Liquid Chromatography on Carbosilochrom and Carbosilica Gel — Silica Adsorbents with a Modified Carbon Surface

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Summary

The silica adsorbent Silochrom C-120 which is homogenous, macroporous and thermally stable, and Spherisorb S20W which is a wide-pore silica gel have been modified by the deposition on them of carbon formed by the pyrolysis of benzene. The adsorbent structures before and after modification have been studied. Columns packed with the Carbosilochrom and Carbosilica gel so obtained were used for studies of their selectivity in the liquid chromatography of an homologous series of polymethyl- and monoalkylsubstituted benzenes, alkyl-naphthalenes, methylphenols and benzoic esters on elution with solutions of methanol + water of different concentrations. An increase in the amount of carbon deposited on the adsorbent and an increase in solvent polarity results in an increase in adsorbent selectivity.

In the case of polymethylsubstituted benzenes this increase is greater than in the case of isomeric monoalkylsubstituted benzenes. For phenols this increase is less than that for the corresponding hydrocarbons. The separating power of the column can be controlled by changing the degree of specificity of the carbosilica and the polarity of the eluent.

Separation of non-polar substances or substances having large hydrocarbon segments occurs on non-specific or weakly specific adsorbents on elution with polar eluents or their solutions. This method has been called reverse phase liquid chromatography (RPLC) [2]. In our previous paper [3] it was shown that this term is not an accurate description of the molecular mechanism of separation in liquid-solid chromatography.

In earlier investigations [4—7] non-polar liquids deposited on a support were used as stationary phases. The main disadvantage of such stationary phases is that in time they are washed out of a chromatographic column. This occurs especially quickly when there is an increase in temperature. At present adsorbents without this disadvantage and adsorbent supports with chemically bonded non-polar and weakly polar stationary phases are used for such separations [2, 9—18]. The most widely used, suggested by J. J. Kirkland [2] is octadecylphase, obtained through the interaction of octadecyltrichlorosilane with a silica adsorbent surface.

In our previous paper [3] we used (for the first time in liquid chromatography) a silica adsorbent modified with a deposit of a pyrolytic carbon. Guiochon and co-workers [19] recently used in liquid-solid chromatography Carbochrome [20, 21] type adsorbents prepared by the pyrolysis of benzene vapour on carbon black particles. This method has been described in our previous papers [20, 21], and is based [22] on the heterogeneous catalytic conversion of benzene accompanied by the formation of carbon deposits on the surface of the adsorbent support which is heated to 700—850°C. This method has been used previously for the modification of adsorbent and support surfaces used in gas chromatography [22]. It was shown [3, 23] that a silica adsorbent modified by carbon layers shows high selectivity to high alkane homologues during elution with a polar eluent and can be used for their separation by liquid chromatography.

In the present work the pore structure and specific surface area of silica adsorbents modified by pyrolytic carbon deposits was investigated and some examples of the application of these adsorbents in liquid chromatography are discussed.
Adsorbents

The wide-pore silica adsorbent aerosilogel [24] (commercial name Silochrom [25]) and silica gel Spherisorb S20W (Phase Separation, Deeside, Great Britain) were used as initial adsorbents. Silochrom is a macroporous silica prepared from aerosil [24]. The structural characteristics of Silochrom are not changed on heating to 850 °C [26], the temperature of benzene pyrolysis. This pyrolysis was carried out on Silochrom C-120 at 850 °C for one hour. The mean surface concentration of carbon products on the modified adsorbent — Carbosilochrom, \( \bar{\alpha}_C \), determined using a Thermogravimetric Analyzer (Paulic-Erdey, Hungary) is 1.3 mg m\(^{-2}\). Preliminary investigation of the thermal stability of silica gel Spherisorb S20W showed that near 700 °C the adsorbent begins to sinter with a decrease in its specific surface area and pore volume. The low thermal stability of this adsorbent support restricted the upper temperature limit of the benzene pyrolysis reaction. Therefore, the modification of S20W was carried out at 750 °C. The extent of benzene conversion at this temperature is not high and the mean value \( \bar{\alpha}_C \) is 0.3 mg m\(^{-2}\). The structural characteristics of the original and modified adsorbents were determined from adsorption isotherms of benzene vapour at 25 °C (Figs. 1 and 2).

Table I shows the specific surface area, \( s \) (calculated from adsorption isotherms of benzene vapour and determined by the BET method [27] taking the area occupied by a benzene molecule in a dense monolayer on silica to be \( \omega_{mc} H_s = 0.49 \text{ nm}^2 \) [28]), the surface area of the adsorbed film, \( s' \) (just before capillary condensation [29]), the pore volume, \( V_p \), the effective Kelvin pore diameter, \( d_K \), and the average pore diameter, \( d = 4 V_p/s \).

Chromatographic Experiments

The chromatographic experiments were carried out on a Perkin-Elmer Chromatograph, model 1220 equipped with UV-detector operating at 254 nm, using stainless-steel columns (30 cm x 3 mm I.D.).

Silochrom C-120 contains particles of irregular form with an average size of ca 80 \( \mu \text{m} \) while silica gel S20W contains spherical particles of diameter ca 20 \( \mu \text{m} \). Columns were filled with adsorbents using a dry method. Water + alcohol mixtures (1:1, 7:3, 3:7) were used as eluents. The flow rate of the eluent was 1 cm\(^3\) min\(^{-1}\) and the column temperature was 50 °C. Capacity factor values, \( k_C \), were determined as the ratio of the corrected retention volume of the adsorbate to the retention volume of a virtually non-adsorbed substance (benzoic acid) under the given conditions of the chromatographic experiment.

Results and Discussion

The results given in Table I and Figs. 1 and 2 show that the original and the modified adsorbents are homogeneously porous and have wide pores. Silochrom C-120 has a somewhat lower specific surface area, \( s \), but a considerably larger pore volume, \( V_p \), and approximately 4 times larger pore sizes, \( d_K \), than silica gel S20W.

As a result of benzene pyrolysis and adsorbent modification we observe a decrease in \( s \) and \( V_p \). In the case of the macroporous and chemically pure Silochrom [26], characterised by high thermal stability, a decrease in \( s \) and \( V_p \) observed after modification at 850 °C is due to partial pore filling by benzene pyrolysis products. After combustion of the carbon which had been deposited in the pores the initial Silochrom structure was reestablished completely. It is significant that in the case of Silochrom C-120 the carbon deposition through pyrolysis does not lead to any change in the pore size \( d_K \) (Table I) and the