Column Packing for Gas Chromatography Containing Immobilized Poly(ethylene Glycol) Stationary Phase

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Key Words
Gas chromatography
Packed columns
Immobilized stationary phase
Poly(ethylene glycol) phase

Summary
Carbowax 20M poly(ethylene glycol) stationary phase was immobilized on Chromosorb W by cross-linking with pluriisocyanate. The properties of the prepared packing material were investigated. Column efficiencies of 10,960 and 7,510 theoretical plates/meter were obtained for n-pentadecane and 1-heptanol, respectively.

Introduction
Immobilization of gas chromatographic (GC) stationary phases by their cross-linking and/or chemical bonding to a support overcomes the shortcomings of coated stationary phases such as limited thermal stability, bleeding and the impossibility to wash the chromatographic column with solvents.

Such methods have been used for many years with capillary columns. Non-polar and moderately polar polysiloxanes have been immobilized either by radical cross-linking with organic peroxides, ozone, aza-compounds, γ-radiation [1–6] or using OH-terminated phases [7–8]. Poly(ethylene glycols) have been immobilized in capillary columns by radical cross-linking with organic peroxides [9–11] or dibutyltin dilaurate [12], especially in the presence of silanes or siloxanes. Recently, catalytic immobilization of poly(ethylene glycol) by chemical reaction between the terminal hydroxy groups and the NCO-groups of a cyanate, producing urethane bonds, has been described [13, 14].

Experimental

Chemicals and Materials
The following major chemicals were used: Carbowax 20M (Carlo Erba, Italy), γ-glycidoxypropyltrimethoxysilane (Union Carbide, USA), Desmodur L 75 (a pluriisocyanate based on toluene diisocyanate; Bayer AG, FRG), and DABCO R-8020 (1,4-diazobicyclo-[2,2,2]-octane; Air Products, Chemical Group, Paulsboro, NJ, USA). Other chemicals of analytical reagent-grade were supplied by Lachema, Brno, Czechoslovakia. Acid-washed Chromosorb W (80–100 mesh) was supplied by Becker (Delft, the Netherlands). The measurements were carried out with glass columns of 1.2 m x 3 mm I.D., using the Chrom 5 gas chromatograph of Laboratory Instruments, Prague, Czechoslovakia.

Procedure
Three types of column packings were prepared. The acid-washed chromatographic support was always first heated at 200 °C for 4 hours.
(a) The first type of packing was prepared by coating the support particles with the solution of Carbowax 20M in dichloromethane in the usual way, using vacuum. The resultant packing material contained 10 wt-% of Carbowax 20M relative to Chromosorb W.
(b) In the case of the second type of packing the support particles were first silylated with the solution of γ-glycidoxypropyltrimethoxysilane in dichloromethane [23] and then coated with Carbowax 20M in the same way as in (a).
(c) In the case of the third type of packing Chromosorb W was silylated as in (b), then coated with a dichloromethane solution containing 10 % Carbowax 20M, 2 % Desmodur L 75 and 0.001 % DABCO R-8020 (relative to the support) [14]. After removing the solvent under vacuum, the coated support was packed into a 3 cm I.D. glass tube with a frit. The packed tube was flushed with nitrogen for 15 minutes at room temperature to remove air, then it was thermally treated by temperature programming at 5°C/min to 140°C and then maintained at 140°C for 4 hours under nitrogen flow. The treated packing material was taken out of the tube and packed into the chromatographic column.

The chromatographic column was always conditioned by programming its temperature at 3°C/min to 200°C and then maintained at this temperature for 14 hours. The separation efficiency was measured at 110°C.

The extractability of the stationary phase film was checked in the following way. The packed column was washed with dichloromethane. A volume of 15 ml corresponds to about five free volumes of the column. After washing the remaining liquid solvent was removed from the column by nitrogen flow and the column was conditioned for 2 hours at 200°C and a nitrogen flow rate of about 30 ml/min. Changes in retention were tested at 100°C with 1-heptanol, 1-octanol, 1-nonanol, n-pentadecane, n-hexadecane and n-nonadecane.

Unless given otherwise the chromatographic conditions were: injector temperature, 180°C; detector temperature, 200°C; and carrier gas (nitrogen) flow rate, 23 ml/min.

Results and Discussion

Table I presents performance data for non-immobilized (Type 1 packing material) and immobilized Carbowax 20M packing (Type 3). The carrier gas was used at two velocities: 5.0 cm/s represents the minimum of the van Deemter plot while 9.5 cm/s represents the carrier gas velocity used in practice to optimize analysis time and column efficiency. The respective volumetric flow rates are 15 and 32 ml/min. The height equivalent to a theoretical plate at the optimum of the van Deemter plot for immobilized Carbowax 20M was 0.09 mm and 0.13 mm for a non-polar (n-pentadecane) and polar (1-heptanol) solute, respectively. Thus the column efficiency is very high: the corresponding number of theoretical plates for the 1.2 m long column were 13,150 and 9,000, respectively. The column efficiency measured for the same solute is approximately twice for immobilized Carbowax 20M than for the non-immobilized phase. Retention of these solutes on immobilized Carbowax 20M is, however, much longer (see the capacity factors in Table III). As column efficiency depends on the capacity factor, we also measured the column efficiency for 1-octanol, 1-nonanol, 1-hexadecane and n-nonadecane (Table I) on non-immobilized Carbowax 20M. Although the capacity factors of 1-nonanol and n-nonadecane are higher on this phase than those of 1-heptanol and n-pentadecane on immobilized Carbowax 20M, the efficiencies of the column containing the non-immobilized phase are lower.

Table II/a–c gives data on the extractability of the stationary phase film by comparing the capacity factors after solvent wash. Naturally, the first 15 ml portion of the solvent washes most of the phase out of the column in the case of non-immobilized Carbowax 20M (Type 1 packing; Table II/a). In the case of the support silylated with γ-glycidoxypropylmethoxysilane and then coated with 10 % Carbowax 20M (Type 2 packing; Table II/b) the stationary phase film is washed out slower and to a lesser extent. Even after washing with 60 ml of dichloromethane the capacity factors do not decrease to the level corresponding to the values for the silylated and uncoated support (1.8, 3.6 and 6.9 for 1-heptanol, 1-octanol and 1-nonanol, respectively).

Consequently, a part of the poly(ethylene glycol) molecules is chemically bonded through the silane to the support. In the case of immobilized poly(ethylene glycol) (Type 3 packing; Table II/c) the capacity factors do not decrease after washing with the solvent: the immobilization of the stationary phase film is complete. It is interesting to note that the retention of the solutes slightly increases after washing with dichloromethane.

Under the same experimental conditions the retention of all the solutes is approximately twice as long on immobilized Carbowax 20M than on packing with non-immobilized phase.

Table I. Comparison of the efficiency of column packings prepared with non-immobilized and immobilized Carbowax 20M*

<table>
<thead>
<tr>
<th>Solute</th>
<th>$u = 5.0$ cm/s</th>
<th>$u = 9.5$ cm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k Plates for 1 m</td>
<td>HETP (mm)</td>
</tr>
<tr>
<td>non-immobilized phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-heptanol</td>
<td>7.8</td>
<td>4.850</td>
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<tr>
<td>1-octanol</td>
<td>11.4</td>
<td>5.330</td>
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<tr>
<td>1-nonanol</td>
<td>20.8</td>
<td>7.160</td>
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<tr>
<td>n-pentadecane</td>
<td>10.7</td>
<td>5.930</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>18.7</td>
<td>7.550</td>
</tr>
<tr>
<td>n-nonadecane</td>
<td>104.8</td>
<td>9.980</td>
</tr>
<tr>
<td>immobilized phase</td>
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<td></td>
</tr>
<tr>
<td>1-heptanol</td>
<td>17.0</td>
<td>7.510</td>
</tr>
<tr>
<td>n-pentadecane</td>
<td>23.3</td>
<td>10.960</td>
</tr>
</tbody>
</table>

* Column dimensions, 1.2 m x 3 mm I.D.; carrier gas, nitrogen. Column temperature: 110°C.