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## COORDINATION POLYMERS AS ADSORBENTS AND STATIONARY PHASES IN GAS CHROMATOGRAPHY

### I. POLY[CHROMIUM(III) DIPHENYLPHOSPHINATE]

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#### SUMMARY

The possibility of using a coordination polymer of chromium(III) with diphenylphosphinic acid as a selective packing for gas chromatography is discussed. The polymer reacts specifically with hydrocarbons that contain a  $\pi$ -bond. The thermodynamic effects of the sorption of various compounds have been calculated and a series of chromatographic separations of test mixtures of hydrocarbons performed.

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#### INTRODUCTION

Gas chromatographic (GC) packing materials that contain metals, particularly transition metals, have become increasingly studied owing to their high thermal stability and selectivity<sup>1-5</sup>. The effect of packing materials of this type on chromatographic separations depends to a large extent on the stability of the charge-transfer (CT) complexes that arise between the metal and the mixture submitted to separation. In such complexes, the electron acceptor is the metal cation and the electron donors are organic compounds that contain  $\pi$ -bonds or free electrons. The role of CT complexes in separations of this type has been considered<sup>6,7</sup>.

Packing materials containing metals can be divided into two groups: (1) liquid stationary phases, in which an inorganic salt or the metal complex is dissolved in a common liquid phase, and (2) adsorbents in which the transition metals are present in the form of salts, oxides or organometallic polymers. The organometallic polymers constitute a group of adsorbents which possess many possibilities in terms of selective action and chemical resistance, although there have been few descriptions their use in GC<sup>4,8-12</sup>.

In searching for polymers with high thermal stability, we considered polymers of di-substituted organophosphinic acids with metals, which are stable above 500°, depending on the organic radical and the metal<sup>13,14</sup>. In this work we investigated the possibilities of using a polymer of diphenylphosphinic acid with chromium(III) in GC. This polymer is stable up to 360°.

## EXPERIMENTAL

### *Apparatus and procedure*

A GCHF 18.3 gas chromatograph (G.D.R.) with a flame-ionization detector (FID) was used. The carrier gas was argon, purified with a mixture of molecular sieves 4A and 5A. Air and hydrogen for the FID were purified in the same manner. The volume flow-rate of the argon was varied between 20 and 40 ml/min and was measured with high precision with a 25-ml flow meter. The pressure of argon before entering the column was measured with a fixed mercury gauge, and atmospheric pressure with a mercury barometer. The temperature of the columns was measured to within 0.1° with a mercury thermometer fixed in the thermostat chamber, and the temperature of the flow meter was also measured to within 0.1°.

The samples of the hydrocarbons examined were introduced on to the column in the form of vapours using a Zimmerman syringe (G.D.R.) of 40- $\mu$ l capacity as described earlier<sup>3</sup>.

The thermodynamic functions were calculated by means of an Odra 1204 digital computer according to the least-squares method from at least five measurements of the retention volumes at different temperatures. All compounds were examined at four temperatures: aliphatic hydrocarbons and halomethanes in the range 150–200° and aromatic hydrocarbons in the range 200–250°. The infrared (IR) spectra of the polymers were measured in potassium bromide in the range 400–4000  $\text{cm}^{-1}$  on a UR-20 instrument (Carl Zeiss, Jena, G.D.R.).

Measurement of the specific surface areas of the supports was accomplished with a Gravimat apparatus (Sartorius Works), using the B.E.T. adsorption model.

### *Columns*

The packing of the columns consisted of poly[chromium(III)diphenylphosphinate] (DPP-Cr) deposited on Spherosil XOB 030 carrier (Rhone-Progil, Paris, France) with a specific surface area 30–50  $\text{m}^2/\text{g}$  and particle size 0.1–0.2 mm. The Spherosil XOB 030 was treated with dimethyldichlorosilane (DMCS), 50 g of the carrier and 20 g of DMCS being heated in 1 l of dry benzene for 24 h under reflux. After silanization, the excess of the solution was decanted, taking care that the Spherosil sample did not come into contact with the air. The unreacted DMCS was deactivated by addition of 100 ml of methanol in anhydrous benzene and heating the mixture for 24 hours under reflux. The carrier thus prepared was washed with dry methanol.

The DPP-Cr was obtained by reaction of diphenylphosphinic acid with chromium(III)chloride dissolved in acetone<sup>15,16</sup>. The crude polymer was dried at 140° and then dissolved in chloroform. The polymer was precipitated from this solution by gradual addition of methanol. This process was repeated twice. The purified polymer was dried at 140° and coated on a previously prepared carrier in amounts of 1%, 2% and 3% (w/w). For this purpose, the necessary amount of polymer was dissolved in 50 ml of chloroform, 6 g of the carrier were added and the solvent was removed in a vacuum rotary evaporator. The absorbent was packed in a stainless steel-column of length 1 m and I.D. 4 mm and then the column was conditioned at different temperatures under a forced flow of dry argon at a flow-rate of 20–40 ml/min.

## RESULTS AND DISCUSSION

The polymer DPP-Cr should have specific action in a chromatographic process involving compounds that are capable of forming CT complexes. It appeared, however, that this effect is hardly evident for packings conditioned at 330°.

Table I gives the relative retention volumes for different compounds on a column containing 3% of DPP-Cr conditioned at 150°, 200°, 250° and 330°. The results in Table I indicate that the specificity of the action of DPP-Cr is the result of conditioning at 330°. This effect can be explained on the basis of differential thermal analysis (DTA) and the IR spectra. The DTA results indicated a steady loss of water from the polymer, starting at 100° up to the decomposition temperature of 360°.

TABLE I

INFLUENCE OF TIME AND TEMPERATURE OF CONDITIONING ON SPECIFICITY OF THE COLUMN (RELATIVE RETENTION VOLUMES)

| <i>Adsorbate</i> |                  | <i>Temperature of column (°C)</i> | <i>3.5 h at</i> | <i>3.5 h at</i> | <i>3.5 h at</i> | <i>8 h at</i> | <i>16 h at</i> | <i>8 h at</i> |
|------------------|------------------|-----------------------------------|-----------------|-----------------|-----------------|---------------|----------------|---------------|
| <i>Compound</i>  | <i>B.p. (°C)</i> |                                   | <i>150°</i>     | <i>200°</i>     | <i>250°</i>     | <i>250°</i>   | <i>250°</i>    | <i>330°</i>   |
| Pentane*         | 36.1             | 90                                | 1.00            | 1.00            | 1.00            | 1.00          | 1.00           | 1.00          |
| 1-Pentene        | 30.0             |                                   | 0.98            | 0.99            | 1.00            | 1.00          | 1.00           | 1.54          |
| 2-Pentene        | 36.6             |                                   | 1.15            | 1.17            | 1.19            | 1.19          | 1.18           | 1.59          |
| Cyclohexane*     | 80.7             | 150                               | —               | 1.00            | —               | 1.00          | 1.00           | 1.00          |
| Cyclohexene      | 83.0             |                                   | —               | 1.15            | —               | 1.16          | 1.16           | 1.62          |
| Benzene          | 80.1             |                                   | —               | 1.24            | —               | 1.29          | 1.28           | 2.66          |
| Benzene*         | 80.1             | 200                               | —               | —               | —               | 1.00          | 1.00           | 1.00          |
| Toluene          | 110.6            |                                   | —               | —               | —               | 1.71          | 1.74           | 2.33          |
| Ethylbenzene     | 136.2            |                                   | —               | —               | —               | 2.82          | 2.93           | 4.62          |
| Styrene          | 145.2            |                                   | —               | —               | —               | 3.36          | 3.56           | 6.55          |

\* Standard.

During the heating, elimination of water from the outer coordination sphere occurs first, then of the water from the inner coordination sphere, and at 330° a lattice process occurs as a result of the reaction of two linear molecules of the polymer by splitting off a molecule of water. This process occurs according to the reaction shown in Fig. 1.

As a result of this process, a polymer lattice builds up, in which the chromium atoms have only five ligands, and consequently one coordination position is not filled. This seems to be the cause of the increased affinity in relation to hydrocarbons and halohydrocarbons that are able to build up CT complexes.

Additional evidence is provided by the IR spectra, that of the polymer conditioned at 330° being different from those of non-conditioned polymers. In particular the band at 3610 cm<sup>-1</sup>, which is characteristic of the free hydroxyl group, is lacking, and the band at 940 cm<sup>-1</sup>, characteristic of the Cr-OH group, also disappears.

Structural changes in the polymer on heating at 330° are also evident because of the colour change from green to brown and the insolubility of such a polymer in organic solvents.

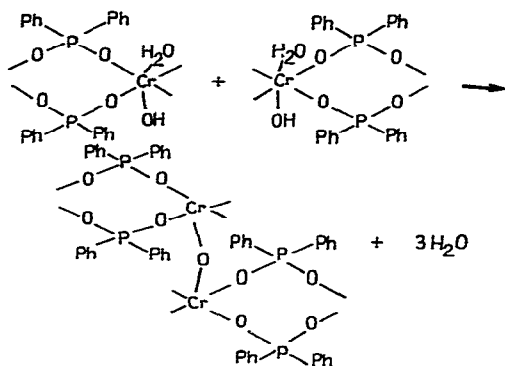


Fig. 1. Mechanism of the thermal formation of unsaturated coordination chromium atoms at 330°.

Table II illustrates the dependence of the specific surface area on the amount of the polymer used. The measurements were made by determining the adsorption of nitrogen at the temperature of liquid nitrogen by outgassing the sample at a temperature of 300° under a pressure of  $10^{-6}$  torr.

TABLE II  
SPECIFIC SURFACE AREAS OF ADSORBENTS (m<sup>2</sup>/g)

| <i>Spherosil</i><br><i>XOB 030</i> | <i>Spherosil</i><br><i>XOB 030</i><br>( <i>DMCS</i> ) | 1% <i>DPP-Cr</i> | 2% <i>DPP-Cr</i> | 3% <i>DPP-Cr</i> |
|------------------------------------|---|------------------|------------------|------------------|
| 48                                 | 36.2  | 39.1             | 44.8             | 45.5             |

Tables III en IV<sub>1</sub> present corrected and relative retention volumes (references for alkenes are corresponding alkanes, for halomethanes dichloromethane, and benzene for aromatic hydrocarbons). From the results, it can be seen that a covering of only 1% of *DDP-Cr* alters considerably the surface of the carrier. Coverage with larger amounts of the polymer produces a large increase in the retention volume. This effect with olefins and aromatic hydrocarbons increases with increasing amount of the polymer. Specific interactions of packing with elifins can result only from polymer and not from the carrier.

Considering that a polymer conditioned at 250° does not show interactions with olefins (Table I) and only conditioning at 330° produces an increase in the specificity of the packing, it can be presumed that the interactions are not caused by phenylphosphinic groups. On the other hand, only the removal of water from the coordination sphere of chromium at 330° renders the specific metal-olefin interactions possible.

The height equivalent to a theoretical plate (HETP) was determined at 200° for a column of length 1 m containing 3% of *DPP-Cr* on *Spherosil XOB 030 (DMCS)*, with heptane and benzene as adsorbates. Argon was used as the carrier gas at flow-rates in the range 1.6–3.7 cm/sec. The HETP under these conditions was 1.04 mm for benzene and 0.95 mm for heptane, which gives 1000 theoretical plates per metre of column length.

TABLE III

CORRECTED AND RELATIVE RETENTION VOLUMES OF ADSORBATES AT 150°

| Adsorbate              | Spherosil XOB<br>030 (DMCS)      |          | 1% DPP-Cr                     |          | 2% DPP-Cr                     |          | 3% DPP-Cr                     |          |
|------------------------|----------------------------------|----------|-------------------------------|----------|-------------------------------|----------|-------------------------------|----------|
|                        | $V^N$ **<br>(ml/m <sup>2</sup> ) | <i>r</i> | $V^N$<br>(ml/m <sup>2</sup> ) | <i>r</i> | $V^N$<br>(ml/m <sup>2</sup> ) | <i>r</i> | $V^N$<br>(ml/m <sup>2</sup> ) | <i>r</i> |
| Pentane*               | 0.0102                           | 1.00     | 0.0131                        | 1.00     | 0.0235                        | 1.00     | 0.0395                        | 1.00     |
| 1-Pentene              | 0.0127                           | 1.24     | 0.0145                        | 1.11     | 0.0293                        | 1.24     | 0.0548                        | 1.39     |
| <i>cis</i> -2-Pentene  | 0.0147                           | 1.44     | 0.0167                        | 1.27     | 0.0318                        | 1.35     | 0.0561                        | 1.42     |
| Cyclopentane*          | 0.0122                           | 1.00     | 0.0161                        | 1.00     | 0.0276                        | 1.00     | 0.0447                        | 1.00     |
| Cyclopentene           | 0.0152                           | 1.25     | 0.0176                        | 1.09     | 0.0324                        | 1.18     | 0.0564                        | 1.26     |
| Hexane*                | 0.0162                           | 1.00     | 0.0278                        | 1.00     | 0.0566                        | 1.00     | 0.1055                        | 1.00     |
| 1-Hexene               | 0.0212                           | 1.31     | 0.0309                        | 1.11     | 0.0690                        | 1.22     | 0.1402                        | 1.33     |
| <i>trans</i> -3-Hexene | 0.0216                           | 1.33     | 0.0315                        | 1.14     | 0.0684                        | 1.21     | 0.1373                        | 1.30     |
| Cyclohexane*           | 0.0185                           | 1.00     | 0.0328                        | 1.00     | 0.0627                        | 1.00     | 0.1102                        | 1.00     |
| Cyclohexene            | 0.0278                           | 1.50     | 0.0428                        | 1.31     | 0.0894                        | 1.42     | 0.1789                        | 1.62     |
| Benzene                | 0.0553                           | 2.99     | 0.0593                        | 1.81     | 0.1321                        | 2.11     | 0.2932                        | 2.66     |
| Dichloromethane*       | 0.0210                           | 1.00     | 0.0248                        | 1.00     | 0.0470                        | 1.00     | 0.0814                        | 1.00     |
| Chloroform             | 0.0254                           | 1.21     | 0.0381                        | 1.53     | 0.0794                        | 1.69     | 0.1338                        | 1.64     |
| Carbon tetrachloride   | 0.0229                           | 1.09     | 0.0373                        | 1.50     | 0.0731                        | 1.55     | 0.1344                        | 1.65     |

\* Standard.

\*\* Definitions:  $V^N = [(t_R - t_M) F_0 j / w_s A_s] (p_0 / 760) (T_c / T_M)$ 

where  $t_R$  is gross retention time,  $t_M$  dead time,  $F_0$  gas flow-rate from column,  $j$  column pressure gradient correction factor,  $w_s$  weight of adsorbent in column,  $A_s$  specific surface area of adsorbent,  $p_0$  column outlet pressure,  $T_c$  absolute column temperature and  $T_M$  flow meter temperature.  $r$  (relative retention volume) =  $V_{alkene}^N / V_{corr. alkene}^N$ ; for aromatics,  $r = V_{arom.}^N / V_{benzene}^N$ .

TABLE IV

CORRECTED AND RELATIVE RETENTION VOLUMES OF ADSORBATES AT 200°

| Adsorbate     | Spherosil XOB<br>030 (DMCS)   |          | 1% DPP-Cr                     |          | 2% DPP-Cr                     |          | 3% DPP-Cr                     |          |
|---------------|-------------------------------|----------|-------------------------------|----------|-------------------------------|----------|-------------------------------|----------|
|               | $V^N$<br>(ml/m <sup>2</sup> ) | <i>r</i> | $V^N$<br>(ml/m <sup>2</sup> ) | <i>r</i> | $V^N$<br>(ml/m <sup>2</sup> ) | <i>r</i> | $V^N$<br>(ml/m <sup>2</sup> ) | <i>r</i> |
| Pentane       | —                             | —        | 0.0039                        | 0.28     | 0.0073                        | 0.27     | 0.0108                        | 0.21     |
| Hexane        | 0.0080                        | 0.74     | 0.0084                        | 0.59     | 0.0142                        | 0.52     | 0.0242                        | 0.47     |
| Heptane*      | 0.0107                        | 1.00     | 0.0142                        | 1.00     | 0.0272                        | 1.00     | 0.0513                        | 1.00     |
| Octane        | 0.0139                        | 1.30     | 0.0254                        | 1.78     | 0.0521                        | 1.91     | 0.1098                        | 2.14     |
| Nonane        | 0.0192                        | 1.79     | 0.0448                        | 3.14     | 0.1011                        | 3.71     | 0.2377                        | 4.63     |
| Benzene*      | 0.0153                        | 1.00     | 0.0153                        | 1.00     | 0.0283                        | 1.00     | 0.0635                        | 1.00     |
| Toluene       | 0.0226                        | 1.47     | 0.0279                        | 1.82     | 0.0571                        | 2.01     | 0.1480                        | 2.33     |
| Ethylbenzene  | 0.0304                        | 1.98     | 0.0457                        | 2.99     | 0.1040                        | 3.67     | 0.2972                        | 4.68     |
| Styrene       | 0.0332                        | 2.16     | 0.0550                        | 3.60     | 0.1371                        | 4.83     | 0.4161                        | 6.55     |
| Chlorobenzene | 0.0239                        | 1.56     | 0.0409                        | 2.67     | 0.0881                        | 3.10     | 0.2230                        | 3.51     |
| Bromobenzene  | —                             | —        | 0.0647                        | 4.23     | 0.1496                        | 5.27     | —                             | —        |

\* Standard.

*Determination of the polarity and affinity of the packing in relation to unsaturated hydrocarbons*

Information on the polarity and affinity of the packing material containing 3% of DPP-Cr on Spherosil XOB 030 (DMCS) for unsaturated hydrocarbons can be

obtained from the increase in the retention indices ( $I_{\text{DPP-Cr}}$ ) in relation to standard retention indices resulting from boiling points, as described by Robinson and Odell<sup>19</sup>:

$$\Delta I = I_{\text{DPP-Cr}} - I_{\text{STD}}$$

where

$$I_{\text{STD}} = 100 \frac{\log \text{BP}_x - \log \text{BP}_n}{\log \text{BP}_{n+1} - \log \text{BP}_n} + 100n$$

where  $\text{BP}_x$ ,  $\text{BP}_n$ ,  $\text{BP}_{n+1}$  are the boiling points of a given compound and  $n$ -alkanes with  $n$  and  $n+1$  carbon atoms, respectively. The highest  $\Delta I$  values (Table V) obtained for aromatic compounds, which indicates a greater affinity of the polymer for these compounds, and the 1-alkenes also have large  $\Delta I$  values. Alkenes with double bonds on the second or third carbon atom show a lower affinity for the polymer. The lowest activity and the smallest  $\Delta I$  values occur for cycloalkanes ( $\Delta I$  negative) and cycloalkenes. These results indicate, that on the surface of the polymer alkanes and alkenes are more easily adsorbed than are cycloalkanes.

TABLE V

EVALUATION OF POLARITY OF ADSORBENT CONTAINING 3% OF DPP-Cr

| Adsorbate              | Standard retention index <sup>19</sup> | 3% DPP-Cr | $\Delta I$ |
|------------------------|--|-----------|------------|
| Pentane                | 500                                    | 500       | 0          |
| 1-Pentene              | 495                                    | 530.4     | +35.4      |
| <i>cis</i> -2-Pentene  | 503                                    | 533.4     | +30.4      |
| Cyclopentane           | 548                                    | 522.0     | -26.0      |
| Cyclopentene           | 532                                    | 545.3     | +13.3      |
| Hexane                 | 600                                    | 600       | 0          |
| 1-Hexene               | 587                                    | 628.0     | +41.0      |
| <i>trans</i> -3-Hexene | 594                                    | 626.9     | +32.9      |
| Cyclohexane            | 644                                    | 621.8     | -22.2      |
| Cyclohexene            | 652                                    | 667.7     | +15.7      |
| Benzene                | 642                                    | 716.5     | +74.5      |
| Toluene                | 747                                    | 827.6     | +80.6      |
| Ethylbenzene           | 844                                    | 919.1     | +75.1      |
| Styrene                | 879                                    | 964.7     | +85.7      |

### Thermodynamics of sorption

The heats of adsorption of aliphatics are greater than those of the corresponding cyclic hydrocarbons. These weaker interactions of the cyclic hydrocarbons may be due to steric hindrance.

The differential heats of adsorption, changes in thermodynamic potential and changes in entropy were calculated from the usual thermodynamic relationship<sup>17</sup>, and the results are presented in Table VI. It can be seen that greater thermal sorption effects occur on the packing containing of 3% DPP-Cr in comparison with the carrier.

The aromatic hydrocarbons are adsorbed the most strongly and their heats of adsorption are close to the heat effects of chemisorption. Such high values of the heats of adsorption can be explained by the interaction of  $\pi$ -electrons of the aromatic rings with chromium atoms. This interpretation seems to be supported by the behaviour of chlorobenzene and ethylbenzene on the adsorbent. Chlorobenzene and ethyl-

TABLE VI

## THERMODYNAMICS OF ADSORPTION

A, Spherosil XOB 030 (DMCS); B, 3% DPP-Cr-Spherosil XOB 030 (DMCS).

| Adsorbate              | $-\Delta H$ (kcal/mole) |       | $\Delta G$ at 150°<br>(kcal/mole) |      | $-\Delta S$ (cal/<br>mole·°K) |      |
|------------------------|-------------------------|-------|-----------------------------------|------|-------------------------------|------|
|                        | A                       | B     | A                                 | B    | A                             | B    |
| Pentane                | 5.42                    | 10.61 | 3.85                              | 2.72 | 21.7                          | 31.5 |
| Hexane                 | 6.43                    | 12.18 | 3.46                              | —    | 23.2                          | 33.3 |
| Heptane                | 7.58                    | 14.14 | 3.12                              | —    | 25.1                          | 36.0 |
| Octane                 | 8.55                    | 15.64 | 2.78                              | —    | 26.8                          | 37.6 |
| Nonane                 | 8.65                    | 17.74 | 2.41                              | —    | 26.2                          | 40.5 |
| 1-Pentene              | 7.06                    | 11.40 | 3.67                              | 2.44 | 25.2                          | 32.7 |
| <i>cis</i> -2-Pentene  | 7.60                    | 11.40 | 3.54                              | 2.42 | 26.3                          | 32.6 |
| Cyclopentane           | 6.00                    | 10.22 | 3.70                              | 2.61 | 22.8                          | 30.3 |
| Cyclopentene           | 7.36                    | 10.75 | 3.52                              | 2.42 | 25.6                          | 31.1 |
| 1-Hexene               | 8.15                    | 13.32 | 3.24                              | 1.65 | 26.85                         | 35.4 |
| <i>trans</i> -3-Hexene | 8.75                    | 13.22 | 3.22                              | 1.67 | 28.25                         | 35.2 |
| Cyclohexane            | 7.23                    | 11.73 | 3.35                              | 1.86 | 24.9                          | 32.1 |
| Cyclohexene            | 9.33                    | 13.00 | 3.01                              | 1.45 | 29.1                          | 34.1 |
| Benzene                | 11.31                   | 13.53 | 3.92                              | —    | 32.4                          | 34.2 |
| Toluene                | 12.72                   | 15.98 | 1.85                              | —    | 34.5                          | 37.7 |
| Ethylbenzene           | 13.77                   | 17.83 | 1.49                              | —    | 36.1                          | 40.3 |
| Styrene                | 13.57                   | 18.09 | 1.44                              | —    | 35.5                          | 40.2 |
| Chlorobenzene          | 10.18                   | 16.55 | 2.07                              | —    | 29.0                          | 38.1 |
| Dichloromethane        | 7.69                    | 11.07 | —                                 | 2.11 | 25.8                          | 31.1 |
| Chloroform             | 7.64                    | 12.10 | —                                 | 1.69 | 25.6                          | 32.6 |
| Carbon tetrachloride   | 7.45                    | 12.09 | —                                 | 1.69 | 25.1                          | 32.6 |

benzene have similar boiling points, whereas the dipole moment of chlorobenzene is higher than that of ethylbenzene; in spite of these properties, the retention data and the heat of adsorption of chlorobenzene are lower than those of ethylbenzene, which can be explained by the electron-withdrawing capability of the chlorine atom on the ring. As a result of this effect, the density of electrons on the aromatic ring is smaller, and therefore the interaction between chromium and the ring is weaker. A similar effect has been described previously<sup>1,18</sup>. The aliphatic hydrocarbons are generally adsorbed more strongly than cyclic hydrocarbons. As we already pointed out, this may be due to steric hindrance.

The  $\Delta G$  and  $\Delta S$  values indicate the much greater action on sorbed compounds of the carrier surface covered by the polymer in comparison with that of an uncovered carrier.

*Separation of test mixtures of hydrocarbons*

Separations of different test mixtures of hydrocarbons were performed on a packing coated with 3% of DPP-Cr and conditioned at 330°. Figs. 2, 3 and 4 show the separations of pentane, 1-pentene, hexane and 1-hexene; cyclohexane, cyclohexene and benzene; and benzene, toluene, ethylbenzene and styrene, respectively. Although the packing is selective towards aromatic hydrocarbons, the separation of a mixture of xylenes cannot be performed.

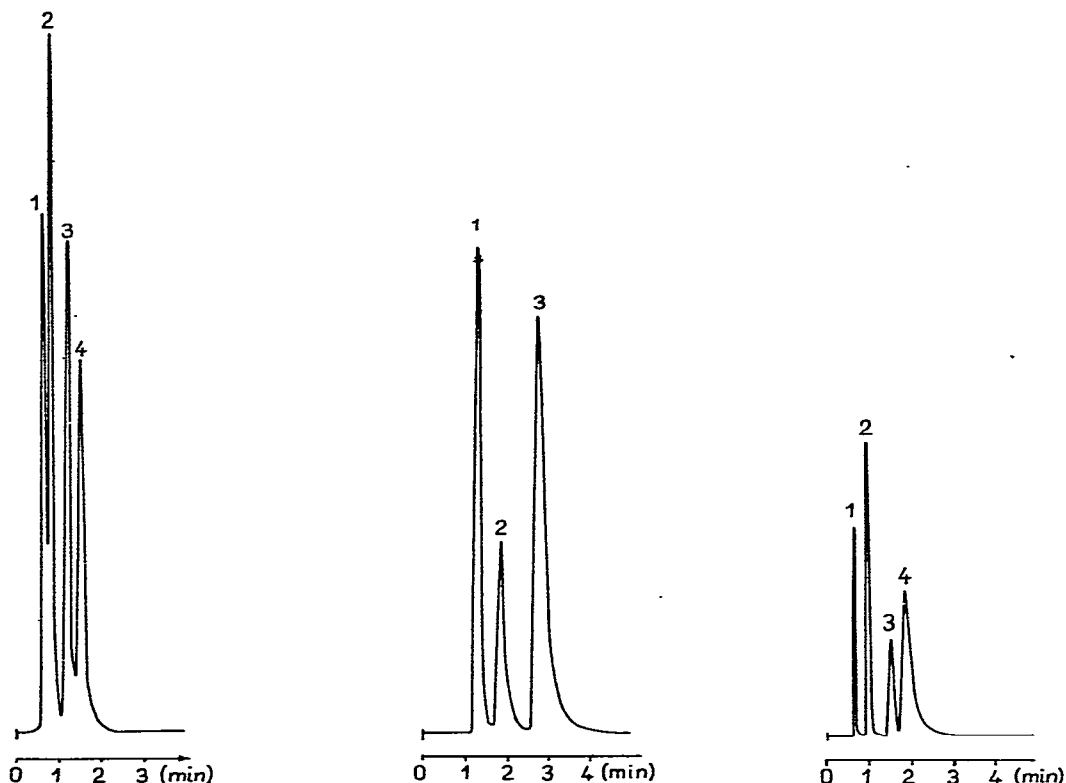


Fig. 2. Separation of pentane (1), 1-pentene (2), hexane (3) and 1-hexene (4) on an adsorbent containing 3% of DPP-Cr on Spherosil XOB 030 (DMCS). Column, 1 m  $\times$  0.4 cm I.D.; column temperature, 150.6°; carrier gas argon at 25 ml/min; detector, FID.

Fig. 3. Separation of cyclohexane (1), cyclohexene (2) and benzene (3). Conditions as in Fig. 2.

Fig. 4. Separation of aromatics: benzene (1), toluene (2), ethylbenzene (3) and styrene (4). Column temperature, 213°; other conditions as in Fig. 2.

## CONCLUSIONS

The use of the polymer of chromium(III) with the diphenylphosphinic acid on a carrier with a DMCS-treated surface provides a good packing for the separation of hydrocarbons, particularly after conditioning at 330°. The sequence of the elution of hydrocarbons depends on the density of  $\pi$ -electrons. The formation of  $\pi$ -complexes between the unsaturated hydrocarbons and the chromium atoms in the polymer might occur.

In CT adsorption chromatography, the choice of the reference phase is particularly difficult, as it is impossible to utilize the model of specific and reference phases from gas-liquid chromatography in gas-solid chromatography (GSC). The salts of alkali metals produce, under GSC conditions, specific reactions<sup>1,20</sup> which, according to the theory of King and Benson<sup>21</sup>, result from electrostatic interactions. In order to estimate the size of the interactions, resulting from the formation of the complex on



the surface of the adsorbent, it is therefore necessary to select the reference metal in such a manner that its electrostatic interaction with the olefins should be similar to the electrostatic interactions of the transition metal forming the complex, *i.e.*, (1) both metals should be incorporated in the same compound or in a similar compound; (2) both metals should have a similar ionic radius; (3) both metals should be oxidised to the same degree. We believe that the determination of the stability constants of  $\pi$ -complexes under GSC conditions is possible only with a system such as a complexing phase-reference phase which fulfils these three conditions.

## REFERENCES

- 1 J. Okamura and D. T. Sawyer, *Separ. Purif. Methods*, 1 (1972) 409.
- 2 W. Szczepaniak and J. Nawrocki, *Chem. Anal. (Warsaw)*, 20 (1975) 3.
- 3 V. Schurig, R. C. Chang, A. Zlatkis and B. Feibush, *J. Chromatogr.*, 99 (1974) 147.
- 4 W. Szczepaniak and J. Nawrocki, *Chem. Anal. (Warsaw)*, 19 (1974) 375.
- 5 O. K. Guha and J. Janák, *J. Chromatogr.*, 68 (1972) 325.
- 6 R. J. Laub and R. L. Pecsok, *J. Chromatogr.*, 113 (1975) 47.
- 7 G. H. Schenk, G. L. Sullivan and P. A. Fryer, *J. Chromatogr.*, 89 (1974) 49.
- 8 W. Kuchen, J. Delventhal and H. Keck, *Angew. Chem.*, 84 (1972) 485.
- 9 J. Delventhal, H. Keck and W. Kuchen, *Angew. Chem.*, 84 (1972) 832.
- 10 J. Delventhal, H. Keck and W. Kuchen, *J. Chromatogr.*, 77 (1973) 422.
- 11 J. Delventhal, H. Keck and W. Kuchen, *J. Chromatogr.*, 95 (1974) 238.
- 12 R. F. Hirsch, H. C. Stober, M. Kowblansky, F. N. Hubner and A. W. O'Connell, *Anal. Chem.*, 45 (1973) 2100.
- 13 B. P. Block, *Inorg. Macromol. Rev.*, 1 (1970) 115.
- 14 S. V. Vinogradova and O. V. Vinogradova, *Usp. Khim.*, 44 (1975) 1084.
- 15 P. Nannelli and H. D. Gillman, *U.S. Pat.*, No. 3,624,244.
- 16 P. Nannelli, H. D. Gillman and B. P. Block, *J. Polym. Sci., Part A-1*, 9 (1971) 3027.
- 17 A. Waksmundzki (Editor), in *Zastosowanie Chromatografii Gazowej w Badaniach Fizykochemicznych*, PAN-Ossolinicum, Wrocław, 1974, p. 99.
- 18 N. H. C. Cooke, E. F. Barry and B. S. Solomon, *J. Chromatogr.*, 109 (1975) 57.
- 19 P. G. Robinson and A. L. Odell, *J. Chromatogr.*, 57 (1971) 1.
- 20 A. V. Kiselew, *Uspekhy Khromatographii*, Nauka, Moscow, 1972, p. 33.
- 21 J. King, Jr., and S. W. Benson, *Anal. Chem.*, 38 (1966) 261.