

CHROM. 8841

## MODIFIED CARBON BLACK IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

HENRI COLIN, CLAUDE EON and GEORGES GUIOCHON

*Laboratoire de Chimie Analytique Physique, École Polytechnique, Route de Saclay, 91120 Palaiseau (France)*

(Received October 7th, 1975)

---

### SUMMARY

The potential use of modified carbon blacks as adsorbent for high-performance liquid chromatography is discussed. The technique of particle hardening through benzene pyrolysis is described. It is shown that the consolidation must be carefully controlled, as too little hardening gives mechanically unstable packings and too much gives a heterogeneous adsorbent of small specific surface area. The advantages of graphitization after hardening are discussed in terms of efficiency and column capacity. The problems of specific surface area, small particle size and efficiency of the adsorbent at relatively large retention are pointed out. Some separations are given in order to illustrate the performance of the adsorbent.

---

### INTRODUCTION

High-performance liquid-solid (adsorption) chromatography (HPLSC) is usually performed by using columns packed with polar adsorbents such as silica gel, alumina or other inorganic solids. Although a great variety of analyses have been performed using these materials, the separation of non-polar compounds is usually very difficult or even impossible. This is also the case with series of homologous solutes. Even very simple separations such as that of benzene, toluene, ethylbenzene, etc. are virtually impossible. For this reason, separations of non-polar compounds are usually carried out by the reversed-phase technique, either in liquid-liquid chromatography (LLC) or on chemically bonded stationary phases<sup>1</sup>. The qualities and disadvantages of these methods have been considered in numerous papers, among which refs. 2-4 are very representative. Many separations using ODS bonded phases (silica modified with *n*-C<sub>18</sub> derivatives) have also been reported<sup>5-8</sup>.

Unfortunately, chemically bonded phases are not stable under all conditions and cannot solve all separation problems. It would be very interesting to have a few non-polar adsorbents that could be used in HPLSC. Telepchack<sup>9</sup> tried natural diamond, but it seems that no further work has been carried out in that direction. Some separations have been performed using porous styrene-divinylbenzene copolymer packings<sup>10</sup> and other porous polymers<sup>11</sup>.

By reference to gas-solid chromatography, it seems that graphitized thermal

carbon black (GTCB) could be an excellent non-polar and non-specific adsorbent. Its poor mechanical properties, however, prevent its direct use in modern liquid chromatography. Its particles are aggregates of small (*ca.* 2000 Å) polycrystalline polyhedrons which break more or less completely when wetted by a liquid. As from previous experience we felt that columns packed with such an adsorbent would have very interesting properties, both from the chromatography and physical chemistry points of view, we tried to modify conventional GTCB in order to obtain a material with which we could pack efficient chromatographic columns. This paper describes the first results obtained. It deals both with the method of preparation and with the chromatographic properties of non-polar carbon surfaces.

## COLUMN PREPARATION

### *Properties of carbon blacks (CB)*

CB is a very fine powder composed of micro-particles of average diameter between 0.01 and 0.5  $\mu\text{m}$ , depending on the variety of the carbon<sup>12</sup>. For most practical purposes, these micro-particles are agglomerated (pelletized) into larger particles of diameter *ca.* 50  $\mu\text{m}$ . As indicated previously, these agglomerates, which are hardly mechanically stable enough to be used in conventional gas-solid chromatography, cannot withstand high flow-rates of solvents without being fractured. The frictional forces that result from the flow of the eluent through the column make the particles dislocate as their cohesion is reduced by the decrease of the interparticular electrostatic interactions in a liquid.

The packing obtained therefore contains particles with a very wide size distribution and, more seriously, the formation of a plug of micro-particles in the column is often observed. On the other hand, the use of the 0.5- $\mu\text{m}$  diameter micro-particles to pack the column is quite impossible. It would be very difficult to prepare a good and reproducible packing with such small particles using the current wet-packing methods. Further, too high pressures would be necessary. Even so, the CB samples composed of the larger (*ca.* 0.5  $\mu\text{m}$ ) micro-particles (Sterling) have a very low specific surface area (5–10  $\text{m}^2/\text{g}$ ). In that case, columns will be easily overloaded and retentions will be too low. It therefore appears necessary to consolidate the agglomerates, but this consolidation should not change the nature of the adsorbent surface or its chromatographic properties.

### *Hardening of GTCB agglomerates*

The structure of carbon black is intermediate between amorphous carbon and graphite and its surface is heretogeneous, both chemically and energetically. For this reason, the performances of carbon blacks as adsorbents in gas chromatography are poor. Although the particle size remains unchanged after graphitization above 2800°, the surface is much cleaner and more homogeneous, especially if a further hydrogen treatment is carried out, and excellent chromatograms are obtained. For applications in HPLSC, GTCB particles have to be hardened and, as shown later, this is effected by benzene pyrolysis. The surface of pyrocarbon, however, is not homogeneous and so a further graphitization step will be necessary anyway. For practical reasons, we chose to consolidate carbon black particles and not GTCB particles.

The hardening was carried out by using a technique previously described by

Barmakova *et al.*<sup>13</sup> for gas chromatographic applications. As pointed out by these workers, it is impossible to use organic or organosilicon substances as adhesives because of their solubilities in the chromatographic eluent and/or because their polar surface changes the adsorption properties of the resulting solid. It is known that high-temperature pyrolysis of organic vapours in an inert gas stream produces pyrolytic carbon on the hot walls of the system<sup>14</sup>. It is also known that a deposit of pyrolytic carbon on carbon black particles increases its hardness<sup>15,16</sup>.

The set-up shown in Fig. 1 is a slightly modified version of those used by Barmakova *et al.*<sup>13</sup> and by others<sup>14,17</sup> who have studied the pyrolysis of benzene and other hydrocarbons into various forms of pyrolytic carbon. A crucible, B, containing the carbon powder is easily introduced through the open end of a large quartz tube, A, which is closed by a mechanical device, b, making the equipment air-tight. The length of the larger tube is such that when the tubular furnace, E, is placed around it, its end, b, is at room temperature.

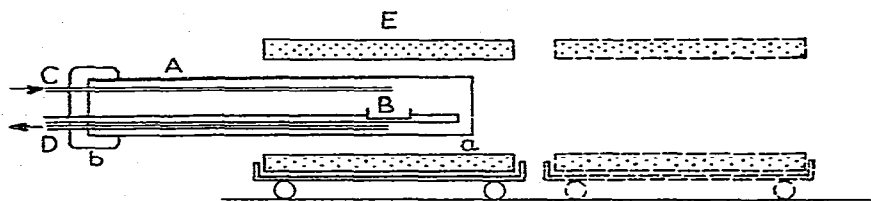


Fig. 1. Pyrolysis set-up. The dashed lines denote the position of the furnace after the pyrolysis reaction. A, Quartz tube closed at (a); B, quartz crucible; C, gas stream inlet; D, gas stream outlet; E, moving furnace.

In most instances, it was necessary to carry out the treatment of several CB samples in order to obtain the correct amount of material to pack one column. The advantage of having a movable furnace, E, is that one need not wait for it to cool when the pyrolysis reaction has been completed. Tube A cools quickly (20–30 min).

In order to prepare the gas mixture, an inert carrier gas (nitrogen) is passed through a temperature-controlled vessel containing the hydrocarbon. Benzene is used as it gives a pyrolytic carbon that can be graphitized in a second step; this is not so with all hydrocarbons<sup>18,19</sup>. During heating and cooling of the quartz tube, pure nitrogen is passed through the equipment.

#### *Effect of the experimental conditions of the pyrolysis*

The parameters that affect the final material are the composition of the gas mixture (molar fraction of benzene,  $N_{Bz}$ ), the pyrolysis temperature ( $T_p$ ), the gas flow-rate ( $D$ ), the specific surface area ( $S_{sp}$ ), the mass of CB treated ( $M$ ), the time of reaction ( $t$ ) and the volume of the reaction chamber. From a few experiments, it seems that the particle size has no influence on the result of the pyrolysis. The relationship between these parameters will be discussed elsewhere<sup>20</sup>. For the present, it is sufficient to know that the smaller is the amount of sample treated, the better are the homogeneity and reproducibility of the final product. This is why it is sometimes necessary to repeat exactly the pyrolysis process on several samples in order to obtain enough material to pack one column.

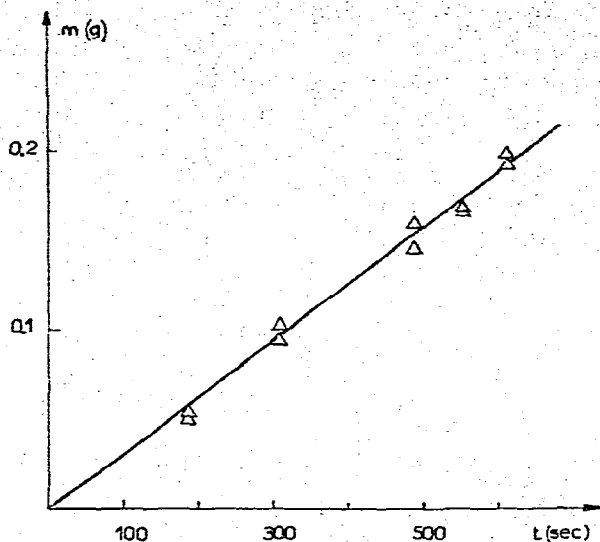


Fig. 2. Relationship between the amount of pyrocarbon deposited,  $m$  (g), and the pyrolysis time  $t$  (sec).  $T_p = 900^\circ$ ;  $N_{Bz} = 0.32$ ;  $D = 1 \text{ cm}^3/\text{sec}$ ;  $S_T = 17.5 \text{ m}^2$ ;  $S_{sp} = 8.5 \text{ m}^2/\text{g}$ .

Different observations have shown that when  $S_{sp}$  is greater than about  $10 \text{ m}^2/\text{g}$ , the specific surface area of the final product is largely determined by the ratio of the mass of pyrocarbon deposited to the sample mass ( $m/M$ ). With small values of  $S_{sp}$  and  $M$ , it was found that the amount of pyrocarbon deposited is proportional to both  $t$  (Fig. 2) and the amount of benzene circulated through the furnace,  $N_0$  (mmole) (Fig. 3):

$$N_0 = DtN_{Bz} \cdot 10^3 \quad (1)$$

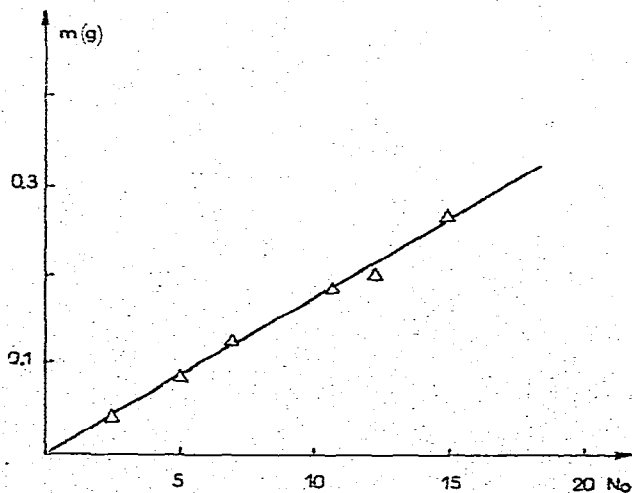


Fig. 3. Amount of carbon deposited versus amount of benzene fed to the reactor.  $T_p = 900^\circ$ ;  $N_{Bz} = 0.20$ ;  $S_T = 6.6 \text{ m}^2$ ;  $S_{sp} = 8.5 \text{ m}^2/\text{g}$ .

It is easier to harden materials with small specific surface areas than those with larger areas.

Better homogeneity of the material would probably be obtained by carrying out the pyrolysis in a fluid bed, but the technical problems involved are too difficult and we have made no attempt so far.

Considering the particle diameter, in HPLSC it is desirable to use small particles between *ca.* 4 and 15  $\mu\text{m}$ , which are difficult to obtain with carbon. Indeed, two forms of CB are available commercially, a powder composed mainly of particles that are too small to be used in chromatography and rather large beads ( $d_p > 40 \mu\text{m}$ ) obtained after pelletization. Sieving the beads gives only a few (5%) small particles ( $d_p$  5–20  $\mu\text{m}$ ), making it necessary to crush the larger beads and to sieve the resulting powder. This is very difficult because the particles agglomerate again during and after sieving and, moreover, the sieves quickly become clogged. Elutriation seems to be impossible because the beads will disaggregate into the original fine powder or because of the density dispersion, as discussed later. The small amount of material that can be prepared in one batch precludes its sieving. Hence the particles we use are relatively large ( $d_p > 15 \mu\text{m}$ ), irregularly shaped and the size distribution is rather large (15–20  $\mu\text{m}$ ), which is prejudicial to good efficiency. The retention behaviour of the carbon surface, however, does not depend on the particle diameter.

The pyrocarbon obtained from benzene pyrolysis has the so-called turbostratic structure: the different planes in which the carbon atoms have a hexagonal distribution present a very low degree of mutual orientation, so that the carbon crystallites are extremely small and the surface is very heterogeneous. By analogy with gas chromatography we considered that graphitization would improve the quality of the adsorbent. Some of the material obtained by the hardening procedure described above was heated at 3000° for 1–2 h.

### *Column packing*

It quickly became apparent that the slurry packing technique<sup>21,22</sup> has to be used, even for particles larger than 20  $\mu\text{m}$ . The slurry packing liquid is a mixture of dibromomethane and acetonitrile. The mixture density is adjusted in order to avoid considerable floating and sedimentation of carbon particles. Indeed, a fine adjustment of the composition is quite impossible and unnecessary, because of the dispersion of the particle density. This dispersion is probably caused by air trapped in pores plugged during the pyrolysis process.

Slurry packing can be performed under high pressure (*ca.* 480 bar) without fracturing the particles if they are sufficiently hardened. We used CB from Cabot, Neuilly, France (Sterling FTFF for small specific surface area and Black Pearls for larger specific surface area). Some samples were previously graphitized (GTCB). Similar results were obtained with both types of products.

## RESULTS

### *Hydrodynamics of columns*

If the CB is not hardened enough, the particles break during packing and the permeability of the column is very low. Further, a slow decrease in permeability during column operation is often observed together with a significant decrease in retention.

Columns packed with material that has been hardened sufficiently are stable and reproducible.

Using the classical Kozeny-Karman equation and the assumption that

$$\frac{\varepsilon_c^3}{180(1-\varepsilon_c)^2} = \frac{1}{1000} \quad (2)$$

(where  $\varepsilon_c$  is the extraparticle porosity), it can be derived from the data in Fig. 4 that the average particle diameters are 30, 19 and 14  $\mu\text{m}$  for columns A, B and C, respectively. These diameters are virtually identical with the lower limits of the size ranges before packing, *viz.*, 31.5–40; 20–25 and 15–20  $\mu\text{m}$ , respectively. The agglomerates are not broken during slurry packing.

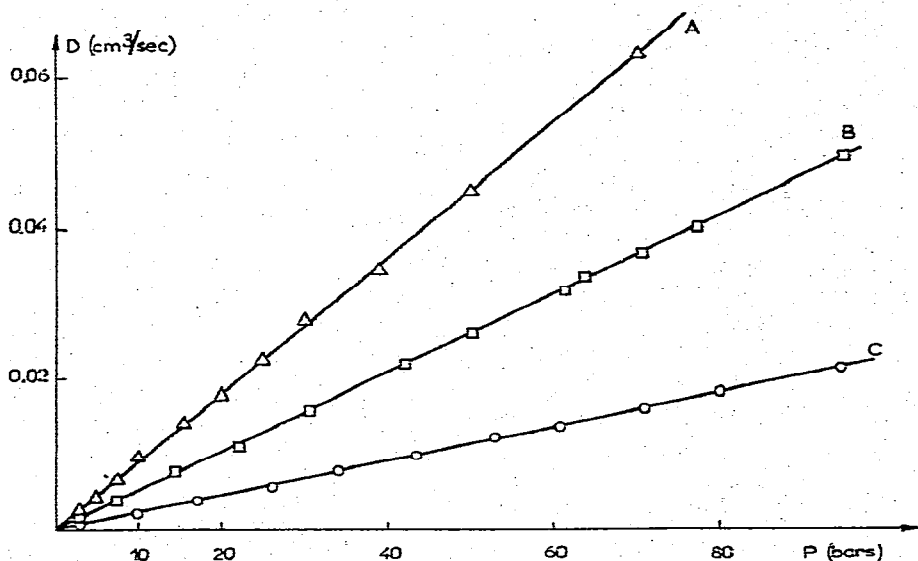


Fig. 4. Acetonitrile flow-rate ( $\text{cm}^3/\text{sec}$ ) versus inlet pressure (bars) for different columns. A:  $L = 70$  cm;  $d_c = 2$  mm;  $d_p$  before packing = 31.5–40  $\mu\text{m}$ ; 14.5% pyrocarbon. B:  $L = 50$  cm;  $d_c = 4$  mm;  $d_p$  before packing = 20–25  $\mu\text{m}$ ; 30% pyrocarbon. C:  $L = 70$  cm;  $d_c = 2.17$  mm;  $d_p$  before packing = 15–20  $\mu\text{m}$ ; 55% pyrocarbon.

### Retention on modified CB

The retention is proportional to the surface area of the adsorbent inside the column. Hardening CB by benzene pyrolysis results in a serious decrease in the specific surface area of the material, which must be taken into account. For columns A, B and C, these decreases are 25, 59 and 79%, respectively. Only the first value is acceptable for the surface area, the retention being too small otherwise. As discussed above, a smaller decrease is associated with a frailer adsorbent and unstable columns are obtained.

This shows how narrow the compromise between hardening and retention is: too much pyrocarbon leads to heterogeneous adsorbent with a low specific surface area, while too little results in unstable columns. A good compromise seems to be a deposit of about 15–20% of the initial amount of carbon black introduced in the pyrolysis set-up for carbon with an initial specific surface area of *ca.* 110  $\text{m}^2/\text{g}$ .

### Column efficiency

Fig. 5 shows the variation of  $\log h$  with  $\log v$ , where  $h$  is the reduced plate height ( $HETP/d_p$ ) and  $v$  is the reduced velocity ( $ud_p/D_m$ ) of the liquid phase. Even at low velocity,  $h$  is large. This may be caused by the formation of bottle-necks or narrow pores during pyrolysis; very slow mass transfer in such pores would result in excessive peak broadening. More probably because of the irregular shape and large size range of the particles, incorrect packing is achieved and a good packing procedure has yet to be designed. Correspondingly the minimum plate height could not be reached whereas classically the minimum of  $h$  is obtained for  $v \approx 2-3$ .

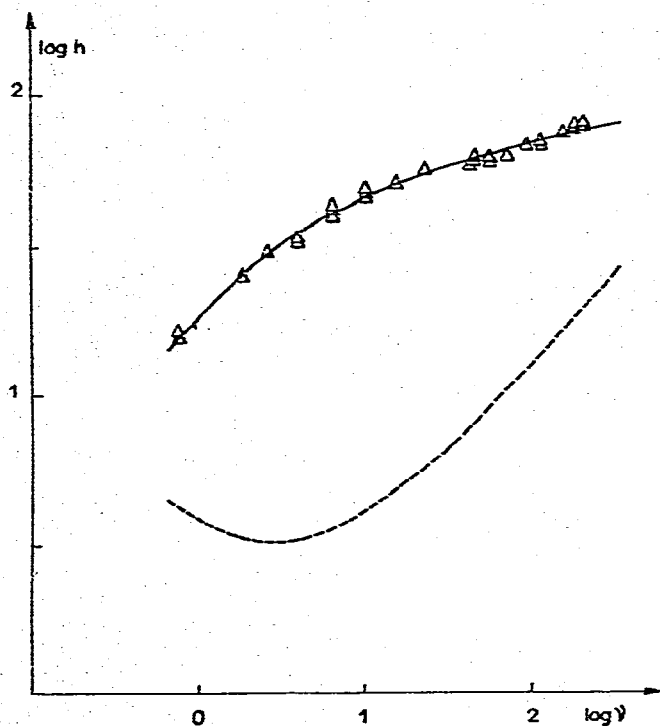


Fig. 5. Reduced plate height versus reduced velocity. Liquid phase: acetonitrile. Solute: phenol ( $k' = 0$ ). Column:  $L = 70$  cm;  $d_c = 2$  mm;  $d_p = 31.5-40 \mu\text{m}$ . Dashed lines denote classical plot with Porasil adsorbent<sup>6</sup>.

### Influence of graphitization

One of the characteristics of hardened CB columns is the very poor efficiency and the large asymmetry of peaks with a capacity factor above *ca.* 1.5. This is presumably due to column overloading through an isotherm effect, because, as already mentioned, the surface area decreases after hardening. By analogy with gas chromatography when GTCB and carbon blacks are used, we thought that graphitization of the material after hardening with a pyrocarbon deposit could improve the qualities of the columns.

The few experiments performed seem to confirm this assumption. Firstly, graphitization improves the kinetics of mass transfer (Fig. 6). For  $k' = 0$ , the same efficiencies are observed with the graphitized and non-graphitized materials. This result shows that the columns are similarly packed and that the packing is reproducible. On the other hand, for retained compounds, the efficiency is much better when using a graphitized adsorbent. Secondly, the graphitization improves the column capacity, as illustrated in Fig. 7. The retention volumes are derived from peak maxima. Extrapolation to a zero sample size seems to give the same value of the retention volumes ( $V_0$ ) for both graphitized and non-graphitized materials. A sample size of  $3.5 \mu\text{g}$  (density *ca.*  $0.2 \mu\text{g}/\text{m}^2$ ) produces a 5% decrease in the retention when the adsorbent is graphitized and 26% when it is not. Further, the peaks are more symmetrical when the adsorbent is graphitized. Graphitization of the consolidated adsorbent particles thus seems to be necessary, at least for CB samples with a small specific surface area.

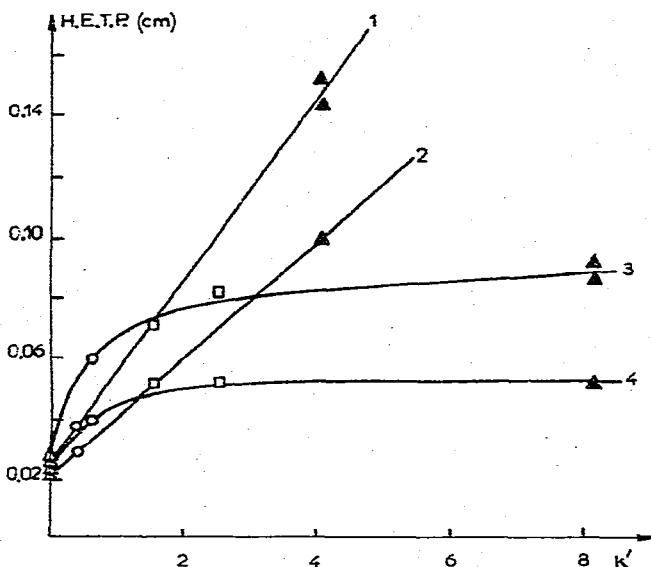


Fig. 6. Influence of graphitization on column efficiency (HETP, cm). All columns:  $L = 70 \text{ cm}$ ;  $d_c = 2 \text{ mm}$ ;  $d_p = 25\text{--}31.5 \mu\text{m}$ . 1, 2 = Non-graphitized material; 3, 4 = graphitized material. Flow-rate: 1, 3 =  $2 \text{ cm}^3/\text{min}$ ; 2, 4 =  $0.5 \text{ cm}^3/\text{min}$ . Solvent: acetonitrile.  $\Delta$  = Benzene ( $0.3 \mu\text{l}$ );  $\circ$  = 1,2,5-trimethylbenzene ( $0.5 \mu\text{l}$ );  $\square$  = 1,2,4,5-tetramethylbenzene ( $4 \mu\text{l}$ );  $\blacktriangle$  = pentamethylbenzene ( $4 \mu\text{l}$ ).

### Choice of solvent

It is known that in reversed-phase chromatography the order of the eluotropic strength of solvents is the reverse of that classically observed on polar adsorbents<sup>23</sup>. To a first approximation it can be said that, in the absence of specific interactions, the more polar the solvent, the weaker is its eluotropic strength. With a given solvent, the more polar the solute, the smaller is the retention. This, however, is only a very rough approximation, as the contribution of the whole solute molecule and especially its molecular area must be taken into account. Nevertheless, it can be predicted that very polar solutes should be eluted with very polar solvents, slightly polar or polarizable



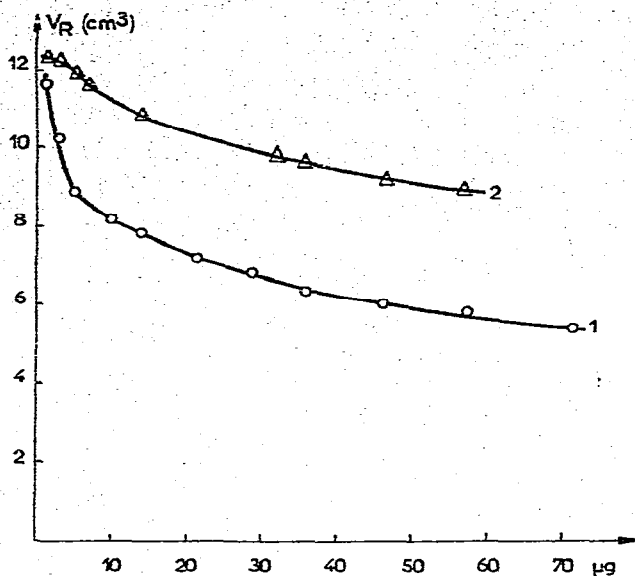


Fig. 7. Influence of graphitization on column capacity. Retention volume ( $V_R$ ,  $\text{cm}^3$ ) versus sample size ( $\mu\text{g}$ ). Columns:  $L = 70$  cm;  $d_c = 2$  mm;  $d_p = 25\text{--}31.5$   $\mu\text{m}$ . Flow-rate:  $2.5$   $\text{cm}^3/\text{min}$ . Solvent: acetonitrile. Solute: *m*-terphenyl. 1 = Non-graphitized material; 2 = graphitized material.

solutes with slightly polar solvents (acetonitrile, ethyl acetate, methylene chloride, etc.) and non-polar solutes with non-polar eluents (hydrocarbons). Water is a very polar solvent but is difficult to use because it wets the carbon surface poorly<sup>24</sup>. Moreover, few organic compounds are soluble in water. Mixtures of water and acetonitrile or methanol, however, can be used conveniently to obtain solvent mixtures with a large range of eluotropic strengths (Fig. 8). As predicted, the retention of solutes increases with the concentration of water. Note also the inversion of elution order between 1,3,4-trimethylbenzene and 3,4,5-trimethylphenol.

The solvent that we most commonly use is acetonitrile; it is relatively polar but has a low viscosity ( $\eta_{15^\circ} = 0.375$  cP). The choice of the most suitable eluent depends, of course, on the characteristics of the column and the compounds to be separated.

#### *Analytical performance and some simple separations*

In order to demonstrate the interest of a non-polar adsorbent, we studied the influence of the carbon number in homologous series on the column capacity factor (Fig. 9). The plots yield almost straight lines for different series, the slopes of the different lines being almost identical. This result is similar to that observed in gas-solid<sup>25-28</sup> or gas-liquid<sup>29-30</sup> chromatography and different from that obtained in LSC using polar adsorbents such as silica gel and alumina.

Fig. 10 shows the separation of methylphenols. The chromatogram is composed of different groups, each being characteristic of the degree of substitution of the phenols. These compounds are separated primarily on the basis of their molecular weight. It is not yet possible to separate all isomers in each group. This situation is

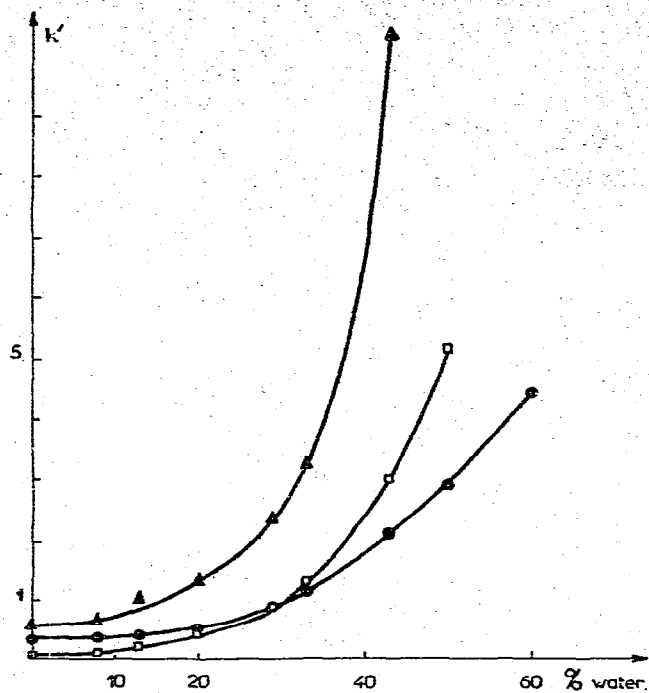


Fig. 8. Variation of column capacity factor,  $k'$ , with volume concentration of water in the solvent (acetonitrile + water). ▲ = 2,3,4,6-Tetramethylbenzene; ● = 3,4,5-trimethylphenol; □ = 1,3,4-trimethylbenzene.

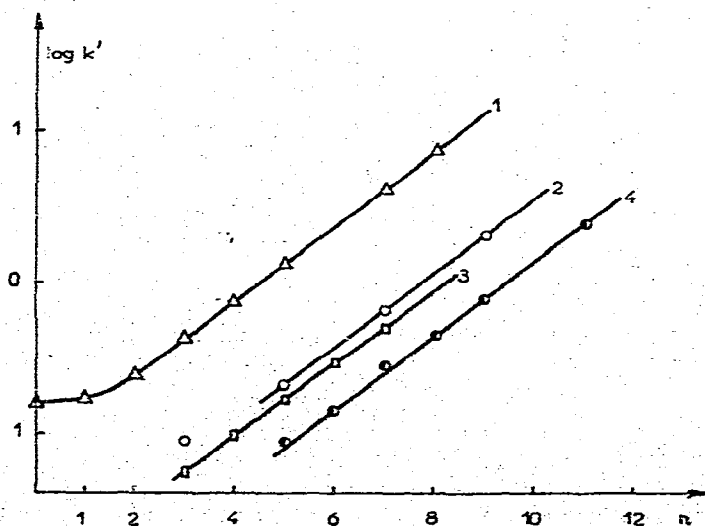


Fig. 9. Variation of logarithm of the column capacity factor with the number of carbon atoms in the molecules of homologous series. Solvent: methanol. 1 =  $\text{CH}_3-(\text{CH}_2)_n-\text{C}_6\text{H}_5$ ; 2 =  $\text{CH}_3-(\text{CH}_2)_n-\text{Br}$ ; 3 =  $\text{CH}_3-(\text{CH}_2)_n-\text{Cl}$ ; 4 =  $\text{CH}_3-(\text{CH}_2)_n-\text{OH}$ .

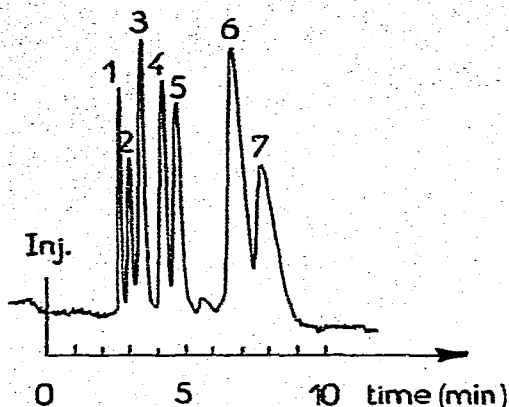


Fig. 10. Separation of phenols. Solvent: acetonitrile. Column:  $L = 70$  cm;  $d_c = 2.17$  mm;  $d_p = 15\text{--}20$   $\mu\text{m}$ . Flow-rate:  $0.5$  cm<sup>3</sup>/min. 1 = Benzene; 2 = phenol; 3 = *o*-cresol; 4 = 2,3-dimethylphenol; 5 = 2,4-dimethylphenol; 6 = 2,4,5-trimethylphenol; 7 = 3,4,5-trimethylphenol.

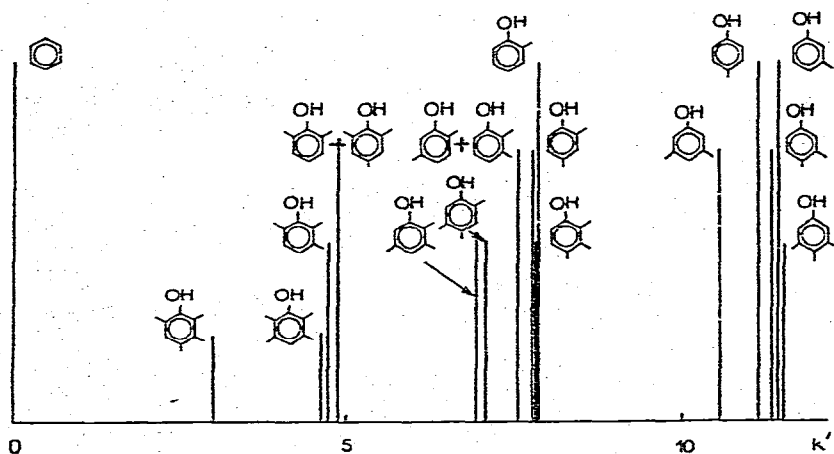


Fig. 11. Column capacity factors of methylphenols on silica gel (Partisil 5, Reeve Angel, Clifton, N.J., U.S.A.) using the solvent mixture *n*-hexane-ethyl acetate (95:5).

very similar to that in gas chromatography with GTCB<sup>31</sup>. Using silica gel as adsorbent in HPLSC, the separation is performed on the basis of the polarity. The retention is therefore largely influenced by the geometry of the phenols. Fig. 11 illustrates the order of elution of phenols on silica gel using *n*-hexane-ethyl acetate (95:5) as eluent<sup>32</sup>. Large overlaps between the different degrees of substitution occur, the three groups of solutes being di-*ortho*-substituted phenols, mono-*ortho*-substituted phenols and phenols with no *ortho*-substitution.

The *n*-alkylbenzenes are very easily separated (Fig. 12). The separation is performed with a low-efficiency column and the resolution is still greater than 2 for each pair of peaks. Again, the order of elution follows the molar weight. Another separation of homologues is illustrated in Fig. 13. This separation is rather tedious using a

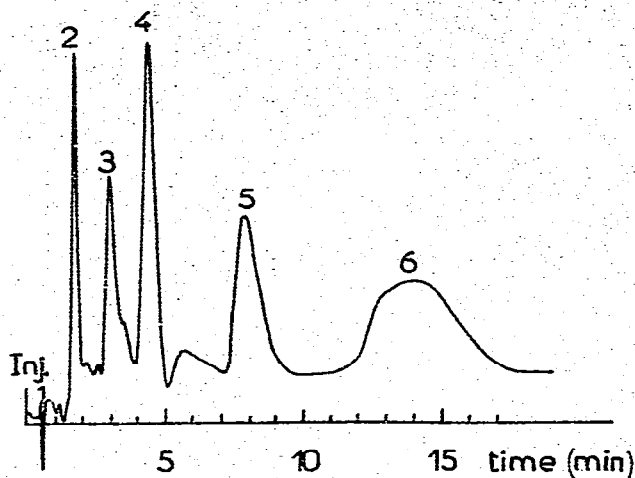


Fig. 12. Separation of *n*-alkylbenzenes. Solvent: acetonitrile–water (46:54, v/v). Column:  $L = 16.5$  cm;  $d_c = 3.7$  mm;  $d_p = 15$ – $20$   $\mu$ m. Flow-rate:  $2$  cm<sup>3</sup>/min. 1 = Unretained solute; 2 = benzene; 3 = toluene; 4 = ethylbenzene; 5 = *n*-propylbenzene; 6 = *n*-butylbenzene.

silica gel packed column but admittedly would be easy in gas chromatography. The use of an acetonitrile–water gradient would certainly allow the separation of a greater number of linear aliphatic alcohols.

Finally, the chromatogram in Fig. 14 illustrates the separation of different aromatic hydrocarbons. A comparison between the capacity factors of these com-

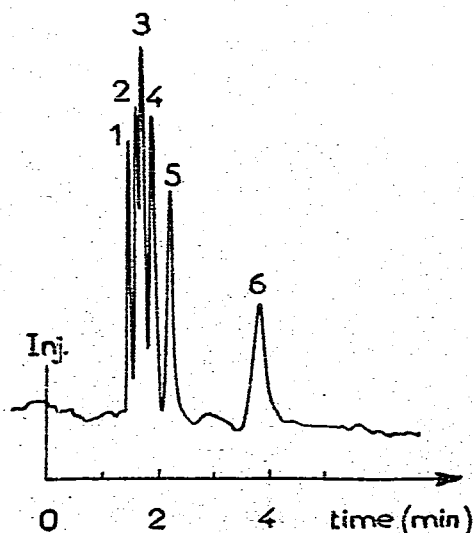


Fig. 13. Separation of *n*-alkanols. Solvent: acetonitrile. Column:  $L = 70$  cm;  $d_c = 2.17$  mm;  $d_p = 15$ – $20$   $\mu$ m. Flow-rate:  $1$  cm<sup>3</sup>/min. 1 = *n*-C<sub>5</sub>H<sub>11</sub>OH; 2 = *n*-C<sub>7</sub>H<sub>15</sub>OH; 3 = *n*-C<sub>8</sub>H<sub>17</sub>OH; 4 = *n*-C<sub>9</sub>H<sub>19</sub>OH; 5 = *n*-C<sub>10</sub>H<sub>21</sub>OH; 6 = *n*-C<sub>12</sub>H<sub>25</sub>OH.

pounds on carbon black, silica gel and alumina is given in Table I. It appears that for this particular separation, carbon is the best adsorbent.

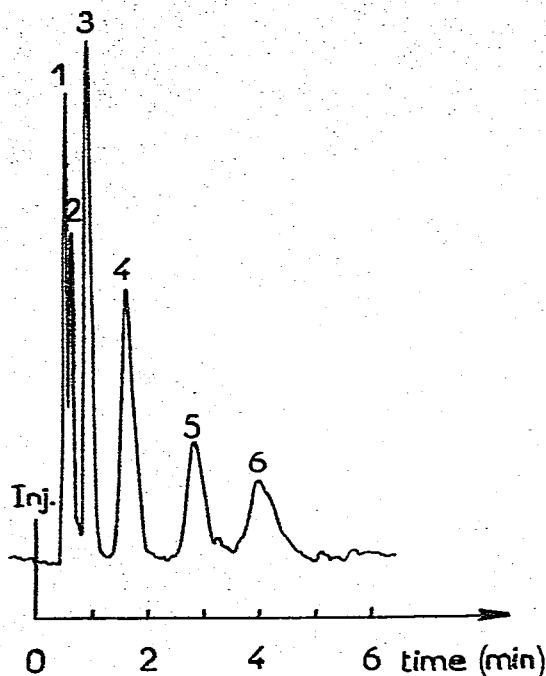


Fig. 14. Separation of naphthalene derivatives. Solvent: acetonitrile. Column:  $L = 70$  cm;  $d_c = 2$  mm;  $d_p = 31.5\text{--}40$   $\mu\text{m}$ . Flow-rate:  $2.8$   $\text{cm}^3/\text{min}$ . 1 = Tetralin; 2 = naphthalene; 3 = 2-methylnaphthalene; 4 = 2,6-dimethylnaphthalene; 5 = fluorene; 6 = 1,3,7-trimethylnaphthalene.

TABLE I  
COMPARISON OF THE RETENTION OF NAPHTHALENE DERIVATIVES ON VARIOUS ADSORBENTS

Solute	Capacity factor		
	Carbon black	Silica <sup>23</sup>	Alumina <sup>33</sup>
Tetralin	0.17	2.20	0.35
Naphthalene	0.40	2.34	0.81
2-Methylnaphthalene	0.94	2.38	0.83
2,6-Dimethylnaphthalene	2.43	2.42	0.93
Fluorene	5.06	3.77	2.24
1,3,7-Trimethylnaphthalene	7.51	—	—

## CONCLUSION

Although the packed columns we have studied still do not have efficiencies as great as those obtained with conventional, polar adsorbents, the first results are very promising. The modified CB has proved to be a good packing for HPLSC. The results are reproducible and the analytical performances are good.

Progress in three different directions should be made in the future in order to help in the development of the use of non-polar adsorbents: (1) to achieve more efficient columns, for example through the use of small particles of narrow size range. (2) To obtain a better efficiency when the capacity factor is important. We expect that a better controlled hardening procedure will improve this efficiency. (3) We must obtain adsorbents of larger specific surface area in order to increase sample sizes. Work is in progress in these different fields.

#### ACKNOWLEDGEMENTS

The gift of samples by Mr. Bourgeois of Cabot France S.A. is acknowledged. This work was carried out under a grant from the D.R.M.E. The laboratory is affiliated to the C.N.R.S. as E.R.A. No. 553.

#### REFERENCES

- 1 I. Halasz and I. Sebestian, *Angew. Chem., Int. Ed. Engl.*, 8 (1969) 453.
- 2 D. C. Locke, *J. Chromatogr. Sci.*, 11 (1973) 120.
- 3 A. Pryde, *J. Chromatogr. Sci.*, 12 (1974) 586.
- 4 R. E. Leitch and J. J. de Stefano, *J. Chromatogr. Sci.*, 11 (1973) 105.
- 5 J. D. Gordon and J. H. Knox, *J. Chromatogr. Sci.*, 10 (1972) 549.
- 6 J. H. Knox and G. Vasvari, *J. Chromatogr.*, 83 (1973) 181.
- 7 J. H. Knox and M. Saleem, *J. Chromatogr. Sci.*, 7 (1969) 745.
- 8 J. A. Schmit, R. A. Henry, R. C. Williams and J. F. Dieckman, *J. Chromatogr. Sci.*, 9 (1971) 645.
- 9 M. J. Telepchak, *Chromatographia*, 6 (1973) 234.
- 10 J. Janák, Z. Jagarić and M. Dressler, *J. Chromatogr.*, 53 (1970) 525.
- 11 O. L. Hollis, *J. Chromatogr. Sci.*, 11 (1973) 335.
- 12 J. Millet, *Les Carbones*, Masson, Paris, 1965, Vol. 1, p. 15.
- 13 T. V. Barmakova, A. V. Kiselev and N. V. Kovaleva, *Kolloid Zh.*, 36 (1974) 133.
- 14 G. Prado and J. Lahaye, *J. Chim. Phys.*, 70 (1973) 1678.
- 15 K. A. Hofman and U. Hofman, *Chem. Ber.*, 59 (1926) 2433.
- 16 A. R. G. Brown, A. R. Hall and W. Watt, *Nature (London)*, 172 (1953) 1145.
- 17 K. I. Makarov and V. K. Pechik, *Carbon*, 12 (1974) 391.
- 18 A. Weintraub and P. L. Walker, in *Third Conference on Industrial Carbons and Graphite, London, 1970*, Society of Chemical Industry, London, 1971, p. 75.
- 19 C. F. Cullis and A. C. Norris, in *Third Conference on Industrial Carbons and Graphite, London, 1970*, Society of Chemical Industry, London, 1971, p. 84.
- 20 H. Colin and G. Guiochon, to be published.
- 21 J. D. Kirkland, *J. Chromatogr. Sci.*, 9 (1971) 206.
- 22 R. E. Majors, *Anal. Chem.*, 44 (1971) 1722.
- 23 L. R. Snyder, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968, pp. 194-195.
- 24 D. C. Locke, *Advan. Chromatogr.*, 9 (1969) 55.
- 25 D. G. Eisen, A. V. Kiselev, A. E. Pilt, S. A. Rang and K. D. Shcherbakova, *Chromatographia*, 4 (1971) 448.
- 26 A. Yu. Zaprometov, E. V. Kalashnikova, A. V. Kiselev and K. D. Shcherbakova, *Zh. Fiz. Khim.*, 46 (1972) 708.
- 27 E. V. Kalashnikova, A. V. Kiselev and K. D. Shcherbakova, *Chromatographia*, 7 (1974) 22.
- 28 A. Lykourghiotis, I. Hadzistelios and N. A. Katsanos, *J. Chromatogr.*, 110 (1975) 287.
- 29 A. B. Littlewood, *Gas Chromatography*, Academic Press, New York, 1962, p. 85.
- 30 S. D. Nogare, R. S. Juvet, Jr., *Gas-Liquid Chromatography*, Interscience, New York, 1966, p. 337.
- 31 C. Vidal Madjar, J. Ganansia and G. Guiochon, in N. Stock (Editor), *Gas Chromatography 1970*, Institute of Petroleum, London, 1971, p. 20.
- 32 A. M. Siouffi and G. Guiochon, to be published.
- 33 M. Martin, J. Loheac and G. Guiochon, *Chromatographia*, 5 (1972) 33.