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### Characterization of Carbonaceous Materials Using Extraction with Supercritical Pentane

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## Characterization of Carbonaceous Materials Using Extraction with Supercritical Pentane

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### Abstract

The use of carbonaceous adsorbents is limited by irreversible adsorption of some compounds, so the use of supercritical pentane as an extracting solvent was examined. Carbon black appeared to be broken down slowly, but continuously, by the pentane. To see if other types of carbon behaved similarly, high purity graphite, technical grade graphites, active carbons, and charcoals were examined. The extracts were characterized by UV spectroscopy, packed column chromatography using flame ionization and flame photometric detectors, and capillary GC/MS. The extracts were characteristic for each class of carbonaceous material. The high purity graphite yielded large, polycyclic aromatic compounds; the technical grade graphites yielded alkanes and alkyl-substituted benzenes and naphthalenes; the active carbons yielded alkanes, dienes, and small amounts of alkyl-substituted benzenes; and the charcoals yielded almost entirely alkanes in small amounts.

### INTRODUCTION

Supercritical fluids have physical properties which give them novel solvent characteristics. The relatively high fluid density results in large

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interactions between solutes and solvent, but flow characteristics result in behavior similar to gases (1). Those properties have been utilized for extractions of hydrocarbons from coal and crude oil (2-5); caffeine from coffee (6); essential oils and flavors from hops, tobacco, and spices (7); and individual oligomers from polymers (8-11). A variety of fluids has been used, including aliphatic hydrocarbons (2, 4, 5, 9, 11), toluene (3), carbon dioxide (6, 7), fluorinated hydrocarbons (10), and *p*-cresol (12). Extracts obtained by using supercritical fluids contain materials that are usually not dissolved by common solvents. The term "destruction" has been coined because the process bears a similarity to both fractional distillation and extraction (2).

The solubilizing power of a supercritical fluid is controlled by a large number of variables, particularly for dynamic (flow-through) systems. The fluid density is very important, and depends primarily on the pressure and temperature. However, the pressure drop across the destruction chamber is also important (11). The pressure drop is mainly dependent on the particle size of the sample material and the flow rate, but inlet pressure and fluid temperature also contribute.

Carbon materials, such as Amoco PX-21 and Sterling MT-FF, have been suggested as suitable materials as adsorbents for trace organic analysis (13). However, some compounds, particularly polychlorinated biphenyls, polychlorinated dibenzofurans, polychlorinated dibenzo-*p*-dioxins, and other large chlorinated aromatic compounds of environmental interest, limit that use as a result of irreversible adsorption (14). From previous work in our laboratory on supercritical fluid chromatography (9, 11, 16), it was thought that supercritical pentane might be a suitable desorbing solvent.

Preliminary work in our laboratory showed that supercritical pentane was a suitable material for extracting polychlorinated hydrocarbons, but significant interference occurred during spectroscopic monitoring at 254 nm. This was attributed to breakdown of the active carbon adsorbent by the supercritical pentane.

The purpose of the current study was to determine if that behavior was general for other carbons and, if so, to see if the resulting extracts could be used to characterize those carbons using various chromatographic and spectrometric methods.

## EXPERIMENTAL

### Chemicals

Technical grade pentane (J. T. Baker Chemical Co., Phillipsburg,

New Jersey) was purified by an extensive procedure (13). Carbons used included two technical grade graphites (Fisher Scientific Co., Fair Lane, New Jersey, and Sargent-Welch Co., Springfield, New Jersey), UCP-901 high purity ( $<3$  ppm sulfur and  $<0.5$  ppm nitrogen) graphite (Ultra Carbon Corp., Bay City, Michigan), Amoco PX-21 active carbon (Amoco, Tulsa, Oklahoma), Sterling MT-FF (Cabot Corp., Boston, Massachusetts), Carbopack B (Supelco, Bellefonte, Pennsylvania), Fisher high purity charcoal (Fisher Scientific Co., Phillipsburg, New Jersey), and Darco G-60 technical grade charcoal (Matheson, Coleman, and Bell, Norwood, Ohio). All carbons were used as received.

### Apparatus

The overall experimental set-up has been described (15, 16), but some modifications were made for this study. First, the sample valve used in previous studies was eliminated, resulting in solvent flow directly from the deaeration column to the spectrophotometer. Second, the pressure and temperature programming options were not utilized in this study.

A Varian 8500 syringe pump (Varian Instrument Division, Walnut Creek, California) delivered pentane to a precolumn,  $1.25\text{ m} \times 1.27\text{ mm}$  i.d., and then to a specially designed high-pressure, high-temperature six-port valve (Model #AH60, Valco Instruments Co., Houston, Texas). Temperatures were monitored by a platinum resistance thermometer, Model PR-11-Z-100-1/4-24<sup>1/2</sup>-E (Omega Engineering, Stamford, Connecticut). Pressure transducers, Model GP-59F-2500 (Transducers, Whittier, California), were used to monitor and control the pressures. A UV-visible spectrophotometer (GCA/McPherson, Acton, Massachusetts) was used to monitor the eluents. A high-pressure flow cell (Altex Scientific, Berkeley, California), rated at 38.3 MPa, was used in the spectrophotometer. Constant flow rates were maintained by a pair of precision metering valves, Model SS-15G (Nupro Co., Willoughby, Ohio) located at the exit end of the spectrophotometric cell. Samples were collected after those valves. Figure 1 is a block diagram of the apparatus.

### Procedures

The carbons were dry packed by the tap and fill method into a 316 stainless steel column,  $0.625\text{ cm o.d.}, 0.42\text{ cm i.d.} \times 25.0\text{ cm}$  (Alltech Associates, Arlington Heights, Illinois). The connectors used at each end of the column were 316 stainless steel Swagelok connectors (Crawford Fitting Co., Solon, Ohio) containing frits of  $2.0\text{ }\mu\text{m}$  porosity (Alltech Associates, Arlington Heights, Illinois).

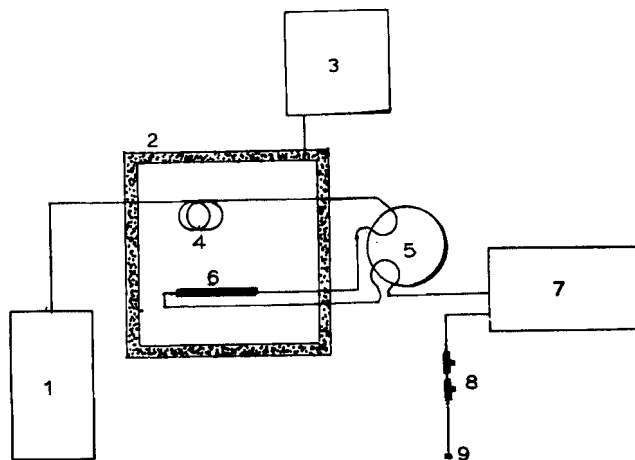


FIG. 1. Experimental apparatus. 1: Varian 8500 pump. 2: Oven. 3: Temperature controller. 4: Pre-column. 5: Switching valve. 6: Sample column. 7: Spectrophotometer. 8: Flow-controlling metering valves. 9: Collection port.

Four successive sets of conditions were used in each destraction, and 5 mL were collected for each at a flow rate of 1.0 mL/min. An initial subcritical extraction (180°C, 3.45 MPa) was done, following which the temperature was raised to 200°C where critical conditions occur. Finally, two extracts were obtained at progressively higher fluid densities (210°C, 6.89 and 10.34 MPa). For each extraction the system was allowed to reach isothermal, isobaric conditions with the pentane flow bypassing the sample column. Then, after switching the flow to the sample column, extracts were collected. "Destructograms" were obtained by monitoring absorbance at 254 nm as a function of time.

UV spectra were taken using a Cary 14 spectrophotometer in the double-beam mode. Infrared spectra were taken on a Perkin-Elmer 599B spectrophotometer. Packed column gas chromatography was done on a Perkin-Elmer 3920 gas chromatograph [with simultaneous flame ionization detection (FID) and sulfur flame photometric detection (FPD)], or on a Perkin-Elmer 900 gas chromatograph [with simultaneous FID and nitrogen thermionic detection (NPD)].

For packed column gas chromatography, a 15- $\mu$ L sample of each extract was injected, the material being absorbed on a 0.64 cm o.d., 0.48 cm i.d.  $\times$  200 cm column of 60/80 mesh Tenax-GC. A temperature program consisting of an initial period of 8 min at 75°C, a ramp to 290°C at 4°C/min, and a final isothermal period at 290°C for 16 min was used.

Capillary gas chromatography was done using a Hewlett-Packard

5720A. A Hewlett-Packard 5930A mass spectrometer interfaced through a jet separator (Scientific Glass Engineering, Austin, Texas) was used in conjunction with the capillary gas chromatograph for GC/MS. Capillary chromatograms were run either on a 20 m  $\times$  0.35 mm i.d. column coated with OV-17 at 25 cm/s linear velocity using a temperature program from 50 to 250°C at 5°C/min or on a 35 m  $\times$  0.35 mm i.d. column coated with SE-54 at 25 cm/s linear velocity using a temperature program from 80 to 280°C at 5°C/min.

## RESULTS

### Destructograms

The material extracted from the carbons came off in large amounts, usually with little difference between the initial and final extracts except for the amounts of sulfur removed. To prove that the hydrocarbons were due to breakdown of the bulk rather than removal of surface contamination, several samples were prepared by washing with methanol and pentane (at room temperature) and destructed. The “destructs” were essentially identical to those used without washing.

The “destructograms” obtained by monitoring the UV absorbance at 254 nm showed trends related to the type of carbon being examined (Fig. 2). When pentane at 180°C and 3.45 MPa was allowed to flow through the sample tube, an initial large absorption was observed. The absorbance was greatest for the two technical grade graphites; the active carbons and the high purity graphite yielded less UV absorbance; the charcoals showed little absorbance. The three successive treatment steps that followed yielded similar results but with less material being extracted than in the first step.

### Spectroscopy

Several types of spectra were taken of the various extracts to get information about the types of compounds present. Ultraviolet spectra (200 to 350 nm) gave some useful information, while visible (350 to 800 nm), infrared, and proton NMR spectra did not. The latter two methods were hampered by the fact that there were only very small concentrations of extracted material in the pentane.

The UV spectra showed trends ongoing from one type of carbon to another (Fig. 3). Graphite extracts showed two absorbance bands, the one at 215 nm being much larger than the one at 270 nm. The absorbance of the latter band changed little from one extract to another even when

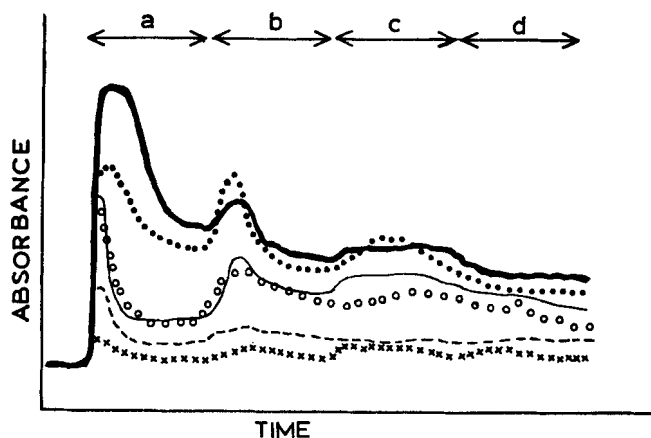


FIG. 2. Destructograms of the carbons as monitored at 254 nm. Conditions: (a) 180°C, 3.45 MPa; (b) 200°C, 3.45 MPa; (c) 210°C, 6.89 MPa; and (d) 210°C, 10.34 MPa. (—) Sargent graphite. (●) Fisher graphite. (—) Sterling MT-FF active carbon. (○) Amoco PX-2I active carbon. (- -) MCB charcoal. (×) Fisher charcoal.

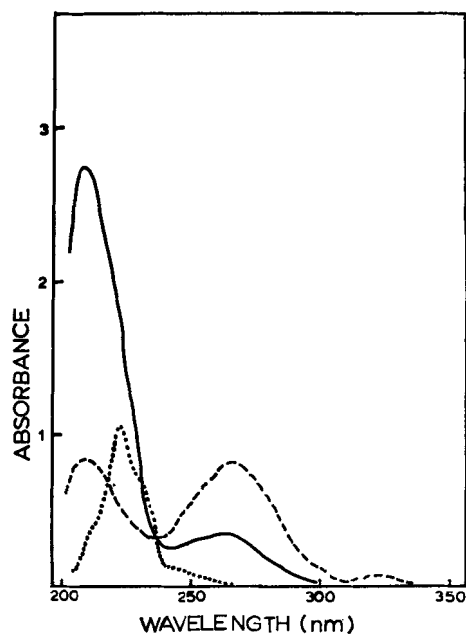


FIG. 3. UV spectra of some typical extracts (180°C and 3.45 MPa). (—) Sargent graphite. (- -) Sterling MT-FF active carbon. (●) Fisher charcoal.

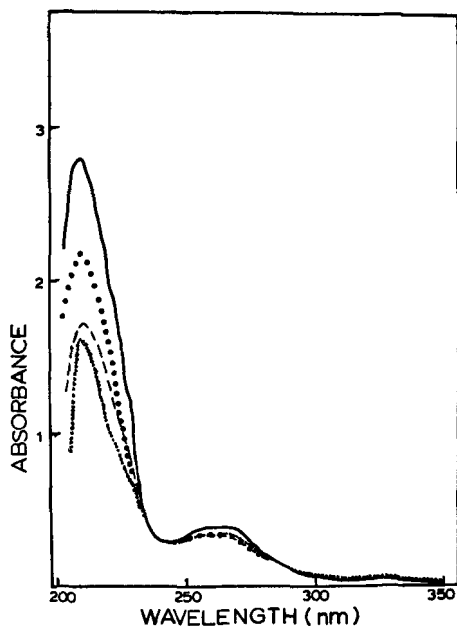


FIG. 4. Changes in the UV spectra of successive Sargent graphite extracts. (—) 180°C, 3.45 MPa. (○) 200°C, 3.45 MPa. (---) 210°C, 6.89 MPa. (●) 210°C, 10.34 MPa.

they were obtained under different extracting conditions (Fig. 4). The 215 nm band, however, decreased significantly from the first extraction at 180°C and 3.45 MPa to the last two extracts obtained using denser fluids and higher temperatures. Extracts for the UCP-901 high purity graphite showed these two bands, but the ratios of the peak absorbances differed from those of the other graphites. The 215 nm band was of similar absorbance (2.2 A vs 2.5 and 2.6 A for the Fisher and Sargent graphites, respectively), but the 270 nm bands were 0.1, 0.5, and 0.4 A, respectively.

The active carbons, Amoco PX-21 and Sterling MT-FF, also showed two bands at 215 and 270 nm. However, their relative sizes were different from those of the graphites. The ratio of the 215 nm band to the 270 nm band ranged from 0.8 to 1.0 for all the extracts obtained for Amoco PX-21 and Sterling MT-FF, with absorbances of 0.7 to 0.8 units. There was no trend in the ratios as a function of pressure or temperature. In addition, the extract obtained for Sterling MT-FF at 180°C and 3.45 MPa showed a small third band at 325 nm having an absorbance of 0.06.

The spectra of the two charcoals had only one distinct band, centered



at 225 nm, with a "tail" that absorbed out to 270 nm. The maximum absorbance of the 225 nm band was 1.1.

### Chromatography

In addition to flame ionization detection in all cases, the use of element specific detection for packed column chromatography and mass spectrometric detection for capillary chromatograms yielded information useful in compound identification. The FID chromatograms of carbons of similar type resembled one another rather closely but differed noticeably from carbons of the other types. UCP-901 high purity graphite gave an extract whose chromatogram (Fig. 5a) was very complex. There were many components of medium and low volatility. The chromatogram for the Fisher technical grade graphite had fewer peaks, but it did have two large peaks (one of low volatility, one of much higher volatility) in common with the UCP-901 extract (Fig. 5b). There were also many smaller peaks present. The Sargent technical grade graphite, however, differed from the other two (Fig. 6a) in that its extract contained many volatile components but few of low volatility.

The extracts of Sterling MT-FF, a partially graphitized active carbon, contained components that covered a wide range of volatility (Fig. 6b).

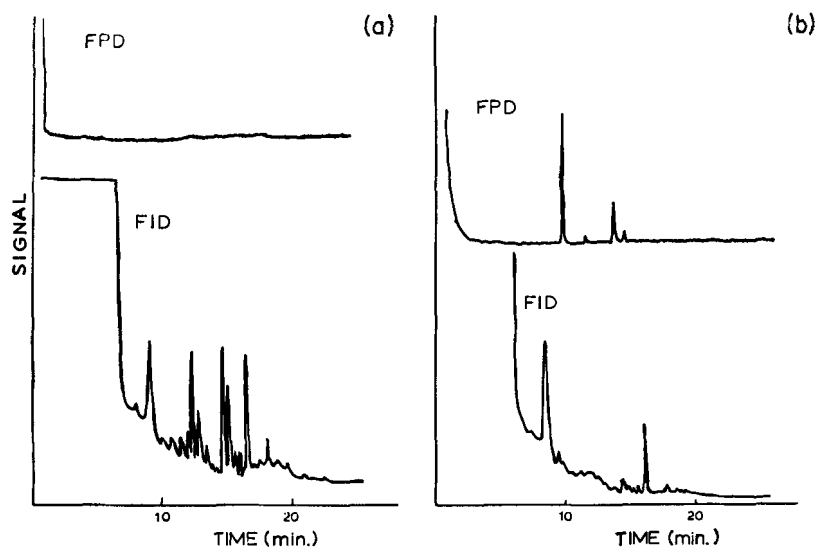


FIG. 5. Packed column chromatograms of the extracts obtained at 180°C and 3.45 MPa for (a) UCP-901 and (b) Fisher graphite.

These were mainly nonvolatile, but there was one major volatile species. Many components had retention times identical to components in the UCP-901 extracts.

The chromatograms of the extracts of the two charcoals were very simple (Figs. 7a and 7b). Two peaks were common to both, one for a very volatile component and one for a heavy component. The Fisher charcoal had more of the first peak and less of the second than the MCB charcoal; it also had another large and several smaller peaks for volatile components. None of the heavy components observed for the extract of the MCB charcoal was found.

The thermionic nitrogen detector showed no response for any of the extracts, implying that the amount of nitrogen present was quite small. However, the flame photometric detector revealed that nearly all of the sulfur was found in the initial extract. Furthermore, all of the samples, except the UCP-901 graphite, had extractable sulfur compounds. The Fisher graphite (Fig. 5b) had four components. One component, the most volatile one, was much larger than the others. The Sargent graphite showed the most response for sulfur of any of the carbons (Fig. 6a), and the chromatogram was very complex. There were about 10 components having the same retention times as the sulfur species in the Fisher graphite

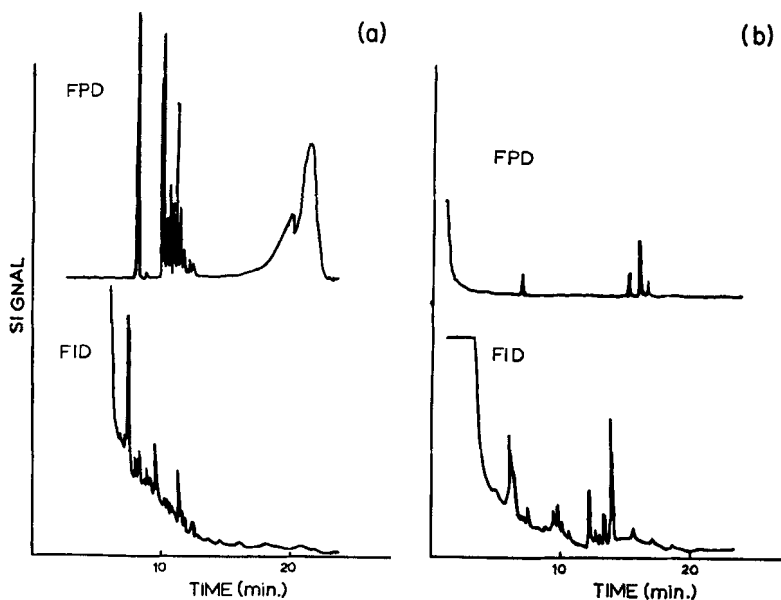


FIG. 6. Packed column chromatograms of the extracts obtained at 180°C and 3.45 MPa for (a) Sargent graphite and (b) Sterling MT-FF.

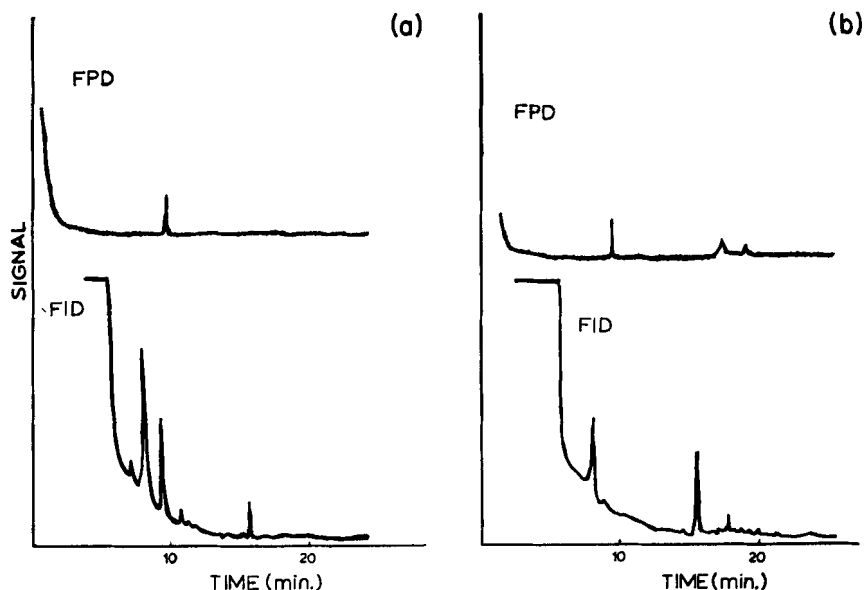


FIG. 7. Packed column chromatograms of the extracts obtained at 180°C and 3.45 MPa for (a) Fisher charcoal and (b) MCB charcoal.

extract. Separate runs showed that there were about six heavier components. Comparison of retention times with standard compounds suggested that these signals were due to substituted thiophenes and benzothiophenes. Unfortunately, the temperature programming capability of the Perkin-Elmer 3920 gas chromatograph did not allow optimization of the separations for both groups of sulfur components.

Sterling MT-FF also showed a sulfur response. Four peaks were observed, all having retention times different from those for the sulfur components in the graphites. One was a very volatile component, and the others eluted between the times of the two groups found in the Sargent graphite. The volatile component appeared to be hexanethiol, while the other peaks corresponded to the retention times of alkyl thiophenes.

The Fisher charcoal had only one sulfur component, with a retention time identical to the first peak in the chromatograms of the technical grade graphites (possibly due to 2-methyl thiophene). The MCB charcoal also had this component plus two smaller ones having retention times similar to the heavier components found in the Sterling MT-FF extract.

Capillary chromatograms yielded further information about the extracts (Fig. 8). The Sargent graphite extract had an extremely complex chromatogram. There appeared to be at least two regularly spaced series of eluting components. One series occurred mainly during the early part

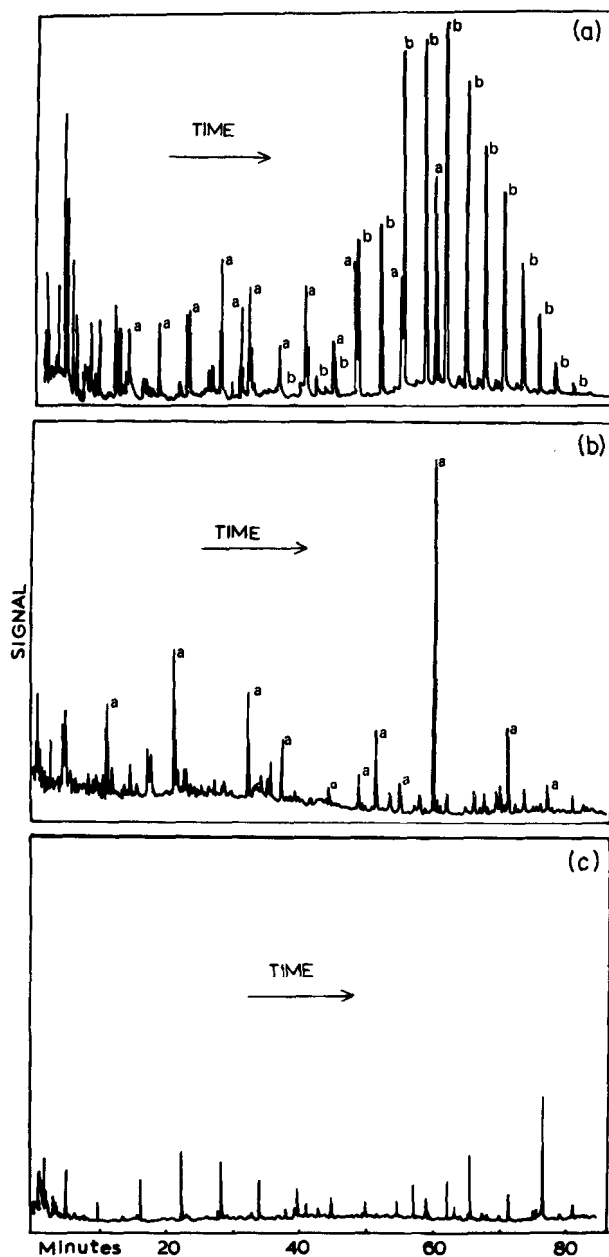


FIG. 8. Capillary chromatograms of the heavy ends (150 to 290°C) of the extracts obtained at 180°C and 3.45 MPa, Column 32 m  $\times$  0.25 mm i.d., coated with SE-54. (a) Sargent graphite where peaks a are alkanes and peaks b are alkyl-substituted aromatics. (b) UCP-901 where peaks a are partially condensed ortho- and peri-fused polycyclic aromatics. (c) Fisher charcoal.

of the chromatogram. The second series occurred at much later retention times and was present in much larger amounts. Mass spectra of the peaks revealed that the first series was due to large alkanes of up to 34 carbons. The second series appeared to be due to substituted benzenes and naphthalenes having substituents that were alkyl groups of up to 33 carbons. Figure 9 is the mass spectrum of the largest chromatographic peak; it appears to be a dimethylheptadecylnaphthalene.

In contrast, the capillary chromatogram of the UCP-901 extract showed no regularly spaced series. Mass spectra indicated that very different components were being removed compared to those from the Sargent graphite. The components were partially condensed ortho- and peri-fused polycyclic aromatic hydrocarbons of up to eight rings, as evidenced by the simple spectra observed for the components. There was little fragmentation, and molecular ions at  $m/e$  244, 257, 271, 284, 308, 324, and 356 were found.

The extract from the Fisher charcoal had a very simple capillary chromatogram. A regular series of components eluted throughout the chromatogram. Mass spectra revealed that this series was due to small alkanes (up to 19 carbons). The fragmentation indicated that the branching was similar to that of the alkane series observed for the extract from the Sargent graphite. (The retention times of these two series also match.)

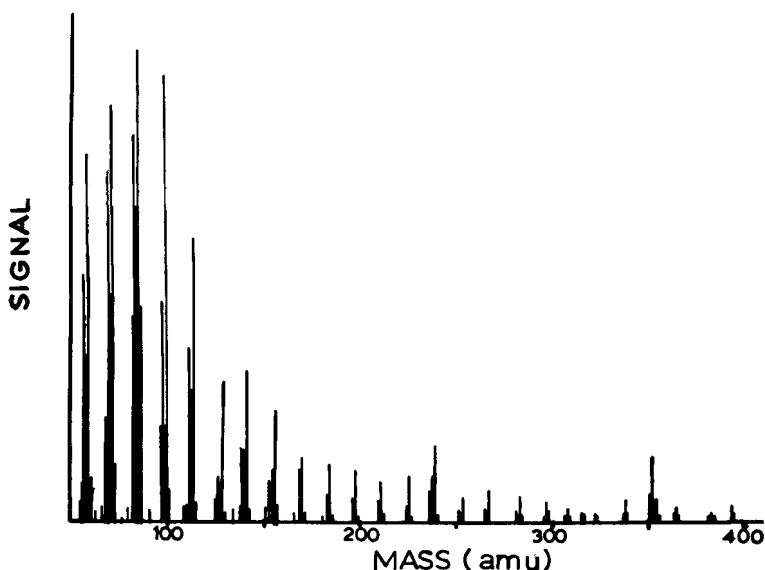


FIG. 9. Mass spectrum of the largest component in the Sargent graphite capillary chromatogram (a dimethylheptadecylnaphthalene).

## DISCUSSION

Extract characterizations can be made by correlating the results of different techniques. The three major indicators were the total amount of volatile species extracted, the relative amounts of different types of species in a given extract, and the changes in those amounts in successive extracts.

First, the extracts of graphites contained many components. A high purity graphite yielded large aromatic compounds, while a lower purity graphite yielded either large alkanes or alkyl-substituted benzenes and naphthalenes. The sulfur components in the low purity graphites were mainly benzothiophenes or dibenzothiophenes (as judged by their UV absorbances at 250 to 280 nm and their similar retention times in packed-column GC). Next, the active carbons (Amoco PX-21 and Sterling MT-FF) appeared to yield diene hydrocarbons (UV absorbance at 215 nm and high volatility) and sulfur components that were either large thiols or benzothiophenes. Finally, extracts of the charcoals were mostly large alkanes, and the small amount of sulfur present was in the form of large thiols.

Second, the extracted hydrocarbons also provide a good means of identifying the general type of carbon material. The high purity graphite gave large aromatic hydrocarbons, while the impure graphites gave alkanes, dienes, and alkyl-substituted aromatics, apparently due to attack at the discontinuities in the graphite lattice. Active carbons also gave alkanes, dienes, and alkyl-substituted aromatics, but they were extracted in much smaller total amounts, especially the dienes. The smaller amounts found for the active carbon reflect its partially graphitized nature. Charcoals yielded little material, and it was largely alkanes.

Third, analyses of successive extracts showed that one extraction using supercritical pentane removed most of the sulfur from the graphites and carbons. The types of extracted sulfur compounds could then be used as a basis for classifying the carbon material. The technical grade graphites yielded alkyl-substituted thiophenes and benzothiophenes, while the active carbons and charcoals yielded thiols and smaller alkyl-substituted thiophenes.

In the light of those results, the use of a carbon as an adsorbent for certain materials, such as polychlorinated hydrocarbons, is not feasible when supercritical pentane is used as the extracting solvent. The adsorbed species cannot be removed without, at the same time, removing much more extraneous material from the carbon itself that will interfere with later determinations of the halogenated compounds. Furthermore, preextraction of the carbon, before using it for the chromatography, is not feasible because material is removed continuously over long periods of time. The

amount of material removed was found to be a function of the amount of carbon used, and, under any set of conditions, the amount varied erratically with time. That behavior suggests a breakdown of the carbon material.

The large amounts of extracted material for the technical grade graphites appeared to be similar to that in extracts obtained by Gangoli and Thodos (3) and Bartle et al. (5) for supercritical extractions of coals. It was postulated in those studies that the supercritical fluid actually attacked the coal, breaking it down and removing the material. The mechanism was assumed to be a solvolysis reaction in which the solvent acted as a hydrogen donor to yield alkane materials from coals having very low hydrogen-to-carbon ratios. The presence of hetero atoms, especially parts per million and parts per billion amounts of alkali, alkali earth, and transition metals, was thought to catalyze the process. The metal contents of the carbons used in the present study were not determined by us, but the manufacturer's specifications showed contents in that range, especially for sodium, iron, nickel, and vanadium. The lack of alkane material in the extracts of high purity graphite supports that theory.

Charcoals, which have long been used to remove organic materials from solution, appear to be the best form of carbon to use because they released the smallest amounts of material compared to active carbons and graphites. Furthermore, because that material is largely aliphatic, it will interfere the least with UV-visible determinations of the aromatic species.

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