

INORGANIC AND ORGANIC ANALYSIS BY INFRARED SPECTROMETRY IN COAL PROBLEMS

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SUMMARY

A group of problems are discussed. In Inorganic work the identification of mineral absorption bands in infrared spectra has been carried out by a combination of spectrometry and coal petrography. The absorption bands of the whole coal that are found to decrease significantly with the removal of mineral matter are easily identified by this means.

An important safety problem in coal mines has been substantially helped by infrared analysis of minerals. The content of rock dust found in the float dust of return airways of coal mines is important and preferably should be determined with speed. The usual procedure is to wait for dust to settle sufficiently to collect 100 mg of sample for chemical analyses. By the application of infrared spectrometry to this problem it is possible to carry out a complete analysis for rock dust content on as little as 2 mg sample. Greater speed is achieved.

In organic work, attenuated total reflectance of shock-heated coal has shown that considerable infrared fine structure is developed relative to the original coal (Spectra by Barnes Engineering Co.). The spectra obtained are, however, not representative of the whole coals. More volatile portions of the coal are found to leave the coal first as expected and to collect first on the ATR prism. Because of the very slight optical penetration of the sample by the spectral beam the spectrometer sees only the initial volatile parts of the coal. This method is therefore very good for concentration of and study of the volatile portions of the coal. A principle use of ATR at the Bureau has been in the study of spectra of sorbates added to coals.

Infrared spectral changes with acid-base interactions (charge-transfer complexes) have been studied by the ATR method. With coal as the acid (acceptor) and pyridine as the base (donor) the same changes in the pyridine spectrum are found as in other charge-transfer complexations involving pyridine.

INTRODUCTION

The application of infrared spectrometry to chemical substances represents the largest use in science of any spectral method. These applications are overwhelmingly in the field of organic chemistry. But infrared spectrometry is also used for analysis of inorganics. In addition to qualitative information it is possible to obtain quantitative information as well. As in organic infrared a straight line relationship usually exists between the concentration of each component in a mixture and the spectral absorption of that component. This paper will treat a few applications of infrared spectrometry to both organic and inorganic problems. In most cases other available spectral methods (mass spectrometry, ultraviolet-visible, nuclear magnetic resonance, electron paramagnetic resonance) are used in conjunction with infrared, but only infrared is discussed here.

INORGANIC APPLICATIONS

Inorganic materials which possess anions of oxygenated systems, namely, carbonates, chlorates, sulfates, silicates, etc., usually possess in their infrared spectra distinct, intense spectral bands. Such substances are amenable to analysis by infrared spectroscopy. One distinct difference between organic and inorganic substances is that inorganics have fewer spectral absorption bands than organics. With fewer bands to work with, analyses of complex mixtures are limited. This is one major reason why infrared analyses of inorganics have not been as popular as analyses of organics. Organic molecules produce profuse spectra because of the large number of atoms involved, and because many of these atoms are usually hydrogens which are responsible for many of the intense bands in the spectra of organic compounds. When hydrogens are present in inorganic compounds, these too show a greater profusion of spectral bands; the bicarbonates are an example.

It is interesting to note that one of the earliest and best text books on infrared, written by German spectroscopists Schaeffer and Matossi^{1/} 36 years ago, discussed the inorganic applications at length, almost to the exclusion of organic applications. It was soon after this period that the greater applicability to organic structures aroused so much activity that it practically swept aside the inorganic applications of infrared. A considerable impetus was given to infrared analysis of inorganics by Miller and Wilkins of Mellon Institute in their publication of a catalog of spectra of inorganic compounds,^{2/} and by Hunt et al. in a publication of infrared spectra of minerals.^{3/} This impetus was needed, although it did not produce any great activity in inorganic analysis until recent years--more than a decade after publication. A recurring difficulty with inorganics is that spectra of unknowns often differ significantly from the spectra of standards. This is a disturbing occurrence and makes difficult the assignment of spectra to specific structures. A list of possible reasons for spectral differences follows: (1) Infrared spectra often differ for different crystal structures of a substance. This is a factor in dealing with pure substances, and is an even bigger factor in the presence of impurities and in mixed salts. Epitaxy can produce differing crystal structures and infrared spectra. (2) Substrates can have a tremendous effect on the spectrum of an inorganic substance. Large spectral changes are well known in the case of organic materials studied *in situ* on catalysts. (3) Reaction may occur between the minute crystals of the sample and the KBr, or other halide, used for infrared pelleting.

In Bureau of Mines work infrared applications in inorganics occurred in connection with: (1) Our early work on coal spectra; unassigned bands thought to be due to ethers in bituminous coal spectra were reported in 1956 to be due to minerals, principally kaolinite;^{4/} (2) spectra of oil shales and other carbonaceous shale produced little information; (3) brief investigations of alkalinized alumina in 1963 gave limited information: the presence of sodium aluminate was indicated, which substantiated the X-ray indications of this group; the presence of sulfates (not definitely assignable) on alkalinized alumina exposed to sulfur oxides has been shown; (4) formation of inorganic carbonates in the pyrolysis of lignites and of peat at 400° C was shown; (5) recent examination of probe samples obtained in combustion experiments showed identifiable sulfates. Further work on (1) will be described.

1. Identification of Mineral Absorption Bands in Coal Spectra

The discovery of the correct assignment of certain absorption bands to minerals^{4/} came about through the observation in 1953 that the spectra of coals and their petrographic components differed considerably. As in other laboratories our suspicions were that these differences were attributable to differences in organic

structure between the coal and its petrographic constituents. But it became apparent that this could not be. A coal such as Pittsburgh seam is very largely vitrain. With only a few percent of the constituents removed from the major component, vitrain, it was not feasible that there should be differences in organic structure between coal and vitrain spectra as great as 5-fold in the intensities of some absorption bands. It eventually became evident that the constituents which were changed many fold in the isolation of vitrain were the mineral components. On comparison of these anomalous absorption bands with the spectra of the few minerals available at that time, it was found that most of the bands were assignable to kaolinite.^{4/} Thus these informative comparisons of spectra represented a very useful combination of spectral and petrographic methods.

Our published investigations on this subject were limited to the 5,000 - 650 wavenumber region.^{5,6,7/} With the advent of instruments for adequate operation below 650 cm^{-1} in the infrared (R. C. Lord has named this region the "middle infrared") it became possible to extend the study of mineral absorption bands through the combination of spectral and petrographic techniques. By a comparison of Pittsburgh coal and vitrain spectra the following bands due to minerals, principally kaolinite, have been observed in the middle infrared: 698, 543, 471, and 420 cm^{-1} . The strongest of these bands are those at 543 and 471. Both bands are attributable to kaolinite. As discussed above some of the intensity differences are extremely large and cannot possibly be attributed to differences in organic structure. For example, the strong band at 543 wave numbers in the coal is 10 times as great as the corresponding absorption intensity in the vitrain spectrum. Such radical differences can only be attributed to mineral absorption. Intensities of these absorption bands can be accurately calculated and used for quantitative determinations of minerals present.

Graphite has been examined in this region of the spectrum. Though strong absorption for graphite was detected out to 290 wave numbers no discrete absorption bands were found. Additional runs out to 100 cm^{-1} have been made by Dr. William Fateley, Mellon Institute, and no specific absorption bands occur.

2. Rock Dust in Float Dust

Infrared spectrometry has recently been applied to analysis of rock dust in float dusts from return airways of coal mines. Sample collection for the purpose of analyzing by wet chemical methods is a difficult problem usually because a considerable amount of dust, about 100 mg, must be collected. This requires more time than desirable; the element of safety is therefore involved. With the use of infrared spectrometry in such a problem only very small samples need be collected. Two mg are ample and collection is rapid.

The dust samples collected in the mine, mixtures of coal and rock dust, are prepared for infrared investigation by mixing 1 part of dust with 100 parts of potassium bromide which is pelleted by a standard technique. The infrared spectrum of the pellet is obtained. Advantageous absorption band or bands are chosen for analytical work. For quantitative analysis it is necessary to check the linearity of the concentration versus spectral absorption by preparing standard samples at various concentrations and measuring their absorption intensities at the appropriate absorption bands. After the linearity of the calibration curve is established, then unknown samples can be prepared in KBr pellets and their spectra obtained. Intensity of absorption at appropriate bands may then be applied to the calibration curve and the concentration of the desired component in the dust is obtained.

The rock dusts dealt with in this investigation were either calcite (CaCO_3) or dolomite, $\text{CaMg}(\text{CO}_3)_2$; calibration curves were obtained for each of the rock dusts plus coal. Though the rocks involved are both carbonates their absorption spectra differ slightly. This is an advantage, as each may be determined in the presence of the other if necessary. Coal also has an absorption spectrum and accordingly the coal dust collected in the mine will produce interfering absorption which must be corrected for. This is most simply done by choosing the calibration band for the carbonates if possible in regions of broad, non-specific absorption of the coal. Then from the spectrum of the mixture of coal and rock dust the absorption band of the rock dust will be superimposed on the broad background of the coal absorption. By drawing a baseline across the base of the absorption band it is possible to correct out the non-specific coal absorption.^{5,6/} The intensity of the rock dust absorption then is measured from this base line to the peak of the absorption band. In this way calibration curves were obtained.

For both calcite and dolomite two absorption bands were obtained for possible analysis. All four bands provided acceptable results, about + 10 percent of the amount present, in the desired range of about 20 to 80 percent rock dust. Results indicate that there is no preference between the two absorption bands studied for each dust. One other carbonate band, at about 7.0 microns, is available for analysis. With its greater intensity this band would be useful for analysis of traces of rock dust in coal dust. In the present problem analysis of traces is not required so the less intense, sharp bands used are preferred. It should be mentioned that only three carbonate bands are available for analysis; as stated earlier, organic materials usually have many bands that can be used. If differentiation between carbonates is required, then two bands only are available, for the strongest band at 7.0 microns is essentially identical in various carbonates.^{2,3/}

ORGANIC APPLICATIONS

1. Attenuated Total Reflectance Spectra. Shock-Carbonized Coals; Sorbates on Coal

Recent investigations on attenuated total reflectance (ATR) of coal were carried out by Bent and Ladner.^{8/} Their results demonstrated the difficulties of utilizing this technique on coals. Very close optical contact is difficult to achieve with the surface plateaus produced by conventional grinding and polishing of coal. These authors demonstrated that the method was more applicable to the spectral investigation of chloroform extracts of shock-carbonized coals.

Volatile products from shock-carbonizing of coals can be condensed directly on the ATR optical element to produce good spectra. However, this technique might be somewhat misleading; on shock carbonizing, the more volatile products and therefore the lower molecular weight products, would be expected to reach the ATR prism first. Because of the slight optical penetration of the sample by the infrared beam in the ATR technique, it is probable that only these most volatile products would be observed in the spectrum. The method is therefore very good for the concentration of and study of the volatile portions of the coal.

Spectra of the volatile products from four shock-carbonized vitrains were investigated by Barnes Engineering Company with an ATR crystal of thallium-bromide-iodide which provides 20 reflections within the crystal. The vitrains were shock-carbonized at 900° C; the volatilized material was collected on the ATR crystal and spectra were determined. Appreciable differences in the spectra of the products from three coal vitrains were observed in comparison with the spectra of the original coal vitrains; greater fine structure and new bands were produced. The fourth sample, shock-carbonized Beulah lignite vitrain showed no spectral changes other than quantitative changes. The spectral changes for the three coal

vitrains are indicated in Table 1. The formation of two doublets is interesting. The doublet at 1625-1600 in the spectra of shock-carbonized products may signify that the 1610 cm^{-1} band in coal is actually attributable to two different chemical species, as suggested by Fujii.^{9/} The doublet at 1440-1400 cm^{-1} is surprising. The origin of these bands is not known; the high temperature used undoubtedly produced considerable reaction.

Table 1.- Infrared spectral differences between ATR spectra of three coal vitrains and the corresponding shock-carbonized products.

Vitrain, coal seam	Infrared frequency, cm^{-1}			
Pittsburgh (hvab)	1610	1450	-	-
Pittsburgh, shock-carbonized	1625-1595 ^{a/}	1440-1402 ^{a/}	1250	1093
Pocahontas (lvb)	1610	1450	-	-
Pocahontas, shock-carbonized	1627-1600 ^{a/}	1443-1400 ^{a/}	1250	1093
Dorrance anthracite	1610	1450	-	-
Dorrance, shock-carbonized	1625-1595 ^{a/}	1440-1398 ^{a/}	1250	1093

a/ Doublets

Interest in attenuated total reflectance at the Bureau of Mines has been principally directed towards the study of sorbates on coals. Good spectra can be obtained when good optical contact is achieved. The interaction between sorbate and the substrate coal can be followed nicely by placing upon the ATR prism a slurry of coal and sorbate. Then the spectrum is scanned repeatedly as the sorbate is allowed to evaporate. If the sorbate is of low volatility a heat lamp can be used to increase the volatility.

Significant spectral changes have been observed for pyridine on coal. (see below.) Whether or not changes in the spectrum of the coal have occurred has not been ascertained because of the broadness of the coal bands and the interference of the intense, sharp, pyridine bands. Observations have also been made on benzene-coal and methanol-coal systems. No significant spectral changes have been seen for either the sorbate or the coal. Spectra of these systems can also be obtained by ordinary transmission spectral methods, but the ATR method provides better spectra, particularly for the sorbate.

2. Charge-Transfer Complexes

Charge-transfer complexes represent one type of weak acid-base interactions. The complexes are formed between electron-rich (donor) molecules and electron-poor (acceptor) molecules.^{10/} Redistribution of electron charge occurs so that the properties of the two moieties are changed; however, definite chemical reaction does not occur and the original moieties are nearly always recoverable by simple processes such as dissolution, or distillation, plus some method of separation. One of the changes experienced by both donor and acceptor molecules in a complex is a change in bond lengths, which produces changes in the vibration spectra; thus infrared spectra can indicate the formation of such complexes.

Observations of the infrared spectra of coal-pyridine systems have led to the belief that charge-complex formation occurs between pyridine (donor) and coal (acceptor). Examination of the pyridine-coal system by the ATR method (described above) provided interesting spectral changes as pyridine is allowed to evaporate. The principal spectral characteristics of the coal-pyridine system are those of pyridine itself with a background due to the coal extract. As evaporation of the pyridine progresses a new band shoulder is formed at about 1000 cm^{-1} and the neighboring band of pyridine at 990 cm^{-1} begins to disappear. As evaporation continues the pyridine band continues to decrease and finally disappears; meanwhile the new coal-pyridine band continues to shift slightly. The final location of the band is 1020 cm^{-1} ; at this point all the remaining pyridine molecules are apparently complexed with the coal extract. The interactions involved in this process are of interest. The results apparently are indicative of the formation of a charge-transfer molecular complex, as pyridine does indeed behave in this manner in the formation of charge-transfer complexes with many electron acceptors.^{10/} We have demonstrated that these same spectral changes occur as phenol is added to pyridine. It is logical to believe that the complexing of coal and pyridine involves the phenolic structures in the coal.

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MEASUREMENT OF THE SURFACE AREAS OF COALS FROM
THE DYNAMIC SORPTION OF CARBON DIOXIDE

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INTRODUCTION

Dynamic-sorption apparatus has been described by Nelsen and Eggertsen¹ and refined by Daeschner and Stross² for use in the determination of the surface area of solids. The essentials of the apparatus have been incorporated in commercially available equipment (Perkin-Elmer's Sorptometer). With the apparatus, the volume of nitrogen sorbed by the sample from a nitrogen-helium gas stream is determined by thermal conductivity measurements. Other mixed-gas systems may be used for special studies. The surface area is calculated using the well-known theoretical principles of Brunauer, Emmett, and Teller³ (BET equation). Surface-area values are in close agreement with those obtained from the use of more conventional apparatus in which pressure-volume measurements are made in a static system. The dynamic-sorption apparatus, however, lends itself more readily to routine measurements, having the advantage over conventional apparatus in speed and simplicity of operation. In addition, the rate of sorption is recorded directly. This can be of value in revealing pore-size variations, particularly in microporous substances where equilibrium is slow in being reached.

It is well-recognized that nitrogen at 77° K. does not reach a large part of the internal surface of coals. This is attributable, for the most part, to activated diffusion^{4,5} although thermal contraction can not be completely ruled out as being responsible for some pore closure. Conversely, it has been concluded that carbon dioxide at 195° K. does reach most of the internal surface^{6,7,8}. Three recent papers^{9,10,11} are substantially in agreement as to the magnitude of the surface-area values obtained using carbon dioxide as the adsorbate. The values are appreciably greater than those obtainable from nitrogen adsorption and do not differ greatly from those obtained using heats of wetting in methyl alcohol^{12,13}.

The primary purposes of the work reported herein are (1) to demonstrate the applicability of continuous-flow measurements to internal surface studies of coals and (2) to report for comparative purposes the surface-area values obtained for the different coals studied. Of special significance are the values obtained for coals from the Illinois Basin. These coals are high volatile A, B, and C bituminous and, to the authors' knowledge, with the exception of the work reported by Machin, Staplin, and Deadmore¹⁴ in which nitrogen and water vapor were used as adsorbates, they have not been studied to any appreciable extent.

EXPERIMENTAL

Apparatus

The adsorption apparatus was quite similar in design and use to the original apparatus described in detail in the afore-mentioned references. Modifications included: (1) needle valves for controlling gas flow rates (2) a disc integrator (Disc Instruments, Inc., Santa Ana, California) attached to a Sargent Model MR recorder for integrating peak areas (3) a reversing switch in the bridge circuit to permit positive adsorption peaks to be recorded for integration as well as positive desorption peaks and (4) a Sorensen QB12-2 D.C. Power Supply (Raytheon Company, South Norwalk, Connecticut).

Samples

Coal samples used in the study and appropriate analytical data are given in Table I. The Illinois high volatile A, B, and C bituminous coals (3 for each rank) represent only a fraction of the total number of coals of similar rank that were studied and include those coals which yielded the extremes of the range of surface-area values found for each rank.

Samples of anatase, silica spheres, bone char, carbon black (Spheron 6), and a silica-alumina catalyst with known surface areas were used to establish the effective cross-sectional area for the carbon dioxide molecule under the given experimental conditions. These substances have been evaluated at several participating laboratories by the BET nitrogen adsorption method and are distributed by the Bone Char Research Project, Inc. (Revere Sugar Refinery, 333 Medford Street, Charlestown 29, Mass.).

Procedure

Operational details for the apparatus are clearly outlined in the work of Nelsen and Eggertsen, as is the transformation of experimental data into a surface-area determination. The conditions used for the coal studies reported here are summarized as follows: A 40 x 120-mesh sample of approximately 0.2 gram is weighed into the sample tube which is then attached to the apparatus, and the sample is outgassed at 90° C. for 1 hour under a flow of helium. A controlled gas mixture of carbon dioxide and helium is permitted to flow over the sample. A dry ice-absolute ethanol bath (approximately 195° K.) is raised into position around the sample tube and adsorption is continued for 16 hours. (The adsorption step for a few samples was conducted for 30 minutes, 2 hours, and 24 hours for comparison purposes.)

After the adsorption step is completed, the gas is desorbed from the sample by removing the dry ice-ethanol bath and quickly replacing it with another bath (glycerol here) at 150° C. The volume of desorbed gas is determined from a calibration curve (detector response versus known volumes of carbon dioxide) and it is this volume that is used for determining the surface area. The relatively high desorption temperature is necessary to remove virtually all the adsorbed carbon dioxide (less than 0.5% of the original volume is retained at this temperature) and it helps provide a sharper, symmetrical desorption peak that is more comparable with calibration data. Thus, errors which may arise from badly tailing peaks are minimized.

From the familiar BET equation, which is assumed to be applicable, a single-point plot using P/P_0 as the abscissa and $P/V(P_0 - P)$ as the ordinate, and with the intercept at 0, yields $V_m = 1/\text{slope}$. The saturation vapor pressure (P_0) used in the calculations was 1450 mm. which allows for a very slightly higher temperature than the value (1.86 atm. at 195° K.) given by Bridgeman.¹⁵ Surface area then is readily determined from V_m , from the area occupied by a carbon dioxide molecule, and from the sample weight which is more carefully determined on the dry sample after the desorption step.

Multipoint plots were used for three coal samples and for all the substances involved in the determination of the effective area occupied by the carbon dioxide molecule. The constant C of the BET equation is large for carbon dioxide as the adsorbate on coal and a multipoint plot passes practically through the origin of coordinates. This enables one to use the single-point method on a more-or-less routine basis, particularly in view of the inherent uncertainties of the BET method with coals and the necessary long adsorption periods.

TABLE I

Selected Analyses of Coals Studied

No.	Sample	Proximate Analysis				Dry, Mm-Free		Heating Value	
		Moisture, %	Moist, Mm-Free Matter, %	Volatile Matter, %	Fixed Carbon, %	Fixed Carbon, %	Moist, Mm-Free Btu per pound		
<u>Illinois hvCb</u>									
1	Madison Co. (#6 coal)	17.6	35.5	46.9	57.0	11,700			
2	Kankakee Co. (#2 coal)	15.2	41.2	43.6	51.4	12,300			
3	Vermillion Co. (#7 coal)	13.1	42.6	44.3	50.8	12,700			
<u>Illinois hvBb</u>									
4	Franklin Co. (#6 coal)	11.2	33.8	55.0	62.0	13,000			
5	Williamson Co. (#6 coal)	7.9	39.1	53.0	57.5	13,700			
6	Saline Co. (#6 coal)	7.6	37.6	54.8	59.3	13,600			
<u>Illinois hvAb</u>									
7	Gallatin Co. (#5 coal)	5.9	39.4	54.7	58.2	14,100			
8	Gallatin Co. (Lower Willis)	2.3	36.9	60.8	62.2	14,900			
9	Gallatin Co. (#6 coal)	3.2	41.7	55.1	56.8	14,600			
10	West Virginia (Pittsburgh seam)	1.7	42.7	55.6	56.6	15,200			
11	West Virginia (Sewell seam)	2.1	29.9	68.0	69.5	- - -			
12	West Virginia (Bakerstown)	2.3	17.9	79.8	81.6	- - -			
13	Utah	5.7	45.0	49.3	52.3	13,700			
14	Kentucky (#5 coal)	2.6	39.1	58.3	59.8	14,700			
15	Arkansas (Hartshorne)	1.6	17.8	80.6	81.9	- - -			
16	Pennsylvania anthracite	2.1	5.1	92.7	94.8	- - -			
17	Meta-anthracite (Leoben, Austria)	0.1	1.8 (d.a.f.)	-	98.2 (d.a.f.)	- - -			
18	Borneo (Silantek)	0.8	25.3	73.9	74.5	- - -			

RESULTS AND DISCUSSION

Molecular Area of Carbon Dioxide

Table II gives the results from which the effective cross-sectional area of the carbon dioxide molecule used as the adsorbate in the studies was established. The cross-sectional area of the nitrogen molecule was taken as 16.3 \AA^2 . The assumption is made that carbon dioxide at 195° K . should give the same surface area as N_2 at 77° K . It is seen that the values are in satisfactory agreement with the exception of that obtained for the carbon black. Slight differences are to be expected, of course, owing to the wide differences in the chemical compositions of the substances used. It would appear that the large difference is due to the presence of a micro-pore system - similar perhaps to that which exists in coals - that also is not permeated during nitrogen adsorption at 77° K .

Excluding the value obtained for the carbon black, the average effective molecular area of carbon dioxide is 22.1 \AA^2 . Calculated from this value, the surface area for Spheron 6 should be about $150\text{-}155 \text{ m}^2/\text{g}$.

Adsorption-Desorption Characteristics

The desorption curve and the portion of the adsorption curve shown in Figure 1 are typical for carbon dioxide adsorbed on coals. During adsorption, a rather sudden uptake of the gas extending over a period of 2-3 minutes is followed by very slow diffusion that may extend over a period of 16 hours. As much as one third of the total adsorption volume is adsorbed by certain high-volatile C bituminous coals during the first 2-3 minutes.

Table III gives some comparative data for various periods of adsorption. Although the table includes only a small sampling of coals, the data clearly show that adsorption is far from complete at 2 hours but also indicate that it is essentially complete somewhere between 2 and 16 hours. The 16-hour period was selected as it was found convenient to conduct adsorption overnight.

Adsorption is much too slow to enable one to use the adsorption curve for the gas-volume determination since calibration curves are practically impossible to construct for the extended removal or addition of a gas introduced at a variable rate into the mixed-gas stream. Fortunately, however, for analysis purposes, desorption is rapid and essentially complete within the first 2-3 minutes of its initiation.

Surface Areas of Coals

Table IV lists the surface-area values for the coals studied. As indicated earlier, a larger number of Illinois coals than shown were investigated and a range of intermediate values was found within the extremes shown here for each rank. Some overlap of values is present between the ranks of Illinois coals as would be anticipated. The range of values from the work of Machin et al. by classical nitrogen adsorption methods is shown for comparative and supplemental purposes.

It is seen that the values from carbon dioxide adsorption are of the same order of magnitude as values obtained from heats of wetting and, thus, also are in agreement with the more recent studies in which carbon dioxide was used as the adsorbate in static systems and to which references have been made. Values for the hvAb coals are the lowest reported thus far from carbon dioxide adsorption on coals, with the exception of meta-anthracite, but they are not any lower than values that have been obtained from heats-of-wetting methods.

Maximal and minimal values among all the coals studied are found essentially within the ranks of Illinois coals. Since the Illinois coals comprise such a narrow

TABLE II

Determination of the Effective Cross Sectional Area of the Carbon Dioxide Molecule

Adsorbent	S.A., m ² /g*		N ₂ S.A. CO ₂ S.A.	Effective Molecular Area of CO ₂ , A ²
	(N ₂ ads.)	(CO ₂ ads.)		
Anatase	10.3	7.9	1.30	22.1
Silica spheres	24.3	18.6	1.31	22.3
Bone char	69	52	1.33	22.6
Carbon black(Spheron 6)	110	117	0.94	16.0
Silica-Alumina catalyst	550	436	1.26	21.4

*Mean of accepted values from several participating laboratories.

**Assuming a cross sectional area of 17.0 A² for the carbon dioxide molecule.

TABLE III

Adsorption of Carbon Dioxide on Coals for Different Adsorption Times

Coal	Volume Adsorbed Per Gram of Sample (ml.)*			
	0.5 hour	2 hours	16 hours	24 hours
Sample 4	27.1	35.1	42.2	42.3
Sample 7	3.3	5.8	10.2	- -
Utah	14.1	17.7	28.3	28.4
Borneo	29.9	38.0	38.4	38.4

*P/P₀ differed slightly among the coals used but was the same for each coal for the different adsorption periods.

TABLE IV

Surface Areas of Coals

No.	Sample	Surface Area, m ² /g		No.	Sample	Surface Area, m ² /g
		CO ₂ ads.	N ₂ ads.*			
	<u>Illinois hvCb</u>		46.8-91.8	10	W. Virginia (Pitts. seam)	43
1	Madison Co. (#6 coal)	292		11	W. Virginia (Sewell seam)	197
2	Kankakee Co. (#2 coal)	248		12	W. Virginia (Bakerstown)	128
3	Vermilion Co. (#7 coal)	184				
	<u>Illinois hvBb</u>		7.2-16.3	13	Utah	145
4	Franklin Co. (#6 coal)	205		14	Kentucky (#5 coal)	66
5	Williamson Co. (#6 coal)	115		15	Arkansas (Hartshorne)	182
6	Saline Co. (#6 coal)	83				
	<u>Illinois hvAb</u>		1.8-4.5	16	Pennsylvania anthracite	262
7	Gallatin Co. (#5 coal)	86		17	Meta-anthracite (Leoben, Austria)	6.0
8	Gallatin Co. (Lower Willis)	57		18	Borneo (Silantek)	290
9	Gallatin Co. (#6 coal)	46				

*From work by Machin, Staplin, and Deadmore.

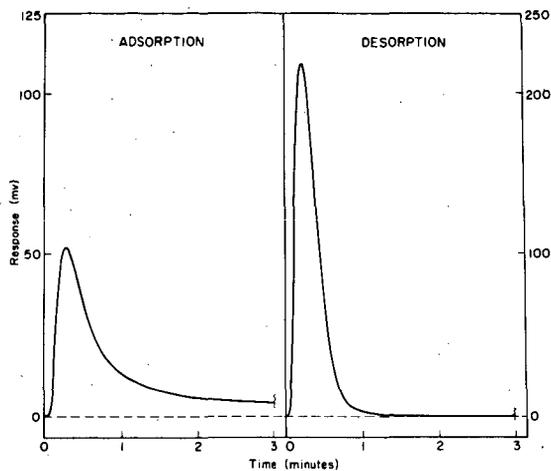


Figure 1. Typical carbon dioxide adsorption and desorption curves for coals (without integrator record)

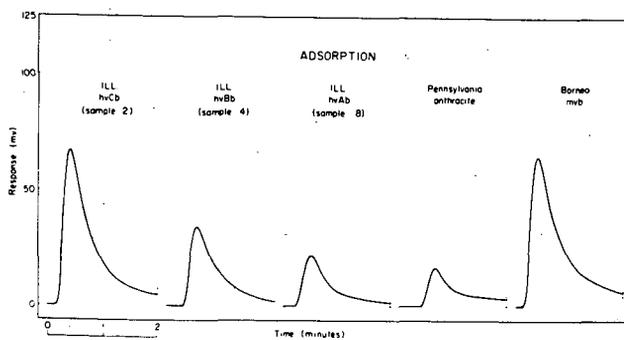


Figure 2. Initial portions of adsorption curves for 0.2-gram samples of various coals (without integrator record)

portion of the overall degree of metamorphism among coals, and since the values for the higher rank coals examined do not change in an orderly manner with increase in rank, there appears to be little basis for attempts to construct a curve relating rank and surface area.

Implications from Initial Adsorption Rates

It is significant that surface-area values for Illinois hvCb coals from nitrogen adsorption isotherms reported by Machin et al. are as high as $91 \text{ m}^2/\text{g}$. A search of the literature failed to uncover a report in which a coal sample produced a surface area this large by nitrogen adsorption. In some of our own studies using nitrogen as the adsorbate in the continuous-flow apparatus, values for sample numbers 2 and 3 were found to be 99 and $48 \text{ m}^2/\text{g}$, respectively. Indications are that a larger proportion of pores of greater diameter than a certain minimal size exists in the hvCb coals permitting greater quantities of nitrogen to permeate the structure at 77° K .

Further proof of this may be seen in a comparison of the initial adsorption rates for carbon dioxide on similar sample weights of several coals shown in Figure 2. All of the coals shown have surface-area values of over $200 \text{ m}^2/\text{g}$, with the exception of the hvAb which should not be used directly in this comparison. It is readily apparent that the rate of carbon dioxide taken up during the first 2-3 minutes differs markedly among the coals. It would appear that the greater rate of adsorption of carbon dioxide by the hvCb coal in comparison with the hvBb, hvAb, and anthracite coals coincides with a greater macropore volume of the coal and would tend to supplement the nitrogen adsorption data from this standpoint. It is tempting to say, without knowledge of the Borneo coal, that the macropore volume decreases with rank, and this appears to be true for the Illinois coals studied thus far. The large volume of carbon dioxide initially adsorbed by the Borneo coal (mvb), however, would tend to negate this concept, and yet nitrogen adsorption for this coal gives a surface-area value of only $0.8 \text{ m}^2/\text{g}$. Thus, it would appear that this coal has very little macropore volume available to nitrogen at 77° K ., and yet it has a large number of pores of sufficient size to permit carbon dioxide to permeate the structure rapidly at 195° K . making it different from anthracite or hvAb coals in this regard. This only serves to emphasize the danger in making generalities about coals from widely differing localities and perhaps formed in widely differing environments.

CONCLUSIONS

It is recognized that in the determination of the surface areas of coals no method reported thus far is completely free of criticism. In the work reported here it is assumed that the BET equation is applicable, and this in itself is subject to some criticism. The abbreviated single-point method used here, however, should be as good as any other method for obtaining useful relative data for practical comparative purposes. In addition, the ability to easily follow the initial adsorption rate should be of advantage in attempts to describe quantitatively the molecular sieve characteristics of various coals.

ACKNOWLEDGMENT

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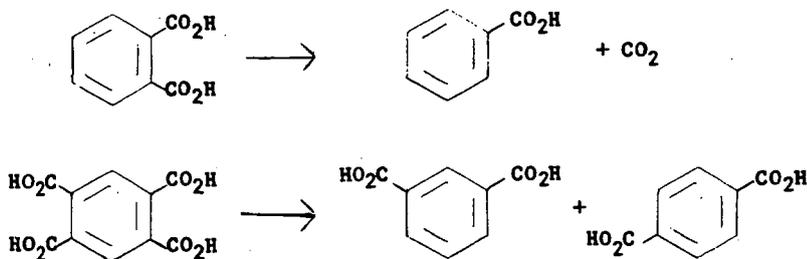
GAS CHROMATOGRAPHIC SEPARATIONS OF BENZENECARBOXYLIC ACIDS DERIVED FROM COAL

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INTRODUCTION

When benzenepolycarboxylic acids are treated with hydrogen and carbon monoxide at elevated temperatures and pressures in the presence of dicobalt octacarbonyl, a reductive decarboxylation reaction occurs^{2/}



The products of the reaction are carboxylic acids containing fewer carboxyl groups than are present in the starting acid. In most cases mixtures of benzenecarboxylic acids are obtained.

Alkaline oxidation of coal produces a mixture containing relatively large amounts of benzenecarboxylic acids.^{2,7/} If these "coal acids" can be decarboxylated by the above reaction, commercially useful products such as isophthalic and terephthalic acids might be obtained. In studying the feasibility of this decarboxylation reaction, it is necessary to have an analytical procedure by which the benzenecarboxylic acids can be separated and analyzed quantitatively. Several chromatographic procedures, including thin layer, column, and paper chromatography, for the separation of this type of acids appear in the literature.^{2,3,6/} All of these procedures, however, are deficient in some respects. The visualization and quantitative estimation of the separated acids is difficult. Moreover, the separation of isophthalic and terephthalic acids was not reported.

The free acids cannot be analyzed by gas liquid chromatography (g.l.c.) because they are not volatile enough and they tend to decarboxylate or form anhydrides at high temperatures. In order to chromatograph acids, derivatives are usually prepared; esters are the most common. Schnitzer and Desjardins^{8/} have described a g.l.c. procedure utilizing methyl esters to separate benzenecarboxylic acids. Complete esterification of all of the acids required the use of diazomethane, a reagent with some undesirable properties. In addition, isophthalic and terephthalic acids were not separated sufficiently for quantitative analysis and tailing of the peaks was noticeable. Trimethylsilyl esters of amino acids,^{1/} phosphonic acids^{5/} and carboxylic acids^{4/} have been prepared and analyzed by g.l.c. Symmetrical peaks are obtained and separations were usually adequate. The preparation of trimethylsilyl esters is also relatively simple experimentally. For these reasons, the preparation and gas chromatographic behavior of the trimethylsilyl esters of benzenecarboxylic acids was investigated and is the subject of this paper.

ACKNOWLEDGMENT

The authors wish to thank Mrs. Joan Gordon for her assistance in the experimental portion of this work. This work was also supported in part by the Union Carbide Corporation.

DISCUSSION

Several methods have been used for the preparation of trimethylsilyl derivatives.^{1,4,5/} All of the reagents investigated for the preparation of trimethylsilyl esters of benzenecarboxylic acids were successful in silylating the acids that contained up to four carboxyl groups. However, the esters of the pentacarboxylic acid and the hexacarboxylic (mellitic) acids either did not form or their formation was not reproducible. A procedure that was found to give consistent results was to reflux the acids with equal volumes of hexamethyldisilazane, trimethylchlorosilane and toluene until the resulting ammonium chloride sublimed and the acids were completely solubilized. This procedure was used to obtain the esters used in this paper.

To carry out a quantitative analysis on benzenecarboxylic acids and on the coal acids, flame ionization detector response factors for each of the acids were determined relative to *m*-toluic acid as a standard. Synthetic mixtures of ten benzenecarboxylic acids plus *m*-toluic acid were prepared, silylated and chromatographed. Figure 1 shows the separation of this synthetic mixture. Once the response factors were determined, other mixtures of the acids containing different weights of each acid were prepared and analyzed using the appropriate response factors. Table 1 compares the known and found values of a sample mixture and shows that the analysis can be made satisfactorily.

Table 1. Analysis of synthetic mixture of benzenecarboxylic acids

Component	Position of carboxyl groups	Composition, percent by weight	
		Known	Found
Benzoic	1	6.5	6.3
Phthalic	1,2	4.3	4.0
Isophthalic	1,3	8.4	8.6
Terephthalic	1,4	6.6	7.1
Hemimellitic	1,2,3	5.5	5.1
Trimellitic	1,2,4	14.2	15.8
Trimesic	1,3,5	12.8	13.4
Pyromellitic ^{1/}	1,2,4,5	20.5	21.4
Pentacarboxylic	1,2,3,4,5	8.6	6.3
Mellitic	1,2,3,4,5,6	12.6	12.0

^{1/} The other tetracarboxylic acids [prehnitic (1,2,3,5) and mellophanic (1,2,3,4)] were not available. From comparison between the chromatograms of the methyl and trimethylsilyl esters, the authors feel that these should also be separable as trimethylsilyl esters.

The newly developed analytical method was then used for determining the nature of the products from the decarboxylation of pure acids. It was found that polycarboxylic acids containing carboxyl groups ortho to each other decarboxylated giving mixtures of acids containing fewer carboxyl groups than were present in the original acid. For example, in aqueous dioxane, pyromellitic acid yields a 2:1 mixture of isophthalic and terephthalic acids while hemimellitic acid yields a 1:1 mixture of benzoic and isophthalic acids. In general, yields are 70 to 90%.

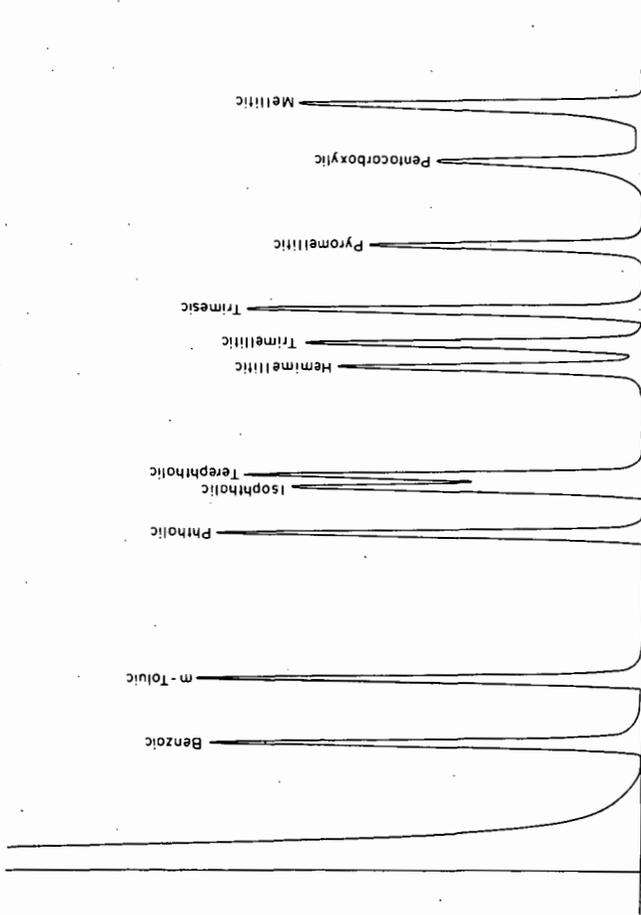


Figure 1. — Separation of benzenecarboxylic acid trimethylsilyl esters.

The coal acids, a mixture obtained from the Dow Chemical Company, and the decarboxylated acids containing a known amount of m-toluic acid were then silylated and chromatographed. Figures 2 and 3 show the type of chromatogram obtained. Using the correction factors which were determined previously, the analysis of the coal acids was carried out. Table 2 summarizes the results. It can be seen that the starting acids contain fairly large amounts of phthalic, hemimellitic, trimellitic, pyromellitic and pentacarboxylic acids. The decarboxylated acids contain large amounts of benzoic, isophthalic and terephthalic acids with only traces of higher acids. Thus it was shown that the decarboxylation reaction essentially converts almost all of the tri-, tetra-, and pentacarboxylic acids to iso- and terephthalic acids and that the benzoic acid results primarily from decarboxylation of phthalic acid. By use of the analytical method described, it was shown that the coal acids were upgraded and converted into valuable products, i.e., benzoic, isophthalic and terephthalic acids, upon undergoing the decarboxylation reaction.

Table 2. Analysis of coal acids

Component	Coal acids, weight percent	
	Before decarboxylation	After decarboxylation
Benzoic	-	4
Phthalic	3.3	Trace
Isophthalic	} 0.4	10
Terephthalic		3
Hemimellitic	2.8	-
Trimellitic	5.5	-
Trimesic	-	> 0.5
Pyromellitic	10.1	Trace
Mellophanic	-	1/
Prehnitic	-	1/
Pentacarboxylic	3.4	Trace
Mellitic	Trace	Trace
Total	25.5	17.5

1/ Traces possibly present; no standards available.

EXPERIMENTAL

Reductive Decarboxylation of Hemimellitic Acid. A solution of 3.1 g. hemimellitic acid (0.0187 mole) and 2.1 g. dicobalt octacarbonyl in 70 ml. dioxane and 15 ml. of water was placed in a 150 ml. Aminco rocking autoclave and pressured to 3500 p.s.i.g. with 1:1 synthesis gas ($H_2:CO$). The autoclave was heated to 200°C. for 5 hr. and allowed to cool overnight. The gases were vented and the reaction mixture taken to dryness under vacuum. The residue was refluxed with dilute hydrochloric acid and again taken to dryness. Most of the product was crystalline, but some gummy material was still present. The product was refluxed with water, cooled, and filtered to yield 3.0 g. of pale, purple solid. A further 0.54 g. of product was extracted from the filtrate with ether.

Gas Chromatographic Analyses. The gas chromatographic analyses were performed on a Micro Tek GC 2000R dual column, programmed-temperature chromatograph equipped with a dual hydrogen flame ionization detector. A 3 foot by 1/8 inch OD stainless steel column packed with 3% Apiezon L on 60 to 80 mesh AW-DMCS treated Chromosorb G was used. Helium at a flow rate of approximately 55 ml. per min. was the carrier gas. Runs were temperature programmed from 90° to 260° at a rate of 7.5° per min. The analysis takes less than one-half hr. under these conditions.

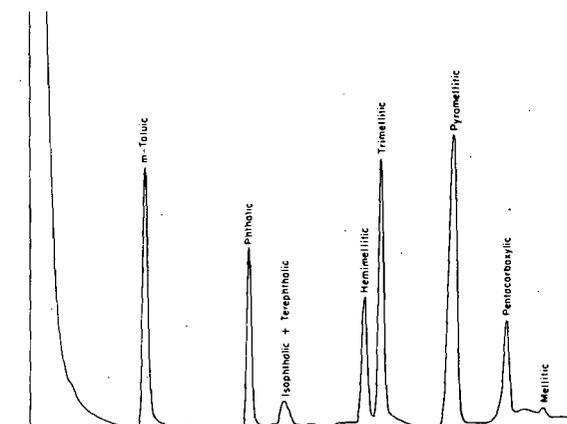


Figure 2 - Cool acids before decarboxylation.

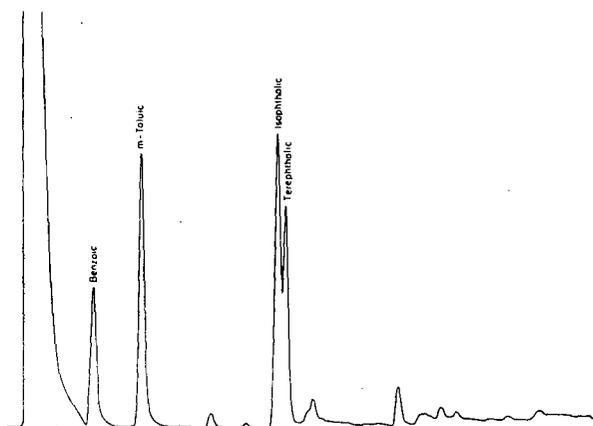


Figure 3 - Cool acids after decarboxylation.

The trimethylsilyl esters were prepared by refluxing the acids with a 1:1:1 mixture of hexamethyldisilazane:trimethylchlorosilane:toluene until the acids were completely solubilized and the resulting ammonium chloride had sublimed. This takes one to two hr. The reaction mixture is kept in a vial sealed with a serum cap to keep out moisture. The fact that the trimethylsilyl ester derivatives are readily hydrolyzable back to the original acid is a useful property of these esters. For example, upon elution from the chromatograph, the ester is trapped out in a capillary tube and exposed to the atmosphere for a short time to affect hydrolysis to the free acid. The infrared spectrum of the acid can then be obtained for positive identification. This has proved extremely helpful for identification since retention times are not reproducible to the degree necessary for identification.

CONCLUSION

By using a g.l.c. separation based on trimethylsilyl esters, it has been possible to rapidly analyze mixtures of carboxylic acids and show that benzenecarboxylic acids undergo a reductive decarboxylation in the presence of hydrogen and carbon monoxide at elevated temperatures and pressures with dicobalt octacarbonyl as a catalyst. The advantages of the trimethylsilyl esters over the methyl esters are that they are easily prepared, chromatograph without tailing, are better separated and are easily converted to the original acid for positive identification. Additionally, with the use of this procedure it has been shown that coal acids undergo this reaction and that valuable products are obtained.

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QUANTITATIVE ULTRAVIOLET ANALYSIS OF C₁₀-C₁₅
NAPHTHALENES IN HYDROCARBON OILS

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INTRODUCTION

The characterization of neutral oils from low-temperature coal tars required the development of a quantitative determination of alkylnaphthalenes according to their degree of substitution.

The near ultraviolet spectrum of naphthalene consists of three principle regions of absorption which, according to Clar's classification (13), are called the β -, para-, and α -band systems and are related to the three band systems of benzene. The principle bands of these systems are located at 220.7, 275.5, and 311.5 m μ (log ϵ 5.08, 3.77, and 2.40, respectively). For the quantitative analysis of C₁₀-C₁₁ naphthalenes, the use of the α -bands has been reported by Neimark (31), Adams (2), and Coggeshall (15). An ASTM method (4) for total naphthalenes in jet fuels using the para bands has been adopted and the extent of interference of other aromatics pointed out. Snyder (34) has said that the ASTM procedure using the para bands for naphthalene determination is inapplicable in gasoline samples because of serious interference of monoaromatics. Mixtures of coal tar neutral oils analyzed in this laboratory (23) also prohibits the use of the para bands because of possible interference from other aromatics. Therefore, the present paper describes a method developed for the analysis of C₁₀-C₁₈ alkylnaphthalenes using the most intense β -band of naphthalenes, thereby improving sensitivity and increasing selectivity by reducing interference from other classes.

EXPERIMENTAL

As part of a recently developed low-temperature coal tar assay (23), total naphthalenes were isolated from a high-quality neutral oil using liquid chromatography on a gas chromatography analog. The detailed procedure for this chromatographic technique has been described (21, 22). For the separation, a weighed quantity close to 1 gram of the high-quality neutral oil was introduced to a 25-ft length of 3/8 in. tubing packed with 80-100 mesh F-20 alumina containing 4 weight-percent water and pretreated with spectral grade cyclohexane. The charge was eluted with cyclohexane under 75 psig nitrogen. Fractions of 14 ml each were collected, and elution of naphthalenes was followed by the automatic recording of a chromatogram with an ultraviolet absorption monitoring device. Ultraviolet spectra were obtained on the cyclohexane solutions from tubes corresponding to the chromatogram peaks, using a Perkin-Elmer 350 ultraviolet spectrophotometer and matched quartz absorption cells.

For the absorptivity data, pure samples of naphthalenes and all methyl- and ethylnaphthalenes C₁₀-C₁₂ were commercially available. Zone refined samples from James Hinton, 358 Chicago Ave., Valparaiso, Fla., were used when possible

and were found to be the highest purity available. Out of the 14 possible isomers of trimethylnaphthalenes, the only commercially available samples were the 1, 3, 7-, the 2, 3, 5-, and the 2, 3, 6- isomers. All samples were weighed on a microbalance for the absorptivity data. A study of the β -band for naphthalene and monomethylnaphthalenes showed that these classes behaved in accordance with the laws of Lambert and Beer and it was assumed that higher homologs also obeyed these laws in the concentrations used.

RESULTS AND DISCUSSION

Elution Chromatographic Separation. - Naphthalene and its alkyl derivatives emerged from the column relatively free from other classes of compounds, thus allowing the application of ultraviolet quantitative procedures. Aliphatic material, biphenyls, hydroaromatics, and monoaromatics were all eluted before naphthalenes, with only a small amount of overlapping. Three-ring compounds such as dibenzofurans, fluorenes, phenanthrenes, and anthracenes are eluted later and do not interfere seriously. Within naphthalenes as a class, the parameter which causes a pronounced change in adsorbability was the degree of substitution, while position-substitution effects and size-of-alkyl group effects were secondary. Thus, all isomers of mono-, di-, tri-, tetra-, and pentaalkylnaphthalenes were eluted as classes and were sufficiently separated from each other, as evidenced by marked changes in the ultraviolet spectra of successive fractions.

Figure 1 for a synthetic mixture of four pure naphthalenes shows that overlapping occurs more extensively in lower classes and that increased alkyl substitution is effective in enhancing class separation. Klemm (25) points out that methylation of naphthalene enhances adsorbability but increasing the bulkiness of the substituent group decreases adsorbability. Snyder's data on naphthalenes agrees with the increase of adsorbability with alkylation (35), but shows very little difference in adsorbability of 1-ethyl-, 1-n-butyl-, and 1-n-hexylnaphthalene (36). Ethyl groups were known to be present in the naphthalene mixtures analyzed; a detailed characterization of a bituminous coal tar (11) and recent gas chromatographic data on the naphthalene fractions isolated from 18 tars (23) showed that monoethylnaphthalenes comprised 16 percent of the total amount for monosubstituted naphthalenes and that ethylmethylnaphthalenes were 16 percent of the total amount for disubstituted naphthalenes.

Figure 2 shows that the wavelength of the β -band for naphthalenes containing alkyl groups other than methyl depends more on the number than on the size of the substituent. Hence, any marked change in adsorbability of an alkyl naphthalene from that of the correspondingly substituted methylnaphthalene would be readily detected by its β -band. Since such a change was not observed either in the elution of neutral oil mixtures or synthetic mixtures containing ethylnaphthalenes, it was assumed that naphthalenes containing ethyl groups are eluted with methylnaphthalenes with the same degree of substitution. Further, it is assumed that their amounts were accurately accounted for because their absorptivities were not significantly different from methylnaphthalenes with the same degree of substitution. Small differences in adsorbability among some of the various isomers in mono-, di-, and trimethylnaphthalenes were observed in pure compound elution runs.

Figure 3 shows the results for a neutral oil from a low-temperature tar produced from a Colorado subbituminous coal in a fluidized-bed with internal heating at 500° C.

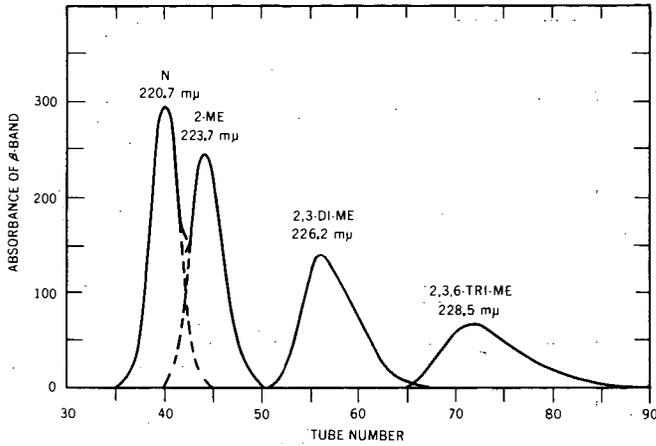


FIGURE 1. - Elution of a Synthetic Mixture of C₁₀-C₁₃ Naphthalenes.

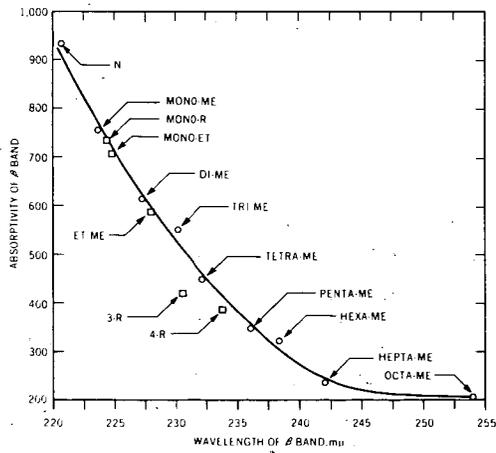


FIGURE 2. - Wavelength and Absorptivity Data for C₁₀-C₁₈ Alkyl naphthalenes.

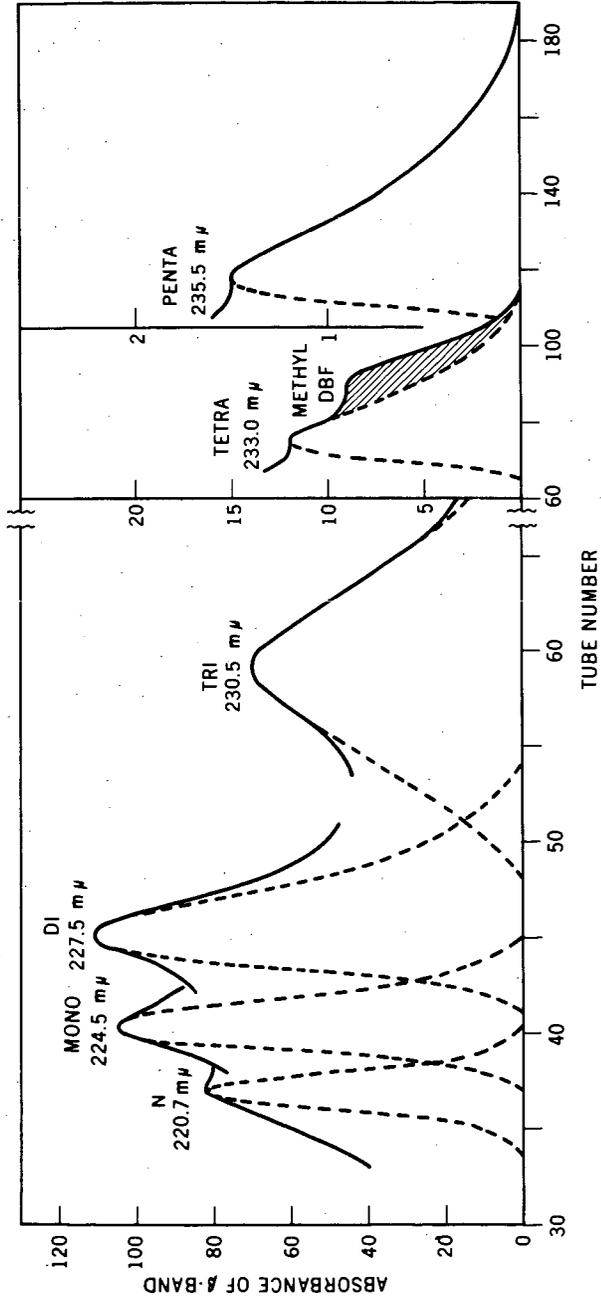


FIGURE 3. - Elution of a Neutral Oil, C₁₀-C₁₅ Naphthalenes.

Since tube number is arbitrary and columns gradually deactivate with extended use, the relative retention of each class to an internal standard can be utilized to aid in the determination of peak tubes, particularly in the broader bands of pentamethylnaphthalenes. For this purpose, 20 μ l of o-ethyltoluene was added to each sample. Since the synthetic mixture shown in Figure 1 and the neutral oil shown in Figure 3 were run several months apart, the peak tube numbers do not agree. However, their relative retentions are comparable. Figure 1 gives relative retentions of 1.5, 1.7, 2.2, and 2.8 for naphthalene and one isomer each of mono-, di-, and trimethylnaphthalene classes, relative to o-ethyltoluene in tube 26. Figure 3 gives relative retention values of 1.4, 1.5, 1.7, and 2.3, respectively, for natural, complex mixtures of these classes, relative to o-ethyltoluene in tube 26.

Determination of Ultraviolet Calibration Data. - It has been observed by Mosby (30) for ultraviolet spectra of C_{14} - C_{16} methylnaphthalenes that with increasing methylation there are bathochromic shifts relative to naphthalene. Dannenberg (16) has shown that for the β -band of naphthalenes there is a constant bathochromic shift of 3 $m\mu$ per alkyl substituent introduced to the ring, independent of its bulkiness and its position in the ring up to the octa-substituted compound. The data presented in Table 1 for C_{10} - C_{18} methylnaphthalenes support this wavelength correlation with the exception of octamethylnaphthalene. A study of both wavelengths and absorptivities was made on C_{10} - C_{18} alkylnaphthalenes, making extensive use of literature data. Ultraviolet spectral data have been reported on all of the 14 possible trimethylnaphthalenes (3, 5, 8, 9, 12, 14, 17, 18, 19, 24, 28, 32, 33), 8 of the tetramethylnaphthalenes (3, 6, 7, 8, 27, 30, 33, 37), 2 pentamethylnaphthalenes (1, 30), 4 hexamethylnaphthalenes (1, 10, 30), 1 heptamethylnaphthalene (1), and octamethylnaphthalene (1, 29). No solvent corrections were applied to the literature data, which are reported both in alcohol and hydrocarbon solvents. Mosby (30) reports that for a tetramethylnaphthalene the only observable difference in methanol and isooctane spectra is a very slight hyperchromic displacement (intensity increase) of the longer wavelength maxima.

As shown in Table 1 and Figure 2 for the β -band there is both a bathochromic and hypochromic displacement (shift to longer wavelength and intensity decrease) as the number of alkyl groups increase in the naphthalene ring. The values of wavelength and absorptivities for the various isomers in each carbon number class are in ranges narrow enough to justify the use of averages. Table 1 presents the arithmetic averages determined for each class of methylnaphthalenes. A plot of carbon number vs. arithmetic average of molar absorptivity yields a linear relationship. However, for application to the present analysis the relationship shown in Figure 2 is shown to have more usefulness. This plot combines both the bathochromic and hypochromic shifts by plotting average absorptivity vs. average wavelength of the β -band for each class of methylnaphthalenes. Values for other alkylnaphthalene classes were added to the plot after the curve for methyl data was drawn. Points shown in squares for monoalkyl-, ethylmethyl-, trialkyl-, and tetraalkylnaphthalenes (where $R = C_{13}$ - C_{16}) were obtained from averages of 26 literature spectra.

While the absorptivities and wavelengths for each class fell into definite ranges, it must be pointed out that the β -band is not insensitive to isomerism. A close examination of the data reveals that in addition to the relationship of absorptivity with degree of substitution, it is also subject to position substitution effects.

TABLE 1. - Ultraviolet data for the β -band of C_{10} - C_{18} naphthalene classes

Class	Source	Average wavelength, $m\mu$	Average absorptivity
Naphthalene	Pure compound	220.7	933
Monomethylnaphthalenes	Pure compounds	223.7	754
Monoethylnaphthalenes	Pure compounds	224.8	709
Dimethylnaphthalenes	Pure compounds	227.3	612
Trimethylnaphthalenes	34 literature values	230.1	550
Tetramethylnaphthalenes	12 literature values	232.1	446
Pentamethylnaphthalenes	2 literature values	236.0	346
Hexamethylnaphthalenes	9 literature values	238.3	321
Heptamethylnaphthalenes	1 literature value	242.0	237
Octamethylnaphthalenes	2 literature values	254	205

TABLE 2. - Ultraviolet data for the β -band of individual C_{11} - C_{12} naphthalenes

Compound	Wavelength, $m\mu$	Absorptivity
1-Methylnaphthalene	223.7	657
2-Methylnaphthalene	223.7	850
1-Ethylnaphthalene	224.8	609
2-Ethylnaphthalene	224.8	808
1, 2-Dimethylnaphthalene	227.5	544
1, 3-Dimethylnaphthalene	227.8	564
1, 4-Dimethylnaphthalene	227.7	352
1, 5-Dimethylnaphthalene	227.3	571
1, 6-Dimethylnaphthalene	226.9	523
1, 7-Dimethylnaphthalene	227.2	692
1, 8-Dimethylnaphthalene	228.2	572
2, 3-Dimethylnaphthalene	226.2	653
2, 6-Dimethylnaphthalene	226.6	868
2, 7-Dimethylnaphthalene	227.3	785

The β -band of naphthalene has been assigned to longitudinal polarization by Klevens (26). The longitudinal direction is defined as being parallel to the long axis of the molecule while transverse is perpendicular to the long axis of the molecule. Jaffé (20) has discussed the importance of the position of substitution upon the longitudinal and transverse polarizations possible within the naphthalene molecule and the effects on wavelength and intensity. However, he does not discuss these effects with regard to the β -band. An examination of all the classes of naphthalenes shows no correlation of structure with wavelength within each class since the ranges are so narrow. It is to be expected that ring substitution will distort the charge distribution within the naphthalene ring and that this effect will influence the intensity of absorption. The following position substitution effects on the absorptivity of the β -band for four classes of naphthalenes were noted:

(1) For monomethylnaphthalenes, Table 2 shows that substitution in the 1-position causes a greater hypochromic shift relative to the value for naphthalene than 2-substitution.

(2) In the class of dimethylnaphthalenes, Table 2 shows that substitution in the 1,4-position produces the greatest hypochromic shift relative to the value for naphthalene while substitution in the 2,6-position produces the least.

(3) A study of the literature data on trimethylnaphthalenes shows that the 1,4,6-isomer has the lowest absorptivity, thus indicating again a greater hypochromic effect with substitution in the 1 and 4 positions.

(4) Within the class of tetramethylnaphthalenes, the 1,4,6,7-isomer has the lowest absorptivity value (320) while the 2,3,6,7-isomer has the largest (686).

Since, as previously stated, ethyl groups are present in coal tar neutral oils and, specifically, monoethylnaphthalenes, it was thought they should be included in the average absorptivities used for the determination of monoalkylnaphthalenes. An arithmetic average of 731 was obtained for the two classes. Since position substitution has a pronounced effect on absorptivity of monoalkylnaphthalenes, a further check on the validity of this average was made by calculating a weighted absorptivity. Data used in obtaining this weighted absorptivity was based on gas chromatographic analysis of each of these four compounds in the isolated naphthalene fractions from 18 individual neutral oils. A value of 757 was obtained which represents a difference of only 3.4 percent from the arithmetic average. In the same manner as for monoalkylnaphthalenes, a weighted average absorptivity was determined for dimethylnaphthalenes. A value differing from the arithmetic average was expected here since there is not an even distribution of the amounts of the 10 dimethyl- isomers in these neutral oils. For example, 1,8-dimethylnaphthalene has not been identified in any coal tar neutral oil. However, a value of 639 was obtained which differs only 4.2 percent from the arithmetic average of 612 for all 10 isomers. In summary, for analysis of coal tar neutral oils, tailored absorptivities of 757 and 639 were used for the mono- and dialkylnaphthalene classes respectively, and absorptivities obtained from the literature were used for the tri-, tetra-, and pentamethylnaphthalenes.

Ultraviolet Analysis. - Throughout successively eluted portions of a neutral oil a regular stepwise bathochromic shift of the β -band occurs and the wavelength of each shift is in good agreement with the wavelength average determined for each class of methylnaphthalenes shown in Table 1. Corresponding to each wavelength shift a peak occurs in the monitor chromatogram. Data from the ultraviolet spectra of individual tubes were used to construct absorbance distribution curves for the β -band of each class of naphthalene, as shown in Figures 1 and 3. The envelope of the ultraviolet absorbance curve is discontinuous, i. e., it is constructed of data from several wavelengths. The plot for a single wavelength was followed as long as that wavelength predominated, i. e., until a combination tube was reached. The absorbance plot was then continued at the new wavelength. In the neutral oil samples analyzed there were consistently six wavelength changes corresponding to C_{10} - C_{15} alkyl naphthalenes. A graphical method was utilized to resolve the individual absorbance distribution curves for each class. Using qualitative changes exhibited throughout the entire ultraviolet spectrum (naphthalene α - and para- bands also vary qualitatively with increasing degree of alkylation), it is possible to follow the key tubes representing the first appearance, the peak and the disappearance for each class of naphthalene, even in the presence of overlapping. These tubes and all combination tubes are then marked on the absorbance plot. The absorbance curve is then drawn according to this information. The dashed lines shown in Figures 1 and 3 indicate this deduced data. Knowledge of curve shapes and characteristic tailing was obtained from pure compound runs. After the absorbance curve for an individual class was constructed in this manner, the absorbance values for each tube were read from this resolved plot and the proper absorptivity used to calculate the weight of that class in a single tube according to the following equation:

$$w = \frac{A \times l4}{a}$$

where w = weight, milligrams;

$l4$ = volume of one tube, ml;

a = absorptivity of the naphthalene class at the β -band;

A = absorbance of the tube at the β -band.

Extensive interference from non-naphthalenic compounds was not encountered. Both ultraviolet and infrared spectra showed that the lower classes of naphthalene were sufficiently separated from the preceding classes of hydroaromatics, biphenyls, and monoaromatics. A small amount of overlapping introduced negligible error since these classes have minimum absorption in the region of the naphthalene β -band and, in addition, have significantly lower absorptivities at their maxima. When there was qualitative evidence of significant amounts of dibenzofurans, fluorenes, phenanthrenes, and anthracenes overlapping the higher naphthalene classes, there was a change in the shape of the distribution curve, as shown in Figure 3 for the tetramethylnaphthalene class. The amount of absorbance due to this interfering compound was graphically subtracted from the absorbance distribution plot, as shown by the shaded area, considering the shape of the naphthalene curve. In the instance of Figure 3, the compound was identified as a methyl dibenzofuran mixture from its ultraviolet bands. Since the method is graphical, it is not necessary to identify the compound to subtract its absorbance. If this graphical approach is prevented by too close an agreement of peak tubes of interfering compound and

naphthalene class, the standard quantitative method of solution of simultaneous equations can be applied. The absorptivities of these more strongly adsorbed compounds at the naphthalene β -band wavelength are minimum since their wavelength maxima are all in the range 250 to 260 μ .

Because of the unavailability of pure samples in the C_{14} - C_{15} naphthalene range, no realistic synthetic mixture could be tested. However, analysis of the relatively simple mixture shown in Figure 1, using absorptivities specific for the compounds present, gave individual errors of not more than 2 percent absolute. Another accuracy test was made on a mixture synthesized to duplicate the percentages of individual C_{10} - C_{13} naphthalenes in a neutral oil sample. This test mixture, containing 14 naphthalenes, gave an ultraviolet absorbance distribution curve that showed the same class elutions as obtained with neutral oils. Average class absorptivities were used to determine the amounts of each class. Results showed that no naphthalene class was in error more than 5 percent absolute.

The 18 neutral oils analyzed by this method varied in composition from 5 to 25 percent total alkyl naphthalenes. In spite of this composition variation, wavelengths of each class remained remarkably constant. These analytical procedures for coal tar neutral oils should be applicable to similar hydrocarbon oils from other sources, such as petroleum and shale oil.

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ANALYSIS OF SULFUR IN COALS BY X-RAY FLUORESCENCE

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ABSTRACT

Determination of the sulfur content of coals by X-ray fluorescence has been investigated. For preliminary studies on sulfur in both organic and pyritic forms, known amounts were added to sulfur-free carbon black.

Pyrite particle size was found to have a significant effect on fluorescence intensities. At constant pyrite content, fluorescence intensity gives a good measure of pyrite particle size in the range from 2 to 150 microns. For determination of sulfur content, samples must be ground to less than 2 microns.

The ratio of sulfur $K\alpha$ and $K\beta$ fluorescence emission is quite dependent on sulfur concentration but almost independent of bonding or sulfur form. The alpha to beta ratio thus is a very good measure of the sulfur concentration, requiring no standard or correction for changes in intensity of the X-ray beam. The alpha to beta ratio, in combination with the $K\alpha$ reading, permits a determination of total sulfur as well as the percentage in pyritic form.

A program is now in progress to determine the sulfur content of over 100 American coals by X-ray fluorescence.

A MICROMETHOD FOR TOTAL SULFUR DETERMINATION IN
NONLEADED LIGHT HYDROCARBON FEEDSTOCKS

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ABSTRACT

Sulfur poisoning adversely affects the life and performance of nickel catalysts used in hydrocarbon reforming and similar operations. The need for a dependable procedure for total sulfur determination led to development of the method described in this paper. The sulfur compounds in a weighed sample are converted to SO_2 by combustion in an oxyhydrogen burner, and oxidized to SO_3 by passage of the combustion products through a hydrogen peroxide solution. An aliquot of the washings is then reduced to H_2S in a solution of hydriodic acid. The resulting H_2S is converted to methylene blue for colorimetric measurement; at the acid concentration used in this method, methylene blue has two absorption peaks: 670 and 745 $\text{m}\mu$. The method is so sensitive that 2 μg of sulfur in a 100 cc volume yields a perceptible color development. By adjusting the amount of sample taken, or the aliquot of sulfate solution, one can determine sulfur levels in the range of 0 to 500 ppm by weight. The only limitation is contamination of low-sulfur samples if the apparatus is not thoroughly rinsed and cleaned after use with high-sulfur samples. Interferences are from metals such as Ca, Ba, and Pb, which cause insoluble sulfates.