CANADA

THE DETERMINATION OF METHYL AND METHYLENE GROUPS IN THE OIL AND RESIN FRACTIONS OF ATHABASCA BITUMEN USING INFRARED SPECTROSCOPY

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THE DETERMINATION OF METHYL AND METHYLENE GROUPS IN THE OIL AND RESIN FRACTIONS OF ATHABASCA BITUMEN USING INFRARED SPECTROSCOPY

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F. E. Goodspeed* and D. S. Montgomery**

ABSTRACT

A method of determining the methyl and methylene carbon present in the oil and resin fractions from the Athabasca bitumen, using infrared absorption spectra, has been developed. Absorption bands in the 3- and 7-micron regions are used, and data on pure compounds serve as a basis for quantitative estimates of these groups. Estimates obtained for the oil fractions were supported by the agreement of the total hydrogen content of the fractions that was obtained from the ultimate analysis with the hydrogen content predicted by this method.

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ÉVALUATION DES GROUPES MÉTHYLE ET MÉTHYLÈNE DANS LES FRACTIONS HUILE ET RÉSINE DU BITUME DE L'ATHABASCA À L'AIDE DE LA SPECTROSCOPIE INFRAROUGE

par

F. E. Goodspeed* et D. S. Montgomery**

RÉSUMÉ

On a mis au point un procédé pour évaluer le carbone méthyle et méthylène présent dans les fractions "huile" et "résine" du bitume de l'Athabasca, à l'aide de spectres d'absorption infrarouges.

On utilise à cette fin les raies d'absorption comprises dans les régions de 3 et de 7 microns, et l'on se sert de résultats correspondant à des composés purs comme bases d'estimations quantitatives de ces groupes.

Les estimations obtenues pour les fractions "huile" furent confirmées par l'accord observé entre la teneur totale en hydrogène de ces fractions, telle que determinée par l'analyse complète, et la teneur en hydrogène prédite par le présent procédé.

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INTRODUCTION

In the research reported here an examination of the absorption spectra of pure hydrocarbons in the 2-15 μ region of the infrared spectrum was made to determine the absorption bands that would be useful in making quantitative estimates of some of the structural groups present in the fractions that were isolated by chromatography from Athabasca bitumen from the Abasand Quarry. This study was associated with an attempt to apply a structural group analysis system which has recently been developed(1) to give an insight into the composition of the oil and resin fractions (2, 3). This structural analysis method required, for solution, five known quantities: C, the total number of carbon atoms per molecule; H, the total number of hydrogen atoms per molecule; the molar volume; the molar refraction; and C_a, the number of aromatic carbon atoms per molecule. Of these quantities, the one most difficult to determine is the total number of aromatic carbon atoms per molecule; for this reason the investigation commenced with an attempt to explore the possibility of estimating this quantity by the use of infrared spectroscopy.

The use of the aromatic C=C absorption band at 6.25 μ for the determination of aromatic carbon has been reported in the literature (4, 5, 6, 7, 8, 9). This absorption has been used in two ways:

1.   Brandes (4, 5), Traxler (6) and Francis (7) correlated the

absorption at 6.25 μ with results from the n-d-m method of hydro-

carbon structural analysis (10).

2.   Burdett (8) and Greenshields (9) used the absorption data

of pure hydrocarbons as a basis for the quantitative measurement

of aromatic carbon in oils.

However, on investigation it was found here that there

was a wide variation in the absorption of the aromatic carbon in the

6.2 μ region, and therefore this absorption band did not appear to

be capable of producing reliable estimates of C_a, particularly as

the fractions from the Athabasca bitumen are of complex composi-

tion. Within simpler mixtures of aromatic compounds, this absorp-

tion can be of some value.

On the other hand, it was found possible to make estimates

of the number of methyl and methylene groups present in pure hydro-

carbons. This forms the subject of the present investigation, to-

gether with the application of this technique to the study of the

fractions from Abasand bitumen.

The spectra of 70 pure compounds were examined in the

3.2 to 3.6 μ and the 7.1 to 7.5 μ regions, since the dominant ab-

sorption bands in the spectra of the oil and resin fractions were in

these ranges. In some cases the quantitative estimates derived by

this method might be used as an independent variable capable of

being incorporated in structural analysis schemes in order to pro-

vide solutions (2, 3).

In the past a considerable amount of work has been reported on the infrared spectra of pure compounds (11, 12, 13), and the assignment of absorption bands has been well established in the regions studied in this report. The analysis of hydrocarbon mixtures with the aid of pure compound reference spectra, using the above regions, has previously been reported (14, 15). Hastings et al (14) and Francis (15) used these regions to determine functional groups in saturated hydrocarbon mixtures with high resolution instruments, whereas the work reported here has been limited to the use of a sodium chloride prism.

In this investigation, the absorption at $7.28\,\mu$ was employed to estimate the carbon in methyl groups and the absorption at $3.42\,\mu$ the carbon in methylene groups, while the absorption at 3.48 to $3.50\,\mu$ served as a verification of the total CH_2 and CH_3. From the study of pure hydrocarbon spectra, the various absorptivity factors per gram of methyl carbon and methylene carbon were determined. The pure hydrocarbons studied included 29 methyl substituted aromatics, 18 other aliphatic substituted benzenes, 7 linear saturates, 3 branched chain saturates, 6 saturates containing 6-membered rings, and 6 hydroaromatic compounds. In some cases the absorptivity factors varied as a result of the effect of other groups present in the compound; however, the range of values was fairly narrow for most of the compounds

studied. Quantitative absorption data calculated from information in the literature (13, 15, 16) supported the uniformity of the data obtained in this investigation and gave some assurance that no large anomalies would have appeared for any of these hydrocarbon types had the spectra of a larger number of compounds been measured.

The appropriate absorption factors, or ranges of factors, for use with the bitumen fractions were selected after study of the 2 to 15 μ infrared spectrum of each fraction. This spectrum indicated the dominant structural groups present in each fraction. Also, in the saturated oil fraction the agreement of the hydrogen content predicted from these estimates with the total hydrogen in the molecule, as determined from the molecular weight and the ultimate analysis, was used to confirm the accuracy of the method.

EXPERIMENTAL

A Perkin-Elmer Model 21 spectrometer with sodium chloride optics was used for the spectral measurements. Carbon tetrachloride solutions of the pure compounds and fractions were prepared in concentrations which gave absorbances of between 0.1 and 0.5 at the wavelength to be measured. A cell with sodium chloride windows and a path length of 0.515 mm was used for all measurements. The pure compounds used to provide the reference spectra were obtained commercially and used without further purification. For all measurements it was possible to set the instrument at zero absorbance at the wavelength to be measured with the cell full of

pure solvent, and thus be able to read the solution absorbance directly. In the 3-micron region the 3.0-3.6 μ range was scanned, and in the 7-micron region the 6.7-7.7 μ range was examined. The slit schedule was set at 927, giving spectral slits of 0.018 μ at 3.4 microns and 0.022 μ at 7.28 microns.

CALCULATION

The absorptivity, in grams per litre per centimetre, at the selected wavelengths was calculated as follows:

$$a_b = \frac{A_b}{cd}, \qquad (1)$$

where a_b = absorptivity (g/1/cm) at the chosen wavelength b,

A_b = absorbance of the solution at wavelength b,

c = concentration of the solution in grams per litre, and

d = cell thickness in centimetres.

The absorptivity per gram carbon in the structural group absorbing was derived as follows:

$$a_c = \frac{M}{12.01n} a_b, \qquad (2)$$

where a_c = absorptivity (g/1/cm) per gram carbon of the type absorbing,

M = gram molecular weight,

n = number of carbon atoms of the type absorbing per molecule,

12.01 = gram atomic weight of carbon, and

a_b = absorptivity from equation (1).

From the a_c determined for a specific carbon type in the pure compounds, an average value may be chosen as applicable to the analysis of an unknown. From Equation (2) the number of carbon atoms of that type present in the unknown may be calculated, using a selected value of a_c along with the absorptivity and molecular weight of the unknown.

In order to evaluate the average absorptivity for one class of compounds, and to establish its reliability in representing a specific structural group, the coefficient of variation was calculated. To do this, the standard deviation is first determined, as follows:

$$s = \sqrt{\frac{\Sigma(x-\bar{x})^2}{n-1}} \qquad (3)$$

where s is the standard deviation,

x is the individual absorptivity value for each compound,

$\bar{x}$ is the average absorptivity, and

n is the number of compounds.

From this the coefficient of variation, V, is then calculated:

$$V = \frac{100s}{\bar{x}} \qquad (4)$$

V is simply the standard deviation as a percent of the average absorbance.

DISCUSSION

The 3-micron Region

In this region the various C-H stretching vibrations in a molecule absorb energy at the following wavelengths:

$3.26 - 3.33\ \mu$ .. Aromatic CH
3.38 and $3.48\ \mu$ .. CH_3 attached to another aliphatic carbon
3.42 and $3.50\ \mu$ .. CH_3 attached to an aromatic ring
3.42 and $3.50\ \mu$ .. CH_2
$3.46\ \mu$ (weak) .. CH aliphatic

This is a very complex region for hydrocarbon absorption. In this work, only a sodium chloride prism was used; hence the resolution of these bands was incomplete.

Many reports on the absorption by hydrocarbons in this region of the spectrum have appeared in the literature, and some of these were useful in evaluating its practical importance in the determination of methyl and methylene carbon. From the data published by Jones (13, 16) on pure hydrocarbons, absorptivity values comparable to those used in this study were calculated. These showed that the absorptivity of linear CH_2 at $3.42\ \mu$ and $3.50\ \mu$ per gram of methylene carbon was virtually constant for the 17 members of the n-paraffin series reported. The absorptivity of CH_3 at $3.38\ \mu$ and $3.48\ \mu$ in the n-paraffin series increases slightly with increase in chain length and is two to three times stronger per gram of carbon than is that for CH_2. The aromatic CH absorption in benzene derivatives, reported by Jones, occurs at several wavelengths and appears to be quantitatively af-

fected by various substitutions on the ring. The absorption of methyl groups attached to a benzene ring at 3.42 μ is considerably less than that of methyl groups in saturated hydrocarbons at 3.38 μ.

The work reported by Francis (15) on high molecular weight saturated hydrocarbons confirms the data on paraffins reported by Jones. In addition, it shows that the absorption of methylene groups at 3.42 μ in long-chain branched saturated hydrocarbons agrees quantitatively with that for n-paraffinic methylene. The absorptivity of cyclohexyl methylene was slightly higher than that of paraffinic methylene, while that of methylene in fused 6-membered rings was comparable to that of paraffinic methylene. The absorptivity at 3.38 μ for methyl groups in the types of saturated hydrocarbons reported by Francis varied considerably. These data, calculated from information in the literature, served to amplify and confirm the uniformity and usefulness of the absorption data obtained during this investigation of the various types of groups present in fractions of the bitumen. However, since it is not possible to transfer quantitative absorption data from one spectrometer to another, this information from the literature, although substantiating the principle of using these bands, could not provide the absorption data necessary to measure the number of methyl and methylene groups per molecule in the materials at hand.

The absorptivities per gram of carbon associated with the types of carbon-hydrogen bonds that are listed on the previous page (except CH at 3.46 μ) were calculated from the spectra of the compounds measured in this investigation; the average value for each type is shown in Table 1. The aromatic CH absorption values vary widely for the substituted isolated aromatic ring. Since the absorption of this group is weak, it was not always possible to measure the absorption, particularly when the aromatic ring became a minor constituent in the compound. The values for the naphthalenes and more condensed aromatic systems were more consistent, except those for hydroaromatic compounds.

The usefulness of the methyl absorption at 3.38 μ was restricted, as a high resolution prism was not used. In the linear saturated compounds it was only possible to obtain a quantitative estimate of the amount of absorption due to this group for the two shortest chains, hexane and heptane. This value agreed with what was reported in the literature. Considerably lower values were obtained for methyl groups in the other types of hydrocarbons. This appears to be true for short chain substitution and where more than one methyl group is attached to a single carbon atom. The methyl absorption at 3.42 μ, where the methyl is attached to an aromatic carbon atom, is much less than methyl absorption at 3.38 μ in saturated compounds.

TABLE 1

Absorptivities of Aromatic and Aliphatic Groups in Various Types of Hydrocarbons

Number and type of hydrocarbon	Aromatic carbon absorptivity(a_c) per gram of carbon g/l/cm				Aliphatic carbon absorptivity (a_c) per gram of carbon g/l/cm					
Range of wavelength / Type of bond	3.26 - 3.30 μ CH		3.30 - 3.33 μ CH		3.38 μ CH_3		3.42 μ CH_3		3.48 - 3.50 μ $CH_2 + CH_3$	
	a_c	V*	a_c	V	a_c	V	a_c	V	a_c	V
11 Methyl benzenes			1.02 (8)	56.0			1.75(10)	13.1	1.02(9)	3.1
12 Methyl naphthalenes	0.525(9)**	7.2	0.581(5)	6.5			1.78(11)	11.1	0.98(10)	12.2
6 Methyl higher condensed aromatic compounds	0.526(6)	19.0			1.94(1)		1.75(5)	16.6	1.10(5)	10.5
Type of bond			CH		CH_3		CH_2		$CH_2 + CH_3$	
			a_c	V	a_c	V	a_c	V	a_c	V
6 Ethyl benzenes			0.550(1)		5.39(6)	5.1	3.68(5)	13.9	1.09(6)	11.7
12 Higher substituted benzenes			0.498(8)	11.3	4.43(9)	19.1	3.35(2)	3.2	1.28(11)	16.4
6 Hydroaromatics			0.998(6)	53.0			2.83(6)	18.4	1.21(5)	13.2
6 Saturated 6-membered rings			0.505(1)				4.18(6)	4.1	1.59(6)	9.4
7 Linear saturates					9.22(2)	3.4	3.89(7)	7.5	1.60(7)	7.8
3 Branched saturates					5.47(2)	16.9	4.12(2)	22.4	1.38(2)	8.7

* V is coefficient of variation.

** Number of spectra included in the average is shown in parentheses.

The methylene absorption at 3.42 μ was fairly consistent within any one type of hydrocarbon, but varied from one type to another. The methylene groups in cyclic 6-membered rings gave the highest and most uniform absorption values of all the types measured. Methylene groups attached to an aromatic ring gave slightly lower values than those in saturated compounds, while those in hydroaromatic compounds gave the lowest values. It should be noted that in some classes of compounds, only one or two values were available to obtain an average for one type of structural group, and the reliability of these values may therefore be open to question.

The absorption at 3.48 μ and 3.50 μ was unresolved, and was treated as one band due to both methyl and methylene vibrations. The absorptivity values in Table 1 were calculated on the basis of total CH_2 and CH_3. This absorption, due to symmetric C-H stretching vibrations, is weaker than the two absorption bands due to asymmetric C-H stretching vibrations in CH_2 and CH_3 at 3.42 μ and 3.38 μ. The coefficient of variation for this composite band is low for almost every type of structure. Again the absorption of these groups was less when associated with aromatic structures than when in wholly saturated compounds; it ranges overall from 0.98 for methyl naphthalenes to 1.60 for linear saturates.

The 7-micron Region .

The absorption between 7.15 and 7.35 μ is due to the carbon-hydrogen bending vibration in methyl groups. Where only one methyl group is attached to a carbon atom a single band occurs at 7.27-7.28 μ. Where two or three methyl groups are attached to a single carbon atom, the band is split so that two or three bands occur within this region. The absorptivities per gram of methyl carbon for the pure compounds studied are shown in Table 2.

Comparable data calculated from information in the literature (13, 15, 16) showed that although this value does vary, it is still within reasonable limits. From the molecular extinction coefficients reported for 18 paraffins by Jones, the calculated absorptivities for methyl carbon gave a coefficient of variation of 10.8. These absorptivities increased gradually with increase in the length of the paraffinic chain. A report published recently on polymers (17) shows that polymethylene absorbs at about the same wavelength, and this could explain the higher absorption values. Absorptivities calculated from Francis' data on high molecular weight saturated compounds vary. This could also be accounted for by the high proportion of methylene groups.

TABLE 2

Absorptivities of Methyl Groups in Various Pure Hydrocarbons

Number and type of hydrocarbon	Wavelength, in microns	Absorptivity per gram of methyl carbon, g/ l/ cm	Coefficient of variation		Remarks
11 Methyl benzenes	7.27	0.656		19.8	Range, 7.24-7.28 μ
12 Methyl naphthalenes	7.27	1.00		31.0	Range, 7.23-7.29 μ; 2, 3 dimethyl band split.
6 Methyl higher condensed aromatics	7.27	1.61		64.6	Interference from aromatic band absorption
7 Ethyl benzenes	7.28	0.97		38.7	
3 n-alkyl benzenes	7.27	1.59		3.4	Includes sec-butyl.
4 Iso-alkyl benzenes	7.23, 7.33	1.22, 1.18	22.7	19.5	
3 Tert-alkyl benzenes	7.19, 7.35	0.66, 1.60	29.5	14.5	
1 Tertpentyl benzene	7.23, 7.27, 7.34	0.74, 0.77, 0.74			
2 Alkyl cyclohexanes	7.28	1.54		1.5	
5 Linear saturates	7.28	1.50		18.3	

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The data in Table 2 show where variations were found. In some cases, these variations may be caused by interfering absorption bands as noted. Methyl groups attached to non-fused aromatic rings do not absorb as strongly as any other type measured. In general, methyl groups closely associated with an aromatic ring absorb less than do those in saturated compounds.

APPLICATION OF THE INFRARED SPECTRAL DATA TO THE STUDY OF THE OIL AND RESIN FRACTIONS

The use of the absorption data in determining methyl and methylene groups is dependent on: (a) the reliability of this absorption in representing quantitatively the number of carbon atoms in methyl and methylene groups, and (b) the ability to choose, from the data on pure compounds, an absorptivity factor that is suitable for the unknown material being studied.

The data in Tables 1 and 2 show that the most reliable absorption bands for these groups are:

7.27-7.28 μ for methyl carbon,
3.42 μ   for methylene carbon, and
3.48-3.50 μ for total methyl and methylene carbon.

Not all the types of compounds reported in Tables 1 and 2 are presumed to be present in the fractions to be analysed. All of these compounds were examined to determine the basic absorption data and to study the effects resulting from the simultaneous presence of various types of structural groups.

From the data collected on pure hydrocarbons it is clear that the amount of absorption by a specific type of vibration in a methyl or methylene group is somewhat dependent on its environment. To ascertain as much information as possible about these environmental factors in the bitumen fractions being analysed, a close examination of each fraction's origin, mode of separation, and spectrum in the 2-15 micron region was necessary.

The oil and resin fractions of the Abasand bitumen were isolated by chromatography. This chromatographic separation took place on the basis of increasing polarity caused by increasing aromaticity and the presence of foreign atoms such as oxygen, nitrogen, and sulphur. This order of increasing polarity is indicated by the alphabetical sequence of the samples, fraction B representing the sample of lowest polarity.

The 2-15 μ spectra of these fractions are shown in Figures 1 to 3. The absorption bands in these spectra, not already discussed, may be attributed to the following structural groups: 5.7-6.0 μ, C=O; 6.25 μ, aromatic C=C; 6.8-6.9 μ, CH_2 and CH_3; 11.0-11.6 μ, 11.6-12.5 μ, 12.35-13.3 μ, 13.0-13.6 μ and 14.1-14.5 μ, varying numbers of unsubstituted adjacent hydrogens on an aromatic ring; and 13.7-13.9 μ, four or more linear CH_2. The spurious band at 2.95 μ in the pellet spectra is due to pellet moisture. The complete spectra of the oils and resin CCl_4 (II) were measured in the liquid phase, using a variable space cell,
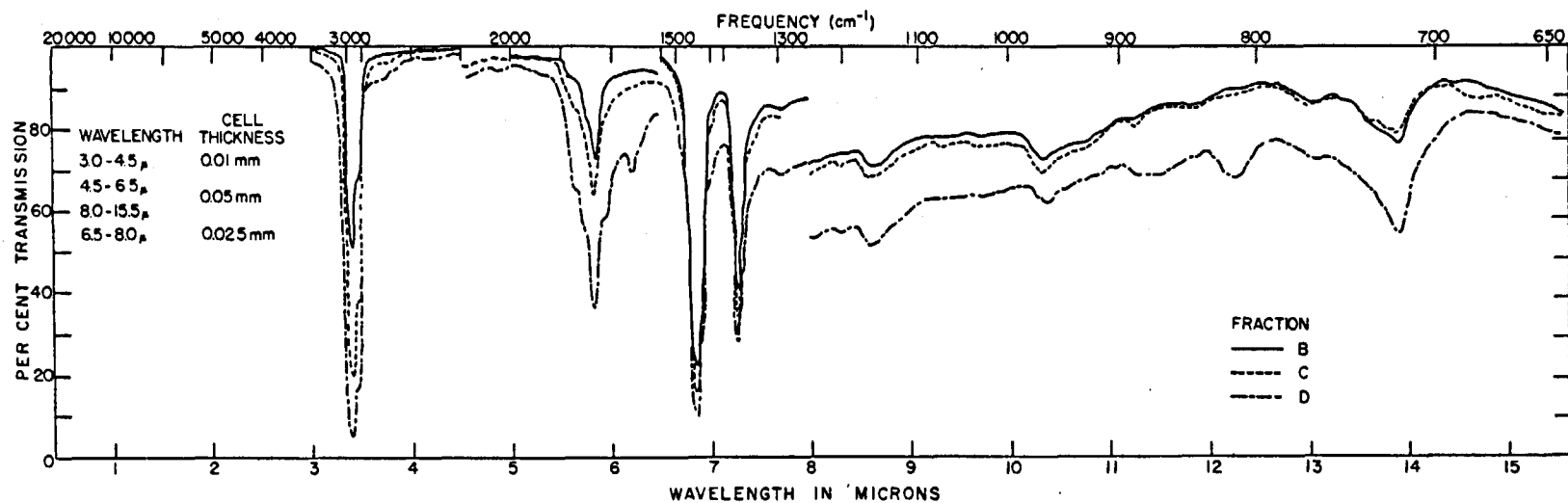
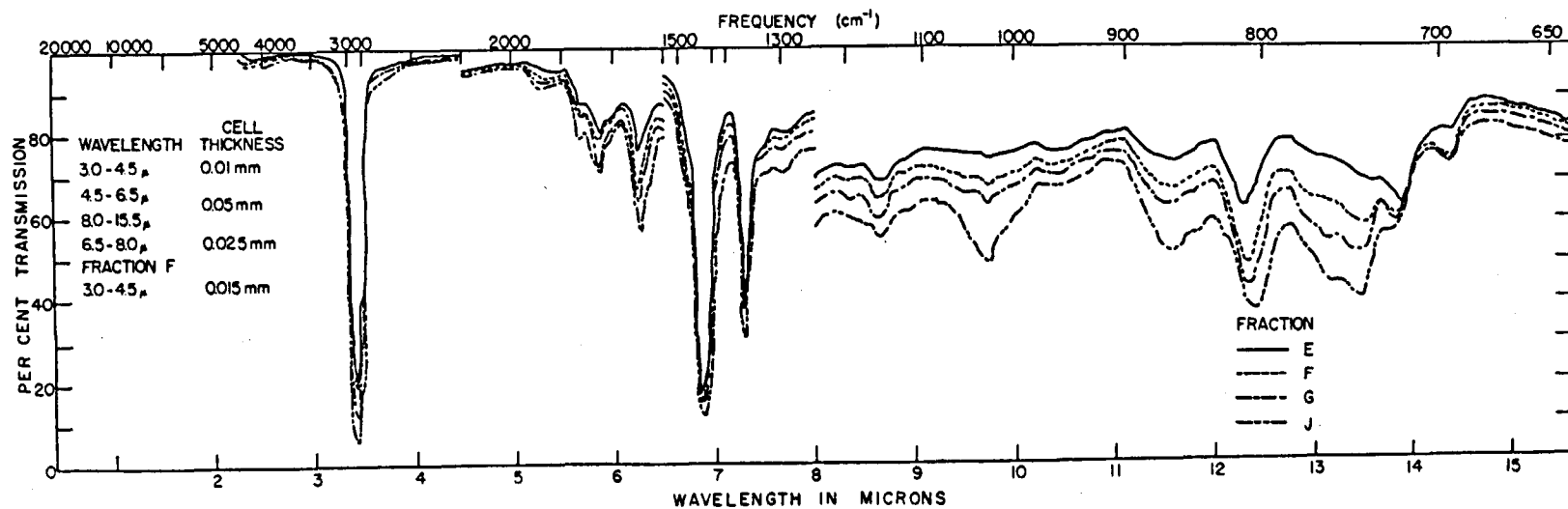FIGURE 1. Infra-red Spectra of Oil Fractions B, C, and D.

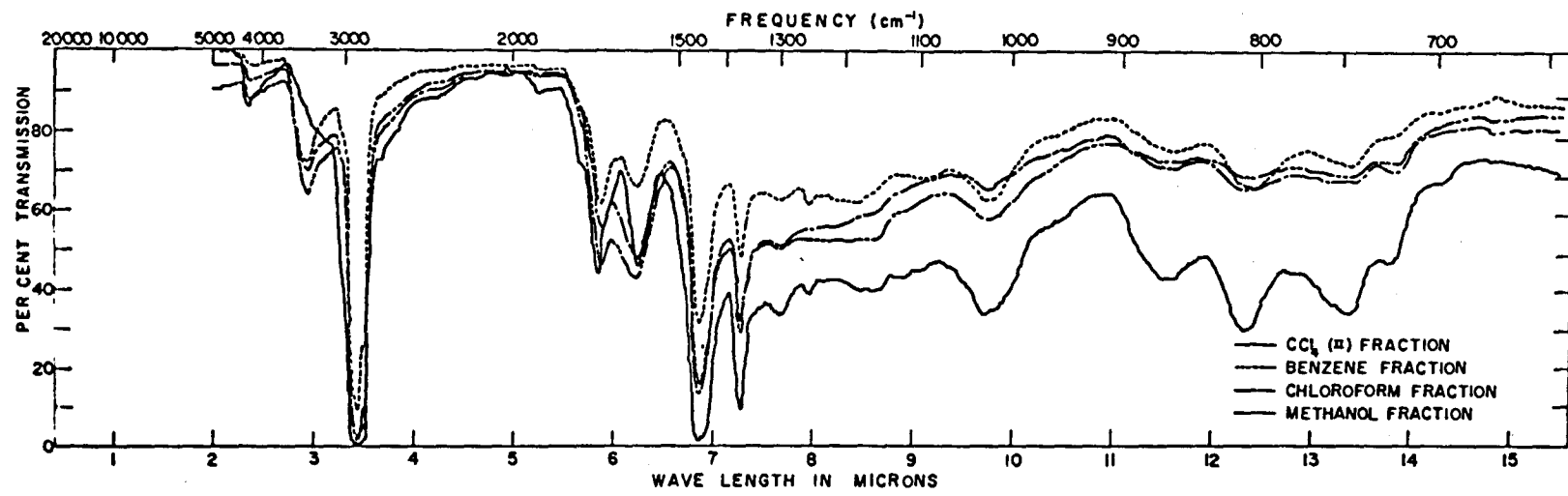FIGURE 2. Infra-red Spectra of Oil Fractions E, F, G, and J

FIGURE 3. Infra-red Spectra of the Resin Fractions

while those of the other resin fractions were done as potassium bromide pellets.

From a detailed examination of the spectra of these fractions, the following first approximations as to their constitution may be made. In the spectrum of each fraction the methyl absorption at 7.28 μ is primarily a single band and sufficiently strong to suggest that there are a number of these groups present. Each fraction has a certain amount of carbonyl absorption at 5.85 μ. Fractions B and C are entirely saturated, with a small amount of carbonyl present. A portion of the methylene groups is present in chains of 4 or more carbon atoms, as indicated by the absorption at 13.85 μ. Fractions D and E are largely saturated, but the weak absorption at 6.25 and 12.25 μ indicates that some aromatic carbon is present. The absorption due to chain methylene groups is stronger than in fractions B and C. The spectrum of D also has a fairly strong and complex carbonyl absorption. Fractions F, G and J, in order, show increasing absorption at 6.25 μ and in the 11 to 15 μ region, due to aromatic carbon and aromatic carbon-hydrogen. The absorption in the 11 to 15 μ region in pure aromatic compounds is very intense; its strength per gram carbon is comparable to, or greater than, that in the 3-micron region due to methylene groups. Therefore, on the basis of absorptivity, the aromatic groups still constitute only a minor part of the molecule.

The four resin fractions are all quite similar, having both saturated and aromatic absorption. The aromatic absorption at 6.25 μ is stronger than that present in any of the oil fractions. In the 11 to 15 μ region the CCl_4 (II) and benzene fractions exhibit stronger absorption relative to the other bands, indicating more unsubstituted hydrogen on aromatic rings. From a study of all the resin spectra, a first approximation indicates that the aromatic carbon constitutes less than half the total carbon in the molecule.

From the above preliminary assessment of the structure of the fractions based on a survey of their absorption in the 2-15 μ region, absorptivity factors applicable to these fractions were selected from values in Tables 1 and 2. Since no exact estimate of the various groups present in the fractions was available, a range of a_c factors was chosen representing compositions ranging from partially aromatic to wholly aliphatic. These ranges were:

1.50	at 7.28 μ for CH_3
3.60-4.00	at 3.42 μ for CH_2
1.30-1.50	at 3.48-3.50 μ for total CH_2 and CH_3

Table 3 lists the fractions, their molecular weights (2, 3), and the absorptivities at the wavelengths used for analysis. These values were used with the above factors, in Equation (2), to calculate the number of carbon atoms present in methyl and methylene groups per molecule of each fraction. These results are presented in Table 4, along with the total number of carbon atoms per molecule.

TABLE 3

Absorptivities of Fractions of Abasand Bitumen

Fraction	Average gram molecular weight	Absorptivity (a_b), g/l/cm		
		$7.28\,\mu$	$3.42\,\mu$	$3.50\,\mu$
B	360	0.284	1.93	1.01
C	317	0.264	1.77	1.01
D	642	0.254	1.78	0.868
E	582	0.236	1.64	0.831
F	431	0.230	1.43	0.748
G	369	0.225	1.34	0.682
J	340	0.218	1.12	0.586
CCl_4 (II)	592	0.213	1.01	0.487
Benzene	821	0.220	0.903	0.430
$CHCl_3$	976	0.225	1.12	0.550
MeOH	834	0.233	0.932	0.512

TABLE 4

Methyl and Methylene Groups Determined from Infra-red Data in Fractions from Abasand Bitumen

Fraction Group	Number of Carbon Atoms in				Total No. of Carbon Atoms
	CH_3	CH_2	CH_2 and CH_3	CH_3 and CH_2 added from	
Wavelength Absorptivity factor	$7.28\ \mu$	$3.42\ \mu$	3.48-$3.50\ \mu$	$7.28\ \mu$ and $3.42\ \mu$	
	1.5	$4.0 - 3.6$	$1.5 - 1.3$		
Oil Fractions					
B	5.7	14.5 - 16.1	20.2 - 23.2	20.2 - 21.8	25.9
C	4.6	11.7 - 13.0	17.8 - 20.5	16.3 - 17.6	22.8
D	9.0	23.8 - 26.4	30.9 - 35.6	32.8 - 35.4	45.2
E	7.6	19.9 - 22.8	26.9 - 31.0	27.5 - 30.4	41.6
F	5.5	12.8 - 14.3	17.9 - 20.6	18.3 - 19.8	30.6
G	4.6	10.3 - 11.4	14.0 - 16.1	14.9 - 16.0	26.3
J	4.1	7.9 - 8.8	11.0 - 12.8	12.0 - 12.9	24.4
Resin Fractions					
CCl_4 (II)	7.0	12.4 - 13.8	16.0 - 18.5	19.4 - 20.8	40.2
Benzene	10.0	15.4 - 17.2	19.6 - 22.6	25.4 - 27.2	54.8
$CHCl_3$	12.2	22.8 - 25.3	29.8 - 34.4	35.0 - 37.5	64.3
MeOH	10.8	16.2 - 18.0	23.7 - 27.4	27.0 - 28.8	53.8

Note: In the above the underlined results are considered the best of those particular fractions.

In keeping with the basis on which the absorptivity factors were chosen, the underlined results are considered to be the best values for those particular fractions, i.e., the high factor for the saturated fractions and the low factor for partly aromatic fractions. Where no value is underlined the most probable value is intermediate in the range, and in most cases this range is relatively narrow. To determine whether these results were fairly accurate, the total number of hydrogen atoms that must be associated with these methyl and methylene carbons was compared with the total hydrogen atoms present in the molecule. These values appear in Table 5.

The results for the oil fractions, shown in Tables 4 and 5, appear to be consistent with the general remarks on their spectra. The values for the total CH_2 and CH_3 determined from the 3.48-3.50 μ band and those from the 7.28 μ and 3.42 μ bands agree throughout the oil fractions. In the saturated fraction, B, the total hydrogen in the CH_2 and CH_3 groups is almost equal to the total hydrogen in the molecule -- which is to be expected, since nearly all the hydrogens should be accounted for by these groups.

The results for the resin fractions are not as consistent. The total amounts of CH_2 and CH_3 determined from the 7.28 μ and 3.42 μ bands are higher than those determined from the 3.48-3.50 μ absorption. The number of hydrogen atoms unaccounted for by the higher infra-red estimates are 5, 4, 3 and 8, respectively, for the four resins (CCl_4 (II) to MeOH). Although it is difficult to estimate the amount of aromatic CH quantitatively, these values for the

TABLE 5

Hydrogen Balance in Fractions from Abasand Bitumen

Fraction	Hydrogen atoms in CH_2 and CH_3 (from 7.28 μ and 3.42 μ) per molecule	Total number of hydrogen atoms per molecule
Oil Fractions		
B	46.1 - 49.3	46.7
C	37.2 - 38.8	41.6
D	74.6 - 79.8	77.0
E	64.6 - 68.4	70.0
F	42.1 - 45.1	49.6
G	35.0 - 36.6	41.0
J	28.1 - 29.9	35.0
Resin Fractions		
CCl_4 (II)	45.8 - 48.6	53.9
Benzene	61.3 - 64.4	68.6
$CHCl_3$	82.2 - 87.2	90.1
MeOH	64.8 - 68.4	76.0

remaining hydrogens appear low, inasmuch as they have to include all of the aromatic hydrogen, the hydrogen in saturated CH, and the hydrogen in OH. When the spectra were re-examined, it was noted that in the 7-micron region there is a higher background absorption in the resins than in the oils; since no compensation was made for this, it is probable that the estimates of methyl carbon are too large. The lower values for total CH_2 and CH_3 estimated from the 3.48-3.50 μ absorption tend to substantiate this conclusion. The number of hydrogen atoms associated with these lower amounts of total methyl and methylene was calculated, using a ratio of 2.35 H per C, (this is equivalent to between 1 CH_3 to 2 CH_2, and 2 CH_3 to 3 CH_2). The numbers of hydrogen atoms unaccounted for by this method are: 10.4 for CCl_4 (II), 15.5 for the benzene fraction, 9.2 for the chloroform fraction, and 11.6 for the methanol fraction. At present, these estimated values for the resins lack confirmation from other sources of information. However, they do indicate the direction for future research. In view of the complex nature of the resin fractions, the mutual agreement between the infra-red estimates based upon different absorption bands indicates that the infra-red absorption data are self-consistent. Consequently these data are potentially useful for securing structural information.

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