Preparation and Characteristics of Two New GC Stationary Phases–Dihydroxy Crown Ether Containing Polysiloxane

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Key Words
Gas chromatography
Dihydroxy crown ether stationary phases
Immobilization by condensation

Summary
Two new kinds of crown ethers: 3,5-dibutyl-unsymmetry-dibenzo-14-crown-4-dihydroxy (cis-, and trans-) with the OH-terminal silicone oil in different proportion were coated on glass capillary columns, and immobilized by condensation using a coupling agent of alkyltrimethoxysilane. Chromatographic characteristics, including column efficiency, polarity, selectivity, phase transition temperature and thermal stability were studied. The columns were compared with PEG-20M in terms of polarity and selectivity. The immobilization and retention mechanisms are also discussed.

Introduction
The use of crown ether polysiloxanes as GC stationary phases has developed rapidly owing to their high thermal stability and unique selectivity [1–5]. In 1985, Blum coated a glass capillary with an OH-terminated polysiloxane stationary phase and then immobilized the coating by a condensation process between terminal silanol groups on the phase and residual silanols on the glass surface. These columns provide high thermal stability and inertness [6].

In this work, two new kinds of crown ethers have been coated and immobilized onto the glass surface by condensing with OH-terminal silicone oil (GY-202) in different proportions with the coupling agent alkyltrimethoxysiloxane. The structure of the crown ethers are shown in Figure 1, each has four different functional groups: a polar polyether ring, an easily polarizable benzene group and a apolar alkyl side chain as well as two hydroxy groups which are convenient for condensation reactions. Because of the structures of these two crown ethers, the columns were expected to have unique selectivity and high thermal stability.

Experimental

Apparatus and Agents
- SC-7 gas chromatography (Sichuan Analytical Instrument Factory, China), equipped with a capillary split injection system, flame ionization detector and N₂ as carrier gas.
- Model GDM glass drawing machine (Shimadzu, Japan).
- 3,5-dibutyl-unsymmetry-dibenzo-14-crown-4-dihydroxy crown ether (cis- and trans-) (offered by Department of Environment Science, Wuhan University, China).
- OH-terminal silicone oil (GY-202, Chengdu Center for Applied Research of Silicone, China).
- alkyltrimethoxysilane (Wuhan University Chemical Factory, China).
- trifluoroacetic acid (Peking Chemicals Factory, China).
- aromatic compounds and chiral alcohol (obtained from the Department of Chemistry Wuhan University, China).

Preparation of the Crown Ether Columns
Glass tubes (O.D. 7.5 mm, I.D. 2.4 mm) were drawn into capillary columns (I.D. 0.30 ~ 0.35 mm). The columns were filled up to 92 % of their volume with 20 % HCl, and heated at 180 °C for 8 h. Subsequently they were rinsed with twice the column volume of 1 % HCl and then blown with N₂ for 1 h. The columns were dried at 280 °C for 2 h, at a programmed rate of 12 °C/min from 30 °C.
The capillaries were statically coated with 0.5 % (w/v) mixed stationary phase (GY-202 with crown ether in different proportions) and alkyltrimethoxysilane (1 % weight of the stationary phase) in methylene chloride at 34 °C. Following the coating procedure the columns were flushed with N₂ for 0.5 h, and then both ends of the column were sealed and heated at 60 °C for 8 h. After this, the ends were opened and the columns were heated to 180 °C at 2 °C/min and held at 180 °C for 4 h. All the columns was rinsed with 5 times column volume of methylene chloride and conditioned at 300 °C for 10 h.

**Results and Discussion**

Immobilization by a condensation reaction is complicated. The possible mechanism of reaction is given in Figure 2.

Finally, the polymer reticular structure was formed in the glass surface and the thermal stability and insolubility of the stationary phase were assessed.

The chromatographic properties of the columns in this study are summarized in Table I. It shows that the column efficiency are about 3000 and 2300 plates per metre for cis- or trans-crown-GY-202 columns respectively when the best proportion is 20:80. The efficiency decreases in proportion to the increase of crown ether content whereas the capacity factors increase with the increasing content of crown ether. This is because the OH-terminal silicone oil (GY-202) can help to spread the stationary phase on the glass surface and the wettability of the crown ether on the surface of the glass is improved when the GY-202 content is increased.

The selectivity and average polarity of those columns, represented by the McReynolds constants are shown in Table II. It can be seen that all the crown ether columns have a higher polarity than that of GY-202. Moreover, the polarity of the cis-crown-GY-202 is similar to that of the trans-crown-GY-202. That is to say the stero-position of the -OH has little effect on the polarity. The columns exhibit a moderate polarity.

We have also plotted log ₜᵣ against the number of carbon atoms for n-alcohols and methyl esters of n-fatty acids

![Figure 2](image)

**Possible mechanism of the condensation reaction.**

### Table I. Characteristics of crown-GY-202 and GY-202.

<table>
<thead>
<tr>
<th>Column No.</th>
<th>Column dimensions (Length (m) x I.D. (mm))</th>
<th>Stationary phase</th>
<th>Capacity factor k’** (Naphthalene at 120 °C)</th>
<th>Efficiency (n/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 x 0.31</td>
<td>trans-crown-GY-202 20:80</td>
<td>2.96</td>
<td>2312</td>
</tr>
<tr>
<td>2</td>
<td>17.5 x 0.31</td>
<td>cis-crown-GY-202 20:80</td>
<td>3.08</td>
<td>2998</td>
</tr>
<tr>
<td>3</td>
<td>15 x 0.32</td>
<td>cis-crown-GY-202 20:80</td>
<td>3.36</td>
<td>1995</td>
</tr>
<tr>
<td>4</td>
<td>14 x 0.34</td>
<td>cis-crown-GY-202 20:80</td>
<td>4.32</td>
<td>231</td>
</tr>
<tr>
<td>5</td>
<td>15 x 0.30</td>
<td>GY-202</td>
<td>2.1</td>
<td>2950</td>
</tr>
</tbody>
</table>

**k’ = tᵣ/to, to was determined directly with methane.**

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