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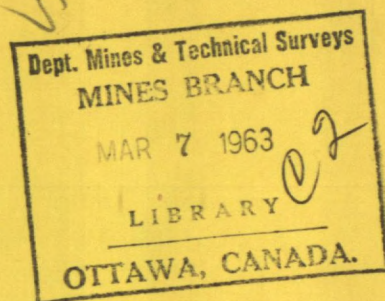
**DEPARTMENT OF MINES AND  
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**A STUDY OF THE ATHABASCA  
BITUMEN FROM THE ABASAND  
QUARRY, ALBERTA, CANADA**

**PART III: CHROMATOGRAPHIC SEPARATION  
OF THE OIL FRACTION, AND  
PROPERTIES AND STRUCTURE  
OF THE OIL COMPONENTS**

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**FUELS AND MINING PRACTICE DIVISION**

**NOVEMBER 1962**

MINES BRANCH RESEARCH REPORT R 104

A STUDY OF THE ATHABASCA BITUMEN FROM THE  
ABASAND QUARRY, ALBERTA, CANADA. Part III:  
Chromatographic Separation of the Oil Fraction, and  
Properties and Structure of the Oil Components.

by

M. L. Boyd\* and D. S. Montgomery\*\*

ABSTRACT

The oil component, which constituted 33.1 percent of the Abasand bitumen, was resolved into a series of fractions by elution chromatography on silica gel. The saturated fraction was further resolved on activated carbon, and the most aromatic portion on both activated carbon and alumina. The following properties were determined for most of the fractions thus prepared: elementary analysis, molecular weight, density (20°C), refractive index ( $n_D^{20}$ ), dispersion, the aniline point, the ultraviolet spectrum and the infrared spectrum. Quantitative estimates of the number of methyl, methylene and aromatic carbon atoms have been made from the infrared spectra. The major fractions were then characterized by the application of three groups of structural analysis methods: (1) a representative group of methods designed for lubricating oils, (2) densimetric methods of van Krevelen, and (3) a method developed by the authors. It was possible to separate out about one-third of the oil component as totally saturated material. The remainder of the material was separated into a series of fractions which contained increasing proportions of aromatic carbon atoms up to about 35 percent. On the average, the oil fractions would appear to contain three rings per molecule.

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Direction des Mines

Rapport de recherches R 104

ÉTUDE DU BITUME ATHABASCA EN PROVENANCE  
DE LA CARRIÈRE ABASAND, EN ALBERTA, CANADA

Partie III: Séparation chromatographique de la  
fraction pétrole, et propriétés et  
structure des constituants du pétrole.

par

M. L. Boyd\* et D. S. Montgomery\*\*

RÉSUMÉ

La portion pétrole, qui représentait 33.1 p. 10 du bitume d'Abasand, a été fragmentée en une série de fractions par voie de chromatographie d'élution sur gel de silice. La fraction saturée a été fractionnée à son tour sur du carbone activé, et la fraction la plus aromatique a été fragmentée, tant sur du carbone activé que sur de l'alumine. On a déterminé ce qui suit dans le cas de la plupart des fractions ainsi obtenues: analyse élémentaire, poids moléculaire, densité (20°C), indice de réfraction ( $n_D^{20}$ ), dispersion, point d'aniline, spectre ultraviolet, et spectre infrarouge. On a fait des estimations quantitatives du nombre de groupes de méthyle, de méthylène et de carbone aromatique à partir des spectres infrarouges. Les principales fractions ont alors été caractérisées par l'application de trois groupes de procédés d'analyse de la structure: (1) un groupe représentatif des procédés qui s'emploient dans le cas des huiles lubrifiantes, (2) les procédés densimétriques de van Krevelen, et (3) un procédé proposé par les auteurs du présent rapport. Il a été possible de séparer environ le tiers de la fraction pétrole présente en tant que matière complètement saturée. Le reste a été séparé en une série de fractions qui contenaient des proportions de plus en plus fortes d'atomes de carbone aromatique, la proportion maximum atteignant environ 35 p. 100. En moyenne, les fractions pétrole semblent contenir trois anneaux par molécule.

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## INTRODUCTION

This report forms Part III of a series of papers (1, 2) on the chemical structure of the Abasand bitumen. The objective of the present investigation was to determine as much as possible about the hydrocarbon framework of the oil component, one of the three major fractions into which the bitumen was arbitrarily separated for this study. The results of the work performed on the asphaltene and resin components have already been reported, in Parts I (1) and II (2) of this series.\*

The preparation of the starting material for this investigation was described in the preceding paper in this series (2). The pentane-soluble portion of the bitumen (77% of the bitumen) was separated on activated Florex\*\* into the resin and oil components. The oil component was taken to be that portion of the bitumen which was eluted with n-pentane from the Florex. In this instance, the oil fraction amounted to 33.1 percent of the bitumen. This report will describe the further resolution of this oil fraction on various adsorbents. The

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\* Since the preparation of Parts I and II, a geochemical study of the Abasand bitumen has been published by Nagy and Gagnon (26). The entire bitumen was fractionated by elution chromatography on silica gel and alumina, and the fractions were characterized by mass spectroscopy. By this means, one fraction (9% bitumen) was shown to contain paraffinic and naphthenic compounds containing one to six rings. Another fraction (18%) was shown to contain alkyl and cycloalkyl benzenes and also substituted naphthalenes, phenanthrenes, benzothiophenes and thiophenophenanthrenes. A third fraction was predominately non-hydrocarbon in character.

\*\* "Florex", Florida fuller's earth manufactured by the Floridin Company, Tallahassee, Florida, U.S.A.



objective of this fractionation was to devise a separation scheme which would bring about a gross separation, according to chemical type, for a relatively large amount of starting material (in this case 200 g) to provide a basis for further analytical separations employing much higher adsorbent-to-oil ratios. The various fractions thus produced were characterized by means of ultraviolet and infrared spectroscopy and by the application of a representative selection of structural group analysis methods designed for oils, including a method developed by the authors.

## THE RESOLUTION OF THE OIL COMPONENT

### Separation on Silica Gel

The approach adopted in the chromatographic work was to make an initial separation on silica gel into two broad fractions, namely saturated-type and aromatic-type compounds respectively, and then to resolve each class by further separation on other adsorbents. It should be noted that, from a practical point of view, the scale of operation used here rather limited the maximum adsorbent-to-oil ratio that would be desirable for the greatest possible separation.

A slight modification of the elution method of Clerc, Kincannon and Wier (3), using a weak initial developer (methylcyclohexane) to displace the saturated hydrocarbon band and to elute the aromatic bands, was selected for the initial separation of the oil fraction. The oil fraction (211.79 grams) was arbitrarily divided into six portions. This division was based on the order of the efflux of the pentane eluate from the Florex column. These portions were each diluted with approximately an equal weight of methylcyclohexane and were added to a silica gel column in the order of their efflux from the Florex. This order of addition was used to take advantage of the separation of the sulphur and aromatic compounds already brought about by the Florex.

The silica gel column consisted of a glass tube, 37 mm x 360 cm, filled to a depth of approximately 250 cm with 2 kg of silica gel\* (+200 mesh). The silica gel was added to the column in the form of a slurry with 3250 ml of methylcyclohexane. The operating pressure under which the chromatography was performed was approximately 8 lb/sq in. After ten litres of methylcyclohexane effluent had been collected, the column was eluted with four litres of toluene.

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\*Davison Chemical Corporation, Baltimore, Maryland, U.S.A.

The separation of the saturates from the immediately following aromatic class was not complete, as shown by the fluorescence of the saturate band. This separation was improved by chromatographing the methylcyclohexane effluent a second time on an identical silica gel column. The methylcyclohexane effluent from the first silica gel column was divided into 34 fractions. The solvent was removed from them, and they were then re-diluted with methylcyclohexane in the ratio of 5 MCH/1 by weight and added to the top of a second silica gel column. The final separation achieved is shown in Figures 1 and 2. The percentage recovery for the silica gel separation was 92.8% (i.e., the loss amounted to 2.37% bitumen). The fact that, two fractionations on silica gel were required to separate the saturates from the aromatics indicated that the gel-to-oil ratio was rather low and should be raised somewhat. The oil devoid of solvent was arbitrarily divided into nine fractions, as indicated in Figure 2. These fractions have been designated alphabetically and will be thus referred to in the remainder of the report. The properties of these fractions are tabulated in Table 1. Fractions A to H were eluted with methylcyclohexane and Fraction J with toluene. Fractions A and B were colourless. Fractions C to J ranged from almost colourless to yellow; they gradually darkened on exposure to light and air.



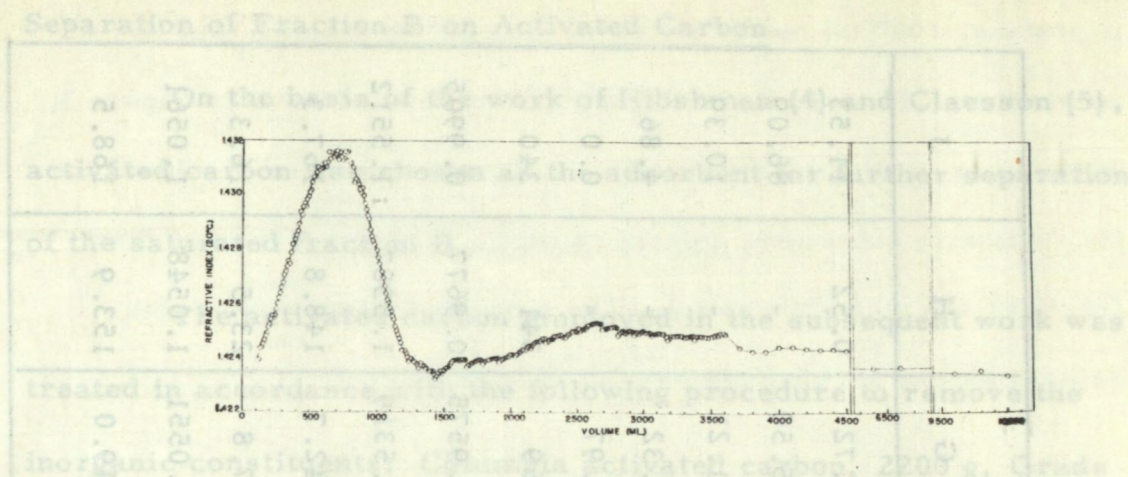


FIGURE 1. Oil fraction of Abasand bitumen eluted with methylcyclohexane from silica gel. The volume and refractive index refer to the effluent solution.

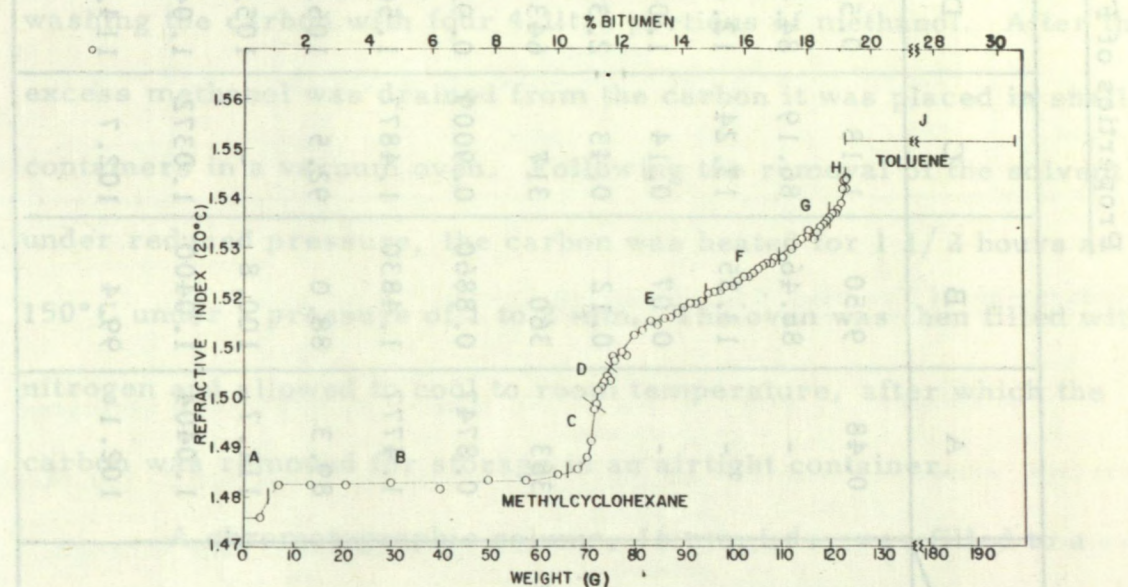


FIGURE 2. Oil fraction of Abasand bitumen eluted with methylcyclohexane and toluene from silica gel. The refractive index and weight refer to the oil devoid of solvent.



TABLE 1

Properties of Fractions A to J

Fraction Property	A	B	C	D	E	F	G	H	J
Wt. % Bitumen	0.48	9.50	1.18	0.51	2.94	2.34	1.72	0.52	11.53
% C	-	86.46	86.19	84.43	85.78	84.74	85.50	-	86.09
% H	-	13.35	13.24	12.09	12.12	11.59	11.21	-	10.39
% S	-	0.07	0.14	1.09	1.66	2.07	2.32	-	4.86
% O (diff.)		0.12	0.43	2.39	0.44	1.60	0.97	-	0.0
Molecular Weight*	363	360	317	643	582	431	369	341	340
$d^{20}$	0.8747	0.8860	0.9009	0.9263	0.9247	0.9420	0.9575	0.9677	0.9905
$n_D^{20}$	1.4777	1.4830	1.4877	1.5044	1.5139	1.5236	1.5319	1.5387	1.5512
$(n_f - n_c) \times 10^4$	89.3	88.0	92.5	106.3	119.1	132.6	142.7	148.8	167.3
Aniline Point	111.7	100.8	-	105.5	85.0	55.7	37.8	23.5	16.3
$n_D^{20} - d/2$	1.0404	1.0400	1.0372	1.0412	1.0515	1.0526	1.0551	1.0548	1.0561
$\frac{(n_f - n_c) \times 10^4}{d}$	102.1	99.4	102.7	114.8	128.8	140.8	149.0	153.9	168.5

\*Determined cryoscopically in benzene.

### Separation of Fraction B on Activated Carbon

On the basis of the work of Hibshman (4) and Claesson (5), activated carbon was chosen as the adsorbent for further separation of the saturated Fraction B.

The activated carbon employed in the subsequent work was treated in accordance with the following procedure to remove the inorganic constituents: Columbia activated carbon, 2200 g, Grade L (48-150 mesh), was washed with ten successive 4-litre portions of distilled water. The carbon was stirred with each portion and then allowed to stand for one hour. After the tenth wash the excess water was drained away and the carbon was extracted with methanol in a large Soxhlet extractor. This extraction was the equivalent of washing the carbon with four 4-litre portions of methanol. After the excess methanol was drained from the carbon it was placed in shallow containers in a vacuum oven. Following the removal of the solvent under reduced pressure, the carbon was heated for 1 1/2 hours at 150°C under a pressure of 1 to 2 mm. The oven was then filled with nitrogen and allowed to cool to room temperature, after which the carbon was removed for storage in an airtight container.

A chromatographic column, 16 mm i.d., was filled to a depth of 308 cm with a slurry of 1200 ml of n-pentane and 300 g of activated carbon. Twenty-one grams of Fraction B in n-pentane was added to the top of the column at an initial concentration of one gram oil to 5 ml pentane. The column was then eluted with 2700 ml

n-pentane, 1000 ml methylcyclohexane, 1000 ml toluene, and 500 ml ethyl ether. The results of this separation are indicated in Figure 3, in which are indicated the quantity of oil removed by each solvent and its refractive index after solvent removal. The properties of these fractions are given in Table 2. The percentage recovery in this separation was 68.6% (loss was 3.13% bitumen).

TABLE 2  
Properties of Fractions B<sub>1</sub> to B<sub>6</sub>

Fraction eluted with Property	B <sub>1</sub> n-Pentane	B <sub>2</sub> Methyl- cyclohexane	B <sub>3</sub> Toluene	B <sub>4</sub> Toluene and Other	B <sub>5</sub> Ether	B <sub>6</sub> Methanol- Toluene Extraction
% Bitumen	2.40	0.61	2.77	0.55	0.05	0.47
$n_D^{20}$	1.46-1.48	1.48-1.49	1.486- 1.495	1.4862- 1.4885	-	1.4917
$d_4^{20}$	0.8917	0.9223	0.8920	-	-	-
Molecular Weight	286	349	460	-	-	-

Separation of Fraction J on Activated Carbon

A column, 11 mm i.d. x 186 cm, was filled with 100 g activated carbon, prewetted with 160 ml methylcyclohexane. Fraction J (10.06 g) was diluted with 60 ml methylcyclohexane and allowed to flow through the column under the action of gravity. The column was then eluted with 350 ml methylcyclohexane, followed by 250 ml toluene-methylcyclohexane (84% toluene, 16% MCH), 350 ml carbon tetrachloride, 500 ml

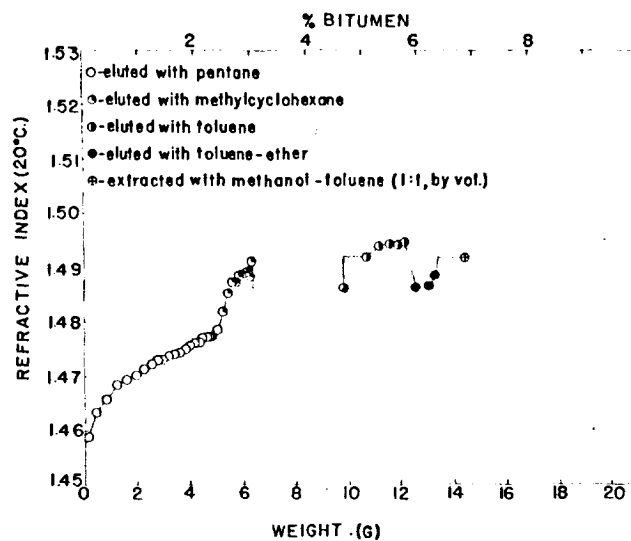


FIGURE 3. Fraction B eluted with a graded series of eluents from activated carbon. The refractive index and weight refer to the oil devoid of solvent.

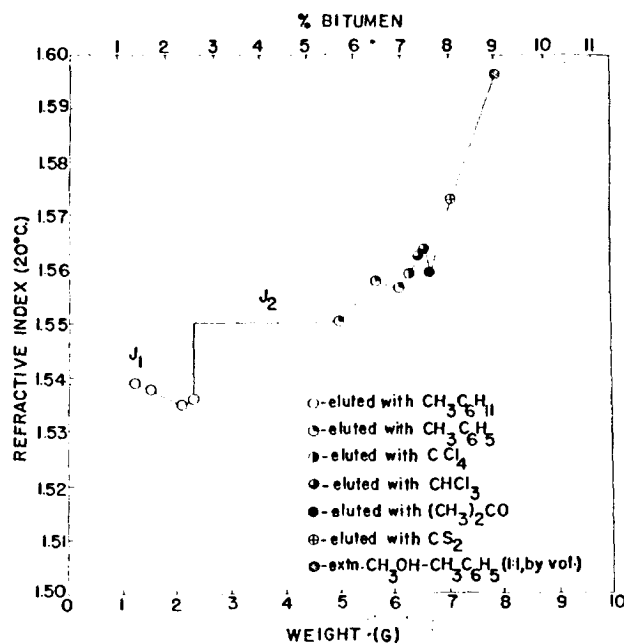


FIGURE 4. Fraction J eluted with a graded series of eluents from activated carbon. The refractive index and weight refer to the oil devoid of solvent.



chloroform, 500 ml acetone, and 350 ml carbon disulphide. The weight removed by each solvent and the index of refraction of each fraction after solvent removal are shown in Figure 4. The properties of the fractions are given in Table 3. The percentage recovery in this separation was 78.3% (loss was 2.50% bitumen).

TABLE 3  
Properties of Fractions J<sub>1</sub> to J<sub>7</sub>

Fraction eluted with Property	J <sub>1</sub> Methylcyclo- hexane	J <sub>2</sub> Toluene- MCH	J <sub>3</sub> CCl <sub>4</sub>	J <sub>4</sub> CHCl <sub>3</sub>	J <sub>5</sub> Acetone	J <sub>6</sub> CS <sub>2</sub>	J <sub>7</sub> Methanol- Toluene Extractions
% Bitumen	2.64	4.37	0.20	0.29	0.15	0.40	0.99
n <sub>D</sub> <sup>20</sup>	1.5382	1.5502	-	1.5636	1.5592	1.5731	-
d <sub>4</sub> <sup>20</sup>	0.9857	0.9809	-	-	-	-	-
(n <sub>f</sub> - n <sub>c</sub> ) × 10 <sup>4</sup>	139.1	161.9	-	188	194.7	207.9	-
Spec. Dispersion	141.2	164.9	-	-	-	-	-
Molecular Weight	412	364	-	-	-	-	-
Aniline Point	38.4	19.0	-	-	-	-	-
% Sulphur	4.96	4.47	-	-	-	-	-
n <sub>D</sub> <sup>20</sup> - d/2	1.0453	1.0598	-	-	-	-	-
Colour	colourless	Pale Yellow	-	-	-	Yellow	-

### Separation of Fraction J on Alumina

Two experiments were made to separate Fraction J on alumina, the first using Merck alumina without further treatment, and the second using alumina activated at 400-450°C for three hours.

In the first experiment, 11.8 g of Fraction J in 60 ml of pentane was added to a column, 11 mm x 180 cm, packed with 197 g of alumina. The column was eluted with n-pentane, pentane-benzene mixtures, benzene, chloroform, and methanol. About twenty samples were collected, stripped of solvent, weighed, and their refractive index and dispersion at 20°C measured. These properties are shown in Figure 5. The percentage recovery from the unactivated alumina amounted to 93.4%.

In the second experiment, 9.7 g of Fraction J in 50 ml n-pentane was added to a similar column containing 156 g of alumina that had been activated by heating for three hours at 400-450°C. The column was eluted with the same series of solvents as in the first experiment. Approximately eighty fractions were collected, stripped of solvent, weighed, and their refractive index and dispersion at 20°C. measured. These properties are shown graphically in Figure 6. The percentage recovery from the activated alumina amounted to 87.4%.

The results of these two experiments showed that activation of the alumina produced a much sharper separation than did the non-activated. The loss entailed in the use of alumina is considerably less than for carbon; for this reason, it is advisable to reserve carbon for the final separation step.

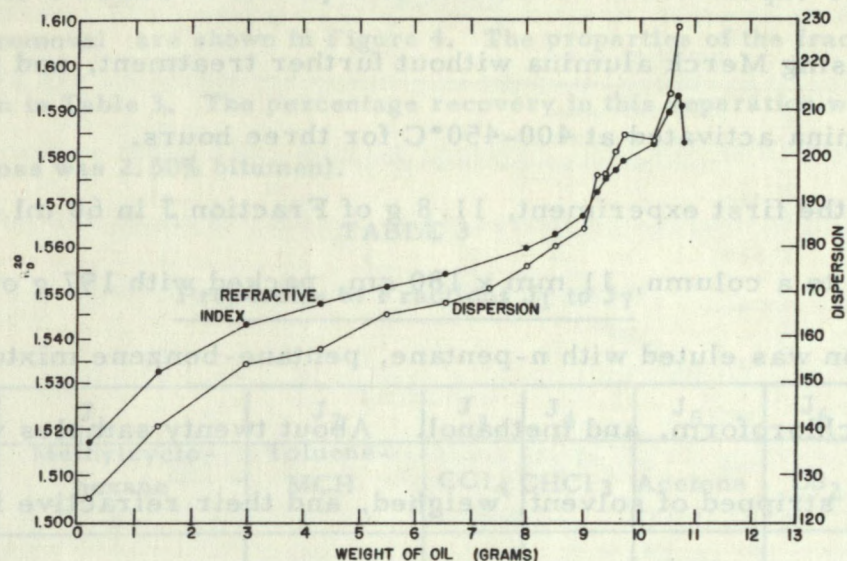


FIGURE 5. Fraction J eluted with a graded series of eluents from non-activated alumina. The refractive index and the weight refer to the oil devoid of solvent.

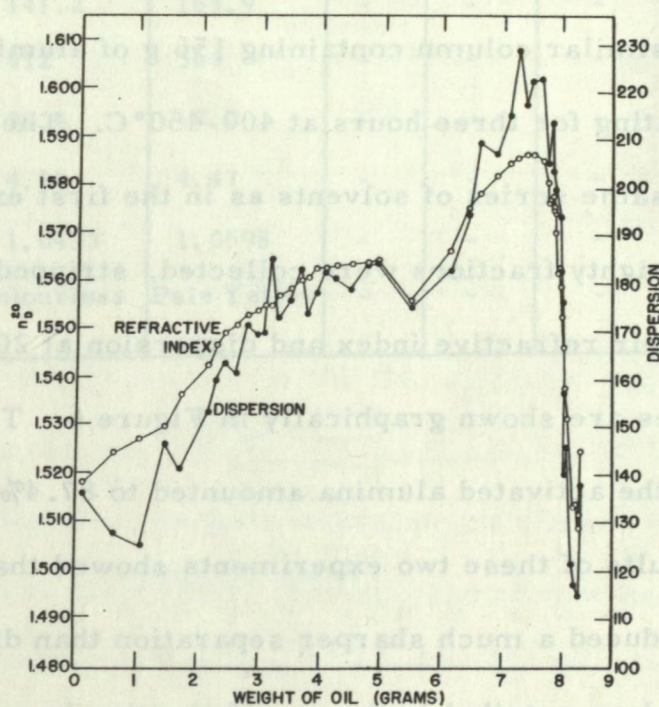


FIGURE 6. Fraction J eluted with a graded series of eluents from activated alumina. The refractive index and the weight refer to the oil devoid of solvent.



## DETERMINATION OF THE STRUCTURE OF THE OIL FRACTIONS

### Structural Information from the Absorption Spectra

The ultraviolet and infrared spectra were measured on a majority of the oil fractions. The primary objective was to determine the aromatic content, since this quantity was required for the application of one of the structural analysis methods. However, in general, it was considered important to learn the main structural features indicated by these spectra.

#### The Ultraviolet Spectra

The ultraviolet spectra were determined for Fractions B to J and also for the fractions obtained by the separation of J on alumina. These measurements were made in n-heptane solution over the wavelength range 210-350 millimicrons, using a Beckman model DK-2 spectrophotometer.

The spectra of Fractions B, C, E, F and J, shown in Figure 7, indicated two principal absorption bands, one at 225 to 230  $m\mu$  and the other at 265  $m\mu$ . These spectra were also plotted in the form log E versus wavelength so that they could be compared with the resin components of the bitumen (2) and with a collection of log E spectra of aromatic hydrocarbons (6). These log E curves are given in Figure 8. In general, these curves possessed a slight indication of individuality when compared with those of the resin components. As would be



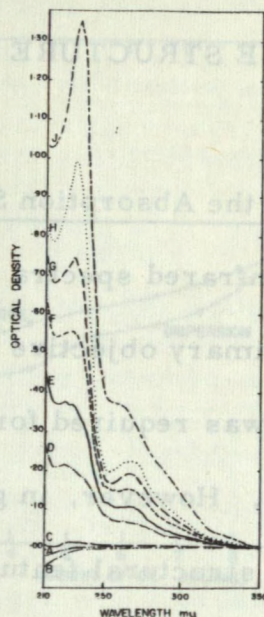


FIGURE 7. Ultraviolet spectra of Fractions B to J.

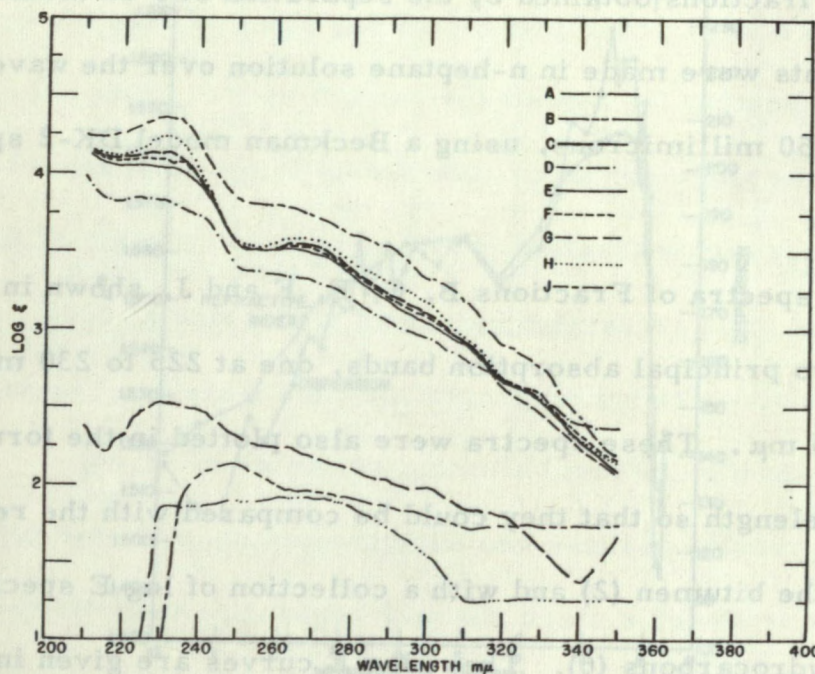


FIGURE 8. Ultraviolet spectra of Fractions B to J. (Log E form)



expected, log E values for all the oil fractions over the wavelength range measured were considerably less than corresponding values for the resin fractions. Owing to the effects of substitution and the influence of carbonyl groups, it was difficult to draw any reliable conclusions as to the average number of aromatic rings per molecule of the oil fractions, although the log E curves would seem to indicate that there were less than three aromatic rings in Fractions D to J. This is somewhat less than the number of aromatic rings estimated for the resin fractions (2).

The spectra of the fractions separated from J on activated alumina are shown in Figure 9. On the basis of the ultraviolet spectra, these fractions could be divided into three classes, distinguished as follows: In the first class (Fraction 3), there was a slight maximum at 265 m $\mu$  followed by a regular increase in absorption to 210 m $\mu$ ; in the second class (Fractions 10 and 25) two maxima were exhibited, one at 265 m $\mu$  and the other at 235 m $\mu$ ; and in the third class (Fraction 34), there was a shoulder at 260 m $\mu$  and two maxima at 242.5 and 215 m $\mu$ .



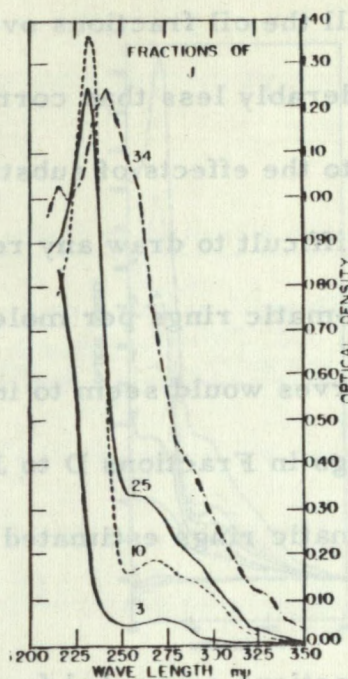


FIGURE 9. Ultraviolet spectra of the fractions isolated from J by chromatography on activated alumina.

#### The Infrared Spectra

The infrared spectra were determined for Fractions B to J and also for the fractions obtained by the separation of J on activated alumina. All spectra were recorded with a Perkin-Elmer double-beam infrared spectrometer. The spectra for Fractions B to J are given in Figure 10. Goodspeed and Montgomery (7) have made a study of the infrared spectra of Alberta bitumen fractions and, for completeness, a brief summary of their findings for Fractions B to J is given below:

The principal absorption bands in these spectra were assigned to the following structural groups:



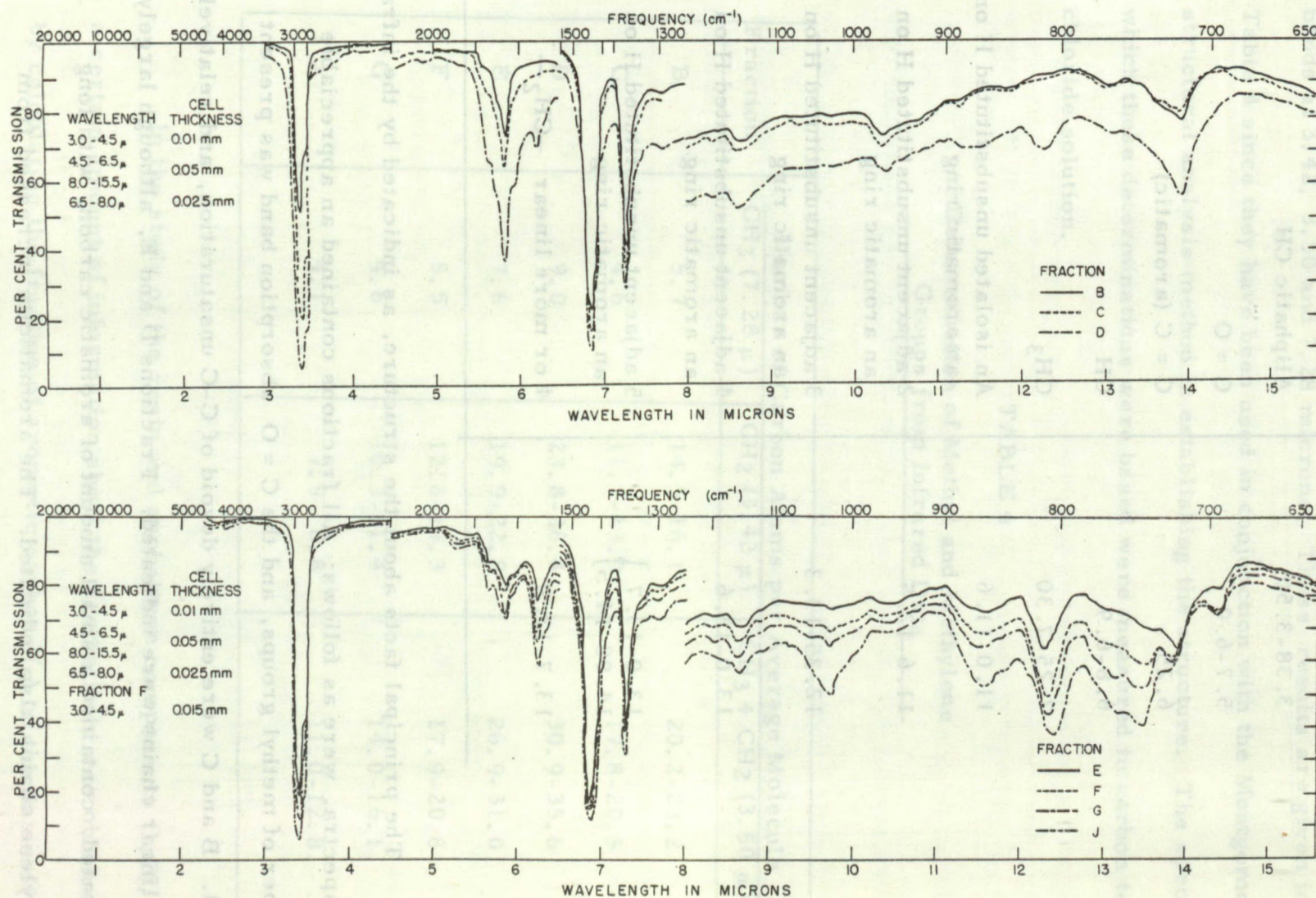


FIGURE 10. Infrared spectra of Fractions B to J.

<u>Wavelength (microns)</u>	<u>Functional Group</u>
3.25-3.35	Aromatic CH
3.38-3.50	Aliphatic CH
5.7-6.0	C = O
6.25	C = C (aromatic)
6.8-6.9	CH
7.25-7.30	CH <sub>3</sub>
11.0-11.6	An isolated unsubstituted H on an aromatic ring
11.6-12.5	2 adjacent unsubstituted H on an aromatic ring
12.35-13.3	3 adjacent unsubstituted H on an aromatic ring
13.0-13.6	4 adjacent unsubstituted H on an aromatic ring
13.0-13.7 } 14.08-14.5 }	5 adjacent unsubstituted H on an aromatic ring
13.7-13.9	4 or more linear -CH <sub>2</sub> -

The principal facts about the structure, as indicated by the infra-red spectra, were as follows: All fractions contained an appreciable number of methyl groups, and the C = O absorption band was present in all. B and C were entirely devoid of C-C unsaturation, and relatively long linear chains were indicated. Fractions D and E, although largely saturated, contained a small amount of aromatic carbon, with long methylene chains also indicated. The aromaticity increased from Fractions F to J, although in general these fractions were not predominantly aromatic.

Goodspeed and Montgomery (7) determined quantitatively the number of methyl and methylene groups, on the basis of the absorption bands at 3.42, 3.50 and 7.28 microns. These results are given in Table 4 since they have been used in conjunction with the Montgomery-Boyd structural analysis method in establishing the structure. The spectra upon which these determinations were based were measured in carbon tetrachloride solution.

TABLE 4  
Determination of Methyl and Methylene  
Groups from Infrared Data

Fraction	Number of Carbon Atoms per Average Molecule		
	CH <sub>3</sub> (7.28 $\mu$ )	CH <sub>2</sub> (3.42 $\mu$ )	CH <sub>3</sub> + CH <sub>2</sub> (3.50 $\mu$ )
B	5.7	14.5-16.1	20.2-23.2
C	4.6	11.7-13.0	17.8-20.5
D	9.0	23.8-26.4	30.9-35.6
E	7.6	19.9-22.8	26.9-31.0
F	5.5	12.8-14.3	17.9-20.6
G	4.6	10.3-11.4	14.0-16.1
J	4.1	7.9- 8.8	11.0-12.8

In the study of the resin and asphaltene components (1, 2), a certain amount of information about the aromaticity was obtained by calculating the fraction of aromatic carbon ( $f_a$ ) on the basis of the absorbance of the 6.25  $\mu$  band of a selected group of pure aromatic



hydrocarbons. These compounds were divided into various groups on the basis of structural differences that were significant from the structural analysis viewpoint. For comparative purposes, this calculation of  $f_a$  was also made for fractions B to J, and the results are summarized in Table 5. Values of  $f_a$ , calculated by Brandes' method (8), have also been included in this table.

The infrared spectra of the fractions obtained by the separation of J on alumina are shown in Figure 11. These spectra were very similar for all fractions. All exhibited strong absorption bands at  $6.2 \mu$ , a fact which, together with the ultraviolet spectra, indicated the aromatic character of these fractions. There were no striking differences in spectral type which would permit of dividing them into groups, as was possible from the ultraviolet spectra.

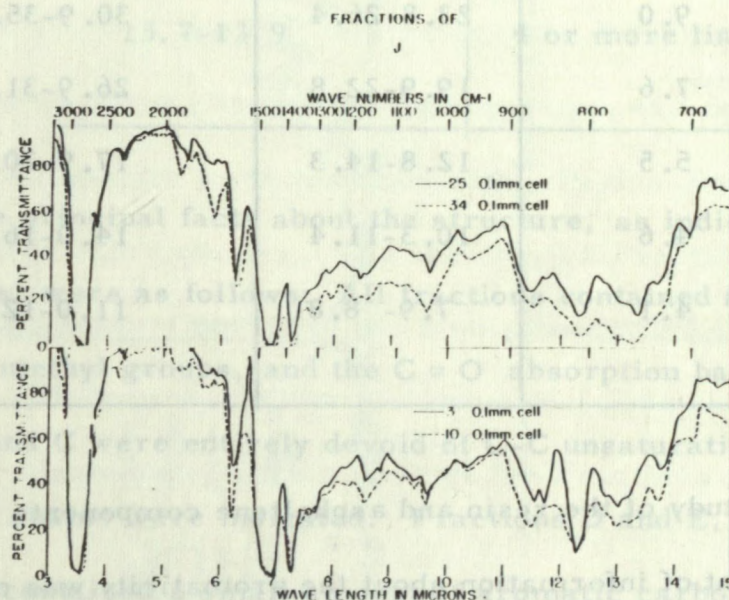


FIGURE 11. Infrared spectra of the fractions isolated from J by chromatography on activated alumina.



TABLE 5

Determination of the Fraction of Aromatic Carbon ( $f_a$ ) on the  
Basis of the Absorbance of the 6.25  $\mu$  Band of Six Types  
of Pure Aromatic Hydrocarbons

Class of Compounds	No. in Class	Mean Value of $f_a$					
		C	D	E	F	G	J
1) Fused aromatics with side chains where $\frac{CH_a^*}{Ca} < 2.0$	4	0.07	0.25	0.20	0.25	0.48	0.52
2) Fused aromatics with side chains where $\frac{CH_a}{Ca} > 2.0$	2	0.03	0.12	0.09	0.12	0.22	0.24
3) Fused aromatics with no side chains and $\frac{CH_a}{Ca} < 2.0$	18	0.12	0.42	0.33	0.42	0.80	0.87
4) Fused aromatics containing cyclic $CH_2$ groups	8	0.11	0.37	0.29	0.36	0.70	0.76
5) Non-fused aromatics	5	0.06	0.22	0.17	0.21	0.45	0.45
6) Methyl naphthalenes	12	0.06	0.12	0.14	0.18	0.21	0.23
7) Brandes' Method (8)	-	-	0.11	0.14	0.23	0.24	0.24

\* $CH_a$  - number of aromatic CH groups or their equivalent per molecule.

$Ca$  - number of junction carbon atoms between aromatic fused rings per molecule.



Characterization of the Oil Fractions by Structural Group  
Analysis Methods

At the present time, one of the most widely used techniques for determining the average structure of petroleum oils is structural group analysis, which is the general term covering a large number of methods based on the correlation of the physical properties and the constitution of oils. Most of these methods determine the percentage of the carbon atoms in aromatic rings, naphthenic rings and paraffinic side chains. In addition, several of the methods make certain assumptions concerning the type of rings present and the degree of condensation; consequently, this allows a calculation of the average number of aromatic and naphthenic rings. A representative number of these methods, developed over the past thirty years, were applied to the oil fractions of the bitumen. They covered the span from the Waterman method of 1935 to the recent (1962) modifications to the n-d-M method of van Ness and van Westen (1951), the latter being the most commonly used method for oils. These methods were chosen on the basis of the properties that were available on the oil fractions.

A second method used to study the hydrocarbon framework of these bitumen fractions was van Krevelen's method of physical constitution analysis based on the elementary analysis and density measurements. Although this system has been designed primarily for coal, it was applied here so that the composition of the oil fractions obtained could be compared with the compositions of the higher molecular weight components of the bitumen to which this method had been applied (1, 2). This method was intended primarily to determine the degree of aromaticity.

The final method of structural analysis applied was one developed by the authors (9). It describes the structure in terms of five hydrocarbon groups, and therefore gives more structural information than do the other methods applied. It has the added advantage of being based on a larger volume of pure compound data than the other methods. The method itself consists of the simultaneous solution of five property equations, based on correlations of the properties (molar volume and molar refraction) of the high molecular weight hydrocarbons of API Project 42. This method was recently applied to the asphaltene and resin components of the bitumen (10), and has been used here to illustrate its applicability to the entire molecular weight range of the fractions into which the bitumen was separated.

#### Representative Group of Methods Designed for Lubricating Oils

Several of the structural analysis methods that have been developed over the past thirty years were applied to the bitumen oil fractions. The results are tabulated in Table 6. These results have been arranged in such a fashion that all methods can be compared on the basis of a given structural group.

A qualitative indication of the nature of Fractions A to J was obtained on the basis of the carbon-type analysis of Clerc, Kincannon and Weir (3). On this basis, Fractions A, B and C were saturates, Fractions D to H were monocyclic aromatics, and Fraction J was composed of dicyclic aromatics.

**TABLE 6**  
**Summary of Carbon-type Analyses**

Percent C <sub>a</sub>														
Fraction Method	A	B	B <sub>1</sub>	B <sub>2</sub>	C	D	E	F	G	H	J	J <sub>1</sub>	J <sub>2</sub>	
n-d-M (11)	0.0	0.2			0.0	4.7	16.6	21.9	25.6	29.3	29.6	19.3	35.5	
Karr's modification (12)						5.3	17.2	22.6	26.4		34.9	21.0	37.1	
n-d-M							18.0	23.7	27.6		33.4	23.7	33.8	
Hazelwood (13) and Karr's							9.9	25.8	41.5	43.6	49.6	52.2	39.9	56.8
S corr. (12)	0.0	0.0					16.9	26.1	31.9	35.2	37.8			
Waterman (14)						13.0	17.2	23.6	27.7	30.2	33.4	24.2	31.6	
Robert (15)		0.0			0.0	2.0	17.0	22.5	25.5		31.0			
Martin and Sankin (16)														
Kurtz et al (17)														
Percent C <sub>n</sub>														
Fraction Method	A	B	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	C	D	E	F	G	H	J	J <sub>1</sub>	J <sub>2</sub>
n-d-M (11)	44.3	48.8				60.5	42.7	20.6	25.5	30.1	27.0	35.2	43.0	16.6
Karr's modification (12)							41.8	19.7	24.4	28.8		24.0	40.3	14.1
n-d-M								17.8	21.9	25.8		26.2	32.2	21.0
Hazelwood (13) and Karr's								21.6	0.0	27.1	31.2	40.0	51.8	22.5
S corr. (12)	41.5	41.5					28.4	22.5	26.8	31.1	34.0	37.4	44.8	34.2
Waterman (14)	44.5	50.4	61.8	65.8	43.5	60.9	49.2							
Martin and Sankin (16)		49.3				63.0	45.0	24.0	30.5	34.5		39.0		
Lipkin, Martin and Kurtz (18)														
Kurtz et al. (1958) (17)														
Percent C <sub>p</sub>														
Fraction Method	A	B	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	C	D	E	F	G	H	J	J <sub>1</sub>	J <sub>2</sub>
n-d-M (11)	55.7	51.0				39.5	52.6	62.8	52.7	44.3	43.7	37.2	37.7	48.2
ndM-Karr's correction (12)							52.9	63.1	53.0	44.8		41.1	38.7	48.8
Hazelwood (13) - Karr's								64.1	54.4	46.6		40.4	44.2	45.3
S corr. (12)	58.5	58.5					48.8	52.6	58.5	29.3	19.2	7.75	8.33	20.8
Waterman (14)							58.5	60.3	49.6	41.2	35.9	29.4	31.0	34.4
Martin and Sankin (16)	55.5	49.6	38.2	34.2	56.5	39.1	50.8							
Lipkin, Martin, and Kurtz (18)		50.7				37.0	53.0	59.0	47.0	40.0		30.0		
Kurtz et al. (1958) (17)														
R <sub>a</sub> The mean number of aromatic rings per molecule														
Fraction Method	A	B	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	C	D	E	F	G	H	J	J <sub>1</sub>	J <sub>2</sub>
n-d-M (11)	0.0	0.01				0.0	0.36	1.21	1.18	1.18	1.25	1.26	0.99	1.62
n-d-M and Karr's S corr. (12)							0.41	1.25	1.22	1.22		1.49	1.08	1.70
Hazelwood (13) and Karr's														
S corr. (12)								1.37	1.33	1.33		1.55	1.25	1.72
Martin and Sankin (16)							1.01	1.32	1.35	1.36	1.38	1.59	1.32	1.61
R <sub>n</sub> - Mean number of naphthene rings per molecule														
Fraction Method	A	B	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	C	D	E	F	G	H	J	J <sub>1</sub>	J <sub>2</sub>
n-d-M (11)	2.4	2.7				3.0	4.5	2.0	1.8	1.9	1.5	1.8	2.7	1.0
n-d-M and Karr's S corr. (12)							4.5	2.1	1.9	1.9		1.6	2.9	1.1
Hazelwood (13) and Karr's S														
corr. (12)								1.8	1.7	1.7		1.6	1.4	1.4
Martin and Sankin (16)							3.3	2.4	2.1	2.1	2.1	2.3	3.4	2.3
C <sub>n</sub> - Number of carbon atoms per molecule in naphthene rings														
Fraction Method	A	B	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	C	D	E	F	G	H	J	J <sub>1</sub>	J <sub>2</sub>
Davis and McAllister (19)		14.7	13.8	19.2	17.7									

The data in Table 6 indicated that some methods were applicable to the entire composition range of the oil fractions (n-d-M and related methods), whereas others were applicable, on the one hand, only to the saturated fractions (Davis and McAllister (19) and Lipkin, Martin and Kurtz (18)) and, on the other, to aromatic fractions (Hazelwood (13) and Martin and Sankin (16)). The methods of Waterman (14) and Davis and McAllister (19) are now only of historical interest, and were included here essentially for this reason. The Waterman method requires the use of the aniline point and is essentially the forerunner of the n-d-M method. The Davis and McAllister method (19) is based on a correlation between molar volume and molecular weight and determines the number of carbon atoms in naphthene rings per molecule. It is included here because it represents probably the earliest attempt (1930) to determine structural information from a correlation of physical properties. It has now been superseded since so many more data are now available. In 1946 Lipkin, Martin and Kurtz (18) developed a method for determining the composition of saturated oils, based on the temperature coefficient of density. This method requires the use of the molecular weight and density (or refractive index) and involves the assumption that both condensed and non-condensed ring structures are present. In 1951 van Nes and van Westen presented the n-d-M (11) method, derived from refractive index, density, and molecular weight. This represents a considerable simplification in oil analyses. This method was not recommended for cases where  $\% C_a / \% C_n > 1.5$ . The determination of the number of

rings  $R_t$  and  $R_a$  per molecule was based on the assumption of six-membered kata-condensed rings. This method was followed by several modifications: in 1954 Hazelwood (13) published a method suitable for aromatic concentrates only, and recently Karr (12) has presented a modification that permits a sulphur correction to be incorporated in both the n-d-M and Hazelwood equations. In 1952, Robert (15) developed an expression relating %  $C_a$  and refractive index, density, and aniline point. In 1953 Martin and Sankin's (16) method appeared for examining aromatic-rich oils. The results of this method are of special interest, since this method is the only one of those applied that involves the use of the specific dispersion. This group of structural analysis methods was concluded with the application of the Density-Refractivity Intercept Method of Kurtz, King, Stout, and Peterkin (17).

These methods have indicated that Fractions A, B and C were saturated, with C containing the smallest proportion of paraffinic side chains. The method of Lipkin, Martin and Kurtz (18) has indicated the nature of the fractionation of B on carbon. The first fraction,  $B_1$ , eluted from the carbon was more cyclic (62%) than B (50%). In the second fraction,  $B_2$ , the amount of naphthenic carbon was even larger (66%), but in the third fraction,  $B_3$ , there was a marked decrease in cyclic content to 43.5%. The Davis and McAllister method gave the actual number of naphthenic carbons per molecule for B,  $B_1$ ,  $B_2$ , and  $B_3$  (14.7, 13.8, 19.2, and 17.7). In Fractions D to J the proportion of

aromatic carbon atoms gradually increased to 30-35% in J. According to Karr's recommendations (12), his modification of the n-d-M method can be considered to give the best analyses for Fractions D to H, and Hazelwood's method (with Karr's sulphur correction) is most suitable for Fraction J. The Martin and Sankin method (16), using specific dispersion, gave values of %  $C_a$  in reasonably close agreement with the Hazelwood-Karr values, but that there were larger differences in %  $C_n$  values, with the Martin-Sankin values being higher than the others. An examination of the Hazelwood analysis of Fractions J,  $J_1$  and  $J_2$  indicated the nature of the separation of J on carbon. In terms of %  $C_a$ ,  $J_1$  contained a smaller proportion (23.7%) of aromatic carbons than did J (33.4), while  $J_2$  contained about the same proportion (33.8%).  $J_1$  contained a larger proportion (32.2%) of naphthenic carbons than J (26.2%), and  $J_2$  a smaller proportion (21.0%). With regard to the %  $C_p$  values, these amounts increased progressively from 40.4% for J to 44.2% for  $J_1$  to 45.3% for  $J_2$ . The number of aromatic rings varied from 1.6 for J to 1.25 for  $J_1$  to 1.7 for  $J_2$ , while the number of naphthenic rings amounted to 1.6 for J and 1.4 for both  $J_1$  and  $J_2$ . Fraction D contained the largest number of rings (4.9), but all other fractions contained on the average very close to three rings.

The oil fractions of the bitumen were compared with a typical midcontinent petroleum oil by plotting the aniline point and specific dispersion on graphs used by Mair, Willingham and Streiff (20) in their study of the lubricant fraction from a midcontinent petroleum. These

graphs are shown in Figures 12 and 13, and consist of aniline point and specific dispersion vs number of carbon atoms per molecule for various groups of pure hydrocarbons. Fractions D and E are the only fractions that lie appreciably outside the molecular weight range of Mair's lubricant fraction. On the basis of both aniline point and specific dispersion, Fractions A, B and C appear free of aromatic contamination. The aromatic-containing fractions vary considerably on the basis of molecular weight. On the basis of aniline point, Fractions D to J (also  $J_1$  and  $J_2$ ) cluster about the curve corresponding to naphthalene homologues, whereas, on the basis of specific dispersion, these same points (except D and E) lie close to the curve for diphenyl methane homologues.

#### Van Krevelen's Structural Analysis Methods

The structural analysis methods developed by van Krevelen and coworkers during the period 1952-1957 have been applied to the bitumen oil fractions. Van Krevelen described the hydrocarbon framework in terms of a ring condensation index  $2R/C$ , which, together with the hydrogen/carbon ( $H/C$ ) ratio, was related to the fraction of aromatic carbon ( $f_a$ ). Three sets of structural calculations were made. These are given in Table 7. They are summarized as follows:

- 1)  $R/C$  and  $f_a$  were calculated by the Densimetric Method (21) requiring the use of density and the elementary analysis.

- 2)  $f_a$  was calculated by the Graphical Densimetric Method (22).

This method is based on the relationship between molar volume per carbon atom ( $M_c/d$ ) and  $H/C$  with  $f_a$  for pure hydrocarbons. A correction to the  $M_c/d$  value for foreign atoms was made.

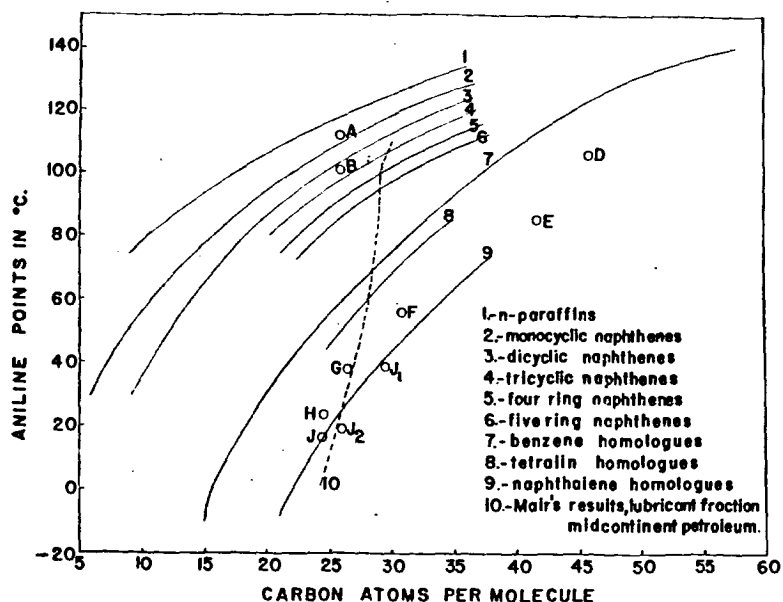


FIGURE 12. Aniline points of various types of hydrocarbons with respect to the number of carbon atoms per molecule.

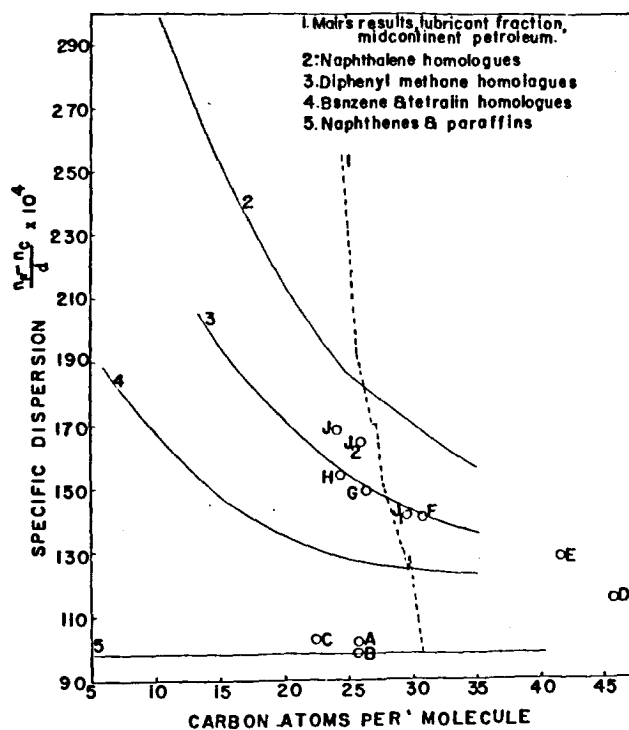


FIGURE 13. Specific dispersion of various types of hydrocarbons with respect to the number of carbon atoms per molecule.



3) Van Krevelen's method of carbon-type analysis, published in 1952 (23), was also applied. This permits the determination of four hydrocarbon groups:  $C_1$ , the fraction of paraffinic and naphthenic  $CH_2$  groups;  $C_2$ , the fraction of carbons that are junctions between fused naphthenic rings;  $C_3$ , the fraction of aromatic  $CH$  groups; and  $C_4$ , the fraction of carbon atoms that are junctions between fused aromatic rings. This method uses  $R/C$  and  $f_a$  obtained by the Densimetric Method and involves the use of an equation, relating  $C_1$  and  $H/C$ , which expresses the statistical probability of the occurrence of a  $CH_2$  group as a function of the  $H/C$  ratio.

The data in Table 7 indicate the following structural information:  $H/C$  values vary from 1.82 for B to 1.45 for J. These are all higher than those for the resin components (2).  $R/C$  values on the average for the oils are about one-third the average value of the resin components (2). This fact would indicate the oil fractions to be less condensed cyclic structures than the resin components. The  $f_a$  values by the two methods are in moderately close agreement, considering the different basis of the methods.

The carbon-type analyses indicate that from 50 to 86 percent of the carbon atoms are paraffinic or naphthenic  $CH_2$  groups. The results of this carbon-type analysis cannot be given the same weight as the graphical densimetric method, owing to the doubtful basis of the probability equation relating  $C_1$  and  $H/C$ .

TABLE 7

Application of Van Krevelen's Structural Analysis Methods

Fraction Property	B	C	D	E	F	G	J
H/C	1.84	1.84	1.72	1.70	1.64	1.58	1.45
S/C	0.0003	0.0006	0.0048	0.0072	0.0092	0.0102	0.0212
O/C	0.0012	0.0037	0.00212	0.0038	0.0142	0.0173	0.0
R/C (densimetric)	-0.028	0.0497	0.080	0.0389	0.0453	0.0473	0.105
f <sub>a</sub> (densimetric)	0.21	0.06	0.12	0.22	0.27	0.33	0.34
R/S			16.6	5.4	5.0	4.6	5.0
Mc/d	15.68	15.48	15.12	15.18	15.02	14.82	14.29
(Mc/d) corr.	15.67	15.44	15.04	15.06	14.79	14.55	14.02
f <sub>a</sub> (graphical densimetric)	0.11	0.07	0.20	0.22	0.25	0.26	0.40
C <sub>1</sub> = CH <sub>2</sub> /C	0.85	0.86	0.75	0.73	0.68	0.63	0.52
C <sub>2</sub> = CH/C	-0.06	0.085	0.13	0.048	0.052	0.046	0.14
C <sub>3</sub> = CH <sub>a</sub> /C	0.20	0.046	0.092	0.19	0.23	0.28	0.27
C <sub>4</sub> = C <sub>a</sub> /C	0.01	0.015	0.028	0.030	0.038	0.049	0.074

The Montgomery-Boyd Method of Structural Analysis

The final method used to elucidate the hydrocarbon framework was the method recently developed by the authors (9). This method describes the hydrocarbon structure in terms of five linkages and permits the determination of these groups by the simultaneous solution of five equations, which represent three chemical and two physical properties. The details of this method, the

equations involved and the method of application have already been reported (9, 10, 24). The calculations were made on an IBM 1620 Data Processing Machine. This method was applied to Fractions B to J.

In brief, the structural groups determined by this method are defined as follows:

$C_1$  = number per molecule of  $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}$  and  $\text{C}$  groups in linear and branched chains.

$C_2$  = number per molecule of  $\text{CH}_2$  groups in saturated rings, including the case where the hydrogen atoms may be replaced by linear or branched chains.

$C_3$  = number per molecule of  $\text{CH}$  groups that are junctions between fused saturated rings, including the case where the hydrogen is replaced by linear or branched chains.

$C_4$  = number per molecule of  $\text{CH}$  groups in aromatic rings, including the case where the hydrogen is replaced by linear or branched chains.

$C_5$  = number per molecule of  $\begin{array}{c} | \\ -\text{C}- \\ | \end{array}$  groups that are junctions between fused aromatic rings as well as junctions between saturated and aromatic rings.

The five equations constituting this method are relationships that express in terms of the five groups the following five properties: the total number of carbon atoms per molecule ( $\Sigma C$ ), the total number of hydrogen atoms per molecule ( $\Sigma H$ ), the total number of aromatic carbon atoms per molecule ( $\Sigma C_a$ ), the molar volume (M.V.), and the molar refraction (M.R., the Lorentz-Lorenz function). Numerical values of  $C_1$  to  $C_5$  were obtained by the simultaneous solution of these five equations by means of a digital computer (an IBM 1620 Data Processing Machine).

$\Sigma C$  and  $\Sigma H$  were calculated from the carbon and hydrogen analyses and the experimentally determined molecular weight. The molar volume and molar refraction were calculated from the molecular weight, the density (20°C), and the refractive index ( $n_D^{20}$ ). As was previously done with the asphaltene and resin fractions, the molar volume and molar refraction were corrected to a foreign-atom-free basis (1, 2, 10). This correction consisted in removing the contribution of the foreign atoms without affecting the structural contributions to the molar volume and molar refraction, and also without altering the number of carbon and hydrogen atoms. In the process of correcting the molar volume and molar refraction, it was necessary to calculate the values of K and E, which represented the amounts by which the molar volume and molar refraction respectively deviated from the values obtained by summing the atomic increments (using Traube's increments). These values are tabulated in Table 8, since they were of interest as they represented the structural contributions to the molar volume and the molar refraction.

Regarding the values used for the fifth property,  $\Sigma C_a$ , the number of aromatic carbon atoms per molecule, some explanation is required. It was felt that the values obtained experimentally (Table 5) and those calculated by the methods previously described (Tables 6 and 7) were not in sufficiently close agreement to permit a reliable single value to be taken for  $\Sigma C_a$  for each fraction. Consequently, as in the case of the asphaltene and resin components of the bitumen, it seemed

TABLE 8

Values of K and E for the Oil Fractions

Fraction	K	K/M. V. exp. x 100	E	E/M. R. exp. x 100
B	-1.78	-0.4	0.10	0.09
C	3.25	0.9	-0.26	-0.3
D	-0.02	0.0	6.58	3.2
E	4.54	0.7	8.20	4.3
F	3.00	0.6	7.66	5.5
G	7.81	2.0	6.90	5.8
J	14.56	4.2	7.05	6.4

that the most informative approach was to determine values of  $C_1$  to  $C_5$  for various arbitrarily chosen values of  $\Sigma C_a$  which covered the entire range of possible values. Fractions B and C were calculated for only one value of  $\Sigma C_a$  -- zero. The previously described properties, the ultraviolet spectra, and the structural analyses seemed to indicate that these fractions were entirely free of aromatics. These various sets of values were then critically assessed on the basis of algebraic and chemical criteria and thus it was possible to confine the structure within reasonably close limits. The derived properties required for the application of this method are shown in Table 9.



TABLE 9  
Derived Properties of the Oil Fractions Required for  
the Montgomery-Boyd Analysis

<div style="text-align: center;">Fraction Property</div>	B	C	D	E	F	G	J
$\Sigma C$	25.9	22.8	45.2	41.6	30.4	26.3	24.4
$\Sigma H$	47.7	41.6	77.0	70.0	49.6	41.0	35.0
$\Sigma S$	0.01	0.01	0.2	0.3	0.3	0.3	0.5
$\Sigma O$	0.03	0.08	1.0	0.2	0.4	0.4	0.0
M. V. exp.	406.3	351.9	693.1	629.4	457.5	385.4	343.3
M. R. exp.	116.0	101.5	205.5	189.9	139.8	119.6	109.8
M. V. corr.	406.1	351.4	686.2	624.3	451.5	379.7	335.5
M. R. corr.	115.9	101.3	202.2	187.3	137.0	116.8	105.8

The computational method was identical with that already reported (1, 2). The results of the application of this method to the oil fractions B to J are tabulated in Table 10.

The results shown in Table 10 were critically assessed on the basis of the same algebraic and chemical criteria as were described for the higher molecular weight components (1, 2). These criteria are: 1) the establishment of a range of  $\Sigma C_a$  values within which all values of  $C_1$  to  $C_5$  were positive (i. e., elimination of all negative numbers); 2) the assumption of the value of 4.0 for the ratio,  $C_R/R$ , the number of cyclic carbon atoms per ring and the subsequent determination of the unique set of values of  $C_1$  to  $C_5$  corresponding

TABLE 10

Results of the Montgomery-Boyd Analysis of the Oil Fractions

Fraction	$f_a$	$\Sigma C_a$	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$
B	0.0	0.0	14.5	7.5	3.9	-0.2	0.2
C	0.0	0.0	10.2	8.8	3.9	-0.1	0.1
D	0.0	0.0	31.6	2.2	11.4	-2.0	2.0
	0.05	2.1*	31.0	2.6	9.5	0.3	1.8
	0.15	6.7	29.9	3.7	4.9	4.9	1.8
	0.25	11.3	28.7	5.8	-0.6	8.6	2.7
E	0.07	3.0	27.4	3.6	7.6	0.4	2.6
	0.17	6.9*	26.4	4.9	3.4	4.0	2.9
	0.26	11.0	25.4	6.9	-1.8	7.0	4.0
	0.36	15.2	24.6	9.7	-7.9	9.3	5.9
F	0.10	3.0	18.3	3.4	5.7	0.5	2.5
	0.22	6.7*	17.5	4.9	1.4	3.5	3.2
	0.32	9.7	16.9	6.5	-2.8	5.4	4.3
	0.42	12.7	16.6	8.5	-7.4	6.9	5.9
G	0.11	3.0	13.1	4.0	6.2	0.6	2.4
	0.26	6.7*	12.3	5.9	1.4	3.3	3.5
	0.36	9.4	11.9	7.5	-2.5	4.7	4.7
	0.46	12.0	11.6	9.3	-6.6	5.7	6.2
J	0.10	2.3	9.3	3.7	9.1	-0.01	2.4
	0.30	7.2*	8.0	6.5	2.7	3.4	3.8
	0.37	9.0	7.6	7.7	0.04	4.2	4.8
	0.50	12.1	7.3	10.0	-5.0	5.4	6.7

\*Obtained by n-d-M method.

to this assumption; and 3) the indirect determination of  $\Sigma C_a$ , which was made on the basis of the quantitative estimate of the methylene and methyl groups from the infrared spectra (Table 4) and thus permitted a unique set of values of  $C_1$  to  $C_5$  corresponding to this value of  $\Sigma C_a$ . The net effect of applying these criteria was to confine the aromaticity to certain limits and hence all the other structural groups were similarly confined. The object of this application was to show that these criteria permitted the structure of each fraction to be defined within a reasonably narrow range.

To apply these criteria, it was necessary to be able readily to read off values of  $C_1$  to  $C_5$  for each fraction for any value of  $\Sigma C_a$  desired. For this reason the data in Table 10 have been presented graphically in Figures 14-18.

#### Application of Criterion I

An examination of Figures 14-18 reveals that physically impossible values for some of the structural groups occur for certain values of  $\Sigma C_a$ . It was possible to establish from these graphs, the range of  $\Sigma C_a$  values in which all five carbon types were positive. These were obtained by reading off the  $\Sigma C_a$  values for each fraction corresponding to  $C_3 = 0$  and  $C_4 = 0$ . It was only within this range that all types were positive. Above the upper limit of  $\Sigma C_a$ ,  $C_3$  became negative and below the lower limit  $C_4$  became negative. It should be noted here that, in the case of the asphaltene and resin fractions, this lower limit was set by  $C_2$  becoming negative. However, in the case of the oil fractions,  $C_2$  did not

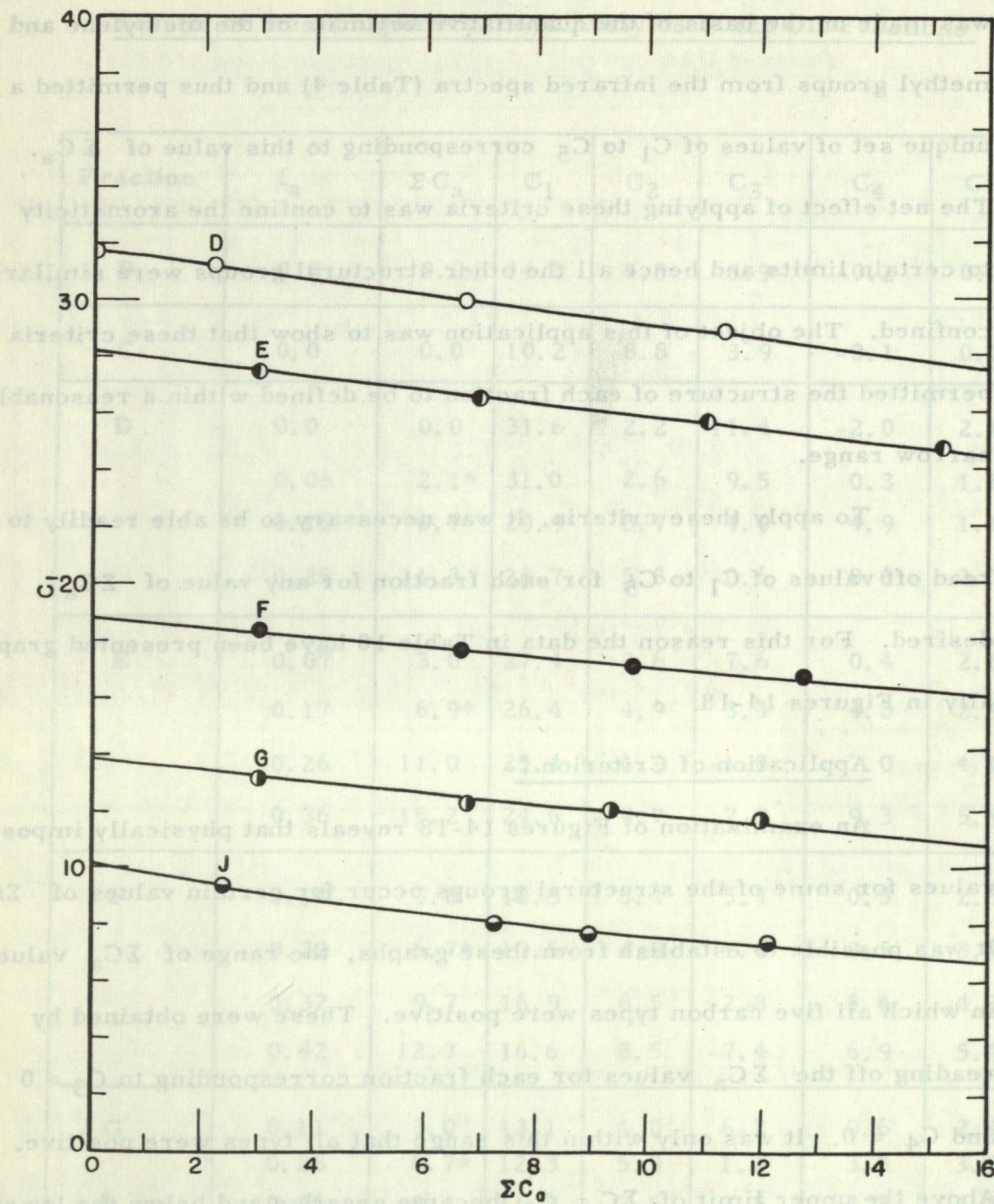


FIGURE 14. Results of the Montgomery-Boyd analysis of Fractions D to J.  $C_1$  versus  $\Sigma C_a$ .



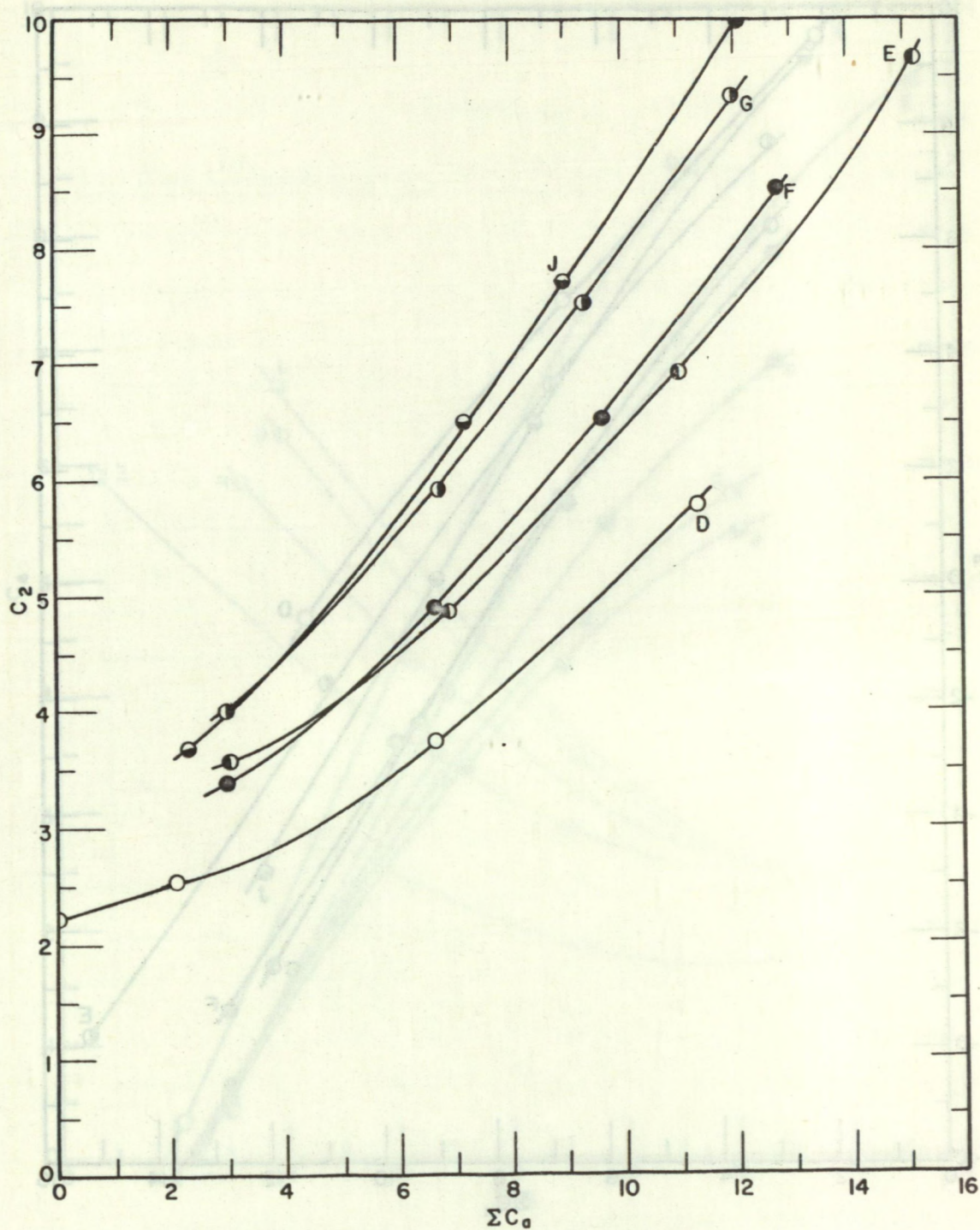


FIGURE 15. Results of the Montgomery-Boyd analysis of Fractions D to J.  $C_2$  versus  $\Sigma C_\alpha$ .



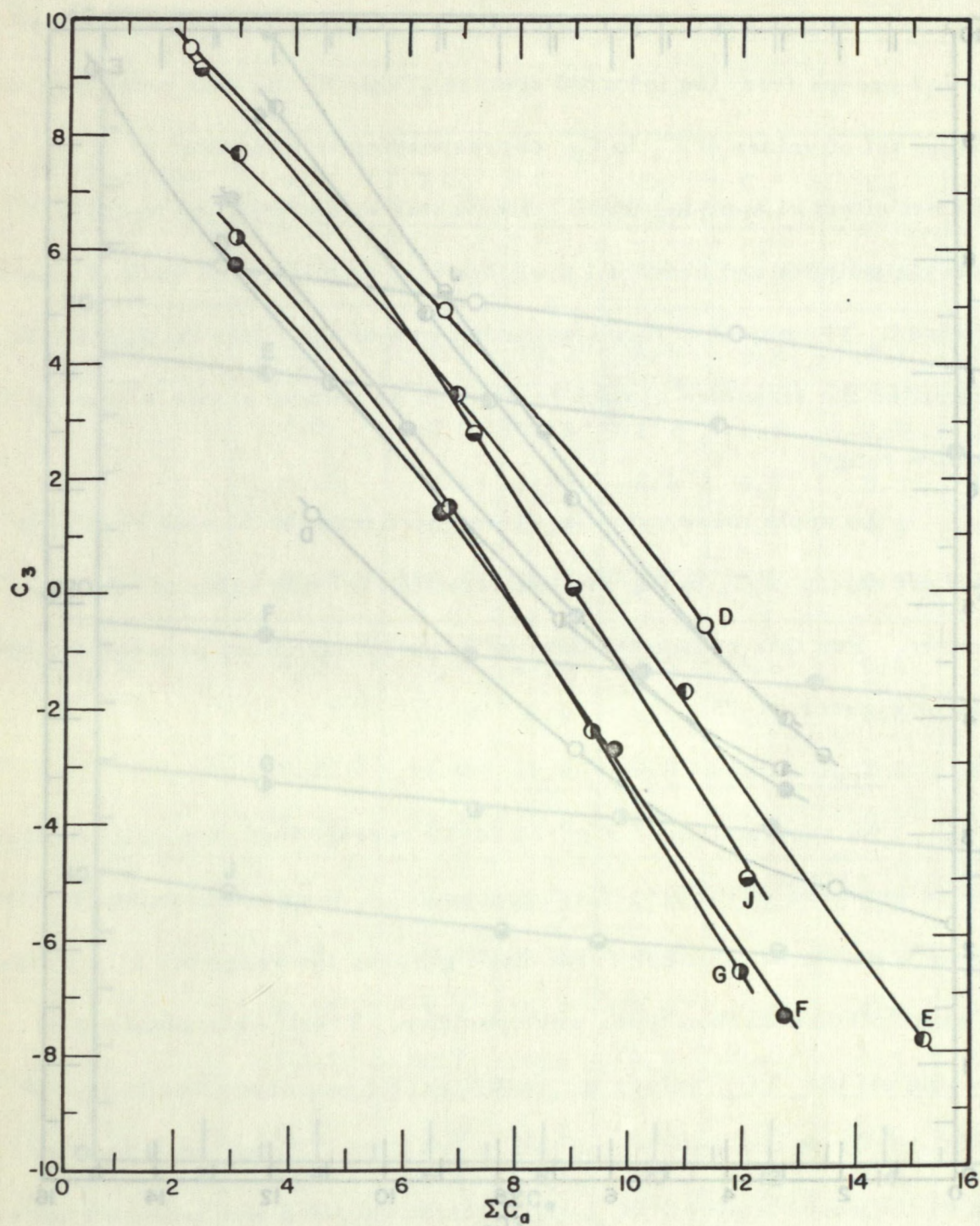


FIGURE 16. Results of the Montgomery-Boyd analysis of Fractions D to J.  $C_3$  versus  $\Sigma C_a$ .



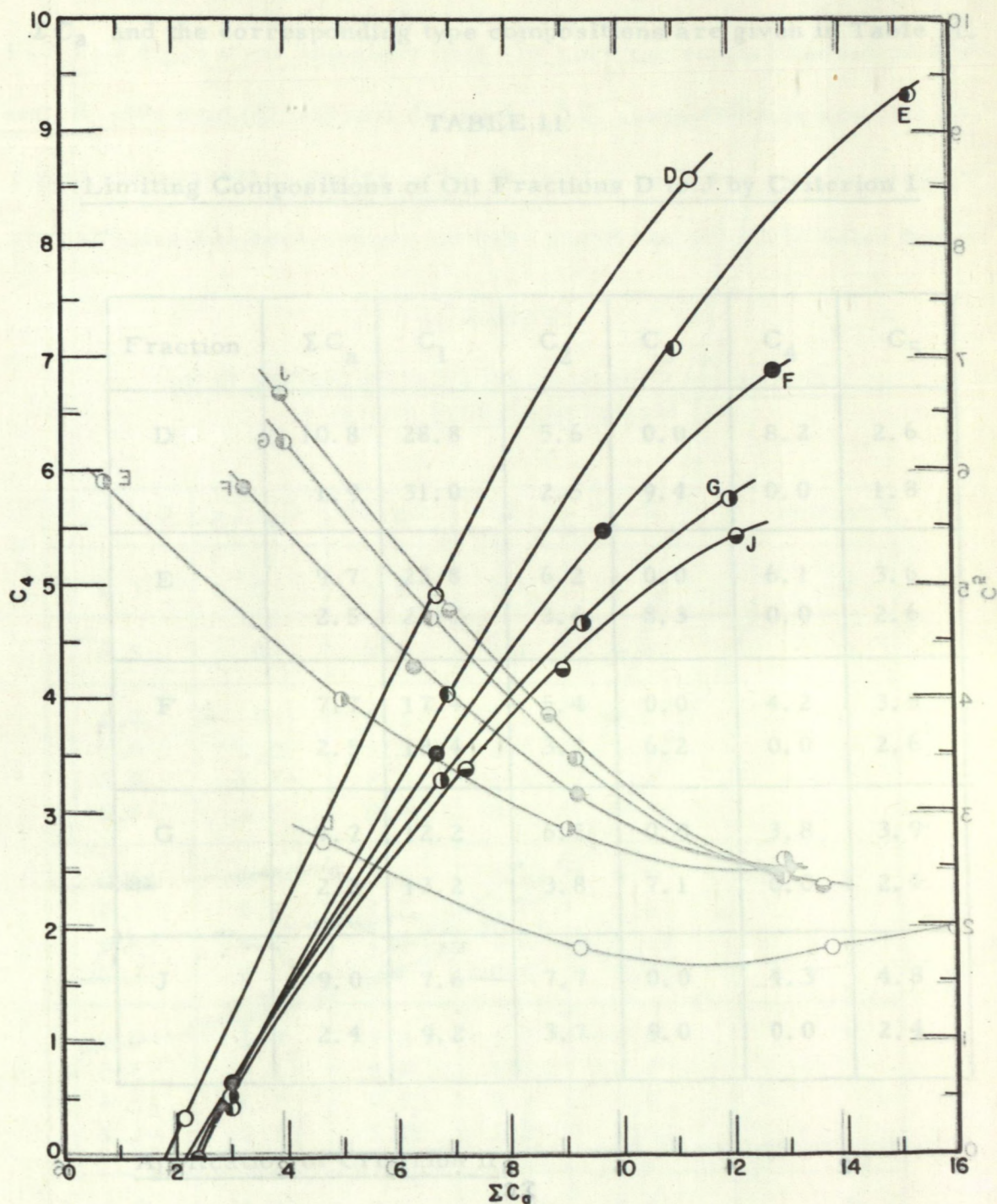


FIGURE 17. Results of the Montgomery-Boyd analysis of Fractions D to J.  $C_4$  versus  $\Sigma C_a$ .



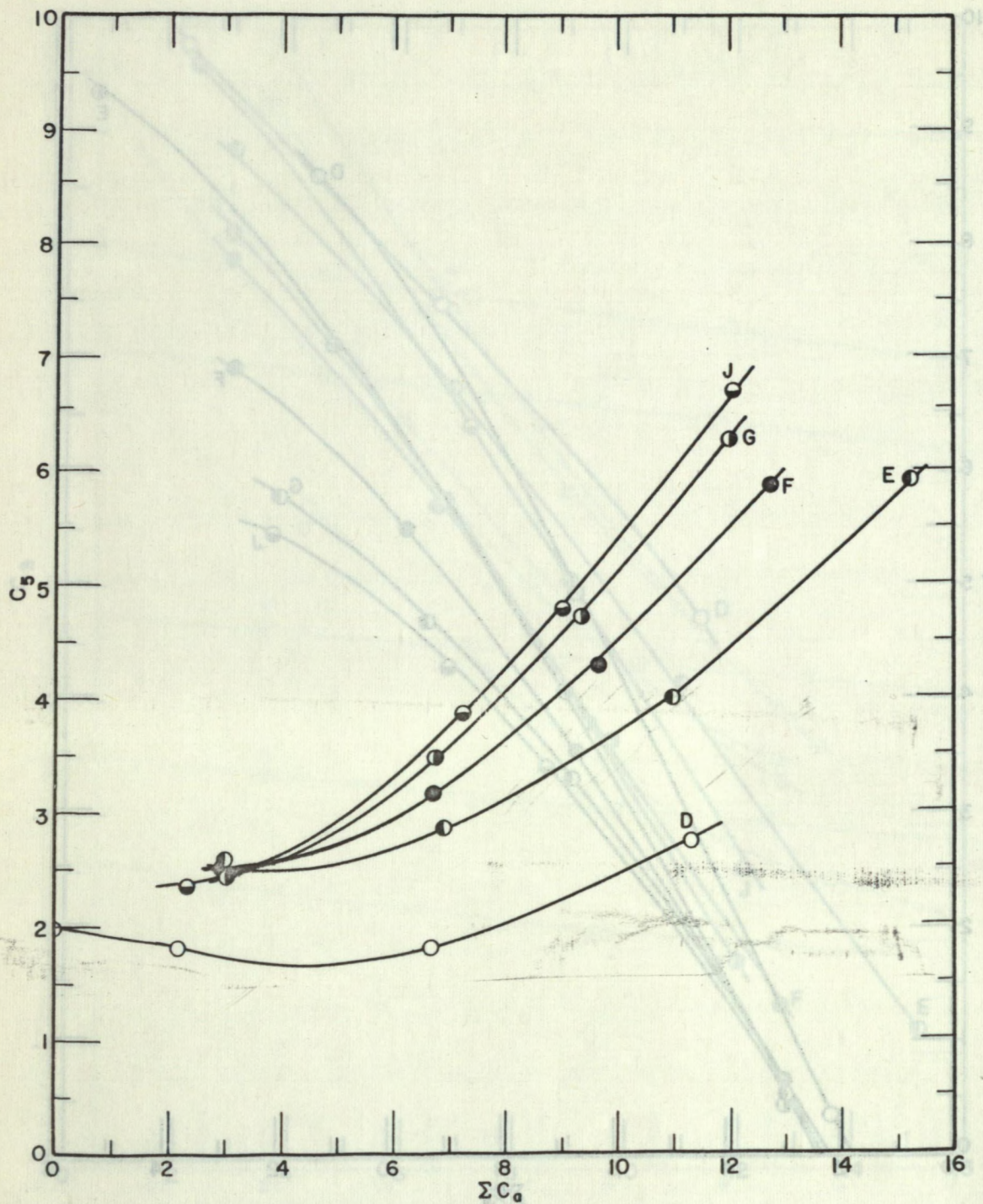


FIGURE 18. Results of the Montgomery-Boyd analysis of Fractions D to J.  $C_5$  versus  $\Sigma C_a$ .



become negative for any positive values of  $\Sigma C_a$ . The limiting values of  $\Sigma C_a$  and the corresponding type compositions are given in Table 11.

TABLE 11

Limiting Compositions of Oil Fractions D to J by Criterion I

Fraction	$\Sigma C_a$	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$
D	10.8	28.8	5.6	0.0	8.2	2.6
	1.9	31.0	2.5	9.4	0.0	1.8
E	9.7	25.8	6.2	0.0	6.1	3.6
	2.5	27.7	3.4	8.3	0.0	2.6
F	7.7	17.4	5.4	0.0	4.2	3.5
	2.5	18.4	3.3	6.2	0.0	2.6
G	7.7	12.2	6.5	0.0	3.8	3.9
	2.2	13.2	3.8	7.1	0.0	2.4
J	9.0	7.6	7.7	0.0	4.3	4.8
	2.4	9.2	3.7	9.0	0.0	2.4

Application of Criterion II

This criterion involves the determination of the type composition corresponding to a value of 4.0 for the number of cyclic carbon atoms/ ring ( $C_R/R$ ). This was done in the following manner. For all sets of results in Table 10, the number of rings per molecule (R) was calculated, using



van Krevelen's ring balance equation ( $C_3 + C_5 = 2R - 2$ ). The number of cyclic carbons atoms per ring was then evaluated from  $(C_2 + C_3 + C_4 + C_5)/R$ .  $C_R/R$  was plotted versus  $\Sigma C_a$  for each fraction (Figure 19). In this manner, it was possible to read off  $\Sigma C_a$  values corresponding to any desired value of  $C_R/R$  and hence read the carbon-type analysis directly

TABLE 12  
Structural Characteristics Corresponding to the  
Montgomery-Boyd Analysis

Fraction	$\Sigma C_a$	R	$C_R/R$	$C_4/C_5$	$C_2/C_3$
B	0.0	3.0	3.7	0	1.9
C	0.0	3.0	4.2	0	2.3
D	0.0	7.7	1.8	0	0.2
	2.1	6.6	2.1	0.2	0.3
	6.7	4.4	3.5	2.7	0.8
	11.3	2.0	8.0	3.1	-9.2
E	3.0	6.1	2.3	0.2	0.5
	6.9	4.2	3.7	1.4	1.4
	11.0	2.1	7.7	1.8	-3.9
	15.2	0.0	$\infty$	1.6	-1.2
F	3.0	5.1	2.4	0.2	0.6
	6.7	3.3	4.0	1.1	3.5
	9.7	1.8	7.7	1.3	-2.4
	12.7	0.2	60.2	1.2	-1.2
G	3.0	5.3	2.5	0.2	0.6
	6.7	3.4	4.0	0.9	4.2
	9.4	2.1	6.8	1.0	-3.1
	12.0	0.8	18.4	0.9	-1.4
J	2.3	6.7	2.2	0.0	0.4
	7.2	4.3	3.8	0.9	2.4
	9.0	3.4	4.9	0.9	208.6
	12.1	1.8	9.2	0.8	-2.0



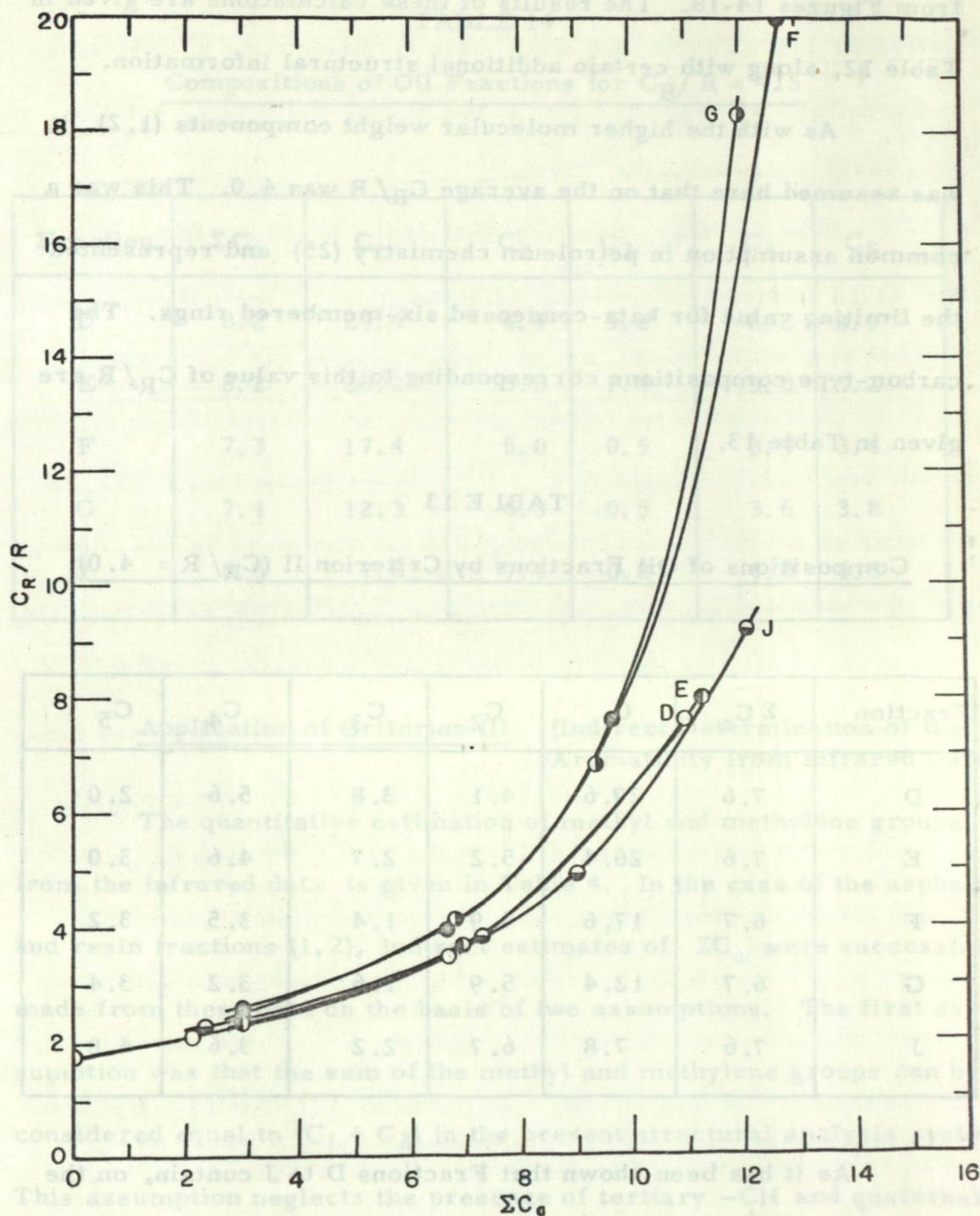


FIGURE 19. The number of carbon atoms per ring versus  $\Sigma C_a$  for the Montgomery-Boyd analysis of Fractions D to J.

from Figures 14-18. The results of these calculations are given in Table 12, along with certain additional structural information.

As with the higher molecular weight components (1, 2), it was assumed here that on the average  $C_R/R$  was 4.0. This was a common assumption in petroleum chemistry (25) and represented the limiting value for kata-condensed six-membered rings. The carbon-type compositions corresponding to this value of  $C_R/R$  are given in Table 13.

TABLE 13

Compositions of Oil Fractions by Criterion II ( $C_R/R = 4.0$ )

Fraction	$\Sigma C_a$	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$
D	7.6	29.6	4.1	3.8	5.6	2.0
E	7.6	26.4	5.2	2.7	4.6	3.0
F	6.7	17.6	4.9	1.4	3.5	3.2
G	6.7	12.4	5.9	1.6	3.2	3.4
J	7.6	7.8	6.7	2.2	3.6	4.0

As it has been shown that Fractions D to J contain, on the average, three rings, at least one of which is aromatic, the ratio of  $C_R/R$  is therefore probably somewhat greater than 4. Consequently, a similar set of carbon-type compositions corresponding to  $C_R/R = 4.5$  is given in Table 14 to reveal the differences in carbon type composition that would be consistent with this higher value  $C_R/R$ .

TABLE 14

Compositions of Oil Fractions for  $C_R/R = 4.5$

Fraction	$\Sigma C_a$	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$
D	8.2	29.4	4.4	3.2	6.2	2.1
E	8.2	26.2	5.5	1.9	5.0	3.2
F	7.3	17.4	5.0	0.5	3.9	3.4
G	7.4	12.3	6.3	0.5	3.6	3.8
J	8.5	7.6	7.4	0.8	4.0	4.5

Application of Criterion III (Indirect Determination of the Aromaticity from Infrared Data) -

The quantitative estimation of methyl and methylene groups from the infrared data is given in Table 4. In the case of the asphaltene and resin fractions (1, 2), indirect estimates of  $\Sigma C_a$  were successfully made from these data on the basis of two assumptions. The first assumption was that the sum of the methyl and methylene groups can be considered equal to  $(C_1 + C_2)$  in the present structural analysis system. This assumption neglects the presence of tertiary  $\begin{array}{c} | \\ -CH \\ | \end{array}$  and quaternary  $\begin{array}{c} | \\ -C- \\ | \end{array}$  saturated carbon atoms counted in the sum of  $C_1$  and  $C_2$  in the structural analysis system. As it is highly probable that there are tertiary and quaternary carbon atoms in the bitumen, it follows that the sum of the methyl and methylene groups estimated from the infrared



data is somewhat less than the sum of  $C_1$  and  $C_2$  in the structural analysis. In this case, the  $\Sigma C_a$  value corresponding to this value of  $(C_1 + C_2)$  was read off a plot of  $(C_1 + C_2)$  versus  $\Sigma C_a$  for the structural group analysis.

In cases where this first estimation failed to yield a value for  $\Sigma C_a$ , a second estimate of  $\Sigma C_a$  was made by further assuming that the sum of the methyl and methylene groups can be considered equal to all the saturated carbon atoms in the molecule as determined by the structural analyses (i. e.,  $C_1 + C_2 + C_3$ ) and hence  $\Sigma C_a$  can be taken as the difference between the total number of carbon atoms per molecule and the sum of the methyl and methylene groups. This second assumption is likely to result in low estimates of the total number of saturated carbon atoms and consequently high values for  $\Sigma C_a$ , since it neglects the possible presence of  $C_3$ -type groups in addition to the limitation of the first assumption. This results in larger errors for the oil fractions than for the resins, since the former have been shown to contain a higher proportion of saturated carbon atoms than the latter. This procedure was repeated with the oil fractions. The plot of  $(C_1 + C_2)$  versus  $\Sigma C_a$  for the structural analysis is shown in Figure 20. The first assumption failed to give an estimate of  $\Sigma C_a$ , since the values of  $(C_1 + C_2)$  obtained from the infrared data were, in every case except Fraction D, lower than the minimum value permitted by the structural analysis system (Figure 20). In the case of Fraction D, the value of  $(C_1 + C_2)$  from the  $7.28 \mu$  and



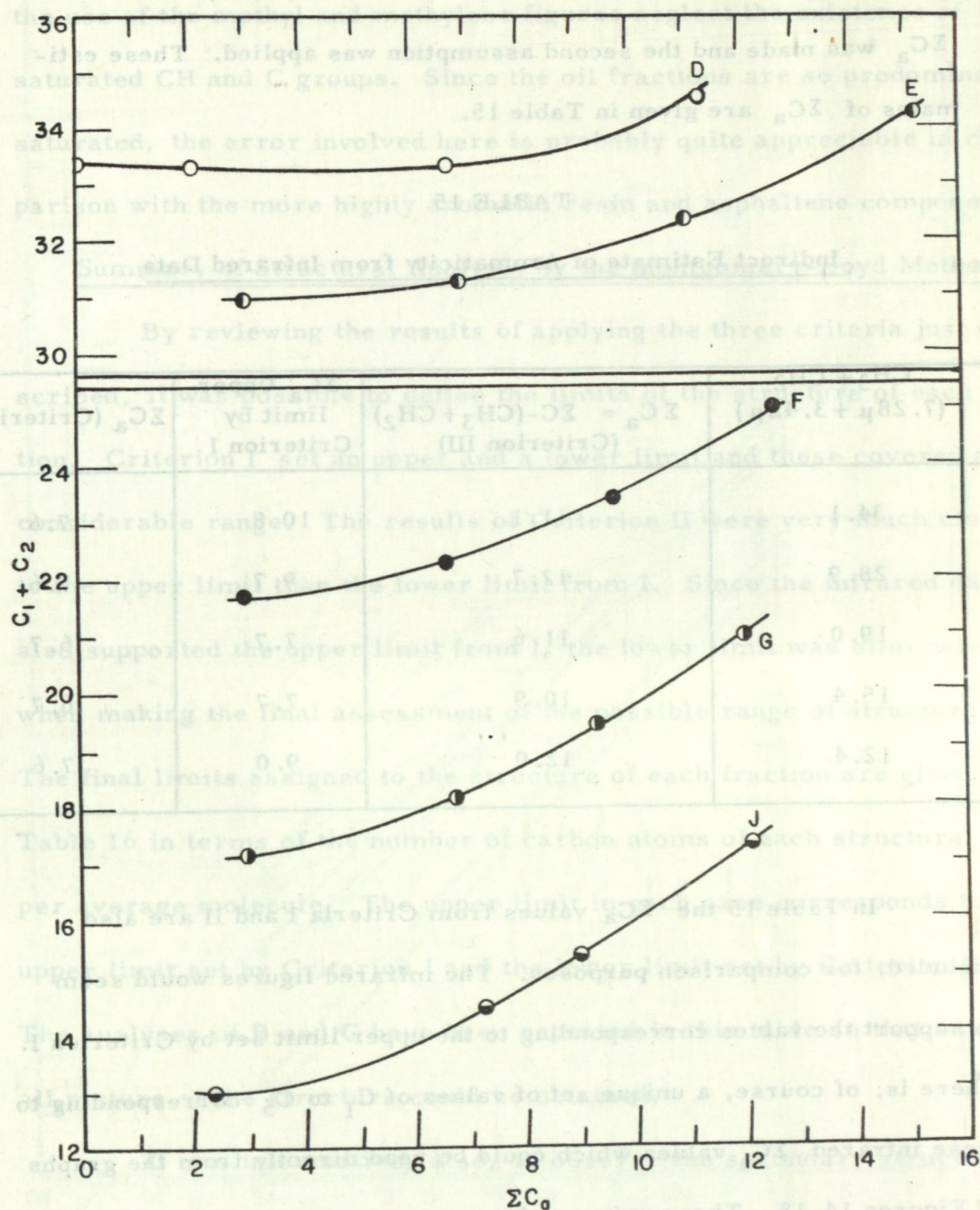


FIGURE 20.  $(C_1 + C_2)$  versus  $\Sigma C_a$  for the Montgomery-Boyd analysis of Fractions D to J.

3.42  $\mu$  bands corresponded to a value for  $\Sigma C_a$  of 10.4. This agreed with the upper limit set by Criterion I. A second attempt to determine  $\Sigma C_a$  was made and the second assumption was applied. These estimates of  $\Sigma C_a$  are given in Table 15.

TABLE 15  
Indirect Estimate of Aromaticity from Infrared Data

Fraction	$CH_3 + CH_2$ (7.28 $\mu$ + 3.42 $\mu$ )	$\Sigma C_a = \Sigma C - (CH_3 + CH_2)$ (Criterion III)	$\Sigma C_a$ Upper limit by Criterion I	$\Sigma C_a$ (Criterion II)
D	34.1	11.1	10.8	7.6
E	28.9	12.7	9.7	7.6
F	19.0	11.6	7.7	6.7
G	15.4	10.9	7.7	6.7
J	12.4	12.0	9.0	7.6

In Table 15 the  $\Sigma C_a$  values from Criteria I and II are also included, for comparison purposes. The infrared figures would seem to support the values corresponding to the upper limit set by Criterion I. There is, of course, a unique set of values of  $C_1$  to  $C_5$  corresponding to these infrared  $\Sigma C_a$  values which could be read directly from the graphs in Figures 14-18. These unique values are not given since it is obvious that they will contain negative numbers ( $C_3$  would be negative). The incompatibility of the infrared results with the structural analysis



results is probably due to the fact that the assumptions made regarding the use of the methyl and methylene figures neglect the existence of saturated CH and C groups. Since the oil fractions are so predominantly saturated, the error involved here is probably quite appreciable in comparison with the more highly aromatic resin and asphaltene components.

#### Summary of Structural Analysis by the Montgomery-Boyd Method

By reviewing the results of applying the three criteria just described, it was possible to define the limits of the structure of each fraction. Criterion I set an upper and a lower limit and these covered a considerable range. The results of Criterion II were very much closer to the upper limit than the lower limit from I. Since the infrared data also supported the upper limit from I, the lower limit was eliminated when making the final assessment of the possible range of structures. The final limits assigned to the structure of each fraction are given in Table 16 in terms of the number of carbon atoms of each structural type per average molecule. The upper limit in each case corresponds to the upper limit set by Criterion I and the lower limit set by Criterion II. The analyses of B and C have been repeated in this table so that an overall picture of the structure could be obtained.

It was informative, also, to observe the secondary structural parameters corresponding to these limiting compositions. For convenience, these parameters were obtained directly from the graphs in Figures 19, 21, 22 and 23, and are given in Table 17.

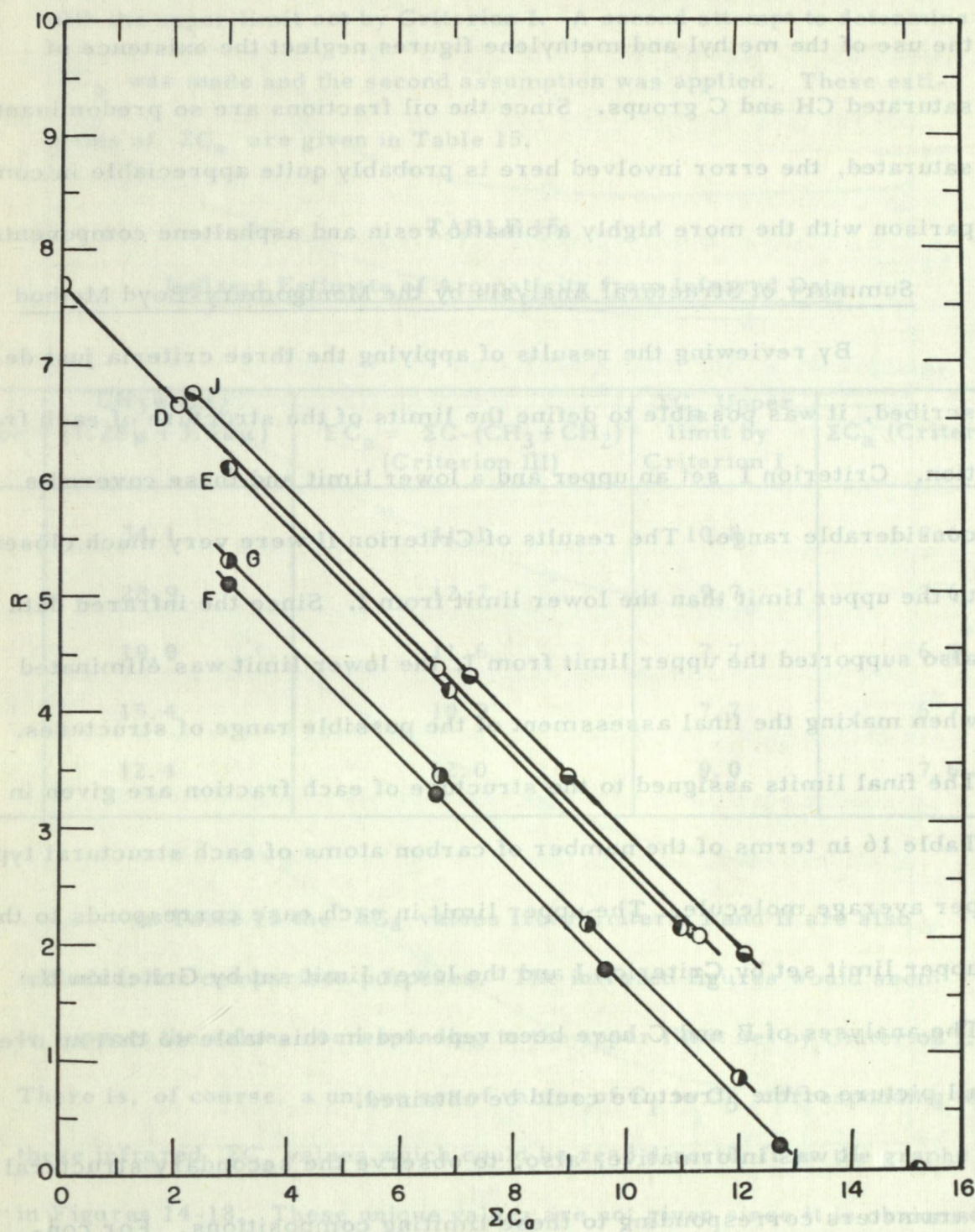


FIGURE 21. The number of rings per molecule versus  $\Sigma C_a$ , for the Montgomery-Boyd analysis of Fractions D to J.



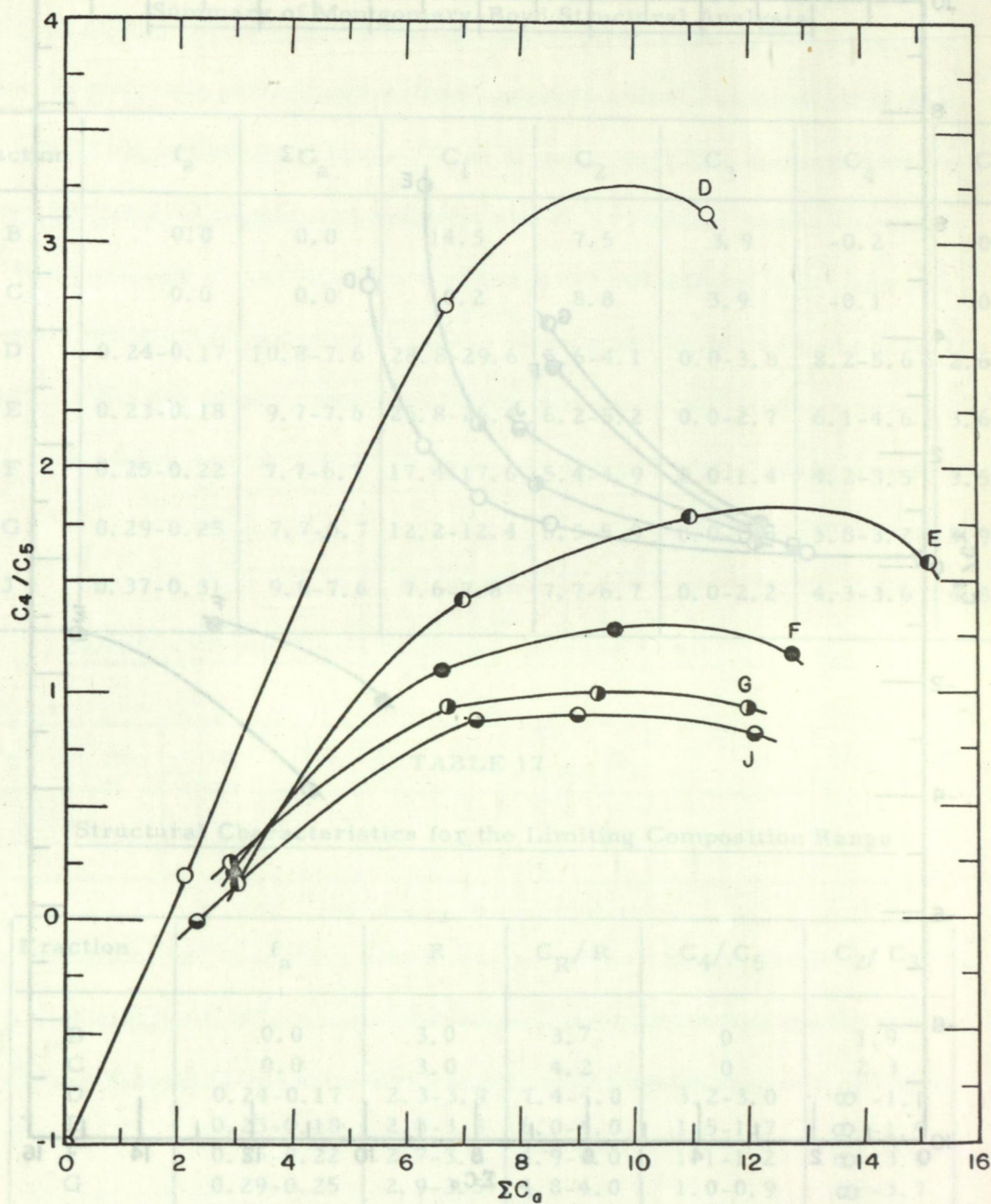


FIGURE 22. Variation of  $C_4/C_5$  with  $\Sigma C_a$  for the Montgomery-Boyd analysis of Fractions D to J.



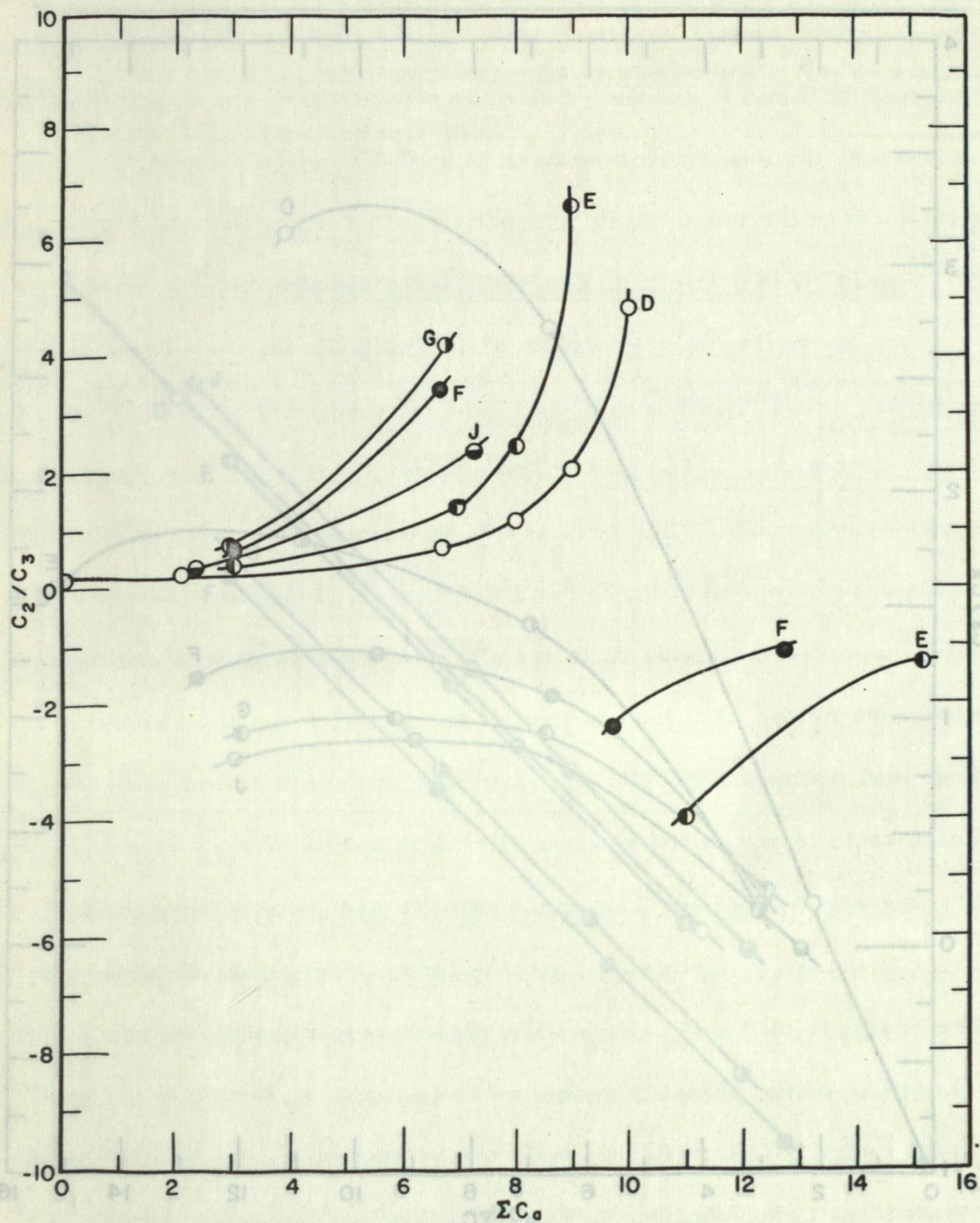


FIGURE 23. Variation of  $C_2/C_3$  with  $\Sigma C_a$  for the Montgomery-Boyd analysis of Fractions D to J.



TABLE 16

Summary of Montgomery-Boyd Structural Analysis

Fraction	$f_a$	$\Sigma C_a$	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$
B	0.0	0.0	14.5	7.5	3.9	-0.2	0.2
C	0.0	0.0	10.2	8.8	3.9	-0.1	0.1
D	0.24-0.17	10.8-7.6	28.8-29.6	5.6-4.1	0.0-3.8	8.2-5.6	2.6-2.0
E	0.23-0.18	9.7-7.6	25.8-26.4	6.2-5.2	0.0-2.7	6.1-4.6	3.6-3.0
F	0.25-0.22	7.7-6.7	17.4-17.6	5.4-4.9	0.0-1.4	4.2-3.5	3.5-3.2
G	0.29-0.25	7.7-6.7	12.2-12.4	6.5-5.9	0.0-1.6	3.8-3.2	3.9-3.4
J	0.37-0.31	9.0-7.6	7.6-7.8	7.7-6.7	0.0-2.2	4.3-3.6	4.8-4.0

TABLE 17

Structural Characteristics for the Limiting Composition Range

Fraction	$f_a$	R	$C_R/R$	$C_4/C_5$	$C_2/C_3$
B	0.0	3.0	3.7	0	1.9
C	0.0	3.0	4.2	0	2.3
D	0.24-0.17	2.3-3.9	7.4-4.0	3.2-3.0	$\infty$ -1.1
E	0.23-0.18	2.8-3.8	6.0-4.0	1.5-1.7	$\infty$ -1.9
F	0.25-0.22	2.7-3.2	4.9-4.0	1.1-1.2	$\infty$ -3.5
G	0.29-0.25	2.9-3.5	4.8-4.0	1.0-0.9	$\infty$ -3.7
J	0.37-0.31	3.4-4.1	5.0-4.0	0.9-0.9	$\infty$ -3.1



Since these fractions contained such a large proportion of saturated carbon atoms, it was of some interest to examine this portion of the molecule more closely. In this discussion, the composition of each fraction has been taken to be the average of the two limiting compositions in Table 16. It was possible to make an estimate of the average chain lengths for the paraffinic side chains. It was assumed that the number of methyl groups (Table 4) determined from the infrared represented the maximum number of linear chains possible. The average chain length was calculated as  $C_1/CH_3$ . These values are located in Table 18.

TABLE 18  
Determination of Average Length of Paraffinic Side Chains

Fraction	B	C	D	E	F	G	J
$C_1/CH_3$	2.5	2.2	3.2	3.4	3.2	2.7	1.9

Another noticeable feature of this portion of the molecule is the large proportion of paraffinic carbon atoms. To illustrate this feature, the percentage of paraffinic carbons in the saturated portion of the molecule has been tabulated in Table 19.

TABLE 19  
Percentage of Paraffinic Carbons in the Saturated Part of Molecule

Fraction	B	C	D	E	F	G	J
$C_1/(C_1 + C_2 + C_3), \%$	56.0	44.7	81.3	78.6	74.8	63.7	48.1

Another interesting structural feature is the ratio  $R_a/S$  which gives some indication of the manner in which the sulphur is associated with the aromatic ring structure. This ratio was calculated for the values of  $\Sigma C_a$  which corresponded to  $C_3 = 0$ . The results are contained in Table 20.

TABLE 20  
Determination of  $R_a/S$

Fraction	S	$R_a$	$R_a/S$
D	0.2	2.3	11.5
E	0.3	2.8	9.3
F	0.3	2.7	9.0
G	0.3	2.9	9.7
J	0.5	3.4	6.8

These values of  $R_a/S$  were all considerably higher than for the resins (2), where this ratio was practically constant at 3.5.

## DISCUSSION

There has been presented here a wide variety of physical and chemical property data, of spectra and of structural analyses, in an effort to characterize the oil component of the Alberta bitumen. A wide variety of methods has been used, some of which were not strictly applicable (e.g. the van Krevelen methods, which were designed for coal and the relatively large number of methods designed for oils of lower molecular weight range than that of the oil fractions being studied here). Our objective has been to obtain an appreciation of the class of material to which the Alberta bitumen belongs, as well as to study the differences indicated by the various methods on the same fractions.

At the commencement of this investigation, it was felt that the Alberta bitumen, from a chemical point of view, could be considered in a class midway between coal and oil. This accounts for the wide range of structural analysis methods applied. The van Krevelen analysis has been used to characterize the asphaltene (1) and resin (2) components, and was used here so that all fractions of the bitumen could be compared on the same basis. The methods designed for oils have been used to show that the oil components of the bitumen can be treated as any petroleum oil. The Montgomery-Boyd five-parameter system has been applied, to illustrate its applicability to the entire molecular weight range encountered in the bitumen; the particular form of its equations (24) made it suitable for this purpose. It also was based on a larger amount of pure compound data.



The infrared and ultraviolet spectra, the aniline point and the specific dispersion correlations of Mair (20), and the qualitative type analyses of Clerc, Kincannon and Weir (3), all gave a qualitative indication of the nature of the fractions. On this basis, Fractions A, B, and C were essentially saturated and D to J contained increasing amounts of aromatic material. A limited amount of quantitative information regarding the total number of aromatic carbon atoms and of methyl and methylene groups was obtained from the infrared spectra. This information was used, in conjunction with the Montgomery-Boyd method, to define the aromaticity and also to determine the average chain length that was found to be relatively constant. Mair's correlations (in Figures 12 and 13) compared the bitumen oil fractions with a midcontinent lubricant fraction. Most of the fractions were in a comparable molecular weight range (except D and E). One striking difference was that the bitumen fractions D to J fell along one chemical-type curve, whereas the curve for the midcontinent oil cut across all the type curves illustrated.

The structural analysis results in Table 6 are all in reasonably close agreement, since they are all based on the same or closely related properties. The largest discrepancy occurred for Fractions D and E. This was considered to be due to their molecular weight being higher than the other fractions and also to the fact that their composition is such (low amount of aromatics) that they could be considered "borderline" cases for the application of methods designed for

saturates only, as well as methods designed for aromatics. These results indicated the degree of separation of the saturates from the aromatics on silica gel, and also the further separation of the saturates on carbon and the aromatics on carbon. Owing to lack of material, it was only possible to characterize the separation of J on activated alumina on the basis of ultraviolet spectra and infrared spectra. There appeared to be a fractionation into three classes on this adsorbent.

The van Krevelen analysis has shown the oil fractions to be less aromatic and less condensed cyclic structures than the resin (2) and asphaltene (1) components.

The Montgomery-Boyd analysis gives quantitative information about five structural groups. However, it is possible to combine these to compare all methods on the basis of the same parameters ( $\% C_a$ ,  $\% C_n$ , and  $\% C_p$ ). On the basis of  $\% C_a$ , all methods gave results in reasonably close agreement except for Fraction D, where the Montgomery-Boyd method and the van Krevelen graphical densimetric method both gave results 13% higher than the results in Table 6. The lack of agreement in Table 6 for this fraction has already been mentioned. It was to be expected that the van Krevelen and Montgomery-Boyd methods would agree, since both are based on pure hydrocarbon data. The Montgomery-Boyd method has the added advantage that it should not be sensitive to molecular weight nor to the relative proportions of carbon types in the molecule. On the basis of  $\% C_n$ , the

Montgomery-Boyd results were consistently low in comparison with the results in Table 6, the difference being the greatest for Fraction D and the least for J. On the basis of the %  $C_p$ , the Montgomery-Boyd results were higher than the other methods, the differences being greatest (12%) for Fraction D and lowest for J. In terms of  $R_t$  with the exception of Fraction D, all methods predict, on the average, three rings per molecule for all fractions. In the case of D, the Montgomery-Boyd method predicted three rings whereas the methods of Table 6 predicted four rings per molecule. Attention is drawn to the fact that these average compositions are not in conflict with the compounds which Nagy and Gagnon (26) have identified in Abasand bitumen.

In addition to the structural parameters already compared, the Montgomery-Boyd method gave quantitative information on the distribution of the cyclic carbon atoms between those in ring junction positions and non-junction positions, both saturated and aromatics. This is best illustrated by observing the ratios  $C_2/C_3$  and  $C_4/C_5$ . For the average compositions from Table 16, the ratio  $C_2/C_3$  varied from a low of 1.2 for Fraction B, gradually increasing to 7 for F, G, and J. The values for  $C_4/C_5$  varied from a low of 0.9 for Fraction J, to a high of 3.0 for Fraction D.

In conclusion, it can be said that much useful information has been gained from all techniques applied. These have shown the oil fraction of the Abasand bitumen to be highly saturated, to contain a relatively large amount of paraffinic carbon, and to be amenable



to the techniques developed for petroleum oils. It has been shown to be less aromatic and of a less condensed cyclic nature than the higher-molecular-weight components, the resins and the asphaltenes.

## CONCLUSIONS

1. The experimental details of the chromatographic methods were largely fixed by the scale of operation desired here to produce the quantities of the fractions required for the characterization methods used. Two separations on silica gel were required to fractionate the saturates from the aromatics. This could undoubtedly be reduced to a single experiment, by increasing the adsorbent-to-oil ratio. The percentage recovery was relatively high here (93%), in contrast to 88% on activated alumina and 68-78% for carbon. The high losses with the latter adsorbent make it desirable to use it as the final stage in any series of chromatographic separations.
2. (a) The ultraviolet spectra indicated all oil fractions to be less aromatic than the resin and asphaltene components. It was possible to divide the most aromatic oil fraction (J separated on activated alumina) into three classes, on the basis of their absorption bands.

(b) From the infrared spectrum the following structural facts were indicated: All fractions contained C = O groups and an appreciable number of methyl groups. Fractions A, B and C were devoid of C-C unsaturation and also contained long methylene side chains; D and E contained a small amount of aromatic carbon, and also long methylene chains. Fractions F to J contained increasing amounts of aromatic carbon, but were still predominantly saturated. The infrared spectra did not show any distinguishable difference between the fractions of J separated on activated alumina.

3. The average composition of the oil fractions, as determined by various three parameter methods designed for lubricating oils, may be represented by the following selection (Table 21) of these analyses.

4. Van Krevelen's densimetric method of analysis predicted values for the aromaticity ranging from 6% for Fraction C to 34% for J. The graphical densimetric method gave values up to 40% for J. The ring condensation index ( $2R/C$ ) varied from 0.08 to 0.21, J having the highest value and E the lowest.

TABLE 21

Representative Carbon-type Analyses of the Oil Fractions

Fraction	%C <sub>a</sub>	%C <sub>n</sub>	%C <sub>p</sub>	R <sub>a</sub>	R <sub>n</sub>	C <sub>n</sub>
A (a)	0.0	44.3	55.7	0.0	2.4	
B (a)	0.2	48.8	51.0	0.1	2.7	14.7 (c)
B <sub>1</sub> (b)		61.8	38.2			13.8 (c)
B <sub>2</sub> (b)		65.8	34.2			19.2 (c)
B <sub>3</sub> (b)		43.5	56.5			17.7 (c)
C (a)	0.0	60.5	39.5	0.0	3.0	
D (d)	5.3	41.8	52.9	0.4	4.5	
E (d)	17.2	19.7	63.1	1.2	2.1	
F (d)	22.6	24.4	53.0	1.2	1.9	
G (d)	26.4	28.8	44.8	1.2	1.9	
H (a)	29.3	27.0	43.7	1.2	1.5	
J (e)	33.4	26.2	40.4	1.6	1.6	
J <sub>1</sub> (e)	23.7	32.2	44.2	1.2	1.4	
J <sub>2</sub> (e)	33.8	21.0	45.3	1.7	1.4	

(a) n-d-M method (11).

(b) Lipkin, Martin and Kurtz (18).

(c) Davis and McAllister (19).

(d) Karr's modification of n-d-M (12).

(e) Hazelwood's method (13) with Karr's sulphur correction (12).



5. The Montgomery-Boyd 5-parameter structural analysis system, in conjunction with the assumption that the average number of carbon atoms per ring was 4.0, has defined the aromaticity and the carbon type composition for most of the oil fractions within the following limits:

TABLE 22  
Summary of Montgomery-Boyd Structural Analysis,  
as Percentages

Fraction	% $\Sigma C_a$	% $C_1$	% $C_2$	% $C_3$	% $C_4$	% $C_5$
B	0.0	56.0	28.9	15.1	0	0
C	0.0	44.7	38.6	17.1	0	0
D	24-17	63.7-65.5	12.4-9.1	0-8.4	18.1-12.4	5.8-4.4
E	23-18	62.0-63.5	14.9-12.5	0-6.5	14.7-11.0	8.6-7.2
F	25-22	57.2-57.9	17.8-16.1	0-4.6	13.8-11.5	11.5-10.5
G	29-25	46.4-47.1	24.7-22.4	0-6.1	14.4-12.2	14.8-12.9
J	37-31	31.1-32.0	31.6-27.5	0-9.0	17.6-14.8	19.7-16.4

6. The average side chain length was essentially constant and amounted to 2.8.

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MLB:DSM:(PES)PH