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

II. REPRODUCIBILITY OF CARBON ADSORBENTS AND THE INFLUENCE OF GRAPHITIZATION ON THEIR PERFORMANCE

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SUMMARY

The reproducibility of the performance of carbon columns has been studied in terms of retention data and efficiency. The repeatability of the data obtained with one column over several months was excellent, in spite of its use for the analysis of a variety of samples with solvents with a wide range of eluotropic strengths. It was found that the retention data on carbon adsorbents are proportional to the total surface area of the adsorbent in the column, within the limits of error of measurement of this parameter, except for polyaromatics. For these compounds, the carbon adsorbents exhibit active sites and the retention increases faster than the surface area. Graphitization had little effect on the retention data or the eluotropic strengths of the solvents.

The column efficiency for inert peaks is good, showing that excellent packings can be obtained with carbon black particles, either graphitized or not. The column efficiency decreases markedly with increasing retention, which seems to be a property of columns packed with large particles of porous adsorbents. Graphitization has also a small effect on this phenomenon and accordingly is much less useful in liquid than in gas chromatography, except in preparative applications, as the loadability is one order of magnitude greater.

INTRODUCTION

The reproducibility of retention data in liquid chromatography (LC) has been the subject of contradictory reports. Some found it excellent¹, while others found it difficult to obtain comparable retention data on different columns packed with particles of the same batch of adsorbent². In fact, the situation is very different for polar and non-polar adsorbents. In the former instance the reproducibility of the water content of the adsorbent, and hence its degree of activation, is critical and it has been demonstrated that the water contents of alumina and silica control the retention to a large extent^{3,4}. Reproducibility of retention data from column to column can be

achieved only if the water content before packing and also the amount of water adsorbed during the packing procedure are controlled. Further, the water concentration in the mobile phase should be kept constant, which is not easy at values below saturation. The reproduction of a given water concentration is even more difficult to achieve. Finally, when not in use, columns should be kept closed, filled with a solvent. All of these steps are critical and often overlooked, which probably explains the poor degree of reproducibility that is often achieved.

When non-polar adsorbents are used in reversed-phase chromatography, the problem is different and simpler. The ubiquitous water is not appreciably adsorbed, and the compounds most strongly adsorbed by non-polar adsorbents do not change appreciably the polarity of the surface. In this instance the reproducibility of retention data depends mainly on the reproducibility of the chemical properties of the surface itself. This is easy with carbon adsorbents derived from carbon black, the surface chemical homogeneity of which is well known.

In this paper we discuss the reproducibility of chromatographic results achieved with carbon adsorbents and the effect of graphitization of the adsorbent. This treatment has a considerable effect on retention data in gas chromatography but the effect is much less important in liquid chromatography.

The preparation and general properties of carbon adsorbents have been described previously^{5,6}.

REPRODUCIBILITY OF CARBON COLUMNS

Adsorption on carbon surfaces is closely related to the size of the adsorbate molecules, which is the opposite of the effect with polar adsorbents, where the main parameter appears to be the polarity of the adsorbate^{5,6}. Of compounds that are liquid at room temperature, water has the smallest molecule and consequently the extent of its adsorption on carbon surfaces is very small. As a result, a column packed with carbon black (CB) particles containing some adsorbed water and eluted with a solvent that has not been adequately dehydrated and the water content of which is not kept constant exhibits the same chromatographic properties as a column with which special care has been taken to keep the water content constant or negligible in both the adsorbent and the eluent.

On the other hand, aromatic impurities have to be carefully removed from the system because of their strong adsorption. However, pollution of either the solvent or the adsorbent by such impurities is less common than pollution by water.

The reproducibility of chromatographic results was studied on the same column used at different times (long-term repeatability) and on columns packed with the same and with different varieties of CB (column-to-column reproducibility). The parameters concerned are the retention data (capacity factors, solvent strengths) and the efficiency (HETP curves and dependence of HETP on the capacity factor).

Long-term repeatability

This property was studied by comparing separations of mixtures carried out at different times, firstly with the column freshly packed (condition I) and secondly after the column had been operated several weeks (condition II), using more than 20 solvents covering a wide range of eluotropic strengths and left open and dry in the

laboratory for 4 months. Plugs of porous PTFE were fitted at both ends of the column so as to prevent any loss of packing material.

The separations of mixtures of methylbenzenes (MB), methylphenols (MP) and diphenols (DP), *i.e.*, weakly polar, polar and very polar solutes, were studied, using as eluents acetonitrile (for MB and MP) and ethyl acetate (for DP). The results are summarized in Table I and Figs. 1 and 2.

TABLE I
REPEATABILITY OF CHROMATOGRAMS ON MODIFIED CARBON BLACKS

Compound*	Capacity factor (k')		Efficiency (N)		Resolution (R_s)	
	I	II	I	II	I	II
Benzene	0.04	0.03	2000**	2100**	2.80	2.76
<i>o</i> -Xylene	0.35	0.33	1350**	1280**	2.40	2.39
1,2,4-Trimethylbenzene	0.81	0.74	1800**	1800**	—	—
1,2,4,5-Tetramethylbenzene	2.04	1.90	2100**	2000**	—	—
<i>p</i> -Cresol	0.42	0.43			>2	>2
2,4-Xylenol	0.89	0.91	632	751	>2	>2
3,4,5-Trimethylphenol	2.96	2.93	345	1050		
MDC	3.61	3.42	1000***	700***	0.91	0.90
ME	4.21	4.13	970***	700***	0.96	0.74
EE	4.89	4.79	960***	830***	>2	>2
MR	8.74	8.87	1500***	1250***	1.27	1.25
ER	10.18	10.45	1600***	1350***		

* For abbreviations see Fig. 2.

** Calculated from injection of the pure compound.

*** Calculated from the chromatogram of a mixture.

The resolution, R_s , is given by

$$R_s = 2 \cdot \frac{t_{R1} - t_{R2}}{W_1 + W_2} \quad (1)$$

where t_{Ri} and W_i are the retention time and bandwidth, respectively, of solute i .

In Fig. 1, the separations of MPs (chromatograms A, B and C) were obtained under conditions I, II and II after the column had been washed with ethyl acetate, respectively. It appears that before washing (B) the elution peaks of phenol derivatives are unsymmetrical and broad, whereas the separation of MBs (not shown)

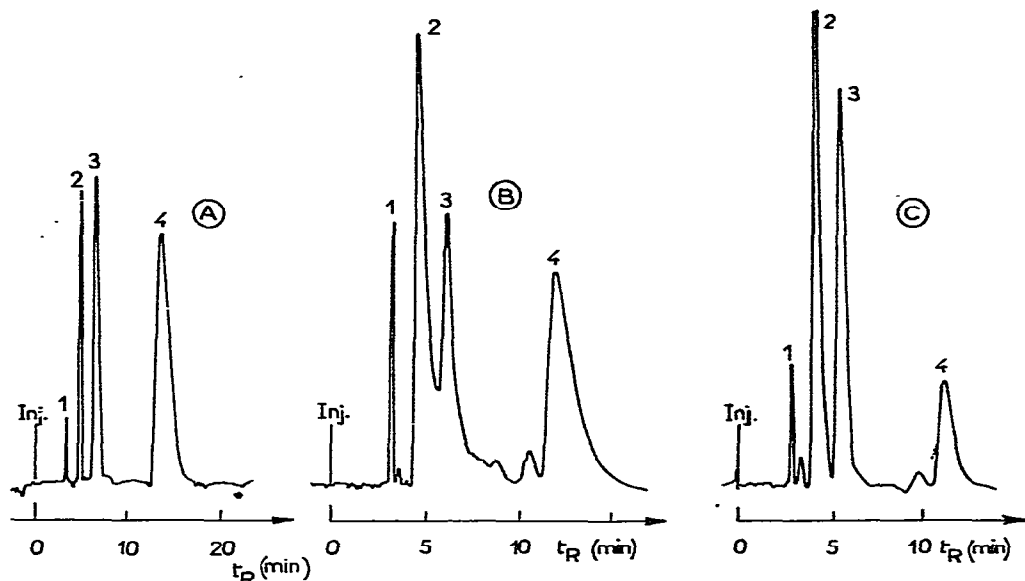


Fig. 1. Reproducibility of the separation of methylphenols. Solvent, acetonitrile; flow-rate, 1 ml/min; Detector, UV (254 nm). column $L = 54$ cm; $d_c = 2.17$ mm; $d_p = 25\text{--}31.5$ μm . Chromatograms, A = freshly packed column (condition I); B = first use of the column under condition II; C = condition II, after flushing with ethyl acetate.

was very good and similar to that obtained under condition I. This suggests that the active sites responsible for the tailing of polar solutes may be provided by polar impurities which are adsorbed on CB and which are soluble in ethyl acetate but not in acetonitrile.

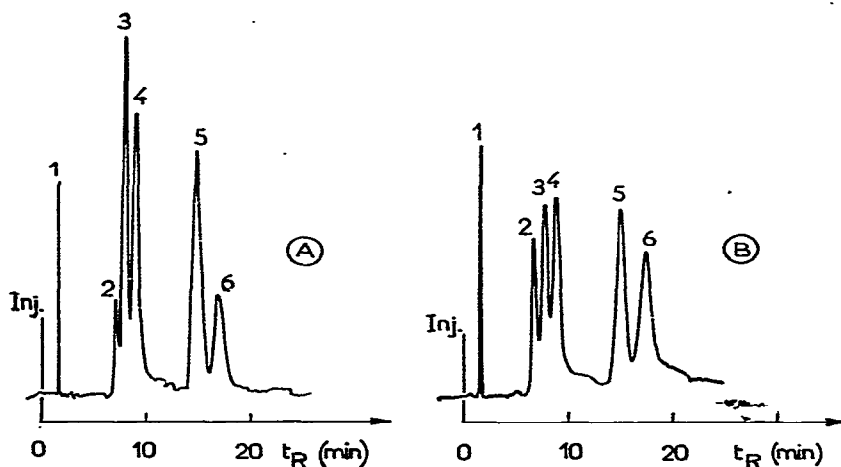


Fig. 2. Separation of diphenol derivatives. Solvent, ethyl acetate; flow-rate, 1 ml/min; detector, UV (254 nm). Peaks: 1 = unretained; 2 = methyl divaricinate (ML); 3 = methyl everminate (ME); 4 = ethyl everminate (EE); 5 = Methyl rhizonate (MR); 6 = ethyl rhizonate (ER). For formulae, see ref. 6.

Comparison of chromatograms A and C indicates that excellent repeatability is achieved after cleaning the adsorbent surface; the new peaks in chromatograms B and C are due to a change of sample mixture. The same good repeatability was observed for the separation of diphenols, as shown in Fig. 2, where chromatograms A and B were obtained under conditions I and II, respectively⁶.

From the data in Table I, it appears that the long-term repeatability of the capacity factor, k' , is generally better than 5%. With regard to column efficiency and resolution, it seems that the analytical properties of columns are constant with time, with only a slight decrease in efficiency.

These results are encouraging for the use of modified CB in high-performance liquid chromatography (HPLC), as they show that there is no problem in keeping columns with constant characteristics. Moreover, because water is not adsorbed on the carbon surface, there is no need for drastic control of the water content of the solvent.

Column-to-column reproducibility

It is of great importance that chromatographic data should be reproducible from one column to another when the columns are packed with the same adsorbent under the same conditions. Not only is such reproducibility necessary when chromatographic measurements are to be used for the determination of physico-chemical constants, but it is also of interest to know if it is possible to predict the retention properties of a column packed with a given carbon adsorbent from the data obtained by using a column packed with another carbon adsorbent.

Both problems were studied in this work, using two kinds of CB: Sterling FT.FF, with a specific surface area (S_{sp}) of about 16 m²/g, and Black Pearls L, with $S_{sp} = 150$ m²/g. Most experiments were carried out using acetonitrile, while in a few ethanol and *n*-heptane were used and gave similar results. The characteristics of the different columns studied are summarized in Table II.

TABLE II
CHARACTERISTICS OF COLUMNS USED IN REPRODUCIBILITY STUDY

Column	Carbon type*	Pyrocarbon coating (%)	Graphitization	Total surface area (m ²)	Liquid hold-up (cm ³)
A	B	55	Yes	47	1.50
B	B	44	Yes	72	1.52
C	B	55	Yes	36	1.09
D	B	43	Yes	193	2.85
E	B	33	Yes	66	1.15
F	B	21	No	79	1.27
G	B	43	No	112	1.77
H	S	14	Yes	18	1.36
I	S	15	No	10.3	1.82
J	S	15	Yes	20	1.93
K	B	44	No	65	1.55
L	B	44	Yes	72	1.56

* B = Black Pearls L; S = Sterling FT.FF.

The fundamental equation in adsorption chromatography relates the capacity factor, k' , the equilibrium distribution coefficient, K , and the characteristics of the column (dead volume V_m and total surface area of the adsorbent A_s):

$$k' = K \cdot \frac{A_s}{V_m} = K \cdot \frac{m S_{sp}}{V_m} \quad (2)$$

where m is the amount of adsorbent in the column.

The ratio of the capacity factors of one solute on two different columns, i and j , using the same eluent is

$$R_{i,j} = \frac{k_i}{k_j} = \frac{m_i S_{spi} V_{Mj}}{m_j S_{spj} V_{Mi}} \quad (3)$$

Eqn. 3 is valid if we assume that the chemical composition of the liquid-solid interface is the same for columns i and j ($K_i = K_j$), and this assumption should be borne in mind when comparing different adsorbents. Moreover, for identity between K_i and K_j , the sample size used must be small enough to ensure a linear adsorption isotherm; the maximum amount that can be injected without producing a change in k' is closely related to the specific surface area of the adsorbent.

Even when using columns packed with particles prepared from the same original adsorbent (*i.e.*, Sterling FT.FF or Black Pearls L), it is likely that $S_{spi} \neq S_{spj}$, as coating with pyrocarbon decreases the specific surface area⁶. Data obtained using such columns are reported in Table III, the theoretical values of $R_{i,j}$ being calculated from eqn. 3. The dispersion of the results is hardly significant, as shown by the small values of the standard deviation; the reproducibility is better than 5%, *i.e.*, within the limits of experimental error. There is also reasonable agreement between the experimental and calculated $R_{i,j}$ values. The deviation is probably due to an imprecise estimation of S_{sp} (S_{sp} values are derived from BET measurements, and it is likely that the gas-solid interface area is slightly different from the liquid-solid interface).

TABLE III
COMPARISON OF RETENTION DATA OBTAINED ON DIFFERENT COLUMNS

Solvent: acetonitrile.

Capacity factor ratio	Mean value	Relative standard deviation	Calculated value
$R_{B,A}$	1.83	0.07	1.55
$R_{A,C}$	1.12	0.03	0.95
$R_{E,C}$	1.88	0.04	1.73
$R_{D,C}$	2.48	0.03	2.05
$R_{D,E}$	1.50	0.08	1.18
$R_{J,H}$	1.12	0.04	0.78
$R_{F,G}$	0.76	0.04	0.98

From eqn. 3 we obtain

$$R_{i,k} = R_{i,j}/R_{k,j} \quad (4)$$

This equation allows a test of the consistency of the results. For instance, the calculated value of $R_{E,C}$ is 1.73, the value derived from direct measurement is 1.88, and $R_{E,D}/R_{C,D}$ is 1.66. All of the columns prepared with the same kind of CB provided very consistent data, regardless of the pyrocarbon coating ratio, provided that account is taken of its effect on the specific surface area.

With regard to carbons of different varieties, significant data are reported in Table IV which suggest that $R_{i,j}$ increases with increasing aromaticity of the solute, being roughly independent of the number of alkyl substituents. The larger the specific surface area before hardening, the larger is the retention of polyaromatic compounds relative to monocyclic compounds. The few results obtained with a carbon with a specific surface area greater than that of Black Pearls L (Black Pearls 800, 254 m²/g) confirm this trend. This effect must be related to another observation, namely that the peaks of conjugated polyaromatic compounds become increasingly unsymmetrical and subject to tailing with increasing specific surface area, while the capacity factors increase considerably with increasing molecular size ($k'_{\text{naphthalene}} = 2.25$ and $k'_{\text{fluorene}} = 40$ on Black Pearls L with acetonitrile as solvent).

TABLE IV

COMPARISON OF RETENTION DATA OBTAINED ON BLACK PEARLS L AND STERLING FT. FF IN ACETONITRILE

Solute	$R_{E,H}$ (4.34)*	$R_{E,J}$ (5.54)*
<i>o</i> -Xylene	4.55	—
1,3,5-Trimethylbenzene	4.35	4.85
1,3,5-Triethylbenzene	4.52	—
1,2,4,5-Tetramethylbenzene	4.57	4.72
Pentamethylbenzene	5.00	4.41
Naphthalene	6.00	5.00
2-Methylnaphthalene	6.01	5.08
Acenaphthalene	6.97	5.85
Fluorene	7.96	7.07

* Theoretical values according to eqn. 3.

It seems that the carbon surface exhibits sites where the adsorption of the large and flat molecules of polyaromatics is particularly important. This is similar to the template effect reported by Knox and Pryde⁷ for completely different adsorbents. The greater the specific surface area, the larger the number and the greater the energy of these sites. This is also in agreement with the energy distribution on the CB surface: the greater the specific surface area, the broader this distribution. This discussion is continued in the next section.

From the analytical point of view, a consequence of this phenomenon is that CB is not a suitable adsorbent for the separation of large conjugated polyaromatics. If, however, it is necessary to use carbon for particular applications, then the analyst should choose a carbon with a small specific surface area or silica gel particles coated with small amounts of pyrocarbon⁸.

EFFECT OF GRAPHITIZATION

When CB is used directly in gas chromatography, without purification after its manufacture, the results are bad, the peaks exhibit pronounced tailing and the column efficiency is poor. This is due (a) to the presence of chemical impurities containing polar groups ($-\text{OH}$, $-\text{COOH}$, $-\text{C}=\text{O}$, $-\text{SH}$) on the CB surface and (b) to the broad energy distribution of adsorption sites. This distribution can be explained as follows. Many of the carbon atoms in CB particles belong to graphite crystallites with the well known hexagonal structure, while others belong to aromatic or aliphatic groups bonded to the atoms at the edges of the crystallites. The adsorption energies are different for the atoms in the centre and at the edges of crystallites surfaces, and also for the atoms in the aliphatic groups. The larger the crystallites, the narrower is the energy distribution. The ratio (α) of the number of "edge atoms" to the number of "bulk atoms" is closely related to the energy dispersion.

Graphitization is a thermal process which allows an increase in the size of crystallites and a decrease in the number of crystal defects, including surface defects, and it can thus reduce the value of α . However, as graphitization cannot produce monocrystals, α cannot be zero. Excellent results are obtained in gas chromatography with graphitized thermal carbon blacks (GTCB). Although good results are obtained in liquid chromatography with non-graphitized CB, we studied the influence of graphitization on retention and efficiency.

Graphitization occurs when the carbon sample is heated at very high temperatures (3000°). The degree of graphitization (g) is

$$g = \frac{3.44 - \overline{d_{002}}}{0.086} \quad (5)$$

where $\overline{d_{002}}$ Å is the distance between two layers of carbon atoms. For pure graphite $\overline{d_{002}} = 3.35$ Å and $g = 1$. $\overline{d_{002}}$ is derived from X-ray diffraction measurements (Debye-Scherrer diagrams). There is a close relationship between g and the conditions of thermal treatment. Whatever these experimental conditions, it seems that when the sample has been heated at a temperature higher than 3000–3100°, g is greater than 0.6. The chromatographic results are very similar for samples of GTCB with g between 0.6 and 0.9. We obtained the best results for $g = 0.7$, but the effect was small and no systematic study has yet been made.

Retention and graphitization

The influence of graphitization on the thermodynamic properties of carbon adsorbents can be studied by means of the capacity factor (k') and the solvent strength (ϵ°).

The differences between capacity factors measured on graphitized and non-graphitized carbon blacks (GCB and NGCB) may depend on the solutes and solvents used. Experiments were carried out with four series of compounds, n -alkylbenzenes (AB and MB), methylphenols (MP) and polyaromatics (PA), the molecules of which have different sizes, polarities and aromaticities. We used ethanol, acetonitrile and n -heptane as solvents. The results for three pairs of columns are reported in Table V, which gives the average values of the ratio $R_{i,j}$. The two columns of each pair were

packed with the same carbons, one of them being graphitized and the other not. Data for $R_{D,G}$ are missing because column G was accidentally destroyed during the experiments. Data for alkylbenzenes in n -heptane are not given because of their very small retentions.

TABLE V

COMPARISON OF RETENTION DATA OBTAINED ON GCB AND NGCB

Solvent	Solute*	$R_{D,G}$ (1.07)**	$R_{L,K}$ (1.10)**	$R_{J,I}$ (1.83)**
Ethanol	AB	0.8	—	—
	MB	1.1	1.2	2.2
	MP	1.9	2.6	2.4
	PA	1.1	1.3	1.7
Acetonitrile	AB	0.9	—	2.3
	MB	1.1	1.3	2.3
	MP	1.1	2.5	2.4
	PA	0.8–1.3	—	1.9
n -Heptane	AB	—	—	—
	MB	—	2.7	2
	MP	—	0.5	0.9
	PA	—	1.3	1.4–1.8

* AB = alkylbenzenes; MB = methylbenzenes; MP = methylphenols; PA = polyaromatics.

** Theoretical values according to eqn. 3.

It appears from Table V that in polar solvents (ethanol and acetonitrile) the retention is generally larger for GCB than for NGCB. The increase in k' seems to be the most important for the polar solutes (MP). The smaller the specific surface area (columns J and I), the less scattered were the $R_{i,j}$ values, which is in agreement with the previous comments about the distribution of adsorption energy. The results were very similar in ethanol and acetonitrile.

When using n -heptane as the solvent, the retention of phenols is less important on GCB than on NGCB. This decrease in k' is probably due to the removal of polar impurities from the surface of CB, such impurities acting as strong adsorption sites for polar solutes. The very small values of $R_{L,K}$ for PA in ethanol and n -heptane are surprising.

It seems that, in general, graphitization increases the adsorption energy of solutes. On the other hand, it also produces a more homogeneous surface, decreasing the number and energy of active sites. These two phenomena have opposite effects on the retention of compounds such as PAs, as previously mentioned; consequently, it is difficult to predict the variation of $R_{i,j}$.

As graphitization changes the retention data, it may also affect the eluotropic strength of solvents. This aspect was studied using mixtures of water and ethanol, where ϵ° decreases from 0 (reference value for pure acetonitrile) to -0.5 (in pure water). According to the following equation, changing the composition of the mixture from pure water to pure acetonitrile produces a 10^4 -fold decrease in k' for a solute with a molecular area of 8.0 units (*i.e.*, 68 \AA^2), which is typical:

$$\log(k'_j/k'_i) = \frac{1}{A} (\epsilon_i^0 - \epsilon_j^0) \quad (6)$$

where k'_j is the capacity factor of the solute of molecular area A in solvent j of elotropic strength ε_j° . By convention A is the molecular area in \AA^2 divided by 8.5 (ref. 9). The terms related to the solvent effect and activity coefficients⁶ are neglected. Different solutes are used to measure ε° , depending on the water content of the solvent (1,2,4-trimethylbenzene, *o*-xylene and benzene). Polar solutes are not used because neglecting the term for the activity coefficients would lead to a large error because of the strong solute-solvent interactions⁶. Data are reported in Fig. 3 for GCB and NGCB, and there is excellent agreement between results obtained with the two adsorbents. Note that the dependence of ε° on the acetonitrile content is almost linear.

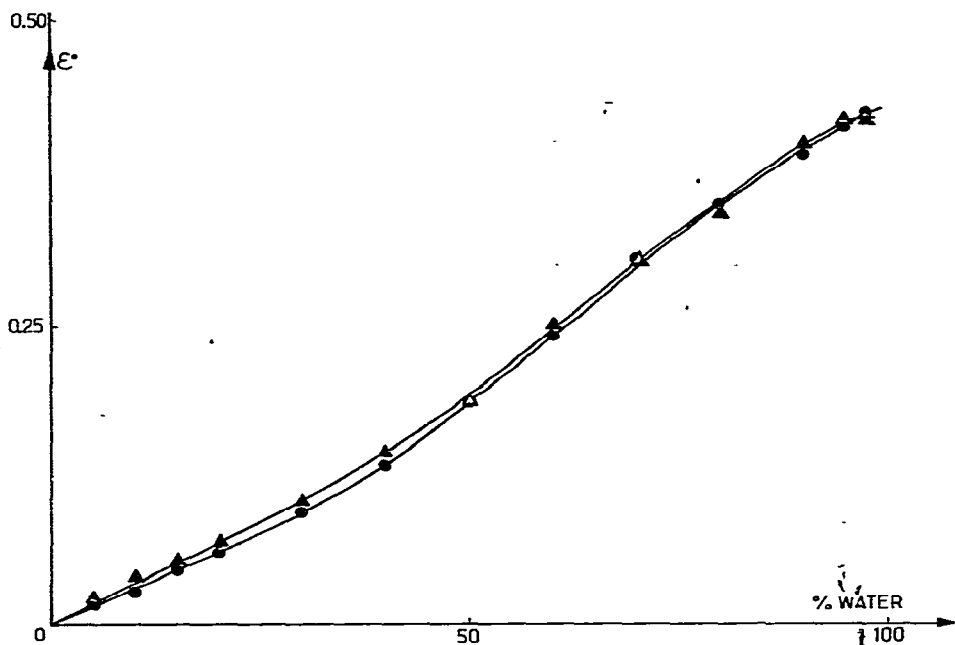


Fig. 3. Solvent strength of ethanol-water mixtures. ●, Graphitized carbon black; ▲, non-graphitized carbon black. Solvent composition is given in volume %.

Let k'^0 and k'^1 be the capacity factors on the graphitized and the non-graphitized adsorbent, respectively. If we assume that the molar area of the solute is the same when adsorbed on GCB or NGCB, eqn. 6 gives

$$\log(k'_j/k'_j) - \log(k'_i/k'_i) = A [(\varepsilon_i^{\circ,0} - \varepsilon_i^{\circ,1}) - (\varepsilon_j^{\circ,0} - \varepsilon_j^{\circ,1})] \quad (7)$$

where $\varepsilon^{\circ,0}$ and $\varepsilon^{\circ,1}$ are the solvent strength when the adsorbent is graphitized and non-graphitized, respectively. If $\varepsilon^{\circ,0} = \varepsilon^{\circ,1}$, then

$$k'_j/k'_j = k'_i/k'_i \quad (8)$$

Eqn. 8 is in good agreement with the data in Table V for polar solvents. The larger deviation for *n*-heptane is probably explained by the activity coefficient term, which is not taken into account in eqn. 6 because of the lack of data in the literature⁶.

In conclusion, it seems that the ϵ° values are almost identical for GCB and NGCB, which is not surprising as ϵ° is a relative parameter.

Graphitization of carbon black can also modify its adsorption capacity, and we studied this aspect by comparing the linear capacities of different columns packed with NGCB and GCB. We have chosen as definition of the linear capacity of a chromatographic column the amount of solute per gram of adsorbent which produces a 10% change in the capacity factor (generally a decrease). This capacity is closely related to the capacity factor of the solute, *i.e.*, to the solute, the solvent and the adsorbent. The comparison is tedious as the solute adsorption is different when measured on GCB and NGCB, but some measurements are reported in Table VI. Data are given only for ethanol as reversed-phase chromatography is associated with polar solvents. It appears from Table VI that graphitization generally improves the column loadability. It is not possible to give a general equation that would account for this improvement as too many parameters must be taken into account.

TABLE VI

LINEAR CAPACITIES OF DIFFERENT COLUMNS IN ETHANOL

Column	Solute*	Capacity factor	Linear capacity	
			$\mu\text{g/g}$	$\mu\text{g/m}^2$
G	1,3,5-TMB	0.55	12	0.11
D	1,3,5-TMB	0.63	260	1.35
G	3,4,5-TMP	0.77	37	0.33
D	3,4,5-TMP	1.67	115	0.60
K	3,4,5-TMP	0.42	24	0.37
L	3,4,5-TMP	1.23	26	0.36
K	2,3,4,6-TeMP	1.17	22	0.34
L	2,3,4,6-TeMP	3.32	21	0.29
I	1-MMN	0.72	3	0.29
J	1-MMN	1.26	9	0.45
I	1,2-DMN	2.02	2.5	0.24
J	1,2-DMN	3.60	8.5	0.43

* TMB = trimethylbenzene; TMP = trimethylphenol; TeMP = tetramethylphenol; MMN = monomethylnaphthalene; DMN = dimethylnaphthalene.

This effect is important for preparative applications and it is preferable to use GCB in such cases. It is worth noting that for all of the solutes we used, the linear capacities are similar, being between 0.1 and 0.6 $\mu\text{g/m}^2$ (with the exception of 1,3,5-trimethylbenzene on column D). These values are somewhat smaller than those obtained with silica gel (0.5–5 $\mu\text{g/m}^2$).

Column efficiency and graphitization

From the previous discussion, it appears that graphitization does not markedly affect the retention. It would be useless in LC if it does not improve column efficiency. During graphitization the carbon layers move, mainly by rotation, the crystallite size increases, and the structure of CB becomes more similar to the graphite structure. It is well known that the graphite planes can slip easily one over the other, thus providing

its lubricating properties. We would therefore expect that graphitization would produce a decrease in the hardness, porosity and specific surface area of the particles. Our method of measurement of hardness⁶ is not sensitive enough to detect small changes in hardness and we did not observe any difference between GCB and NGCB. As far as we are concerned, packings with GCB are as stable as those with NGCB.

Conversely, S_{sp} decreases markedly upon graphitization. For instance, for Black Pearls 46 $S_{sp} = 650 \text{ m}^2/\text{g}$ before and $150 \text{ m}^2/\text{g}$ after graphitization. This effect, however, is less important when CB is coated with a large amount of pyrocarbon, and when the specific surface area of the original NGCB is small. For example, graphitization of Sterling FTFF modified with 30% pyrocarbon produces a decrease in S_{sp} of less than 3%.

Precise porosity measurements have not yet been made, but the different columns packed in the laboratory with samples of CB differing only in graphitization treatment have similar permeabilities and hold-up volumes, suggesting constant porosities (both internal and external).

The packing performances were tested by measuring the variation of the HETP for an inert compound at various flow velocities and fitting the data with the equation

$$h = \frac{B}{v} + Av^{0.33} + Cv \quad (9)$$

were B is assumed to be 2 (refs. 5 and 6). Data obtained with different columns (*D* and *G*, *L* and *K* and *J* and *I*) are similar and results are given in Table VII for the last two columns only. The results in Table VII suggest that the packings are good in both instances (for "good" columns *A* is between 1 and 2.5 and *C* between $0.5 \cdot 10^{-2}$ and $5 \cdot 10^{-2}$) and that the efficiency is slightly better for GCB. This result should be connected with the observation that the mechanical stability of particles is unchanged or decreased very slightly by graphitization. A characteristic feature of CB columns is the relationship between efficiency and retention. The *C* term in eqn. 9 is a function of k' .

TABLE VII
COEFFICIENTS OF THE HETP EQUATION ($k' = 0$)

Column	<i>A</i>	<i>C</i>	h_{min}	v_{opt}
<i>J</i>	1.79	$0.8 \cdot 10^{-2}$	3.25	2.50
<i>I</i>	2.77	$1.9 \cdot 10^{-2}$	4.50	1.80

Different expressions have been derived for this coefficient^{10,11}, but they do not agree. In fact, nearly any type of *C* vs. k' plot can be found experimentally from HETP curves.

The decrease in HETP with increasing k' is much less important for LC columns packed with fine silica particles than that found here for CB, but Loheac *et al.*¹² found a comparable decrease in efficiency when using silica particles as large as the CB particles used here.

Experiments were performed to determine whether graphitization can improve the efficiency for retained compounds. Plots of N/N_0 against k' are shown in Figs. 4 and 5, with acetonitrile and *n*-heptane as solvents, N_0 and N being the number of theoretical plates for unretained and retained solutes, respectively. N_0 is independent of the solute and is merely a function of the flow velocity of the mobile phase.

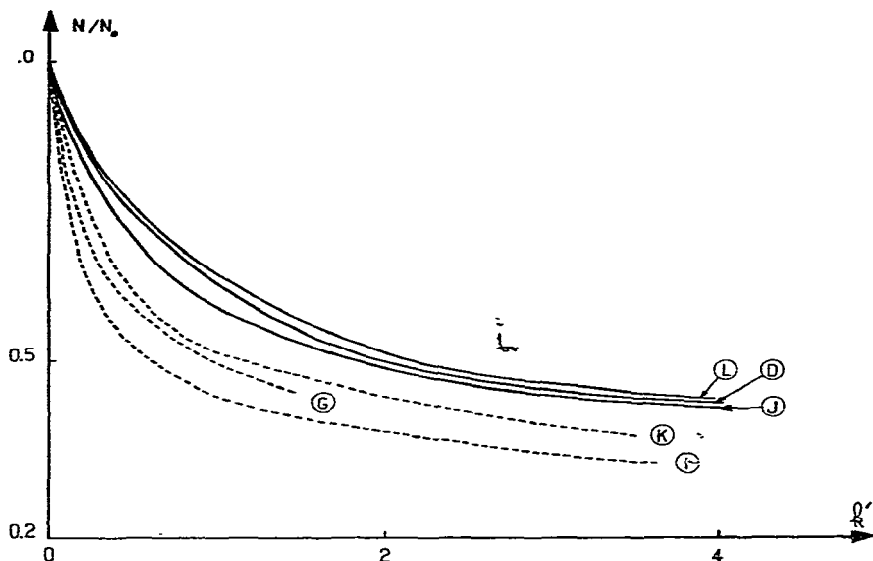


Fig. 4. Variation of efficiency with capacity factor for several columns, using acetonitrile as solvent (cf., Table II). Solid lines refer to graphitized and broken lines to non-graphitized carbon black.

Using acetonitrile as solvent, the efficiency for GCB (solid lines in Fig. 4) is slightly better than that for NGCB (broken lines). For the sake of clarity, the points for the various solutes are not reported but it should be pointed out that the experimental points that correspond to compounds of very different polarities are all very near the curves shown, which indicates that there is a strong correlation between N and k' . Few measurements were carried out at large values of the capacity factor, but it seems that, at least for GCB, HETP decreases only very slowly for $k' > 7$.

The situation is different when the solvent is apolar (*n*-heptane, Fig. 5). It is not possible to use polar solutes because of the large peak asymmetry. The behaviour of GCB columns is different when dealing with monoaromatics (solid lines 1, 3 and 4) and polyaromatics (solid lines 2 and 7). In the former instance the plots show a minimum at k' values which increase with increasing specific surface area. On the other hand, when using NGCB the efficiency decreases steadily with increasing k' in all instances, which suggests that graphitization is important mainly for the use of non-polar solvents because it cleans the surface, removing polar impurities whose effect is small with polar solvents. However, as we have shown above, CB does not seem to be a good adsorbent for the separation of polyaromatics, especially with a non-polar solvent. The results are better with polar solvents, but then the retention of these solutes become important.

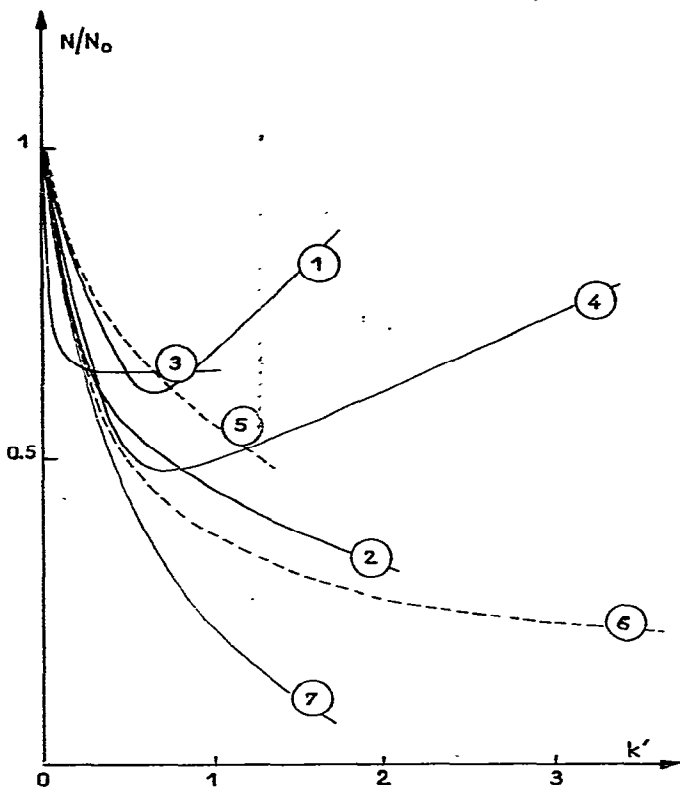


Fig. 5. Variation of efficiency with capacity factor for several columns, using *n*-heptane as solvent (cf., Table II). 1 = MB on column *D*; 2 = PA on column *J*; 3 = MB on column *J*; 4 = MB on column *L*; 5 = MB on column *K*; 6 = MB and PA on column *I*; 7 = PA on column *L*.

In conclusion, it must be pointed out that as reversed-phase chromatography is associated with the use of polar solvents, the influence of graphitization on the performance of carbon adsorbents is small in liquid chromatography.

‡

CONCLUSION

The influence of graphitization on the chromatographic properties of carbon black is of moderate importance in liquid chromatography. The decrease in retention, for instance, can easily be obviated by using a weaker solvent. The greater efficiency of graphitized carbon is interesting, especially when using apolar solvents such as *n*-heptane. The possibility of packing columns with fine particles (5–10 μm) will partially offset the importance of this effect. Further, it is possible that the decrease in the number of theoretical plates with increasing capacity factor will be less critical for smaller particles than for the larger particles used here (30–50 μm).

It is really of interest to use graphitized carbon only in preparative chromatography, as the loadability of the columns is greater and the efficiency is less sensitive to the amount of solute injected. With regard to physical measurements, it is essential

to use graphitized carbon black because its structure is well known and the experimental conditions for hardening have no influence on the thermodynamic properties.

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