

CHROM. 12,345

## A PTFE-BASED CARBON ADSORBENT IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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### SUMMARY

A new type of carbon adsorbent, prepared by reduction of PTFE, was studied and modified with the aim of obtaining a material with a relatively homogeneous, non-polar surface for applications in high-performance liquid chromatography. Three types of sorbent differing in the specific surface area, oxygen remainder and porosity were investigated.

The chromatographic behaviour of various solutes, both in non-polar (*e.g.*, pentane) and polar (aqueous buffer) media, has been studied. The plots of natural logarithm of the capacity factor *vs.* the carbon number were reasonably parallel for a homologous series with different functional groups. The influence of the ionization of some amino acids on their retention over the whole pH range has been shown.

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### INTRODUCTION

Carbon adsorbents comprising the basic adsorbents used in chromatography were highly favoured by classical liquid chromatographers before the advent of gas chromatography (GC). They were widely used both for the study of adsorption of substances without prototropic groups (hydrocarbons)<sup>1,2</sup> and of substances containing them (acids, bases and ampholytes)<sup>3-6</sup>. The effect of pH on the adsorption was studied in most cases. Some papers describe the shape of the adsorption isotherms<sup>2,6</sup>, other are concerned with the heats of wetting<sup>7,8</sup>. The straightforward exploitation of these data in recent studies of carbon adsorbents is hampered especially by the poorly defined surface properties of the adsorbents.

An intense search for new adsorbents has occurred owing to the rapid prolifer-

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ation of high-performance liquid chromatography (HPLC). Carbon adsorbents are of special interest mainly due to their selectivity for isomeric substances. A carbon adsorbent in the form of natural diamond was used by Telepchak<sup>9</sup>. In spite of its unique mechanical properties and nearly non-polar surface, this material has not found application due to its too low specific surface area. Another attempt at the preparation of carbon adsorbents was made by carbonization of organic polymers<sup>10,11</sup>, but only scarce chromatographic data are available. The first promising work was the deposition of pyrolytic carbon on thermal carbon blacks<sup>12,13</sup>. The resulting material is characterized by a high selectivity for homologous compounds and geometrical isomers. Unfortunately, the linear capacity was low and the efficiency decreased rapidly with increasing capacity factor. Another method of preparing carbon-like adsorbents involves coating of silica particles with a carbon layer<sup>14-16</sup>. A pyrolytic decomposition of benzene at temperatures up to 900°C places very stringent requirements on the silica to be covered. This material seems to have the best efficiency, so far, however there are problems with the degree of coating. At low coverages a combined retention mechanism is to be expected, while peeling of the surface layer may occur at high degrees of coating. Jansta *et al.*<sup>17</sup> succeeded in preparing a new carbon adsorbent by a low temperature (below 100°C) electrochemical reduction of poly(tetrafluoroethylene) (PTFE). The carbon powder obtained exhibits very good mechanical properties for packing HPLC column<sup>18</sup> without any subsequent treatment. The structure and physico-chemical parameters of this material were thoroughly investigated<sup>19,20</sup>, and demonstrated its great promise for applications based on sorption. In agreement with a high content of oxygen (13-16%, w/w), the polarity of the surface was confirmed<sup>18</sup> using HPLC.

The present paper describes the preparation of these new carbon adsorbents with a low content of oxygen and a relatively non-polar surface and HPLC studies of their chromatographic parameters. Some simple chromatographic applications were also tested.

## EXPERIMENTAL

### *Materials*

Three types of carbon adsorbents were prepared from a solid mixture of carbon and lithium fluoride (resulting from the reduction of PTFE with a lithium amalgam<sup>17,21</sup>), dispersed nearly at a molecular level.

*Sample No. I.* LiF was leached from the initial mixture with water and the fraction of required particle size, 3-12  $\mu\text{m}$ , was obtained by sedimentation in water (the content of this fraction was 73%, w/w). The sample was then dried *in vacuo* at 300°C to an end pressure of 0.01 Pa and heated at 950°C in helium for 1 h. Oxygen bound to the carbon surface during the wet part of the preparation process escaped irreversibly in the form of CO<sub>2</sub> during the thermal treatment.

*Sample No. II.* The initial mixture was heated to 950°C in helium (melting point of LiF is 842°C) for 1 h. The LiF formed droplets, which could be separated to a large extent after cooling on a mesh. The residue of LiF was then dissolved in water and the oxidation of the carbon surface mentioned above did not occur. The carbon material was fractionated (6-13  $\mu\text{m}$ ) by sedimentation in a 0.1% (w/w) aqueous detergent solution (Empicol LXV, containing chiefly sodium laurylsulphate;

Albright and Wilson, Whitehaven, Great Britain), on the basis of the hydrophobicity of the surface. The detergent adsorbed on the surface was then removed by heating to 700°C in hydrogen and by washing out the resulting inorganic salts with water. The sample was finally dried at 300°C *in vacuo*.

*Sample No. III.* The sample was treated under the same conditions as with sample No. II, but after dissolving the LiF residue the sample was dried at 300°C *in vacuo* and heated in argon at 2400°C for 1 h. The required fraction, 5–15 μm, was obtained from the bulk using an air classifier (Gonell).

For all the sorbents the BET-specific surface areas were calculated from the adsorption isotherms for N<sub>2</sub> (77°K), measured on a Sorptomatic 1826 apparatus (Carlo Erba, Milan, Italy). The values of the porosity ( $\epsilon_t$ ) were obtained from the total volumes of liquid nitrogen adsorbed at a relative pressure of  $p/p_0 = 1$ .

### Methods

The chromatographic columns were packed using the slurry-packing technique<sup>18</sup>. The slurry contained 5% (w/w) of carbon adsorbent in tetrachloromethane. After treatment in an ultrasonic bath for 5 min, the slurry was pressed in the column by heptane under a pressure of 20–30 MPa.

A Varian Model 8500 liquid chromatograph and a Pye-Unicam Model LC 3 UV variable-wavelength detector were used. The experiments were carried out with Varian N.316 stainless-steel columns (25 × 0.21 cm I.D.) or home-made stainless-steel columns (30 × 0.43 cm I.D.), under isocratic conditions at 23°C. The samples of hydrocarbons and their derivatives were purchased from API (New York, N.Y., U.S.A.); reagent-grade chemicals for the preparation of the slurry were obtained from Lachema (Brno, Czechoslovakia). The solvents were dried on a silica-alumina column activated at 150°C, and distilled. Redistilled water was used.

The retention times were measured from the switching on of the pump to the maximum of the peak using a stopwatch. The peak parameters were determined graphically using a chart speed of 20 cm/min.

The effect of the flow-rate on the column efficiency was described by the reduced parameters of the plate height  $h = H/d_p$  and the velocity  $v = ud_p/D_m$ , where  $H$  is the height equivalent to a theoretical plate, evaluated using a bi-Gaussian fit<sup>22</sup>,  $u$  is the linear velocity in cm/sec,  $d_p$  is the effective particle diameter in cm as determined by Karch *et al.*<sup>23</sup> and  $D_m$  is the molecular diffusivity in cm<sup>2</sup>/sec of an inert solute and was approximated by the relationship of Chang and Wilke<sup>24</sup>.

Small non-polar molecules (*e.g.*, 2-methylbutane) were used for the measurement of the mobile phase hold-up times in non-polar eluents, while NaNO<sub>3</sub> was used in buffer solutions. When the choice of an inert molecule was difficult, the procedure suggested by Guardino *et al.*<sup>25</sup> for the calculation of the dead time from retention in a homologous series was used. The capacity factor was evaluated in the usual way as  $k' = (t_R - t_0)/t_0$ . The molecular areas of the solvents were calculated according to<sup>25</sup>

$$A_M = (V/N)^{2/3} \text{ m}^2 \quad (1)$$

where  $V$  is the molar volume in m<sup>3</sup>/mol of the eluent and  $N$  is Avogadro's number in mol<sup>-1</sup>.

The analysis of the data was performed on a TI 59 minicomputer and/or on a HP 9830 A computer.

## RESULTS AND DISCUSSION

### *Sorbent properties and column efficiency*

The three procedures described above yield a carbon material with a relatively low content of oxygen, widely differing in the specific surface area and the particle size distribution, suitable for HPLC application. The determined physical properties are summarized in Table I. The sorbent polarity was tested using a mixture of *m*- and *p*-carborane isomers. In contrast to the results obtained on a carbon adsorbent with a high oxygen content<sup>18</sup>, the capacity factors for carborane isomers on the sorbents studied were lower than 0.3 in hexane. All the sorbents are sufficiently hard to allow a reproducible packing of HPLC columns.

TABLE I  
BASIC PHYSICAL PROPERTIES OF CARBON ADSORBENTS

Sample No.	Specific surface area, $S_{sp}$ ( $m^2/g$ )	Porosity $\epsilon$ ,	Effective particle diameter, $d_p$ ( $\mu m$ )	Oxygen content (% w/w)
I	2000	0.74	9.5	1.6
II	1300	0.76	13.0	0.5
III	20	$\rightarrow 0$	9.2	$\rightarrow 0$

Fig. 1 shows the variation of  $h$  (the reduced plate height) with  $v$  (the reduced velocity). The experimental data were fitted to the Giddings equation<sup>27</sup>:

$$h = B'/v + \frac{A'}{D' + 1/v} + C'v$$

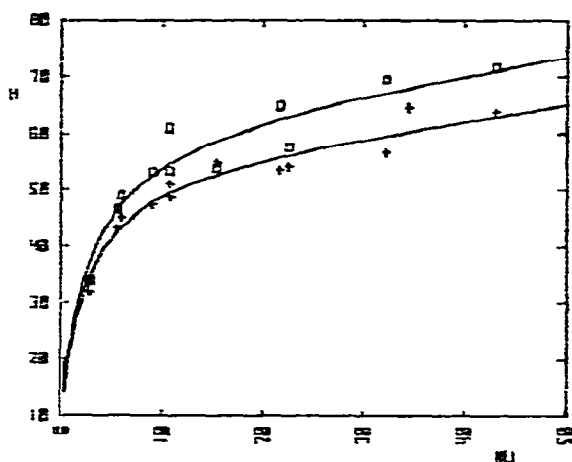


Fig. 1. Plots of the reduced plate height versus the reduced velocity. Operating conditions: adsorbent, No. II; column,  $30 \times 0.43$  cm I.D.; eluent, diethyl ether; detector, refractive index; temperature,  $23^\circ C$   $\pm$ , Dodecane;  $\square$ , tetradecane.

Due to the low diffusivity coefficient in liquids ( $\approx 10^{-5}$  cm<sup>2</sup>/sec), the measurements were not carried out in the region of  $v$  where the first term of eqn. 2 is predominant. The estimated value of parameter  $B'$  was 2, in agreement with the literature<sup>13</sup>. The parameters of eqn. 2 are given in Table II. The irregular shape of the adsorbent and the large particle size range account for the relatively high values of  $A'$ . Values of parameter  $C'$  given in refs. 13 and 15 (both for carbon particles and carbon-coated silica particles) range between 0.30 and 0.48 for  $k' \approx 1$ . Regardless of ambiguity in determining the value of  $C'$  at reduced velocities below 50, it seems that for a carbon type of adsorbent the mass transfer resistance plays the predominant role in efficiency at higher  $k'$ .

TABLE II  
COLUMN EFFICIENCY DESCRIBED BY EQN. 2

For operating conditions see Fig. 1.

Capacity factor	Solute	$A'$	$B'$	$C'$	$D'$	$v_{opt.}$	$h_{min.}$
1.25	Dodecane	28	2	0.23	0.50	0.31	14
2.25	Tetradecane	28	2	0.45	0.28	0.30	14

#### Retention in homologous series

As expected, the carbon adsorbents are eminently suitable for the separation of homologous series. Figs. 2-4 show some examples of such separations. The almost linear relationship between the natural logarithm of the capacity factor and the number of carbon atoms is shown in Fig. 5. Assuming that Snyder's competitive model of adsorption<sup>28</sup> is valid for our adsorbents with neat eluents, the retention should be governed by dispersion forces. The correlation between the elution order and  $A_i\sqrt{\gamma_i}$  (where  $A_i$  is the molecular area of the solute and  $\gamma_i$  is the surface tension)<sup>29</sup> or the molar refraction<sup>30</sup> was not satisfactory. A specific property of this type of carbon adsorbent is its high affinity for double bonds, which is not encountered on bonded phases of the ODS type<sup>31</sup> or, as is generally supposed, on charcoal<sup>28,32</sup> and which is difficult to explain on the basis of the available data.

#### Effect of eluent properties

With carbon adsorbents, the mobile phase elution strength is related, to a first approximation, to the molecular area<sup>13</sup>. The plot of the mean value of  $A$  (the slope of the relationship  $\ln k' = An + B$ , where  $k'$  is the capacity factor and  $n$  is the number of carbon atoms) against the mobile phase molecular area calculated from eqn. 1 is given in Fig. 6, together with data obtained by other authors. The departure from the straight line is probably due to (a) a solvophobic effect and/or (b) an incorrectly determined surface area occupied by the molecule of the eluent (the shape of the adsorption isotherms would be of great interest).

#### Examples of separations

Fig. 7 shows the separation of aromatic hydrocarbons. The preferential adsorption of aromatics on carbon adsorbents is well known. This was the reason why the adsorbent of low specific surface area was utilized.

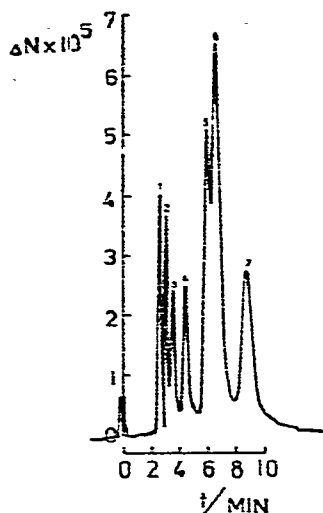


Fig. 2. Chromatogram of a mixture of aliphatic hydrocarbons. Operating conditions: adsorbent, No. II; column,  $25 \times 0.21$  cm I.D.; eluent, pentane; flow-rate, 20 ml/h; detector, refractive index; temperature,  $23^\circ$ . Peaks: 1 = 2-methylbutane; 2 = octane; 3 = decane; 4 = dodecane; 5 = tetradecane; 6 = 1-tetradecene; 7 = hexadecane.

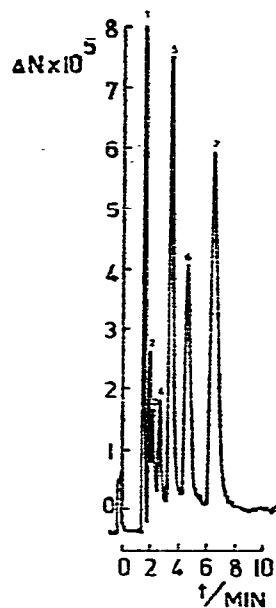


Fig. 3. Chromatogram of a mixture of chlorinated hydrocarbons. Operating conditions: adsorbent, No. I; column,  $25 \times 0.21$  cm I.D.; eluent, heptane; flow-rate, 20 ml/h; detector, refractive index; temperature,  $23^\circ$ . Peaks: 1 = pentane; 2 = 1-chlorohexane; 3 = 1-chlorooctane; 4 = 1-chlorodecane; 5 = 1-chlorododecane; 6 = 1-chlorotetradecane; 7 = 1-chlorohexadecane.

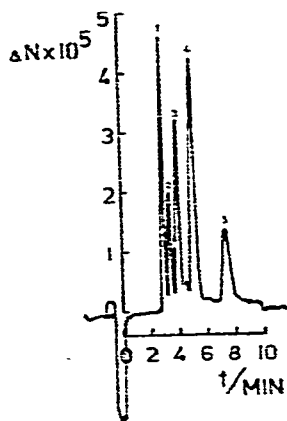


Fig. 4. Separation of a mixture of 1-alkanols. Operating conditions: adsorbent, No. II; column,  $30 \times 0.43$  cm I.D.; eluent, methanol; flow-rate, 80 ml/h; detector, refractive index; temperature,  $23^\circ$ . Peaks: 1 = water; 2 = 1-propanol; 3 = 1-butanol; 4 = 1-pentanol; 5 = 1-hexanol.

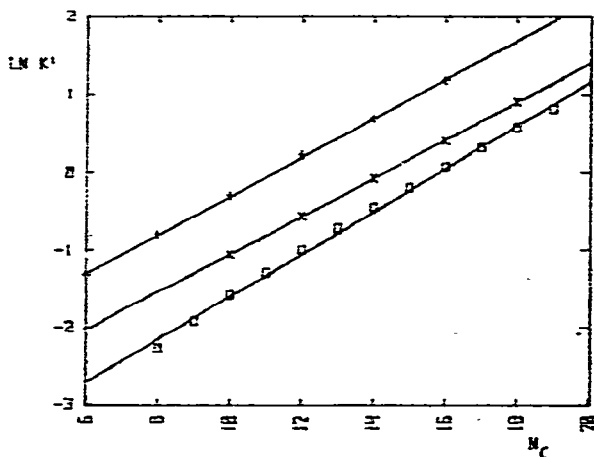


Fig. 5. Graph illustrating the relationship between the natural logarithm of the capacity factor and the number of the carbon atoms. Operating conditions: adsorbent, No. I; column,  $25 \times 0.21$  cm I.D.; eluent, heptane; flow-rate, 20 ml/h; detector, refractive index; temperature, ambient.  $\square$ , Alkanes;  $\times$ , 1-alkenes;  $+$ , 1-chloroalkanes.

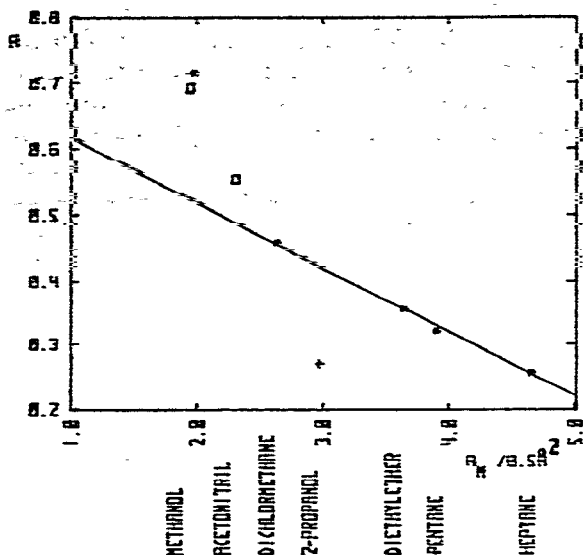


Fig. 6. Plot illustrating the effect of the eluent molecular area on the mean value of the slope of the lines from Fig. 5. ★, Experimental data (operating conditions as in Fig. 4); +, the value calculated from ref. 14; □, the data evaluated graphically from refs. 12 and 13.

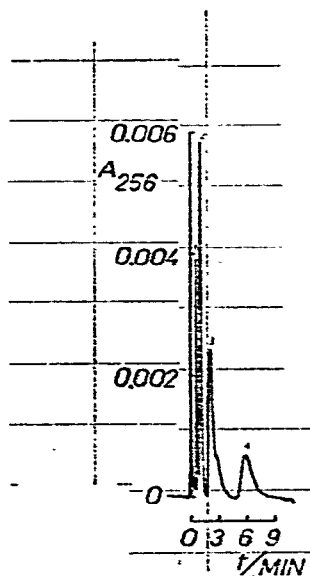


Fig. 7. Chromatogram of a mixture of aromatic hydrocarbons. Operating conditions: adsorbent, No. III; column, 25 × 0.21 cm I.D.; eluent, diethyl ether; flow-rate, 60 ml/h; detector, UV; temperature, ambient. Peaks: 1 = benzene; 2 = 4-bromobiphenyl; 3 = *m*-terphenyl; 4 = anthracene.

The fact that our carbon adsorbent has a low polarity and resists alkaline solutions (where adsorbents based on silica gel fail), suggests its application over the whole pH range. Recently an extensive theory of the chromatographic behaviour of ampholytes in buffer solutions of different pH was published<sup>33-35</sup>. From that work

one would expect the adsorbent to interact solely with the solutes and not with the buffer components. This assumption is not valid for our carbon adsorbent as is evident from Figs. 8 and 9. In a neat water eluent these samples interact with the adsorbent much more strongly than in a buffer solution of the same pH. In our case the material behaves more like a dynamically loaded ion exchanger<sup>36</sup> than an adsorbent. Table III illustrates the dramatic change in the capacity factor for ampholytes with changing pH of the mobile phase. These results are promising as they suggest the possibility of separating biologically active amino acids without any derivatization.

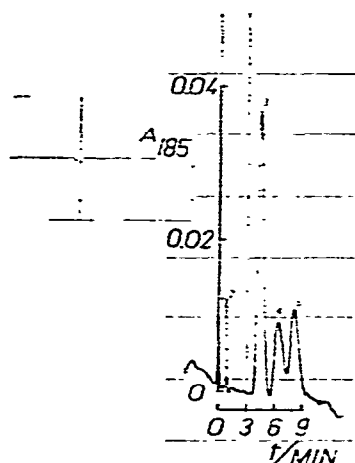


Fig. 8. Separation of some protein amino acids. Operating conditions: adsorbent, No. II; column,  $30 \times 0.43$  cm I.D.; eluent, 0.1 M phosphate buffer, pH = 2.1,  $I = 0.1$  ( $\text{Na}_2\text{SO}_4$ ); flow-rate, 240 ml/h; detector, UV; temperature, ambient. Peaks: 1 = L-ornithine; 2 = L-lysine; 3 = L-arginine; 4 = L-histidine; 5 = L-leucineamide.

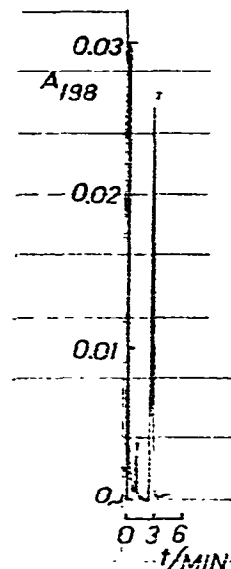


Fig. 9. Separation of two basic amino acids. Operating conditions: adsorbent, No. II; column,  $30 \times 0.43$  cm I.D.; eluent, 0.05 M  $\text{NaH}_2\text{PO}_4$  and 0.05 M NaOH buffer, pH = 9.5,  $I = 0.1$  ( $\text{Na}_2\text{SO}_4$ ); flow-rate, 240 ml/h; detector, UV; temperature, ambient. Peaks: 1 = L-ornithine; 2 = L-lysine.

TABLE III

VARIATION OF CAPACITY FACTOR OF BASIC AMINO ACIDS WITH pH OF MOBILE PHASE

Operating conditions: adsorbent, No. III; column,  $25 \times 0.21$  cm I.D.; eluent, Britton-Robinson buffer,  $I = 0.15$  ( $\text{Na}_2\text{SO}_4$ ); detector, RI; temperature, ambient.

pH	Solute capacity factor	
	L-Arg	L-His
6.8	0.28	0.30
8.7	0.43	0.26
11.5	1.35	0.99



## CONCLUSIONS

A low-polarity carbon adsorbent has been prepared that differs from all carbon adsorbents prepared so far in having defined and reproducible surface properties and being easy to pack into HPLC columns with a reasonable efficiency. The chromatographic behaviour of the sorbents prepared, the effect of the eluent and solute interactions were studied. The main advantage of the new type of carbon adsorbent is the possibility of transferring it into an aqueous solution and working with buffer eluents over the whole pH range. Some analytical applications have been illustrated.

## ACKNOWLEDGEMENTS

The authors are grateful to B. Gaš and P. Foch for their help with the computer data handling and to I. Cannie (Pye Unicam) for the loan of the detector.

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