previously<sup>5,6</sup>. The bonding procedure was significantly different to that employed in an earlier study<sup>9</sup>. The bonded phases were packed in stainless-steel tubes (100 × 4 mm I.D.).

### *Physico-chemical and chromatographic measurements*

The measurements of specific area ( $S_{\text{BET}}$ ) and mean pore diameter ( $D$ ) of the CPG supports were carried out using nitrogen sorption on a Model 1806 Sorptomatic (Carlo Erba, Milan, Italy). The surface boron concentration was determined by isotachophoretic measurements<sup>16</sup>.

The density of coverage was calculated on the basis of the Berendsen and De Galan equation<sup>17</sup> from C, H, N data. For this purpose a Model 185 C, H, N, analyser (Hewlett-Packard, Palo Alto, CA, U.S.A.) was used.

A Pye Unicam LC 20 liquid chromatograph equipped with a UV detector operating at 254 nm was used (Pye Unicam, Cambridge, U.K.). The samples were injected by means of a Rheodyne 7120 injector (Rheodyne, Berkeley, CA, U.S.A.) using a 10- $\mu\text{l}$  sample loop.

Methanol (POCH) and methanol-water mixtures were used as mobile phases. Water was purified in our laboratory<sup>18</sup> and its conductivity was about  $10^{-6} \text{ S m}^{-1}$ .

The columns were packed at 45 MPa according to a modified upward slurry method as described by Buszewski *et al.*<sup>19</sup>. The slurry consisted of silica (8%, w/w) in tetrachloromethane-methanol (90:10). Methanol was used as a driving solvent.

## RESULTS AND DISCUSSION

Table I gives the specific surface areas of porous glasses heated for various periods of time at 893 K. It appears from the data that heating of the initial glass

TABLE I

DENSITIES OF COVERAGE BY C<sub>18</sub> CHEMICALLY BONDED PHASE

CPG<sub>0</sub> = initial glass; CPG<sub>2</sub>, CPG<sub>20</sub> and CPG<sub>70</sub> = glasses heated for 2, 20 and 70 h, respectively; C<sub>B<sub>2</sub>O<sub>3</sub></sub> = surface boron concentration; S<sub>BET</sub> = specific surface area.

Column No.	Sample	C <sub>B<sub>2</sub>O<sub>3</sub></sub> (μg m <sup>-2</sup> )	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Coverage	
				Carbon percent from CHN anal	α <sub>RP</sub> (μmol m <sup>-2</sup> )
1	CPG <sub>0</sub>	0.09	215	—	—
2	CPG <sub>2</sub>	3.82	186	—	—
3	CPG <sub>20</sub>	17.96	161	—	—
4	CPG <sub>70</sub>	29.32	128	—	—
5	CPG <sub>0</sub> + ODMCS	—	—	4.56	0.93
6	CPG <sub>2</sub> + ODMCS	—	—	5.57	1.35
7	CPG <sub>20</sub> + ODMCS	—	—	—	—
8	CPG <sub>70</sub> + ODMCS	—	—	5.83	2.05
9	CPG <sub>0</sub> + ODMCS + A	—	—	8.38	1.82
10	CPG <sub>2</sub> + ODMCS + A	—	—	11.09	2.90
11	CPG <sub>20</sub> + ODMCS + A	—	—	10.72	3.20
12	CPG <sub>70</sub> + ODMCS + A	—	—	8.79	3.23

causes a decrease in the specific surface area, as reported in the literature<sup>7-9,11</sup>; this is related to changes in the silica lattice of the porous glass and to the diffusion of boron atoms from the bulk material to the surface. The former effect increases the density of the silica skeleton and the latter modifies the chemical nature of the surface by enriching it in boron atoms<sup>11,12</sup>.

Also shown in Table I is the amount of boron extracted from the surface of each glass. Because the individual glasses differ in their specific surface areas, these

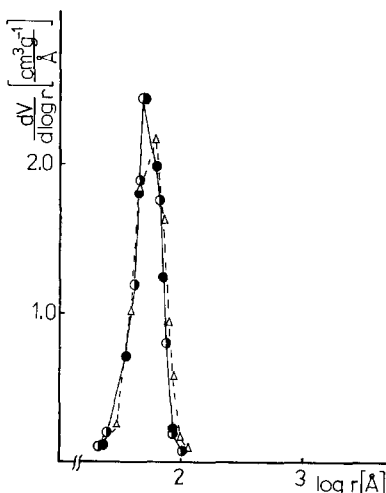


Fig. 1. Pore-size distribution functions for (●), initial glass, (●) glass heated for 2 h and (△) glass heated for 20 h.  $V$  = pore volume,  $r$  = pore radius.

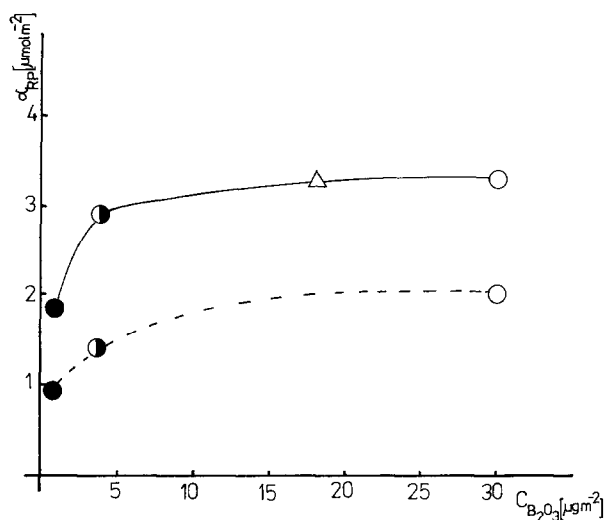


Fig. 2. Relationships between density of coverage,  $\alpha_{RP}$ , and surface boron concentration,  $C_{B_2O_3}$ , for packings with activator (solid line) and without activator (dashed line).

values are given per square metre. These results indicate that extending the time of thermal treatment increases the surface boron concentration.

Fig. 1 shows additionally the influence of thermal treatment on the pore-size distribution of used CPG.

The boron-enriched CPGs were employed as supports for chemically bonded  $C_{18}$  phases. Two series of reversed-phase (RP) packings were prepared. In the first series only monochlorodimethyloctadecylsilane was used as a bonding agent. The second series was obtained in a similar manner but in the presence of morpholine as activator<sup>5,6</sup>. The data in Table I show for both series of sorbents a correlation between the surface boron concentration and the amount of bonded alkyl phase (Fig. 2). This result confirms the previously reported trend<sup>7,9</sup>.

The densities of coverage of the surfaces by  $C_{18}$  ligands are not as high as previously reported<sup>9</sup> because the bonding procedure was carried out under conditions in which water was not specifically excluded. It should be noted that  $-BOH$  groups are more reactive and show higher adsorption properties than  $-SiOH$  groups<sup>20,21</sup>. Considering the results for both series of materials, it is seen that the use of an activator ensures higher surface coverage densities. It appears that the modification with an activator is not as sensitive to the presence of water as the same bonding reaction without an activator. In addition, morpholine activates the surface hydroxyl groups as well as the modifier<sup>5,6</sup>. The CPGs used in this investigation as a support for chemically bonded phases contain more residual  $Na_2O$  than the wider porous glasses employed previously<sup>7,11</sup> and, as a consequence, lower surface coverage densities by  $C_{18}$  occur in both series of materials studied.

The chromatographic properties of the prepared sorbents were investigated and Table II gives the measured parameters characterizing the packed columns. Two effects observed from these data are that an increase in the surface coverage density by  $C_{18}$  ligands causes both an increase in the number of theoretical plates and an

TABLE II  
COLUMN CHARACTERISTICS (BIPHENYL SOLUTE)

$k'$  = capacity factor;  $n_T$  = number of theoretical plates for a 100-mm column;  $h$  = reduced plate height;  $v$  = reduced flow-rate;  $f_{AS}$  = asymmetry factor.

Column No.	$k'$	$n_T$	$h$	$v$	$f_{AS}$
5	3.45	995	10.03	5.01	1.27
6	2.36	940	10.61	4.83	1.23
7	—	—	—	—	—
8	2.79	1180	8.47	4.67	1.13
9	3.62	1065	9.36	3.02	1.05
10	3.52	1070	9.32	3.07	1.10
11	3.47	1645	6.09	2.59	1.09
12	3.51	1980	5.05	2.37	1.08

increase in chromatographic peak symmetry. According to Bristow and Knox<sup>22</sup> our packed columns are "good" if we take into account the mean particle size diameter,  $\bar{d}_p = 10 \mu\text{m}$ .

Fig. 3 ( $\alpha = k'_{\text{benzene}}/k'_{\text{phenol}}$  as a function of mobile phase  $k$  composition) confirms

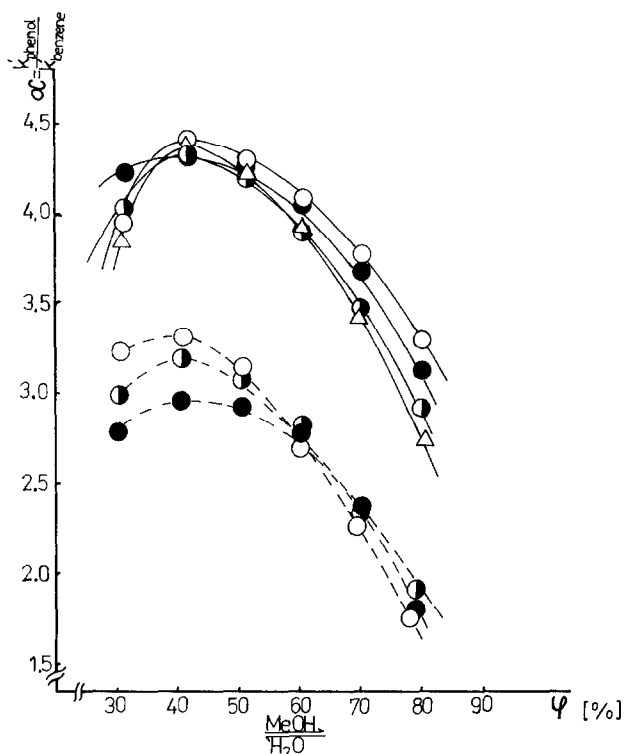


Fig. 3. Dependence of selectivity of prepared columns on mobile phase composition for (●) initial glass and glass heated for (○) 2 h, (△) 20 h and (□) 70 h. Lines as in Fig. 1. MeOH = Methanol.

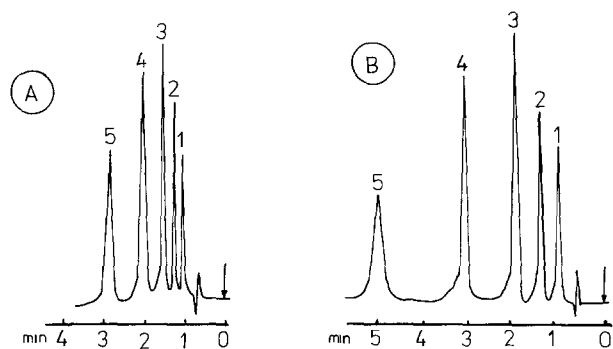


Fig. 4. Separation of alkylbenzenes on packings obtained by bonding of ODMCS to GPC heated for 70 h: (A) without activator; (B) with activator. Separation conditions: column, 100 × 4 mm I.D.; mobile phase, methanol-water (70:30); flow-rate, 1 ml/min. Peaks: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = propylbenzene; 5 = butylbenzene.

an earlier conclusion concerning the increase in the hydrophobic properties of packings<sup>23</sup>. The selectivity values are higher for sorbents prepared in the presence of an activator. The comparison of  $\alpha$  as a function methanol concentration is interesting. An explicit influence of surface boron concentration (surface coverage densities by  $C_{18}$ ) on the height of the curve is seen for materials 5–8 (curves 5–8), whereas this sequence is not evident with materials 9–12 (curves 9–12). This could be explained by a similarity of separation mechanisms in the given range of coverage density<sup>9</sup>. However, the maxima of the  $\alpha$  vs. methanol concentration curves occur at the same mobile phase composition (methanol-water, 40:60) for all the materials.

Some examples of chromatographic separations on the most densely bonded  $C_{18}$  materials (8 and 12) are shown in Fig. 4. The elution volumes of the solutes studied are higher on the more hydrophobic sorbent 12 (Fig. 4b).

In spite of the low coverage densities by chemically bonded  $C_{18}$ , the investigated materials can be used successfully for separations of different mixtures. The retention data show the good quality of the columns. The sorbents are comparable to those prepared on bare silica gel<sup>10</sup>. The results obtained were confirmed by similar relationships published by Okamoto and Jinno<sup>10</sup>. The coverage densities reported here are significantly higher than those on packings synthesized by Okamoto and Jinno<sup>10</sup>. It is characteristic that the coverage densities of CPG surfaces (even if not additionally enriched with boron) are higher than those of silica gel surfaces<sup>8,10,24</sup>. This suggests the necessity for further investigations on the application of CPG as supports of chemically bonded phases.

Future investigations should take into consideration (i) the optimal conditions of the modification reaction; (ii) the control of the content of  $Na_2O$  in the initial narrower pore glass; (iii) the control of the surface free hydroxyl group concentration; (iv) the comparison of the properties of hydroxyl groups bonded to surface boron and silica atoms; and (v) the influence of the presence of surface boron or sodium atoms and alkyl groups on the composition of the surface layer.

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