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THE ANALYSIS OF OILS FROM HYDROGENATION AND SUPERCRITICAL

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GENATION AND SUPERCRITICAL GAS
EXTRACTION

ENQUIRIES TO : J R KERSHAW

DIVISION : CHEMISTRY

FUEL RESEARCH INSTITUTE OF SOUTH AFRICA

REPORT NO. 58 OF 1976

THE ANALYSIS OF OILS FROM HYDROGENATION AND SUPERCRITICAL GAS
EXTRACTION

SYNOPSIS

The oils from dynamic and static hydrogenation, supercritical gas extraction
and soxhlet extraction were separated into a number of fractions by
adsorption chromatography on silica-gel. The fractions from this chro-
matographic separation were investigated by ultra-violet and infra-red
spectroscopy, and gas chromatography. The chemical nature of the alip-
hatic and aromatic hydrocarbons as well as the hydroxyl containing com-
pounds are discussed, and compared and contrasted between the various
processes.

INTRODUCTION

Within the Institute, a number of coal liquifaction processes are being
studied. To understand these processes properly, it is necessary to
analyse the product and ascertain its chemical composition. This report
describes and compares the chemical nature of the oil formed by dynamic
and static hydrogenation, and supercritical gas extraction of the same
coal.

EXPERIMENTAL

Coal used

Sigma (West Belt), 0,59 mm - 0,25 mm (30 - 60 B.S. mesh). Analysis of
this coal is given in Table 1.

Samples studied

"Oils", (hexane soluble fraction) from the following coal solvation
methods:

A. 'Dynamic' hydrogenation at 25 MPa[1]

Hydrogenation using an entrained bed of coal, through which hydrogen was continuously passed. The volatile liquid products were condensed in a receiver, using dry-ice/ethanol as the coolant. The autoclave was heated to 450°C and maintained at that temperature for 1 hour. Tin (1% of the coal), as stannous chloride, was used as a catalyst. The product was removed from the reactor with benzene, which was then evaporated, under reduced pressure to give the extract.

B. 'Dynamic' hydrogenation at 17 MPa[1]

The same as A, except at the lower pressure.

C. 'Static' hydrogenation at 25 MPa[1]

Hydrogenation in a closed rotating autoclave. The autoclave was heated to 450°C and maintained at that temperature for 1 hour. Tin (1% of the coal), as stannous chloride, was used as a catalyst. The product was extracted from the autoclave with benzene, which was then evaporated, under reduced pressure to give the extract.

D. 'Static' hydrogenation at 17 MPa[1]

The same as C, except at the lower pressure.

E. Supercritical gas extraction at 450°C[2, 3]

Toluene at 17 MPa was passed through the coal, heated to 450°C and maintained at that temperature for 1 hour. The toluene and extract were condensed and the toluene removed by evaporation under reduced pressure.

F. Supercritical gas extraction at 350°C[2, 3]

The same as E, but at the lower temperature.

G. Solvent extraction at atmospheric pressure

Soxhlet extraction using boiling chloroform/methanol (3:1 by volume) for 100 hours. The solvent was removed under reduced pressure.

Figure 1 shows that the extraction is nearly complete after 100 hours, though there is still a little that can be extracted.

The "oils" were obtained from the total extracts by extraction with excess n-hexane.

Fractionation of the "oils"

The oils were separated into fractions by adsorption chromatography on silica-gel. The column was eluted successively with n-hexane (12 fractions), n-hexane/toluene (increasing proportions of toluene, 5 fractions), toluene, chloroform and methanol.

In some cases further purification was carried out by adsorption chromatography on alumina or silica-gel.

Analysis

Infra-red (i.r.) and ultra-violet (u.v.) spectra were measured for each fraction from the columns. Infra-red spectra were measured as smears on sodium chloride plates using a Perkin-Elmer 567 grating spectrophotometer. While ultra-violet spectra were measured as a solution in hexane, or methanol, (spectroscopic grade) using a Unicam SP 1700 instrument. The u.v. spectra of a large number of aromatic compounds were measured for comparison.

Gas-liquid chromatographic (g.l.c.) analysis was carried out on 1,25 m x 3 mm stainless steel columns with 10% SP 2100 methyl silicone oil on 100 - 120 mesh Supelcoport, using a Perkin-Elmer 3920 chromatograph with flame ionisation detector. Various temperature programmes were employed with heating rates of $4^{\circ}C$ and $8^{\circ}C$/min. G.l.c. analysis was also carried out with a 50 m x 0,25 mm i.d. capillary column, (wall-coated open tubular) using OV 101 silicone fluid stationary phase on the same chromatograph. Various temperature programmes were used with heating rates of $1^{\circ}C$, $2^{\circ}C$ and $4^{\circ}C$ per minute.

RESULTS

Infra-red (i.r.) and ultra-violet (u.v.) spectroscopy

The fractions, from column chromatography, have been grouped as aliphatic hydrocarbons, aromatic hydrocarbons and hydroxy containing compounds. This latter group was assigned as those fractions from the chromatogram, which showed an hydroxyl absorption in the i.r. spectrum. They all also showed characteristic aromatic absorptions. These results are summarised in Table 2.

Dynamic hydrogenation (samples A and B)

The i.r. spectra of the first fractions from the columns showed that this was aliphatic and contained no double bonds. In the C-H stretching region (ca 3000 cm^{-1})[4-7] the absorption due to methylene groups was much stronger than that due to methyl groups. This indicates that the fractions contain mainly n-alkanes of reasonable chain length. A weak absorption in the region 720 - 735 cm^{-1} is attributable to chains having 4 or more methylene groups.[4,5] The second fraction to be eluted was similar but showed an increase in the methyl absorption compared to the methylene absorption, indicating more branched chained alkanes.

The u.v. spectra of the first aromatic fractions showed the presence of the naphthalenic structure. Strong peaks at ca 224 nm, 266 nm, and 275 nm and weak ones at 309 nm, 318 nm and 323 nm were present. The shape and ratio of the absorbances were similar to those of the naphthalenes recorded. The characteristic naphthalenic odour was also noticed with these fractions. The i.r. spectra of these fractions showed in the 3000 cm^{-1} region much more aliphatic than aromatic hydrogen. This might well be indicative of hydroaromatic structures. In the "aromatic region" (1000 - 650 cm^{-1}) strong peaks were found at 812, 785 and 743 cm^{-1} indicating[4,6,7] 1, 2, 3, 4-tetra- (or 1, 4-di-), 1, 2, 3-tri-, 1, 2-di-substitution. A weak peak at 1260 cm^{-1} was noticed in these fractions which could be due to an aromatic ether.

The next aromatic structure to be shown by u.v. spectroscopy was the pyrene structure[X] (1) with characteristic strong peaks at 319 and 334 nm.[8,9]

X U.v. spectra do not indicate the nature or position of substituents (if any).

Fractions which showed a strong absorbance in these areas were chromato-graphed twice on alumina to obtain a sample, which gave a spectrum very similar to that of pyrene (see Figure 2). The amount of the pyrene struc-ture was calculated from the u.v. spectra and is recorded (Table 3).
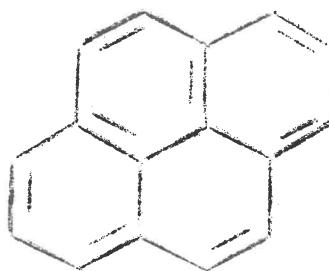

(1)

The calculation was based on the heights, above the background absorbance, of the 319 and 334 nm peaks. (A spectrum of pyrene was used as a stan-dard). It was noticed that on purification, by chromatography, the total amount of pyrene calculated increases, which is probably due to the ab-sorbance of other aromatic structures "masking" the pyrene peaks at 319 and 334 nm. It was assumed that the substituents on pyrene rings do not significantly affect the molar absorptivity (molecular extinction coeffi-cient) (based on unsubstituted pyrene) of the ca 319 and 334 nm peaks. This is a reasonable assumption as the values for the amounts of pyrene present are undoubtably low due to the "masking" effect of other aroma-tics and the values are only intended to be a guide for comparison of processes, not as absolute values.

The same fractions which contain pyrenes, also showed peaks at ca 292, 299, 377 and 397 nm. The former could be due to a phenanthrene structure (2). While the 299 nm peak, which is eluted just after the 292 could be from a substituted phenanthrene.[10] The 377 nm peak which was larger than the 397 nm peak and was eluted just before it on the column was tentatively assigned to an anthracene, substituted in rings A or C. On further chro-matography a peak emerged at ca 356 nm with the 377 nm peak; anthracenes have a peak at ca 356 nm. The 397 nm peak indicated a 9,10-disubstituted
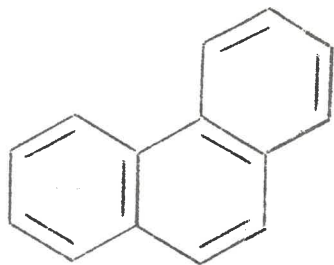
(2)
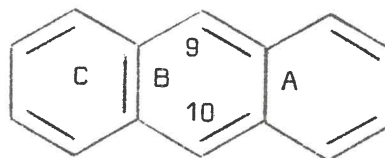
(3)

anthracene.[10] (Dibenz (a, h) anthracenes also have a peak ca 397 nm,[9,10] but they have stronger peaks at ca 348, 332 and 320 nm, and as these were not observed, this structure is less likely).

The i.r. spectra of the pyrene fractions, in the 3000 cm^{-1} region, have stronger aromatic C-H absorptions, compared to the methylene and methyl C-H stretching vibrations, than the earlier fractions indicating less hydroaromatic structures. In the "aromatic region" the spectra were very complicated but the major substitution patterns indicated were 1, 2, 3, 4-tetra- (or 1, 4 di-), 1, 2-di- and mono- substitution of the benzene rings. Weak absorbances at ca 1250 cm^{-1} and 1180 cm^{-1} may indicate the presence of an aryl ether[4] and a benzofuran,[11,12] or similar type oxygen heterocycle, respectively.

The next structure to be shown by u.v. spectroscopy was the benzo (a) pyrene (4)[X] structure. This has characteristic peaks at ca 363 and 383 nm.[9] Further purification of these fractions gave a spectrum very similar to that of benzo (a) pyrene (see Figure 3). The amount of benzo (a)

(4)

(5)
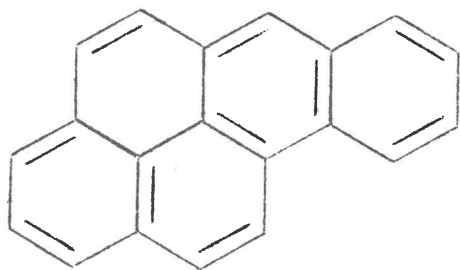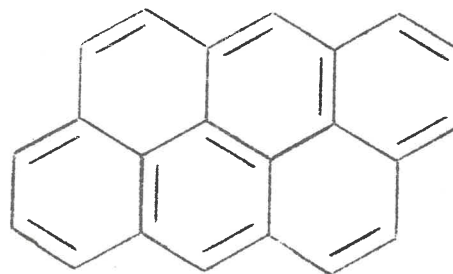
X The correct I.U.P.A.C. name for this compound is benzo (def) chrysene. However, the more common name of benzo (a) pyrene is used. 3, 4-Benzopyrene and 1, 2-benzopyrene have also been used to describe this ring system.

pyrene was estimated from the u.v. spectra and is recorded (Table 3). The calculation was based on the heights above the background absorbance of the 363 and 383 nm peaks. Benzo (a) pyrene is one of the most carcinogenic compounds known[9], and has been extensively measured in a wide variety of environments during pollution studies[13]. Weak absorption maxima were also noticed at ca 422 and 430 nm. The position and ratio of these two peaks indicates the dibenzo (def, mno) chrysene (anthanthrene) structure (5) (see under sample G).
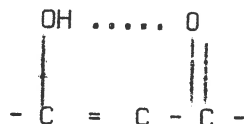
The i.r. spectra of these fractions show in the 3000 cm^{-1} region higher aliphatic C-H absorption compared to the aromatic C-H absorption for sample A than B. This indicate that further reduction has taken place at the higher pressure. In the "aromatic region" the spectra were very complicated, but the major substitution patterns indicated were 1,2-di- and 1, 2, 3, 4-tetra- (or 1,4-di-) substitution.

The final aromatic fractions show strong absorption in the u.v. above 300 nm but no peaks were apparent. The i.r. spectra had peaks at 1128 cm^{-1} and 1261 cm^{-1} indicating alkyl and aryl ethers, respectively.

The hydroxyl containing fractions have a strong absorbance in the u.v., showing their aromatic nature, but no fine structure. The strength of the absorbance above 300 nm indicates that there are polyaromatic ring structures in these fractions.

In the i.r. spectra, the position and shape of the OH absorption changes. With first fractions sharp peaks at ca 3532 cm^{-1} and 3420 cm^{-1} were found, while in the later fractions the OH absorption was much broader and at a lower frequency, due to increased hydrogen bonding. The aromatic C-H stretching frequencies were much weaker than the aliphatic C-H stretching frequencies, in the 3000 cm^{-1} region. Weak carbonyl frequencies were noticed between 1650 and 1700 cm^{-1} (aromatic carbonyl groups in different environments) and at ca 1720 (aliphatic carbonyl). It appears as though most of the hydroxyl groups are phenolic as indicated by the strength of the aromatic C-O stretch compared to the aliphatic C-O stretching frequencies. However, there were peaks which indicated alpihatic C-O

stretching frequencies and therefore some of the hydroxyl groups as being alcoholic rather than phenolic in nature. In the later hydroxy containing fractions the 1600 cm^{-1} was very strong and broad compared to other peaks in the spectra. It is possible that a chelated carbonyl structure (eg 6) could enhance the 1600 cm^{-1} absorption. These structures are known to

$$OH \ldots\ldots O$$
$$| \qquad ||$$
$$- C = C - C -$$

(6)

give rise to very intensive absorptions.[4, 14 - 16]

Static hydrogenation (Samples C and D)

The i.r. spectra of the aliphatic fractions were very similar to those from the dynamic hydrogenation.

There were a number of differences between the aromatic fractions from the static and dynamic hydrogenations. The first aromatic fractions were shown by u.v. spectroscopy to contain naphthalenes. The i.r. spectra of these fractions showed much higher aliphatic C-H absorption, compared to aromatic C-H absorption than with the equivalent fractions from the dynamic hydrogenation. This indicated that further reduction of the aromatic rings occurs when the sample is confined in the autoclave. Further indication of this reduction was the weakness of the 1600 cm^{-1} absorption and the absorptions in the "aromatic region" when compared to other peaks in the spectra. These changes were especially noticeable with the hydrogenation carried out at 25 MPa.

The u.v. spectra also indicated that the following structures were present: pyrene, benzo (a) pyrene, anthanthrene, phenanthrene, anthracene, 9,10-disubstituted anthracene. However, there were less of the specific structures especially pyrene, and in general the u.v. spectra showed less fine structure. The i.r. spectra of the pyrene fractions in 3000 cm^{-1} region showed more aliphatic hydrogen in relation to the aromatic hydrogen when

compared to the equivalent fractions from samples A and B. Whereas, the i.r. spectra of the benzo (a) pyrene fractions were similar to those from the dynamic hydrogenation. A weak peak at ca 1180 cm^{-1} was again noticed in the i.r. of the pyrene fractions.

The i.r. spectra of the hydroxy containing compounds were very similar to those for the dynamic method.

Supercritical gas extraction (Samples E and F)

The i.r. spectra of the aliphatic fractions were similar to those from the other samples studied.

The i.r. spectra of most of the early aromatic fractions were not as expected, having far more sharp peaks than could be expected from a complex mixture obtained from coal. One fraction slowly solidified and was recrystallised from methanol as colourless needles. This was assigned as bibenzyl (7) on grounds of its m.p., 52 - 3°C (lit.,[17] 52,5^{o}C) and was undepressed on admixture with an authentic sample. The i.r. spectrum was also identical with that of an authentic sample and with that reported.[6]
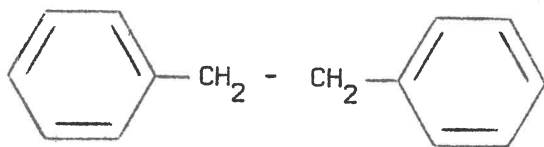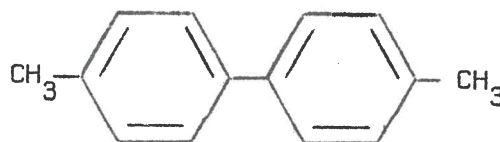
(7)   (8)

The retention time on g.l.c. analysis was the same as that of the authentic compound and they were identical by co-injection (see g.l.c. section). The i.r. spectra of the samples before separation showed, especially the sample obtained at 450°C, a large amount of bibenzyl.

The large amount of one single compound "masks" the i.r. and u.v. spectra of many of the aromatic fractions. Pyrene and anthracene structures were indicated by the u.v. spectra and the later fractions showed the presence

of benzo (a) pyrene and anthanthrene structures.

The final aromatic fractions showed strong aromatic C-H stretching absorption. In the "aromatic region" peaks attributable to a fair amount of phenyl groups were present. The spectra also showed weak peaks indicating the presence of aryl and alkyl ethers.

The hydroxyl fractions show no fine structure in the u.v., but the absorbance shows the aromatic nature of these fractions. The hydroxyl fractions show strong OH absorption, the absorption was broader and at a lower frequency, later the fraction came off the column. The aromatic C-H stretching frequencies were much weaker than the aliphatic C-H frequencies. In the carbonyl region, there were strong absorbances at ca 1650 - 1690 cm^{-1} (aromatic carbonyl) and ca 1730 cm^{-1} (aliphatic carbonyl). As with the samples from hydrogenation the 1600 cm^{-1} peak in the later fractions was extremely strong. The majority of the hydroxyl groups were indicated to be phenolic by the intensity of the aryl C-O stretching frequency but there was an appreciable amount of alcoholic hydroxyl groups indicated by the i.r. spectra. In the "aromatic region" the spectra indicated that phenyl groups and 1,2-disubstituted benzene rings were present in appreciable amounts.

Solvent extraction at atmospheric pressure (Sample G)

The i.r. spectra of the aliphatic fractions were similar to those from the other samples, indicating a predominance of n-alkanes.

The u.v. spectra of the first aromatic fractions showed the presence of naphthalenes. The i.r. spectra of these fractions had a strong aliphatic C-H absorption in relation to the aromatic C-H absorption. This may be caused by an appreciable amount of hydroaromatic structures or long aliphatic chains on the naphthalenes. 1, 2, 3, 4-Tetra- (or 1,4 di-) aromatic substitution was indicated to be the most common with these fractions.

The next structure to be shown by u.v. spectroscopy was that of pyrene. Phenanthrenic, anthracenic and 9,10-disubstituted anthracenic compounds were also indicated by the u.v. spectra to be present in these fractions.

Anthracenes were eluted from the column before 9,10 disubstituted anthra-
cenes. The i.r. spectra in the "aromatic region" were very complex, but
those peaks which could ascribed to a 1,2 disubstituted and 1, 2, 3, 4,-
tetra (or 1,4-di-) substituted benzene rings were the strongest. Two
absorptions near 1190 cm^{-1} and one weaker one at 1263 cm^{-1} were assigned
to the C-O frequency in oxygen heterocycles[11, 12] (eg benzofuran) and
aryl ethers[4,6], respectively.

The next structure to be shown by u.v. spectroscopy is benzo (a) pyrene.
Peaks at 402, 421 and 429 nm were also present in these fractions. The
429 and 421 peaks were at the same wave length and were in approxamately
the same ratio as two major peaks in dibenzo (def, mno) chrysene (anthanthrene)[X]
(5) (see Figure 4). The 402 nm peak is probably by its relative intensity
a combination of the 399 and 405 peaks of anthanthrene and the 402 peak
of benzo (a) pyrene. The later aromatic fractions showed strong aromatic
C-H stretching absorbance and strong absorbance attritutable to 1,2
disubstituted benzene rings.

The spectra of the hydroxyl fractions were similar to those from samples
E and F.

Gas-liquid chromatographic analysis
The chromatograms of the aliphatic fractions showed as principal com-
ponents a regular series of peaks attributed to straight-chain alkanes.
These were identified by having the same retention time as standards and
were identical by co-injection with these standards. Some branched chained
alkanes were identified by identical retention times and by co-injection
with standards. The n-alkanes up to nonadecane were also identified by
their identical retention times on the capilliary column, and were identical
by co-injection on this column. The isoprenoid alkane, pristane (2, 6,
10, 14-tetramethylpentadecane) was identified as being present in the
aliphatic fractions of all the samples. It was necessary to use a
capillary column to seperate pristane from n-heptadecane, and pristane

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X In older literature referred to as dibenzo (cd, jk) pyrene

was identified by having an identical retention time with an authentic
sample and being identical on co-injection with that sample. Quantitative
analysis was based on peak areas. A known amount of n-nonane or n-penta-
decane was added as an internal standard. A brief study showed the
n-alkanes had the same instrumental response. The concentrations of the
alkanes are summarised in Table 4.

G.l.c. analysis of the first aromatic fractions, from the hydrogenation
samples (A-D) using the capillary column, showed the presence of tetralin,
naphthalene, 1- and 2-methyl-, 1, 3- and 1,5-dimethyl naphthalenes by
their identical retention times with standard samples and identical on
co-injection. The monomethylnaphthalenes were there in greater amounts
than the others, while 1, 3-dimethylnaphthalene was more plentiful than
its 1,5-dimethyl isomer. The ratio of tetralin to naphthalene was
measured for these samples (see Table 5).

The solvent extraction product (sample G) had appreciable amounts of
1- and 2-methyl-, 1,3- and 1,5-dimethylnaphthalenes but only a small
amount of the parent compound.

The g.l.c. analysis of the aromatic fractions from supercritical gas
extraction (E and F), using the capillary column, showed the presence
of the same major compound in a number of fractions. This compound has
been identified as bibenzyl (7) on the grounds that it had the same
retention time and was identical on co-injection with an authentic
sample. p,p'-Bitolyl (8) was also present in these fractions and was
identified by identical retention time and by co-injection with an
authentic sample. The position of other peaks in the chromatogram was
where other bitolyls would be expected.

A sample of the "lighter" fractions of the product from the dynamic
hydrogenation (conditions as in sample A but using Landau as the coal)
was collected prior to benzene extraction and has been examined by g.l.c.
using the capillary column. The following compounds were identified
(identical retention times and identical on co-injection with authentic
samples): n-pentane, n-hexane, n-octane, n-nonane, benzene, toluene,

o-, m- and p-xylenes, ethylbenzene, cumene (isopropylbenzene), mesitylene (1, 3, 5-trimethylbenzene), p-cymene (1-methyl - 4-isopropylbenzene). In general, the amounts of both the n-alkanes and the aromatics decreased with increasing molecular weight.

DISCUSSION

Hydrogenation (samples A - D)

The yields of oil for the dynamic hydrogenation were much greater than for the static hydrogenation (see Table 2). It appears that when the product was left in the autoclave, polymerisation occured as high asphaltene (hexane insoluble, benzene soluble) yields were obtained by static compared to dynamic hydrogenation for a number of coals.[1] Comparing dynamic and static hydrogenation at 17 MPa (samples B and D), it is noticed that it is mainly the amount of aromatic hydrocarbons which is reduced in the static case. Presumably, aromatic compounds at high temperatures polymerise, via free radicals, to give larger and less soluble aromatic units.

The aliphatic fractions had similar compositions (see Table 4), mainly consisting of n-alkanes. The amount of the n-alkanes, in general, decreased with increasing chain length. It was noticeable, however, that there was a maxima at the $n-C_{23}$ alkane. This was the most common compound in the aliphatic fraction from solvent extraction. The amount of the $n-C_{23}$ alkane was greater with the dynamic system rather than the static and the lower rather than higher hydrogen pressure. It appears as if hydrocracking of the larger aliphatics occurs and also additional material is obtained from the breakage of aliphatic side chains and linkages in the coal structure. Hydrocracking of the alkane chain is less likely to occur with the dynamic system, where compounds can be "blown out" of the system, than with the static system.

The aromatic fractions show greater differences between the dynamic and static systems than the aliphatic fractions. The i.r. of the first aromatic fractions indicated that further reduction had occurred with the static system. This was further shown by the naphthalene/tetralin ratio (see Table 5) which completely changes.

An estimate of the amount of pyrene and benzo (a) pyrene structures (see Table 3) shows that the amount of pyrenes, especially, is much lower with the static than the dynamic system. Pyrene and most simple alkyl derivatives have boiling points below the reaction temperature ($450^{\circ}C$), whereas benzo (a) pyrene has a boiling point above this temperature. It, therefore, seems likely that most of the pyrenes will be removed from the autoclave in the dynamic method but much less of the benzo (a) pyrenes, though some may be carried over in the hydrogen stream.

The polyaromatic compounds probably can undergo two competing reaction pathways. The first is hydrogenation to give an hydroaromatic which then may undergo further hydrogenation with cleavage of a ring to smaller molecules, eg the reduction of anthracene to benzene, toluene and xylene. The second is polymerisation _via_ free radicals to give larger aromatic
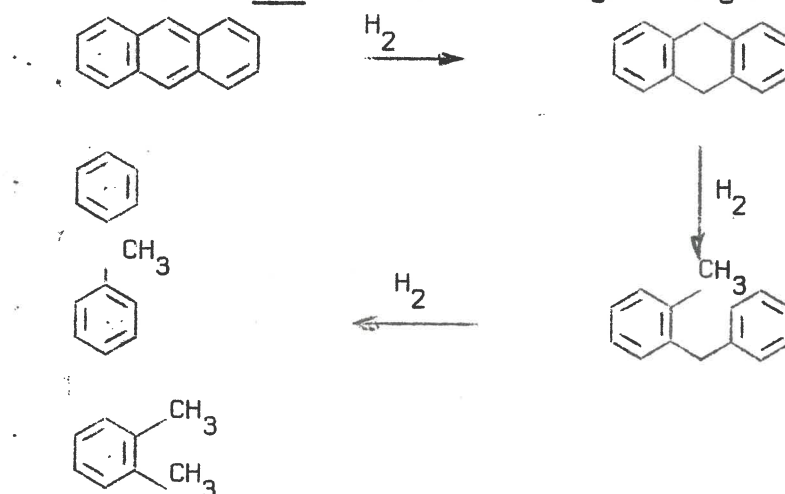
structures, eg dimerisation of naphthalene to picene (9) and benzo (j) fluoranthene (10). The high yields of asphaltenes produced with static
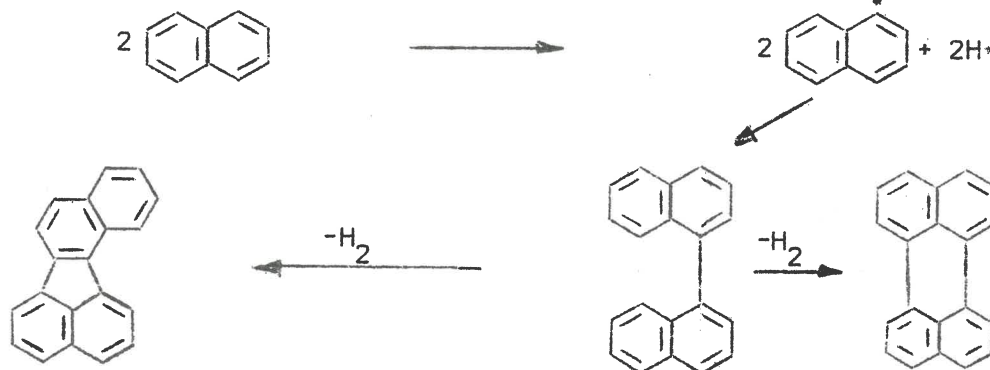
(10)   (9)

hydrogenation indicates that the latter is the preferred pathway.

It is noticeable that while the amount of the pyrene structure (on a coal basis) (see Table 3) is approximately the same with the dynamic system at 25 and 17 MPa, the amount of the benzo (a) pyrene structure increases considerable at the higher pressure.   Maybe benzo (a) pyrenes need more vigerous conditions to remove them from the coal lattice.
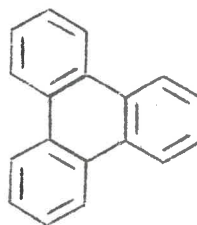
Supercritical gas extraction (samples E and F)

The aliphatic fraction from the supercritical gas extraction at 350° has a similar composition to that from soxhlet extraction (see Table 4) and the amount of aliphatics was of the same order (see Table 2).   The odd over even composition and the low concentration of n-alkanes below n-C_{17} are features not expected if thermolysis had taken place.[18] Thus, the extract, at least as far as the alkanes are concerned, is not significantly degraded during the gas extraction process at $350^{\circ}C$.   A similar conclusion was reached by Bartle et.al.[19]

At $450^{\circ}C$, however, there is considerable change in the composition of the aliphatic fraction compared to solvent extraction.   The composition and the amount were intermediate between mild solvent extraction and hydrogenation.

The aromatic fractions were dominated by one compound, bibenzyl (7), formed by thermolysis of toluene via the free radical (11).   The high temperature pyrolysis of toluene has been studied,[20 - 24] and the major

CH_2
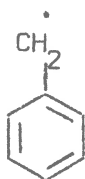
(11)   (12)

products are bibenzyl and benzene.   p, p'-Bitolyl (8), which was shown by g.l.c. analysis to also be in the product from supercritical gas ex-

traction, has previously, been detected on pyrolysis of toluene.[24]
Other workers have shown the presence of a mixture of bitotyls (dimethyl-
biphenyls) in the product from thermolysis of toluene.[23] It is worth
noting that at high temperatures naphthalene, anthracene and phenanthrene
are formed from toluene.[20 - 22, 24]

The amount of bibenzyl increases considerably when the extraction tempe-
rature is raised from 350° to 450°C. It has been previously reported[19]
that bibenzyl is formed when coal is supercritically extracted with
toluene. However, in this case the percentage of bibenzyl in the extract
was much lower. The following factors may effect the relative amount
of bibenzyl in the coal solvation product: (a) temperature of extraction,
(b) the time which the solvent spends at that temperature, (c) ratio of
solvent to coal, (d) the yield of extract, and (e) the nature and amount
of the inorganic matter in the coal.

Though a fairly high proportion of the oil comes from toluene and not
from the coal, nevertheless, at 450°C a reasonable yield of oil from the
coal was obtained.

General

All the aliphatic fractions showed the presence of the isoprenoid alkane,
pristane. Pristane has previously been found in coal extract, e.g. from
solvent extraction at room temperature,[25, 26] soxhlet extraction,[27, 28]
supercritical gas extraction,[19] and low temperature carbonisation.[29]
A relatively high amount of an isoprenoid hydrocarbon is a useful guide
to a biological source of geological deposits.[30 - 32] The n-alkanes
from solvent extraction and also the supercritical gas extraction at
350°C (samples F and G) had a predominance of those with odd carbon
number over those with even carbon number; a feature characteristic
of biogenic origin.[25, 32, 33]

The aromatic fractions showed the presence of the naphthalene, pyrene(1),
benzo (a) pyrene (4) and anthanthrene (5) structures while those of
phenanthrene (2), anthracene (3), and 9,10-disbustituted anthracene
were indicated. These same aromatics structures were present in the

hydrogenation samples and in the sample from soxhlet extraction, which takes place at a temperature (ca 60°C) too low for the breakage of bands to occur.   It is assumed that at this temperature the solvent dissolves compounds held in the pores of the coal, Vahrman's "molecular sieve" theory.[34]   The fact that the same aromatic structures were obtained from high pressure hydrogenation as were obtained from mild solvent extraction indicates either that the coal contains the same aromatics structures in the coal lattice as are held in the coal pores, or that even with hydrogenation, a sizeable proportion of the product comes from included compounds in the coal pores rather than from rupture of the coal skeleton.

It is known that on heating aliphatic compounds at high temperatures, a complex mixture which contains mainly aromatic compounds is formed.[35] More recently it has been shown[36] that certain naphthalenes during hydrogenation cyclise with dehydrogenation to give phenanthrenes. However, the author feels that as the same aromatic structures are shown in appreciable amounts in both the solvent extraction sample and the dynamic hydrogenation samples, then these structures are present in coal and are not formed during dynamic hydrogenation.

Looking at the aromatic structures present, there appears to be a series, except for the anthracenes, from naphthalene to phenanthrene (2) to pyrene (1) to benzo (a) pyrene (4) to anthanthrene (5) in which one more ring is formed each time. Both anthanthrene and benzo (a) pyrene are not very soluble in hexane and it is possible that some of these compounds could be left in the asphaltene fraction. The amount of pyrenes, especially, appears to be a significant proportion of the aromatic hydrocarbon fraction.

U.v. spectroscopy shows some polyaromatic hydrocarbons better than others in a complex mixture, e.g. anthracene is easier to detect than phenanthrene and pyrene easier than triphenylene (12). It is quite possible that certain aromatic structures are present in significant amounts but are not detected by u.v. spectroscopy.

The i.r. work indicated that the aromatic fractions contain hydroaromatics and oxygen heterocycles, such as benzofuran, as well as aromatic and aliphatic ethers.

The main difference between the hydroxyl fractions from the hydrogenation experiments and from the other methods was the relatively weak carbonyl absorption in the former. Reduction of carbonyl groups to hydroxyl groups presumably occurs. The intense peak at 1600 cm^{-1} in the later hydroxyl fractions may be due in part to a chelated carbonyl structure (see Results). The high intensity of this absorption has been noted in the i.r. spectra of coals and has been the subject of considerable discussion. Friedel has summarised the work[14 - 16] and he feels that a chelated carbonyl structure is the most likely explanation (see also ref. 37). However, the expected shift of the 1600 cm^{-1} peak in chars, from 0^{18} labelled precursors, did not occur.[38]

FURTHER WORK

It is envisaged that further work falls into two categories. The first is to use the same techniques to further investigate coal liquifaction processes. For example, whether the same aromatic structures are found in oils from other coals or whether different aromatic structures are shown. The effect of such parameters as type and amount of catalyst, temperature, residence time on the chemical composition of the product should also be investigated. A study of the composition of the product from other processes such as carbonisation and an investigation of the nature of asphaltenes could be useful in understanding the structure of coal and the mechanism of the conversion to liquid products.

The second category is the use of other analytical techniques to study the composition of the products. For example, fluorescence spectropotometry might throw further light on the aromatic structures present. Useful work using this spectroscopic technique has been carried out on poly-aromatic hydrocarbons in high-boiling petroleum distillates.[39, 40] 'H Nuclear magnetic resonance (n.m.r.) spectroscopy would be useful for investigation of the chemical type of the hydrogen atoms in the product while 13_C n.m.r. spectroscopy could be used to study the nature of the

carbon atoms (see refs. 37 and 41 and references therein). Mass spectro-
metry and liquid chromatography could also play an important role in un-
ravelling the complex composition of coal liquifaction products.

CONCLUSION

The oils from all the samples were very similar, structurally. The u.v.
spectroscopic studies showed the following aromatic structures; naphtha-
lene, pyrene, benzo (a) pyrene and anthanthrene, while those of anthracene
and phenanthrene were indicated. These same structures were found in
samples from mild soxhlet extraction and high pressure hydrogenation and
no other structures were shown by u.v. spectroscopy. Hydroaromatic
structures and oxygen heterocycles such as benzofuran were indicated by
i.r. spectroscopy to be present. The hydroxyl fractions were mainly
phenolic in nature, but nevertheless, contain an appreciable amount of
aliphatic hydroxyl groups. These fractions also had strong carbonyl
absorptions with the samples from solvent extraction and supercritical
gas extraction, while with the hydrogenation samples only weak carbonyl
absorptions were present. The aliphatic hydrocarbons present were main-
ly n-alkanes. The isoprenoid alkane, pristane, was found in all the
samples.

A considerable amount of a solvent derived compound, bibenzyl, was found
in the oil from supercritical gas extraction, especially at $450^{o}C$. This
emphasises the need in any solvent based process to study the composition
of the product for solvent thermolysis products.

The approach of separation of the oil into a relatively large number of
fractions by adsorption chromatography, followed by investigating these
fractions using u.v. and i.r. spectroscopy, and g.l.c. has given con-
siderable information on the nature of the oils. The results described
here, show that this method could well be used for further studies of
the nature of coal liquifaction products.

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TABLE 1

ANALYSIS OF COAL USED

	%	% d.a.f.
H_2O	6,6	
Ash	29,6	
Volatile matter	21,9	34,3
Fixed carbon	41,9	
Carbon		76,71
Hydrogen		4,42
Nitrogen		1,55
Sulphur		1,08
Oxygen		16,24
H/C Ratio		0,69

TABLE 2

OIL YIELDS AND COMPOSITION

| Method | Oil | Aliphatics | | Aromatics | | Hydroxyl compounds | |
	% coal (d.a.f.)	% oil	% coal (d.a.f.)	% oil	% coal (d.a.f.)	% oil	% coal (d.a.f.)
A	25,2	9,0	2,3	51,9	13,1	31,6	8,0
B	17,3	9,7	1,7	55,6	9,6	29,5	5,1
C	7,0	13,7	1,0	48,3	3,4	35,3	2,5
D	12,4	12,1	1,5	40,2	5,0	43,1	5,3
E	16,3 (11,2)[X]	3,0	0,5	80,0	13,0 (7,9)[X]	13,6	2,2
F	0,88 (0,69)[X]	10,6	0,09	44,1	0,39 (0,20)[X]	41,1	0,36
G	0,41	12,8	0,05	34,8	0,14	47,1	0,19

X Figures in brackets are the approximate figures after the estimated amount of bibenzyl has been substracted.

TABLE 3

AMOUNT OF PYRENE AND BENZO (a) PYRENE STRUCTURES

Method	Pyrene		Benzo (a) pyrene	
	% Aromatic fraction	% Coal (d.a.f.)	% Aromatic fraction	% Coal (d.a.f.)
A	2,8	0,37	0,91	0,12
B	3,8 (6,3)X	0,36 (0,61)X	0,49	0,05
C	1,1	0,04	0,21	0,007
D	0,54	0,03	0,11	0,006
G	1,2	0,002	0,83	0,001

X After further purification by chromatography on alumina.

TABLE 4
CONCENTRATION OF ALKANES

Alkane	SAMPLE (% Total Alkanes)						
	A	B	C	D	E	F	G
nC_9	5,0						
nC_{10}	5,9						
di Me-C_9	3,5						
Me-C_{10}	1,6						
nC_{11}	6,1						
nC_{12}	5,5		2,7	3,7			
di Me-C_{11}	4,3						
nC_{13}	6,1	5,8	5,7	4,7	3,8	0,2	
nC_{14}	4,9	5,8	6,3	5,4	4,3	0,7	0,2
nC_{15}	4,0	4,7	6,8	5,5	3,9	1,0	0,5
nC_{16}	3,9	4,3	7,5	6,7	4,1	1,2	0,8
nC_{17}	3,5	4,1	5,8	5,2	3,6	1,4	1,3
Pristane	2,0	present	present	2,0	3,8	4,6	5,1
nC_{18}	3,3	3,1	5,1	5,1	4,6	2,6	1,8
nC_{19}	3,0	3,4	4,5	4,7	4,8	2,9	2,0
nC_{20}	3,3	3,7	4,1	3,8	4,9	4,2	2,9
nC_{21}	3,2	4,3	3,2	3,2	4,4	5,8	4,0
nC_{22}	3,5	5,2	3,2	3,5	4,0	6,7	4,8
nC_{23}	3,8	5,5	3,2	3,8	4,3	10,9	13,5
nC_{24}	3,0	4,1	2,6	3,4	3,0	6,0	4,9
nC_{25}	2,3	2,8	1,7	2,8	2,7	7,7	10,3
nC_{26}	1,3	1,4	1,1	1,8	1,7	2,5	1,9
nC_{27}	0,9	0,8	0,8	1,4	1,7	2,8	3,5
nC_{28}	0,4		0,6	1,1	1,8	2,1	1,7
nC_{29}	0,3		0,5	0,9	1,7	2,6	2,4
nC_{30}	0,1		0,3	0,5	1,3	1,7	1,2
nC_{31}	0,1		0,3	0,4	1,4	1,3	1,6
nC_{32}	present		0,2	0,2	1,0	1,0	0,3
nC_{33}					0,7	0,7	0,4
nC_{34}					0,4	0,4	0,2
Total identified	85	59	66	68	69	71	65

TABLE 5

NAPHTHALENE
TETRALIN   RATIO FOR HYDROGENATION SAMPLES

Method	$\dfrac{\text{Naphthalene}}{\text{Tetralin}}$ Ratio
A	3,8
B	ca 4
C	0,5
D	0,6
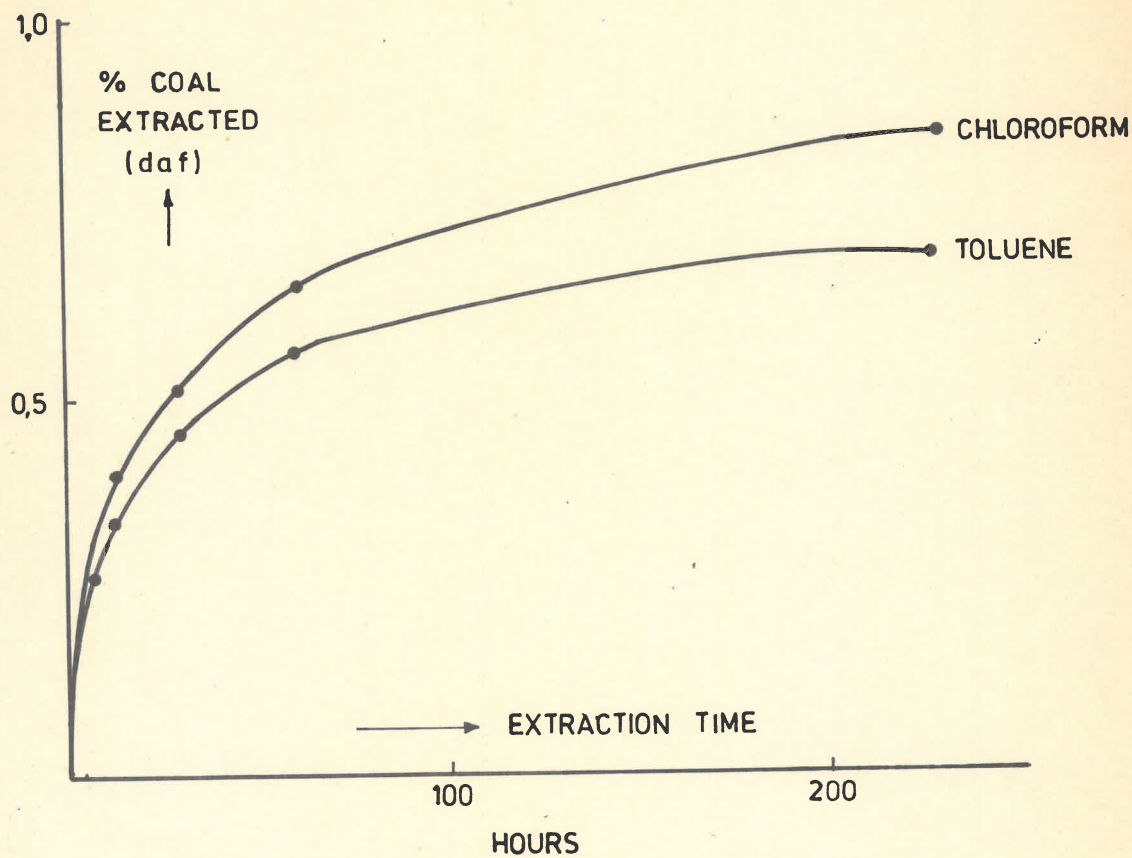
FIGURE 1: SOXHLET EXTRACTION OF SIGMA COAL.
USING CHLOROFORM AND TOLUENE AS SOLVENTS.

SAMPLE B

FRACTION
FROM
SAMPLE B

FRACTION FROM SAMPLE B,
CHROMATOGRAPHED

ABSORBANCE

FRACTION FROM
SAMPLE B
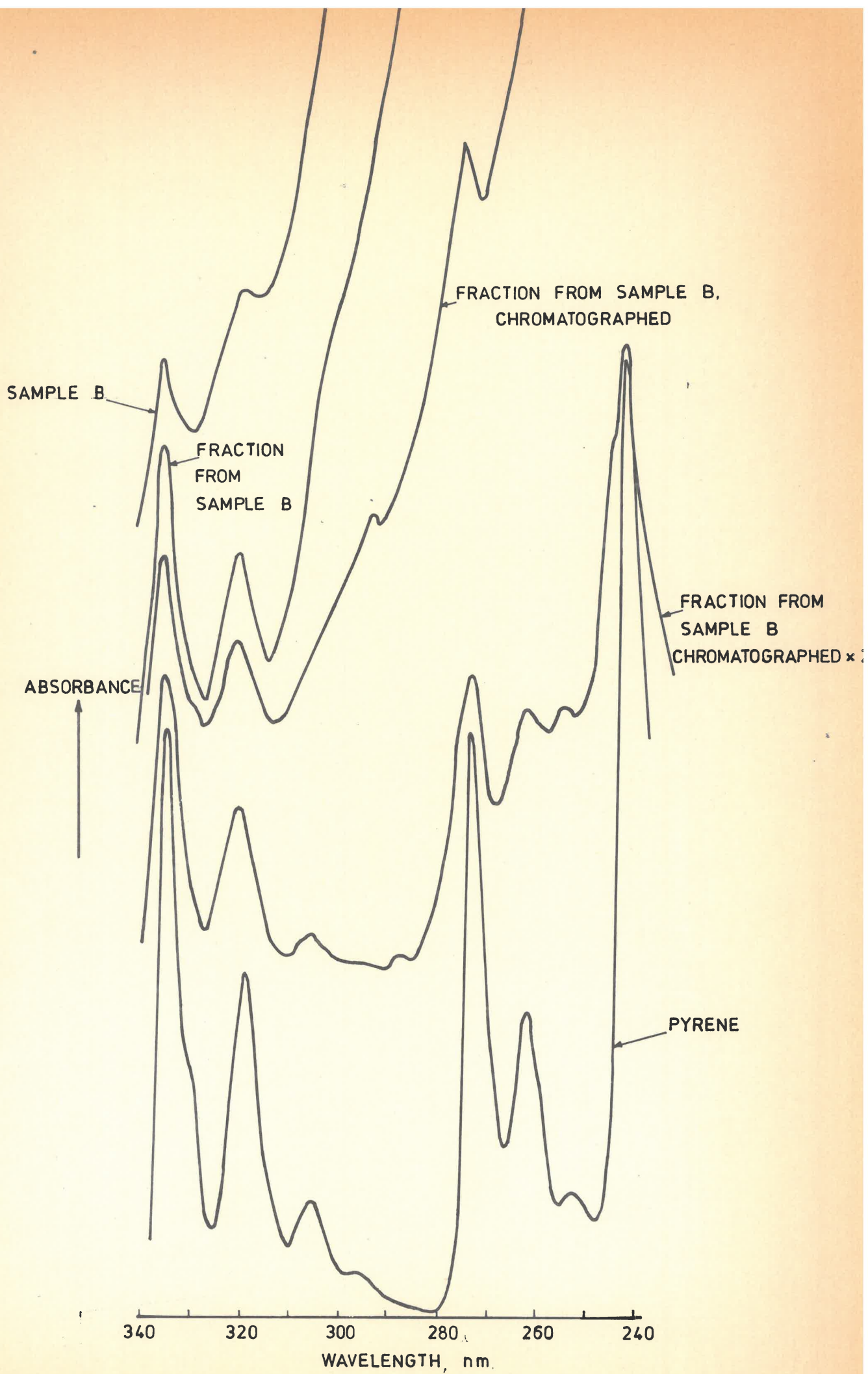CHROMATOGRAPHED × 2

PYRENE

340   320   300   280   260   240

WAVELENGTH, nm

FIGURE 2a: U.v. SPECTRA OF PYRENES IN HEXANE
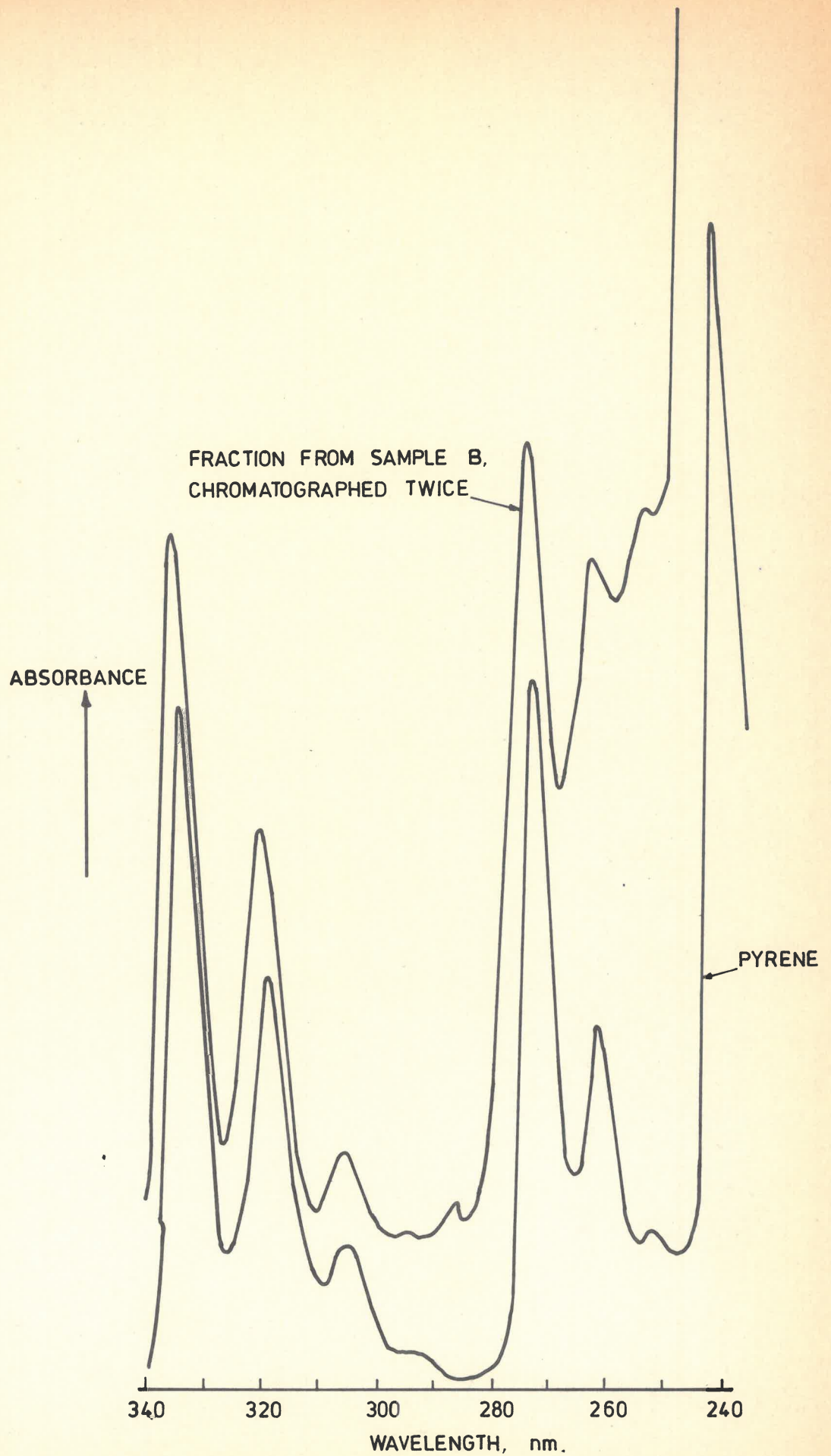
FIGURE 2 b: U.v. SPECTRA OF PYRENES IN METHANOL

a) BENZO (a) PYRENE IN HEXANE
b) c FURTHER PURIFIED IN HEXANE
c) FRACTION FROM SAMPLE A IN HEXANE
d) FRACTION FROM SAMPLE G IN HEXANE
e) BENZO (a) PYRENE IN ETHANOL
f) c FURTHER PURIFIED IN ETHANOL

ABSORBANCE

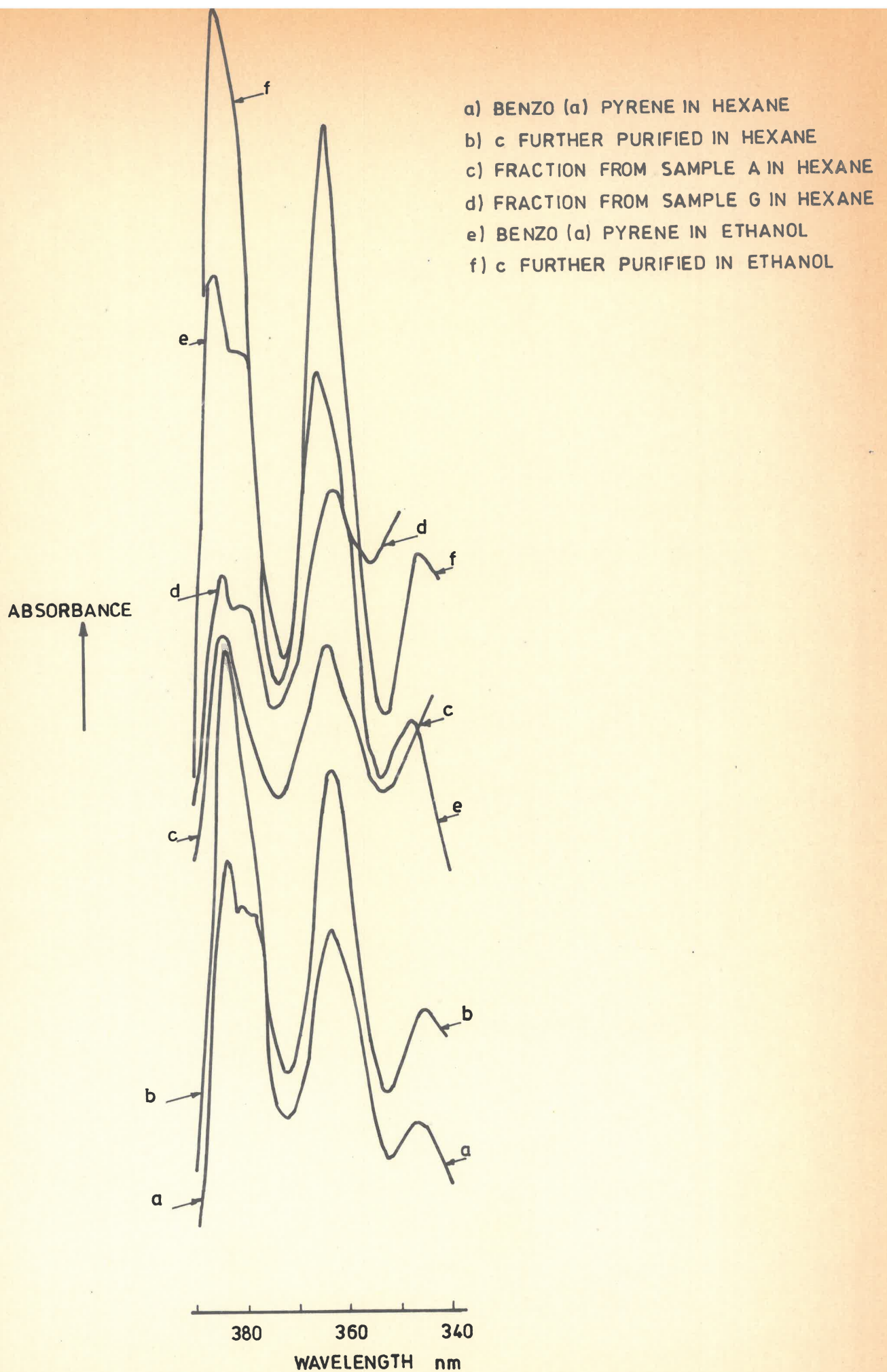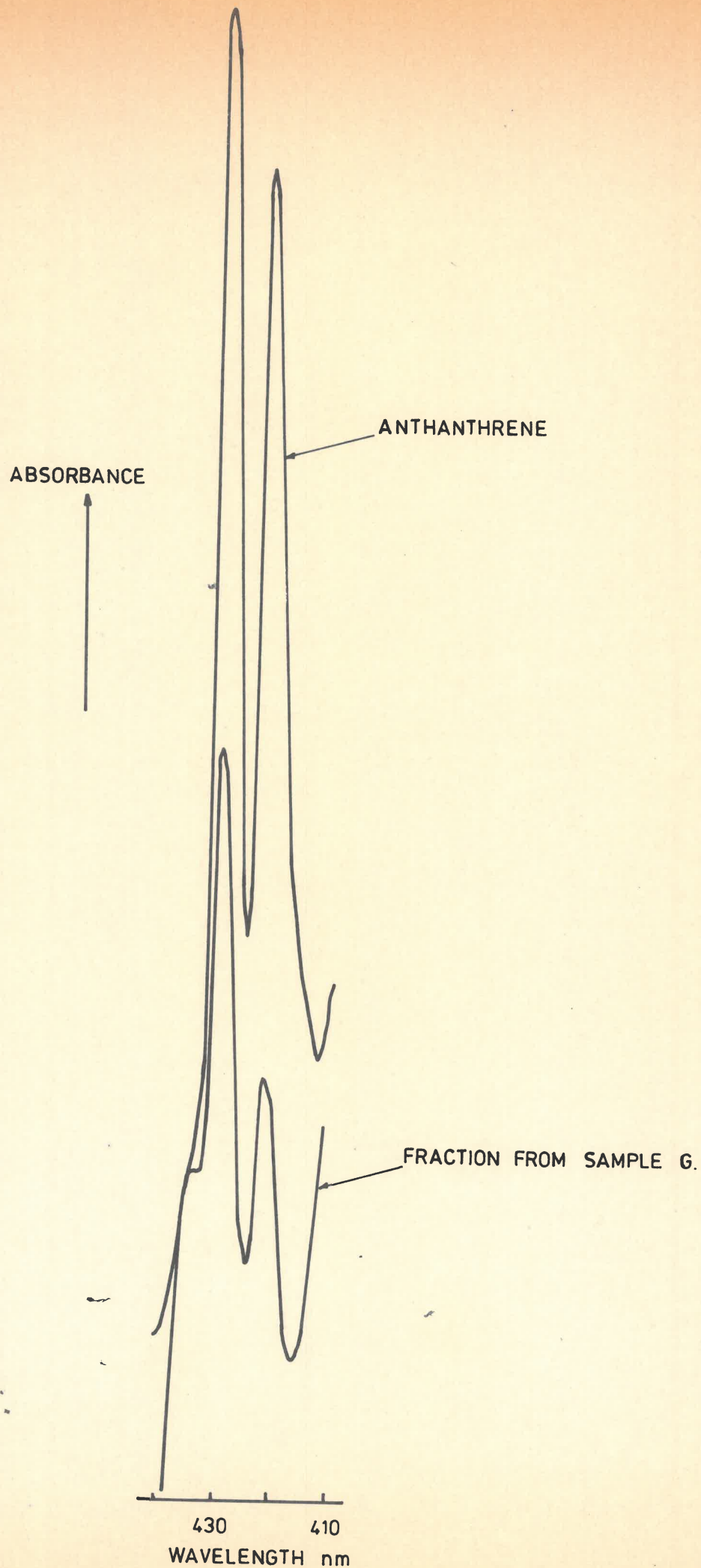380   360   340
WAVELENGTH   nm

FIGURE 3: U.v. SPECTRA OF BENZO(a) PYRENES

FIGURE 4: U.v. SPECTRA OF ANTHANTHRENES IN HEXANE