DEVELOPMENT AND USE OF CARBON ADSORBENTS IN HIGH-PERFORMANCE LIQUID–SOLID CHROMATOGRAPHY

I. CARBON-COATED SILICA PARTICLES

H. COLIN and G. GUIOCHON

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

SUMMARY

　　The technique for coating silica particles with a layer of pyrocarbon is described. The conditions of preparation are important as they determine both the chromatographic performance and the degree of agglomeration of particles during coating.

　　The effect of the coating was studied in terms of both efficiency and retention data. For the silica studied (Spherosil XOB 75), moderate amounts of pyrocarbon (less than 15%) gave the best results; greater degrees of coating give a large decrease in efficiency with increasing retention, while smaller degrees of coating give very small retentions and polar adsorbents.

　　Some simple separations are shown to illustrate the analytical characteristics of these adsorbents.

INTRODUCTION

　　Reversed-phase chromatography is based on non-specific intermolecular interactions between (1) adsorbent and solute and (2) adsorbent and eluent. A chromatographic process based only on dispersive (non-specific) forces needs a non-specific and consequently non-polar adsorbent. As recently pointed out by Bebris et al.[1], the basic foundations are identical in classical liquid–solid chromatography (LSC) (using silica or alumina) and in reversed-phase chromatography. In particular, all interactions (adsorbent–solute, adsorbent–solvent and solvent–solute) must be taken into account in order to understand the mechanism of retention.

　　However, contrary to Bebris et al.[1], we do not think that it is unreasonable or misleading to continue to use the term "reversed-phase". It allows a more precise definition of the type of interactions that will be responsible for the retention and consequently for the separations. Obviously, we must always bear in mind that no basic difference exists between the two instances. The retention of a solute is due to its positive adsorption and consequently to negative adsorption of the solvent. However, at the molecular level, the difference between reversed-phase and classical LSC is that only non-specific interactions occur in the former while specific interactions are important in the latter. This aspect is important.

TABLE I

EXPERIMENTAL CONDITIONS FOR THE PREPARATION OF CARBON-COATED SILICA PARTICLES

L = column length; d_c = column diameter; d_p = particle size.

Column	L (cm)	d_c (cm)	d_p (μm)	Support	Coating (%)	Pyrolysis temperature (°C)	Benzene saturator temperature (°C)	Flow-rate (cm³/min)	Reaction time (min)	Amount treated (g)
A	65	2.17	31.5-40	Spherosil (XOB75)	0.3*	900	29	34.6	1	3.51
B	65	2.17	31.5-40	Spherosil (XOB75)	0.8*	900	29	34.6	3	3.51
C	65	2.17	31.5-40	Spherosil (XOB75)	1.5*	900	29	63.15	3	3.52
D	65	2.17	31.5-40	Spherosil (XOB75)	4.0	900	29	63.15	10	3.52
E	65	2.17	31.5-40	Spherosil (XOB75)	15.4	900	29	63.15	31	3.56
F	65	2.17	31.5-40	Spherosil (XOB75)	53**	947	30.5	57.9	40	3.23
G	65	2.17	31.5-40	Spherosil (XOB75)	140**	947	30.5	57.9	100	3.40
H***	11.5	4.17	6	Partisil 5	4.1	904	36.5	64	3	0.70
I***	12	4.17	6	Partisil 5	13.6	904	36.5	65.8	4	0.76
J***	11.3	4.17	6	Partisil 5	24.8	904	36.5	65.8	10	0.76
R	75	2.17	31.5-40	Sterling FT,FF	13 (graphitized)	947	39	98	30	24

* Calculated from previous experiments.
** The precision is low as the particles stick to the wall.
*** Silica coated with the first set-up (without stirring particles, see ref. 2).

We have described in previous papers[2,3] the treatment of carbon black (CB) particles to obtain a mechanically stable adsorbent for LSC and various chromatographic applications. It has been mentioned[3] that the problem of obtaining small particles that are hard enough to stand the high pressure drop that is commonly used in packing techniques and in many experiments could be solved by coating silica particles with carbon. Bebris et al.[1] have published some preliminary results. This paper describes the results we have obtained recently with different silica particles. One of the most important results is that it has proved possible to prepare a new adsorbent that exhibits chromatographic properties that are similar to those of pure carbon.

Carbon black-coated silica is thermally very stable and is not sensitive to pH insofar as the silica is not destroyed and can be used in any solvent. As for pure carbon, the equilibration time when changing the solvent is very small and the reproducibility of the chromatographic data obtained is very good. It is also possible to change the chromatographic properties by decreasing the amount of pyrocarbon coated on the silica particles. It is thus possible to adjust retention and to optimize efficiency.

PREPARATION OF CARBON-COATED SILICA PARTICLES (CCSP)

It is well known that high efficiencies in high-performance liquid–solid chromatography (HPLSC) are achieved by the use of small particles (ca. 5 μm in diameter), and we have mentioned previously the difficulties encountered in trying to make carbon particles in that range[3]. We thought that coating fine silica particles with pyrocarbon would be a means of avoiding these problems. In their recent paper, Bebris et al.[1] gave little information about the preparation technique and the properties of the product obtained, and no chromatograms were shown.

The coating procedure used in this work is identical with that described previously for carbon-black hardening[2-4]. The set-up provides for continuous stirring of the powder during the pyrolysis process, which increases both the production and the homogeneity of the final product. More details will be given in a later paper[5]. Four different silica gels were used: Partisil 5 (Reeve Angel, Clifton, N.J., U.S.A.), Lichrosorb Si 60 5 μm (Merck, Darmstadt, G.F.R.) and Spherosil XOA 600 and XOB 75 (Rhone-Progil, Antony, France). Only systematic results obtained with large (30–40-μm Spherosil) and small (ca. 5-μm Partisil) particles are reported here (cf., Table I).

In order to make possible an exact measurement of the amount of pyrocarbon coated, the silica was first dehydrated at 900° for 3 h under a stream of pure nitrogen. It is strongly advised that fine silica particles (5 μm) should not be stirred during this step, as large particles (up to several hundred microns) would be formed by pelletization; these pellets are then hardened by the pyrocarbon coating (cf., Fig. 1).

Carbon coating was carried out at 950, 900 and 875°. While the weight loss during dehydration is approximately the same at all three temperatures, it seems that the agglomeration is less important at 875°. Moreover, we observed that the pyrolysis reaction gives better results at the lowest temperature. The experimental conditions under which ten different samples and a reference sample of pure carbon were prepared are given in Table I.

The carbon layer should cover completely all of the silica surface and be thick enough to offset the sorption properties of silica. Hence it would seem that a large
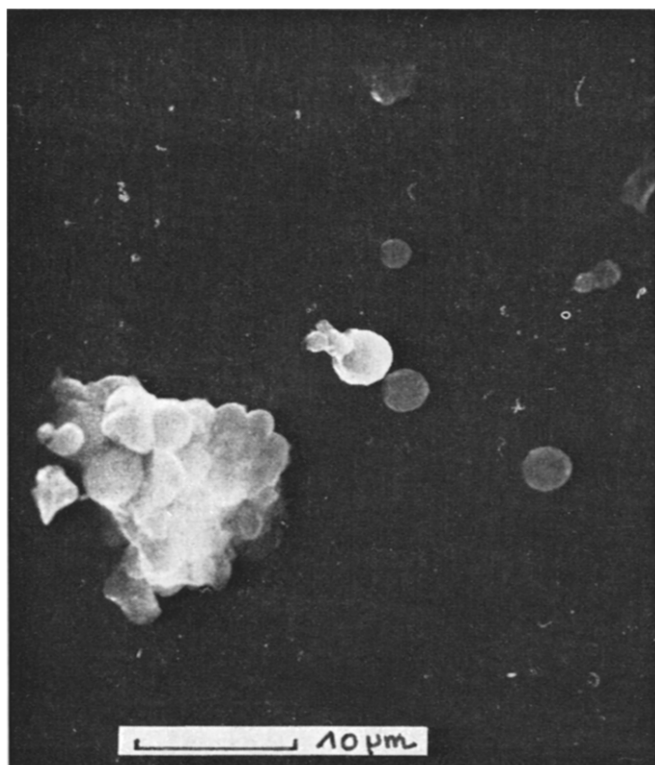
Fig. 1. Scanning electron microscope photograph of carbon-coated silica. Agglomerate of Spherosil particles made during dehydration.

amount of pyrocarbon is necessary. However, it rapidly became clear to us that it is impossible to coat more than about 50–55% (w/w) of carbon on any of the 5-μm silica particles used, otherwise all of the particles become stuck together into hard, compact agglomerates that cannot be broken down into the individual particles. At present we do not know whether this limit results from a property of carbon formation or of the experimental set-up.

The upper limit of the degree of pyrocarbon coating is sharp; 5-μm particles have been coated with 41% and 53% of pyrocarbon without any notable agglomeration (observation under optical microscope), while all attempts to coat more than 60% produced particles that were agglomerated to a large extent, if not completely. When coating larger particles, this problem is much less critical. For instance, using a 31.5–40-μm sieve fraction, coatings exceeding 140% were possible without agglomeration, although the particles stuck to the pyrolysis tube wall. For hardened carbon black[2], the greater is the degree of coating, the more metallic grey were the particles; at low degrees of coating they were black.

Photographs of particles of carbon-coated silica obtained with a scanning electron microscope are shown in Figs. 2, 3 and 4. Unfortunately, the secondary emission coefficients of silicon and carbon are very similar, so these substances cannot be readily distinguished on the photographs.
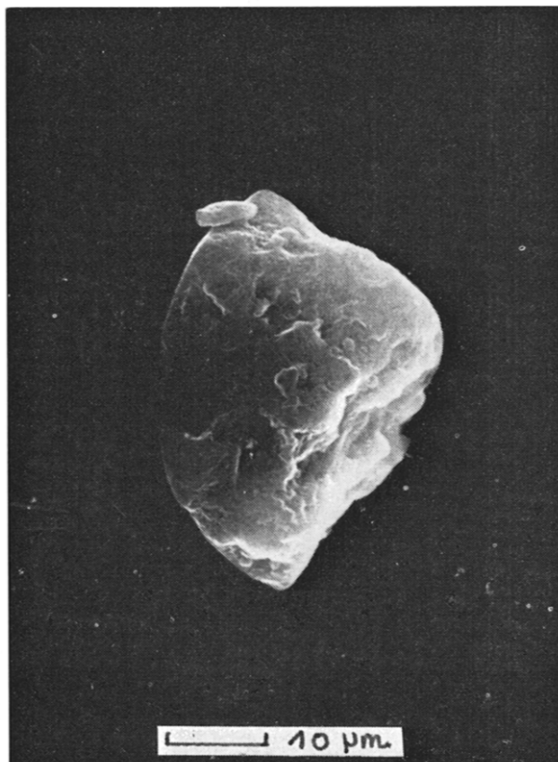
Fig. 2. Detail of a particle of Spherosil coated with 0.84% of pyrocarbon (cf., Table I, B).

Fig. 3. Detail of a particle of Spherosil coated with 15.4% of pyrocarbon (cf., Table I, E).

The clear spots in Fig. 2, showing a silica with a low carbon coating (0.8%), are probably carbon. This is in agreement with the generally accepted assumption that benzene pyrolysis does not produce carbon layers directly on the whole silica surface but various substances of higher molecular weight that eventually give droplets and condense further in the liquid state. Figs. 3 and 4 show that at high degrees of coating the particles lose their spherical shape. Large amounts of carbon form around the particle core but, as will be shown later, the porosity and specific surface area remain large.

STUDY OF COLUMN EFFICIENCY

All columns are packed using the slurry technique. The slurry liquid is a mixture of dibromoethane and acetonitrile (ca. 76:24, v/v), accurate adjustments being made, depending on the degree of coating. A suspension is prepared with 10% (w/w) of coated silica particles. The packing pressures are 300 bar for larger particles and 600 bar for the smaller. Some experimental data are shown in Fig. 5 for two columns, B and G (cf., Tables I and II). The curves are very similar for non-retained solutes, showing that the packing technique is reproducible, but are different for retained solutes.
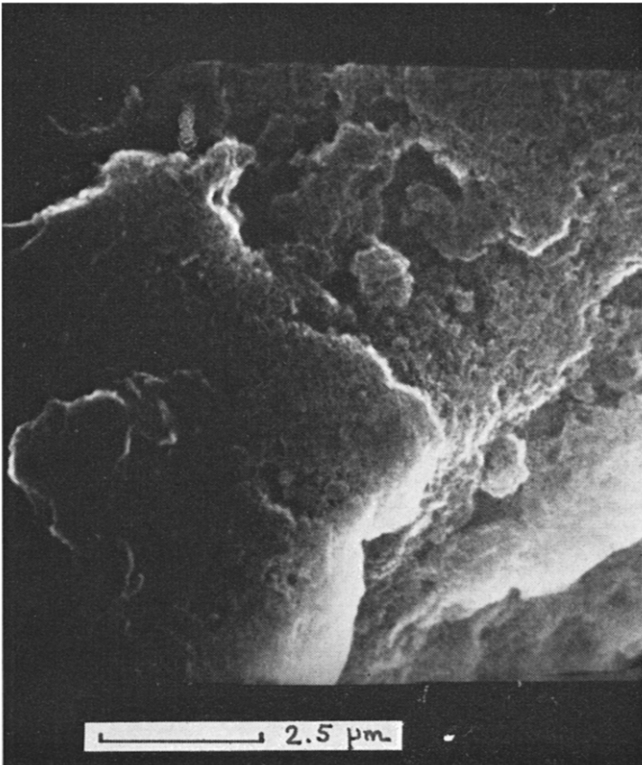
Fig. 4. Detail of the centre of particle shown in Fig. 3.

Usually it can be assumed that the reduced plate height h ($= H/d_p$), and the reduced velocity v ($= ud_p/D_m$) are related by the equation of Knox and co-workers[6–8]:

$$h = \frac{B}{v} + Av^{0.33} + Cv \tag{1}$$

which is an approximation of the original rigorous Giddings equation[9]:

$$h = \frac{B'}{v} + \frac{A'}{D' + \dfrac{1}{v}} + C'v \tag{2}$$

In a previous paper[3], HETP curves were fitted by eqns. 1 and 2 assuming that $B = B' = 2$, as it is difficult and time consuming to make HETP measurements in the range of flow-rates where B (and B') are the controlling terms, especially when using large particles. We used the well known non-linear least-squares fitting technique in order to calculate the parameters. The diffusion coefficients that appear in the expression of the reduced velocity are derived from the classical Wilke and Chang equation[9]:

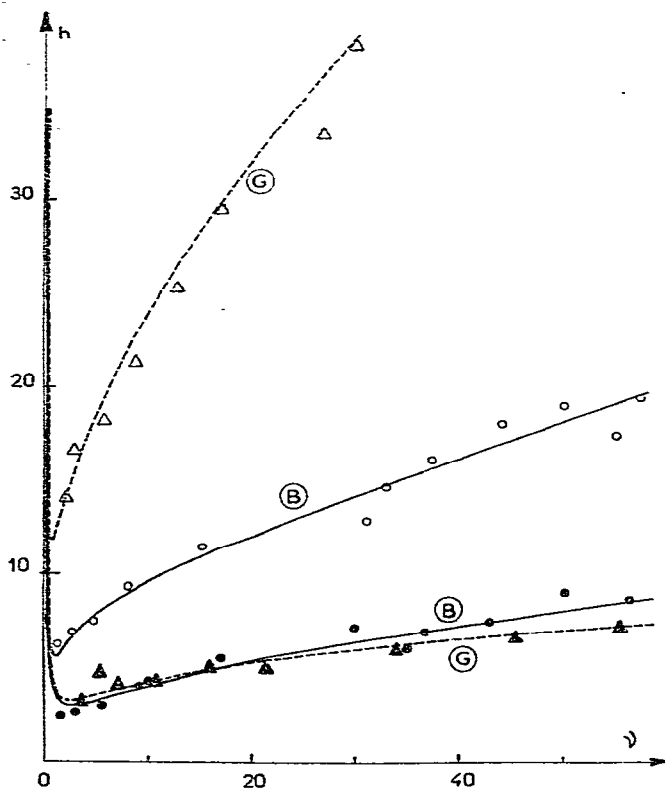$$D_m = \frac{7.4 \cdot 10^{-10} (\psi M)^{\frac{1}{2}} T}{\eta V^{0.6}} \tag{3}$$

Fig. 5. Reduced plate height (h) *versus* reduced velocity (v) for columns B and G in acetonitrile. Broken lines, column G; ▲, benzene; △, 1,8-dimethylnaphthalene. Solid lines, column B; ●, benzene; ○, 2,3,5-trimethylnaphthalene.

We previously used a value of 1.5 for the association parameter ψ of acetonitrile[2,3]. Recently, Fawcett and Caton[10] measured the diffusion coefficient of anthracene in acetonitrile, and it appears from their data that a better estimate of ψ in eqn. 3 is 2.14. This value is used here for the calculation of the reduced velocity.

The results are summarized in Table II, and show that by using the slurry technique it is possible to pack good columns with either small or large particles. With large particles, we packed long columns and obtained $h_{min.}$ values of between 2.4 and 3.5 and A values of about 2 (*cf.*, columns A–G). Obviously, with such columns high efficiencies correspond to very low flow-rates of the eluent (typically *ca.* $7 \cdot 10^{-3}$ cm/sec) and consequently time-consuming analyses. With small particles (columns H, I and J), although the packing is less good ($h_{min.} = 4$–5.5), high efficiencies are obtained at large solvent flow-rates (*ca.* $5 \cdot 10^{-2}$ cm/sec), which permits good separations to be effected in a short time (see below).

The increase in $h_{min.}$ is probably due to the formation of some small agglomerates of the particles during pyrolysis. No attempt was made to eliminate agglomerates smaller than 20 μm.

It can also be seen from Table II that the best results in terms of efficiency are

TABLE II

HETP EQUATIONS FOR THE DIFFERENT COLUMNS

Column	Unretained solute					
	Equation 1	h_{min}	v_{opt}	Equation 2	h_{min}	v_{opt}
A*	$2/v + 1.92\, v^{0.33} + 5.26\ 10^{-2}\, v$	3.52	2.20	$2/v + \dfrac{0.85}{0.12 + 1/v} + 7.16\ 10^{-2}\, v$	2.50	1.80
B*	$2/v + 1.67\, v^{0.33} + 3.81\ 10^{-2}\, v$	3.16	2.40	$2/v + \dfrac{0.93}{0.16 + 1/v} + 5.71\ 10^{-2}\, v$	2.51	1.70
C*	$2/v + 1.97\, v^{0.33} + 9.46\ 10^{-2}\, v$	3.67	2.00	$2/v + \dfrac{1.53}{0.29 + 1/v} + 13.89\ 10^{-2}\, v$	3.15	1.60
D*	$2/v + 1.87\, v^{0.33} + 6.45\ 10^{-2}\, v$	3.48	2.10	$2/v + \dfrac{1.22}{0.22 + 1/v} + 9.71\ 10^{-2}\, v$	2.85	1.60
E*	$2/v + 1.23\, v^{0.33} + 4.18\ 10^{-2}\, v$	2.55	2.90	$2/v + \dfrac{1.475}{0.51 + 1/v} + 7.39\ 10^{-2}\, v$	2.60	2.30
F*	$2/v + 3.11\, v^{0.33} + 1.71\ 10^{-2}\, v$	4.91	1.60	$2/v + \dfrac{0.76}{0.05 + 1/v} + 3.77\ 10^{-2}\, v$	2.43	1.70
G**	$2/v + 1.92\, v^{0.33} + 0.00\ 10^{-2}\, v$	3.40	2.40	$2/v + \dfrac{1.10}{0.16 + 1/v} + 2.19\ 10^{-2}\, v$	2.68	1.70
H**	$2/v + 2.12\, v^{0.33} + 66.22\ 10^{-2}\, v$	4.71	1.30	$2/v + \dfrac{5282.2}{2816.2 + 1/v} + 95.26\ 10^{-2}\, v$	4.64	1.40
I**	$2/v + 3.60\, v^{0.33} + 0.00\ 10^{-2}\, v$	5.45	1.50	$2/v + \dfrac{4379.8}{1018.2 + 1/v} + 0.00\ 10^{-2}\, v$	4.3	—
J**	$2/v + 2.48\, v^{0.33} + 0.00\ 10^{-2}\, v$	4.11	2.00	$2/v + \dfrac{4985.4}{1677 + 1/v} + 0.00\ 10^{-2}\, v$	3.0	—

* Injection of 2 μl.
** Injection of 1 μl.

obtained with degrees of coating between 1 and 15 % (columns B–E). On the one hand, one should expect that for non-retained compounds the larger the degree of coating, the better the column. This would be for mechanical reasons and because of a decrease in the intraparticle resistance to mass transfer. It is explained by the reduction in pore depth as thicker layers of pyrocarbon are coated on the silica surface and the obstruction of finer pores. However, as already observed[2,3] with carbon black, the efficiency is closely related to the retention and depends on the solvent used and the solute for a given column. The ratio of the numbers of theoretical plates for two solutes with different retentions depends on the flow-rate, generally being smallest near the minimum of the HETP curve. The coefficients C and C' are much more important for retained than for non-retained solutes and even A and A' are larger. The variation increases with increase in the degree of coating. It appears, however, that moderate amounts of pyrocarbon provide the best columns.

etained solute

v	Equation 1	h_{min}	v_{opt}	Equation 2	h_{min}	v_{opt}
.08	$2/v + 9.15\, v^{0.33} + 3.79\ 10^{-2}\, v$	11.01	0.70	$2/v + \dfrac{9.06}{0.42 + 1/v} + 29.78\ 10^{-2}\, v$	7.86	0.60
.60	$2/v + 4.07\, v^{0.33} + 6.35\ 10^{-2}\, v$	6.06	1.30	$2/v + \dfrac{6.05}{0.69 + 1/v} + 19.10\ 10^{-2}\, v$	5.75	0.90
.69	$2/v + 4.90\, v^{0.33} + 9.68\ 10^{-2}\, v$	6.99	1.10	$2/v + \dfrac{4.71}{0.40 + 1/v} + 22.87\ 10^{-2}\, v$	5.54	0.80
.85	$2/v + 3.61\, v^{0.33} + 12.76\ 10^{-2}\, v$	5.65	1.30	$2/v + \dfrac{3.57}{0.41 + 1/v} + 22.60\ 10^{-2}\, v$	5.05	1.60
.025	$2/v + 2.19\, v^{0.33} + 25.47\ 10^{-2}\, v$	4.22	1.60	$2/v + \dfrac{21.21}{6.077 + 1/v} + 36.06\ 10^{-2}\, v$	4.95	2.00
.73	$2/v + 4.36\, v^{0.33} + 14.53\ 10^{-2}\, v$	6.47	1.20	$2/v + \dfrac{2.03}{0.13 + 1/v} + 20.0\ 10^{-2}\, v$	3.99	1.00
.71	$2/v + 9.83\, v^{0.33} + 28.15\ 10^{-2}\, v$	11.80	0.70	$2/v + \dfrac{13.44}{0.52 + 1/v} + 46.47\ 10^{-2}\, v$	9.56	0.50

Finally it should be noted that the values of the parameters A, B and C obtained by the fitting technique should be used with care. For instance, 0.00 is sometimes obtained for C in eqn. 1, and such a value obviously has no physical meaning. A realistic calculation of the parameters is possible only if measurements of h over very large range of v values are carried out, which is generally not done because of the experimental difficulties. This is especially so for columns H, I and J; for these small-particle columns, measurements of h have been made only around the minimum. If the values derived for A are meaningful, this is not so for C, the contribution of the corresponding term being small in this region.

RETENTION ON CARBON-COATED SILICA PARTICLES

The comparison of the columns is made using three solvents with widely dif-

ferent polarities: high (a 1:1 mixture of water and acetonitrile), medium (pure ace-tonitrile) and no polarity (*n*-heptane). This choice allows the study of retention patterns in a large range of eluotropic strength, $\varepsilon°$ (ref. 3). The influence of the silica skeleton, if it remains, will show up differently for polar and non-polar solutes and depends on the solvent.

Polar solvent

Polar solvents generally have a weak eluotropic strength on carbon[3,11]. If specific interactions can take place between the solvent and the adsorbent, $\varepsilon°$ would be even larger than with pure carbon. This decrease can be explained as follows.

The pyrolysis is accompanied by thermal treatment of the silica. Adsorption on thermally modified silica is much weaker than on ordinary silica, although it re-mains high for polar compounds[12]. Adsorption on carbon is very substantial[2,3], but if the layer of pyrocarbon is too thin, the silica located under it can influence the re-tention on carbon. In this way, a polar solvent may be more strongly adsorbed than on carbon because of specific interactions with the underlying silica, and hence $\varepsilon°$ is larger. This effect also happens near the edges of carbon spots in the case of partial coverage, where solvent molecules will be more retained because of the interactions with the silica.

If a monolayer of pyrocarbon is expected to be coated on the silica, the corre-sponding amount of carbon (weight-% increase) is high (*cf*., Table III). In practice, as the coating is not homogeneous, much larger degrees of coating are necessary than the values given in Table III. In our work, for instance, we used Spherosil XOB 75. The specific surface area before dehydration was 108 m²/g (stated by the manufac-turer) and after dehydration 99 m²/g (measured). In fact, it is possible that the pyro-carbon does not cover all of the silica surface but plugs some pores, reducing the sur-face area. This may happen only seldom, as shown by the measurements reported in Table IV. These results are surprising as they show that the specific surface area does not decrease regularly with increase in the degree of coating, as happens for carbon black. Possibly the pyrocarbon coating is porous and in the range 0–15% of carbon the two effects, reduction of the skeleton surface area and increase in the pyrocarbon pore surface area, cancel each other. The surface measurements are in excellent agreement with the results of retention data measurements.

TABLE III

DEGREE OF COATING NECESSARY TO OBTAIN A MONOLAYER OF CARBON ON SILICA

Average density of graphite, 2.25 g/cm³.

Specific surface area (m²/g)	Weight-% increase
10	0.77
50	3.85
100	7.69
400	30.78

TABLE IV

SPECIFIC SURFACE AREA OF SILICA (SPHEROSIL XOB 75) COATED WITH PYRO-CARBON

Degree of coating (%)	Specific surface area (m²/g)
0	99.8
0.3	85
0.8	99.5
4.0	74
15.4	90

Concerning the adsorption of a non-polar solute, two effects can modify the column capacity factor (k') when increasing the degree of coating: the surface area available for carbon solute interaction increases, and the eluotropic strength of the solvent tends towards the value observed on pure carbon. For a polar solute, it may be necessary to take into account specific adsorption on silica. However, it is impossible to make any quantitative prediction as we are dealing with two very different adsorbents, giving rise to adsorption forces that are difficult to compare, and we do not even know how the ratio of the surface areas of silica and carbon varies with the degree of coating.

The results of a comparison between retention data on different columns using various solutes are given in Table V. We should point out that the retentions on column A were very small and difficult to measure accurately (especially relative retentions). Table V includes the column capacity (k') and the relative retention (α), the reference solute being 1,2,3-trimethylbenzene, the retention of which can be measured with good precision on the different columns. The use of α allows a more significant comparison to be made between the columns as it eliminates the possible effect of surface area. The corresponding retention data on pure carbon (Sterling FT.FF hardened with 13% of pyrocarbon and graphitized) are also given. However, as will be pointed out in a forthcoming paper, these data must be used with caution. Indeed, it will be seen that even columns of carbon are difficult to compare when packed with adsorbents of different specific surface areas. We chose a carbon giving retentions similar to those on CCSP. Capacity factors of some solutes are plotted *versus* the amount of pyrocarbon in Fig. 6. It seems that the results for column D are too low, while the other results are self-consistent. The same effect does not occur with column D when the other solvents are used (see below). For this reason, it is not possible to exclude an error in the composition of the solvent mixture used in this instance (too much acetonitrile). However, the general form of the plot shows that the retention first increases very rapidly with increase in the degree of coating and then tends towards a limit. The data for column G are in agreement with the other data and a large reduction in specific surface area.

The relative retentions are only slightly different from those measured on column R, suggesting that the effect of the variation of apparent eluotropic strength is not very important: $\varepsilon°$ drifts slowly towards the values on pure carbon. The effect of $\varepsilon°$ is better illustrated in Fig. 7 which is a plot of log k' *versus* the number of methyl groups for two homologous series (methylbenzenes and methylphenols). Nearly

TABLE V

COMPARISON BETWEEN RETENTION DATA ON DIFFERENT COLUMNS (cf., TABLE I) WITH WATER–ACETONITRILE (1:1) AS SOLVENT

Solute*	Parameter	Column							
		A	B	C	D	E	F	G	R
Benzene	k'	0.03	0.16	0.08	0.13	0.18	0.46	0.19	0.18
	α	0.50	0.41	0.17	0.13	0.10	0.07	0.11	0.06
Phenol	k'	0.00	0.12	0.06	—	0.12	0.24	0.08	0.13
	α	0.00	0.32	0.12	—	0.07	0.04	0.05	0.04
2,4-Xylenol	k'	0.03	0.15	0.13	0.23	0.52	—	0.35	0.88
	α	0.50	0.39	0.26	0.23	0.29	—	0.20	0.28
2,3,4-TMP	k'	0.06	0.28	0.37	0.67	1.74	4.74	1.03	3.44
	α	1.00	0.73	0.76	0.66	0.97	0.73	0.60	1.08
2,3,4,6-TeMP	k'	0.12	—	0.74	1.90	3.33	12.26	2.85	8.77
	α	2.00	—	1.50	1.86	1.86	1.88	1.66	2.75
β-Naphthol	k'	0.11	0.39	0.58	1.07	2.17	8.17	1.11	4.85
	α	1.90	1.03	1.18	1.05	1.21	1.25	0.65	1.52
Naphthalene	k'	0.12	0.60	0.96	1.80	3.13	—	2.00	5.03
	α	2.00	1.57	1.94	1.76	1.75	—	1.17	1.58
n-Propylbenzene	k'	0.00	—	0.23	0.41	0.75	2.20	0.79	0.89
	α	0.00	—	0.46	0.40	0.42	0.34	0.46	0.28
n-Butylbenzene	k'	0.00	0.33	0.36	0.75	1.26	4.22	1.51	1.60
	α	0.00	0.86	0.72	0.74	0.71	0.64	0.88	0.50
1,2,3-TMB	k'	0.06	0.38	0.49	1.02	1.79	6.54	1.72	3.19
	α	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
1,2,3,4-TeMB	k'	0.19	0.83	1.14	2.87	5.15	19.11	4.86	11.63
	α	3.15	2.17	2.31	2.81	2.88	2.92	2.83	3.65

* TMP = trimethylphenol; TMB = trimethylbenzene; TeMP = tetramethylphenol; TeMB = tetramethylbenzene.

parallel straight lines are obtained in all instances and the two lines corresponding to each column are close to each other. The larger the degree of coating, the larger are the slopes, suggesting a small decrease in ε°.

In conclusion, with this polar solvent, the chromatographic properties of CCSP are similar to those of carbon when the degree of coating is large enough.

Medium-polarity solvent

The variation of solvent strength with degree of coating and its effect on retention is less important when the polarity of the eluent is lower. The retentions of some solutes for the different columns are given in Fig. 8, and results for more compounds are given in Table VI. The curves are very similar to those in Fig. 6, but their initial slopes are smaller. This is in agreement with a smaller variation in the apparent eluotropic strength of the solvent, and is confirmed by the results in Table VI.

Owing to malfunction of the equipment, column D was accidentally destroyed during these measurements so some results in acetonitrile and all results in n-heptane are lacking for this column.

Non-polar solvent

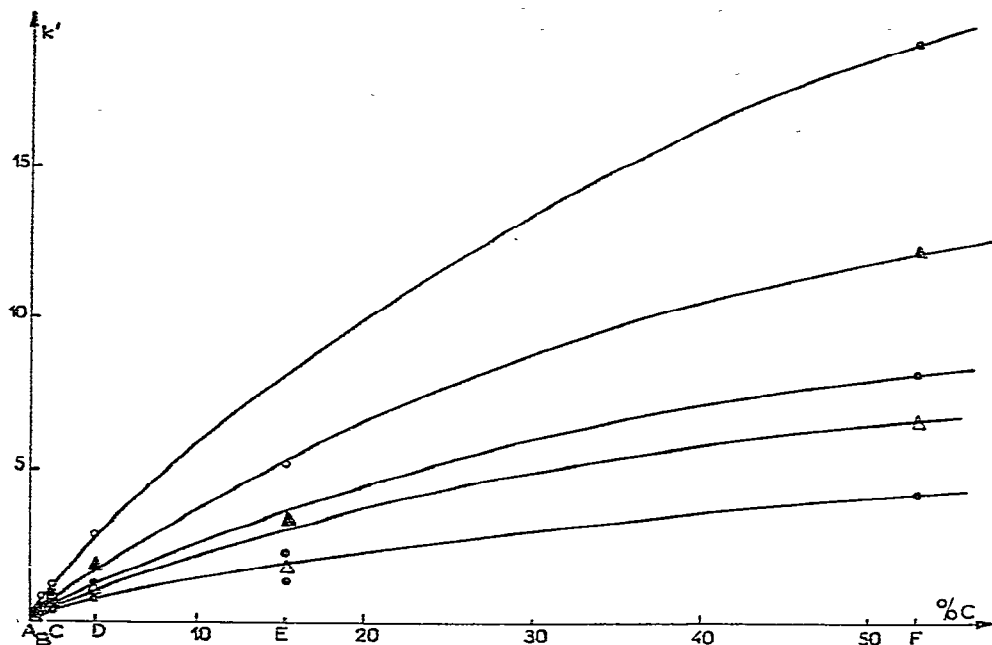Although this is of little direct analytical interest, experiments using a non-

Fig. 6. Capacity factors (k') of various solutes *versus* degree of carbon coating with water–acetonitrile (1:1) as solvent. ○, 1,2,3,4-tetramethylbenzene; ▲, 2,3,4,6-tetramethylphenol; ◉, β-naphthol; △, n-butylbenzene; ◑, 1,2,3-trimethylbenzene.
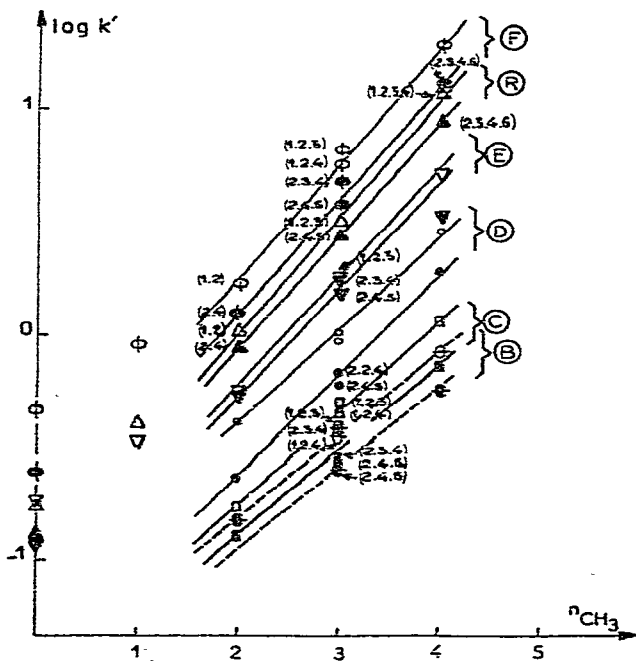

Fig. 7. Variation of log k' in homologous series. Open symbols, methylbenzenes; closed symbols, methylphenols.

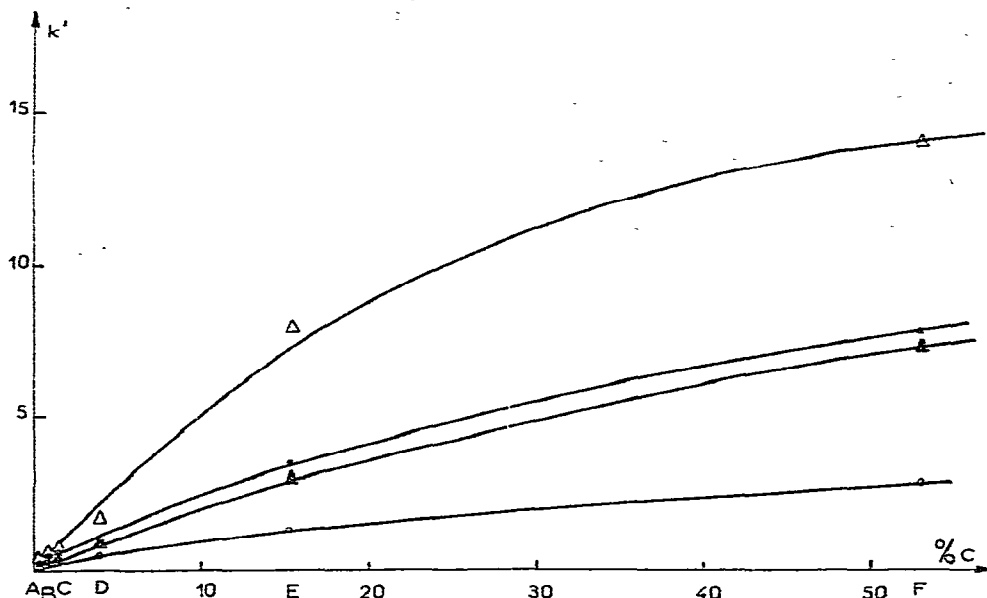Fig. 8. Capacity factors (k') of various solutes *versus* degree of carbon coating with acetonitrile as solvent. △, 2,3,5-Trimethylnaphthalene; ●, hexamethylbenzene; ▲, 1,8-dimethylnaphthalene; ○, 2-methylnaphthalene.

polar solvent are the best means of testing the influence of the silica substrate, which is well measured by the retention of polar compounds. Indeed, a non-polar solvent is very weakly adsorbed on the silica surface. Conversely, a polar solute, for which interactions with the solvent are small while specific interactions with the adsorbent are large, will be strongly adsorbed on the silica. The retentions of such compounds will increase with the surface area of the uncovered silica. On the other hand, the retention of non-polar solutes will increase with increasing area of the carbon-liquid interface and with an increase in the degree of coating.

The results are reported in Table VII and Fig. 9. As expected, the relative retention of polar compounds decreases with increase in the degree of coating.

As can be seen in Fig. 10, the elution peaks of polar solutes are asymmetric and accurate measurements are not possible. As their adsorption takes place essentially on silica, the linear capacity of the adsorbents is necessarily very small, especially at large degrees of coating, and hence the columns are easily overloaded. No further effort was made to assess the influence of column overloading and its variation with increasing retention and degree of coating. Nevertheless, it appears from Table VII that polar solutes are slightly retained on pure carbon.

The values obtained with column A, which contains virtually no pyrocarbon, are much smaller than those reported by Scott and Kucera[12]. As an example, for Partisil 5, the lowest degree of coating used was 4.12%, and for this column (H) the k' value of naphthalene was 0.25 while that given by Scott and Kucera was 1.25. Although this effect might result in part from a lower specific surface area of our silica particles, it also demonstrates the dehydration effect of the thermal treatment that

TABLE VI

COMPARISON BETWEEN RETENTION DATA ON DIFFERENT COLUMNS (cf., TABLE I) WITH ACETONITRILE AS SOLVENT

Solute*	Parameter	Column							
		A	B	C	D	E	F	G	R
Naphthalene	k'	0.04	0.06	0.06	—	0.44	1.38	0.12	0.45
	α	0.11	0.09	0.09	—	0.06	0.10	0.07	0.05
2-MMN	k'	0.09	0.12	0.18	0.45	1.30	2.82	0.28	1.18
	α	0.25	0.20	0.26	0.27	0.21	0.20	0.17	0.11
1,8-DMN	k'	0.18	0.29	0.38	0.85	2.97	7.32	0.71	2.75
	α	0.50	0.47	0.55	0.51	0.37	0.52	0.44	0.32
2,3,5-TMN	k'	0.36	0.61	0.69	1.68	7.94	14.00	1.60	8.52
	α	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Acenaphthylene	k'	0.10	0.22	0.27	0.63	2.94	5.40	0.57	2.24
	α	0.28	0.37	0.39	0.38	0.37	0.39	0.36	0.26
Fluorene	k'	0.25	0.51	0.58	1.26	6.50	13.10	0.94	5.70
	α	0.78	0.84	0.84	0.75	0.82	0.94	0.59	0.67
β-Naphthol	k'	0.09	0.10	—	0.45	0.71	1.40	0.17	1.45
	α	0.24	0.17	—	0.27	0.09	0.10	0.11	0.17
2,4-Xylenol	k'	0.04	0.00	0.03	0.05	0.13	0.29	0.04	0.19
	α	0.11	0.00	0.04	0.03	0.02	0.02	0.02	0.02
2,3,4-TMP	k'	0.03	0.05	0.05	—	0.31	0.98	0.13	0.69
	α	0.07	0.09	0.07	—	0.04	0.07	0.08	0.08
1,2,3-TMB	k'	0.00	0.02	0.04	—	0.14	0.41	0.07	0.20
	α	0.00	0.04	0.07	—	0.02	0.03	0.04	0.02
2,3,4,6-TeMP	k'	0.05	0.08	0.11	0.37	0.64	1.68	0.28	1.22
	α	0.13	0.12	0.15	0.22	0.08	0.12	0.17	0.14
1,2,3,4-TeMB	k'	0.03	0.06	0.08	—	0.46	1.10	0.22	0.60
	α	0.08	0.10	0.11	—	0.06	0.08	0.14	0.07
PMB	k'	0.07	0.14	0.14	—	1.06	2.46	0.58	1.66
	α	0.20	0.23	0.20	—	0.13	0.18	0.36	0.19
HMB	k'	0.17	0.40	0.40	—	3.54	7.74	1.93	6.40
	α	0.48	0.64	0.58	—	0.45	0.55	1.20	0.75

* MMN, DMN and TMN = mono-, di- and trimethylnaphthalene, respectively; PMB, HMB = pentamethyl- and hexamethylbenzene, respectively. Other abbreviations as in Table V.

TABLE VII

COMPARISON BETWEEN RETENTION DATA ON DIFFERENT COLUMNS (cf., TABLE I) WITH n-HEPTANE AS SOLVENT

| Solute	Parameter	Column							
		A	B	C	D	E	F	G	R
Naphthalene	k'	0.05	0.09	0.14	—	0.37	0.92	0.09	0.16
	α	0.15	0.16	0.20	—	0.16	0.15	0.19	0.09
Acenaphthylene	k'	0.13	0.18	0.23	—	0.86	2.24	0.21	0.58
	α	0.38	0.31	0.34	—	0.38	0.36	0.46	0.32
Fluorene	k'	0.34	0.59	0.68	—	2.26	6.11	0.45	1.84
	α	1.00	1.00	1.00	—	1.00	1.00	1.00	1.00
Phenol	k'	16.4	16.0	13.4	—	6.05	9.40	2.56	0.23
	α	48.0	27.0	19.7	—	2.68	1.54	5.64	0.12
o-Cresol	k'	Too high	6.2	8.4	—	3.83	5.72	1.62	0.18
	α		23.7	12.3	—	1.70	0.94	3.56	0.09
2,4-Xylenol	k'	Too high	6.2	8.3	—	3.83	5.95	1.62	0.16
	α		23.7	12.2	—	1.70	0.97	3.56	0.09
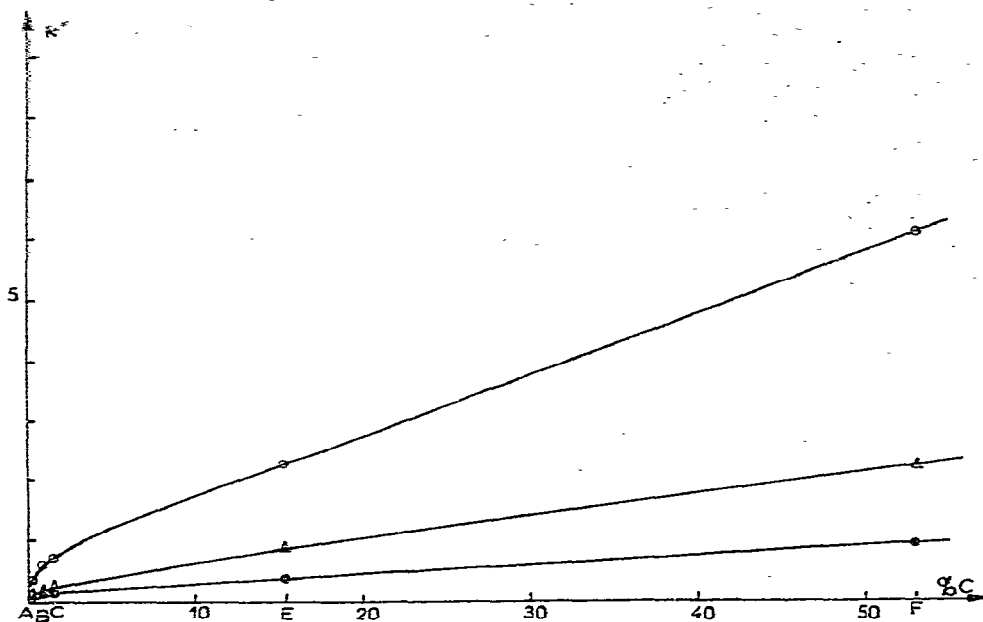
Fig. 9. Capacity factors (k') of various solutes *versus* degree of carbon coating with *n*-heptane as solvent. ○, fluorene; △, acenaphthylene; ●, naphthalene.
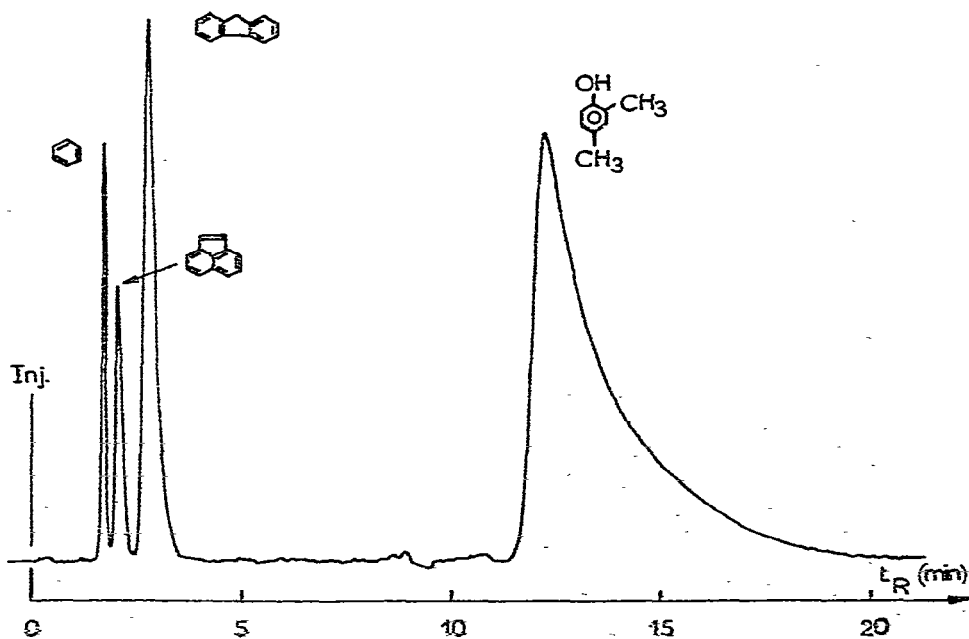

Fig. 10. Elution of non-polar and polar solutes in *n*-heptane. Column B; 0.98 cm⁵/min; UV detector.

accompanies the pyrolysis. No column of thermally treated uncoated silica has been packed.

    These results are in agreement with those of Bebris *et al.*[1]. It does not seem possible to mask the properties of the underlying silica completely. This does not make it difficult, however, to obtain good analytical results with polar eluents.

ANALYTICAL PROPERTIES OF CARBON-COATED SILICA PARTICLES

    A few simple separations are considered here in order to illustrate some characteristics of CCSP.

    The three chromatograms in Fig. 11 represent the separations of a mixture of phenol and alkylbenzenes. The solvent was water–acetonitrile (1:1) and the flow-rate 0.4 cm³/min in all instances. Chromatogram I was obtained with column R, and II and III with columns E and B, respectively. Separations I and II are very similar, the resolution of phenol and benzene, however, being better on CCSP. When injected alone, the capacity factors for these solutes are 0.18 and 0.13 on column R. The k' values are
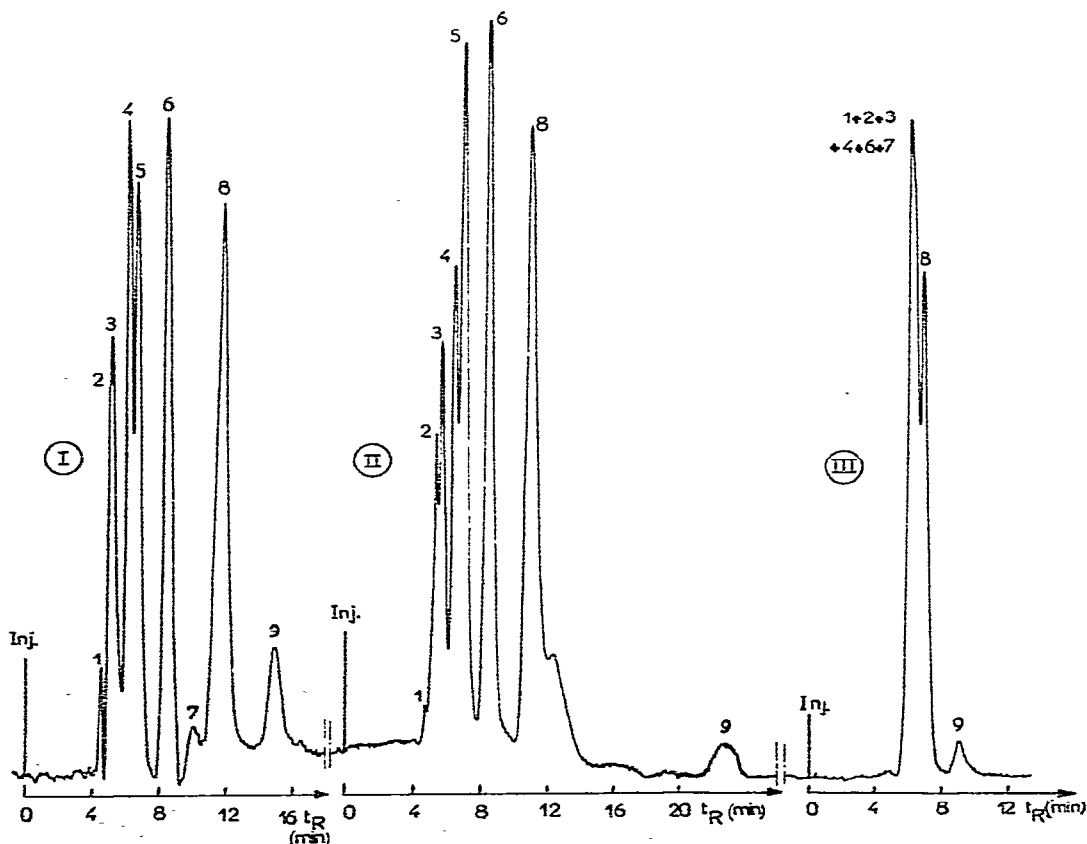

Fig. 11. Separations of phenol and alkylbenzenes on different adsorbents: I, column R; II, column E; III, column B. Solvent, water–acetonitrile (1:1); flow-rate, 0.4 cm³/min; UV detector. Peaks: 1 = acetonitrile (solvent for sample); 2 = phenol; 3 = benzene; 4 = toluene; 5 = ethylbenzene; 6 = *n*-propylbenzene; 7 = impurity; 8 = *n*-butylbenzene; 9 = impurity.

0.15 and 0.10 when the measurements are made from the chromatogram I. This effect, which is probably due to local column overloading during the beginning of the chromatographic process, is currently under investigation. Chromatogram III suggests, on the other hand, that the degree of carbon coating (0.84%) is insufficient: only n-butylbenzene is slightly retained and can be identified in the mixture.

Fig. 12 shows the separation of some polynuclear aromatic compounds with n-heptane as eluent. The decrease in efficiency with increasing retention is very important, as illustrated in Fig. 13. This effect is due in part to the large flow-rate used ($u = 0.54$ cm/sec, $v = 90$). For $k' = 2.2$, the column exhibits three-fold fewer theoretical plates than for a non-retained solute. When dealing with the mixture water–acetonitrile, however, the decrease in efficiency is lower: only 1.7-fold fewer plates for $k' = 2.1$ (n-pentylbenzene) than for $k' = 0$. On the other hand, the peak symmetry seems to be good in all instances.
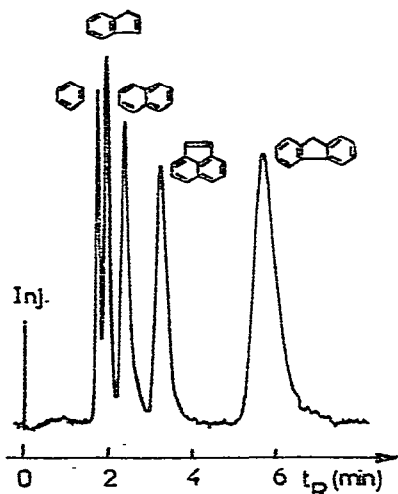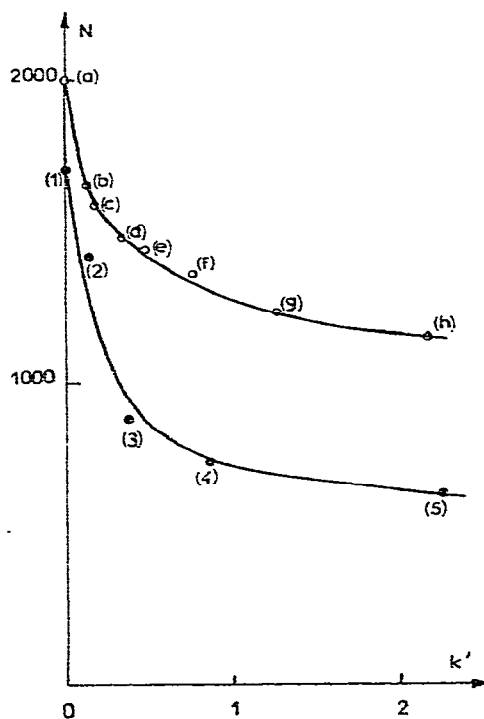

Fig. 12. Separation of polynuclear aromatic compounds. Column E. Solvent, n-heptane; flow-rate, 1.2 cm^3/min; UV detector.

Fig. 13. Variation of the number of theoretical plates (N) with retention (k') at constant flow-rate. Column E. Solvent: open symbols, water–acetonitrile (1:1) (0.4 cm^3/min); closed symbols, n-heptane (1.2 cm^3/min).

The separation shown in Fig. 14 has been performed previously using water–acetonitrile (6:4) on carbon black[3]; we carried it out here with the 1:1 mixture on column F. The retention of aromatic nitro compounds is twice as great on column F, while those of benzene and toluene are only 1.3-fold greater. This effect is due in part to the fact that all retentions are higher on column F than on column R. Furthermore,

a decrease in the water content of the mixture sometimes increases the retention of polar compounds[5].

Finally, the separations of a mixture of polymethylphenols is shown in Fig. 15. It is, in fact, the analysis of a "pure" commercial 2,3,5,6-tetramethylphenol sample. Peaks 2, 3 and 4 have been tentatively identified as those of other methylphenols. This separation was performed on Partisil 5 coated with 14% of pyrocarbon (column I). The efficiency is not high ($N = 1110$ for 2,3,5,6-tetramethylphenol; $k' = 1.0$; $h = 15$), but the time of analysis is very short. Also, as pointed out previously, the coating of fine powders is tedious and is accompanied to some extent by agglomeration of particles, resulting in an increase in the HETP values.
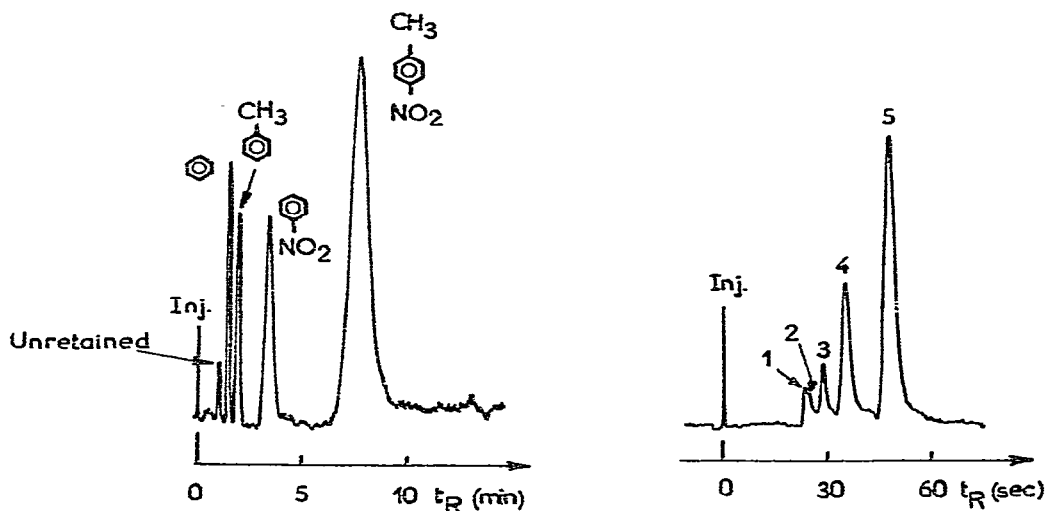

Fig. 14. Separation of a mixture of compounds of very different polarities. Column F. Solvent, water–acetonitrile (1:1); flow-rate, 2 cm³/min; UV detector.

Fig. 15. Separation of methylphenols. Column I. Solvent, acetonitrile; Flow-rate, 2.55 cm³/min ($v = 3.5$); UV detector. Peaks: 1 = unretained; 2 = 2,4-xylenol (?); 3 = 2,4,6-trimethylphenol; 4 = 2,3,4,6-tetramethylphenol; 5 = 2,3,5,6-tetramethylphenol.

CONCLUSION

The coating of silica particles with pyrocarbon can be a good method for providing suitable adsorbents for reversed-phase HPLSC. The correct amount of carbon to be deposited depends on the type of silica used, and the experimental conditions of preparation seem to be very important. Moreover, the optimal conditions are probably not the same for all types of silica particles.

This work was carried out essentially using Spherosil XOB 75, which explains why the few results obtained with Partisil 5 were not very good.

It is possible to modify fine particles of 5-μm diameter, which would permit very efficient columns to be packed. This possibility is attractive insofar as it is extremely difficult to prepare pure carbon particles in this size range. The silica particles have very good mechanical properties and can be regularly shaped, which makes packing

easy. On the other hand, carbon-coated silica cannot be graphitized. Although we have not yet assessed the consequences of this treatment, our preliminary results seem to show that it improves the chromatographic performances of the packings.

Work will be carried out on the use of other silica and aluminosilicate materials. The main drawback, however, seems to be the virtual impossibility of completely eliminating the influence of silica: at low degrees of coating a large part of the silica surface is not covered. It seems that at high degrees of coating the coating does not adhere well to the underlying material and peels off during the cooling, leaving part of the silica exposed. This would explain the results in Table IV and the polarity of the adsorbent in column G.

ACKNOWLEDGEMENT

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