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NEW CARBON ADSORBENT FOR HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

A carbon adsorbent prepared by reduction of poly(tetrafluoroethylene) with alkali-metal amalgams can be used as a mechanically stable packing for high-performance liquid chromatography. Physical properties of the material are presented, and the structure of the particles is discussed. The separations of some aliphatic alcohols, aromatic compounds and isomeric carboranes are used to illustrate the performance of the adsorbent.

INTRODUCTION

Carbon materials, which are of interest in adsorption liquid chromatography, usually exhibit poor mechanical properties. Their grains are mostly agglomerates which gradually disintegrate in a chromatographic column under normal high-performance liquid chromatographic (HPLC) conditions. This is accompanied by undesirable progressive changes in the hydrodynamic properties of the column. Recently, studies have been made of the preparation of carbon black grains for HPLC, which were hardened by graphitization and deposition of carbon layers prepared by pyrolysis of suitable hydrocarbons^{1,2}. Other papers describe the preparation of silica micro-particles covered by carbon films^{3,4}.

An interesting carbon material was recently isolated from the products of reduction of poly(tetrafluoroethylene) (PTFE) with alkali-metal amalgams at 25–100° (ref. 5). These temperatures are unusually low for the preparation of carbon by decomposition of organic materials, and the carbon made from PTFE contains hardly any definable products of pyrolysis on its surface. The reduction of PTFE was shown to proceed via an electrochemical mechanism in the solid state⁶. PTFE is known to

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possess a high degree of crystallinity, and it was shown⁷ that the structure of the carbon produced may be correlated with that of the starting material. This results in an unusual reproducibility of the properties of the carbon particles. The present paper describes the first results of tests of the new carbon adsorbent as a column-packing material for HPLC.

EXPERIMENTAL AND RESULTS

Properties of the PTFE carbon

The preparation of the carbon has already been described⁵. PTFE was quantitatively reduced with lithium amalgam *in vacuo* at 100°. The carbon was isolated from the resulting solid mixture of products (C:2 LiF) by extraction of the lithium salt with water. The suspension of carbon particles in water was filtered and dried *in vacuo* at 350°. A carbon powder was obtained in this way without any supplementary operations (grinding, fractionation, etc.).

The particle size distribution (Fig. 1) was determined by use of a Sartorius sedimentation balance. The calculation of the particle diameters was based on Stoke's law, *i.e.*, the particles are assumed to be spherical. Owing to the lamellar shape of the particles of PTFE carbon, which will be discussed below, particle sizes given in Fig. 1 are only relative. Almost all of the measurements described in this paper were performed with a material which was prepared from the original carbon powder by separation of particles smaller than 4 μm and greater than 12 μm using a fractionated sedimentation in water. Elementary analysis of the dry product yielded 86% C, 1% H and oxygen as the residue. Less than 0.01% of Li and less than 1% of ash containing Ca, Si, Mg and Fe from the starting PTFE were found. Fluorine was present only in an amount equivalent to the lithium residue.

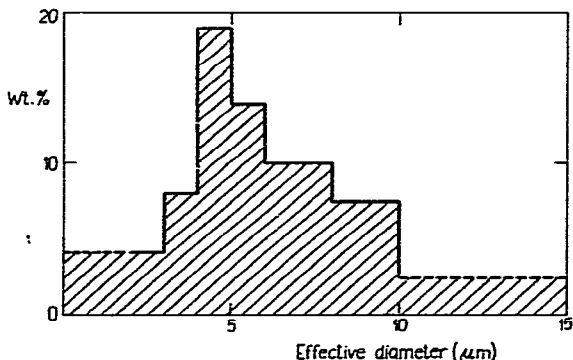


Fig. 1. Frequency polygon of the PTFE-carbon particles.

The polymer used as a starting material is a highly crystalline compound with lamellar morphology. It consists of elementary lamellae whose thickness is of the order of tens of nanometres. The macromolecular chains are stacked along the smallest dimension of the lamella. Along the chain, regions with compact chain packing (so-called nodules) alternate with disordered regions. Hence the nodules are the basic morphological structure unit in the polymer. The molecules of PTFE are formed by

very long linear unbranched chains of carbon atoms, closely surrounded by spirals of fluorine atoms. The C-F bonds are split by the electrochemical reduction. The fluorine ions formed are too large to be mobile in the solid phase and their electric field provokes diffusion of Li^+ into the bulk of the solid reaction products. Thus solid lithium fluoride "covers" are formed around the reduced carbon chains of poly-yne ($-\text{C}\equiv\text{C}-$)_n or polycumulene ($=\text{C}=\text{C}=-$)_n. The relatively high oxygen content in the PTFE carbon, obtained during extraction with water, may be explained by the reactivity of the chains of carbon atom freed from the solid phase during dissolution of LiF , *i.e.*, by the reaction of the carbon with water. This reactivity suggests the possibility of lateral bonding of the carbon atom chains with the formation of a firm continuous carbon skeleton.

Observations with a JSM 35 scanning electron microscope (JEOL, Tokyo, Japan) showed that the particles in the carbon powder had a multilayer structure and were composed of a few lamellae (the micrograph was published in ref. 7). The longitudinal dimension of the particles varied in the range *ca.* 2–50 μm (statistical mean $12 \pm 9 \mu\text{m}$). The true density of the carbon particles, obtained by the pycnometric method, was 2.17 g/cm^3 ; the bulk density of the dry powder after a vigorous shaking was 0.142 g/cm^3 . The dry particles could be compressed under a pressure of 400 MPa without substantial permanent deformation.

The adsorption properties of the PTFE carbon are unique in comparison with all of the known adsorbents: up to 1.25 ml of benzene are adsorbed by 1 g of the carbon at 25°. The specific surface area of the carbon is extremely high: values of *ca.* 2500 m^2/g were calculated from the BET adsorption isotherm of argon (in liquid nitrogen). Capillary condensation effects, which normally occur on charcoals, were excluded experimentally⁵. A specific surface area of 1550 m^2/g was calculated from low-angle X-ray scattering⁷. The very good reproducibility of the properties of the PTFE-carbon powder, arising from the constant properties of the elementary particles in the starting polymer, was confirmed experimentally for numerous samples. The preparation of the carbon is so simple that the production of tens of grams is possible on a laboratory scale.

Column preparation and apparatus

The balanced-slurry packing technique⁸ was used. The slurry-packing liquid was tetrabromoethane-dioxan-tetrachloromethane (38:31:31) or tetrachloromethane. No difference in the column efficiency was observed with the change of the slurry-packing liquid. An amount of 0.8 g of the PTFE carbon was suspended in 40 cm^3 of the slurry-packing liquid and after treatment in an ultrasonic bath for 5 min the slurry was transferred to a packing apparatus⁹. Stainless steel columns (300 × 3 mm I.D.) were filled under a pressure of 20 MPa and this pressure was maintained until 1 l of heptane had been pumped through the column. Slurry packing can be performed under a pressure of 47.0 MPa without fracturing the particles and loss of column permeability.

Columns were operated at a pressure of 2.0–8.0 MPa and no decrease in permeability was observed during operation. The home-made chromatograph was equipped with a VCM-150 membrane pump, a differential UV-detector operating at 254 nm (Development Works of the Czechoslovak Academy of Sciences), a Model 2025/50 differential refractometer (Knauer, Oberursel, G.F.R.) and a TZ 21 S line

recorder (Laboratorní Přístroje, Prague, Czechoslovakia). All of the solvents were purified by passage through a column of activated alumina and were distilled before use.

Hydrodynamics and efficiency of the columns

Values of the average particle diameter, d_p , were calculated from the inlet pressure and flow-rate of heptane (0.5–5.0 ml/min) by use of equation of Karch *et al.*¹⁰. For columns filled with unfractionated carbon powder (Fig. 1), $d_p = 7.0 \mu\text{m}$; for columns filled with a carbon powder from which particles smaller than $4 \mu\text{m}$ and larger than $12 \mu\text{m}$ had been removed, $d_p = 9.4 \mu\text{m}$.

Fig. 2 shows the variation of the theoretical plate height h with flow-rate. The efficiency obtained does not correspond to the column efficiency obtained with silica particles of similar particle size on chemically bonded stationary phases¹¹. However, the efficiency obtained with the unfractionated carbon powder is quite good for chromatographic applications, especially on a preparative scale. Comparison of the fractionated and unfractionated material shows that an increase in efficiency could be attained using normal fractionation methods. A characteristic of columns containing carbon black is the large asymmetry of peaks having a capacity factor greater than 2.0. Colin *et al.*¹ also observed this phenomenon and explained it in terms of a low column capacity. A monotonous decrease in the retention time with increasing sample loading was observed for the PTFE carbon. For sample sizes from 5.4 to $140 \mu\text{g}$ of *o*-terphenyl per gram of the adsorbent, the retention time decreased by 8% (corresponding to a 16% decrease in the capacity factor) in methylene chloride at a flow-rate of 1.28 ml/min. PTFE carbon exhibits a greater column capacity than those achieved by Colin *et al.*¹.

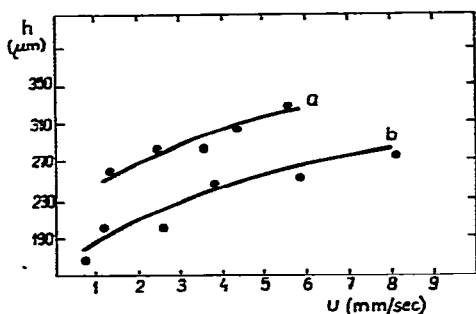


Fig. 2. Peak broadening as a function of the velocity of the mobile phase. Eluent, heptane; sample, pentane ($k' = 0$). (a) Column ($200 \times 3.3 \text{ mm I.D.}$) packed with unfractionated carbon particles (see Fig. 1). (b) Column as in (a) but packed with fractionated carbon particles.

Simple analytical applications

Non-polar adsorbents are used in reversed-phase liquid chromatography, where their advantages are usually used for the separation of polar samples and homologous solutes. Fig. 3 demonstrates the influence of hydrocarbon chain length on the retention behaviour of aliphatic alcohols. The k' value increases with increasing length of the non-polar chain of the monofunctional *n*-alcohols. When *n*-heptane or methylene chloride is used as a solvent, aromatic compounds of widely differing polarity can be separated (Table I). The retention sequence of biphenyl and *o*-terphenyl

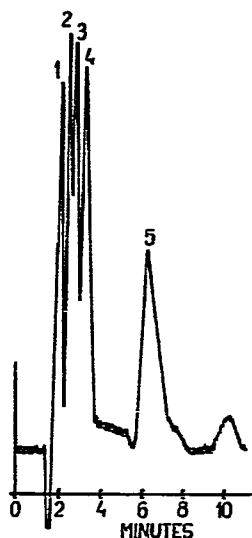


Fig. 3. Separation of aliphatic alcohols. Eluent, acetonitrile; column (300×3.3 mm I.D.) packed with fractionated PTFE carbon; flow-rate, 0.77 ml/min; pressure drop, 3.2 MPa. Peaks: 1 = ethanol; 2 = *n*-butanol; 3 = *n*-amyl alcohol; 4 = *n*-hexyl alcohol; 5 = *n*-nonyl alcohol.

TABLE I
RETENTION OF SOME AROMATIC COMPOUNDS

Solute	Capacity factor k'		
	PTFE carbon		Silica ^{12,13,***}
	A*	B**	
Benzene	0.11	0.19	0.59
Biphenyl	6.33	4.63	1.88
<i>o</i> -Terphenyl	2.11	1.25	4.88
Nitrobenzene	3.67	1.75	15.65

* Column, 300×3.3 mm I.D.; flow-rate, 1.03 ml/min; pressure drop, 3.6 MPa; eluent, dichloromethane–heptane (1:1).

** Column, 300×3.3 mm I.D.; flow-rate, 1.28 ml/min; pressure drop, 5.6 MPa; eluent, dichloromethane.

*** Eluent, heptane.

was reversed in comparison with the behaviour on silica gel. The change in retention with the change of solvent system is in agreement with the position of the solvent in the eluotropic series established for carbon adsorbents by Colin *et al.*². Fig. 4 shows an excellent separation of carborane isomers $B_{10}C_2H_{12}$ with a resolution $R > 3.0$. For this particular separation, the PTFE carbon offers great selectivity and is the best adsorber known.

CONCLUSIONS

These first experiments with the new carbon adsorbent made from PTFE show its applicability for HPLC. The material may be used in the form which results from

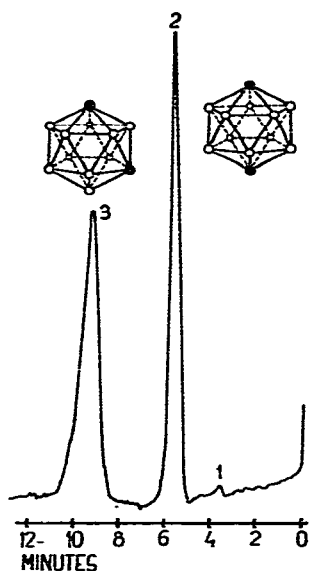


Fig. 4. Separation of carborane isomers. Eluent, heptane; column (300 × 3.3 mm I.D.) packed with fractionated PTFE carbon; flow-rate, 1.23 ml/min; pressure drop, 3.0 MPa. Peaks: 1 = solvent impurity; 2 = *p*-carborane (0.60); 3 = *m*-carborane (1.66).

the electrochemical preparation without supplementary treatment. Its efficiency can be increased by using fractionated particles. However, owing to the lamellar shape of the particles, a more effective procedure seems to be the preparation of PTFE micro-particles of an optimum shape followed by the formation of a carbon film on their surface by reduction. In comparison with silica gel, the carbon material may be of use in the separation of unstable compounds which are sensitive towards water and protic solvents. It is the best adsorbent, having a high selectivity, for the separation of carborane isomers.

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