ADVANCES IN COAL SPECTROMETRY

Absorption Spectrometry

By R. A. Friedel, H. L. Retcofsky, and J. A. Queiser

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ADVANCES IN COAL SPECTROMETRY

Absorption Spectrometry

by

R. A. Friedel,[1] H. L. Retcofsky,[2] and J. A. Queiser[3]

Abstract

THE IMPORTANCE of infrared and ultraviolet-visible spectrometry in studies of the structure of coal and similar substances is described. Special experimental techniques have been developed for these studies. Thin sections of coal are preferred, but halide pellets are easier to prepare. Information obtained from infrared spectra on chemical functional groups has been discussed; the importance of both intensities and wavelengths of absorption bands has been emphasized. Functional groups assigned include aliphatic and aromatic CH, methylene and methyl groups, hydrogen-bonded hydroxyls, hydrogen-bonded and chelated carbonyls, phenolic structures, minerals, and aromatic structures that are benzenoid or polynuclear.

Infrared studies of structures of coal extracts, distillates, and reaction products of various processes, both chemical and physical, are discussed. Coallike infrared spectra of chars of model compounds have been utilized extensively in studies of coal structure.

Ultraviolet-visible absorption spectra of coals show a lack of fine structure and low spectral intensities. These results have been applied to the questions of the chemical and physical structure of coal, particularly the question of polynuclear aromaticity of coals. The color of coal is also treated. The physical-chemical origin of the color of coal may be due to free radicals, as interesting correlations of ultraviolet-visible spectra with electron paramagnetic resonance have been obtained. The optical color of coal has been explained and simulation of the color changes observed in thin sections has been carried out. The spectra and structure of coal derivatives and other carbonaceous materials are also discussed. Possible sources of error in absorption spectral measurements are pointed out.

Limited measurements of the ultraviolet-visible reflectance spectra of coal are described.

Introduction

The first portion of this bulletin is devoted essentially to a discussion of studies of coal structure by infrared and ultraviolet-visible spectrometry and the information on coal structure to be obtained from investigation of coals, coal derivatives, and similar carbonaceous materials. Special techniques required will be discussed in detail. Emphasis is placed on work carried out by the authors and the conclusions based on this work; references to all pertinent work in other laboratories are covered.

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Ultraviolet-visible spectra were being used in 1955 in this laboratory in an attempt to determine the maximum possible concentrations of polynuclear condensed aromatics in Pittsburgh hvab coal vitrain. At that time the results of various investigative techniques were indicating that the hvab coals were about 85 percent aromatic, that 7-ring polynuclear aromatics predominated, and that the polynuclear aromaticity of such coals was about 80 percent. The spectral data did not agree with these results. The early work on absorption spectra of solid coals was carried out by Friedel and coworkers (*48, 65–66*) [4] and later work was done by Ergun and coworkers (*42–43*).

Acknowledgments

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[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

INFRARED SPECTROMETRY

The early infrared investigators of coal (27–28, 132) utilized the techniques of the thin section, the mineral oil mull, and destructive distillation, and these techniques are still used extensively today. The most notable additions in recent years have been the halide-pellet technique, the use of many different extracts, and attenuated total reflectance (ATR). In the early 1950's considerable work was done at the Pittsburgh spectrometry laboratory of the Bureau of Mines: The spectra of coal and extracts were given along with structure assignments (111) followed later by other work on coal and carbohydrate chars (63, 130–131). Work was also being published on techniques and band assignments in coal spectra by Hadzi (79), Gordon and coworkers (76–77), Cannon (25), Bergmann and coworkers (7), van Vucht and coworkers (142), J. K. Brown (18–19), Friedel and Queiser (64), Roy (122), Brooks and coworkers (16), Fujii and Yokoyama (72), Kinney and Doucette (92), and others. Bergmann and coworkers were the first to report the use of the KBr pellet technique on coals. Van Vucht (142) and Gordon (76–77) published the first collections of spectra of several different ranks. Recent advances in coal structure research by infrared have been in the assignment of absorption bands in the coal spectrum, based on extensive spectra-structure correlations, intensity information, and on the knowledge gained from infrared spectra of coal before and after various chemical reactions (4, 36, 51, 54, 91, 109).

The ranks and the approximate ranges of carbon, hydrogen, and oxygen contents of coals to be discussed are given in table 1.

SAMPLE PREPARATION

For the investigation of solid coals three techniques have been used principally: (1) Ground thin sections, (2) mulls, and (3) halide pellets.

TABLE 1.—Ranks of coals and their general ranges of elemental analysis, maf basis, weight-percent

	Carbon	Hydrogen	Oxygen
Lignite (brown coals)	<77	>5	>19
Subbituminous	78–80	5–6	11–18
Bituminous	80–91	4–5	3–10
Anthracite	>91	2–4	2–3

Ground Thin Sections

Ground thin sections have been used with success in the Bureau of Mines laboratories (51, 64). Although not used extensively, the technique has been instrumental in serving as a standard for coal spectra. Spectra obtained with thin sections do not have the interfering bands of a mulling agent or the spurious bands introduced during preparation of halide pellets. One of the greatest advantages of the thin section method has been its avoidance of the scattering problem in the short wavelength infrared region where the use of either mulls or pellets is difficult. Formerly, the general background absorption that increases toward short wavelengths in mull and pellet spectra of coals was attributed to scattering by particles, or to scattering plus unknown electronic absorption. The thin section technique was used to demonstrate that Pittsburgh coal vitrain (84 percent carbon) does not scatter above 2 microns and that strong electronic absorption occurs below 2 microns (49, 64).

The preparation of a ground thin section involves the grinding of the section by hand, using a glass plate with some adhesive to hold the coal. Grinding is done down to a thickness of about 15 to 20 microns for bituminous coals, and then the adhesive is dissolved in a solvent and the section floated away from the glass plate. H. J. O'Donnell has prepared sections for Bureau spectral work by pipetting the solvent out of an evaporating dish and guiding the coal section or fragment down onto a slotted brass disk (131, 133). Salt plates can also be used. The coal section is taped to the mount and is then ready for the spectrometer. Disadvantages of the method include: (a) It is not applicable to some coals and macerals, (b) the thickness may not be uniform and thickness determinations by various methods are limited to accuracies of a few percent for very thin sections (66), (c) the fragmentation of the prepared thin section sometimes leaves no crack-free portion large enough for examination by conventional spectrometry; in such cases microspectrometry is applicable, (d) difficulties may arise in obtaining a section with low mineral content, (e) there is a possibility of oxidation occuring during the long time necessary for their preparation; but this difficulty is probably no more serious than oxidation of a powdered sample while grinding for preparation of a halide pellet. Despite these difficulties reproducible spectra

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can be obtained, and the method serves as a good standard for coal spectra.

Mulls With Petroleum Oil or Halocarbon Compounds

Cannon and Sutherland (27–28) used the mull technique, although the results were not very good because of tremendous scattering due to large particle sizes. J. K. Brown (18–19) succeeded in obtaining very good spectra by this technique and presented an excellent collection of many coal spectra over a large range of ranks. As usual with mull work, there is considerable difficulty with interference of the mineral oil bands. It is common, however, to utilize perfluoro or perchloro mulling agents to obtain spectra in those regions where hydrocarbon oils interfere. One great advantage of the mull technique is that finely ground particles are protected from exposure to air and water, and the heat of grinding is dissipated in the mulling agent.

Coal is an extremely difficult substance to grind. In order to obtain good spectra Brown found it necessary to hand grind with mortar and pestle as long as 8 hours (18–19). This requirement moves coal into a separate class relative to most chemicals which require only a few minutes or seconds of grinding with a mulling agent. The pelleting technique also requires that coal be ground for long periods.

Halide Pellets

The pellet technique has become the most popular method of obtaining infrared spectra of coals (3, 7–9, 40, 64, 72, 76–77, 82, 92, 95, 142). Potassium bromide (KBr) has been used principally, by others and in this laboratory, as the alkali halide matrix. KBr and coal are ground together, then pressed into a pellet in an evacuable die. At the Bureau of Mines pellets customarily are made 0.5 mm thick with coal concentrations of 1 percent. Disadvantages in the use of pellets of coal include: (a) Coal requires many hours of grinding with attendant increase of contaminants, (b) spurious bands not attributable to contaminants are produced in the mixing and grinding of halide and coal. Fortunately coal is an amorphous substance and does not undergo any spectral changes due to crystalline modifications, which are common difficulties in pelleting.

Long Grinding and Attendant Contamination

The grinding of KBr and bituminous coal of 84 percent carbon must be carried on for at least 16 hours on a mechanical vibrator in order to eliminate scattering in the 2- to 6-micron region. Under these conditions contamination from the hard steel or carbide vial is not noticeable. However, grinding for longer times can produce contamination and resulting background absorption and scatter. Local high temperatures are undoubtedly produced by dry grinding and can easily cause some decomposition or oxidation.

Spurious Bands

Although KBr does not possess any band in the 2- to 15-micron spectrum, the mixing and grinding together of KBr and water-containing substances such as inorganic hydrates and coal produce very intense bands at 2.95 and 6.12 microns and a weaker band at 4.90 (10, 101). These bands produced by the combination of KBr and H_2O are easily detected by comparing the spectra of pellets and mulls; for example, the mull spectrum of $Na_3PO_4 \cdot 12H_2O$ has its H_2O band at 3.13 microns, but in a pellet the H_2O band appears at 2.95 microns, resulting in erroneous assignments. The three bands are undoubtedly due to H_2O and will be referred to as $KBr–H_2O$ bands. The intensity of these bands increases almost directly with time of grinding. Even with KBr alone a pellet with a negligible H_2O band at 3.00 microns will, upon grinding for 1 minute in room air, show a sixfold increase in the H_2O band—and this band will be centered at 2.95 rather than at 3.00 microns.

KBr is not nearly as hygroscopic as generally supposed; 100 grams of KBr in saturated air take up only 0.007 gram of water (123). The principal trouble experienced with KBr pellets does not involve water in the KBr itself. KBr has been allowed to sit on a laboratory table for days without picking up sufficient moisture to cause any appreciable increase in H_2O absorption in the spectrum of the pellet; however, pellets prepared by grinding this exposed KBr produce intense $KBr–H_2O$ absorption bands. Milkey has shown that the interfering bands are much less intense if coarse KBr is used (108). Careful and extensive drying of the KBr and of coal samples as well as preparation of the mixture by grinding in inert atmospheres does not seem to prevent the development of these bands with extended grinding.

The effect of pressure in pellet preparation was investigated by comparing spectra of a KBr pellet of coal and of the KBr-coal mixture in a mull. No difference was observed. KCl-coal pellets were also made; the same water bands occurred, with the most intense band shifted very slightly to 2.97 microns.

It was found that the production of intense KBr–H₂O bands is due to an interaction involving KBr and the water in the sample. Water is present in coal as such even if the coal is dried under vacuum at 105° C. Roberts (*120*) has reported the occurence of the same bands in pellets of steroids and has attributed them to traces of water in the sample. Durie has reported the same bands in the preparation of KCl pellets of polynuclear aromatics (*39*).

Figure 1 indicates the effect of extremely long mechanical grinding and the accompanying great intensity of the KBr–H₂O bands at 2.95 and 6.12 microns (also the weaker 4.90-micron band). The KBr pellet spectra in figure 1 were obtained with an 0.5 mm pellet of 1 part coal and 200 parts KBr. Of this 1 part coal, approximately 2 percent is moisture, or a total of only 0.04 percent water in the pellet; the resulting specific extinction coefficient, K, assuming that all of the water in the coal is contributing to the intensity of the 2.95-micron band, is about 4.0 l/g cm (dashed curve in fig. 1). The sharpness of the 2.95-micron band that develops with very slight grinding may indicate that it is due to oriented water molecules on the surface of the freshly cleaved KBr crystallites. An X-ray investigation was made of these mixtures; no lines that might be assigned to a new KBr–H₂O crystal structure were found.

Because of the suspected orientation of the water molecules, a logical attempt was made to eliminate them by heat treatment of the pellets. Such treatment successfully decreased the intensity of the bands but did not eliminate them. Roberts, however, found in the case of steroid pellets that these bands could be eliminated completely by heating to 100° C (*120*). Although this treatment was not completely successful in the case of coal pellets, the bands are eliminated by determination of the spectra in hot cells operated at 175° C. It is found, however, that with cooling of the sample the bands again reappear, at reduced intensity.

The elimination of the water bands from spectra by means of hot cells is satisfactory, though inconvenient. Further attempts were made to prepare pellets which would not possess these bands. Grinding of the coal and the KBr separately, followed by mixing without grinding is not successful. Grinding the two components together is necessary for the elimination of scattering at short wavelengths. The freeze-drying technique is not very applicable to coals since they are mainly insoluble in any solvent. One promising
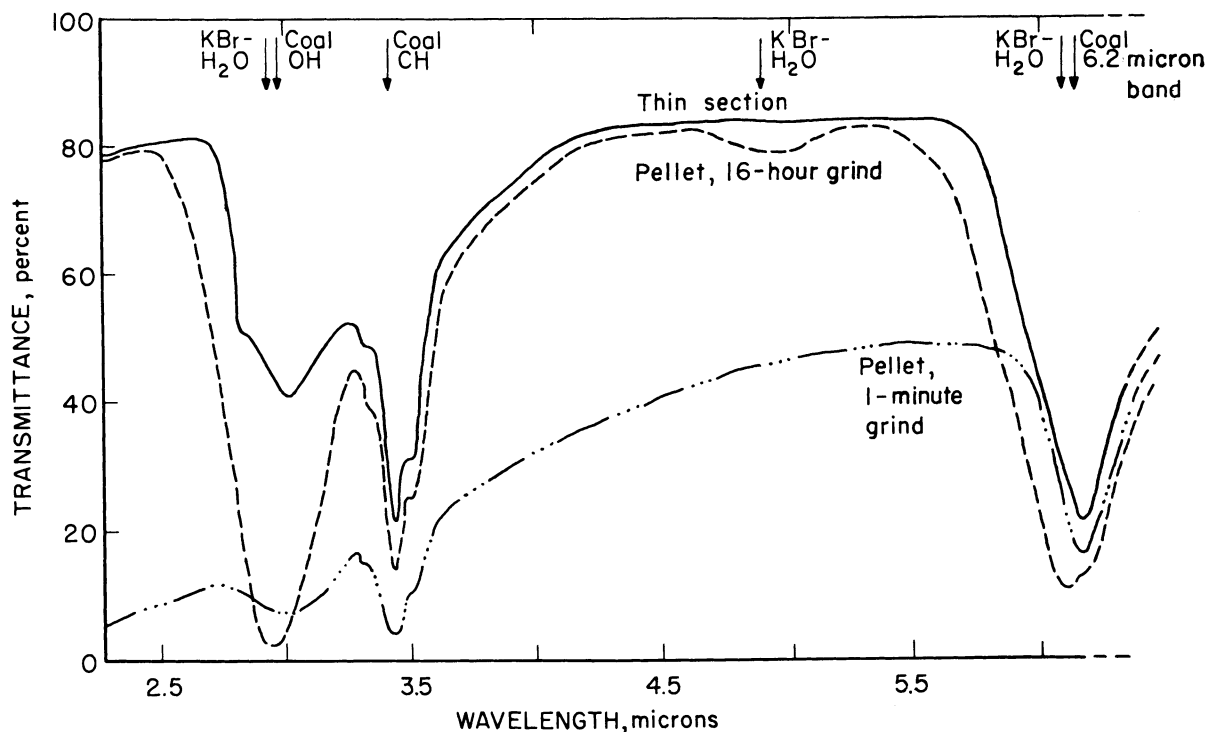
FIGURE 1.—KBr–H₂O Effect on the Spectrum of Pittsburgh Vitrain.

method appears to be that developed by Durie (*39*). KBr pellets of the sample prepared in the usual way were found to have absorption at the water band positions. If, however, grinding of the sample with KBr was done under a covering liquid, carbon tetrachloride, water bands in the resulting pellet did not appear, indicating that perhaps the troublesome water was coming from the atmosphere. Experience with adding H_2O to KBr had indicated that water *per se* was not troublesome. As shown by the preparation of a pellet using Durie's technique with a liquid containing 5 percent water (95 percent ethanol), the resulting KBr pellet of coal had no false KBr–H_2O absorption. It is suggested therefore that the success of Durie's technique may be due to the fact that the covering liquid provides a means of conducting the heat of grinding away from the KBr surfaces and prevents activated adsorption of the H_2O molecules on the KBr surfaces. It is equally possible, however, that the adsorption process requires H_2O in the vapor state. The difficulty with this method for pellets when applied to coal is that a substance such as carbon tetrachloride apparently can not be eliminated from the coal completely at temperatures below thermal decomposition of the coal. Thus one is faced with the prospect of replacing one set of bands with another. Other liquids such as hydrocarbons may be better. Use of water itself as a covering liquid has some promise, although initial attempts were frustrated by the necessity of grinding the sample after the evaporation of the water because of the recrystallization of the KBr. If this process is tried in a freeze-drying system it may be successful.

Grinding at liquid nitrogen temperatures has also been attempted in the hope that properties of the coal would be altered sufficiently so that grinding would occur more readily. This unfortunately was not found to be the case. In routine preparation of coal samples for spectral measurements the KBr–H_2O bands are most easily avoided and time is saved by grinding for short times, in spite of the scattering at short wavelengths (fig. 1, bottom spectrum).

In this laboratory spectra are determined in thin sections when feasible, but by far the majority of spectra are determined with KBr pellets; spectra in all figures except figures 2, 4, and 7 were obtained with KBr pellets.

COAL, STRUCTURE ASSIGNMENTS

Structure assignments are based on the infrared spectra of many coals and vitrains. The coal vitrains principally studied are listed as follows, along with their ultimate analyses (moisture- and ash-free), in weight-percent:

Coal	C	H	N	S	O[1]
Anthracite: Glen Burn, Curtiss-Wright No. 3, Pennsylvania	92.5	3.1	1.2	1.0	2.2
Low-volatile bituminous:					
Pocahontas No. 3, Wyoming County, W. Va.	89.82	4.46	1.53	.59	3.6
Fulton, Huntingdon County, Pa.	91.20	4.64	1.42	.96	1.8
Hocloz, Liege, Belgium	89.01	4.55	1.53	.91	4.0
Medium-volatile bituminous: Sewell, Wyoming County, W. Va.	89.32	5.15	.99	.64	3.9
High-volatile A bituminous:					
Pittsburgh, Allegheny County, Pa.	84.20	5.50	1.59	.81	7.9
Illawara, New South Wales, Australia	84.61	5.47	1.90	.57	7.5
Powellton, Logan County, W. Va.	84.94	5.08	1.61	.47	7.9
High-volatile C bituminous:					
Rock Springs No. 7, Sweetwater County, Wyo.	76.87	5.81	2.06	.88	14.3
Illinois No. 7, Harmatten, Vermillion County, Ill.	78.31	5.54	1.36	1.59	13.2
Lignite:					
Velva, Ward County, N. Dak.	71.9	5.3	.7	.6	21.5
Kincaid, Burke County, N. Dak.	67.89	5.49	.34	.50	25.7

[1] By difference.

Samples used in obtaining spectra were principally vitrains, the major constituent of most coals. One advantage in the use of vitrains instead of whole coals is that mineral interference is greatly decreased.

Spectral information on the structure of coal is obtained by reference to spectra-structure correlations. Band assignments were originally made strictly on this basis, but eventually organic and physical-chemical methods were called upon to assist the infrared interpretations. Methods that will be discussed in conjunction with infrared determinations on coal include solvent extraction, petrographic separations, pyrolysis, vacuum distillation, chemical and electrolytic reduction, catalytic hydrogenation and dehydrogenation, oxidation, chlorination, charring of model compounds and of isotope-labeled compounds, photolysis, nuclear irradiation, flash and laser irradiation, electrical discharges, charge-transfer complexing, and microbiology.

Wavelength Assignments

Structure assignments in figure 2 and table 2 include assignments reported previously (18–19, 25, 63–64, 80, 142) along with assignments based on more recent studies of chemical reactions. There remains some disagreement and the preferred assignments in table 2 are not necessarily exclusive. Alternative assignments are given.

One of the greatest uses of the infrared spectrum has been the indication of the absence of certain groups which were thought to be present. At various times such groups as simple alcohols, ketones, esters, acids, paraffin chains, and olefins have been considered in coal structure work; but infrared spectrometry has shown such groups to be present in small amounts, if at all. Such structures might still be present as parts of more complex structures.

The collection of spectra of many different ranks of coal (fig. 3) (72) is also helpful because of the possibility of correlating
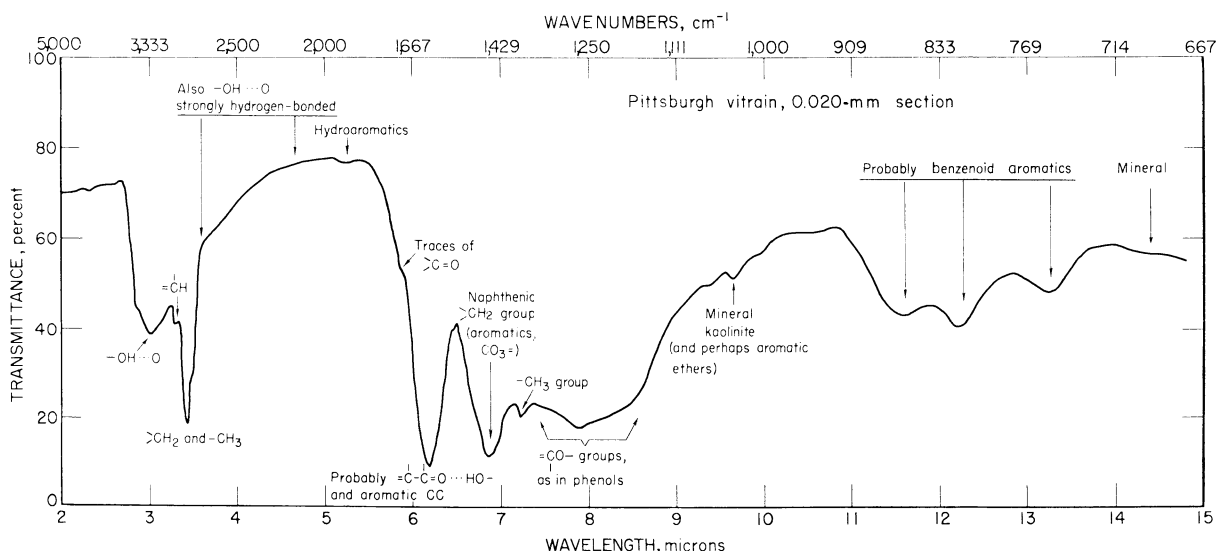
FIGURE 2.—Infrared Spectrum of Vitrain From Pittsburgh Seam Coal; Assignments of Bands to Molecular Structures.

TABLE 2.—*Band assignments for the infrared spectra of coals.*

Wavenumbers, cm⁻¹	Wavelength, microns	Estimated intensities [1]	Assignment
>5000	<2.0	—	Electronic absorption; overtones of vibration bands (weak).
3500	2.86	(sh,vw)	Single-bridge –OH (or –NH).
3300	3.0	(s)	Polymeric associated –OH (or –NH); phenols.
3030	3.30	(w)	Unsaturated CH, probably aromatic.
[2] 2950	3.38	(sh,w)	CH_3.
2920	3.42	(s)	Naphthenic and/or aliphatic CH_x.
2860	3.50		
2780 to 2350	3.6 to 4.25	(m)	More strongly hydrogen-bonded –OH than that at 3.0 microns.
1900	5.25	(vw)	Aromatic bands, prevalent for 1,2-distribution and 1,2,4-trisubstitution.
1780	5.6		
1700	5.9	(vw)	C=O.
1610	6.2	(vs)	C=O ··· HO– (and/or aromatic CC with –O– substituent); carboxylates.
1590 to 1470	6.3 to 6.8	—	Shoulder at 6.65, but no bands except in lignites; most aromatics have bands here.
1450	6.9	(vs)	CH_2 and CH_3; also aromatic CC or ionic carbonate.
1375	7.27	(w)	CH_3 groups.
1330 to 1110	7.5 to 9.0	(vs)	CO in phenoxy structures (for low-rank coals, CO in aliphatic structures).
1040 to 910	9.6 to 11.0	—	Clay minerals such as kaolinite; some phenoxy structures.
860	[3] 11.6	(m)	Isolated H's; 1,2,4-, 1,2,4,5-, 1,2,3,4,5- in benzenoids.
833	[3] 12.0	(vw)	Two adjacent H's; for example, 1,4- in benzenoids (in high-rank coals).
815	[3] 12.3	(m)	Isolated H and/or 2 adjacent H's; for example, 1,2,4- and 1,2,3,4- in benzenoids.
750	[3] 13.3	(m)	Four adjacent H's; for example, 1,2- in benzenoids.
700	[3] 14.3	(vw)	Mineral. Or 5 and 3 adjacent hydrogens; for example, monobenzenoids or 1,3- benzenoids.
690 to 400	14.5 to 25.0	—	Mineral bands; general absorption.
400 to 80	25.0 to 125	—	See "For Infrared, 25 to 125 Microns."

[1] (s)=strong, (m)=moderate, (w)=weak, (v)=very, (sh)=shoulder.
[2] Shoulder.
[3] Aromatic CCH in single and/or condensed rings, 11.6 to 14.3 microns.
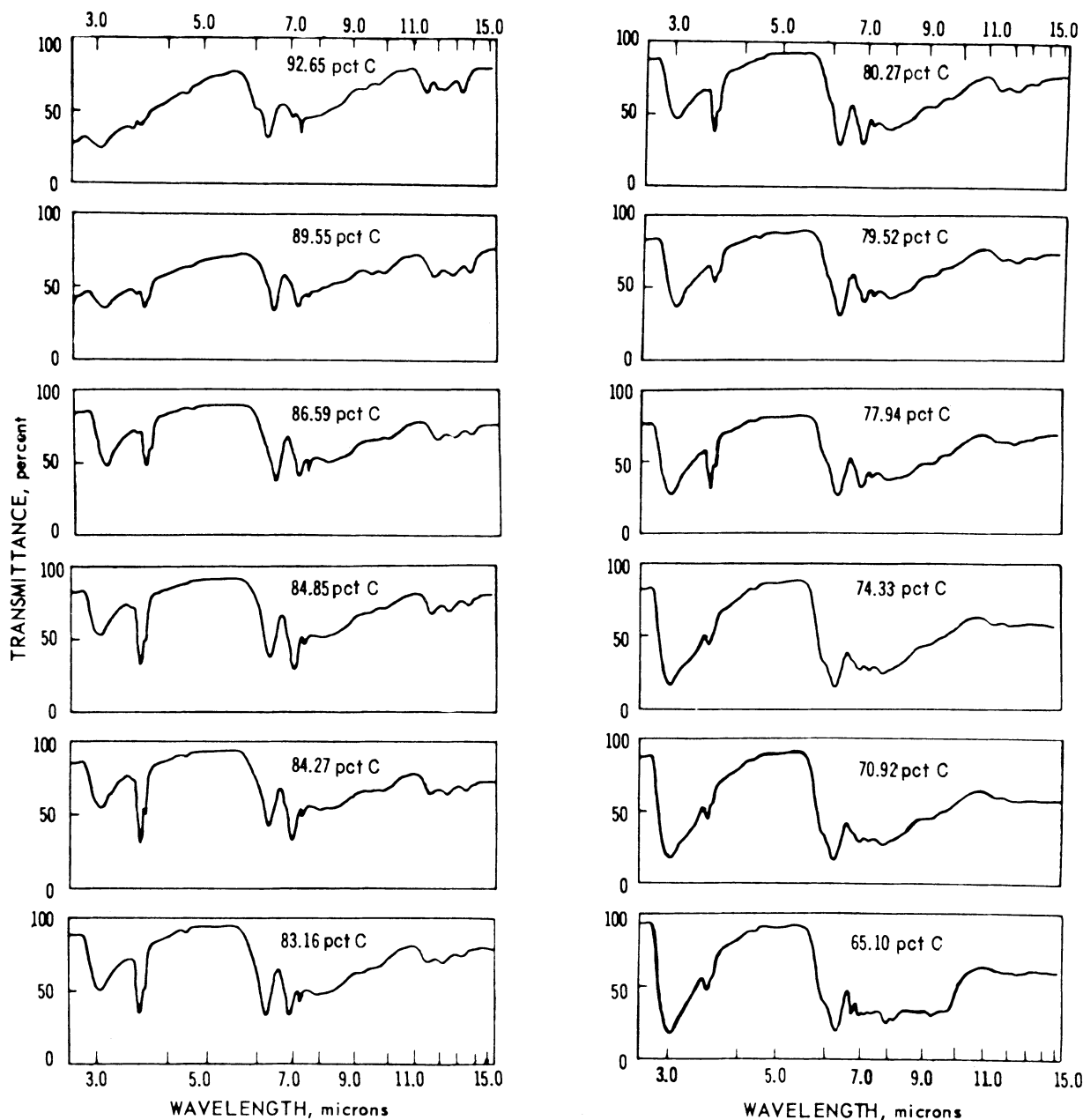
FIGURE 3.—Infrared Spectra of Coals of Various Ranks (Carbon Contents) (72).

gradual spectral changes with changes in functional group bands and elemental analyses. Some of the definite changes observed for increasing rank are the increase of the aromatic relative to the aliphatic CH, the decrease in hydroxyl absorption, the surprisingly slight changes in the long wavelength aromatic bands and in the 6.2-micron band, and the gradual change in absorption in the 7- to 9-micron region which is probably related to the decreasing oxygen content. The

position of the OH/NH absorption indicates a predominance of hydrogen-bonded groups. There is, however, a trace of unbonded OH groups as indicated by a weak band shoulder at 2.8 microns.

Discussion of some of the individual bands follows.

Under 2.0 Microns

The presence of electronic absorption has been demonstrated in the spectra of chars

(*94, 106*) and of coals (*64, 49*). In figure 4 transmittance of a thin section of bituminous coal vitrain is seen to drop sharply below 2 microns. No combination or overtone bands could entirely account for the observed absorption, and scatter is minimized as a possibility by the use of a thin section. This result is presumably consistent with the semiconductor properties of coals. The energy difference between the filled and empty electronic shells is shown by this spectrum to be sufficiently small so that the energy gap lies in the edge of the infrared region. The energy gap for Pittsburgh vitrain is located at about 0.85 micron and thus has a value of 1.5 electron volts (*49*). For an anthracite thin section the energy gap is 0.3 ev (4.5 microns) (*51*).

3 Microns

From the apparent lack of aliphatic C–O absorption at 9.0 and 9.5 microns and the presence of phenolic C–O absorption in the 8-micron region, the OH group in coal is assigned to phenols. Combined infrared and chemical evidence has shown that the OH is indeed phenolic (*23*). Much of this absorption may also be due to water that is not removable from the coal at ordinary temperatures. A point of difficulty in connection with this band in the spectra of KBr pellets of coal is the interference of the anomalous KBr–H_2O bands developed by grinding.

The broad absorption from 3.5 to about
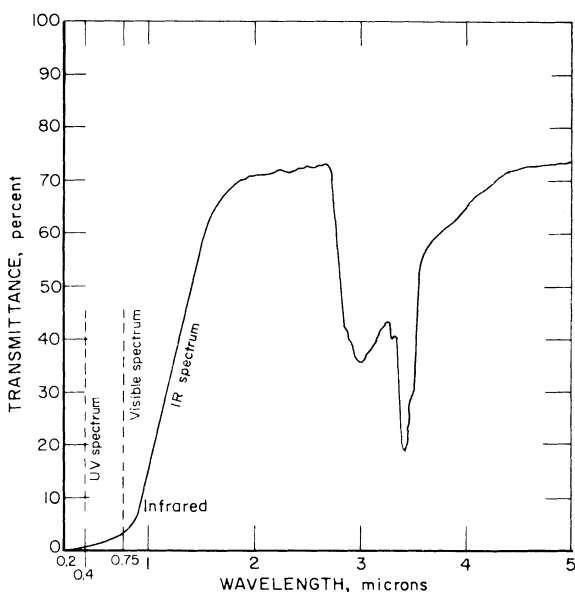
FIGURE 4.—Electronic Absorption Shown by Thin Section (0.020 mm) of Pittsburgh Vitrain.

4.25 microns is apparently due to –OH (or –NH) groups that are more strongly hydrogen-bonded than the –OH groups contributing to the 3.0-micron band. Hydroxyl groups in strongly chelated structures might be responsible for this absorption.

3.25- to 3.50-Micron Region

See "Intensity Assignments."

5.9 Microns, Carbonyl Groups

In the medium- and high-rank coals absorption at this wavelength is very weak, when present. Simple aliphatic carbonyl groups are seldom present in appreciable concentrations. This band often develops because of oxidation of the coal in handling. Preparation of thin sections does not cause this; grinding of KBr and coal can produce carbonyl absorption unless carried out in an inert atmosphere.

6.2 Microns

This assignment remains controversial. It is still not definitely determined whether the band is due to aromatic structures and/or a chelated and conjugated carbonyl structure. (This is discussed more fully under "Intensity Assignments.")

6.9 Microns

The usual assignment of this band solely to CH_2 and CH_3 groups is incorrect; additional structures are involved. (This is discussed more fully under "Intensity Assignments.")

7.5- to 9.0-Micron Region

The 7.5- to 9.0-micron region is assigned to aromatic ethers and phenols.

9- to 11-Micron Region

Some of the broad absorption from 9 to 10 microns is probably due to C–O groups. But the bands at 9.67 and 10.0 microns are the principal bands in the spectra of kaolins and other clay minerals (*64*). Kaolinite also produces weaker bands at 10.7 and 11.0 microns which are found in the spectra of coals with appreciable mineral contents. Other minerals identifiable in various spectral regions, include carbonates and silicas.

11- to 14-Micron Region

These bands have always been assumed to be due to aromatic structures (*18–19, 25, 63–64, 142*). It has been debated whether or not these aromatic structures were simple benzenoids or polynuclear condensed structures. This point is not likely to be settled by infrared spectra of coals alone. It is not

necessary to assume the presence of poly-nuclear aromatics in order to explain these bands; benzenoid structures can account for them. Types of substitution which are assignable to these groups of bands, whether in benzenoids or in polynuclear condensed aromatic structures, are given in table 2. Assignments are based on spectra of both phenols and hydrocarbons.

From the infrared spectrum it can not be determined whether or not these bands are actually aromatic bands, although an aromatic origin is strongly suggested by the increase with rank of the intensities of both the 11- to 14-micron bands and the 3.30-micron aromatic CH band. An attempt was made to obtain further information on this question by means of spectra of chars prepared from a completely deuterated paraffin. (See "Chars of Model Compounds.")

15- to 25-Micron Region

In the spectra of bituminous coals from the Pittsburgh bed specific absorption is found between 15 and 25 microns, but it is usually assignable to minerals (55) because the bands decrease or disappear from the spectrum of the vitrain which has a low mineral content. General absorption occurs throughout this region (64).

Intensity Assignments

Information on intensity is also of importance in studying the structure of coal. The spectral intensities, K values, for the absorption bands of Pittsburgh vitrain (51) are given in table 3. Intensities of various absorption bands and the structural information obtained from them are discussed with regard to Pittsburgh vitrain and other coals.

TABLE 3.—*Intensities of infrared absorption bands for Pittsburgh hvab vitrain thin sections*

Wavelength, microns	K, 1/g cm	Baseline anchor points, microns
3.0	0.14	2.7 – 4.75
3.3	.038	3.2 – 3.6
3.42	.17	3.2 – 3.6
5.3	.004	5.05– 5.5
6.2	.49	5.5 –10.8
6.9	.36	5.5 –10.8
7.27	.013	7.18– 7.37
7.9	.26	5.5 –10.8
9.67	.052	5.5 –10.8
10.0	.030	5.5 –10.8
11.6	.098	10.8 –14.75
12.3	.092	10.8 –14.75
13.3	.056	10.8 –14.75
14.3	.008	10.8 –14.75

The CH Stretching Bands

The combined intensities (peak absorbances) of the aliphatic and aromatic CH bands do not approach the amount expected for Pittsburgh vitrain, having 5.5 percent hydrogen (67). By comparing the CH intensities of many types of model compounds and correcting the coal spectrum for the H in OH, the CH bands in the coal spectrum are found to represent only about half the expected intensities. The C–H absorption per H atom of a pyridine extract is about 25 percent higher than that for the original Pittsburgh vitrain, even though the hydrogen contents are closely similar. Also, the CH bands in coal hydrogenation asphaltene do show the high intensity expected for the known hydrogen content of the substance, based on model compounds. The low peak intensities of the CH stretching bands in solid coal vitrain thus require that (a) the missing hydrogens must be of an unfamiliar type, or (b) hydrogen-containing groups are absorbing in regions not customarily expected for such groups, or (c) coals are sufficiently inhomogeneous so that measurement of the true absorption is not attained.

Recent comparisons of absorption area intensities in the 11- to 14-micron regions for extracts of Pittsburgh vitrinite with pure compound data have shown that assignments can be made to specific groups of aromatic structures (114, 134).

6.2-Micron Band

The major question is whether the 6.2-micron band is due to aromatic CC or chelated conjugated carbonyls (18–19, 32, 64, 70, 117). Both assignments have many adherents. The high intensity of absorption of the 6.2-micron band decreases with increasing rank. A correlation with oxygen content thus appears feasible. The band might be due to (1) a high concentration of aromatic structures or (2) a chelated conjugated carbonyl structure, such as in acetylacetone, kojic acid, hydroxyacetophenones, etc. If such oxygenated structures are important contributors to this band then the aromaticity of coal does not need to be large. With assignment of this strongest band to an oxygenated structure the principal structures in coal might be aliphatic. Other structures which must be considered here are the phenolic or phenoxy structures which have intense 6.2-micron bands (18–19, 64, 68). The comparatively weak absorption at the 9.7-micron phenoxy region does not encourage the assignment of the 6.2-micron band to aromatic structures; however, weak absorption may mean only

that the aromatic rings are highly substituted. Recent unpublished work on absorption areas indicates that phenols are not intense enough to produce the 6.2-micron band.

The chelated carbonyl is probably the more logical assignment. The amount of oxygen required for chelated conjugated carbonyl structures is very slight because the 6.2-micron band produced by these structures is very broad and intense ($K_{=0} \approx 25$ l/g cm, for O in chelated $C=O$): whereas in Pittsburgh vitrain the "intense" 6.2-micron band is actually rather weak, $K = 0.49$ l/g cm (table 3) (67). Thus, only 2 weight-percent oxygen is needed to produce the 6.2-micron band in the spectrum of Pittsburgh vitrain. Similar small amounts of oxygen could produce the 6.2 micron bands for other coals, as well as for chars of oxygenated compounds. The conclusion that oxygen is not involved in the 6.2-micron and (35) does not appear to be justified. Studies of chars of model compounds, to be discussed, indicate that oxygen is involved in the absorption at 6.2-microns. However, the work of Friedman and co-workers (68) on the formation of trimethyl-silyl ethers does not show the decrease in intensity at 6.2-microns that should occur.

Additional structures to be considered include the carboxylates (16). Bonds between the organic and inorganic constituents of the coal may be involved in the 6.2-micron band; there is chemical evidence indicating that carboxylates may be involved (38). Interference of the KBr–H_2O complex described above, is unfortunately a frequent contributor to absorption near 6.2 microns.

Relative Intensities of the CH Stretching and Bending Vibrations

Relative intensities of the CH stretching and bending vibrations give important structural information. The baseline intensities for the CH stretching vibration at 3.4 microns in aliphatic compounds customarily are stronger than those of the CH bending vibration in the 6.9 region. In the spectra of coals the reverse is found (table 3). This reversal is not known to occur in any reference compounds, as the stretching intensity is always greater than the bending intensity, as pointed out by Elofson (40). Thus there must be some other species absorbing strongly at 6.9 microns in addition to the CH groups. What this grouping might be is not known. It could be a small amount of a mineral carbonate which absorbs very strongly in this region. Another possibility would be an aromatic structure.

Relative Intensities of the Bands in the 9- to 11-Micron Region

Relative intensities of the bands in the 9- to 11-micron region in the spectra of vitrain and of whole coal led to the assignment of mineral structures to these bands. Coal petrography, a purely physical method, was used to assign these bands. It is possible with a petrographic microscope to remove pieces of mineral from a powdered coal in order to study the effect of changing mineral concentrations on the coal spectrum. The only spectral differences occurred in the 9- to 11-micron region and the intensities followed the mineral content of the samples. Reference spectra indicated that the minerals were principally of the kaolin type (64).

Relative Intensities of the Aromatic Bands

Relative intensities of the aromatic bands are of use in assigning structures. In the lower rank coals the predominating band is that at 12.3 microns, which is assignable to structures such as 1,2,4-trisubstituted benzenoid. In higher rank coals a shift in intensities occurs and the 13.3-micron band becomes very intense, indicating the predominance of disubstituted benzenoid structures or polynuclear aromatic structures having similar arrangements of hydrogens.

Other Infrared Methods

Two relatively new infrared methods have been applied to the study of coal: (1) Far infrared and (2) infrared luminescence.

Far Infrared, 25 to 125 Microns

Pittsburgh coal vitrain has been investigated out to 125 microns. Although there is general absorption throughout this region there is no indication of specific bands, nor is there any indication of the occurrence of energy gaps. In the 15- to 25-micron region Pittsburgh coal does have weak absorption bands, as reported previously, but these are apparently assignable to mineral rather than to organic structures in the coal (55).

Graphite was also investigated out to 125 microns. No absorption bands nor energy gaps were found.

Infrared Luminescence

In the usual method of investigation for visible luminescence under mercury light it is easy to observe strong luminescence for solutions of hydrogenation asphaltene and of coal extracts. It is difficult or impossible, however, to detect luminescence for solid coal, asphaltene, or extract. With the new method

of infrared luminescence developed by Gibson (73) solid asphaltene has been found to luminesce as strongly as a solution of asphaltene. Solid extract and coal vitrain also luminesce, though very weakly (59).

The occurrence of luminescence in the infrared and not in the visible may be indicative of species that have strong electronic absorption at long wavelengths; that is, in the edge of the visible or in the near infrared. Possible species are very large polynuclear condensed aromatics, very long conjugated systems, charge-transfer complexes, or free radicals. Free radicals are thought to be the most logical source of this luminescence.

EXTRACTS AND DISTILLATES FROM COAL

A large amount of infrared work has been done on coal extracts (20, 27, 93, 111, 135). In general it can be said that the higher the percentage of coal which the extract represents, the greater will be the similarity of the infrared spectrum to that of the original coal. For those extracts obtained from solvents which will extract only 1 or 2 percent of the coal, the similarity is not very great. One reason for the use of extracts is the avoidance of temperature effects in the preparation of spectral samples. Even though it is impossible to dissolve coals completely in any solvent the avoidance of temperature effects can be important. One of the important solvents is pyridine, which extracts about 25 to 30 percent of soluble material from bituminous coals. Such an extract is conceded to represent a sizable proportion of the coal and information obtained from it is therefore considered valid. As shown by Brown the spectra of the pyridine extract and of the original coal are practically identical (20). However, pyridine extracts of Pittsburgh vitrain from this investigation show almost a 25-percent increase in intensity per H atom from the CH stretching band. Apparently pyridine preferentially extracts materials having more intensely absorbing CH structures.

Extracts can be examined as pellets, mulls, films, or solutions. Pyridine is quite opaque in the infrared and there is little opportunity to observe the broad coal bands in the spectra of pyridine solutions among the sharp bands of pyridine. Mull spectra of extracts are usually good. Homogeneous, nonscattering films of pyridine extract are difficult to obtain by casting. However, fairly homogeneous films can be obtained by placing a warm solution of extract on two rocksalt plates to form a sandwich; then upon slowly sliding the two plates apart solid pyridine extract is deposited as a clear film. The principal use of spectra of extracts is to support the information obtained from spectra of coal itself; but this information must be used cautiously as the extract does not represent the whole coal.

Distillates are also used for the study of the structure of coal. Because of the high temperatures involved there is danger of decomposition of the coal structure. Whether or not this is important in the case of infrared spectra is debatable, because it has been shown that there are only slight differences in the spectra of coal and of distillates prepared at about 400° C (19, 113). The spectra are also similar to the spectra of coal derivatives obtained at similar temperatures, such as the spectrum of hydrogenation asphaltene (64) and resins from low temperature tar which Karr has investigated (90).

REACTION PRODUCTS

More spectral information on the functional groups in coal can be obtained by the use of chemical reactions, with investigation of the infrared spectra before and after reaction..

Temperature Effects: Spectra of Residues

Temperatures between 300° and 400° C begin to produce decomposition in most coals. The spectra of the products of decomposition differ markedly from the spectra of the original coal. Effects of temperature on functional groups in coal have been studied by carrying coals through a temperature program (1, 18–19, 64, 122). It is found, for example, that the band assignable to OH structures in bituminous coals disappears at about 500° C. The band attributable to phenoxy structures at 8 microns decreases in intensity at 300° C but does not disappear even at 550° C. The CH stretching band intensities decrease (18–19, 64, 80).

The longest wavelength aromatic band, 13.3 microns, increases with temperature; it also increases with increasing coal rank. The 6.2-micron band demonstrates its great stability in remaining unchanged through temperatures approaching 600° C. The increasing background absorption hinders the study of coals at higher temperatures. A bituminous coal heated to 600° C is practically opaque to about 9 microns (18–19) owing to electronic absorption.

Catalytic Hydrogenation; Reduction

Hydrogenation is an important reaction of coal that was used extensively in Germany during World War II to produce fuels and chemicals. The reaction is usually carried out at temperatures of 400° to 450° C at hydrogen pressures of several thousand pounds; the reaction is a hydrogenolysis in which hydrogen stabilizes the reactive species that are produced. It is a useful reaction in conjunction with infrared spectra for studying coal structure. The infrared spectrum of asphaltene obtained from coal hydrogenation at 450° C resembles the spectrum of the original coal (fig. 5) (64). Asphaltene prepared at 400° C has almost the same spectrum as vitrain except for increased aliphatic and aromatic CH stretching and bending bands at 3.3, 3.4, 6.9, and 7.3 microns, and in the 11- to 14-micron aromatic region. The intensity of the 6.2-micron band becomes weaker in the asphaltene spectrum while the aromatic bands increase, indicating perhaps that these bands do not arise from the same structure. However, as shown by the work of Reggel and co-workers (119) in the reduction of coal with lithium-ethylenediamine, the aromatic bands at long wavelength and the 6.2-micron band both decrease, while the CH bands increase (fig. 6).

The definite similarity of spectra of coal hydrogenation asphaltene to the spectra of petroleum asphalts has been noted (fig. 5) (64). The spectral differences are quantitative rather that qualitative; the petroleum asphalts have greater amounts of aliphatic structures and less of aromatic structures. Also given in figure 5 is a spectrum of coal tar obtained from high-temperature carbonization; the spectral fine structure is indicative of the chemical compounds produced from coal at high temperatures.

Hydrogenation of a carbohydrate has given interesting speculative information relative to coal structure. Nearly identical liquid (fig. 7) and solid products were obtained from the hydrogenation of sucrose and coal (116).

Chemical reduction of coal has been carried out by Reggel and co-workers using lithium-ethylenediamine (119) and by Given and co-workers using lithium-ethylamine (74). The infrared results indicated that in spite of extensive reduction the remaining aromatic character of the coal was appreciable. Extensive electrolytic reduction has been successfully carried out on coal (75, 103). Infrared has been of considerable help in characterizing the reduced coal. The aliphatic character of the product promotes good transmission throughout the spectrum; the extent of reduction is clearly indicated. However, there has as yet been no identification by infrared of new compounds or specific structures in reduced coals.

Catalytic Dehydrogenation

Catalytic dehydrogenation has been carried out on coal (118). KBr pellet spectra of the products show extensive scattering and have not been particularly helpful in characterizing the products. The loss of hydrogen should mean that aromatic structures are being produced by dehydrogenation, but infrared has not been able to detect such structures. Artifacts are an added difficulty in this work, for the solvents used thus far have entered into the catalytic reaction. The resulting chemical compounds or polymers then cling tenaciously to the coal. Though these substances are small in amount their strong intensities stand out prominently in the nonspecific spectrum of the dehydrogenation product.

Oxidation

Oxidation of coal produces expected changes in spectra (1, 7, 31, 71, 122, 142): Increase in OH absorption, decrease of the aliphatic CH, an intense new band at 5.9 microns for aliphatic carbonyls principally in carboxyl groups, and an increase in the broad absorption in the 8-micron C–O absorption region. The long wavelength aromatic bands appear to decrease significantly with oxidation, although the band at 6.2 microns does not change (7, 142). Fujii has shown that the 6.2-micron band increases with oxidation (69); this may be a real change or an apparent change caused by the intense band produced at 5.9 microns by oxidation.

Hydroxyl Group Determination

Acetylation of coals and infrared investigation (16, 23) of the products have provided important indications that OH groups in coals and coal extracts are almost exclusively phenolic. The spectra of acetylation products show by the presence of an absorption band at 5.68 microns that the ester groups become bonded to aromatic rings.

An important reagent for determining hydroxyls is hexamethyl disilazane (98, 126). The product from this reagent has incorporated in it silicon groups whose absorption bands are admirably suited for infrared quantitative analysis of hydroxyl oxygen in vitrains (68).
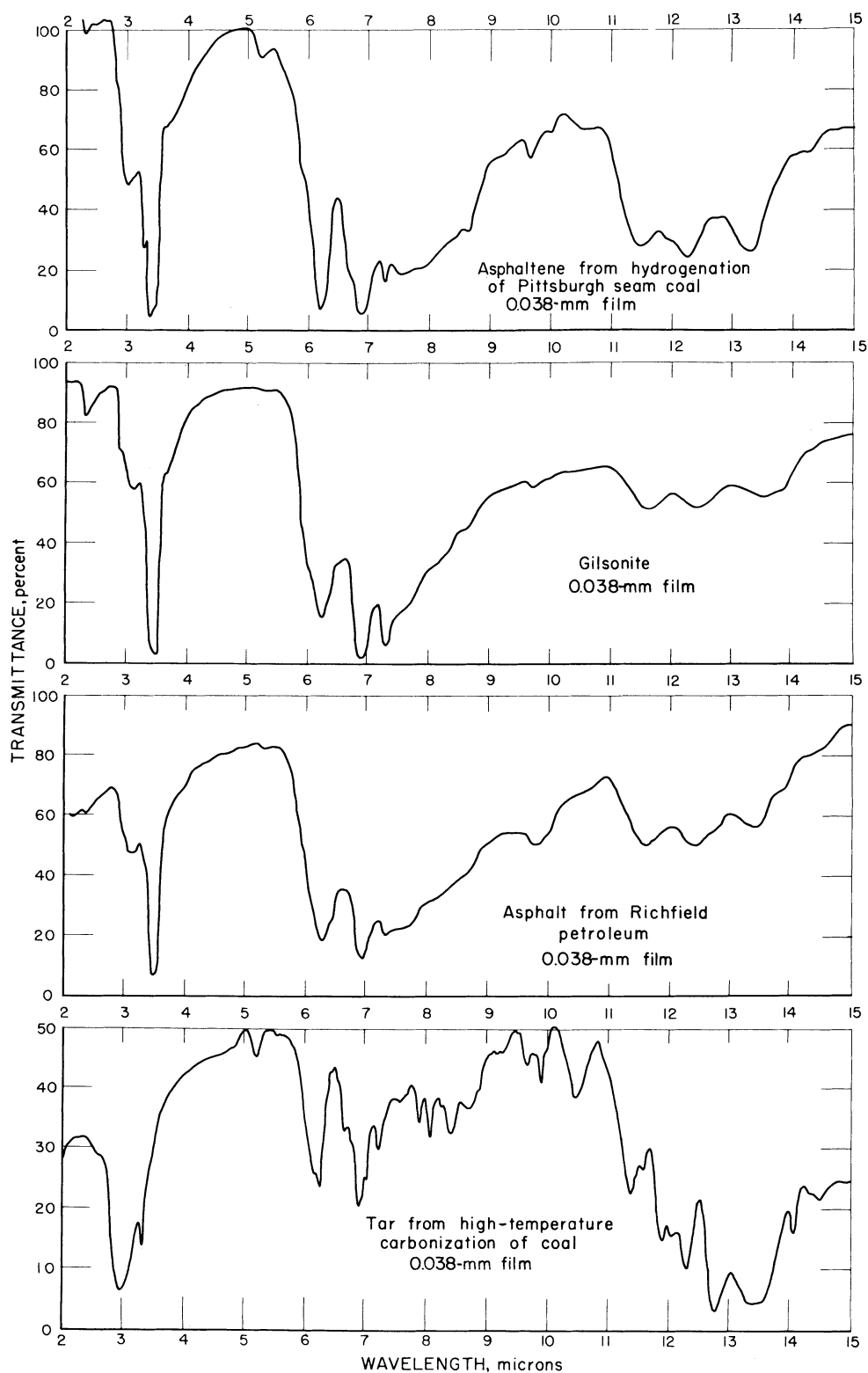
FIGURE 5.—Comparison of Infrared Spectra of 450° C Coal Hydrogenation Asphaltene With Gilsonite, Petroleum Asphalt, and Coal Tar (64).
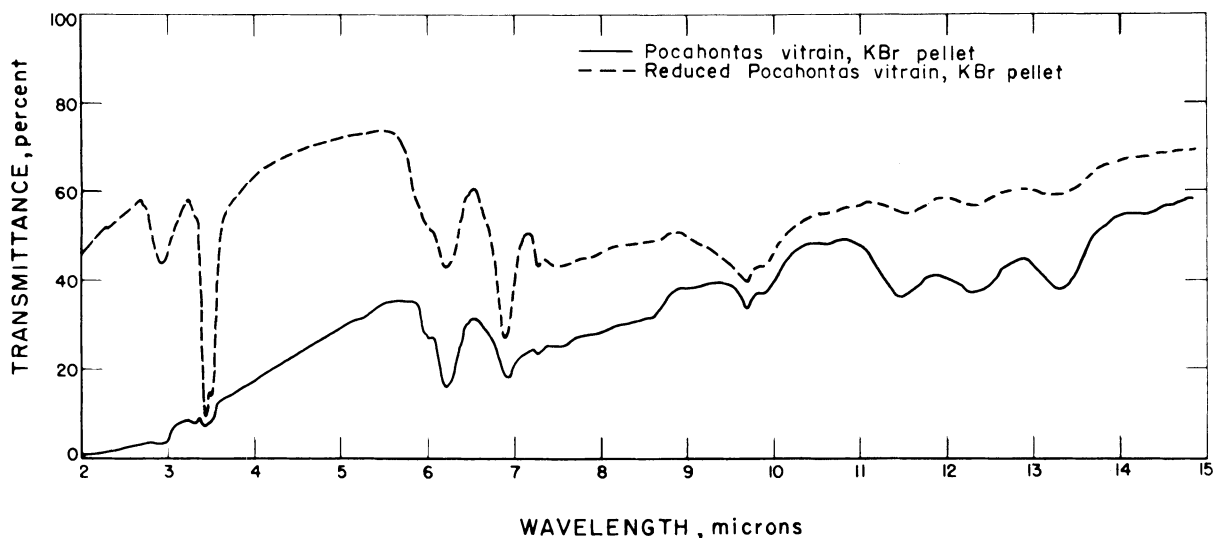
FIGURE 6.—Infrared Spectra of Pocahontas Coal Vitrain (90.5 Percent Carbon) and a Fraction Obtained From Reduction With Lithium and Ethylenediamine (54).
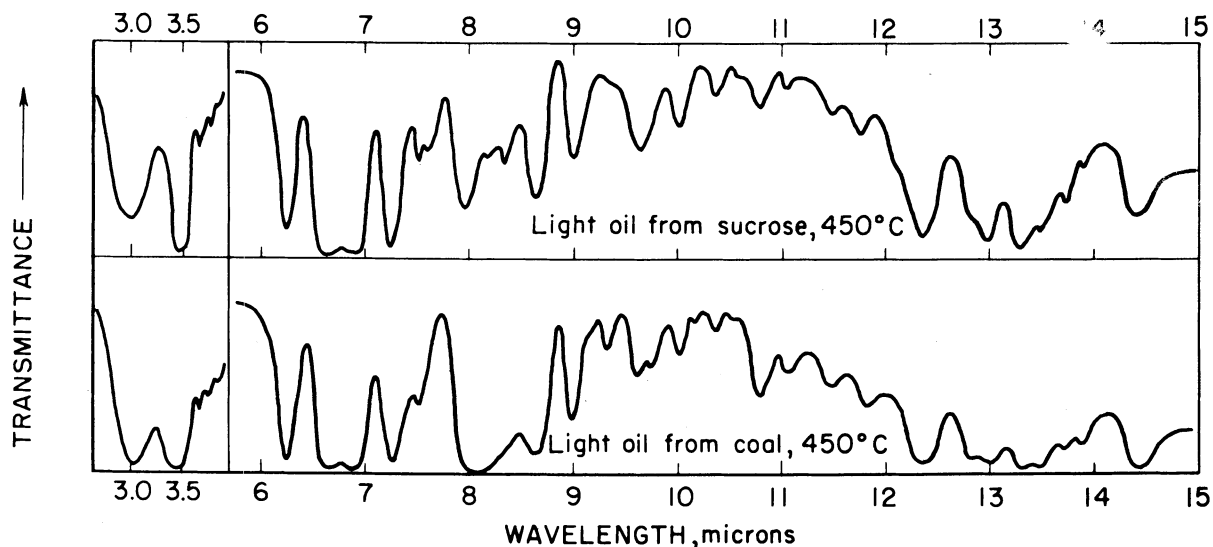
FIGURE 7.—Infrared Spectra of Light Oils From Hydrogenation of Coal and Sucrose (116).

Chlorination and HCl Treatment

In reaction with PCl₅ brown coals have been shown to possess active aliphatic hydrogens which can be replaced by chlorine (16). CH absorption bands decrease in intensity and C–Cl bands appear.

The reaction of brown coals with HCl shows a strong increase in the absorption intensity at 5.9 microns (16, 40). Alkali treatment removes the band completely and reacidification produces reappearance of the band, indicating carboxyl groups. A sharpening of the 6.2-micron band with acidification indicates a probable contribution from carboxylates.

CHARS OF MODEL COMPOUNDS

Indirect studies on coal structure can be made through spectral investigations of chars of various kinds (18–19, 54–55, 63–64, 67, 94, 130). Information pertinent to the origin of coals and other carbonaceous deposits can be obtained from such studies. It is commonly thought that a char from almost any material will give a coallike infrared spectrum, but this is not the case. Chars prepared from various carbohydrates and other oxygen-containing compounds at 300° to 500° C invariably produce spectra having the strongest band near 6.2 microns. Not all of these chars

will show the other characteristic coal bands, particularly the aromatic bands at 11.6, 12.3, and 13.3 microns. Carbohydrate chars all show these bands. Apparently a sizable percentage of OH groups in the starting material is necessary to produce chars having the best

coallike spectra (54). The close comparison of the spectra of coal and carbohydrate chars exists over a large range of temperatures; for example, the aromatic bands in the spectra of cellulose charred at 300°, 400°, and 500° C resemble respectively the aromatic
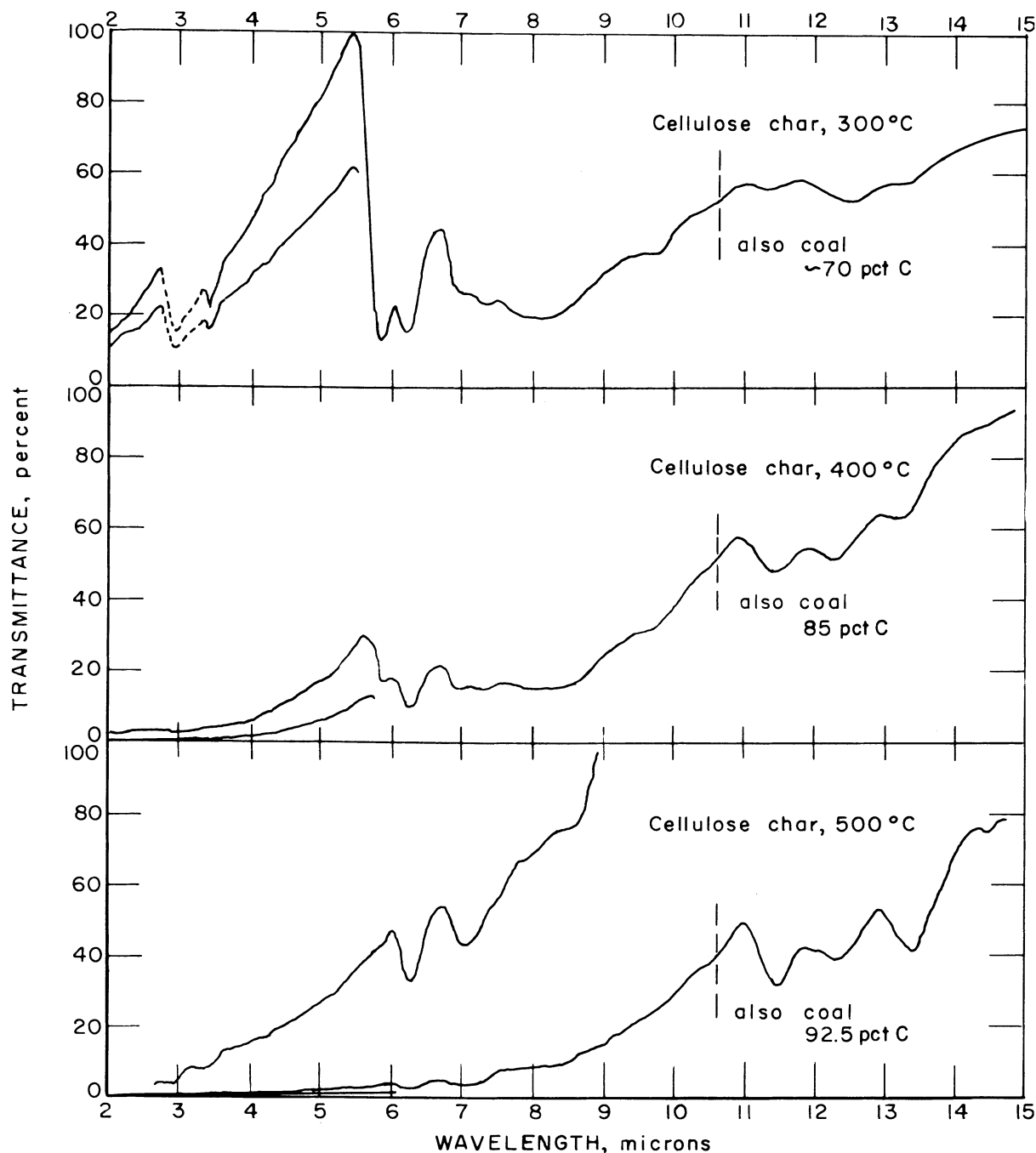
FIGURE 8.—Infrared Spectra of Chars at Various Temperatures; Correlations With Coal. Percent transmittance values refer to the partial spectra, 2 to 6 microns; other spectra are expanded arbitrarily. All spectra are char spectra; "also coal, _____ pct C" signifies that the char spectra in the region from 10.5 to 15 microns are identical to the spectra of coals of the given carbon content.

bands in the spectra of coals of 70, 85, and 92 percent carbon (fig. 8).

Char prepared from an aromatic hydrocarbon, anthracene, at 500° C in the absence of oxygen, has a spectrum with no coallike bands (fig. 9). On the other hand, char prepared from an aliphatic hydrocarbon, n-octacosane, at 450° C does produce most of the typical coallike spectrum (fig. 10). However, the spectrum is not completely coallike, since the 6.2-micron band is much weaker than the other typical coal bands (6.9, 7.3, 11.6, 12.3, 13.3). This finding indicates that a major part of the 6.2-micron coal band might be due to an oxygenated (carbonyl) structure; the weak 6.2-micron band that does occur in the octacosane char may be due to aromatic structures.

In order to check this conclusion oxygen was introduced into the chars merely by forming the chars in the presence of air. Oxidative pyrolysis of anthracene and of n-octacosane produces spectra with strong coallike 6.2-micron bands (figs. 9 and 10). These are considered good indications that the 6.2 micron band in these chars is produced by
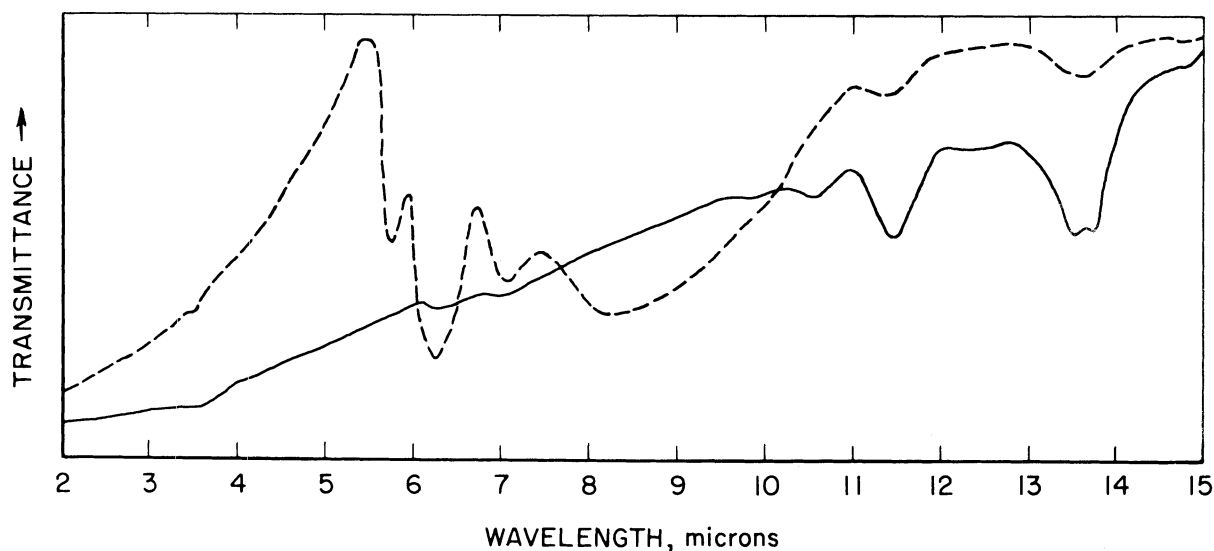
FIGURE 9.—Infrared Spectra: ——— Anthracene Char, 500° C in Inert Atmosphere; ――― Anthracene Char, 500° C in Air After Preheat at 300° C in Air.
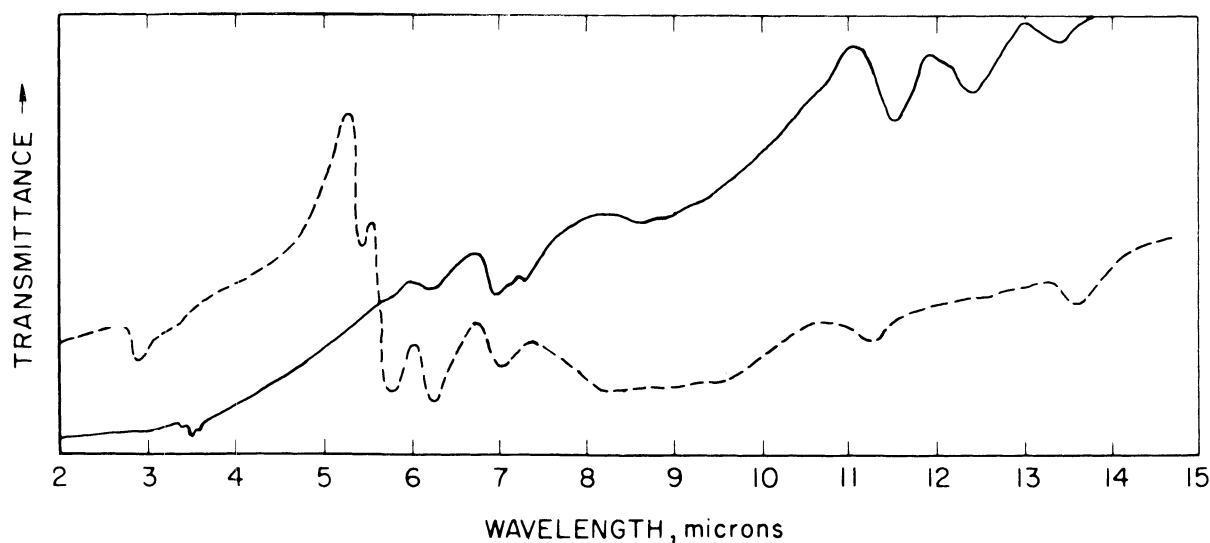
FIGURE 10.—Infrared Spectra: ——— n-Octacosane Char, 450° C in Inert Atmosphere; ――― n-Octacosane Char, 450° C in Air After Preheat at 350° C.

oxygenated structures. Among oxygenated structures the chelated carbonyls are the only structures having intense bands at 6.2 microns. The similarity of the spectra from anthracene and n-octacosane indicates that most of the absorption bands are due to oxygenated structures. Recent studies of pure phenols show their 6.2-micron bands are too weak to account for the intense 6.2-micron band in coal spectra.

In an attempt to assign certain infrared absorption bands, particularly the aromatic bands, a completely deuterated paraffin was charred in the presence of oxygen (54). The aromatic bands did not appear in the 11- to 15-micron spectrum of the char; they were shifted to wavelengths beyond the NaCl region, to 15–19 microns (55). Thus these bands in the spectrum of coal are assignable to the vibrations of hydrogens on unsaturated carbon atoms because substitution of D for H on such structures shifts the absorption bands to longer wavelengths, by a factor of about the square root of 2. Broad absorption occurs at the 7-micron CH bending region even though the deuterated char is essentially free of CH groups; that is an additional indication that the 6.9-micron band in the coal spectrum is not due entirely to C–H vibrations. A band at 6.2 microns is strong in the deuterated char and is thought to be due to a chelated carbonyl structure.

Additional labeling experiments are being carried out. For further characterization of the 6.2-micron band O^{18}-labeled compounds will be used to produce coallike chars. If the band is due to a chelated carbonyl structure a measurable shift to longer wavelengths will be observed for the labeled char.

HIGH ENERGY EFFECTS

Photolysis

The possibility that photochemical changes occur in coals on being taken out of coal mines led to the investigation of photolysis of coals by Bent and Brown (5). Irradiation of finely ground coal in water with a medium pressure mercury arc under an atmosphere of either nitrogen or air produced no change in the infrared spectrum. However, the benzene extract of the coal irradiated under the same conditions showed a strong bleaching and formation of a precipitate. Considerable oxidation takes place. If the benzene extract is irradiated in the absence of air under otherwise the same conditions there is not nearly so much change. Thus a considerable photooxidation is indicated.

Photolysis with a mercury lamp of a suspension of coal in carbon tetrachloride also produced a decrease in CH absorption and incorporation of Cl into the coal structure (5).

Nuclear Irradiation

Coals irradiated in various ways have been investigated by infrared. Generally infrared spectra have not shown any changes in solid coals produced by gamma, X-ray, or electron irradiation; changes in infrared spectra have occured for the most part only for neutron irradiation at high flux (57). It is possible that infrared spectra might detect changes produced in solid coals by other modes of irradiation if the samples are investigated immediately. Gamma irradiation of a slurry of coal in CCl_4 has produced a large amount of a low-molecular-weight soluble substance (45). The infrared spectrum of this material obtained at the Bureau of Mines showed large changes, including production of intense ester bands and incorporation of CCl bonds. The reactions involved are not known; artifacts may well be involved. The greatest changes in solid coal have been found for neutron irradiation at a flux of the order of 10^{19} neutrons per square centimeter (57). Five coals of various ranks from lignite to low-volatile bituminous were investigated. Infrared spectra of the irradiated coals were more diffuse after the treatment, but specific absorption bands were unchanged, indicating that no appreciable changes in rank had occurred (fig. 11). Irradiation had least effect on the spectrum of the lignite (77.8 percent carbon) and the greatest effect on the high rank coals of about 90 percent carbon. The diffuseness of the spectra probably indicates an appreciable increase in molecular weights due to cross-linking reactions initiated by the irradiation.

Laser and Flash Irradiation

Experiments have also been carried out using flash irradiation and laser irradiation (128). Drastic chemical and physical changes in the coal are produced by these two high-energy processes. Low-molecular-weight gases and a char are produced. The char is not easily characterized by infrared. It is similar in character to high-temperature carbons which are known to be intractable.

Electrical Discharges

Considerable work is being done on coal subjected to electrical discharges such as
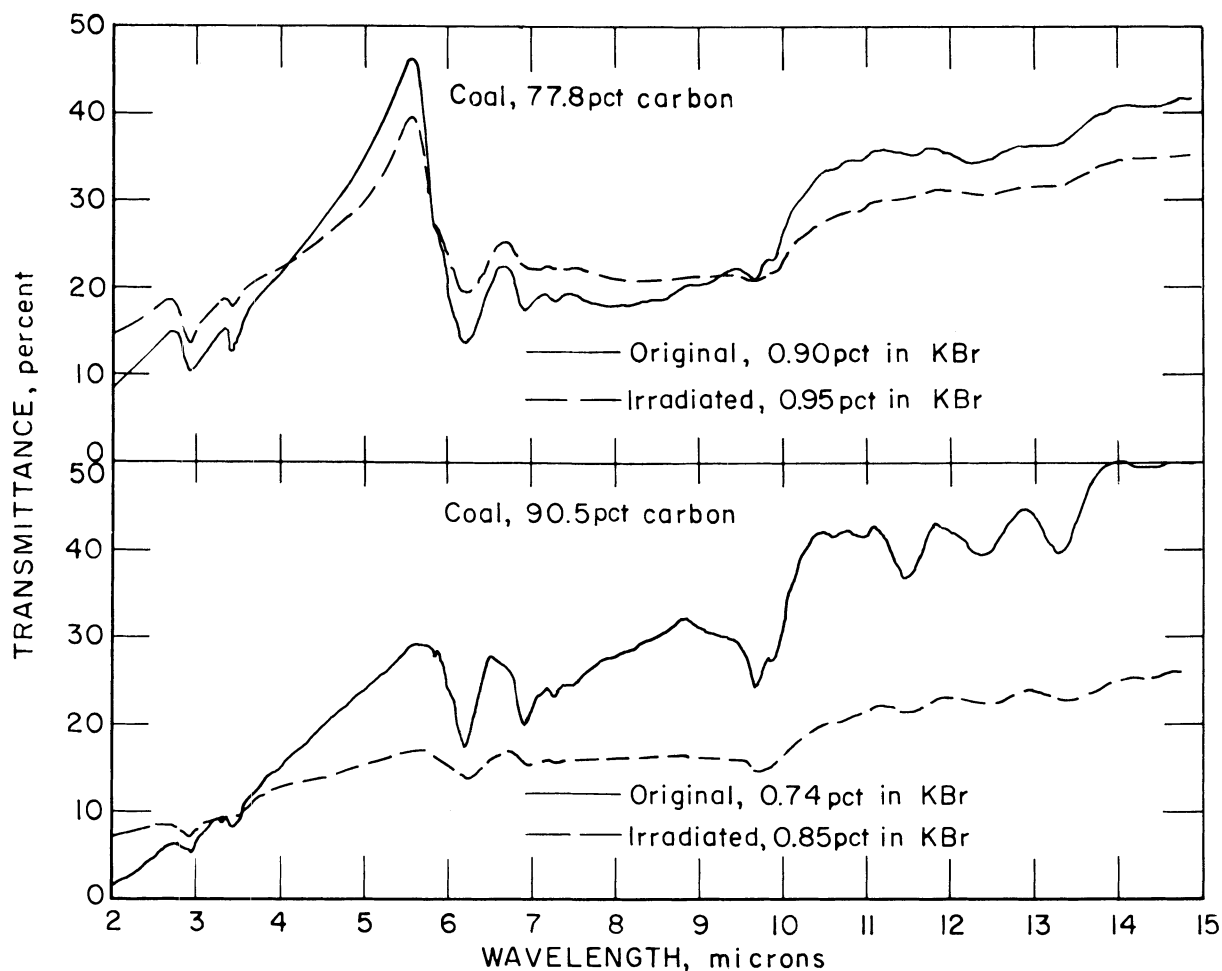
FIGURE 11.—Effect of Pile Irradiation on the Infrared Spectra of Coals Containing 77.8 and 90.5 Percent Carbon.

corona, microwave, plasma-jet, spark, etc. Infrared has been of some help in the investigation of products of coal subjected to atomic species produced in microwave plasma. However, even with pure compounds, it has been difficult to characterize the solid residues obtained from electrical processes. Microwave (143) and negative glow discharges in methane have produced solids that give broad-banded infrared spectra. Similar work has been carried out on electrical discharges in vapors of large hydrocarbons; it has been interesting to find that the infrared spectra of the products are similar (54). It appears that these electrical processes promote the complete decomposition of both small and large molecules followed by reassembling of the atoms or groups in random fashion. It is, however, possible from a study of the CH bands of these solids to establish the aliphatic and aromatic character of the product.

OTHER STUDIES

Microbiology

Work is being carried on in this field for several purposes, one of which is to search for a microorganism that will attack coal. This is a difficult problem because of the discovery that coal contains a very active antibiotic substance (121). In associated studies of bacterial attack on pure compounds infrared has been helpful in the identification of microbiological reaction products.

Sorbed Species on Coal

The sorption properties of coals have been studied extensively; the behavior of many molecules has been observed. The ability of H_2O and methanol to penetrate coal is especially intriguing; the infrared spectrum of

coal with methanol sorbed on it is of interest, but the absorption intensity of coal itself makes it difficult to study sorbates by the usual transmission methods. In preliminary attempts good spectra of methanol on coal have not yet been obtained. The method of attenuated total reflectance (ATR) holds considerable promise for sorption studies on coal. Pyridine on coal has been observed and changes in the pyridine spectrum were clearly observed, as discussed in the next paragraph.

Charge-Transfer Complexing

The structure of coal may to some extent involve a combination of donor and acceptor molecules to form charge-transfer complexes. The high free-spin concentration shown by electron paramagnetic resonance is another indication that charge-transfer complexes may be involved. At present studies are being carried on in an attempt to evaluate the charge-transfer complexing capabilities of coal as a donor or an acceptor. It may be a fairly good acceptor substance, because of the complex which seems to be formed with pyridine. The spectrum of coal extract in pyridine is very similar to the infrared spectra of pyridine with other acceptor molecules.

It is planned to investigate the possibility that coal may be a combination of unknown donor and acceptor molecules. The appreciable aromatic content of the coal would seem to signify the presence of appreciable amounts of donor molecules. The character of the acceptor molecule is difficult to estimate at this time.

AROMATICITY OF COAL

The aromaticity of coals and the types and sizes of aromatic structures in coal have been intriguing questions. The first infrared work on aromaticity was done by Brown and Hirsch who demonstrated that ratios of aliphatic to aromatic hydrogens can be obtained from the CH stretching bands (*21*). After correcting for the presence of OH groups the ultimate analysis of the coal was used to calculate the ratio of aliphatic to aromatic hydrogen atoms. Assuming that aliphatic carbon atoms are in CH_2 groups the content of aliphatic carbon was calculated. Then the aromatic carbon content was obtained by difference. The result for 84-percent-carbon coal is 72 percent aromatic carbon atoms, in single ring and/or polynuclear aromatic structures. The aromatic carbon content increases rapidly with increasing carbon content and reaches 92 percent aromatic carbon for coal of 93 percent carbon. The degree of substitution in the aromatic rings is apparently high for 84-percent-carbon coal and the principal aromatic nuclei are probably one to three rings. In 93-percent-carbon coals the substitution is less and the aromatic nuclei are larger, which is in keeping with the decreased aliphatic material in these coals (*21*).

The important study of hydrogen distribution has been continued by the recent infrared and nuclear magnetic resonance work of Tschamler, deRuiter, and Oth (*114–115, 134*), Ladner and Stacey (*96–97*), the infrared work of Fujii (*72*), and other nonspectral works (*37, 104, 109*). Present data on the distribution of hydrogen in coals between aromatic and aliphatic structures have been obtained from absorption area measurements and comparisons with model compound data. Nuclear magnetic resonance data from soluble coal derivatives have indicated the appropriate infrared calibration data. Aromatic hydrogen distribution has been obtained by a detailed study of wavelengths and intensities of the long wavelength aromatic bands as previously discussed. (See table 2 and accompanying discussion). The near infrared work of deRuiter (*33*) has shown that the intensities of the second overtones of the aliphatic and aromatic CH stretching vibrations are nearly equal for many compounds. Accurate hydrogen distribution can be calculated; the data are valid over a reasonably large range of aromaticities.

Recent results from combined infrared and nuclear magnetic resonance data on the distribution of aliphatic hydrogen into CH, CH_2, and CH_3 groups in coal have shown that the concentration of CH_3 groups is considerably higher than former estimates (*6, 115*). Infrared intensity measurements of the CH_3 band had previously indicated that the methyl group content of coals was small (*22*) and this is probably due to the fact that appropriate calibration data are difficult to choose. Nuclear magnetic resonance data on soluble coal derivatives are now indicating that considerably higher amounts of methyl groups are present in coal. Through combined data present estimates for CH_3 and CH_2 groups are good; the content of CH groups is still in doubt, as is the question of aliphatic quaternary carbon atoms in coal.

The total aromaticity of coal and the polynuclear aromaticity of coal have been studied

by various nonspectral methods (*138*). The spectral methods applied to coal and coal derivatives include ultraviolet-visible (*34, 48, 56, 65–66, 125, 141*), nuclear magnetic resonance (*22, 47*), and mass spectrometry (*127, 129*). Initial studies of the ultraviolet-visible spectrum indicated that a bituminous coal possesses low polynuclear aromaticity (*48, 54, 65–66*), but this conclusion is controversial. More recent work has indicated that the original estimate of low polynuclear aromaticity may be correct (*56*). Asphaltene from coal hydrogenation has also been assigned a low polynuclear aromaticity (*47, 54, 65*). Petroleum asphaltene is believed to have an even lower polynuclear aromaticity from measurements by infrared (*64*), although results from proton magnetic resonance indicate the presence of some large polynuclear aromatics (*144*).

ULTRAVIOLET-VISIBLE SPECTROMETRY

The electronic absorption spectra of aromatic systems have long been used as important chemical tools. Usually, the presence of polynuclear condensed aromatics is determined qualitatively and quantitatively by the absorption bands in the ultraviolet-visible spectrum. For those substances that have no specific absorption bands, the ultraviolet-visible spectrum can still be valuable for determining limits of polynuclear aromaticity. Such measurements are important in the investigation of carbonaceous materials that are low in hydrogen content and are usually considered highly aromatic; if extensive polynuclear aromaticity is not substantiated by ultraviolet-visible spectra, then it behooves the researcher to look at other possible molecular structures. For example, quantitative determinations of low limits of polynuclear aromaticity in bituminous coal vitrain require the presence of large amounts of aliphatic and cyclic structures; the low hydrogen content necessitates the presence of many tetrahedral carbon-carbon bonds, in three-dimensional diamondlike structures (53–54, 66).

In support of the ultraviolet findings, one interpretation of infrared spectra of bituminous coals has questioned the presence of large amounts of polynuclear condensed aromatics in coal (64).

ULTRAVIOLET-VISIBLE SPECTRA AND THE POLYNUCLEAR AROMATICITY OF COAL AND COAL DERIVATIVES

Coal

The first attempts to use the ultraviolet-visible spectra of coals to determine limits of polynuclear condensed aromatics are described in a publication in 1957, in conjunction with a discussion of the color of coal (48).

Color of Coal; Absorption Maxima

Spectral measurements in the ultraviolet and visible regions were made on Pittsburgh vitrain (84 percent carbon) (table 4) in an attempt to measure possible concentrations of polynuclear condensed aromatics. Spectra of thin sections in the visible region and of potassium bromide pellets in the ultraviolet region, showed that absorption increases gradually from the edge of the infrared through the visible and through the near ultraviolet region to 2,100 A. The only specific absorption is a broad band shoulder near 2,650 A which is typical of low-temperature chars and of strongly oxidized aliphatic substances (fig. 12).

Quantitative measurements in the visible spectrum and semiquantitative measurements in the ultraviolet spectrum were made in order to determine absorption intensities
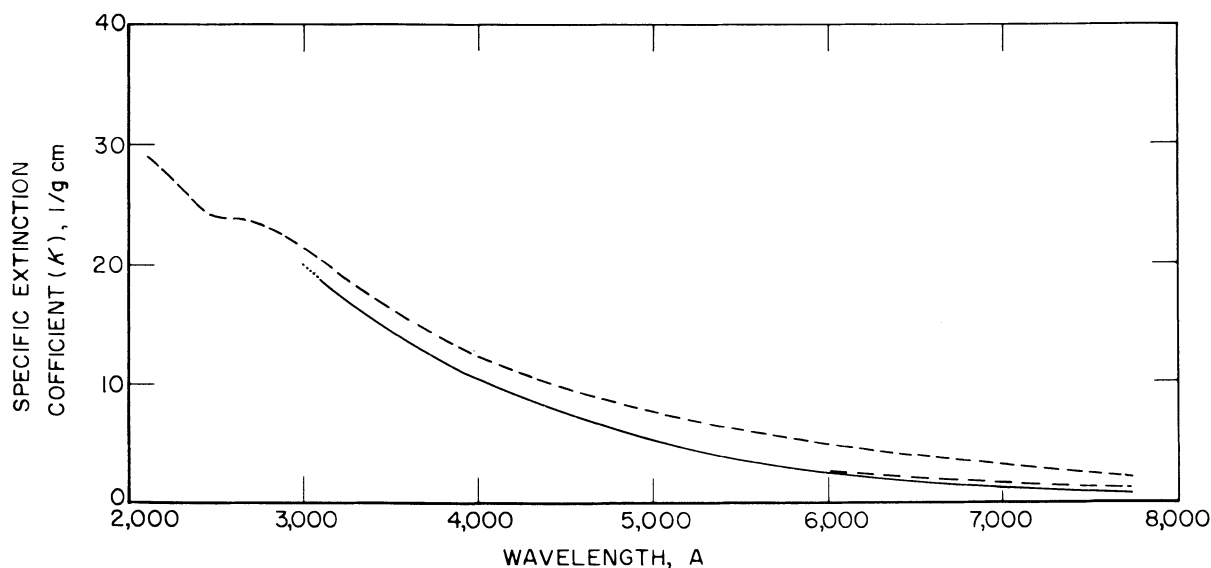

FIGURE 12.—Spectra of Pittsburgh Vitrain, Thin Section (———) and Potassium Bromide Pellets (– – –).

TABLE 4.—*Ultimate analyses*

Material	Composition, weight-percent, maf				
	C	H	N	S	O[1]
Vitrain, Pittsburgh high-volatile A Pittsburgh seam	83.7	5.3	1.6	0.8	8.6
Vitrain, Velva lignite	71.9	5.3	.7	.6	21.5
Pitch, Koppers mp 80° to 85° C	91.7	4.7	1.2	.5	1.9
Asphaltene, from 400° C hydrogenation of Pittsburgh seam coal	86.7	7.3	1.4	.5	3.9

[1] By difference.

(specific extinction coefficients, K). The K values for Pittsburgh vitrain at two wavelengths were compared with the K values of the principal absorption bands of various polynuclear condensed aromatics and of conjugated polyenes as shown in table 5. Violanthrene, a highly colored polynuclear condensed aromatic compound has a K value of 200 for its absorption band at 4,920 A; at the same wavelength Pittsburgh vitrain has a K value of 5.6. In the unlikely case that all absorption intensity of Pittsburgh vitrain at 4,920 A is due to violanthrene, the maximum possible amount of violanthrene nuclei would be about 2.8 percent. Different types of polynuclear aromatics would be expected in coal, but such a proposal is countered by the absence of the spectral structure that should result from such a complex mixture. The most important limitation is the absorption intensity, that can be seen in table 5 to be too low in bituminous coals to substantiate high concentrations of polynuclear condensed aromatics or of conjugated polyenes.

The weak color intensity of bituminous coals is also shown by the absorption index,

TABLE 5.—*Intensities of principal absorption bands of various polynuclears and of conjugated polyenes; comparison with intensities of bituminous vitrain*

	λ, A	Specific extinction coefficient, K, 1/g cm
Coal: 84-percent-carbon vitrain, Pittsburgh seam	4,000	10.0
Do	4,920	5.6
Compound (solutions):		
Violanthrene [1]	4,920	200
Anthanthrene [1]	4,330	289
Dibenzo[a,i]pyrene [1]	3,970	295
Dibenzo[a,h]pyrene [1]	3,135	561
Coronene [1]	3,018	771
Fluorenone [2]	2,574	498
Anthracene [2]	2,534	1,160
Phenanthrene [2]	2,520	393
Naphthalene [2]	2,220	762
Octatrienol [3]	2,650	434
Decatetraenol [3]	2,990	432
Do	3,110	432

[1] Reference *29*.
[2] Reference *61*.
[3] Reference *11*.

0.025 at 5,460 A, calculated from absorption measurements on thin sections of Pittsburgh vitrain. A higher value, 0.04, was obtained by Huntjens and van Krevelen (*86*) for a thin section of Velsen vitrain. Absorption indices calculated by various workers from reflectance measurements are appreciably higher than 0.025 (*14, 26*). This discrepancy is presumably due to the fact that the reflectance equation is practically insensitive to absorption indices in the range of 0.025.

The color of coal is not logically attributable to small amounts of polynuclear condensed aromatics since, as Hirsch has stated, polynuclears of the sizes indicated by X-ray measurements do not possess the color of coal (*84*). The color of coal may be attributable to the structures with unpaired electron spins, presumably free radicals, shown to be in coal by paramagnetic resonance measurements (*88, 136*). Free radicals absorb radiation over wide wavelength ranges, as does coal, and in some cases free radical spectra also are devoid of spectral structure. Free radicals constitute only a fractional percentage of the coal (*88, 136*) and their structures are unknown; they might be polynuclear condensed aryl radicals, semiquinones, triarylmethyls, etc. It is possible that the dark colors of many different reaction residues with nonspecific absorption spectra might be due to free radicals.

If the color of coal is due to free radicals, the visible absorption intensity should increase with increasing numbers of free radicals. The existence of such correlation would not constitute proof; but absence of any correlation would nullify the hypothesis. A correlation has been sought for free radicals and absorption intensity in high-volatile bituminous vitrain and lignite vitrain. Ratios of the specific extinction coefficients at three wavelengths are compared in table 6 with the ratio from Ingram's values for concentrations of free radicals in coals of 84 percent carbon and 72 percent carbon (*87*). A good correlation is obtained (*48*). The trend shown by increasing ratios of coefficients

TABLE 6.—*Correlation of color intensity and free-radical content of 84-percent-carbon and 72-percent-carbon vitrain thin sections*

Line	Vitrain	Specific extinction coefficient, K, 1/g cm			Free radicals per gram
		7,000 A	5,460 A	4,000 A	
1	Pittsburgh vitrain (84 percent carbon)	1.22	3.7	10	0.42 x 10¹⁹
2	Velva lignite vitrain (72 percent carbon)	1.25	2.6	6.1	.15 x 10¹⁹
	Ratio, line 1/line 2	1.0	1.4	1.6	2.8

with decreasing wavelengths in the visible spectrum indicate that the ultraviolet intensity ratios may approximate the free radical ratio. This correlation indicates but does not prove that free radicals are an important cause of the color of coal. Other Bureau work demonstrated a similar correlation; color intensity and free radical concentrations both decreased with lithium-ethylenediamine reduction of a series of coal vitrains (*119*).

Absorption Areas

In addition to the method based on comparison of peak intensities of model compounds with coal, possible concentrations of polynuclear condensed aromatics in vitrain can also be estimated by the method of comparison of total areas of absorption curves. This method was not wholly successful for coal because the very thin sections required did not permit determinations over the entire spectral range. However, the values obtained through a combination of thin sections and KBr pellets (fig. 12) give reasonable data and the most reliable data obtained to date on solid coal. For coal derivatives the method is entirely applicable.

Sample Preparation

Thin Section.—Thin sections of vitrains were mounted on pieces of optical quartz by means of an optical adhesive. Small portions of the section that were free of holes and mineral occlusions were masked off for the measurements. Mechanical determinations of thickness were made by various methods: Micrometer measurement of xylene-washed pieces of the section removed by melting the adhesive and sliding the section onto glass; determinations of weight and area of a removed section or portion of it; and measure-

ments by a Leitz Tolimeter [5] before and after a section is chipped off the adhesive. For 10-micron sections all of these methods are accurate to within 0.5 micron. The 10-micron sections are uniform in thickness, but the sections thinner than 5 microns vary in thickness so that only average values can be obtained.

The most accurate thickness determination has been the method based on absorbances (optical densities). A thick section, 20 microns, is measured to within ±0.5 micron by a micrometer or Tolimeter and its absorbance density is measured at a given wavelength. Reflectance measurements are made at this wavelength and corrections are made to the absorbance for reflection losses. Then the absorbances of very thin sections, corrected for reflection losses, are used to calculate the optical thickness of these sections. This method is considered more accurate than those which measure mechanical thickness, because the optical thickness is independent of variations in thickness and of inhomogeneities such as submicroscopic holes.

Potassium Bromide Pellets. — Potassium bromide pellets were prepared by placing the sample, potassium bromide, and two stainless-steel or agate balls in a stainless-steel or agate capsule mounted on a motor-driven vibrating arm. The balls strike the ends of the capsule 60 times per second. This grinding is important in attempting to achieve uniform distribution and narrow range of particle size in order to obtain accurate optical density measurements. Pressing of 0.5-inch-diameter pellets, about 0.5 mm thick, was done in an evacuable die at 20,000-lb thrust. Concentrations are expressed in the same units as solutions; that is, grams of sample per liter of potassium bromide plus sample. The curve in figure 12 for 68.5 g/l nearly matches the spectrum of the thin section, but this concentration is too high to permit measurements below 6,000 A. The curve for 1.37 g/l lies above the curve for the thin section, since the apparent absorption includes an appreciable percentage of scattering.

As mentioned previously, the only spectral structure found is a broad band shoulder near 2,650 A. The same band has been found to exist in a great many coal derivatives as well as in chars prepared from oxygen-containing compounds. The infrared spectra of these materials often differ but the strong

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[5] Reference to specific makes or models of equipment is made for identification only and does not imply endorsement by the Bureau of Mines.

6.2-micron band invariably occurs; this band has been attributed to aliphatic hydrogen-bonded, conjugated carbonyls (64) as in the α-hydroxy pyrone, kojic acid:

H - - - - O
| ||
O   C

O   CH₂OH
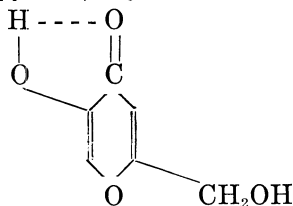
Also, the ultraviolet spectra of this and similar compounds show their only band to be near 2,650 A, the location of the coal absorption band. Other aliphatic structures such as β-diketones also show their strongest infrared and ultraviolet absorption bands in the same spectral regions as the 6.2-micron and 2,650 A coal bands. These chelate structures are very intense absorbers; only small amounts would be needed to produce the typical coal bands.

Aromaticity

The results of statistical analyses (141) on 84-percent-carbon vitrain have indicated that the vitrain consists of high concentrations of aromatic structures, with an average of 5 to 6 aromatic rings. A comparison of K's in the ultraviolet region for a group of 5- and 6-ring polynuclear condensed aromatic hydrocarbons in dilute solution has been made with K's found for vitrain thin sections. K's for vitrain thin sections have been obtained down to 3,000 A; corrections have been made for absorption of the adhesive, which becomes appreciable below 3,400 A and is prohibitive below 3,000 A.

In table 7 the K's of Pittsburgh vitrain are compared with the average K for the most intense band for 27 5-ring compounds and for 20 6-ring compounds. Differences in K's are large; the possible concentration of mixtures of these 5- and 6-ring compounds in Pittsburgh vitrain could be 8.5 and 6.0 percent, respectively. A more direct quantitative comparison was made by determining the average K at a certain wavelength, 3,050 A, for all of the 5- and 6-ring compounds and comparing this average with the K of vitrain at the same wavelength. For a mixture containing equal amounts of all 47 of the 5- and 6-ring polynuclear condensed aromatics, the maximum possible percentage of such a mixture that could be present is 13 percent. The compounds used in these determinations include a large number of benzfluorene-type compounds containing one five-membered nonaromatic ring. The K's of these are ap-

TABLE 7.—*Specific extinction coefficients of Pittsburgh vitrain and of polynuclear condensed aromatics with 5 and 6 rings*

Material	K, 1/g cm	Maximum in 84 percent C vitrain, weight-percent
Coal vitrain:		
84 percent C, 3,500 A_____	15	—
84 percent C, 3,000 A_____	20	—
84 percent C, 3,050 A_____	[1] 19	—
Polynuclear condensed aromatics in dilute solution:		
5-ring compounds:		
Band maxima, 3,500–2,900 A_	[1, 2] 236	[3] 8.5
At 3,050 A_____	[1] 143	[4] 13
6-ring compounds:		
Band maxima, 3,260–2,910 A_	[1, 5] 337	[6] 6.0
At 3,050 A_____	[1] 144	[4] 13

[1] Average.
[2] Range, 132–1,606.
[3] 20/236.
[4] 19/143.
[5] Range, 167–1,080.
[6] 20/337.

preciably less than K's of compounds consisting entirely of six-membered aromatic rings. The K of Pittsburgh vitrain therefore would allow a somewhat greater concentration of benzfluorene types than of the intensely absorbing acene types.

The potassium bromide pellet spectrum should indicate any sharp change in an absorption curve, at least qualitatively. This premise was investigated by comparing complete spectra of solids and solutions of soluble substances. Experiments on coal-derived asphaltene and coal-tar pitch were carried out to determine whether the potassium bromide pellet spectra of these materials can parallel the spectra of solutions or thin films of the same materials over the entire spectrum. Spectra of asphaltene and coal-tar pitch solutions were determined (figs. 13 and 14). By proper choice of grinding conditions, potassium bromide pellets of these same materials (whole pitch and asphaltene gave
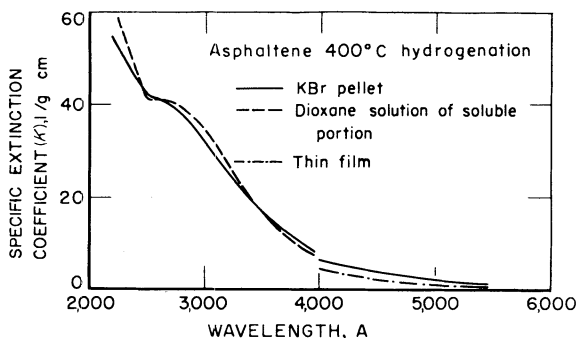
FIGURE 13.—Comparison of Ultraviolet-Visible Spectra of Solution, Film and KBr Pellets.
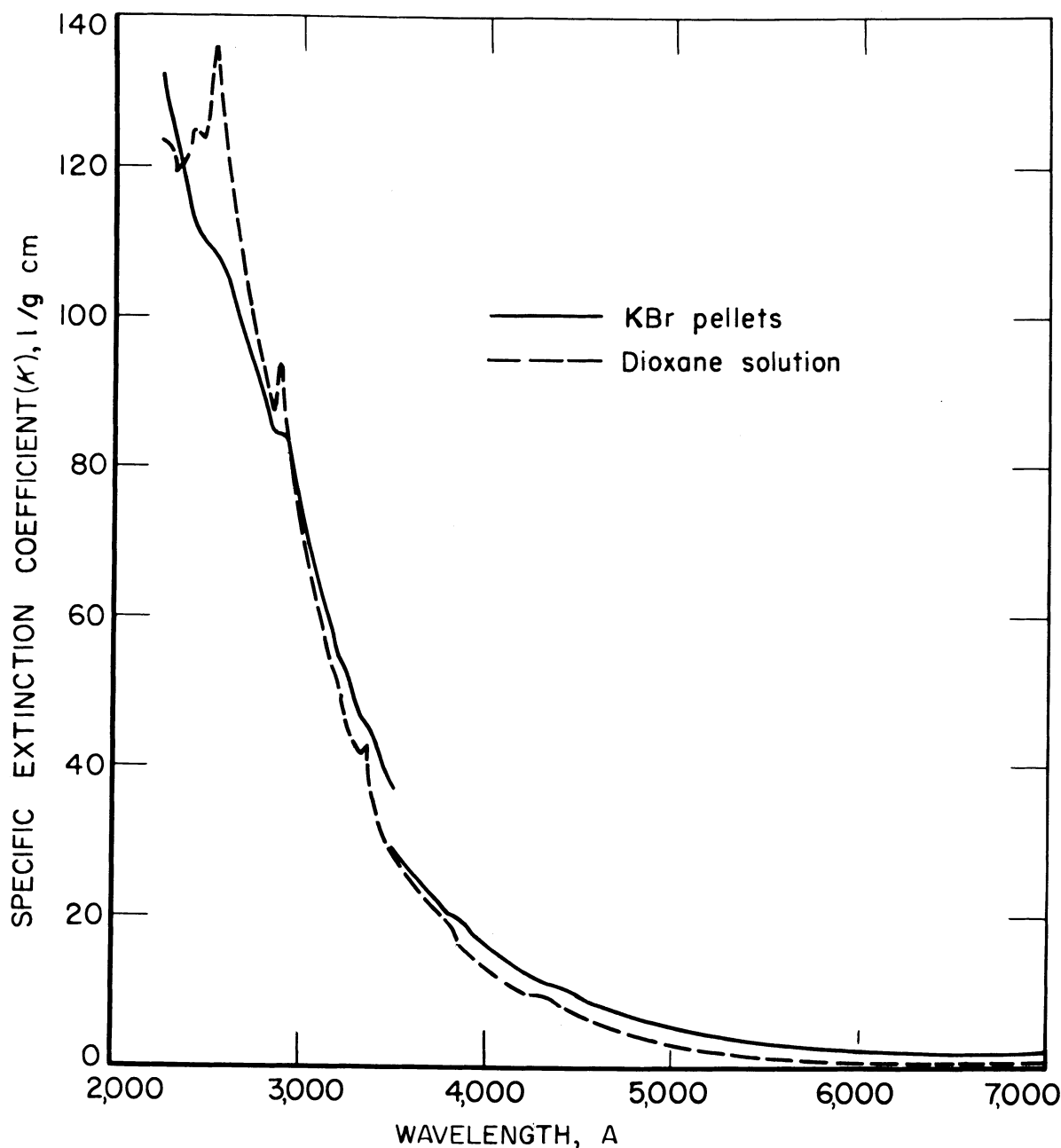
FIGURE 14.—Comparison of Ultraviolet-Visible Spectra of Solution and KBr Pellets of Coal-Tar Pitch.

pellet spectra identical to those of the dioxane-soluble portions) were prepared to match the solution spectra at the longer wavelengths. The spectra were then found to match at the short wavelengths. Inflections in the potassium bromide pellet spectrum of pitch indicate the rapid absorption increases and decreases (fine structure) of the solution spectrum. The existence of these fine-structure inflections in the spectrum of the pitch-potassium bromide pellet gives additional credence to the belief that vitrain spectra actually possess no fine structure.

The measurement of absorption areas was made for 84-percent-carbon vitrain and for a group of compounds. The ratio of absorption areas of vitrain and each compound gives the maximum possible percentage of that com-

TABLE 8.—*Integrated areas under ultraviolet-visible absorption curves of solutions of poly-nuclear condensed aromatic compounds; calculation of maximum allowable concentration in vitrain from the absorption area (uncorrected) of 84-percent-carbon vitrain*

Compound	Solvent	Absorption area,[1] $\int K\nu\, d\nu$, l/g cm^2	Maximum possible concentration in 84-percent-carbon vitrain, weight-percent
Coal vitrain, 84 percent C		[2] 0.00235	--
Naphthalene	Ethanol	.0102	23
Tetradecahydrocoronene	n-Heptane	.0120	20
1,2'-Dinaphthyl	Ethanol	.0110	21
2-(1'-Naphthyl)-1-naphthol	do	.0103	23
Anthracene	Cyclohexane	.0113	21
Phenanthrene	do	.0088	28
1,4-Chrysenequinone	1,4-Dioxane	.0084	28
Pyrene	Ethanol	.0076	31
Chrysene	do	.0097	24
6-Hydroxychrysene	do	.0094	25
1,2-Benzanthracene	do	.0090	26
Naphthacene	Benzene	.0095	25
1,2,5,6-Dibenzofluorene	Ethanol	.0082	29
Violanthrene	Benzene	.0099	24
Coronene	Ethanol, benzene	.0083	28
Dicoronyl	do	.0093	25
Average		----	25
16-component mixture, equal weights		----	25

[1] ν is the frequency range covered by the absorption region, over which integration of the absorption area is carried out.
[2] Uncorrected for reflection losses, light-scattering by vitrain, or absorption by benzenoid structures, nonaromatics, and free radicals.

pound, if the unlikely assumption is made that all of the area under the vitrain curve is due to the compound. The percentage values given in table 8 are still appreciably less than the 70 to 75 percent total aromatics supposedly present in 84-percent-carbon vitrain. Areas under the compound curves do not differ greatly, in spite of the wide range of structures, 2 to 9 rings. Thus approximately the same maximum concentrations of total polynuclear condensed aromatics would be obtained for almost any combination of these compounds.

Objections might be raised to the use of spectra determined in liquid solution to compare with spectra in solid solution as in coal. The literature indicates that absorption bands become sharper and more intense in solid solution at low temperature, but no information could be found on spectra of solid solutions at room temperature. Accordingly solutions of anthracene in paraffin wax were prepared and spectra were determined on the solid solution at room temperature. Fine structure and band widths were the same and K values were also the same practically as those obtained with dilute solutions (fig. 15). Absorption areas differed by only 4 percent (54).

Another point of possible error that has been proposed is the suppression of absorption intensities in systems of high polynuclear aromaticity. This possibility was eliminated by measuring the long wavelength bands of perylene in aliphatic and aromatic

solvents—dioxane, benzene, and methylnaphthalenes. The expected minor shifts in band positions and intensities are observed and the areas show variations of less than 1 percent for the three different solvents (fig. 16) (65).

Derivatives of Coal and Other Carbonaceous Materials

The polynuclear aromaticities of several derivatives of coal and petroleum have been calculated by determination of integrated areas under their absorption curves using area data obtained from polynuclear aromatic model compounds. Derivatives of both coal and petroleum are represented among the substances listed in table 9. It is important to emphasize that the polynuclear aromaticity values given here are reliable values because they were determined on solutions. Accordingly accurate measurements in

TABLE 9.—*Measurements of maximum polynuclear condensed aromaticity for various substances (65)*

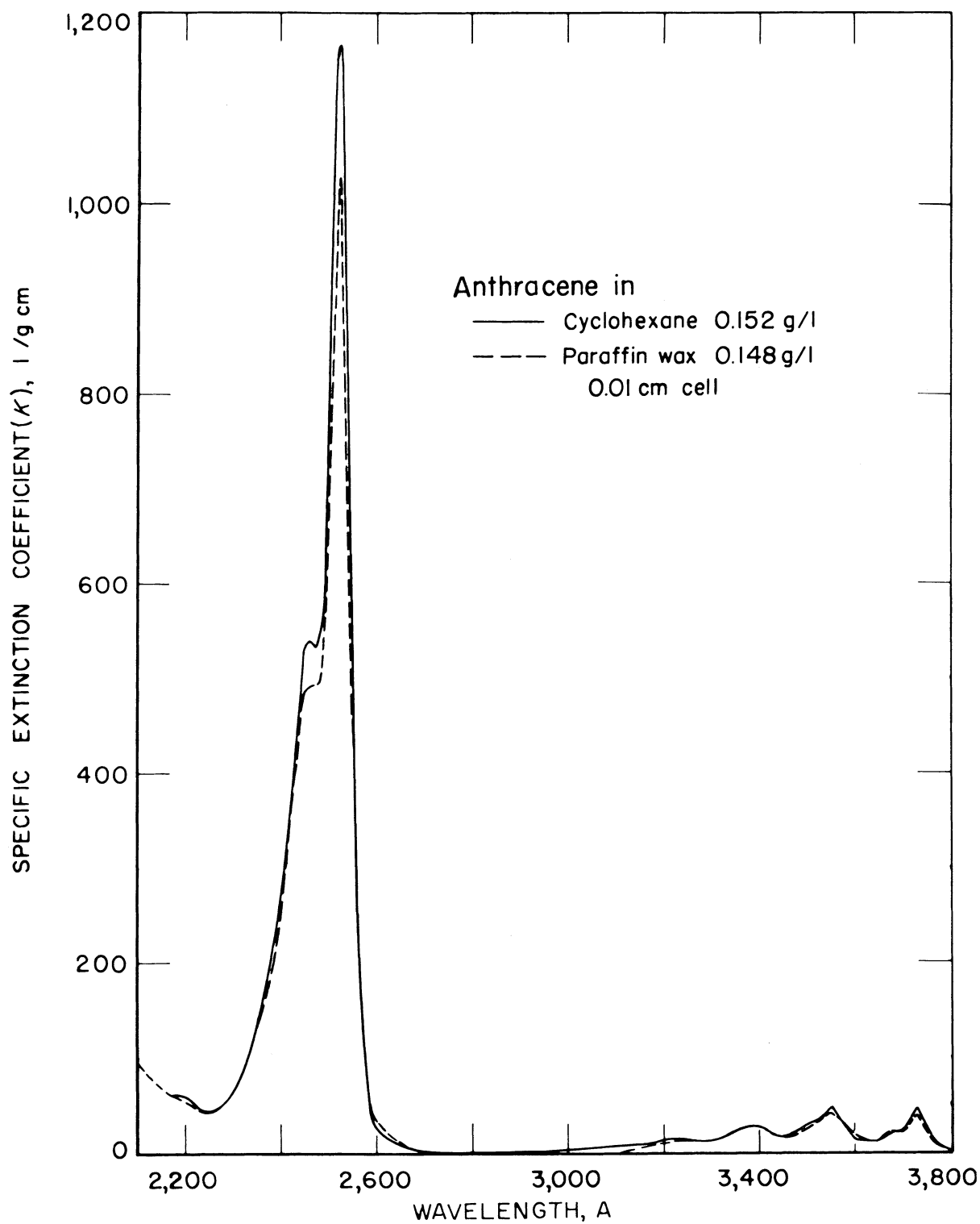|	Maximum polynuclear condensed aromaticity, weight-percent
Coal, pyridine extract in pyridine	45
Coal, pyridine-benzene-petroleum ether extract	60
Asphaltene from coal hydrogenation at 400° C, 87 percent carbon, in dioxane	20
Heavy oil from coal hydrogenation at 400° C	35
Coal tar	80
Coal-tar pitch, melting point 80° to 85° C, dioxane solubles	70
Asphaltene from petroleum, Kern River	25

FIGURE 15.—Comparison of Spectra of an Aromatic Compound in Liquid and Solid States.
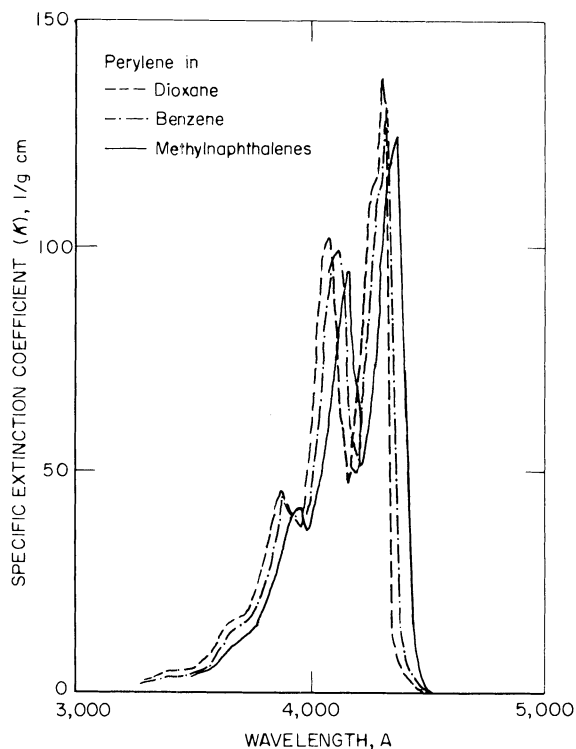
FIGURE 16.—Demonstration of Absorption by a Poly-nuclear Condensed Aromatic Compound in Nonaromatic and Completely Aromatic Solvents.

the ultraviolet region were made simply by working at proper dilutions. Thus the absorption area could be determined for the necessary range of spectral absorption; potassium bromide pellets were utilized below 3,000 A, but the errors involved are now thought to be large. In the case of solid coal, ground sections could not be made sufficiently thin to obtain measurements on bituminous vitrains below 3,000 A. (The inapplicability of microtomed thin sections for spectral measurements is discussed as follows.)

The data in table 9 represent maximum values of polynuclear aromaticities. In several cases the solutions are not true solutions; the extracts formed partially colloidial suspensions. Particles in such solutions may cause scattering of light which results in high absorption values and high aromaticities. Nevertheless the values obtained are indicative of polynuclear aromaticity. The lowest values are those for asphaltenes. This result is supported by nuclear magnetic resonance analysis of coal and petroleum derivatives (67). Ring sizes are apparently larger, however, for petroleum derivatives (67).

Ultraviolet-Visible Absorption-Electron Paramagnetic Resonance of Asphalt Solutions

Absorption Spectra and Magnetic Resonance Spectra of Asphaltene (47)

The spectra of asphaltene in solvents deviate considerably from the usual Beer's Law behavior; K's increase as the concentration decreases (fig. 17 in dioxane). Charge-transfer complexes do not appear to be involved, since the spectra show that asphaltene dissociates in a solvent into more strongly absorbing components. Free radicals (unpaired electron spins) have been found in alphaltenes from coal (48) and from petroleum (78) as well as in coals (88, 136), and crude oils (78, 112); a correlation of color intensity with content of unpaired electrons has been made for coal vitrain (48, 119) and for crude oils (24).

Electron paramagnetic resonance measurements show that the content of unpaired electrons per gram of asphaltene also increases with decreasing concentration in dioxane, presumably through dissociative formation of free radicals which increase with dilution (fig. 17). The correlation indicates that changes in color intensity for this asphaltene are attributable mainly to changes in concentration of unpaired electrons. Similar deviations have been found for other coal and petroleum derivatives. Dissociation may explain the variations in molecular weights with method of determination.

Spectral measurements and unpaired electron determinations on asphaltene in carbon disulfide show an even greater deviation from the expected linearity. Unpaired electrons per gram for asphaltene in carbon disulfide approach the values found for Pittsburgh coal and vitrain (table 10). No saturation of spin resonances was observed.

TABLE 10.—*Unpaired electron spins per gram of coal, vitrain, and asphaltene, solid and in solvents; comparison solution, vanadyl etioporphyrin* [1]

	Free spins per gram	Line width, gauss
Pittsburgh coal	9.4 x 10^18	5.0
Pittsburgh coal vitrain	6.5 x 10^18	8.1
Asphaltene, solid	0.32 x 10^18	9.0
Asphaltene, 295 g/l in dioxane	0.68 x 10^18	6.1
Asphaltene, 29.5 g/l in dioxane	1.8 x 10^18	6.0
Asphaltene, 2.95 g/l in dioxane	1.3 x 10^18	6.0
Asphaltene, 59.2 g/l in CS_2	4.4 x 10^18	6.4

[1] Measurements by D. E. O'Reilly, Gulf Research & Development Company.
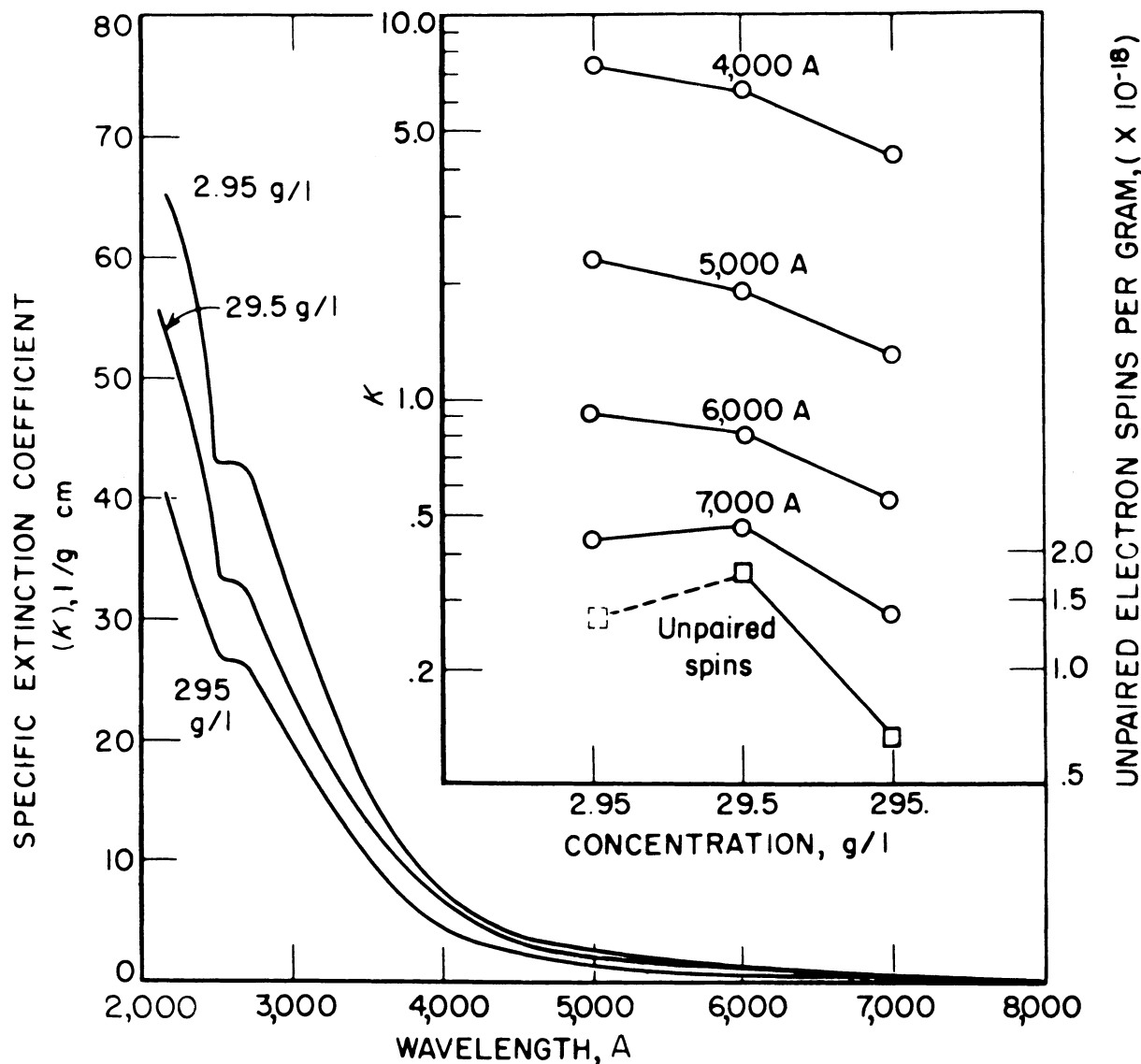
FIGURE 17.—Ultraviolet-Visible Spectra of Asphaltene in Dioxane. Correlation of Beer's law deviations with content of unpaired electron spins per gram. [ ], weak signal.

Line widths given in table 10 illustrate the expected similarity of the solid substances, vitrain and asphaltene. The narrow line width for coal is attributable to other coal constituents containing less hydrogen. The electron magnetic resonance data are presently being rechecked. The original data (47) are questionable because dissolved oxygen had not been removed from the solvent. It is possible that relaxation times and therefore intensities may have been affected by molecular oxygen.

Proton magnetic resonance measurements were made of asphaltene in carbon disulfide at 125° C (fig. 18). The broadness of peaks is probably due to the many magnetically inequivalent protons in asphaltene. Peak 2 is assignable to saturated CH groups on phenyl rings or on unsaturated groups; peak 3 is assignable to saturated CH groups on saturated carbon atoms. The sharp peak on top of peak 3 indicates a few protons on freely rotating chains or CH_3 groups. Peak 1 is due to protons on benzene rings or on phenols. Naphthalenic protons may be present in small amounts; protons on larger polynuclear condensed aromatic systems at lower field are considerably fewer in number, if
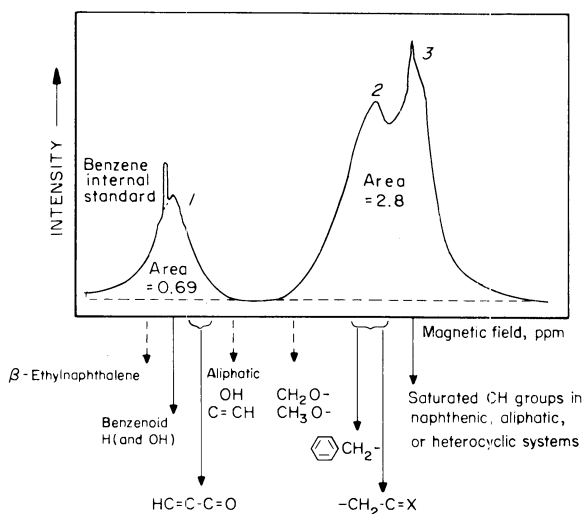
FIGURE 18.—NMR Spectrum of Asphaltene in Carbon Disulfide at 125° C. Measurements by Varian Associates.

present. The ratio of areas, peaks 2 and 3 to peak 1, shows that the protons on saturated C atoms are 4.1 times the benzenoid protons.

These data may indicate large molecules containing many hydroaromatic structures,

but some polynuclear condensed aromatics, and a few weak bonds easily broken to form free radicals. These were the first high-resolution NMR data of a coal derivative to be published (47).

ULTRAVIOLET-VISIBLE REFLECTIVITY SPECTRA (53)

Reflectivity

The spectra of specular reflectivities have been determined in the ultraviolet-visible region for Pittsburgh coal vitrain, 84 percent carbon. Previously, the absorption spectrum in this region was reported along with calculated absorption indices, k (66); the value for k at 5,461 A was found to be appreciably smaller than published values obtained from reflectivity measurements (26, 48). From the reflectivity spectrum (fig. 19), refractive indices, n, over the entire spectral region have been calculated (table 11) by Fresnel's equation:

$$R = \frac{(n-1)^2 + n^2 k^2}{(n+1)^2 + n^2 k^2}.$$

Because of the low magnitude of the absorption indices, this quantity is nearly insignifi-
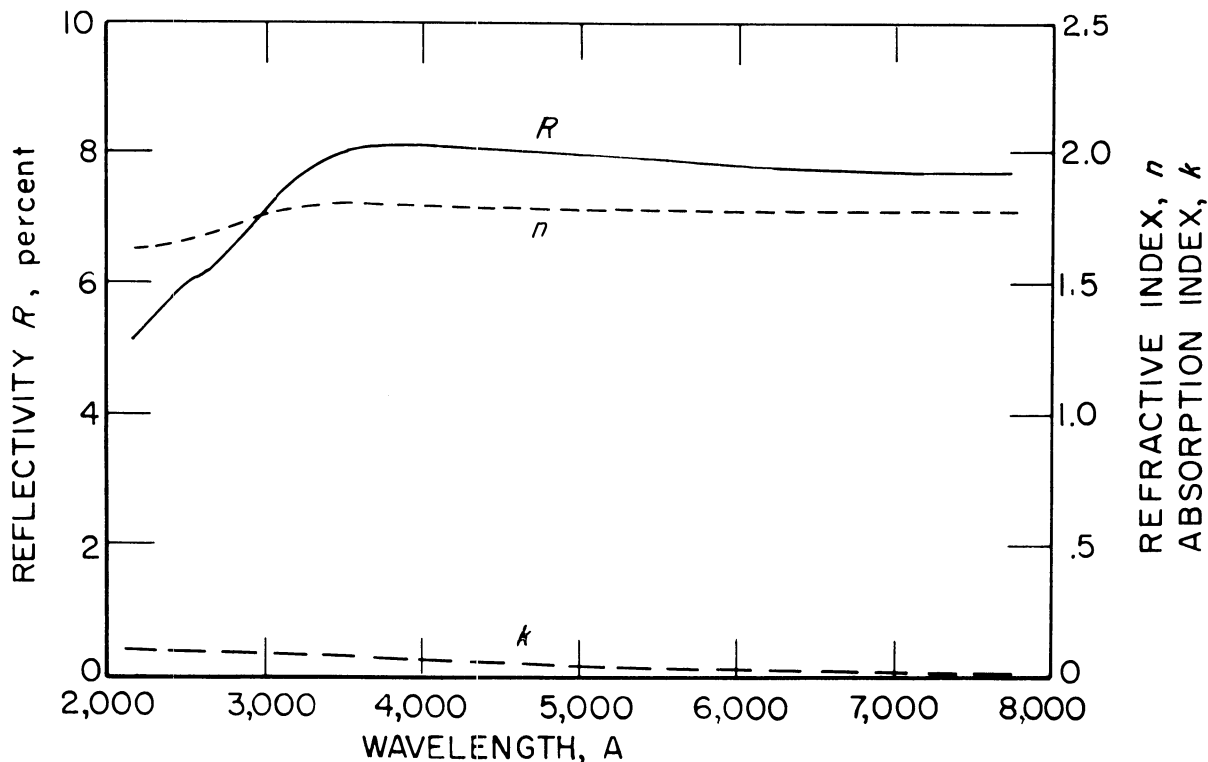
FIGURE 19.—Ultraviolet-Visible Spectrum of Specular Reflectivity and the Optical Constants, n and k; Pittsburgh Vitrain.

TABLE 11.—*Reflectivities (R), specific extinction coefficients (K), and the optical constants, refractive index (n), and absorption index (k), of Pittsburgh vitrain*

λ, A	K	k	R, percent	n
7,750	0.8	0.006	7.66	1.766
7,000	1.2	.011	7.69	1.767
6,000	2.5	.020	7.75	1.771
5,461	3.7	.026	7.88	1.779
5,000	5.4	.035	7.93	1.781
4,000	10.0	.052	8.11	1.788
3,500	14.5	.066	8.02	1.778
3,000	[1] 20.0	[1] .079	7.17	1.715
2,760	[1] 23.0	[1] .088	6.49	1.664
2,500	[1] 24.0	[1] .086	6.04	1.633
2,200	[1] 28.0	[1] .093	5.37	1.583
2,150	[1] 29.0	[1] .093	5.13	1.563

[1] Tentative data based on measurements on KBr pellets.

cant in the calculation of refractive indices. However, the interdependence of the two indices was taken into account by successive alternate calculations of refractive indices from Fresnel's equation and of the absorption indices from

$$k = \frac{2.303\lambda \; A}{4\pi x n},$$

where λ is the wavelength of light in centimeters, A is the absorbance, and x is the sample thickness in centimeters.

The experimental reflectivity curve remains smooth throughout the spectrum, with no sharp discontinuities. One weak, broad shoulder appears at 2,650 A. The reflectivity and refractive index spectra decrease appreciably at short wavelengths in the ultraviolet region. This decrease may be due to changes in absorption properties in this region, or it may possibly be due to increased scattering of the coal substance at these wavelengths.

Reflectivity measurements were made on polished pieces of Pittsburgh vitrain with a Cary spectrophotometer equipped with a specular reflectance attachment; a front-surface aluminized mirror was used as the comparison, and reflectivity values for fused quartz were used as spectral standards.

Aromaticity of Coal

In regions of strong spectral absorption, an increase is expected in both the refractive index and the absorption index, and hence in the reflectivity. In coal, such marked increase in absorption does not occur anywhere in the ultaviolet-visible spectrum. As can be seen from the data for reflectivity and refractive index, there also is no substantial increase in these values at any place in the spectrum (*83*).

These data are of particular significance in view of X-ray measurements (*41, 83*) which indicate that the ring sizes of aromatics that may be in Pittsburgh vitrain should be 1-to-3 and 2-to-4 rings. Thus the possible condensed aromatic nuclei are limited to 2-to-4 rings such as are found in naphthalene, phenanthrene, fluorene, chrysene, and other compounds. The strongest absorptions of all of these are confined to a narrow region of the short-wavelength ultraviolet, so that both reflectivity and absorption should show marked increases with definite spectral fine structure in this narrow region, but they do not. Most of the 16 2-to-4 ring polynuclear condensed aromatics, naphthalene through pyrene, have their strongest band in the region 2,100 to 2,550 A with K values from 205 (fluorene) to 1,230 (anthracene). Five of the 2-to-4 ring group have their maximum absorption band between 2,550 and 2,750 A with K values from 360 (2,3-benzofluorene) to 1,640 (napthacene). On the basis of K values, the allowable percentages of these compounds that could be present in Pittsburgh vitrain varies from 1.4 to 14 percent. These maximum percentages of individual aromatics are not additive owing to considerable overlapping interference in this short spectral region.

If the principal structures in bituminous coal vitrain are not polynuclear condensed aromatic in nature, the predominant structures may be aliphatic and alicyclic and/or benzenoid. The shortage of hydrogen, oxygen, and other elements may require that the saturated structures contain extensive systems of tetrahedral carbon-carbon bonds — that is, quaternary carbon atoms in diamond-like structures (*53*).

ABSORPTION ERRORS

Fluorescence Errors

Light from a fluorescing substance is emitted in all directions; the portion of this light that reaches the detector while determining absorption spectra of flourescing substances can cause significant errors in the absorption data. At high levels of absorption the amount of incident energy transmitted through a sample to the detector is rather small. Part of any fluorescence energy given off by the sample may also reach the photocell and become a significant part of the total light energy detected. The apparent absorption will then be less than the true absorption. It is therefore essential in measuring the absorption of fluorescent materials to work in
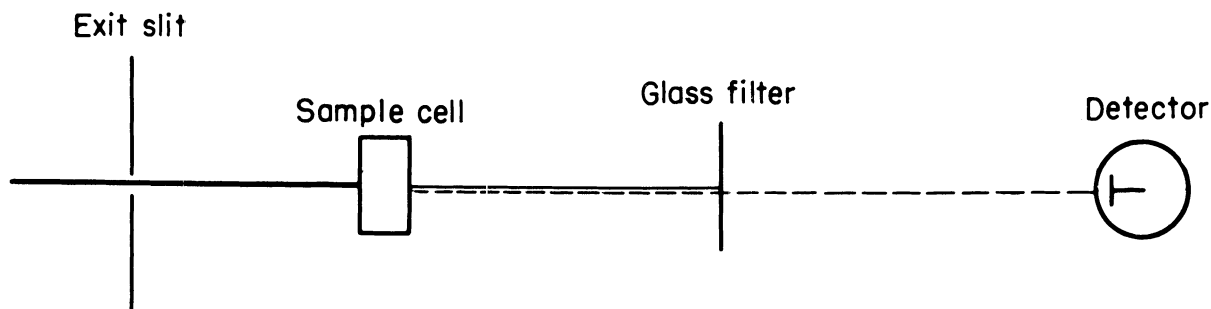
FIGURE 20.—Fluorescence Test, Filter Method. ———, incident and transmitted energy; – – –, portion of fluorescence energy that reaches detector.

regions of absorption intensity that are low enough that intensity is linear with concentration and with sample thickness. Braude and coworkers (*12–13*) demonstrated the sizable errors that can arise from fluorescence of the sample in instruments in which the sample is located between the exit slit and the detector. Vandenbelt (*137*) has demonstrated the effect of fluorescence in the spectra of anthracene solutions and has shown the typical absorption-law plots needed to detect the nonlinearity produced by errors due to fluorescence.

For the necessary investigation of fluorescence interference for solid films or for solutions available at only one specific concentration, the usual absorption-law method is not usable.

Filter Method

The essential requirement in detecting fluorescence interference is that the fluorescence must constitute a large part of the spectral beam that reaches the detector. The simplest approach to this requirement is to produce intense absorption in the region to be investigated; the presence of fluorescence can then easily be detected in that region. A suitable filter method for qualitatively detecting fluorescence interference in certain regions of the spectrum has been described by Friedel (*52*) and was used to detect the fluorescence of quartz and to test for flourescence interference in absorption spectra of benzene vapor. Mehler and coworkers independently developed the same method (*107*) later and demonstrated different applications.

A filter inserted in the optical beam removes ultraviolet energy of wavelengths below the cutoff of the filter; any fluorescence energy of wavelengths above the filter cutoff

will be transmitted (fig. 20). With a 0.24-mm microscope-slide coverglass as the filter, the absorption is very intense below 2,900 A (fig. 21); in this region the fluorescence of quartz is easily demonstrated by inserting 3-mm fused quartz plates between the monochromator and the glass filter. The difference between the curves for the glass filter and the quartz samples represents fluorescence energy emitted by the quartz. The spectra of one, two, and three quartz plates demonstrates the additivity of the fluorescence. The fluorescence emitted by the samples is a total fluorescence, including all wavelengths of the quartz fluorescence spectrum. But only
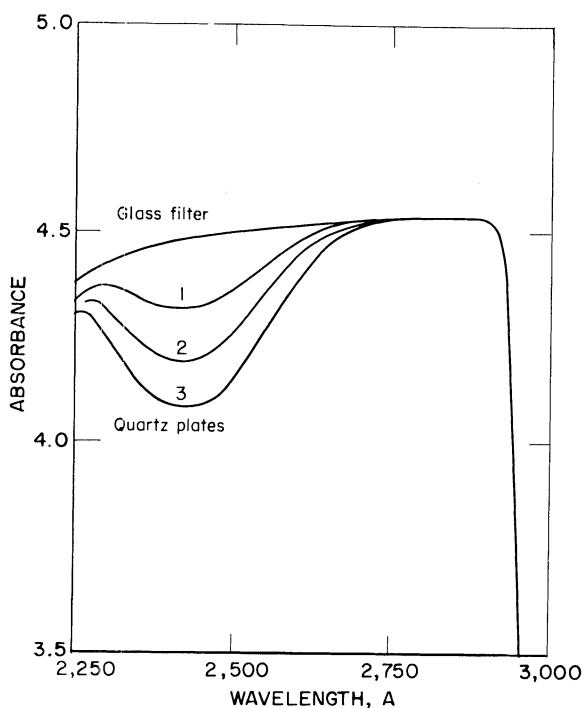

FIGURE 21. Fluorescence of Quartz.

the portion of that spectrum with wavelengths greater than the filter cutoff, 2,900 A, is registered by the detector and produces the curves given in figure 21. The minimum observed at 2,400 A represents the point of maximum activation of fluorescence and is not to be interpreted as a fluorescence band. The amount of fluorescence involved is extremely small; for the spectrum of one quartz plate the difference at 2,400 A from the glass filter spectrum is equivalent to 0.001-percent transmittance. A weak absorption band for quartz occurs at the same wavelength, 2,400 A.

Figure 22 illustrates the fluorescence of an anthracene solution by the filter method. The maximum activation of fluorescence interference is found at the wavelength of the most intense absorption band, 2,520 A.

The disadvantage of the filter method is the necessity of using wide slits and reference screens in order to measure very weak fluor-
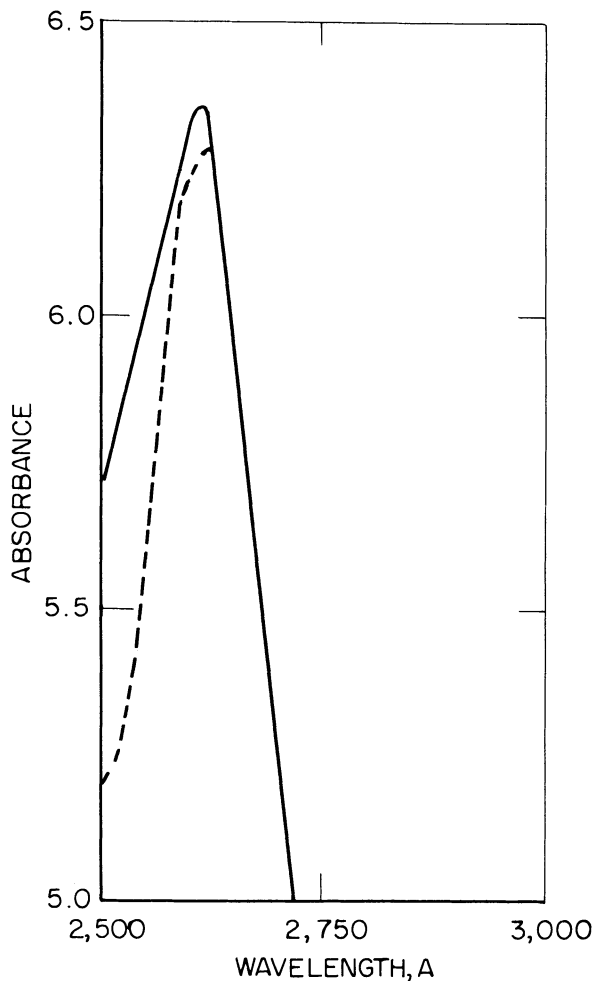
escence. Under these conditions of very low resolution, there is no quantitative indication of the fluorescence interference encountered under actual operating conditions at high resolution.

Path-Length-Extension Method

A method applying Lambert's law to the investigation of fluorescence interference throughout the spectrum under conditions of high resolution has been developed (65). The method is applicable to the determination of fluorescence interference of a specific solution or of a thin film. Fluorescence is increased relative to absorption by increasing the sample path length by (1) using either one or two cells of the same solution and (2) by rotating the cells at given angles in order to obtain greater path lengths. The two cells are rotated in opposite directions in order to return the optical beam to its original path (fig. 23). Special cell holders permit rotation of the cells at angles of 0°, 15°, 30° and 45°. The resulting increases in path length were approximated by direct measurements and by computations for each angle using a beam of 5,800 A and solvent in the cells. Calibration of the data in a particular wavelength region for errors in path lengths and differences in refractive indices were carried out by making measurements on a specimen of sample having absorbances in the linear range. For example, measurements were made on a dilute solution of anthracene in cyclohexane for which absorbances were below 0.7; reflectance losses at the various angles were determined from solvent spectra. Corrections of 1 percent or less were applied to the absorbance versus path-length values in order to produce linearity. These corrections could then be applied to data for a sample of anthracene in cyclohexane being investigated for fluorescence interference.

Table 12 and figure 24 give the results obtained on an anthracene solution having absorbances of 3.0 to 3.5 at the 2,520 A band. The deviations from linearity are a direct measurement of the fluorescence interference for a 2.0-cm thickness of this particular anthracene solution. The ability to make such measurements on the solution itself is necessary in the investigation of fluorescence interference in nonlinear systems, such as a highly concentrated solution of asphaltene for which absorption plots for testing linearity would be inapplicable.

Thin Films

The path-length-extension method can be applied to the detection of fluorescence inter-

FIGURE 22.—Fluorescence Test.
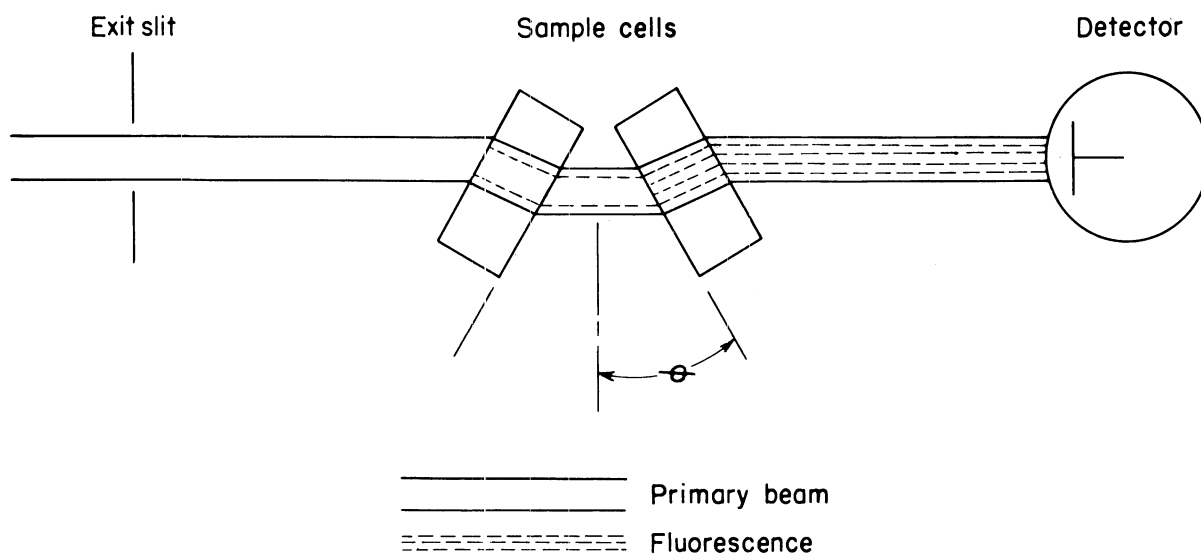
FIGURE 23.—Fluorescence Test, Path-Length-Extension Method. $\Theta = 0°$, 15°, 30°, and 45°.

TABLE 12.—*Path-length-extension method: Fluorescence interference at the 2,520 A anthracene band; deviation from absorption law linearity*

Number of 1.0-cm cells	Angle	Absorbance (A)	Total cell thickness x, cm	A/x	Deviation from linearity, percent
1	0°	1.620	1.0004	1.616	--
2	0°	3.164	2.0007	1.581	2.35
2	15°	3.226	[1] 2.022	1.595	1.19
2	30°	3.320	[1] 2.121	1.565	3.34
2	45°	3.50	[1] 2.269	1.543	4.69

[1] Corrected by means of absorbance measurements in the linear range.
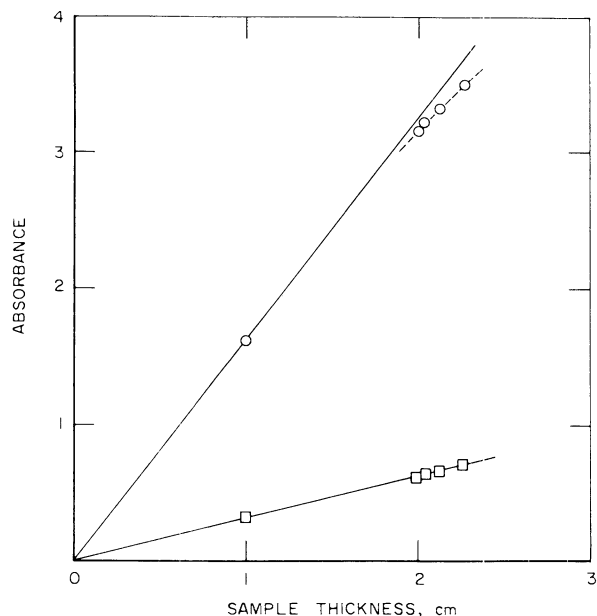
FIGURE 24.—Path-Length-Extension Method, Fluorescence Interference With Absorption, Anthracene in Cyclohexane. □, Calibration Data in Linear Range; ○, Sample Data.

ference in thin films. This application is troublesome because reflectance losses at the various angles must be determined by auxiliary means. Also, refractive index data are needed for the absorption region being investigated.

A simpler, though less informative, Lambert's law test for fluorescence interference in thin films involves the use of (1) a sample film and (2) a very thin film of the same substance. It is possible to check for fluorescence interference by comparing the sum of the two absorbances measured separately, A_1 and A_2, with the absorbance of the two films measured together, A_{1+2}. After applying reflectance corrections, if $A_1 + A_2 > A_{1+2}$, then fluorescence interference is indicated and a thinner sample film becomes necessary. Correcting for reflectance can be carried out with measurements obtained on a specular reflectance attachment or by plotting absorbance versus thickness for two thin films of low absorbance (81).

Potassium Bromide Pellets

To calculate possible concentrations of naphthalenes, the smallest polynuclear condensed aromatic system, it is necessary to obtain quantitative measurements as low as 2,100 A. The use of potassium bromide pellets in measuring the near-ultraviolet spectrum of Pittsburgh vitrain below 3,000 A is open to two serious objections: (1) False absorption due to scattering of radiation by sample particles; (2) insufficient absorption due to insufficient reduction of particle sizes. In the first instance radiation losses due to scattering will produce an apparent increase in the absorption of the sample; in the second, the number of particles is too small to intercept the incident radiation efficiently, so that an apparent decrease in absorption results. Grinding alone does not yield particle sizes small enough to remove these two sources of error in ultraviolet spectra. The error due to inefficient absorption is worst for strongly absorbing substances; even for more weakly absorbing substances, such as vitrain from bituminous coal, it cannot be reduced enough to obtain reliable absolute absorption spectra of KBr pellets. A uniform distribution of particles and a narrow size range are also important.

A balance can be obtained between these two opposing errors for a band-free spectrum, such as that of vitrain, by an appropriate choice of grinding conditions. The absorption spectrum of a vitrain thin section from 3,000 to 7,750 A can thus be closely paralleled by the spectrum of a KBr pellet of the same vitrain (fig. 12); grinding time, 4 hours. A reliable extension of the data to 2,100 A can be made by means of the spectrum of the potassium bromide pellet. Such an extension would be in error if the vitrain spectrum should undergo a sharp increase or decrease in absorption. No such sharp change occurs.

The accuracy of the data obtained with KBr pellets is still questionable. The only other data obtained on solid coals give absorption values that are considerably higher (42–43, 105) than these, both for ground thin sections and for KBr pellets. But the values obtained by Ergun and coworkers on sections cut with a diamond-knife microtome may be high because of artifacts produced in the cutting process. It was considered advisable to recheck the values obtained on ground thin sections. If these could be established as correct there is a possibility that the KBr pellet values may also be correct.

Thin Sections

The visible spectrum of ground sections has been rechecked on thick sections for which accurate measurements of thickness were possible (56). The spectrum obtained for a 10.3-micron hole-free section is curve d of figure 25; the spectral region below 5,000 A is not accessible with sections of this thickness. The previously published composite spectrum (66) for six sections varying in thickness from 2 to 10 microns is curve c. Curve a, a portion of the published spectrum of a microtomed section 550 A thick (42–43), shows K values greater than those of curve d by factors from 7.8 at 6,400 A to 4.3 at 5,000 A. The content of condensed polynuclear aromatics allowed by curve d in this spectral region would be smaller by similar factors.

The differences may be due to holes in the ground sections, or to light losses from scattering or interference effects which would produce high apparent K values for weakly absorbing samples such as ultrathin sections. The use of the thicker ground sections with higher absorbance values can avoid appreciable errors from scattering or interference effects; at very high absorbance values, however, minute holes can produce errors. Inter-
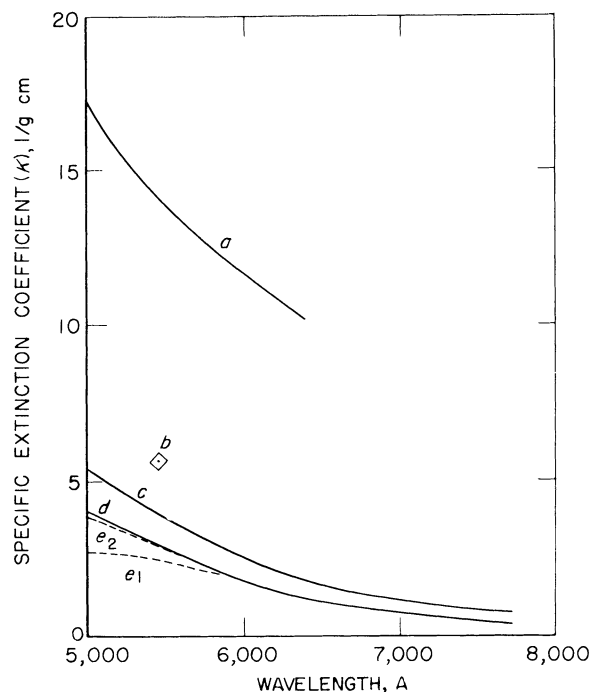

FIGURE 25.—Visible Spectra of Thin Sections. a, Microtome sections (42–43); b, ground section, 5,460 A (138, p. 361 and erratum sheet); c, ground sections (48, 66); d, ground section without holes; e_1, ground section with 0.07 percent holes; e_2, section e_1 with holes covered.

ference effects are important for sections thinner than 1 micron. Scattering errors can result from disruption of the coal structure which may occur as an artifact of the microtome knife action (17, 105); scattering would be greater in the ultraviolet region than in the visible.

The possible errors from holes in ground sections have been investigated by obtaining spectra on a portion of a thin section which contained holes to the extent of 0.07 percent of the sample area (curve e_1). The spectrum shows that the presence of holes is not a negligible factor. Holes are easily detected spectrally by observing a shoulder or levelling-off of the spectrum. K values for the 10.3-micron section, observed to be free of holes, are up to 57 percent larger at 5,000 A. Curve e_1 begins to level off into a shoulder at absorbance 3.5 at 5,200 A; the error is large at that point, but the data are usable from 7,750 to 5,900 A, where the spectral curve begins to deviate. In the original work sections with holes, observable visually or spectrally, were discarded.

That the shoulder is produced by holes is shown by covering the holes with india ink (curve e_2). The shoulder disappears and the spectrum returns essentially to that of the hole-free section (curve d).

The translucence and transparence of ground sections to sodium light is more in accord with the spectral data from curve d; the measured transmittance at 5,890 A for the 10.3-micron ground section was found by Friedel to be 0.043 percent (56).

This value differs considerably from the intense absorption indicated by Ergun's spectral data from ultrathin sections (42–43); at 5.890 A the data from curve a require that the light transmitted by a 10.3-micron ground section would be effectively zero: Transmittance $= 2.5 \times 10^{-16}$. The comparison at longer wavelengths also shows a large discrepancy. The data of Friedel (56) on thin sections prepared by grinding indicate that the transmittance at 6,350 A for a 10-micron thick section is 1.3 percent (fig. 25, curve a). On the other hand the data of Ergun and coworkers (42–43) using microtomed sections predict for a 10-micron section at 6,350 A a transmittance of only 1.3×10^{-11} percent. This very low value shows that there would be no transmission of observable color. The former value of 1.3 percent is more compatible with the translucence, often transparence, observed for a 10-micron section (56).

K values at 5,460 A for ground section data are 3.7 (curve c) and 2.9 (curve d). These values compare with the value of Huntjens

and van Krevelen for a ground section (86, 138 p. 361 and erratum sheet); their absorption index, 0.04 gives a K value of 5.6 (point b, fig. 25).

SIMULATION OF THE COLOR OF COAL (58)

The color of bituminous coal and other carbonaceous materials has been variously attributed to large polynuclear condensed aromatics (2, 124, 140), free radicals (8, 47–48), charge-transfer complexes (99, 124), and free pi-electrons (138, p 362). Final proof of the structural cause of color is missing. This section will discuss the spectroscopic properties of coal and other substances, and their relationship to color.

Thick sections of coal vitrain are black, or opaque, in the visible region of the spectrum. For thin sections, however, the transmitted color progessively changes from brown to red to yellow with decrease in thickness (26, 102). The yellow color is characteristic of the thinnest section that can be successfully made by the normal procedure. Recent success in the C.S.I.R.O. [6] laboratories in the grinding of a thin section to form a wedge suggest that, at thicknesses represented by regions near the tip of the wedge, white light is transmitted; that is, the coal is clear and colorless. Similar variations in color with thickness are observed for carbonaceous derivatives such as some heavy oils, asphalts, etc., from coal and petroleum. An explanation is advanced for these color changes, and the production of identical color changes with thickness is demonstrated with pure compounds that are lightly colored or colorless.

Published absorption spectra for bituminous coals (42–43, 48, 56, 66) (usually as thin vitrain sections, fig. 26a) show that there are no absorption bands, but only general absorption throughout the visible region of the spectrum. This absorption, which is greatest at the short wavelength limit of the visible region, constitutes the "wing" of stronger general absorption in the ultraviolet region. Thus coal transmits more light at the red end of the spectrum than at the blue end. If absorption bands were present in the visible region little or no color change would occur with thickness.

The fact that absorption of vitrain thin sections at each wavelength in the visible region obeys Lambert's law of absorption (that is, the optical density is a linear func-
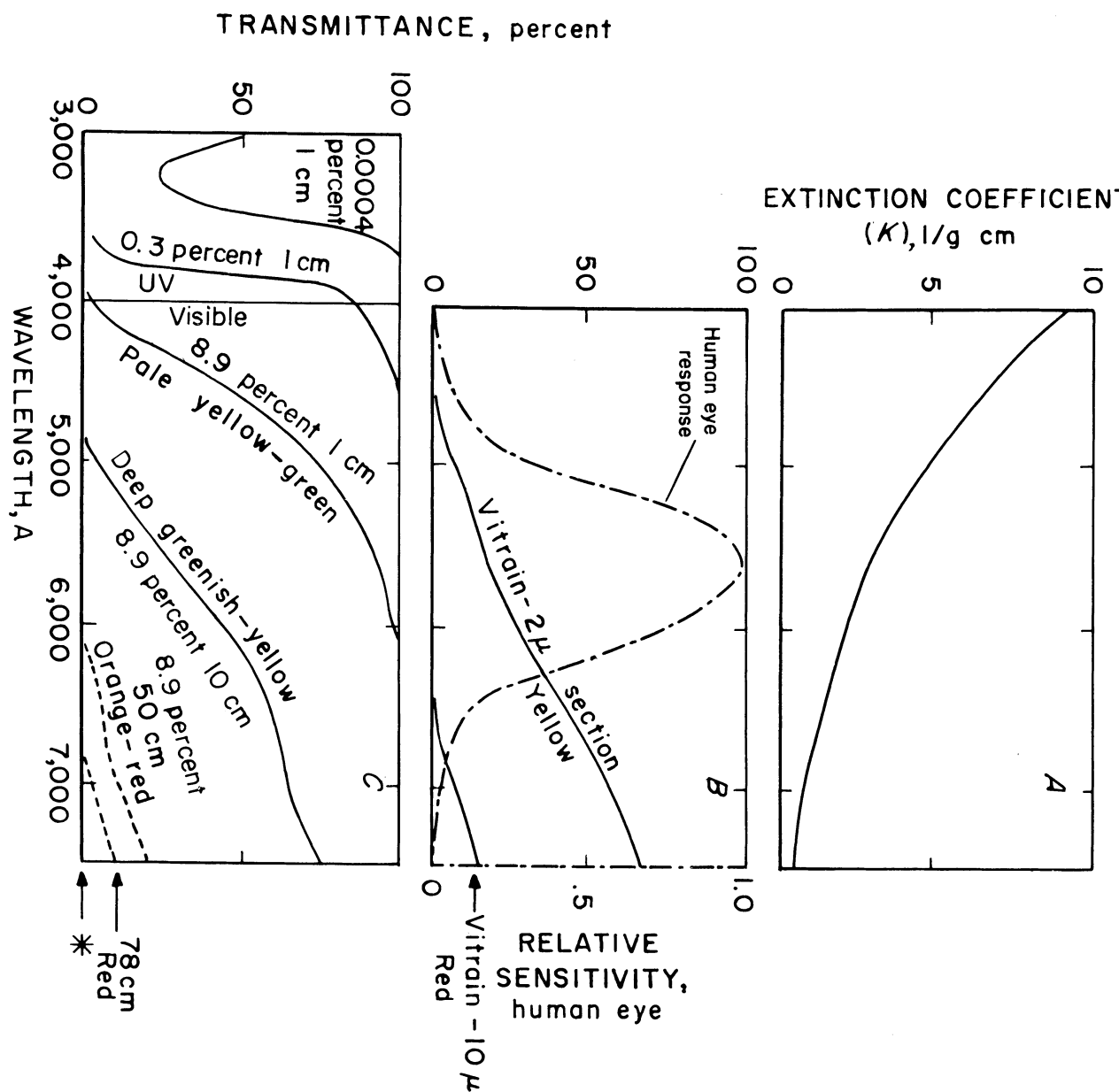
FIGURE 26.—*A*, Absorption Spectrum of Pittsburgh Vitrain (84 Percent C) Determined With Ground Sections; *B*, Schematic Curves for Two Bituminous Vitrain Sections and Response Curve for the Human Eye; *C*, Curves for the Sodium Salt of *p*-Hydroxyacetophenone. ———, transmittance curves and colors for solutions; – – –, calculated curves and colors observed through long cells; *, for a cell of 191 cm the calculated transmittance, 7,500 A, is 0.2 percent and the color is dark brown to opaque.

tion of the thickness) establishes that the observed color changes are of physical rather than chemical origin. In other words, these changes are not due to changes in the chemical structure or to oxidation of the vitrain induced by grinding.

The observed color of a substance is a function of the spectral response of the human eye and of the spectral distribution of the light transmitted or reflected by the substance (*15, 89*). The sensitivity of the eye is a maximum near 5,550 A, which is at the

yellow end of the green and falls rapidly both to shorter and longer wavelengths with cut-offs near 4,000 and 7,500 A (fig, 26B). Thus, for thin sections of coal the decreasing sensitivity of the eye towards the blue end of the visible region, below 5,550 A, is coupled with decreasing transmittance for the coal (fig. 26B); but decreasing sensitivity of the eye towards the red, beyond 5,550 A, is partly compensated by the increasing transmittance of the coal. Therefore the eye receives greatest stimulus from the red end of the spectrum. To explain the variation with thickness from colorless through yellow and orange to red and brown the thin sections of coal may be regarded as optical filters with shallow transmittance cutoffs at the short wavelength end. For very thin sections this cutoff becomes significant only at some wavelength below 4,000 A in the ultraviolet and white light is transmitted with negligible attenuation; the section appears colorless. However, as the thickness increases the absorption edge progressively passes through the visible and the apparent color changes from colorless → greenish yellow → yellow → orange → red → brown. This effect is illustrated in figure 26B by schematic curves for two coal sections; for 2- and 10-micron sections for a bituminous vitrain the predominant colors would be yellow and red respectively.

If the color transmited by coal were due to a narrow, symmetrical transmission band an increase in thickness of the coal would cause only a deepening of the color. The color would not change because spectral changes on each side of the transmission band would nullify each other.

The optical filter explanation for the color changes in coals receives support from the fact that these changes can be simulated in a simple laboratory experiment using selected pure compounds. The sodium salt of p-hydroxyacetophenone, a colorless compound, was selected for this purpose because its only absorption band lies in the near ultraviolet at 3,240 A and has a "wing" that extends nearly into the visible region. The absorption spectrum in the visible region of solutions of this sodium salt were measured with progressively higher concentrations and/or path lengths (fig, 26C); changes from colorless to opacity were noted. At the concentrations normally used to obtain accuracy in the measurement of the optical density at peak absorption in the visible region (fig. 26C) was negligible and the solution was colorless. With increasing concentrations absorption in the visible became increasingly significant

and progressed towards longer wavelengths. In parallel the color changed from colorless → yellow-green → yellow → orange → red → brown → opacity.

Similar color changes through part of the visible region were observed for solutions of other compounds, both organic and inorganic, having "wing" absorption in the visible spectrum. Compounds and the colors observed were as follows: 2-Methylanthracene (colorless, green-yellow, yellow), picric acid (yellow, orange), sodium picrate and sodium dichromate (orange, red, brown, opacity). Because of low solubilities and steep absorption curves it was not practical to produce color changes to complete opacity in all cases.

With reference to the intensity of absorption it is essential that spectral data and visual observations of color be reconciled. As discussed previously the low intensity values reported by Friedel (56) for ground thin sections are more compatible with colors observed through the sections than are the anomalously high values reported by Ergun and coworkers (42–43) for ultrathin sections.

Ultraviolet Absorption and Reflectance Maxima for Polycrystalline Graphite (67)

The positions of the absorption and reflectance maxima of graphite in the ultraviolet region are of particular interest because of the prediction by Coulson and Taylor from band theory calculations on pi-electron states that a difference of 5ev exists between the valence and conduction bands (30). An absorption band should occur in the neighborhood of 5ev (about 2,500 A).

Reflectance spectra have been measured and spectra of refractive indices and extinction coefficients for polycrystalline graphite have been calculated by Humphreys-Owen and Gilbert (85). The absorption spectrum of a graphite single crystal has been reported by Ergun and coworkers (42–43).

The present work describes a simple technique for obtaining both reflectance and absorption spectra of polycrystalline graphite; values obtained from the wavelength positions of the maxima are somewhat different from those of Humphreys-Owen and Gilbert.

The samples of graphite for reflectance and absorption measurements in the ultraviolet-visible region were prepared by melting granules of polyethylene that melts at 80° C, pressing the melt into thin films, and then rubbing powdered graphite (spectral grade or Madagascar) vigorously on the polyethy-

lene film. The resulting films of graphite enable accurate wavelength determinations of the absorption and reflectance maxima.

The reflectance maximum for polycrystalline graphite is located at 2,540 A (table 12). Because of the broadness of the maximum, this value is similar to values reported by Humphreys-Owen and Gilbert (85). These authors found values between 2,560 and 2,750 A, but the best specimens gave maxima at 2,560 and 2,580 A which compare favorably with 2,540 A.

The absorption maximum in the extinction coefficient spectrum of polycrystalline graphite is located at 2,750 A (table 13). This observed value is at considerably longer wavelength than the value calculated by Humphreys-Owen, 2,490 A.

The reflectance maximum is located at shorter wavelength than the absorption maximum. With materials having intense absorption, such as graphite, it is usually expected that the reflection maximum will lie at the same position as the absorption maximum, or slightly on the long wavelength side of it. This will be true unless the refractive index becomes very large at a different

TABLE 13.—*Ultraviolet spectral positions of reflectance and absorption maxima of polycrystalline graphite, spectral grade, rubbed on polyethylene films*

	Maximum, A
Reflectance spectrum:	
Humphreys-Owen, observed	[1] 2,570
This work, observed	2,540
Difference	−30
Extinction coefficient spectrum:	
Humphreys-Owen, calculated	[1,2] 2,490
This work, observed	2,750
Difference	260

[1] Reference 85.
[2] Maximum for a single crystal of graphite is reported at 2,590 A (42).

wavelength. Present results indicate, therefore, that the refractive index of graphite becomes large at the observed maximum, 2,540 A. At this position it is more important than the absorption in determining the wavelength of the reflectance maximum. The presence of another absorption band at shorter wavelength could produce a reflectance maximum at 2,540 A. But there is no indication of an additional absorption band.

CONCLUSIONS AND COMMENTS ON COAL STRUCTURE

Progress on the question of the structure of coal continues, and spectroscopy is one of the chief contributors to this progress. It is possible to formulate detailed structures satisfying the available evidence from many sources, on functional groups, aromatic nuclei, etc. The apparent repeatability of the coal unit or "molecule" promotes the attempt to speculate on structure and to meet the challenge to unravel the structure.

Two controversial facets of the coal "molecule" have been of particular interest to the authors: The questions of (1) five-membered rings and (2) polynuclear condensed aromatic structures. For many years the opinion that five-membered ring structures are plentiful in coal has been based on the many cyclopentyl and indan structures found in products from coal hydrogenation experiments (*44, 50, 60, 62, 110, 145–146*). The temperatures involved in these experiments are low enough to permit the belief that the five-membered structures are present in the unreacted coal.

With regard to polynuclear condensed aromatics the estimated average size for medium rank coals has decreased in the past decade from many rings down to the present 1 to 3 condensed rings. Present evidence for the range of ring sizes and their concentrations seems overwhelming, but it is unsafe to state that the present values are final. As suggested several years ago, polynuclear aromatics are not needed to explain the color of coal; the free electrons, presumably free radicals, can do that (*48*).

The interested reader is referred to three recent books containing information on the structure of coal: Lowry (*100*), van Krevelen (*138*), and Francis (*46*).

SUMMARY

Many facets of the infrared spectral investigation of the structure of coal and coal derivatives have been treated: Sample techniques, specific wavelength assignments, structural information obtained from intensities, identification and characterization of reaction products, high-energy processes, aromaticity of coal, and briefly, sorbed species and charge-transfer complexes.

In ultraviolet-visible spectrometry the principle effort has been devoted to the determination of optical constants, refractive indices and extinction coefficients throughout the spectra of coals and graphite, the estimation of polynuclear aromaticity of coals, correlation of data with other spectral techniques such as infrared and electron paramagnetic resonance spectrometry, absorption errors that lead to erroneous interpretations, physical-chemical explanations for the color of coal such as free radicals, and an optical explanation of and simulation of the color of coal.

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