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STRUCTURE AND PERFORMANCE OF POROUS GRAPHITIC CARBON IN LIQUID CHROMATOGRAPHY

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SUMMARY

The structure of the porous carbon (designated PGC) has been studied in detail by X-ray diffraction, scanning electron microscopy, electron diffraction, and high-resolution electron microscopy. These techniques provide a self-consistent picture: PGC which has not been heated above 1000°C is an amorphous glassy carbon containing micropores and mesopores. PGC which has been heated to above 2000°C has the atomic-molecular structure of a 2-dimensional graphite which is essentially indistinguishable from that of graphitised carbon black (GCB), both being made up from crystallites of around 100 Å in size. By contrast, at the colloidal level, PGC and GCB are very different: where GCB consists of loosely aggregated colloidal units having only weak Van der Waals bonding between them, PGC has a strong sponge-like structure, capable of withstanding considerable shearing forces, such as those met with in high-performance liquid chromatography (HPLC).

During the heating of PGC from 1000°C to above 2000°C, needle- and plate-like structures are also formed. These consist of dense 3-dimensional crystalline graphite. They have negligible surface area and are not useful in chromatography.

The porous 2-dimensional graphite (PGC) consists of 3-10 μm spherical particles which are about 80% porous and have a specific surface area of about 150 m²/g. This material has been used for HPLC and gives peak shapes comparable to those from bonded silica gels of the same particle size. PGC acts as a very strong hydrophobic adsorbent with unique selectivity. Its elution patterns are compared to those from a commercial ODS-bonded silica for methyl benzenes, phenols, ethers, monosubstituted benzenes, amines, and acids. Examples are shown of HPLC separations of simple analgesics. Deactivation by adsorption of high-molecular-weight impurities and reactivation of PGC is also briefly noted.

INTRODUCTION

In 1982 Gilbert *et al.*¹ described the production and performance in gas and

liquid chromatography (GC and HPLC) of a new carbon material which they called "porous glassy carbon" (PGC). The material was produced² by impregnating a silica gel template with a phenol-hexamine mixture, polymerising this mixture within the pores of the silica gel, pyrolysing the resin in nitrogen, dissolving out the silica template, and finally heating the remaining porous carbon to a temperature in excess of 2000°C. Large-particle material (100–200 μm) was examined as a GC adsorbent and small-particle material (< 40 μm) as an HPLC material. In GC, the material showed selectivity and retention which was very similar to that of Carbo-pack B, a commercial graphitised carbon black (GCB) marketed by Supelco. In HPLC, the material behaved as a strong hydrophobic adsorbent but at that stage in development gave rather poor peak shapes with strongly retained solutes¹.

Shortly before the publication of this paper¹, Ciccioli *et al.*³ had shown that carefully fractionated 20- μm Carbo-pack B gave excellent results in LC with a high degree of peak symmetry, even for strongly retained solutes. Unfortunately, the fragility of this material made it impracticable as a routine HPLC packing material. Nevertheless, these two papers^{1,3} showed that a porous graphitised carbon would probably be the ideal carbon material for HPLC, if it could be made strong enough. Accordingly, a more appropriate name for the carbon developed by Gilbert *et al.* might be "porous graphitised carbon". Fortunately, the initials PGC cover both descriptions equally well.

The present work presents evidence from X-ray analysis and electron microscopy to support this contention and it establishes the close similarity between the bulk and surface atomic arrangements in PGC and GCB. However, unlike GCB, which is composed of loosely aggregated colloidal particles and very fragile, PGC has a continuous sponge-like structure with a mechanical strength comparable to that of silica gels having similar porosity and is therefore of adequate strength for both GC and HPLC.

The sample of PGC tested by Gilbert *et al.*¹ in HPLC showed significant peak tailing when compared to the GCB tested by Ciccioli *et al.*³. This difference can probably be attributed to imperfections in the graphitic surface of PGC. In this paper, we show that improved methods of preparation of PGC have led to samples which exhibit chromatographic properties in HPLC very similar to those of ODS-bonded silicas in terms of peak symmetry and sharpness.

STRUCTURE OF CARBONS

Many varieties of carbon are produced industrially on a large scale⁴. The most important of these are: electrographite (for industrial electrodes), nuclear graphite (as a moderator in nuclear reactors) active carbons or charcoals (for adsorption of vapours, extraction of organics from water, decolourising), carbon blacks (fillers in rubber), glassy carbons, and carbon fibres.

Electrographites and nuclear graphites, as the names suggest, are "graphitised". This term, as used commercially, implies little more than that the materials have been heated to high temperatures (*e.g.* 3000°C). The actual degree of graphitisation achieved may vary widely over the range of materials which are loosely termed "graphitised" and is discussed in more detail below. The other forms of carbon are not normally heated much above about 1000°C in the course of manufacture and are

therefore amorphous. Active carbons are made from cokes and charcoals by controlled oxidation, and possess highly oxygenated surfaces, bearing functional groups such as $-\text{OH}$, $=\text{O}$, $\text{C}-\text{O}-\text{C}$, COOH , etc. They behave as polar adsorbents and are hydrophilic, whereas graphite is hydrophobic. Carbon blacks are made by combustion of oils in a deficiency of oxygen, and are converted to graphitised carbon blacks (GCB) by heating in an inert atmosphere to 3000°C . Carbon blacks are generally hydrophobic. Glassy carbons and carbon fibres are produced by controlled pyrolysis of materials such as phenol-formaldehyde resins and poly(acrylonitrile) fibres in an inert atmosphere. They are amorphous but will develop some degree of graphitisation, as discussed later, when heated to temperatures above 2500°C .

For good chromatographic performance an adsorbent such as carbon must have adequate surface area and a uniform free energy of adsorption of solutes at low surface coverage. Too low a surface area leads to inadequate load capacity, whereas an energetically heterogeneous surface leads to tailed peaks. In general, active carbons have strongly heterogeneous surfaces and are unsuitable for chromatography, unless the most active sites can be eliminated. These sites occur mainly in micropores and can be removed by heating to high temperatures. However, as shown by Unger *et al.*⁵, who explored this route to effective chromatographic carbons, the removal of micropores reduces the surface area to such a degree that the material is of very limited usefulness in HPLC.

The requirements for a good chromatographic carbon would thus appear to be a high surface area, a graphitic surface, and good structural strength. Unfortunately, industrial graphites are all designed to be dense and non-porous, while the carbon blacks, which have the necessary area, are much too fragile. Glassy carbons, like industrial graphites, are also dense and non-porous. It is thus evident that no industrial carbon can readily be converted into a carbon suitable for chromatography, and the few attempts to modify them for this purpose^{5,6} or to develop special carbons by electrochemical reduction⁷ have failed. This previous work has been re-

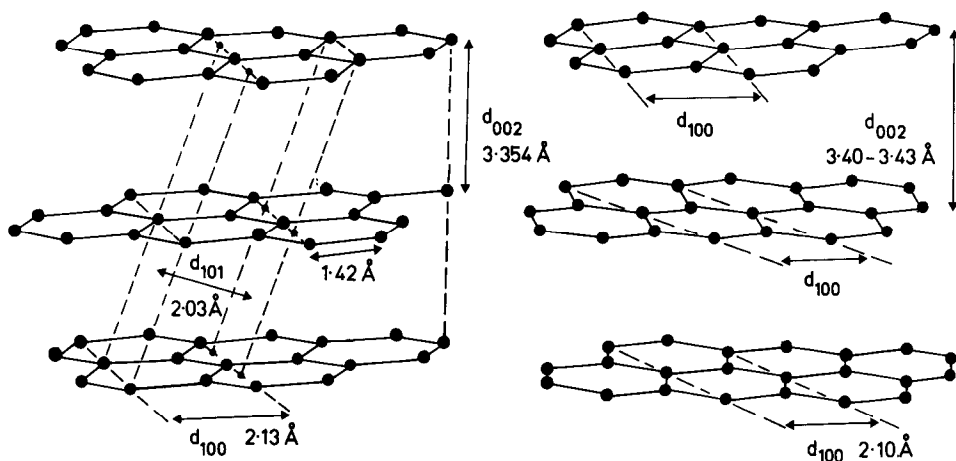


Fig. 1. Atomic structures of graphites. Left: Bernal structure of perfect 3-dimensional graphite with ABAB... layer registration. Right: Warren structure of two-dimensional turbostratic graphite with no layer registration.

viewed comprehensively by Knox and Unger⁸. We therefore believe that the process described by Knox and Gilbert² may offer a unique method of producing chromatographic carbons.

The term "graphitised carbon" is widely misused and misunderstood. As noted above, "graphitised" generally means that a particular carbon has been heated to a temperature in the region of 3000°C in a graphitising furnace. In crystallographic terms, the degree of graphitisation of such a carbon may fall within wide limits, supposedly "graphitised" carbons ranging from almost amorphous materials to perfect three-dimensional crystalline graphites. There are, in fact, three distinct forms of carbon to which the term "graphitised" can reasonably be applied and which have well-defined crystal structures. Two of these forms are shown in Fig. 1. The Bernal structure of perfect three-dimensional graphite⁹ as shown in Fig. 1 consists of layers of carbon atoms, organized in a hexagonal array and ordered ABABAB... This form of graphite is termed hexagonal graphite. A second, rarer form of three-dimensional graphite, the Lipson and Stokes form, also exists, but here the layers are ordered ABCABC... This is termed rhombohedral graphite¹⁰. In both crystalline forms the layer spacing is 3.354 Å and the atomic spacing within the layers is 1.42 Å. Perfect graphite is rarely formed synthetically from amorphous solid carbon, since the bonding between the carbon atoms within the graphitic planes is extremely strong, while the interlayer bonding is weak. Thus, graphitisation tends to develop by the formation of graphitic sheets which are initially randomly oriented. The reorganization of these sheets into ordered three-dimensional graphite requires such a high activation energy that formation of three-dimensional crystalline graphite is generally impossible below 3000°C. Thus, most synthetic carbons, when heated to about 3000°C, assume the second structure shown in Fig. 1. This is a two-dimensional graphite in which graphitic sheets are randomly oriented relative to one another. In

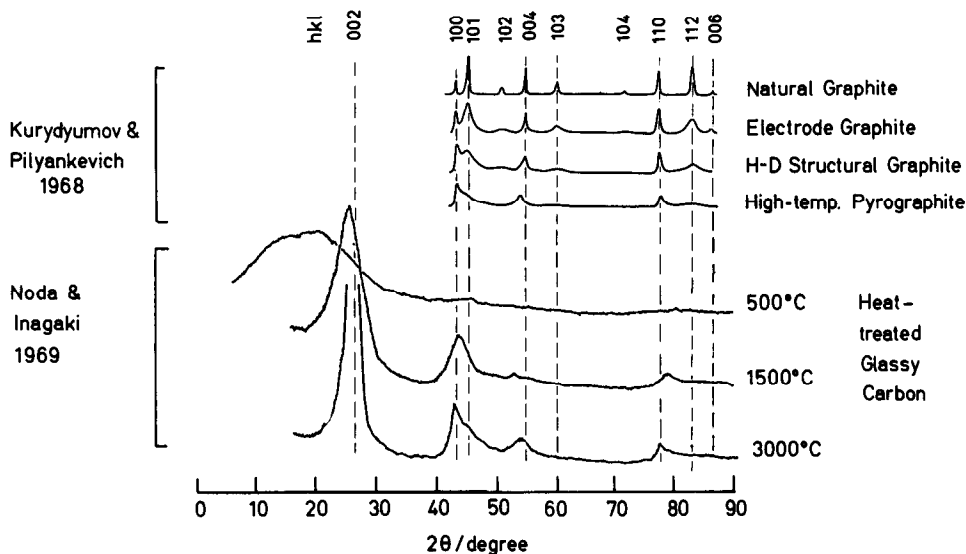


Fig. 2. Published X-ray diffractograms of various carbons, showing different degrees of crystallinity (see refs. 15 and 16).

two-dimensional graphites the layer spacing is slightly greater than in three-dimensional graphites at 3.40–3.43 Å, and the atomic spacing within the layers is slightly less. Two-dimensional graphites are often said to have a turbostratic structure, a term first coined by Warren¹¹ in referring to graphitised carbon blacks. Glassy carbons, when heated to high temperatures, appear to assume a similar structure, except that, unlike carbon blacks, which are composed of loosely aggregated colloidal units, high-temperature glassy carbons are thought to be made up of intertwined graphitic ribbons¹². At an early date, Franklin¹³ discussed the problem of two-phase graphites and the process of graphitisation and concluded that many carbons consisted of mixtures of amorphous and graphitic crystallites. She also distinguished between “hard” and “soft” carbons, depending upon whether they could be readily graphitised or were difficult to graphitise. However, it appears that at that time the distinction between three-dimensional and two-dimensional graphites was not well understood. In general, turbostratic, two-dimensional graphites are not converted into three-dimensional graphites below 3000°C.

While three-dimensional graphites rarely arise from heating amorphous solid carbons, they can nevertheless arise by high-temperature pyrolytic deposition from organic vapours in the gas phase¹⁴. Presumably, properly oriented layers are laid down in the first place, and no reorganization is required.

Fig. 2 shows X-ray diffraction patterns of various carbons, taken from the literature^{15,16}. The X-ray diffractogram of true graphite (topmost tracing) shows a range of sharp (hkl) reflections and, in particular, a prominent 101 reflection of greater intensity than the 100 reflection. The small angular spread of the reflections indicates relatively large crystallites (see below). As the degree of graphitisation decreases, the (hkl) reflections first become diffuse and then disappear altogether, leaving only the (hk0) and (001) reflections, which are characteristic of two-dimensional graphites. A good example is the tracing for “high-temperature pyrographite” which gives only a 002 peak (not shown), a 004 peak, and a typical asymmetric 100 peak. In such materials, the 002 and 004 reflections occur at slightly lower angles than in true 3-dimensional graphites, indicating that the graphitic planes are slightly further apart (3.40–3.43 Å, compared to 3.354 Å). The tracings in the lower part of Fig. 2 show that glassy carbon, as produced at 500°C, possesses no structure and gives only very diffuse reflections at about 20° and possibly at 40–50°. As the material is heated, these diffuse reflections become sharper, and by 3000°C they have become the 002, 004, and 100 reflections of two-dimensional graphite. The X-ray diffractogram of glassy carbon heated to 3000°C is almost identical to that of “high-temperature pyrocarbon” but with wider peaks indicating smaller crystallites.

Fig. 3 shows X-ray diffractograms of a number of so-called graphitised carbons, along with the ungraphitised carbon black Vulcan®. These diffractograms were obtained with the equipment employed for the main part of the X-ray study reported below. Ungraphitised Vulcan black (Cabot Corporation) shows a relatively wide reflection at 25° and a second, more diffuse reflection at 45°. With heating, these peaks become narrow and move to higher angles into the positions of the 002 and 100 peaks for graphitised carbon black, as shown at the top of Fig. 3. This diffractogram of GCB shows the symmetrical 002 and 004 reflections and the unsymmetrical 100 reflection, which is characteristic of two-dimensional graphites. Carbon fibre shows less extensive two-dimensional graphitisation, as indicated by the wider and

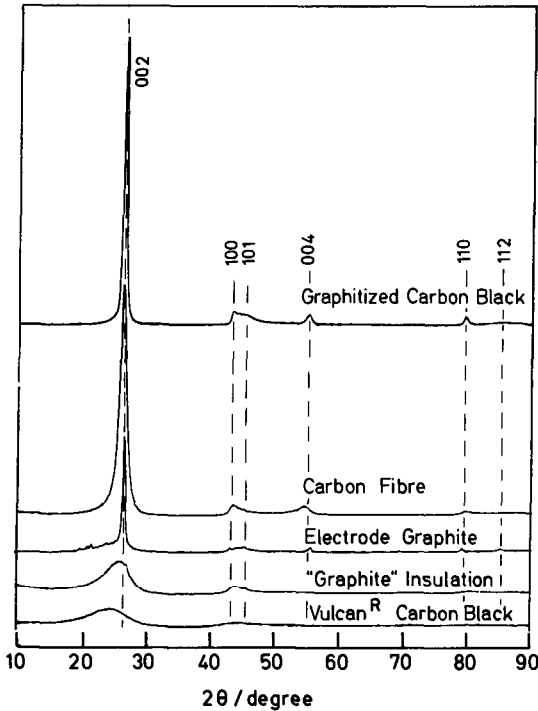


Fig. 3. X-ray diffractograms of commercial carbons, obtained in this study.

less symmetrical 002 and 004 reflections. In this tracing there is slight evidence of some three-dimensional graphitisation, as shown by the blip at the position expected for the 101 reflection. Electrode graphite gives a much sharper 002 reflection, superimposed on a broad, amorphous background reflection, and shows definite evidence of a 101 peak, superimposed on a wide unsymmetrical 100 peak. This material appears to have a significant proportion of three-dimensional crystallites within an otherwise amorphous or two-dimensional graphitic matrix. Finally, "graphite furnace insulation", supplied in the form of a felt, shows only slightly more graphitisation than does Vulcan carbon black.

The angular widths of X-ray reflections, discounting instrumental broadening, gives useful information about crystallite size. In the case of graphites the width of the 002 and 004 reflections (usually measured at half the maximum peak height) give an indication of the mean stack height of the graphitic planes, while the width of the (100) reflection indicates the mean diameter of the graphitic sheets. The relationship was originally derived by Scherrer¹⁷:

$$L = k\lambda/B \cos \theta \quad (1)$$

where L is the crystallite dimension, λ is the wavelength of the X-rays, B is the peak width in radians, θ is the Bragg angle of reflection, and k a constant around unity.

There has been considerable discussion as to the best value for k ¹⁸⁻²⁰. For the

002 reflection, 0.84 is thought to be an optimum value, while for the unsymmetrical 100 peak, Biscoe and Warren²⁰ advocate a value of 1.84. Using these values, a typical stack height in a graphitised carbon black (uppermost tracing in Fig. 3) would be about 50 Å, and a typical plate diameter about 100 Å. These values correspond to crystallites having about 15 graphitic layers with about 3000 C-atoms in each layer.

EXPERIMENTAL

Equipment, materials, and methods

Thermogravimetric analysis was carried out with a Stanton Redcroft TG770 thermogravimetric analyser (Stanton Redcroft, London, U.K.). Scanning electron microscopy was carried out on a Cambridge Instruments type 604 stereoscan instrument (Cambridge Instruments, Cambridge, U.K.) fitted with a Praktica LC camera. Samples of PGC were deposited on aluminium stubs and coated with gold to prevent accumulation of charge. The coating was carried out with an E5100 coating unit (Polaron Equipment). Transmission electron microscopy and electron diffraction were carried out using a JEOL 200-CX instrument (JEOL UK, Colindale, London, U.K.) at Cambridge University. The instrument, operated at 200 keV, was fitted with a top-entry goniometer stage, modified to enable the specimens to be moved parallel to the incident beam (z-lift), as described by Thomas *et al.*²¹. Under the operating conditions used, it had a resolution of 2.4 Å. Specimens for examination were deposited from a suspension in acetone onto carbon "holey" films. Only particles positioned over the holes were imaged under high resolution.

X-ray diffraction was carried out on a Philips powder diffractometer (Pye Unicam, Cambridge, U.K.). Samples on slide holders were loaded by an automatic sample changer (type PW 1170/02). The goniometer (type PW 1050/80) was mounted on a highly stabilized X-ray generator (PW 1130/10) that provided Cu K_{α1,2} radiation of a mean wavelength of 1.5418 Å. Angular scanning was by a motor control unit, type PW 1394. Detection was by a channel control unit, type PW 1390, and fed to a pen recorder, Type PM 8203. Normally, a scan rate of 0.5°/min was used (in 2θ units) with a time constant setting of 4.

High-temperature treatment of PGC up to 2500°C was carried out by the Atomic Weapon Research Establishment (Aldermaston, U.K.), by Carbon Lorraine (Gennevilliers, France), and by Dr. C. Jenkins (Department of Metallurgy, University of Swansea, U.K.). Samples were generally heated slowly in argon from ambient temperature to 2500°C over a period of several hours.

The rocking autoclave used in the preparation of the silica gel template was designed and constructed by C. W. Cook & Sons (Birmingham, U.K.) and was rated to 300 bar at 400°C; it had a 2-l capacity.

The furnace used to pyrolyse the silica-polymer particles in the preparation of PGC could heat up to 2 l of material to 1100°C in a rotating monel tube. The tube could be purged with nitrogen through a rotary seal. The furnace was designed and constructed by Carbolite Furnaces (Bamford Mill, Sheffield, U.K.).

Liquid chromatography was carried out using laboratory-assembled components from a variety of sources. Pumps used were an Altex Model 110 (Beckman RIIC, High Wycombe, U.K.), a Kontron Model 410 (Kontron Intertechnique, St. Albans, U.K.) and a Du Pont chromatographic pump, Type 861001 (Du Pont, Hitch-

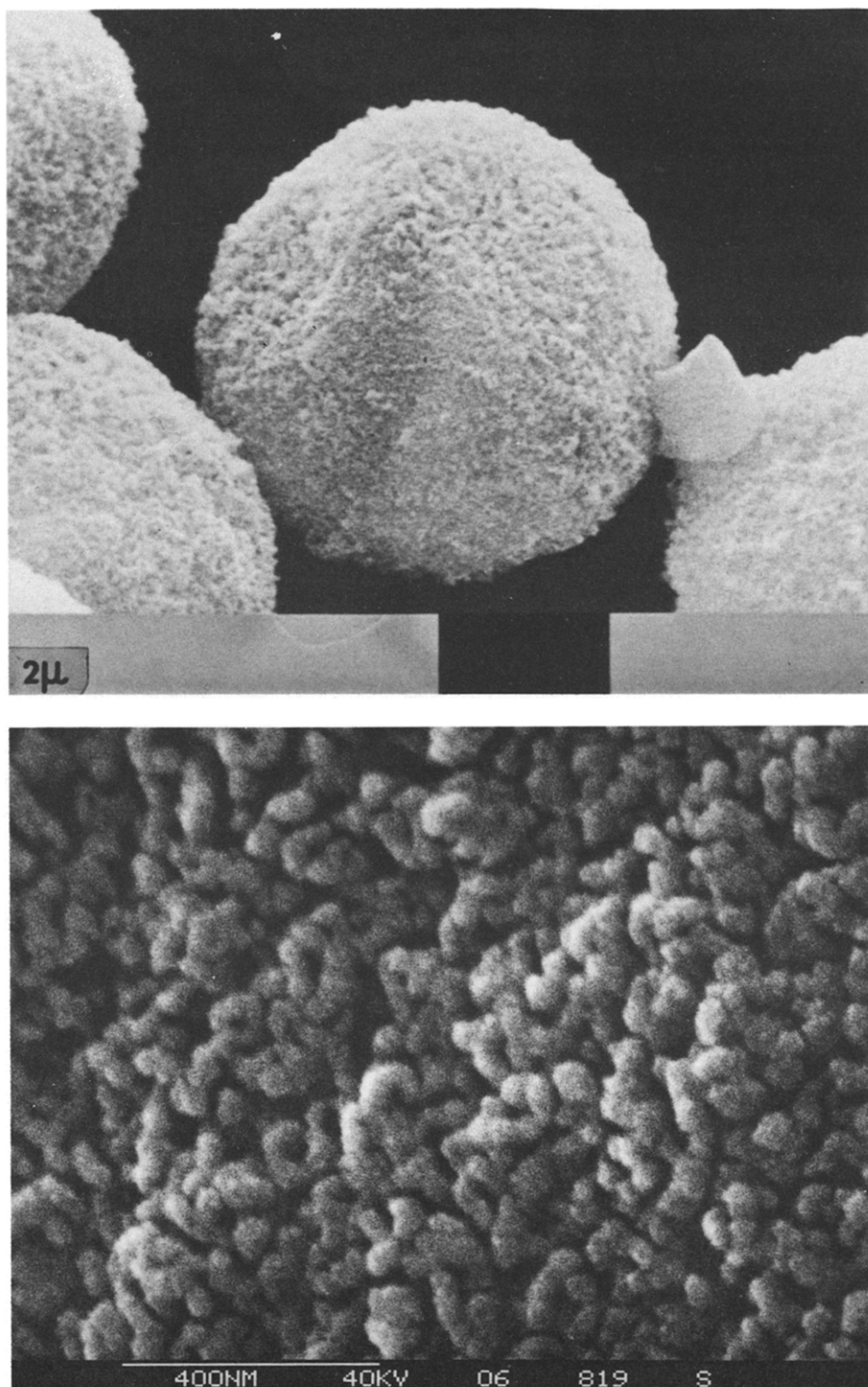


Fig. 4. Scanning electron micrographs of PGC. Upper: spherical particle of PGC; black band represents 2 μm . Lower: high magnification of surface; white horizontal line represents 400 nm.

in, U.K.). Detectors used were a Cecil Model 212 UV spectrophotometer (Cecil Instruments, Cambridge, U.K.) and a Kratos Model 773 UV spectrophotometer (Spectros International, Urmiston, Manchester, U.K.). Injection was by a Rheodyne valve (Shandon Southern Products, Runcorn, U.K.). Columns were from Shandon Southern Products and were 100 mm long, 5 mm bore. PGC was packed using a Shandon slurry packer at 100 bar. Both the slurry support liquid and the follower liquid were acetone. It was important to use ANALAR-grade or HPLC-grade solvents for column packing because of the strong adsorption by PGC of any high-molecular-weight impurities. Columns were normally operated at 1 ml/min with pressure drops of 50–75 bar.

Chemicals used in the preparation of PGC were BDH ANALAR Reagents (BDH, Poole, U.K.). HPLC eluents were obtained from Rathburn Chemicals (Walkburn, U.K.). ODS Hypersil was obtained from Shandon Southern Products.

BET surface areas were measured using a laboratory-constructed instrument.

Pore volumes were determined by a laboratory-constructed low-pressure (up to 30 bar) mercury porosimeter or by liquid titration.

Preparation of PGC

The template required for the production of PGC should be a well-bonded silica gel of high porosity. The spherical silica gel was specially prepared and had a

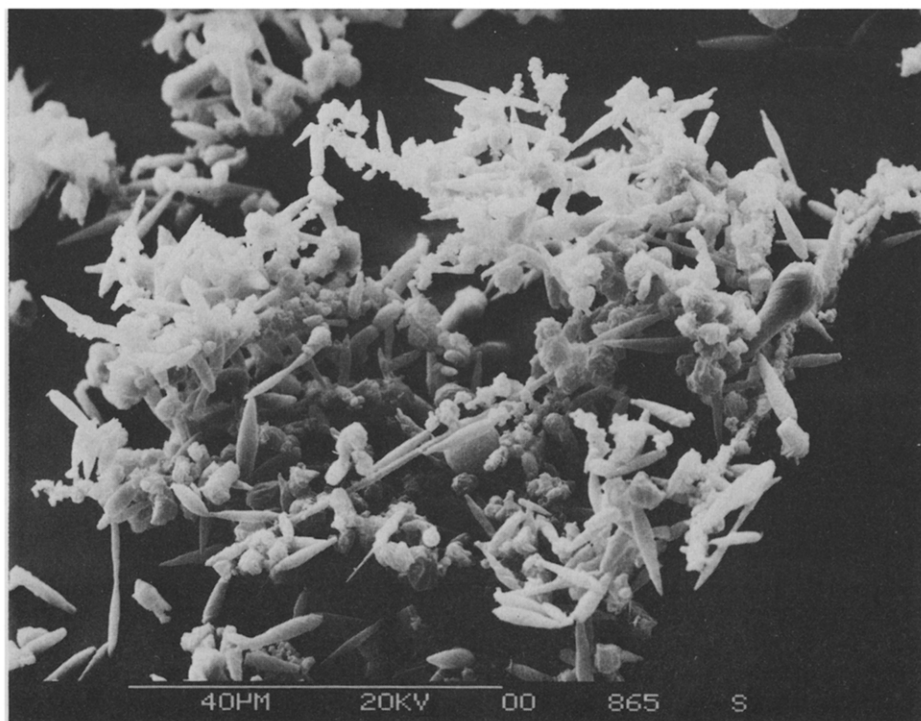


Fig. 5. Scanning electron micrograph of sample of “needles”, separated from spheres of PGC; horizontal white line represents 40 μ m.

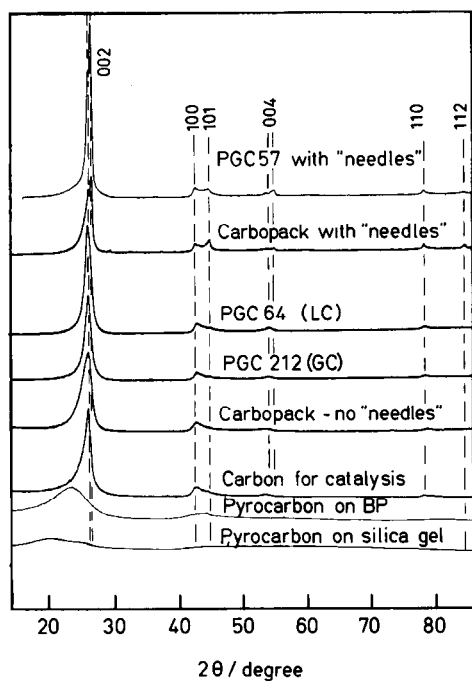


Fig. 6. X-ray diffractograms of potential chromatographic carbons.

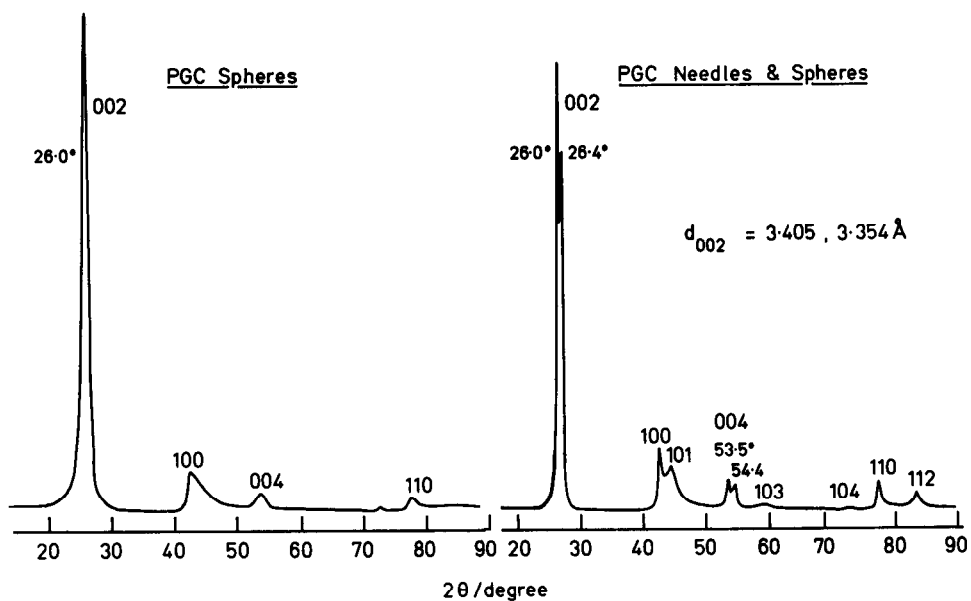


Fig. 7. X-ray diffractograms of PGC 201 (2600°C) with and without needles present.

pore volume of 1.4 cm³/g with a specific surface area of 50 m²/g. The mean particle diameter was 7 μm. This template was impregnated with a melt of phenol and hexamine in a 6:1 weight ratio. The impregnated material was heated gradually to 150°C to form phenol-formaldehyde resin within the pores of the silica gel. This silica-polymer was then heated slowly to 900°C in a stream of oxygen-free nitrogen in a specially designed rotary furnace. Approximately 50% of the weight of the polymer was thereby lost, and the density of what remained was increased to about 2 g/cm³. The silica-carbon particles were then treated with hot aqueous potassium hydroxide to dissolve the silica template. Dissolution of silica was determined with a Stanton Redcroft TG770 thermogravimetric analyser to be at least 99% complete. The remaining porous glassy carbon had a BET surface area of 450–600 m²/g and a pore volume of 2.0 cm³/g, corresponding to a particle porosity of about 80%. This carbon was then heated to 2500°C in oxygen-free argon. The final carbon had a surface area of about 150 m²/g and a pore volume similar to that of the carbon before high-temperature treatment. The carbon retained the spherical form and the particle size of the original silica template. The scanning electron micrographs in Fig. 4 clearly show the spherical shape of the particles and their sponge-like structure.

After high temperature firing, most samples of PGC contained needle-like or spine-like structures with lengths of a few micrometres and diameters of around 1 μm. An example of some needles separated from spherical particles is shown in Fig. 5. Both the porous spheres and the needles were examined by X-ray diffraction and by electron microscopy.

RESULTS AND DISCUSSION

X-ray diffraction

Fig. 6 shows diffractograms of a number of carbons which have been proposed for use in chromatography. "Pyrocarbon on silica" was prepared by Colin and Guiochon²² by deposition from benzene vapour at 900°C into the pores of silica gel.

TABLE I
BRAGG SPACING AND CRYSTALLITE SIZE IN VARIOUS CARBONS

Material*	θ_{002} (deg)	d_{002} (Å)	θ_{100} (deg)	d_{100} (Å)	θ_{101} (deg)	d_{101} (Å)	L_c^{**} (Å)	L_g^{***} (Å)
Graphite	13.3	3.35	21.2	2.13	22.3	2.03	—	—
Needles	13.3	3.35	21.2	2.13	22.3	2.03	—	—
Carbopack B	13.0	3.43	21.2	2.13	—	—	50	100
PGC64 (2350)	13.0	3.43	21.2	2.13	—	—	70	100
PGC205 (2500)	13.0	3.43	21.2	2.13	—	—	70	140
PC on BP	12.2	3.65	21.0	2.15	—	—	15	20

* The bracketted figure in designation of PGC gives the highest temperature in °C to which the PGC was heated. PC on BP = pyrocarbon on Black Pearls, kindly supplied by Dr. H. Colin, Ecole Polytechnique, Palaiseau, France.

** Constant $k = 0.86$ in eqn. 1.

*** Constant $k = 1.84$ in eqn. 1.

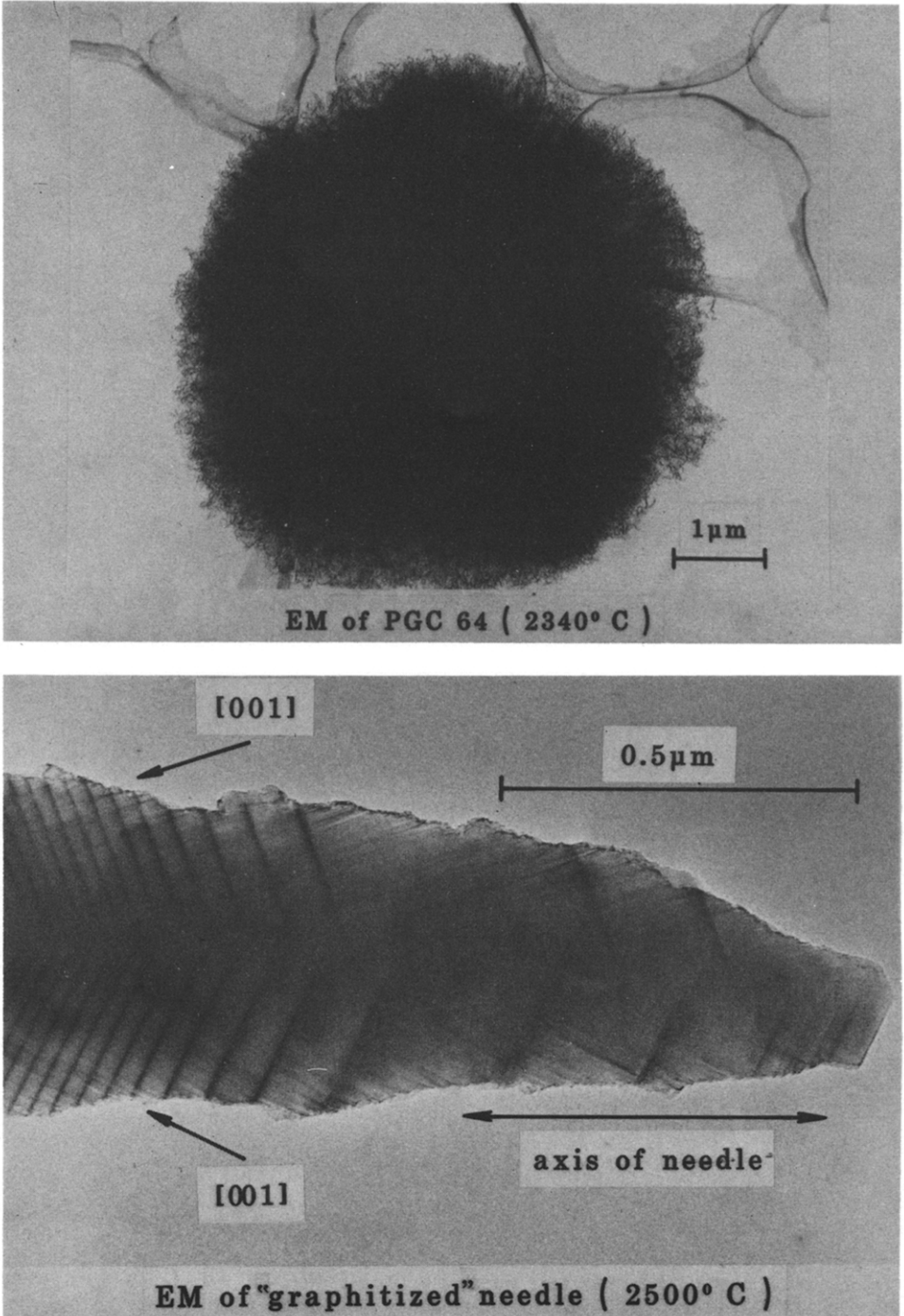


Fig. 8. Transmission electron micrographs. Upper: Spherical particle of PGC. Lower: "Needle", showing twinning.

“Pyrocarbon on Black Pearls” was similarly prepared using Black Pearls (a carbon black) as the supporting structure. Neither material shows significant graphitisation and, indeed, the tracing for the “Pyrocarbon on BP” shows the expected diffuse reflections of a carbon black (Fig. 3). The still wider reflections for “Pyrocarbon on silica gel” are analogous to those of low-temperature glassy carbon (Fig. 2). Neither of these materials gave satisfactory chromatograms in liquid chromatography⁷.

“Carbon for Catalysis” was an active carbon which had been treated at a high

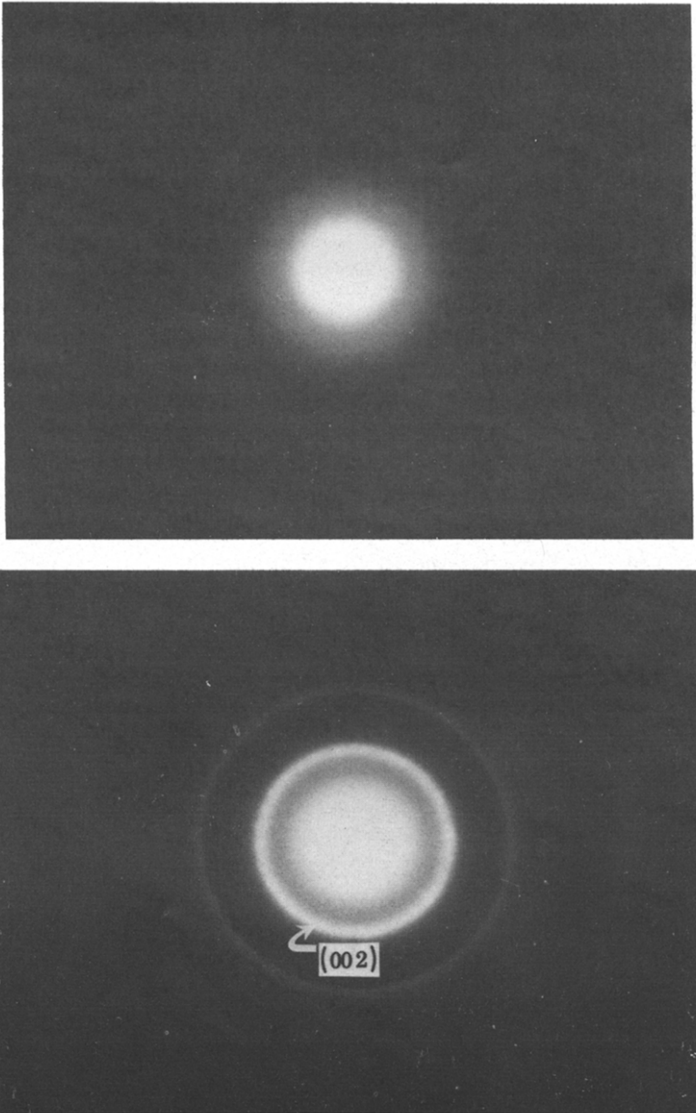


Fig. 9. Electron diffractograms of PGC. Upper: sample, as prepared at 1000°C. Lower: after heating to 2500°C, showing 002 and other diffractions.

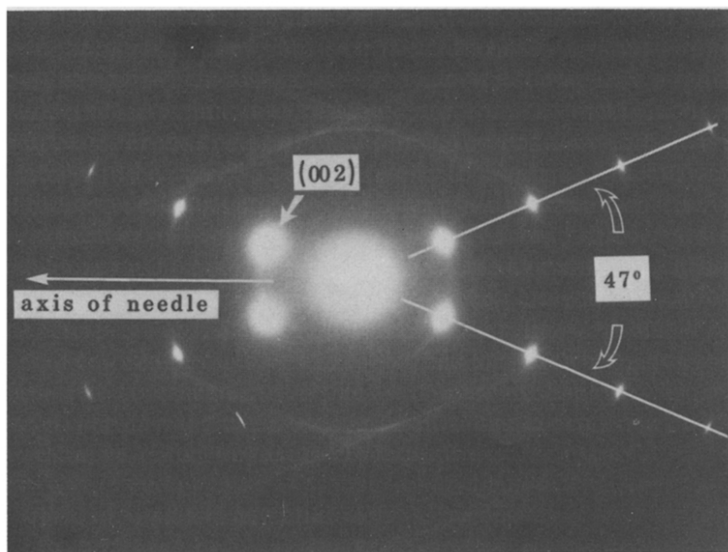


Fig. 10. Electron diffractogram of "needle", showing twinning.

temperature by a proprietary process. It shows two-dimensional graphitisation, but the rather wide asymmetric 002 peak characteristic of a material with a relatively high proportion of amorphous material. "Carbopack" from which needles have been removed shows a more symmetrical 002 reflection, indicating good graphitisation—but its width suggests that the crystallites are small. Both PGC64 and PGC212 show narrower 002 reflections, indicating good graphitisation with larger crystallites. When needles are present in "Carbopack" and PGC, additional 002 and 004 reflections are present, as well as 101 reflections. This is illustrated more clearly in Fig. 7.

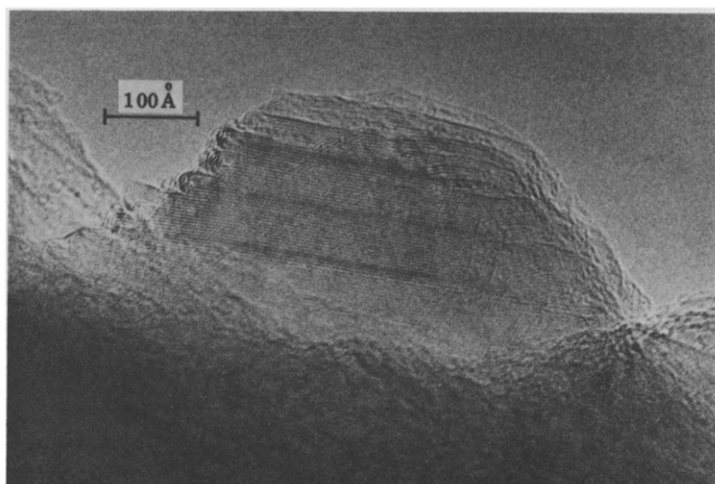


Fig. 11. High-resolution electron micrograph of plate or needle, heated to 2500°C.

The additional peaks indicate that the material containing needles consists of two distinct phases. The needles appear to be three-dimensional pyrolytic graphite, while the spherical, porous particles are two-dimensional graphite with the wider 1-spacing of about 3.40 \AA . Often, a shoulder is seen on the 002 reflection of PGC samples heated above 2000°C . We believe that this shoulder arises from a small proportion of needles in these samples.

Typical crystallite sizes from some PGC samples are given in Table I. The

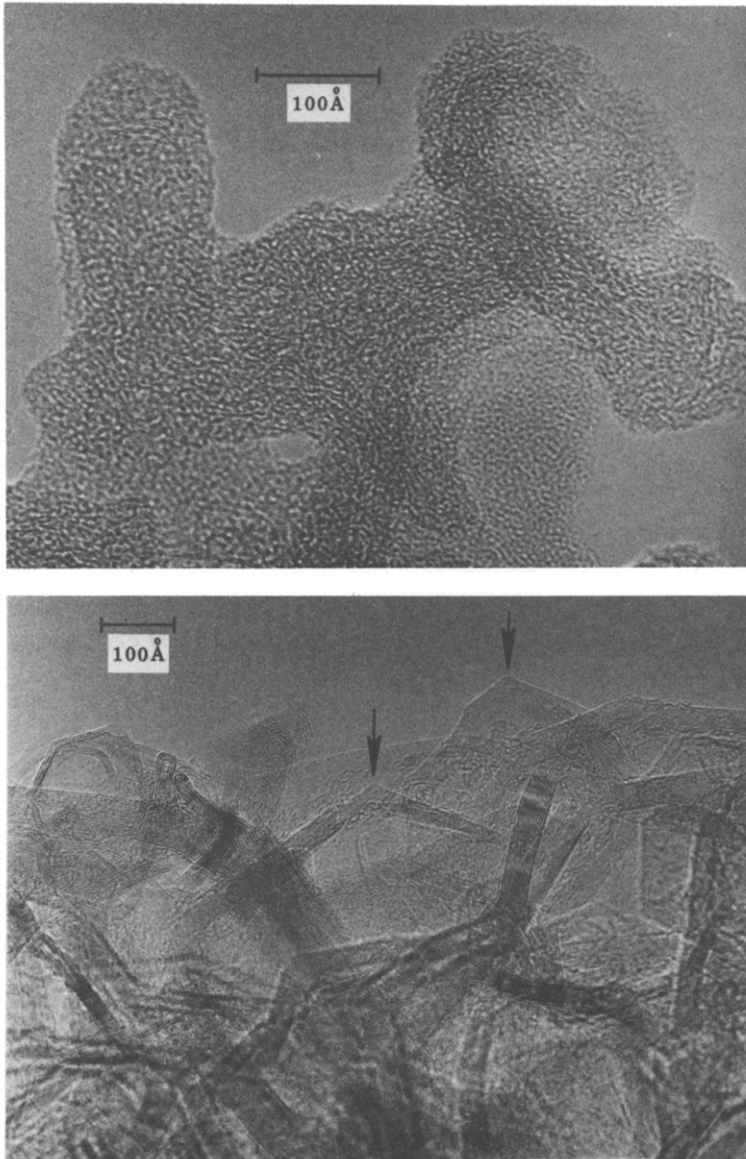


Fig. 12. High-resolution electron micrographs of PGC. Upper: PGC, as prepared at 1000°C . Lower: after heating to 2340°C .

crystallite sizes are typical for two-dimensional graphites and are comparable to the thickness of the connecting bridges in the sponge-like PGC structure. These may be estimated to be about 100 Å on the basis of a surface area of 150 m²/g.

Electron diffraction and transmission electron microscopy

Fig. 8 shows transmission electron micrographs of a spherical particle of PGC and of a "needle". The porous nature of PGC contrasts with the much denser structure of the needle. The needle shows clear evidence of twinning with an angle between the layers of about 45°. Fig. 9 shows two electron diffractograms of the spherical particulate material, the upper of PGC heated to 1000°C, the lower of material heated to 2500°C. The presence of the 002 band and the increased sharpness of the diffraction patterns in the latter are consistent with the evidence from X-ray analysis which indicate layer ordering during high-temperature treatment. The lower diffractogram clearly shows the crystal spacing of two-dimensional graphite. Fig. 10 shows the electron diffractogram from a needle. The two sets of reflections correspond to two sets of crystal planes at an angle of 47°, in complete agreement with the transmission electron micrograph of Fig. 8.

Fig. 11 shows high-resolution electron microscopy (HREM) of a fragment of a pyrolytic carbon needle. The graphitic layers are clearly visible. Fig. 12 shows HREM of PGC. The upper part shows the totally amorphous structure of the material, heated only to 1000°C, while the lower part shows the high degree of two-dimensional graphitisation of PGC after heating to 2500°C. Particularly notable are the straight, parallel lines, indicating ordered graphitic sheets, and the sharp angles at which the "booklets" of sheets meet. Also seen are a number of rounded corners and several groups of curved or bent sheets. There is also some evidence of surface

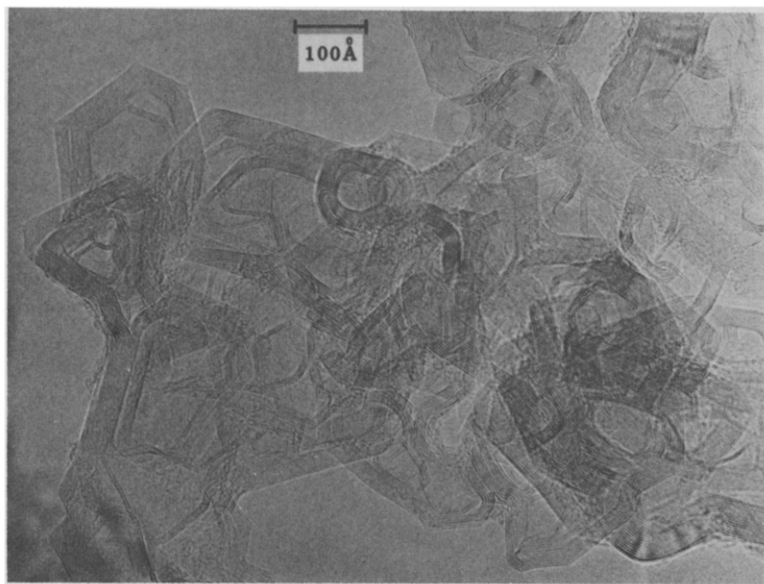


Fig. 13. High-resolution electron micrograph of Carbolpack B, a typical graphitized carbon black.

defects. Fig. 12 should be compared with Fig. 13, which shows HREM of graphitised carbon black. Again, one notes flat sheets, meeting at well-defined angles, rounded corners, and bent or distorted sheets. The degree of two-dimensional graphitisation shown in Fig. 12 and 13 are very similar. However, there is a striking difference between the two: Fig. 13 shows that graphitised carbon black is made up of colloidal particles which are not interconnected, whereas Fig. 12 shows that PGC is in the form of a continuous structure in accord with our original intention in developing a template method for producing PGC.

HREM of PGC shows that the crystallites comprise tens of layers of graphitic sheets, thus giving stack heights of 30–60 Å, in agreement with the X-ray evidence cited in Table I. The widths of the sheets appear somewhat greater than their thicknesses.

Conclusions from X-ray analysis and electron microscopy

From the foregoing, a number of firm conclusions can be drawn regarding the nature and structure of PGC:

- (1) PGC heated to 2500°C is a two-dimensional graphitised carbon.
- (2) PGC heated to 2500°C has an atomic structure almost identical to that of a graphitised carbon black, but its structure at a colloidal level (*i.e.* > 1000 Å) is quite different. PGC has a sponge-like form, whereas GCB is made up of loosely aggregated colloidal particles.
- (3) PGC, when heated only to 1000°C, is totally amorphous, but HREM clearly shows its sponge-like structure.
- (4) On heating PGC from 1000 to 2500°C, pyrolytic deposition of carbon needles takes place, presumably from organic vapours liberated just above 1000°C, rather than from evaporation of carbon itself. The atomic arrangement in these

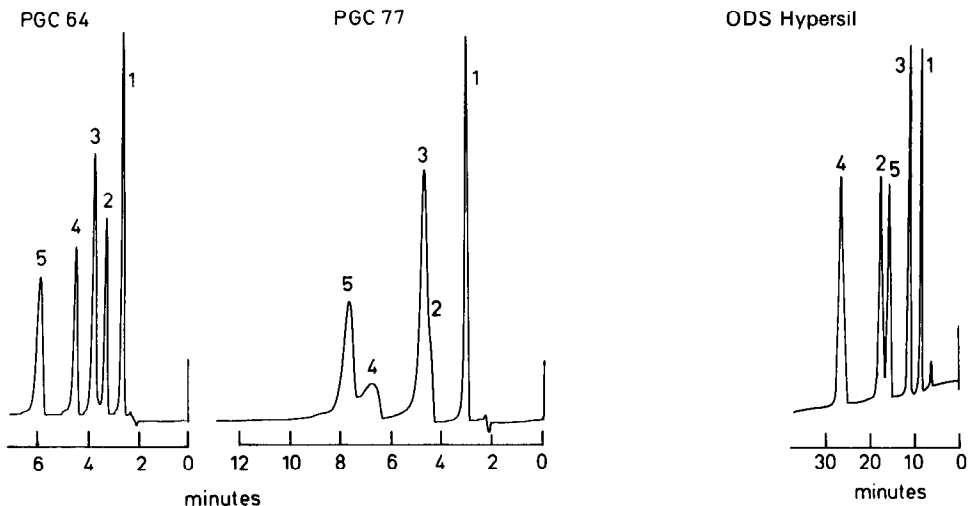


Fig. 14. Comparative chromatograms, showing separations on good and bad samples of PGC (Eluent: methanol–water, 95:5). Peaks: 1 = phenol; 2 = anisole; 3 = *p*-cresol; 4 = phenetole; 5 = 3,5-xylenol. Fig. 15. Separation of mixture of Fig. 14 on ODS Hypersil (methanol–water, 60:40). Peaks as in Fig. 14.

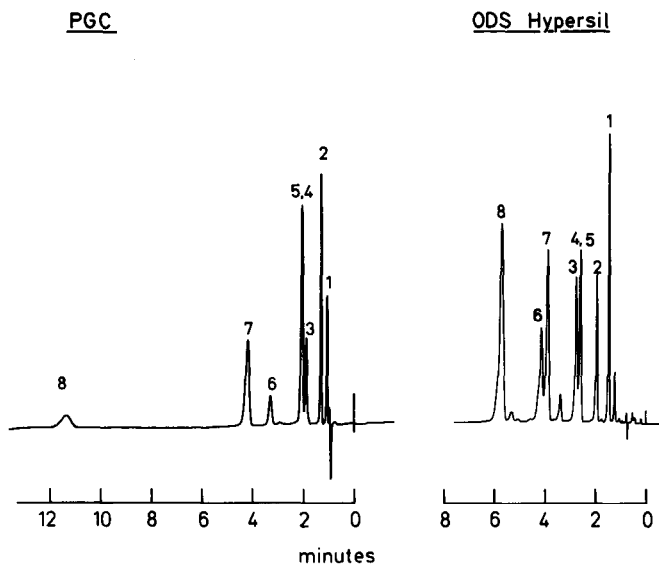


Fig. 16. Separations of methylbenzenes on PGC64 (methanol-water, 95:5) and on ODS Hypersil (methanol-water, 70:30). Peaks: 1 = benzene; 2 = toluene; 3 = *m*-xylene; 4 = *p*-xylene; 5 = *o*-xylene; 6 = 1,3,5-trimethylbenzene; 7 = 1,2,4-trimethylbenzene; 8 = 1,2,4,5-tetramethylbenzene.

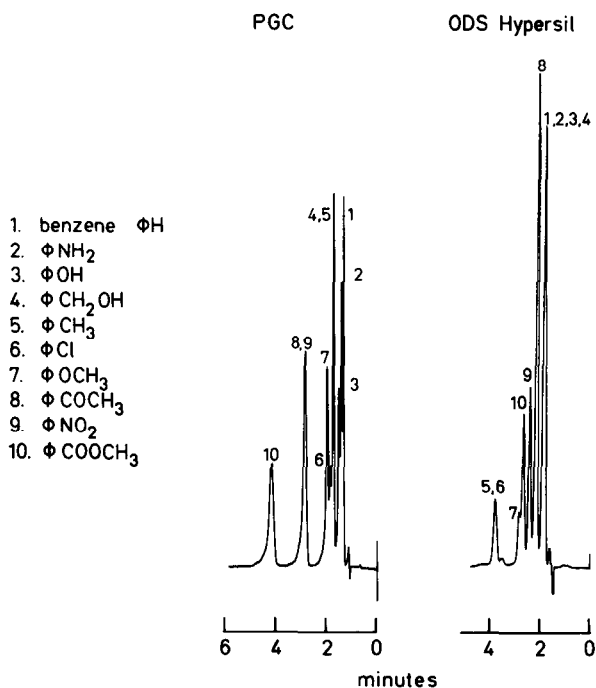


Fig. 17. Separations of monofunctional derivatives of benzene on PGC64 (methanol-water, 90:10) and on ODS Hypersil (methanol-water, 70:30).

needles is that of a three-dimensional crystalline graphite. Whereas the spheres of PGC are highly porous, the needles have no porosity.

(5) For chromatographic purposes, the needles, having no significant surface area, are of no value and should, if possible, be removed or, preferably, their formation should be avoided. The chromatographically useful particles are those of the porous two-dimensional graphite.

(6) The original intention of producing a porous graphite of adequate surface area and appropriate structure for chromatography has been achieved.

Liquid chromatography: typical separations

Figs. 14–22 show illustrative chromatograms on PGC. Figs. 15–19 show comparisons of separations on PGC and ODS Hypersil.

One of the problems encountered in the production of PGC for liquid chromatography is illustrated in Fig. 14. Satisfactory batches of PGC, such as PGC64, show well-shaped peaks with good plate efficiency, whereas unacceptable batches, such as PGC77, show tailed peaks and higher capacity factors. Comparing the two chromatograms, it is particularly noted that the peaks for the ethers, anisole and phenetole, are more strongly retained relative to the phenols on PGC77, and that the

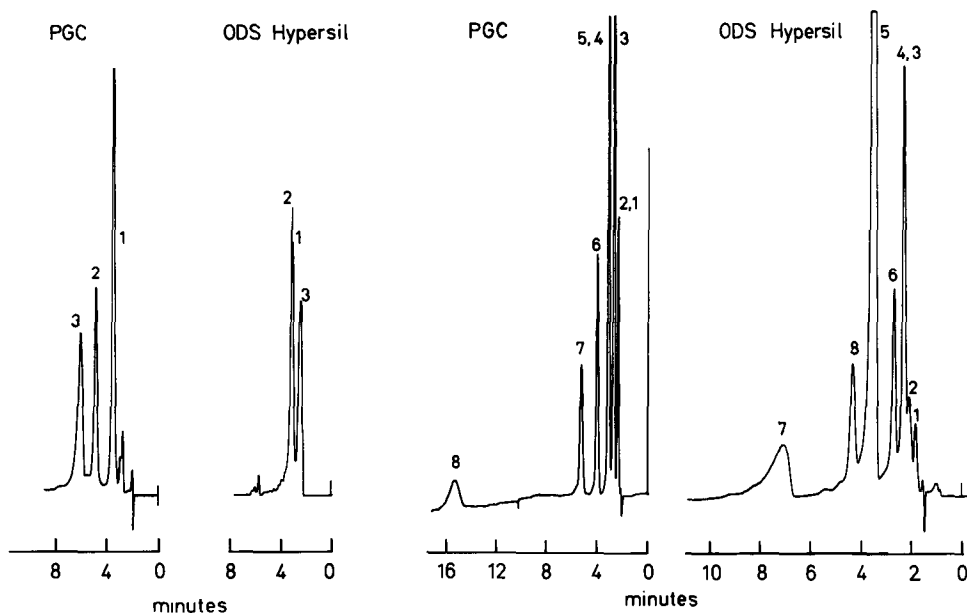


Fig. 18. Separations of acids on PGC64 and ODS Hypersil (acetonitrile–water, 90:10). Peaks: 1 = benzoic acid; 2 = *o*-toluic acid; 3 = salicylic acid.

Fig. 19. Separations of amines on PGC64 (methanol–water, 95:5) and on ODS Hypersil (methanol–water, 70:30). Peaks: 1 = aniline; 2 = pyridine; 3 = 2-methylpyridine; 4 = methylaniline; 5 = dimethylaniline; 6 = ethylaniline; 7 = diethylaniline; 8 = benzylamine.

peak for phenetole is badly tailed. It appears that the unacceptable material arises when traces of oxidation can occur, either during the pyrolysis to 1000°C or during the subsequent heating above 1000°C.

Fig. 15 shows the separation of the same mixture on ODS Hypersil. It is noted that the selectivity with regard to phenols vs. ethers is different, although the order within each group is the same. On ODS Hypersil, the ethers are more retained relatively to phenols than on PGC.

Fig. 16 shows comparative separations of methylbenzenes. Attention is drawn to the reversal of the order of elution of *m*-xylene and *o*- plus *p*-xylenes. The elution order for carbon has been explained by Kiselev and Yashin²³ on the basis that when *o*-xylene and *p*-xylene are adsorbed onto the flat graphitic surface, four carbon atoms contact the surface (two from the methyl groups and two from the ring) whereas with *m*-xylene only three atoms contact the surface (two from the methyl groups and one from the ring). A similar order reversal is noted with 135 and 124 trimethylbenzenes. In addition, PGC shows a greater spread of retention than does ODS Hypersil.

Fig. 17 compares separations of a range of singly substituted benzenes. Again, similar peak symmetry and plate efficiencies are observed, but significant differences in elution order. In particular, solutes 4 and 7-10 appear much later on PGC, whereas 5 and 6 appear later on ODS. The more strongly retained solutes on PGC are those with the greater number of C, N and O atoms in the functional groups. Fig. 18 shows comparative separations of some acids, again showing different selectivities. From PGC, the acids are eluted in the order of molecular weight.

Fig. 19 illustrates the superior performance of PGC when used for the separation of amines. Whereas ODS Hypersil gives tailed peaks for several of the solutes, no tailing is observed with PGC. Tailing on ODS silica is presumably due to the effect of residual silanol groups. This is confirmed by the late elution of the most tailed peaks (dimethylaniline, 5, and diethylaniline, 7) from ODS Hypersil.

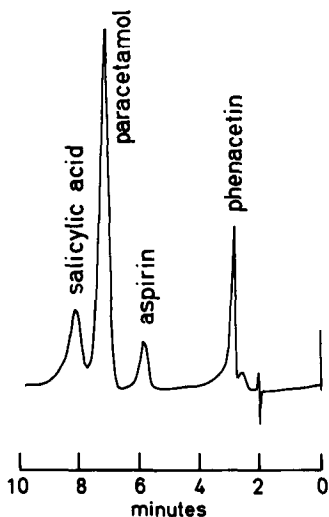


Fig. 20. Separation of simple analgesics on PGC64 (methanol-water-acetic acid, 94:5:1).

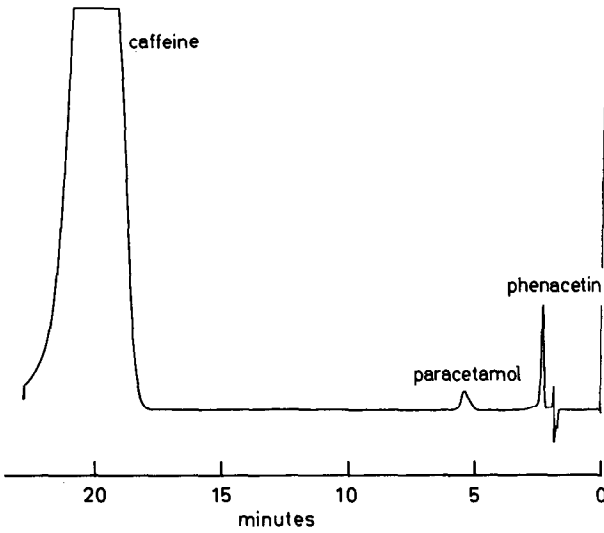


Fig. 21. Separation of analgesics on PGC64 (methanol-water, 95:5).

Figs. 20 and 21 show separations of typical analgesic mixtures on PGC.

Fig. 22 illustrates an aspect of LC on PGC which is likely to be of great importance in the future. A column of PGC after long use became deactivated so that the retention of solutes was much reduced. The column was stored for several

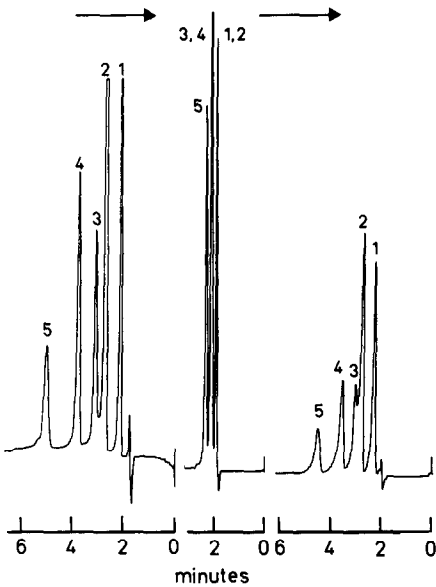


Fig. 22. Deactivation and reactivation of PGC64. From left to right: column, as originally tested with methanol-water (95:5); column, after becoming deactivated; column, after reactivation by washing with dioxane. Solutes as for Fig. 14.

months and was subsequently eluted with pure dioxane, whereupon the original activity returned. This observation leads to some important conclusions.

Firstly, if PGC becomes deactivated, it can generally be reactivated by washing with a suitable solvent. This makes it clear that the deactivation observed must have been due to the adsorption of some high-molecular-weight impurity in the eluent. Accordingly, it is important when using PGC that the eluents contain no traces of plasticisers, etc., and it is probably desirable to include a precolumn before the analytical column to avoid contamination. Secondly, we note that, even when deactivated, PGC provides excellent peak shape. Controlled deactivation of PGC by the preadsorption of high-molecular-weight additives may thus provide an important method of modifying its adsorption characteristics. It may be noted that it is probably impossible to derivatise the graphitic surface of PGC, which is made up of a totally aromatic sheet of carbon atoms. Pre-adsorption of long-chain additives provides the nearest equivalent to the chemical bonding method so widely used with silica gel.

In general, it is noted from the examples just given that, for roughly equal degrees of retention, eluents for PGC contain high proportions of the organic component (90–100%), whereas eluents for ODS silica contain considerable proportions of water (around 50%). Evidently, the very strong retention by PGC may be a disadvantage when eluting molecules of high molecular weight. However, as with silica gel, the addition of a strongly adsorbed modifier can be used to reduce and modify this activity. Accordingly, we anticipate that by adsorbing long-chain molecules, bearing different functional groups, it will be possible not only to control the degree of retention by PGC but also to modify the selectivity of PGC in novel ways. Extensive work in this area has been carried out on modifications of GCB for use in GC by adsorption of small quantities of high-molecular-weight modifiers^{2,4,2,5}.

Conclusions —Chromatographic

- (1) PGC acts as a strong hydrophobic adsorbent in LC.
- (2) PGC can be operated under typical HPLC conditions of pressure and flow-rate.
- (3) Spherical PGC (7 μm) gives peak sharpness (number of plates) very similar to a typical bonded silica gel.
- (4) PGC requires eluents containing a higher proportion of organic components than does ODS-bonded silica gel; typically 95% methanol compared to 50% methanol.
- (5) PGC gives good peak shapes for elution of a wide range of monofunctional benzenes (phenols, ethers, acids, and amines) and for some simple analgesics.
- (6) PGC can be deactivated by prior adsorption of high-molecular-weight additives.

CONCLUSION

PGC is a two-dimensional graphite with a unique sponge-like structure which gives it good mechanical strength, adequate for HPLC, while maintaining an adequate surface area (around 150 m^2/g) and porosity (around 80%). PGC has unique chromatographic properties, being the only truly hydrophobic adsorbent. It shows strong retention of simple organics and novel stereoselectivity. It gives chromatograms of high efficiency.

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