



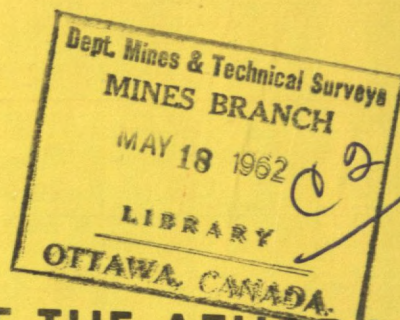
CANADA

DEPARTMENT OF MINES AND  
TECHNICAL SURVEYS, OTTAWA

MINES BRANCH  
RESEARCH REPORT

R 88

*Price 25 cents.*



# A STUDY OF THE ATHABASCA BITUMEN FROM THE ABASAND QUARRY, ALBERTA, CANADA

PART II: THE INITIAL CHROMATOGRAPHIC  
SEPARATION OF THE PENTANE  
EXTRACT AND THE STRUCTURE  
AND PROPERTIES OF THE  
RESINOUS COMPONENTS

M. L. BOYD & D. S. MONTGOMERY

FUELS AND MINING PRACTICE DIVISION

DECEMBER 1961

## Mines Branch Research Report R 88

A STUDY OF THE ATHABASCA BITUMEN FROM THE  
ABASAND QUARRY, ALBERTA, CANADA. Part II: The  
Initial Chromatographic Separation of the Pentane Extract,  
and the Structure and Properties of the Resinous  
Components.

by

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

## ABSTRACT

The pentane-soluble portion, which constitutes 77% of the Abasand bitumen, was chromatographed on activated fuller's earth by the elution technique. This procedure resulted in a separation of the resinous and oil components. The resins were fractionated into four groups by the use of a succession of increasingly polar solvents. The following properties are given for each resin fraction: ash content, emission spectra of the ash, elementary analysis, molecular weight, density at 20°C, refractive index at 20°C, infra-red spectrum, ultraviolet spectrum, and visible spectrum. One resin fraction, CCl<sub>4</sub>(I), was further chromatographed on silica gel, to determine the amount of saturated material. Quantitative estimates of the number of methyl and methylene groups, and also the number of aromatic carbon atoms, have been made from the infra-red spectrum. Each resin fraction has been characterized by the application of van Krevelen's structural analysis system, and also by two new methods devised by the authors. The chemical structure of each fraction has been expressed in terms of five structural groups, and a quantitative estimate has been made of the degree of condensation of the aromatic rings.

---

\* Senior Scientific Officer and \*\* Senior Scientist, Fuels and Mining Practice Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

Direction des mines

Rapport de recherches R 88

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

Partie II: Séparation chromatographique initiale  
des constituants solubles dans le pentane;  
structure et propriétés des composants  
résineux.

par

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

RÉSUMÉ

La fraction soluble dans le pentane, qui représente 77% du bitume de l'Abasand, a été chromatographiée sur de la terre à foulons activée en utilisant les procédés d'élution. Par cette méthode, on a obtenu une séparation des constituants résineux et huileux. Les résines furent fractionnées en quatre groupes en employant successivement des solvants de plus en plus polarisés. Pour chaque fraction de résine on indique les propriétés suivants: teneur en cendres, spectre d'émission des cendres, analyse élémentaire, poids moléculaire, densité à 20°C, indice de réfraction à 20°C, spectre infrarouge, spectre ultraviolet, et spectre visible. On a de plus chromatographié sur un gel de silice la fraction de résine  $\text{CCl}_4$  (I) afin de déterminer la quantité de matières saturées. A partir du spectre infrarouge, on a estimé quantitativement le nombre de groupes méthyle et méthylène, ainsi que le nombre d'atomes de carbone aromatique. Chaque fraction de résine a été caractérisée par l'application du procédé d'analyse structurale de Van Krevelen, ainsi que par deux nouvelles méthodes proposées par les auteurs du présent rapport. La structure chimique de chaque fraction a été exprimée en termes de cinq groupes de structure, et l'on a fait une estimation quantitative du degré de condensation des anneaux aromatiques.

---

\*Chargée de recherches principale, et \*\*Scientiste principal,  
Division des combustibles et des techniques de l'exploitation  
minière, Direction des mines, ministère des Mines et des Rel-  
evés techniques, Ottawa, Canada.

## CONTENTS

	<u>Page</u>
Abstract .....	i
Résumé .....	ii
<u>Part II:</u> <u>The Initial Chromatographic Separation of</u> <u>the Pentane Extract, and the Structure and</u> <u>Properties of the Resinous Components</u>	
Introduction.....	1
Preparation and Analysis of the Resin Fractions .....	7
Preliminary Experiments to Establish the Desired Level of Activity of the Adsorbent .....	7
The Chromatographic Analysis of the Pentane Extract .....	13
The Chromatography of CCl <sub>4</sub> (I) Fraction on Silica Gel .....	22
Structural Information from the Absorption Spectra of the Resin Fractions .....	24
The Ultraviolet Spectra .....	24
The Visible Spectra .....	26
The Infra-red Spectra .....	26
Test for Lignin-like Structures .....	33
Application of van Krevelen's Method of Structural Analysis to the Resin Fractions .....	33
Application of the Montgomery-Boyd Structural Group Analysis Method (Scheme MB1) .....	40
Application of the Modified Montgomery-Boyd Structural Group Analysis Method (Scheme MB2)...	54
Discussion .....	56
Application of Criterion I .....	76

	<u>Page</u>
Application of Criterion II .....	77
Application of Criterion III (Indirect Determination of the Aromaticity from Infra-red Data).....	79
Conclusions Concerning the Structure of the Resin Fractions .....	89
Acknowledgements .....	91
References .....	92

-----

## FIGURES

<u>No.</u>		<u>Page</u>
1.	Chromatographic separation of pentane extract on activated and unactivated Florex ..	9
2.	Result of elution analysis of the pentane extract on unactivated Florex. (The refractive index and weight refer to the solvent-free material.) .....	10
3.	Result of elution analysis of the pentane extract on activated Florex. (The refractive index and weight refer to the solvent-free material.) .....	11
4.	Pentane extract eluted with n-pentane from Florex. (The refractive index and the volume refer to the effluent solution) .....	15
5.	Pentane extract eluted with n-pentane from Florex. (The refractive index and the weight refer to the oil devoid of solvent.) .....	16
6.	Summary of chromatographic analysis of the pentane extract on Florex .....	18
7.	Result of elution analysis of C Cl <sub>4</sub> (I) fraction on silica gel. (The refractive index and weight refer to the solvent-free material.) ..	23
8.	Ultraviolet spectra of the resin fractions .....	25
9.	Visible spectra of the resin fractions. (The concentrations are shown in mg per 100 ml benzene) .....	27
10.	Infra-red spectra of the resin fractions. ....	29
11.	Application of van Krevelen's H/C versus O/C diagram .....	34
12.	Results of the Montgomery-Boyd analysis (Scheme MB 1) of the resins. C <sub>1</sub> versus ΣC <sub>a</sub> .....	49

## FIGURES (Cont'd)

<u>No.</u>		<u>Page</u>
13.	Results of the Montgomery-Boyd analysis (Scheme MB 1) of the resins. $C_2$ versus $\Sigma C_a$ .....	50
14.	Results of the Montgomery-Boyd analysis (Scheme MB 1) of the resins. $C_3$ versus $\Sigma C_a$ .....	51
15.	Results of the Montgomery-Boyd analysis (Scheme MB 1) of the resins. $C_4$ versus $\Sigma C_a$ .....	52
16.	Results of the Montgomery-Boyd analysis (Scheme MB 1) of the resins. $C_5$ versus $\Sigma C_a$ .....	53
17.	Results of the Montgomery-Boyd analysis (Scheme MB 1) of the resins, expressed as fractions of the total carbon. $C_1 / \Sigma C$ versus $f_a$ .....	65
18.	Results of the Montgomery-Boyd analysis (Scheme MB 1) of the resins, expressed as fractions of the total carbon. $C_2 / \Sigma C$ versus $f_a$ .....	66
19.	Results of the Montgomery-Boyd analysis (Scheme MB 1) of the resins, expressed as fractions of the total carbon. $C_3 / \Sigma C$ versus $f_a$ .....	67
20.	Results of the Montgomery-Boyd analysis (Scheme MB 1) of the resins, expressed as fractions of the total carbon. $C_4 / \Sigma C$ versus $f_a$ .....	68
21.	Results of the Montgomery-Boyd analysis (Scheme MB 1) of the resins, expressed as fractions of the total carbon. $C_5 / \Sigma C$ versus $f_a$ .....	69

## FIGURES (Cont'd)

<u>No.</u>		<u>Page</u>
22.	Variation of $C_2/C_3$ with $f_a$ for the Montgomery-Boyd analysis of the resins (Scheme MB1) .....	70
23.	Variation of $C_4/C_5$ with $f_a$ for the Montgomery-Boyd analysis of the resins (Scheme MB1) .....	71
24.	The number of carbon atoms per ring versus $f_a$ for the Montgomery-Boyd analysis of the resins (Scheme MB1) .....	72
25.	Rings/ molecule versus $f_a$ for the Montgomery-Boyd analysis of the resins (Scheme MB1) .....	73
26.	$(C_1 + C_2)$ versus $\Sigma C_a$ for the Montgomery-Boyd analysis of the resins (Scheme MB1) .....	74

## TABLES

1	Physical Properties of the Resin Fractions .....	20
2	Emission Spectra of Resin Ash Samples .....	21
3	Determination of Methyl and Methylene Groups from Infra-red Data .....	30
4	Determination of the Fraction of Aromatic Carbon ( $f_a$ ) on the Basis of the Absorbance of the $6.25\mu$ Band of Pure Aromatic Hydrocarbons .....	32
5	Results of the Application to the Resins of van Krevelen's Densimetric Methods .....	37
6	Van Krevelen's Structural Group Analysis of the Resin Fractions .....	39
7	Values of K and E for the Resins .....	44
8	Derived Properties of the Resin Fractions Required for the Montgomery-Boyd Analysis ..	45



## TABLES (Cont'd)

<u>No.</u>		<u>Page</u>
9	Results of the Montgomery-Boyd Analysis of the Resins .....	48
10	Application of Modified Montgomery-Boyd Analysis .....	56
11	Structural Characteristics of the Resins from the Montgomery-Boyd Analysis .....	64
12	Montgomery-Boyd Analysis (MB1) of the Resins Expressed as Fractions of the Total Carbon ..	75
13	Limiting Compositions of Resin Fractions by Criterion I .....	77
14	Composition of Resin Fractions by Criterion II ( $C_R/R = 4$ ) .....	79
15	Indirect Determination of the Aromaticity from Infra-red Data .....	80
16	Second Indirect Estimate of Aromaticity from Infra-red Data .....	82
17	Composition of Resin Fractions by Criterion III .....	83
18	Summary of Results by Scheme MB1 .....	84
19	Structural Characteristics of the Resins for the Limiting Composition Range .....	84
20	Determination of $R_A/S$ for the Resin Fractions .....	89

PART II: THE INITIAL CHROMATOGRAPHIC SEPARATION  
OF THE PENTANE EXTRACT, AND THE STRUCTURE AND  
PROPERTIES OF THE RESINOUS COMPONENTS

INTRODUCTION

Preliminary experiments, described in Part I<sup>(1)\*</sup> of this series, had shown the desirability of removing the asphaltene fraction from the Abasand bitumen as an initial step to facilitate the chromatographic separation of the remaining resin and oil fractions. The high molecular weight of the asphaltene fraction interferes with the flow of the solvents and increases the difficulty of selecting the solvents, which must possess a low viscosity and an increasing level of polarity and yet must possess sufficient solvent power to avoid precipitation.

In the present research report, Part II of the series, a number of preliminary experiments are described relating to the selection and the control of the activity of the adsorbent, but the major work consisted in the chromatographic separation of a pentane solution containing 495 g of the pentane-soluble fraction that represented 77% of the Abasand bitumen. The products obtained from this chromatographic separation were characterized by a number of structural analysis schemes, including two new methods devised by the authors.

At the outset there appeared to be two possible methods of fractionating the pentane extract: (1) distillation, and (2) chromato-

---

\* References are listed at the end of the report in the order in which they are numbered in the text.

graphic separation. Distillation under reduced pressure had already been applied to the bituminous sand itself. <sup>(2)</sup> At a temperature low enough to minimize cracking, 250°C, it was possible to distill only 20% of the bitumen at a pressure of 0.1 mm; consequently, this approach did not appear attractive as a means of fractionating 77% of the bitumen. Another consideration favouring chromatographic separation was that a separation according to chemical type rather than by molecular weight suited the structural analysis methods that were in the course of development. Extensive work had already been done on the chromatographic separation of low-molecular-weight petroleum fractions by Mair, <sup>(3)</sup> and Smit <sup>(4)</sup> showed that higher-molecular-weight petroleum fractions could be separated by elution chromatography. The extremely mild conditions under which separation took place suggested that this technique might be employed with a minimum of alteration in the hydrocarbon structure. Since one of the major objectives of this work, as emphasized in Part I, was to map the structure of the hydrocarbon framework of the bitumen fractions in an approximate manner, it was essential to employ methods that would not alter the hydrocarbon structure in the course of the separation. These considerations led to the choice of elution chromatography as the most promising separation technique available.

It has been known for many years that fuller's earth is capable of removing the dark-coloured bodies from bitumen. This

method dates back to the original work of Marcusson<sup>(5)</sup> who separated native asphaltic materials into asphaltenes, resins, and oil. According to this method, the asphaltenes were first precipitated and then the petroleum ether-soluble portion was adsorbed on fuller's earth. The oil fraction was eluted with the petroleum ether, and the resins with chloroform. This method has been extended by many investigators by using alumina or silica gel as adsorbent, and various solvents have also been employed. Grader<sup>(6)</sup> studied the composition of bitumens. He employed alumina as adsorbent and made an arbitrary separation of the resins by the use of a series of solvents of increasing desorbing power (carbon tetrachloride, benzene, and chloroform). Hubbard and Stanfield<sup>(7)</sup> improved the reproducibility of the arbitrary separation of the oils from the resins considerably, by employing alumina of a given particle size, activated in accordance with a definite procedure; in addition, provision was made for eluting the alumina with pentane at a fixed temperature.

A number of investigators have already applied this separation to the Alberta bitumen. Krieble and Seyer<sup>(8)</sup> and Katz<sup>(9)</sup> have applied Marcusson's original method, and Pasternack and Clark<sup>(10)</sup> have applied Streiter's<sup>(11)</sup> modification, using n-pentane in place of petroleum ether and ethyl ether for extracting the resins. Gishler<sup>(12)</sup> used a 9:1 mixture of benzene-methanol for extracting the resins. The use of such a wide variety of solvents, and the variations in the nature of the fuller's earth, have resulted in the

resin content of the Athabasca bitumen varying from 15 to 24%.<sup>(10)</sup>

The establishment of a chromatographic scheme for a complex mixture of unknown hydrocarbons and hetero-compounds such as are found in the bitumen differs in some respects from the procedure followed for the separation of a mixture of known compounds. When the compounds are known, a systematic study of the adsorption behaviours can be made following the technique of Weil-Malherbe.<sup>(13)</sup> The relative rates of band movement may also be followed as was done by Le Rosen.<sup>(14)</sup> Under certain circumstances special adsorbents may be synthesized, as shown by Pauling and Dickey.<sup>(15)</sup>

When very little is known of the chemistry of the mixture to be separated, it is desirable to secure the following preliminary information before undertaking separation on a large scale. It is important to know the approximate molecular weight distribution of the material to be separated. Oils with a molecular weight below 200 may be chromatographed using the displacement technique employed by Mair.<sup>(3)</sup> Above this value, it is essential to use elution chromatography. When the molecular weight reaches approximately 800, care must be taken to avoid the precipitation of a portion of the resins by the polar desorbent (methanol). This can be avoided by the use of an appropriate mixture of a good solvent, such as chloroform, with the desorbent. A graded series of eluents must also be selected, of increasing polarity, which have a sufficiently high solvent power to avoid precipitation. This

problem has essentially been solved by Grader,<sup>(6)</sup> as far as the bitumens are concerned.

It is most important that an adsorbent be selected which does not bring about reactions in the substances being separated. W. Trappe<sup>(16)</sup> has shown that a catalytic transformation of cholesterol occurred only on acid clays; consequently, a neutral fuller's earth, Florex, supplied by the Floridin Company\* and stated to have a pH of 7.9 to 8.2, was selected for this research to avoid acid or base catalysis of reactions of the compounds present in the bitumen.

The activity of the adsorbent, i. e. its capacity to adsorb the bituminous substances, is carefully controlled by drying the adsorbent. If the adsorbent is made too active by drying, the resins cannot be eluted with even the most polar desorbent. It is desirable to have almost complete recovery of the sample placed on the column, and at the same time to have sufficient activity to achieve a high level of separation. The only means of determining the correct level of activity in relation to the graded eluents is to dry different batches of the adsorbent and test them. High losses on the adsorbent can be minimized, to some extent, by pre-wetting the adsorbent with solvent. This practice has been found to have considerable merit.

---

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

The previous work described in the literature suggested the suitability of both fuller's earth and alumina as adsorbents for the chromatographic analysis in question. The experiments of Smit<sup>(4)</sup> indicated that silica gel might have the advantage that not only would the resinous bodies be removed but also a separation of the paraffins from the aromatic compounds in the oil fraction would be achieved. An experiment was therefore performed, using 48/200 silica gel (Davison Corporation) in a column 1 cm in diameter x 60 cm high, at a weight ratio of gel to pentane extract (P.E.) of 17/1 and an initial concentration of 2 grams pentane extract in 30 ml n-pentane. The effluent was dark in colour, indicating a poor separation of the oil from the resinous constituents. To achieve a sharp separation would have required a gel of finer particle size, and probably a gel/P.E. ratio of the order of that used by Smit (100/1). Since unactivated Florex XXS (60/100 mesh) was capable of separating the dark-coloured resinous material at an adsorbent-to-P.E. ratio of 10/1, there appeared to be little merit in using silica gel at this stage of the separation process.

One disadvantage in the use of fuller's earth, as compared with alumina, is that some of the inorganic constituents are eluted by the more polar solvents and contaminate the sample as far as the

trace element composition of the ash is concerned. In the present work this consideration was outweighed by the availability and cheapness of Florex as compared with alumina.

## PREPARATION AND ANALYSIS OF THE RESIN FRACTIONS

### Preliminary Experiments to Establish the Desired Level of Activity of the Adsorbent

The following preliminary experiments on 12-gram samples of pentane extract, using 120 grams unactivated Florex in a column 1.1 x 182 cm, were made to determine the optimum conditions for the separation of the resinous bodies. The oil fraction, which was defined as the material eluted from the Florex with n-pentane, amounted to 46% of the bitumen, and the benzene-elutable material (resins) amounted to 16%. The molecular weight of this oil fraction was determined to be 381\*, and that of the resin 920\*. The sulphur content of the former was 3.1%, and of the latter, 6.7%. The high molecular weight obtained for the resin fraction confirmed the view that elution chromatography was one of the few ways to bring about a separation without causing thermal damage to the large molecules. The bromine number of the oil fraction was measured, to compare the value with other animal and vegetable oils and to obtain an estimate of the number of olefinic double bonds. The bromine number was found to be 16.2 g Br<sub>2</sub> per 100 g oil, which is low as compared with animal and vegetable oils and indicates a relatively low number of olefinic double bonds (0.39 double bond

---

\* Determined cryoscopically in benzene.



molecule) or other linkages which react with bromine. However, it does suggest that precautions should be taken to protect the samples from photo-oxidation reactions.

The question of the desirable amount of thermal activation of the Florex prior to use was next considered. To clarify this problem, 12 grams of pentane extract were added to each of two columns 1.1 x 182 cm--one filled with 120 g of Florex activated by heating in an oven at 150°C for 3 hours, and the other filled with the same weight of unactivated Florex. Neither column was pre-wetted with solvent. Summaries of these experiments are given in Figures 1, 2 and 3. It was evident, from the results shown in these figures, that the thermal activation of the fuller's earth had a profound influence upon the separation of the oil from the resin fraction and upon the recovery of the bitumen attainable with the graded series of eluents. Figures 2 and 3 also show that Florex caused a marked segregation of the sulphur-containing compounds.

In view of the differences that arose on slight heating of fuller's earth, it was not surprising that different investigators have found difficulty in securing a reproducible separation of the oil from the resin fraction. As natural bituminous materials contain a large number of compounds differing slightly in adsorptive properties, small variations in the adsorbent cause appreciable differences in the quantity of oil and resin obtained.

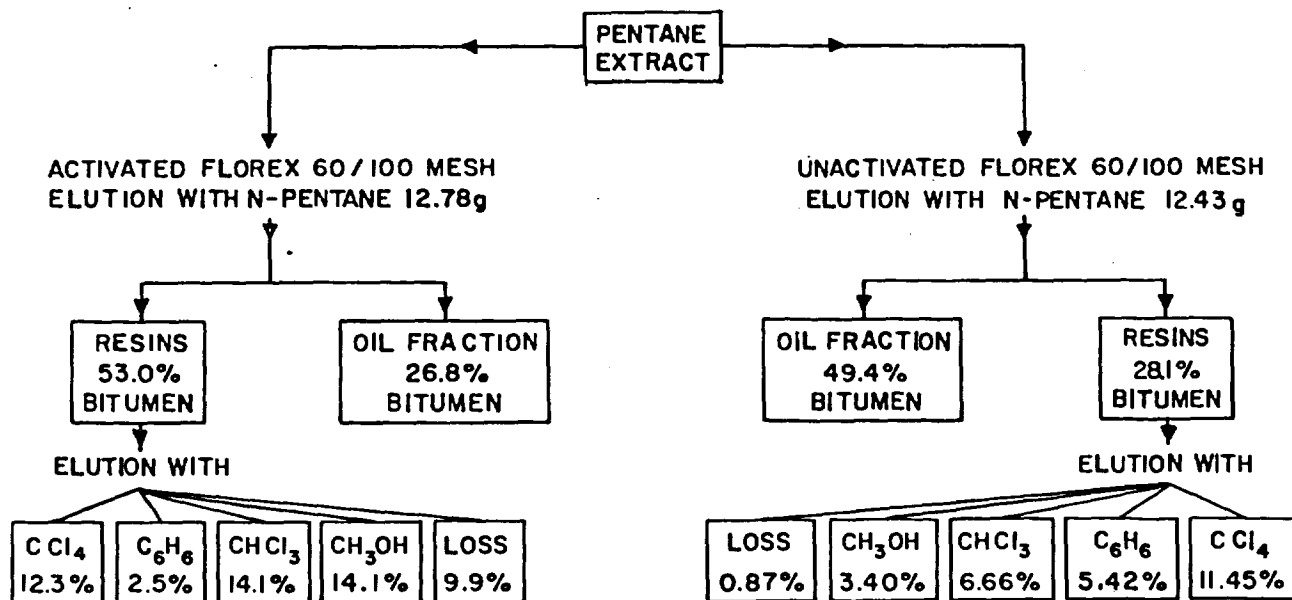


Figure 1. Chromatographic separation of pentane extract on activated and unactivated Florex.

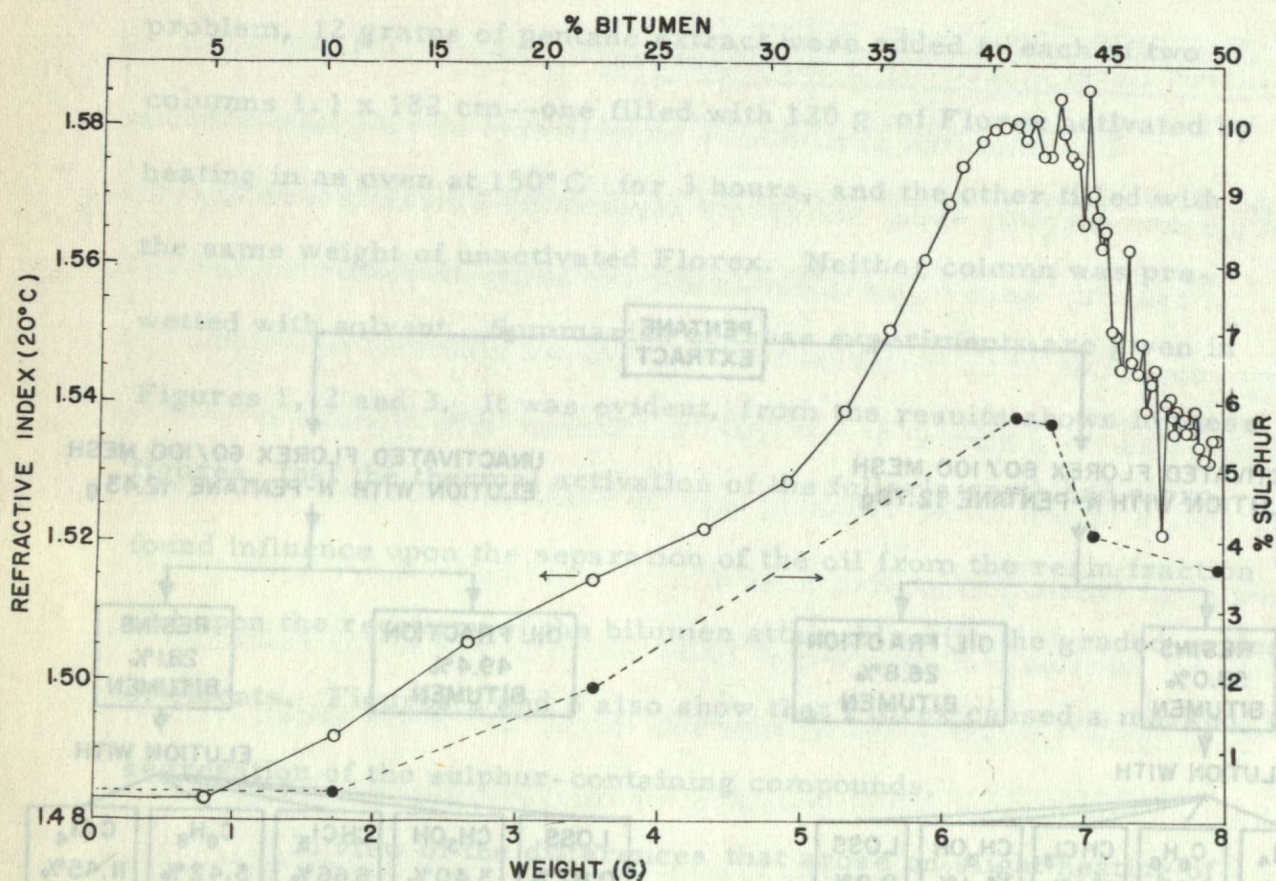


Figure 2. Result of elution analysis of the pentane extract on unactivated Florex. (The refractive index and weight refer to the solvent-free material.)

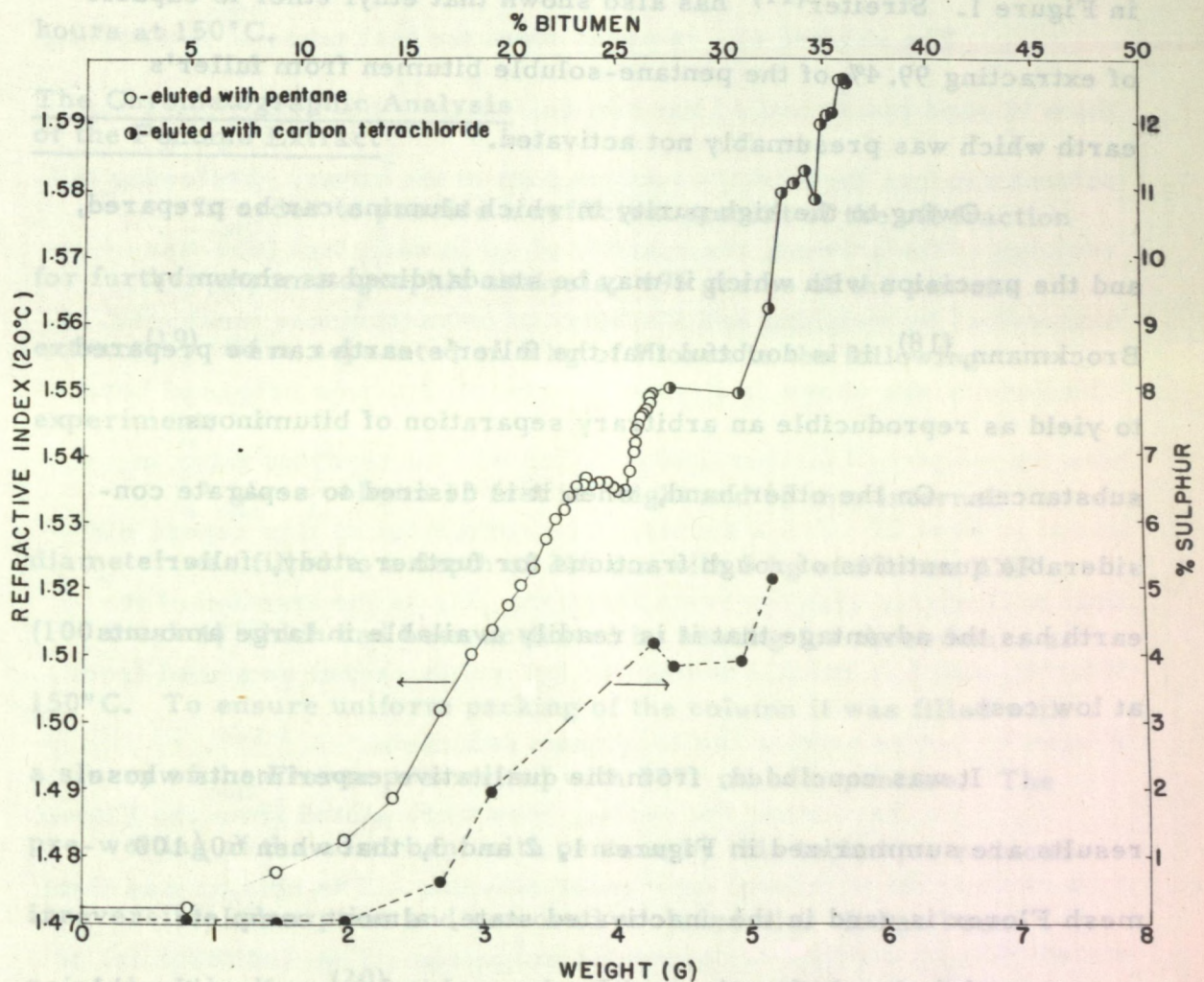


Figure 3. Result of elution analysis of the pentane extract on activated Florex. (The refractive index and weight refer to the solvent-free material.)

Pfeiffer<sup>(17)</sup> has stated that, in general, a disadvantage of the adsorption technique for the separation of bitumen lies in the difficulty of extracting the bitumen quantitatively from the adsorbent. If Florex is not activated, or only very slightly activated, an almost quantitative extraction is possible with the series of solvents shown in Figure 1. Streiter<sup>(11)</sup> has also shown that ethyl ether is capable of extracting 99.4% of the pentane-soluble bitumen from fuller's earth which was presumably not activated.

Owing to the high purity in which alumina can be prepared, and the precision with which it may be standardized as shown by Brockmann,<sup>(18)</sup> it is doubtful that the fuller's earth can be prepared to yield as reproducible an arbitrary separation of bituminous substances. On the other hand, when it is desired to separate considerable quantities of rough fractions for further study, fuller's earth has the advantage that it is readily available in large amounts at low cost.

It was concluded, from the qualitative experiments whose results are summarized in Figures 1, 2 and 3, that when 60/100 mesh Florex is used in the unactivated state, almost complete recovery of the resin fraction can be secured, whereas considerable loss is encountered when this grade of Florex is activated for three hours at 150°C. The unactivated Florex permitted some of the highly coloured resinous bodies to be eluted with n-pentane, and to avoid this it was proposed to use a finer grade of Florex (+100 mesh).

One of the difficulties encountered when the adsorbent was not pre-wetted was that considerable heat of wetting was evolved, accompanied by the desorption of gases, which resulted in gas evolution that upset the flow pattern of liquid in the column. In the proposed large-scale experiment it was therefore planned to pre-wet the column and to counteract the resultant loss of activity by drying the clay for three hours at 150°C.

#### The Chromatographic Analysis of the Pentane Extract

In order to provide a sufficient amount of the oil fraction for further chromatographic analysis, 495 grams of the pentane extract<sup>(19)</sup> were separated on 5 kg of Florex in the following experiment:

A glass column 12 feet in height and 65 mm internal diameter was filled to a depth of 216 cm with 5 kg of Florex XXF (100 mesh +) which had been activated by heating for three hours at 150°C. To ensure uniform packing of the column it was filled with a slurry of the Florex pre-wetted with 7771 ml of n-pentane. The pre-wetting of the adsorbent with pentane by this technique reduced irreversible adsorption and removed occluded air. It has been pointed out by Karr<sup>(20)</sup> that much of the irreversible adsorption is probably due to decomposition of the adsorbate to a char by the heat of adsorption. The adsorbent was activated slightly to compensate for the deactivation caused by pre-wetting. A solution of

2500 ml n-pentane containing 495 g of pentane extract was added to the top of the column. This was eluted with 11.5 litres of n-pentane. The effluent, containing what will be referred to as "the oil fraction of Athabasca bitumen", was divided into 258 10-ml cuts followed by a cut of 3300 ml. The index of refraction of each cut was measured with an Abbé refractometer and plotted as shown in Figure 4.

The solvent was removed from the test tubes by supporting them in sand inside heated vacuum desiccators and withdrawing the solvent vapours through the vacuum port in the cover. Following the removal of the solvent, the quantity of oil in each test tube was determined by weighing and the index of refraction was measured. The results are shown in Figure 5. The oil fraction prepared here was the subject of further study, which will be reported later in detail in Part III of this series. The remainder of this report will deal exclusively with the resin fraction; this is the fraction of the bitumen which is soluble in pentane but which cannot be eluted from Florex by pentane under the conditions described.

To fractionate the resins, they were eluted from the Florex by a succession of increasingly polar solvents. The column was first eluted with 15.2 litres of carbon tetrachloride. The first 4800 ml of the effluent were withdrawn in 100-ml fractions. The index of refraction was measured and a 10-ml aliquot was removed for the determination of the concentration of the resin. The remainder of the solution was placed in a 5-litre flask and the solvent was distilled

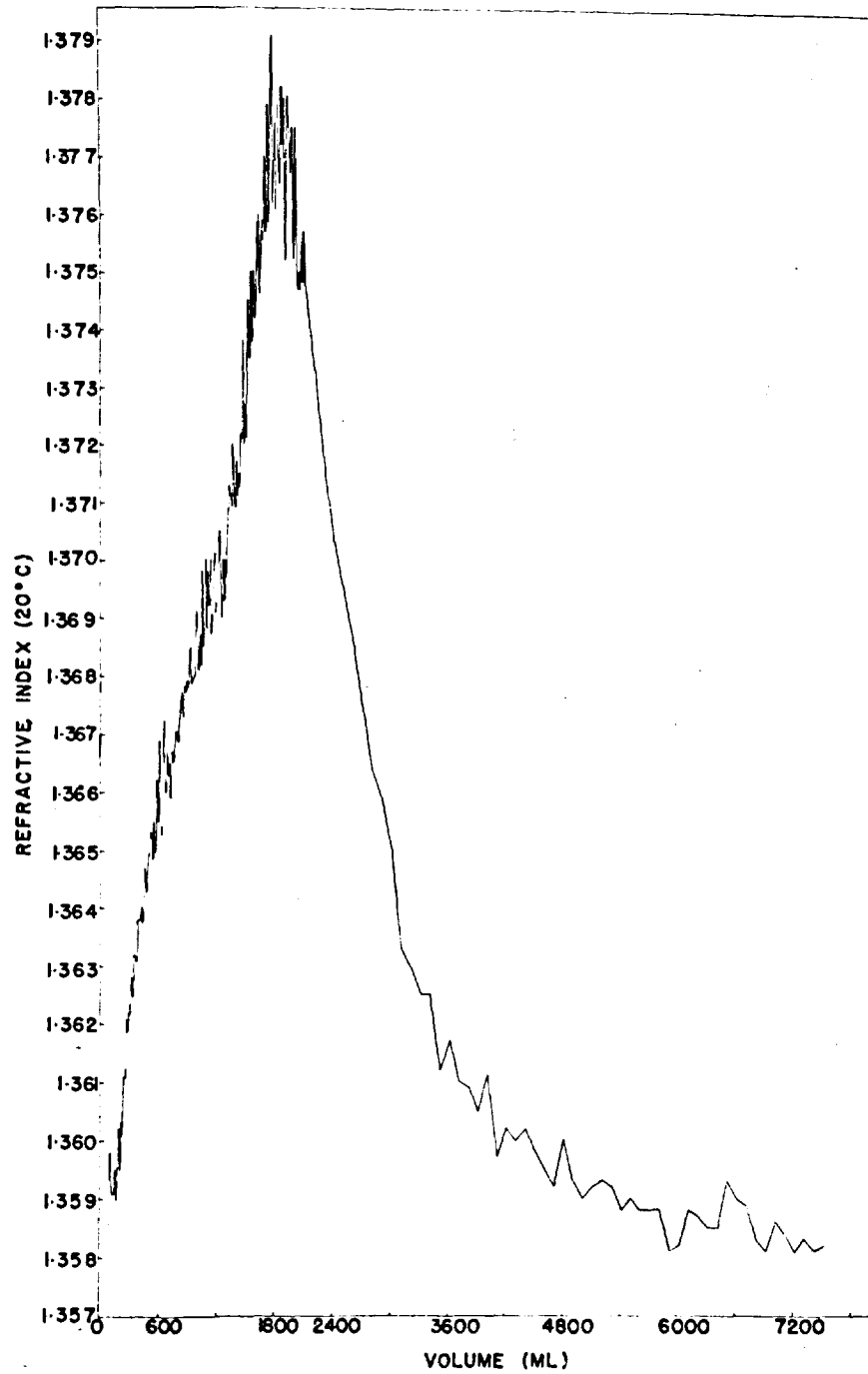


Figure 4. Pentane extract eluted with n-pentane from Florex. (The refractive index and the volume refer to the effluent solution.)



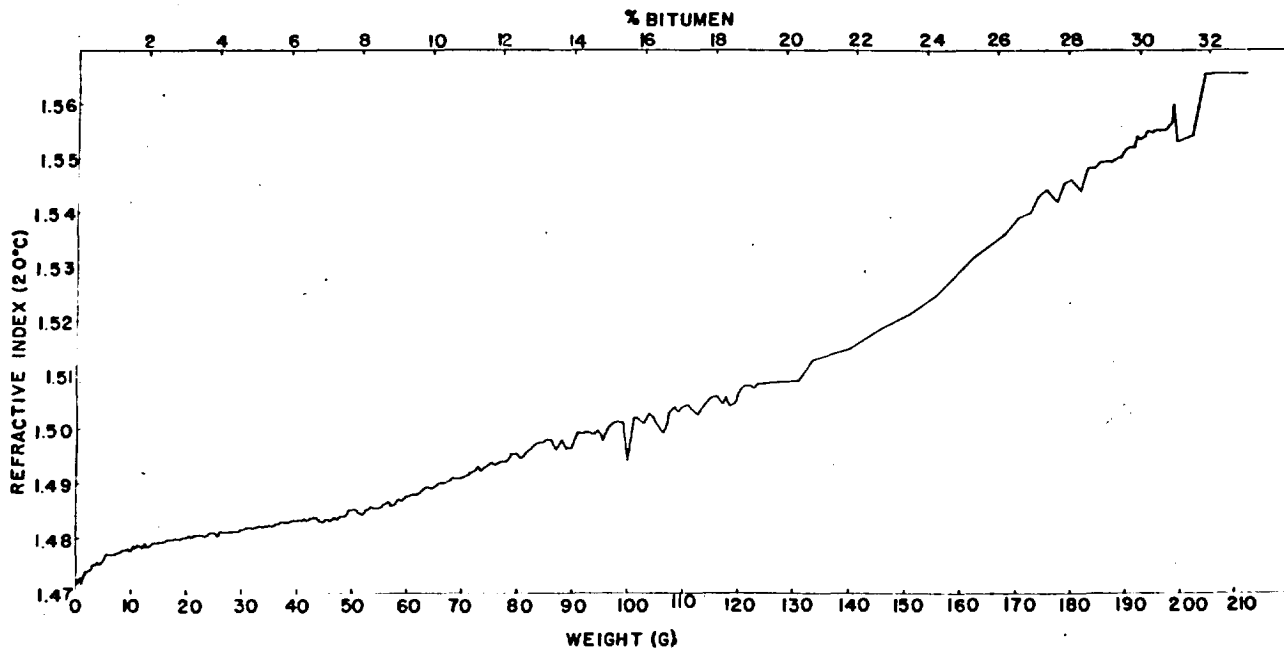


Figure 5. Pentane extract eluted with n-pentane from Florex. (The refractive index and the weight refer to the oil devoid of solvent.)

off until a viscous liquid remained. The distillation was then continued at reduced pressure (4mm) for approximately 24 hours, to remove the remaining solvent. The resin content of the 10-ml samples was determined by removing the bulk of the solvent in heated vacuum desiccators until the danger of bumping was reduced. The test tubes were then transferred to a vacuum oven and heated for three hours at 110°C, under a pressure of approximately 1 cm. to remove the residual solvent. The following cuts of 5000 and 5400 ml, respectively, were collected in large flasks prior to solvent removal at reduced pressure. The column was then eluted with 10 litres of benzene, 10 litres of chloroform and 7 litres of methanol, in succession. The weights removed by each solvent, expressed as percentages of the original bitumen, are shown in the summary in Figure 6.

In this report, the series of resin fractions eluted by these solvents will be referred to by the name of the solvent with which they were eluted. Thus, C Cl<sub>4</sub>(I) fraction refers to the first fraction eluted with carbon tetrachloride; C Cl<sub>4</sub>(II), the second fraction eluted with this solvent; C Cl<sub>4</sub>(III), the third fraction eluted with this solvent; and the benzene, chloroform and methanol fractions were eluted with each of these respective solvents.

When the ash content was determined on the resin fractions, it was found that the chloroform and methanol fractions showed abnormally high ash contents (1.4% for the chloroform fraction and

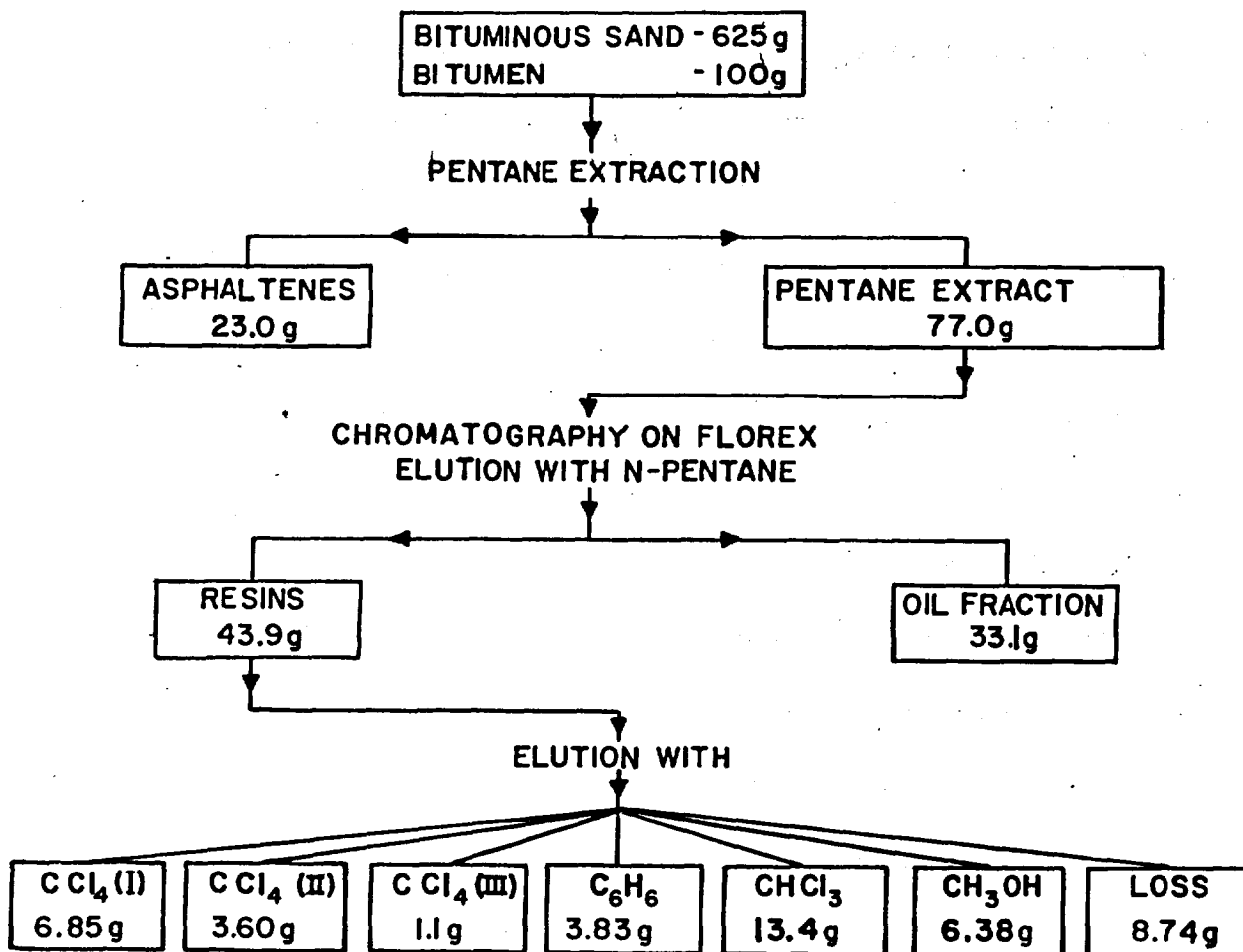


Figure 6. Summary of chromatographic analysis of the pentane extract on Florex.

11.9% for the methanol fraction), which were probably due to some Florex being present as well as inorganic salts extracted from the Florex by the methanol and the chloroform in the actual fractions. Consequently, these samples were further purified by re-dissolving them and filtering the solutions. Some difficulty was encountered in removing the last traces of chloroform from the chloroform fraction, even at reduced pressure. The chloroform appeared to be so firmly bound to the resin that the attempt to remove it was abandoned, and the fraction was analyzed for chlorine in order to enable a correction to be made to the properties for this constituent. The determination of chlorine revealed the presence of 3.44% chloroform in this fraction.

The physical properties of these fractions are given in Table 1. The ultimate analysis refers to an "ash-free" basis.

TABLE 1

Physical Properties of the Resin Fractions

Property	C Cl <sub>4</sub> (I)	C Cl <sub>4</sub> (II)	C Cl <sub>4</sub> (III)	C <sub>6</sub> H <sub>6</sub>	CHCl <sub>3</sub>	CH <sub>3</sub> OH
Ash %	0.03	0.30	0.06	0.62	1.19	2.46
C %	83.68	81.60	—	80.18	79.17	77.42
H %	9.44	9.17	—	8.42	9.31	9.19
S %	6.23	6.90	6.06	6.87	6.73	6.96
N %	—	0.72	—	0.66	0.95	1.02
O % (by diff.)	—	1.61	—	3.87	3.84	5.41
Molecular Weight	519	592	577	821	976*	834*
d <sub>4</sub> <sup>20**</sup>	1.058	1.060	1.052	1.116	1.085	1.085
n <sub>D</sub> <sup>20***</sup>	—	1.594	—	1.631	1.612	1.609

\* These molecular weights were determined cryoscopically in phenanthrene; the remainder, cryoscopically in benzene.

\*\* Determined by water displacement.

\*\*\* Determined by calculation from reflectance measurements in air and water.

The emission spectra of the ash are given in Table 2.

TABLE 2

Emission Spectra of Resin Ash Samples

Sample	Elements - Weight Percent of Ash														
	Si	Mn	Mg	Pb	Cr	Sn	Ni	Fe	Al	Mo	Ca	V	Ti	Cu	Zn
C Cl <sub>4</sub> (I)			7.5				0.005	3.0				0.001			
C Cl <sub>4</sub> (II)			7.5				0.01	3.0				0.001			
C Cl <sub>4</sub> (III)			7.5				0.005	6.0				0.001			
Benzene			1.0				1.5	1.5				2.5			
Chloroform	0.7	1-2	6.0	0.07	0.02	0.02	0.25	0.3	0.25		3.0	2.8	0.025	0.075	2.2
Methanol	0.056	1-2	9.0	-	-	-	0.08	0.15	0.005		3.0	0.023	0.005	0.05	-

The Chromatography of C Cl<sub>4</sub>(I)  
Fraction on Silica Gel

The C Cl<sub>4</sub>(I) fraction was re-chromatographed on silica gel to determine the amount of saturated material present in this fraction. This was considered necessary to give some indication whether the separation on the Florex was one based upon chemical type as well as upon molecular weight. The column used in this separation was 16 mm in diameter and 500 cm in height. This was filled with 500 grams of silica gel (Davidson, through 200 mesh) in the form of a slurry with 2400 ml n-pentane. 10.2 g of C Cl<sub>4</sub>(I) in 50 ml of n-pentane was added to this column, and was eluted with the following solvents: 1 litre n-pentane, 850 ml methylcyclohexane, 1 litre toluene, 500 ml chloroform, and 600 ml methanol. The effluent was collected in 10-ml cuts, whose refractive indices were determined. These samples were stripped of solvent as described previously (in the Florex separation) and their refractive indices again determined, and the quantity of residue in each test tube was determined by weighing. The results of this experiment are shown in Figure 7. This graph shows that the C Cl<sub>4</sub>(I) fraction contained very little saturated material, approximately 3.25%, as indicated by the small amount of material of low refractive index shown by the chromatogram.

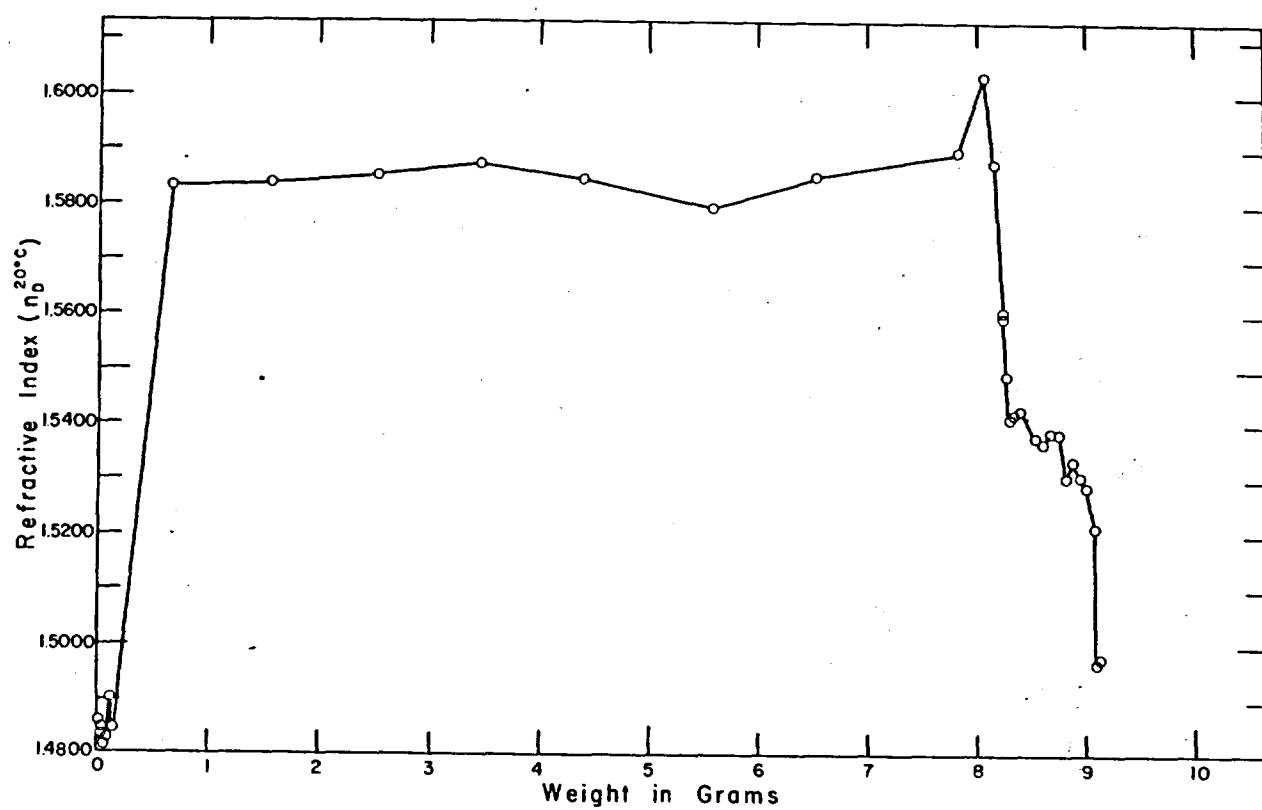


Figure 7. Result of elution analysis of  $\text{C Cl}_4(\text{I})$  fraction on silica gel. (The refractive index and weight refer to the solvent-free material.)



## Structural Information from the Absorption Spectra of the Resin Fractions

The ultraviolet and infra-red spectra of the resin fractions were measured in an attempt to determine the aromatic content of these fractions in particular, and to learn whether they revealed any additional structural features. The visible spectra were also determined to learn whether or not porphyrin pigments were present.

### The Ultraviolet Spectra

The ultraviolet spectra were determined for all six of the resin fractions (C Cl<sub>4</sub>(I), C Cl<sub>4</sub>(II), C Cl<sub>4</sub>(III), and the benzene, chloroform and methanol fractions), using n-heptane as solvent in the range 350-210 millimicrons and methylene chloride in the range 350-450 millimicrons. These spectra shown in Figure 8 were plotted in the form log E versus wavelength so that they could be compared with a collection of log E spectra of aromatic compounds. (21) The resin fractions possessed no distinct features when compared with the spectra of aromatic compounds. By comparing the manner in which the log E values declined with increasing wavelength, there was some evidence to support the fact that the number of condensed aromatic rings per molecule was approximately five. (22) However, due to the effects of substitution upon the spectra, and the influence of carbonyl groups, it was difficult to draw any reliable conclusions on the aromatic character of the resins from

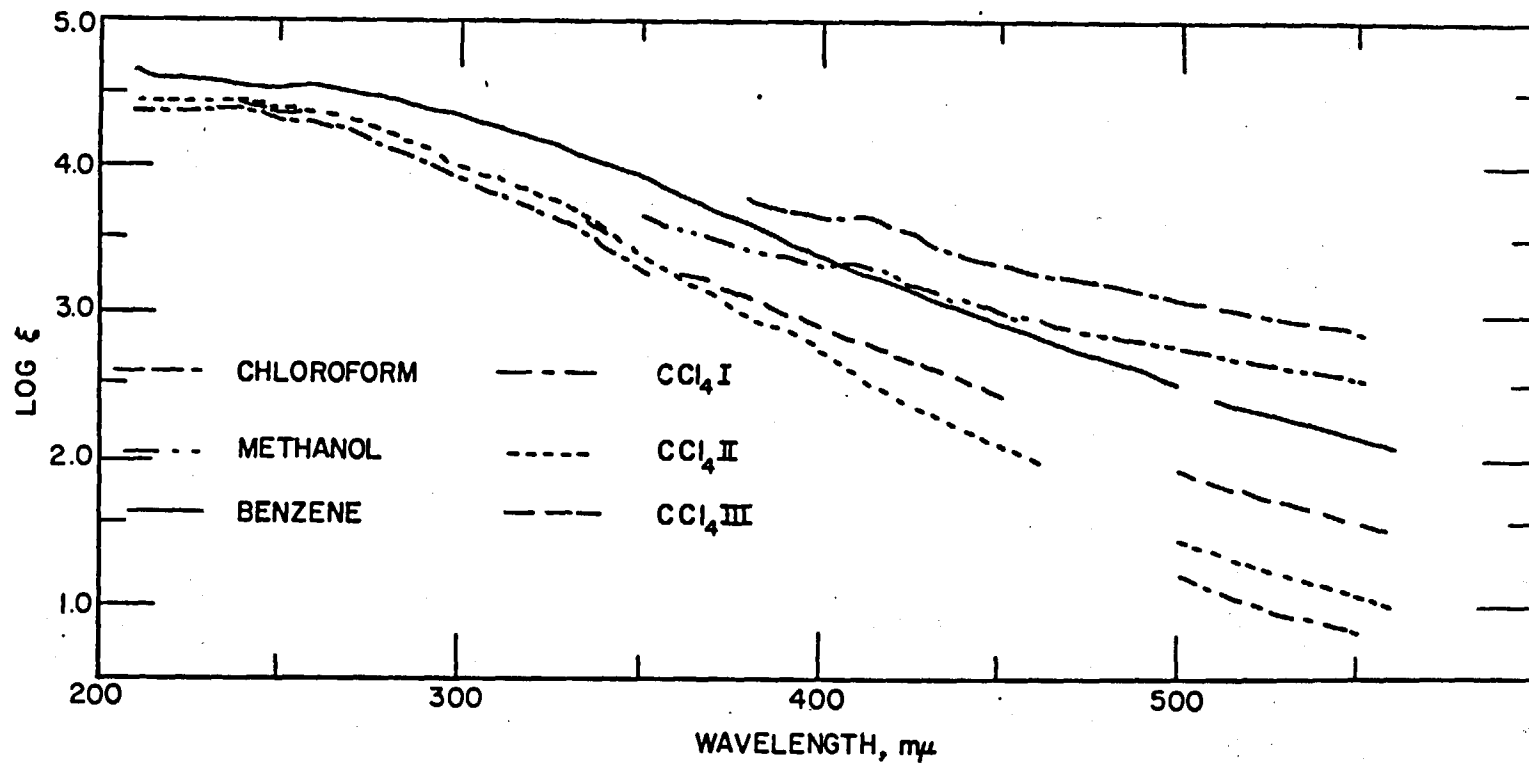


Figure 8. Ultraviolet spectra of the resin fractions.

their ultraviolet spectra. However, it was felt that the ultraviolet spectra set a lower limit for the number of condensed aromatic rings.

### The Visible Spectra

Many bituminous substances are known to contain vanadium salts of porphyrin aggregates. (23) It has been shown that the most striking spectral structure in the visible range found in bituminous substances consists of absorption bands associated with the porphyrin pigments. (23, 24) The typical vanadium porphyrin complex spectrum has maxima at 570, 531 and 408 m $\mu$ . As part of an extensive survey of porphyrin pigments in bituminous substances being made in the Mines Branch the absorption spectra in the visible range of the resin fractions were determined. Figure 9 shows the spectra in the visible range for the methanol, chloroform and benzene fractions dissolved in benzene. These curves indicate that the porphyrins occur only in the chloroform and methanol fractions, since the maxima at 410 and 575 m $\mu$  occur in the spectra for these two fractions and there is little evidence of any structure in the curves for the benzene fraction.

### The Infra-red Spectra

The infra-red spectra of four of the resin fractions [C Cl<sub>4</sub>(II), benzene, chloroform, and methanol] were determined. The C Cl<sub>4</sub>(II) fraction was "fluid" enough for its spectrum to be measured in the liquid state. The spectra of the remaining three

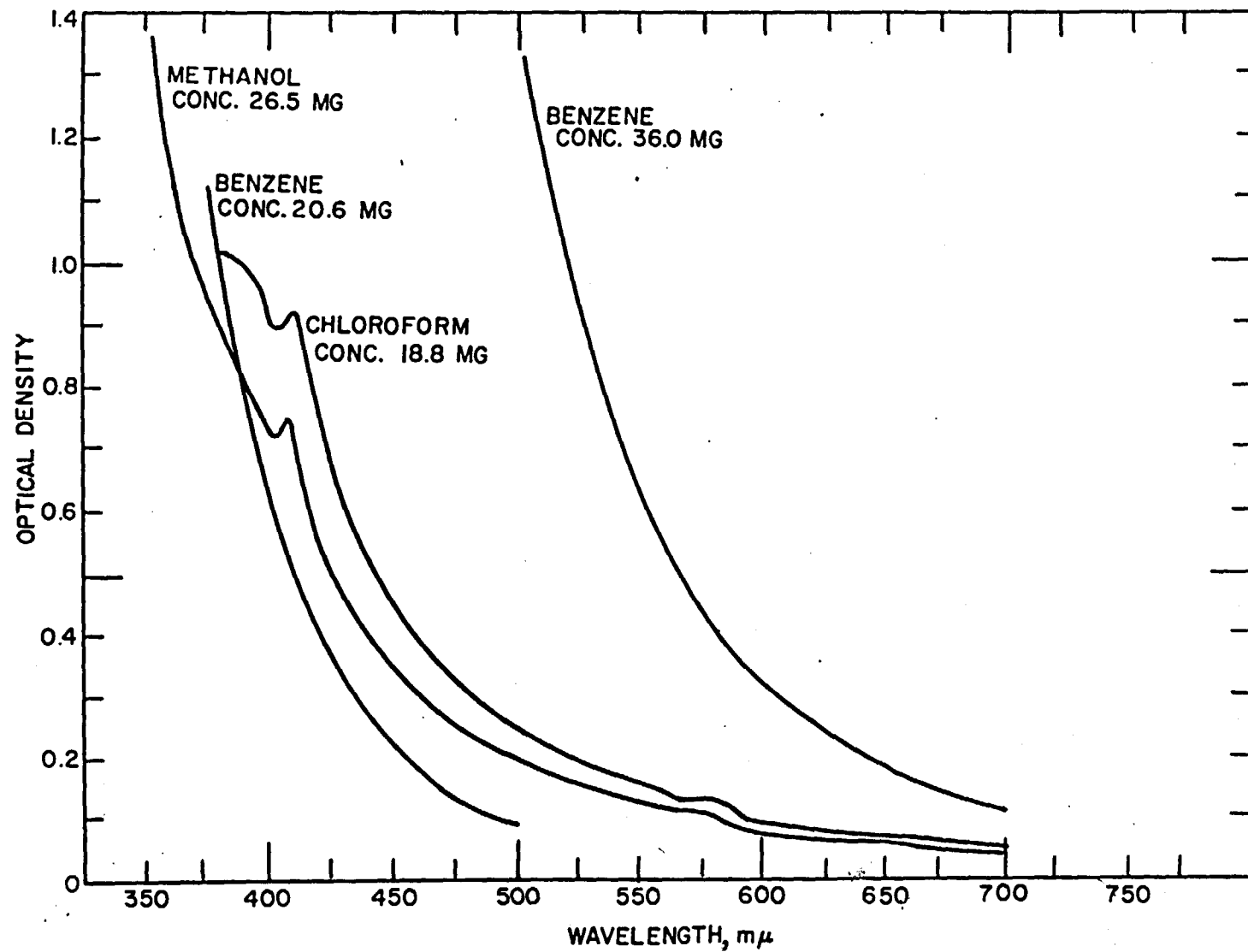


Figure 9. Visible spectra of the resin fractions. (The concentrations are shown in mg per 100 ml benzene.)

fractions were measured, using the KBr pellet technique. All spectra were recorded with a Perkin-Elmer double-beam infrared spectrometer and are shown in Figure 10. The absorption bands in these spectra may be assigned to the following functional groups:

<u>Wavelength</u> (microns)	<u>Functional group</u>
2.95	moisture in KBr pellet
3.0	N-H
3.25-3.35	aromatic CH
3.38-3.50	aliphatic CH
5.7 - 6.0	C=O
6.25	C=C
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	5 adjacent unsubstituted H on an aromatic ring
14.08-14.5	4 or more linear -CH <sub>2</sub> -
13.7-13.9	

Use has been made of the absorption bands at 6.25, 3.42, 3.50 and 7.25 microns to provide quantitative information about the amounts of the aromatic carbon, methylene and methyl groups respectively. The spectra also indicated the presence of several other groups: carbonyl, aromatic CH, and linear CH<sub>2</sub>. It was not possible to make use of the latter two groups quantitatively. The main concern here is the hydrocarbon skeletal structure; hence, non-hydrocarbon linkages will not be discussed.

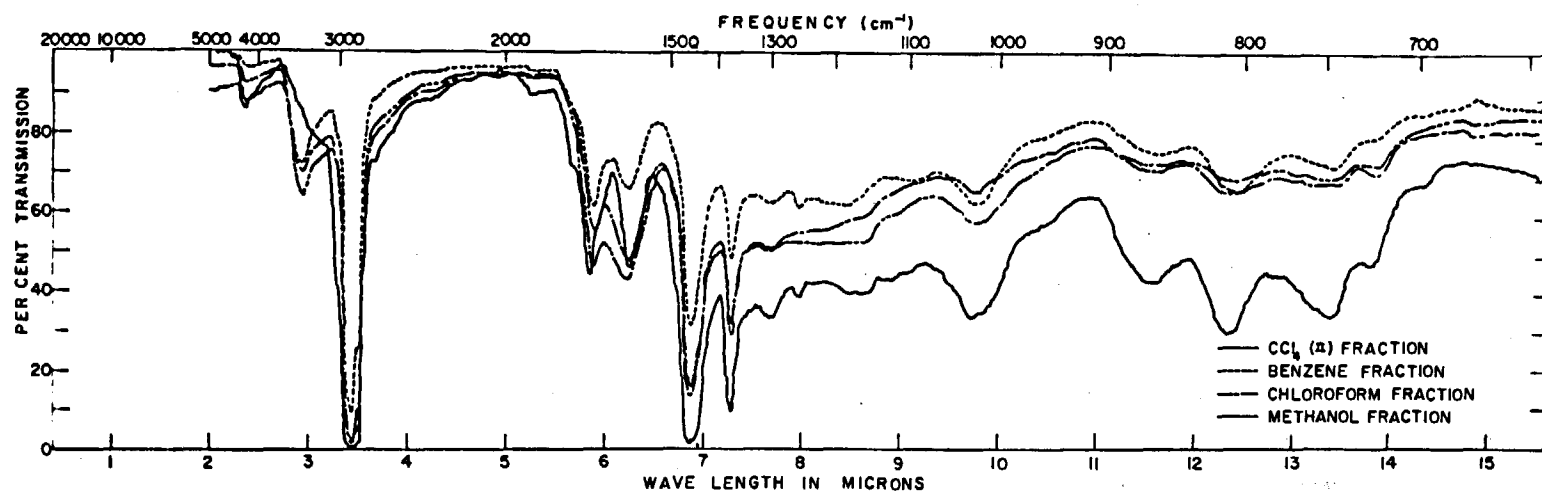


Figure 10. Infra-red spectra of the resin fractions.

The results of the quantitative determination of the methylene and methyl groups are tabulated in Table 3. This determination was based on the absorption bands at 3.42, 3.50 and 7.25 microns. The spectra from which these determinations were made were measured in carbon tetrachloride solution. The basis of this method and the details of the calculations will be reported elsewhere.

TABLE 3

Determination of Methyl and Methylene Groups from Infra-red Data

Resin Fraction	Number Carbon Atoms per 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 $\mu$ )
CCl <sub>4</sub> (II)	7.0	13.3	17.2
Benzene	10.0	16.5	21.0
Chloroform	12.2	24.2	32.0
Methanol	10.8	17.3	25.4

As was pointed out in Part I, much use has been made of the absorption band at 6.25 microns to determine the aromaticity. (25) However, it was found that this absorption band is affected both by the type of substitution on the aromatic ring and by the degree of condensation. This implies that to achieve high accuracy the fractionation of the unknown must be extensive and the selection of the model compounds must correspond closely with those being analyzed. The resin fractions represent fairly broad fractions and

very little is known of their structure, so that the selection of satisfactory model compounds is a difficult problem. Nevertheless, it was felt desirable to calculate the fraction of aromatic carbon ( $f_a$ ) for the resin fractions on the basis of various aromatic hydrocarbons of different types containing aliphatic and alicyclic groups. The spectra of thirty-seven aromatic hydrocarbons were used for this purpose. These spectra were selected from spectra determined in the Mines Branch and for this analysis were divided into six classes on the basis of structural differences which had a bearing upon the absorbance of the  $6.25 \mu$  band and that were significant from the structural analysis point of view. The object of this aromatic carbon calculation was to attempt to exclude certain hydrocarbon structures rather than to define the types most likely to be present. The results of these calculations are summarized in Table 4.



TABLE 4

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

Class of Compounds	No. in Class	Mean Value of $f_a$			
		C Cl <sub>4</sub> (II)	Benzene	Chloroform	Methanol
1. Fused aromatics with side chains where $\frac{*CH_a}{Ca} < 2.0$	4	0.38	0.57	0.77	0.87
2. Fused aromatics with side chains where $\frac{CH_a}{Ca} > 2.0$	2	0.18	0.27	0.36	0.41
3. Fused aromatics with no side chains and $\frac{CH_a}{Ca} < 2.0$	18	0.68	1.01	1.36	1.54
4. Fused aromatics containing cyclic CH <sub>2</sub> groups	8	0.57	0.84	1.13	1.28
5. Non-fused aromatics	5	0.33	0.49	0.67	0.75
6. Methyl naphthalenes	12	0.17	0.25	0.34	0.38
7. Brandes' method <sup>(26)</sup>	-	0.32	0.47	0.64	0.72

\*CH<sub>a</sub> = number of aromatic CH groups or their equivalent/ molecule.

Ca = number of junction carbon atoms between aromatic fused rings/ molecule.

### Test for Lignin-like Structures

The supposed vegetable origin of the bitumen suggested that it be examined for lignin-like compounds.

C. Maule<sup>(27)</sup> has devised a spot test, using potassium permanganate for the detection of ligneous material in membranes, in which the ligneous material becomes coloured bright red. This test was applied to two of the resin fractions (C Cl<sub>4</sub>(III) and the benzene fraction). This test was conveniently carried out on a microscope slide. The substances to be tested were first allowed to react with a few drops of potassium permanganate solution (1 gram in 100 ml water) for five minutes. The slide was then washed with dilute HCl for 2 or 3 minutes, followed by washing with dilute ammonia. No red colouration was observed in either case, thus indicating the absence of ligneous-type structure.

### Application of van Krevelen's Method of Structural Analysis to the Resin Fractions

Van Krevelen's graphical statistical analysis,<sup>(28)</sup> which in Part I was applied to the crude bitumen and the asphaltenes, has now been extended to the resin fractions. The application of this method is shown in Figure 11. This graph revealed that the points representing the various resin fractions lay close together and were practically coincident with the point which represented the resins from the Alberta bitumen prepared by Katz.<sup>(9)</sup> The H/C ratios of the resins varied over the range 1.25-1.41 as compared with a

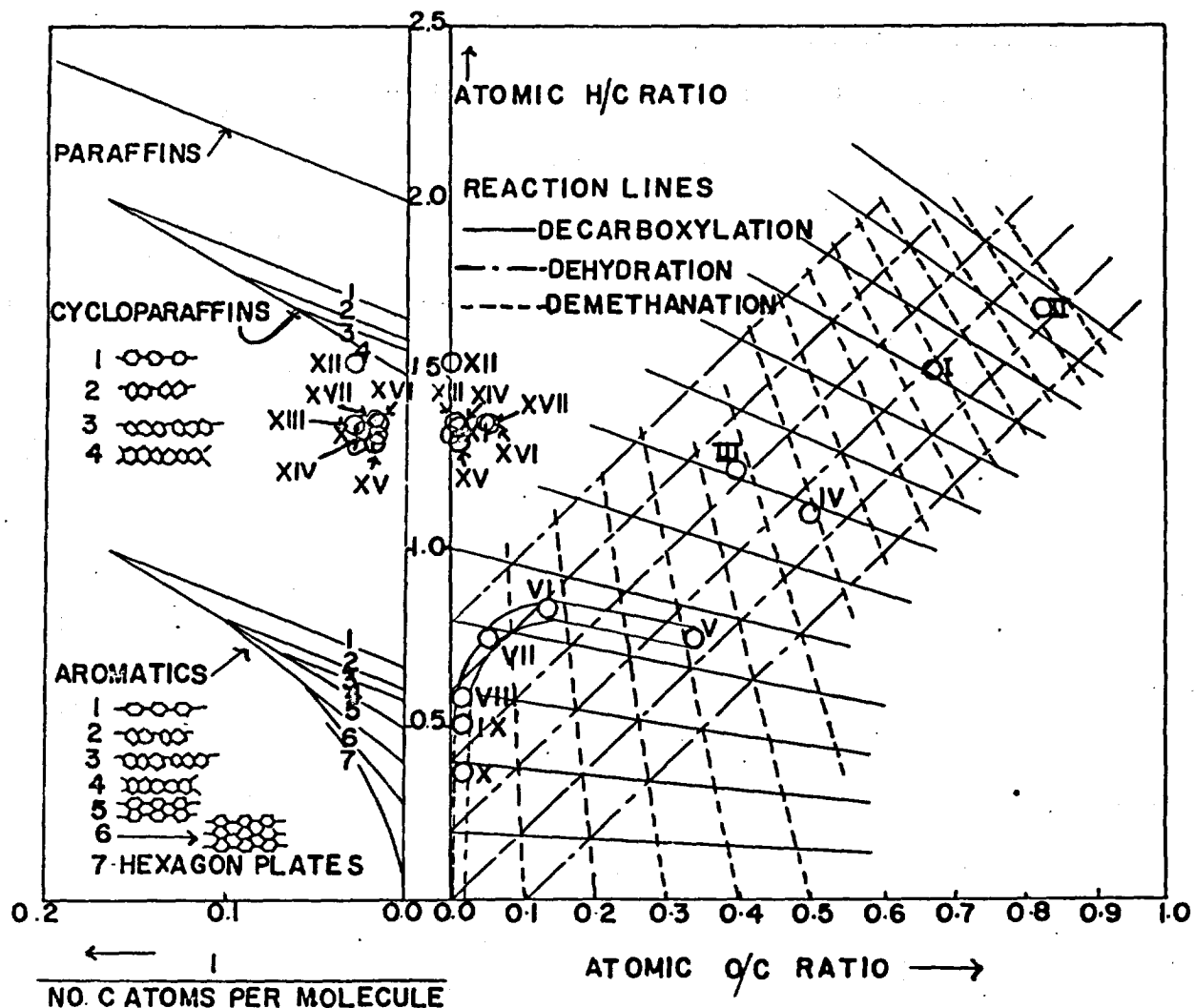


Figure 11. Application of van Krevelen's H/C versus O/C diagram.

Van Krevelen's data: I, wood; II, cellulose; III, lignin; IV, peat; V, brown coal; VI, low rank bituminous coal; VII, medium rank bituminous coal; VIII, high rank bituminous coal; IX, semi-anthracite; X, anthracite.

Katz: XI, Alberta bitumen - resins; XII, Alberta bitumen - oily constituents.

Mines Branch: XIII,  $\text{CCl}_4$ (I) resin fraction; XIV,  $\text{CCl}_4$ (II) resin fraction; XV, benzene resin fraction; XVI, chloroform resin fraction; XVII, methanol resin fraction.

value of 1.52 which Katz obtained for the oily constituents and with the value of 1.20 which was obtained for the asphaltene fraction in the present investigation (Part I). It is particularly noteworthy that the points representing the resins on this graph lie well apart from the transformation path envisaged by van Krevelen for coal formation from cellulose and lignins.

Van Krevelen's more recent structural group analysis methods<sup>(29)</sup> have been applied to the resin fractions. This was done principally to determine the degree of aromaticity of these fractions. It was recognized that van Krevelen's methods were designed primarily for coals, which were essentially highly condensed aromatic systems and thus quite probably different from bituminous materials. However, it was considered that the results obtained would prove useful in indicating the comparative differences between the resin fractions (that is, it would clarify the basis on which this fractionation took place) and in conjunction with the Montgomery-Boyd method<sup>(36)</sup> would form a reasonable basis for defining the chemical structure of these fractions.

The same procedure in this application was used here as has been described in Part I for the asphaltene fraction. This will be briefly summarized here for convenience. Van Krevelen has described the structure in terms of the ring condensation index,  $2R/C$ , which together with the  $H/C$  ratio was related to the fraction of aromatic carbon ( $f_a$ ). The fraction of aromatic carbon ( $f_a$ ) was

calculated by three different equations for each of the resin fractions.

These are as follows:

Method I - van Krevelen's Densimetric Method. (30)

$$(1) \frac{1}{d} = \frac{9.9 + 3.1H/C + 3.75 O/C + 1.5N/C + 14S/C - (9.1 - 3.65H/C)R/C}{12.01 + 1.008H/C + 16.0 O/C + 14.008N/C + 32.06S/C}$$

$$(2) f_a = 2 - H/C - 2R/C$$

Method II - Method I with the experimental molecular weight

incorporated into equation (1). This permitted the use of a

more accurate form of equation (2).

$$(3) \frac{M}{d} = 9.9C + 3.1 H + 3.75 O + 1.5 N + 14 S - (9.1 - 3.65H/C) R$$

$$(4) f_a = 2 - H/C - 2 \frac{(R - 1)}{C}$$

Method III - van Krevelen's Graphical Densimetric Method. (31)

This method was based on the graphical relationship between

$\frac{Mc}{d}$  and  $H/C$  with  $f_a$  for pure hydrocarbons. The following

two quantities were calculated:-

$$(5) \frac{Mc}{d} = \frac{1}{d} \left[ 12.01 + 1.008 H/C + 16.0 O/C + 14.008 N/C + 32.06 S/C \right]$$

$$(6) \left[ \frac{Mc}{d} \right]_{\text{corr.}} = \frac{Mc}{d} - \left[ 8.1 O/C + 6.4 N/C + 12.5 S/C \right]$$

$f_a$  was then read directly from van Krevelen's graph of  $\frac{Mc}{d}$  versus  $H/C$ . The results of these calculations are tabulated in Table 5.

It should be noted that, for cases where naphthenic rings are present, Method III was recommended only for those cases where  $f_a$  was greater than 0.25. (32)

TABLE 5

Results of the Application to the Resins of van Krevelen's  
Densimetric Methods

Property	C Cl <sub>4</sub> (II)	Benzene	Chloroform	Methanol
H/C	1.34	1.25	1.40	1.41
O/C	0.0149	0.0363	0.0364	0.011
S/C	0.0318	0.0321	0.0319	0.034
N/C	0.0075	0.00711	0.0102	0.052
R/C(I)	0.160	0.210	0.216	0.169
R (I)	6.45	11.49	13.90	9.08
$R/S = [R/C(I)/S/C]$	5.05	6.53	6.78	4.97
$f_a$ (I)	0.339	0.330	0.167	0.252
R (II)	6.43	11.52	13.88	9.14
$f_a$ (II)	0.390	0.365	0.199	0.287
Mc/d	13.89	13.42	13.98	14.29
(Mc/d) corr.	13.32	12.68	13.22	13.37
R (III)	3.82	6.58	6.75	5.11
$f_a$ (III)	0.47	0.51	0.39	0.40

Method IV

An additional set of structural calculations was made on the basis of another set of equations of van Krevelen.<sup>(33)</sup> This will be referred to as Method IV. For the purpose of studying coal the various hydrocarbon groups were divided into four classes:

$C_1 = \text{CH}_2 / C$ , the fraction of  $\text{CH}_2$  groups (paraffinic or naphthenic) in the molecule;

$C_2 = \text{CH} / C$ , the fraction of carbon atoms which are junctions between fused naphthenic rings;

$C_3 = \text{CH}_a / C$ , the fraction of aromatic CH groups; and

$C_4 = C_a / C$ , the fraction of carbon atoms which are junctions between fused aromatic rings.

Van Krevelen set forth the following relationships between these four types of linkages, based on the definitions of the symbols and the mass balance:

$$(7) \quad C_1 + C_2 + C_3 + C_4 = 1$$

$$(8) \quad 2C_1 + C_2 + C_3 = \text{H} / C$$

$$(9) \quad C_2 + C_4 = 2R / C$$

$$(10) \quad C_3 + C_4 = f_a$$

The individual values of  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  could not be calculated from this set of equations since it did not consist of four independent equations. In fact, there are three unknowns (the fourth is known, since the sum is one) and only two independent properties, density and  $\text{H} / C$ . The right-hand sides of the above set of equations are not independent but are related to one another by the following

equation, since by definition  $f_a$  and  $R/C$  are related to  $H/C$ :

$$(11) \quad f_a = 2 - H/C - 2R/C$$

An algebraic rearrangement of any group of three of the set resulted in the fourth equation. Van Krevelen overcame this difficulty by developing a relationship between  $C_1$  and  $H/C$ . This equation resulted from a statistical analysis of macromolecular model structures and expressed the probability of the occurrence of a  $CH_2$  group as a function of the  $H/C$  ratio. Hence, van Krevelen was able to determine  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  from the following set of equations:

$$(12) \quad C_1 = 0.5 (H/C)^{3/2} - 0.29 (H/C)^{1/2} \text{ when } H/C > 0.6$$

$$(13) \quad C_2 \approx 1 - f_a - C_1$$

$$(14) \quad C_3 \approx 1 - 2R/C - C_1$$

$$(15) \quad C_4 \approx 1 - H/C + C_1$$

The values of  $f_a$  and  $R/C$  used in this method were those obtained from equations (1) and (2) described previously. The results of this method are tabulated in Table 6.

TABLE 6

Van Krevelen's Structural Group Analysis of the Resin Fractions

Fraction	$C_1$	$C_2$	$C_3$	$C_4$
$CCl_4$ (II)	0.44	0.22	0.24	0.10
Benzene	0.38	0.29	0.20	0.13
Chloroform	0.49	0.35	0.08	0.08
Methanol	0.49	0.26	0.17	0.08



It is pointed out that this method has been applied to bitumens and asphalts by Varga, Hesp and Haidegger<sup>(34)</sup> and also by Padovani, Berti and Prinetti.<sup>(35)</sup>

Application of the Montgomery-Boyd Structural Group Analysis Method (Scheme MBI)

The new method of structural group analysis that has recently been developed by the authors<sup>(36)</sup> has been applied also to these resin fractions as the concluding stage in an effort to elucidate the structure of this portion of the bitumen. The method and the manner of its application here have already been described in Part I in connection with its use in studying the asphaltene fraction; for completeness, they will be briefly reviewed here. The total number of carbon linkages in the molecule was considered to be divided into the following five types:

- $C_1$  = number per molecule of  $CH_3$ ,  $CH_2$ ,  $CH$  and  $C$  groups in linear and branched chains.
- $C_2$  = number per molecule of  $CH_2$  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  $CH$  groups which 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 CH groups in aromatic rings, including the case where the hydrogen is replaced by linear or branched chains.

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

It should be noted that this system of atomic groups does not make provision for non-fused polycyclic substances.

Three chemical and two physical properties have been expressed in terms of these five structural groups in the form of the following five empirical equations:<sup>(36)</sup>

$$(16) \quad C_1 + C_2 + C_3 + C_4 + C_5 = \Sigma C$$

$$(17) \quad 2C_1 + 2C_2 + C_3 + C_4 = \Sigma H$$

$$(18) \quad C_4 + C_5 = \Sigma C_a$$

$$(19) \quad \begin{array}{l} \text{M.V.} \\ \text{at} \\ 20^\circ \text{C,} \\ 1 \text{ atm.} \\ \text{press.} \end{array} = C_1 \left( \frac{16.38 + 30.61}{\Sigma C} \right) + C_2 \left( \frac{13.20 + 28.48}{\Sigma C} \right) + C_3 \left( \frac{10.981 + 20.679}{\Sigma C} \right) + C_4 \left( \frac{12.406 + 14.042}{\Sigma C} \right) -$$

$$1.96 \frac{C_1}{\Sigma C} + \frac{10.13 C_2}{\Sigma C} + C_5 \left( \frac{5.124 - 5.238}{\Sigma C} \right)$$

$$(20) \quad \begin{array}{l} \text{M.R.} \\ \text{at} \\ 20^\circ \text{C,} \\ 1 \text{ atm.} \\ \text{press.} \end{array} = C_1 \left( \frac{4.623 + 2.314}{\Sigma C} \right) + C_2 \left( \frac{4.468 + 0.868}{\Sigma C} - 0.245 \frac{C_1}{\Sigma C} \right) + C_3 \left( \frac{3.693 + 0.3395}{\Sigma C} \right) +$$

$$C_4 \left( \frac{4.5445 - 1.021}{\Sigma C} - 0.396 \frac{C_1}{\Sigma C} - \frac{5.701 C_2}{\Sigma C} \right) +$$

$$C_5 \left( \frac{5.734 - 14.333}{\Sigma C} \right)$$

The method of group analysis consisted of the simultaneous solution of these equations by means of a digital computer to yield numerical values for  $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$  and  $C_5$ . The five properties used in this method were 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). The first two of these properties,  $\Sigma C$  and  $\Sigma H$ , were calculated from the carbon and hydrogen analyses and the experimentally determined molecular weight. Since this method of structural analysis is applicable only to hydrocarbons, it was necessary to make some corrections to the molar volume and the molar refraction to "convert" them to a "foreign-atom-free" basis. The method used here, and considered adequate to a first approximation for the present purpose, consisted essentially in removing the foreign atoms without affecting the structural contributions to the molar volume and the molar refraction and also without making any changes in the number of carbon and hydrogen atoms. These "corrected" values of the molar volume and the molar refraction were calculated by the use of the following equations, which were modified forms of those used by van Krevelen:<sup>(37)</sup>

$$(21) \text{ M.V.} = 9.9 \text{ C} + 3.1 \text{ H} + 3.75 \text{ O} + 1.5 \text{ N} + 15 \text{ S} - \text{K}$$

$$(22) \text{ M.R.} = 2.558 \text{ C} + 1.039 \text{ H} + 1.65 \text{ O} + 2.48 \text{ N} + 7.64 \text{ S} + \text{E}$$

For the calculation of K and E above, which represented the structural contributions to the molar volume and the molar refraction respectively, the values used for M.V. were derived from the experimental values of the molecular weight and density at 20°C, the values used for M.R. were derived from the refractive index ( $n_D^{20}$ ) and the molar volume (20°C), and the values for C, H, N, O and S were determined from the elementary analyses and the molecular weight.  $\text{M.V.}_{\text{corr.}}$  and  $\text{M.R.}_{\text{corr.}}$  were then calculated from the following equations, using values of K and E thus obtained:

$$(23) \text{ M.V.}_{\text{corr.}} = 9.9 \text{ C} + 3.1 \text{ H} - \text{K}$$

$$(24) \text{ M.R.}_{\text{corr.}} = 2.558 \text{ C} + 1.039 \text{ H} + \text{E}$$

The values of K and E obtained for the resin fractions have been tabulated in Table 7. They were included because they represented the amounts by which the molar volume and molar refraction respectively deviated from the values that were obtained by summing the appropriate atomic increments (using Traube's atomic increments).

TABLE 7

Values of K and E for the Resins

Fraction	K	$K/MV_{\text{exp}} \times 100$	E	$E/MR_{\text{exp}} \times 100$
C Cl <sub>4</sub> (II)	28.48	5.1	19.17	10.1
Benzene	54.00	7.3	32.93	12.5
Chloroform	57.38	6.4	33.29	10.6
Methanol	37.93	4.9	29.63	11.1

As has already been stated, the MB1 method required that the number of aromatic carbon atoms per molecule be experimentally determined. This property is not readily determined directly for bituminous materials. Table 4 revealed the wide variation that was obtained in calculating the fraction of aromatic carbon atoms from the 6.25 micron band of the infra-red spectrum. There was also considerable variation in the values calculated according to van Krevelen's structural analysis methods. Consequently, as with the asphaltene fraction, it was felt that the most informative approach was to determine values of  $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$  and  $C_5$  for various arbitrarily chosen values of  $\Sigma C_a$  which covered the entire range of possible values. It will then be shown how certain structures could be eliminated on the basis of algebraic and chemical criteria.

The derived properties required for the application of this method are tabulated in Table 8.

TABLE 8  
Derived Properties of the Resin Fractions Required  
for the Montgomery-Boyd Analysis

Property	Resin Fraction			
	C Cl <sub>4</sub> (II)	Benzene	Chloroform	Methanol
ΣC	40.2	54.8	64.3	53.8
ΣH	53.86	68.6	90.1	76.0
ΣN	0.30	0.39	0.66	0.61
ΣS	1.28	1.76	2.05	1.81
ΣO	0.60	1.99	2.34	2.82
M. V. exp.	558.5	735.7	899.5	768.7
M. R. exp.	189.5	262.1	312.7	266.2
M. V. corr.	536.6	701.2	859.0	730.0
M. R. corr.	178.0	244.4	291.5	246.2

The computational method of solution used here was the same as reported in Part I. Since two of the five property equations were quadratic (the M. V. and M. R. equations), the method of solution consisted essentially in solving two quadratics simultaneously. This involved an iterative procedure. In the method as originally reported for application to pure hydrocarbons, <sup>(36)</sup> the iterative procedure was started at  $C_1 = C_2 = 0$  (i. e., no prior knowledge of the values of  $C_1$  and  $C_2$ ) and only one solution was obtained. This proved satisfactory for pure hydrocarbons, but when the method

was applied to the Alberta bitumen fractions certain difficulties were encountered: firstly, an increasing number of cases occurred which failed to converge, and, secondly, cases arose where physically impossible solutions were obtained which failed to check with solutions obtained by graphical plotting of the quadratics. This led to the modifications of the original program for the IBM 650 computer. The objective of the new program was to obtain all mathematically possible solutions between  $\pm \Sigma C$ . This was done by reducing the set of five equations to two quadratics and then determining one solution by the Newton-Raphson iteration method, starting the iteration method with  $C_1 = C_2 = \Sigma C$ . It was found that starting with  $\Sigma C$  eliminated the cases of non-convergence, ensured that the solution obtained at this stage was the physically possible one (i. e. in first quadrant), and, in most cases, required a smaller number of iterations than the original program. The remainder of the mathematical solutions were then obtained by factoring the first root out of the corresponding quartic equation and thus progressing by the standard methods of matrix algebra through the cubic equation and then the quadratic. In some cases, only one solution was obtained, but in others three were obtained. No case ever arose where there were two solutions in the first quadrant (i. e. both physically possible).

In the case of multiple solutions the physically possible one was read off by inspection, or, where there was no solution in the

first quadrant, the set of values of  $C_1$  to  $C_5$  having the smallest sum of negative structural groups was taken. A negative quantity of a structural group has, of course, no physical significance. A solution that involves numerically small negative numbers may be regarded as more plausible than one involving large negative numbers.

The results of the application of this method to the resin fractions obtained in the manner just described are tabulated in Table 9 and expressed graphically in Figures 12-16.



TABLE 9

Results of the Montgomery-Boyd Analysis of the Resins

Resin Fraction	$f_a$	$\Sigma C_a$	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$
C Cl <sub>4</sub> (II)	0.17 <sup>c</sup>	6.83	19.77	-0.52	14.12	1.28	5.55
	0.27	10.85	17.79	0.68	10.87	6.07	4.78
	0.34 <sup>a</sup>	13.63	16.59	2.20	7.79	8.55	5.08
	0.39 <sup>b</sup>	15.68	15.86	3.64	5.02	9.88	5.80
	0.47 <sup>d</sup>	18.77	15.00	6.19	0.24	11.28	7.49
	0.55	22.10	14.30	9.25	-5.44	12.25	9.85
Benzene	0.25 <sup>c</sup>	13.70	24.62	-2.55	19.04	5.44	8.26
	0.33 <sup>a</sup>	18.07	22.03	-1.16	15.86	11.00	7.07
	0.36 <sup>b</sup>	20.01	21.00	-0.03	13.82	12.84	7.17
	0.51 <sup>d</sup>	27.95	18.01	7.00	1.84	16.74	11.21
	0.60	32.90	16.71	12.29	-7.10	17.70	15.20
Chloroform	0.17 <sup>a</sup>	10.74	35.16	1.15	17.25	0.23	10.51
	0.20 <sup>b</sup>	12.80	34.32	1.64	15.54	2.64	10.16
	0.34 <sup>c</sup>	21.09	30.55	5.73	6.12	11.42	10.48
	0.39 <sup>d</sup>	25.09	29.35	8.01	1.86	13.54	11.55
	0.50	32.20	26.99	14.33	-9.22	16.68	15.52
Methanol	0.15	8.07	32.52	-0.60	13.81	-1.65	9.72
	0.25 <sup>a</sup>	13.55	30.38	0.09	9.78	5.28	8.27
	0.29 <sup>b</sup>	15.43	29.60	0.58	8.19	7.45	7.98
	0.38 <sup>c</sup>	20.40	27.65	2.86	2.89	12.09	8.31
	0.40 <sup>d</sup>	21.50	27.27	3.57	1.46	12.86	8.64
	0.50	26.90	25.68	7.95	-6.73	15.47	11.43

- a - van Krevelen Method I.  
b - van Krevelen Method II.  
c - infra-red, 6.25  $\mu$  band compared to methyl naphthalenes (12 compounds).  
d - van Krevelen Method III.

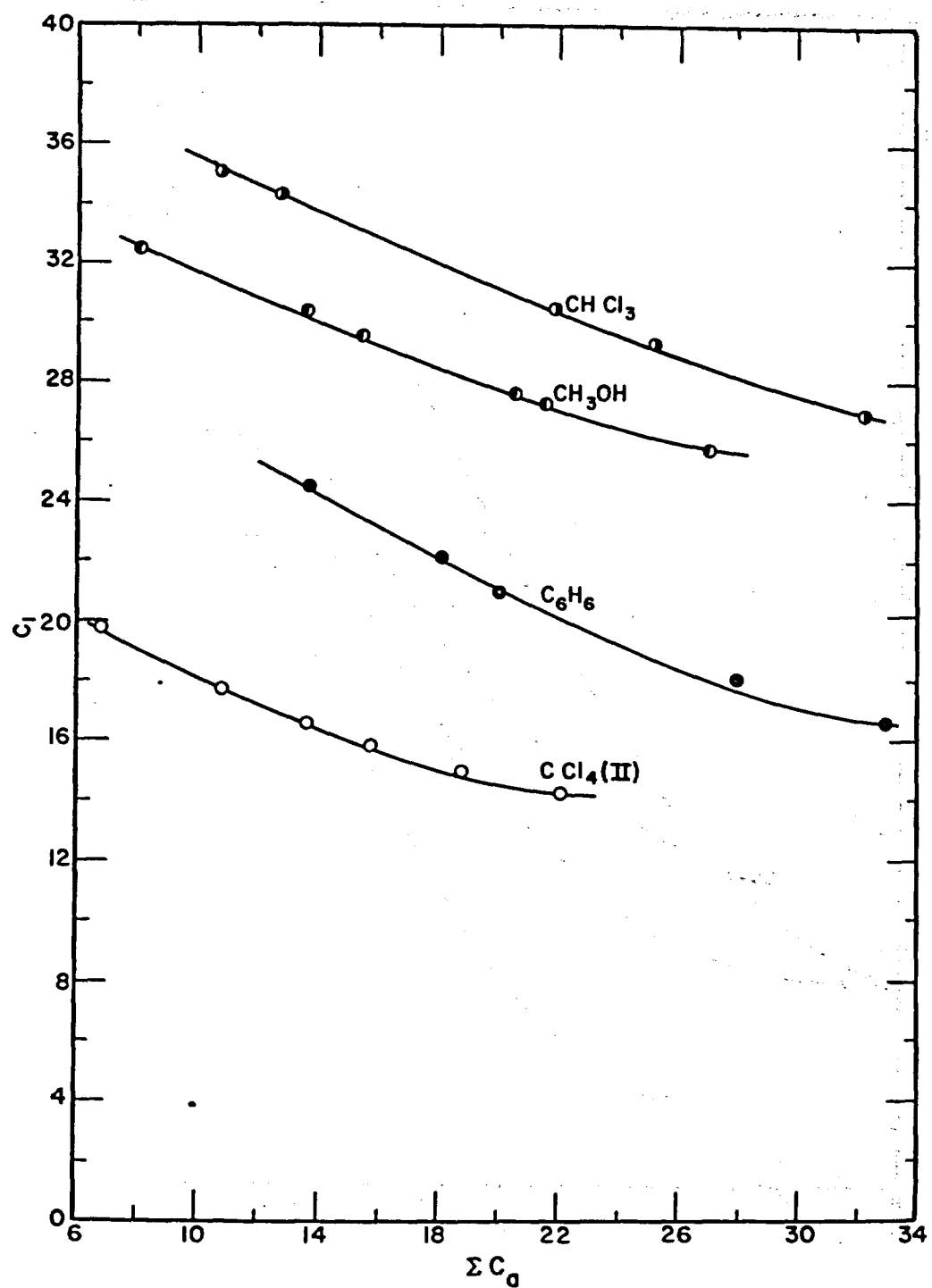


Figure 12. Results of the Montgomery-Boyd analysis (Scheme MB 1) of the resins.  $C_1$  versus  $\Sigma C_0$ .

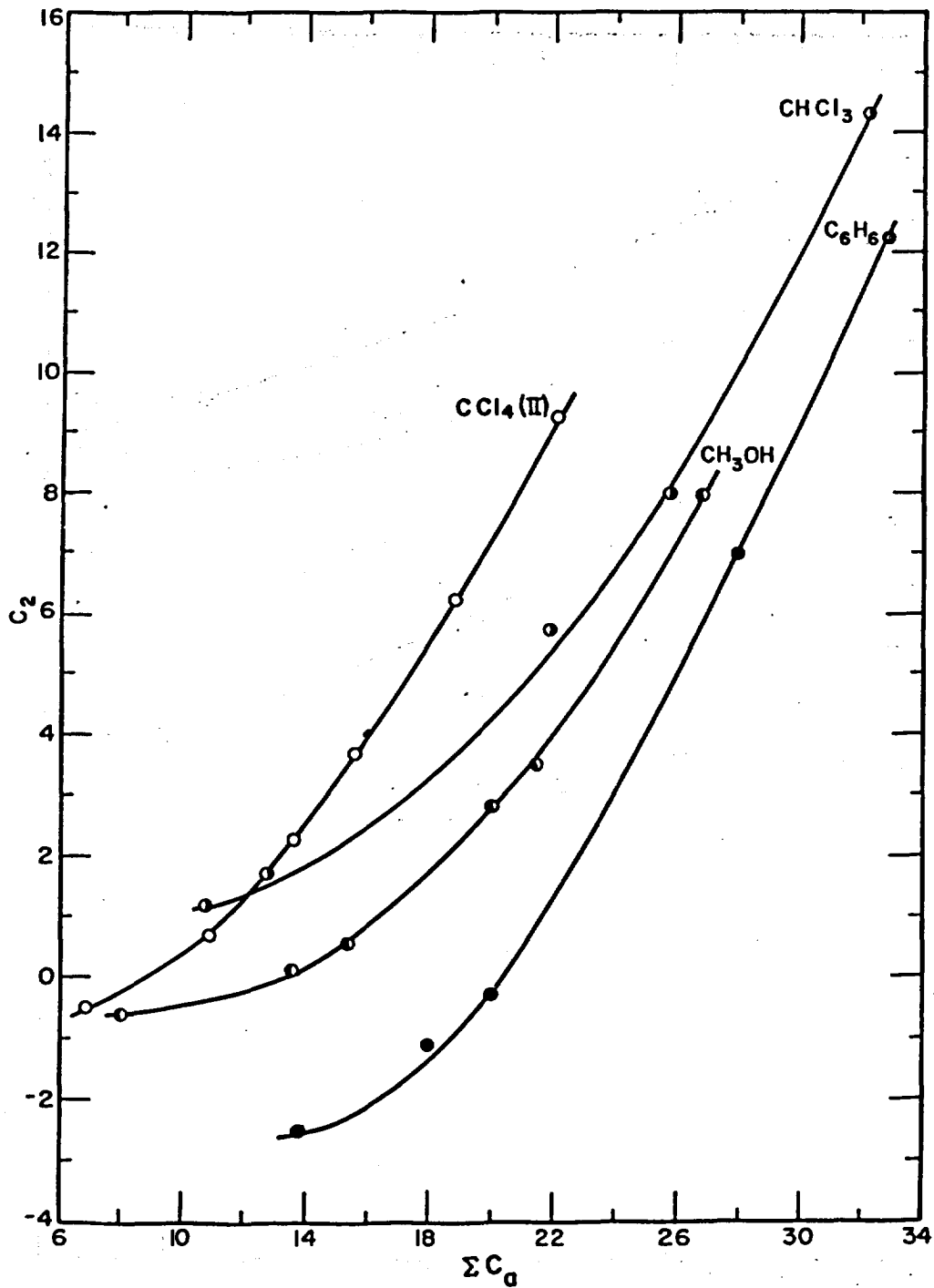


Figure 13. Results of the Montgomery-Boyd analysis (Scheme MB1) of the resins.  $C_2$  versus  $\Sigma C_a$ .

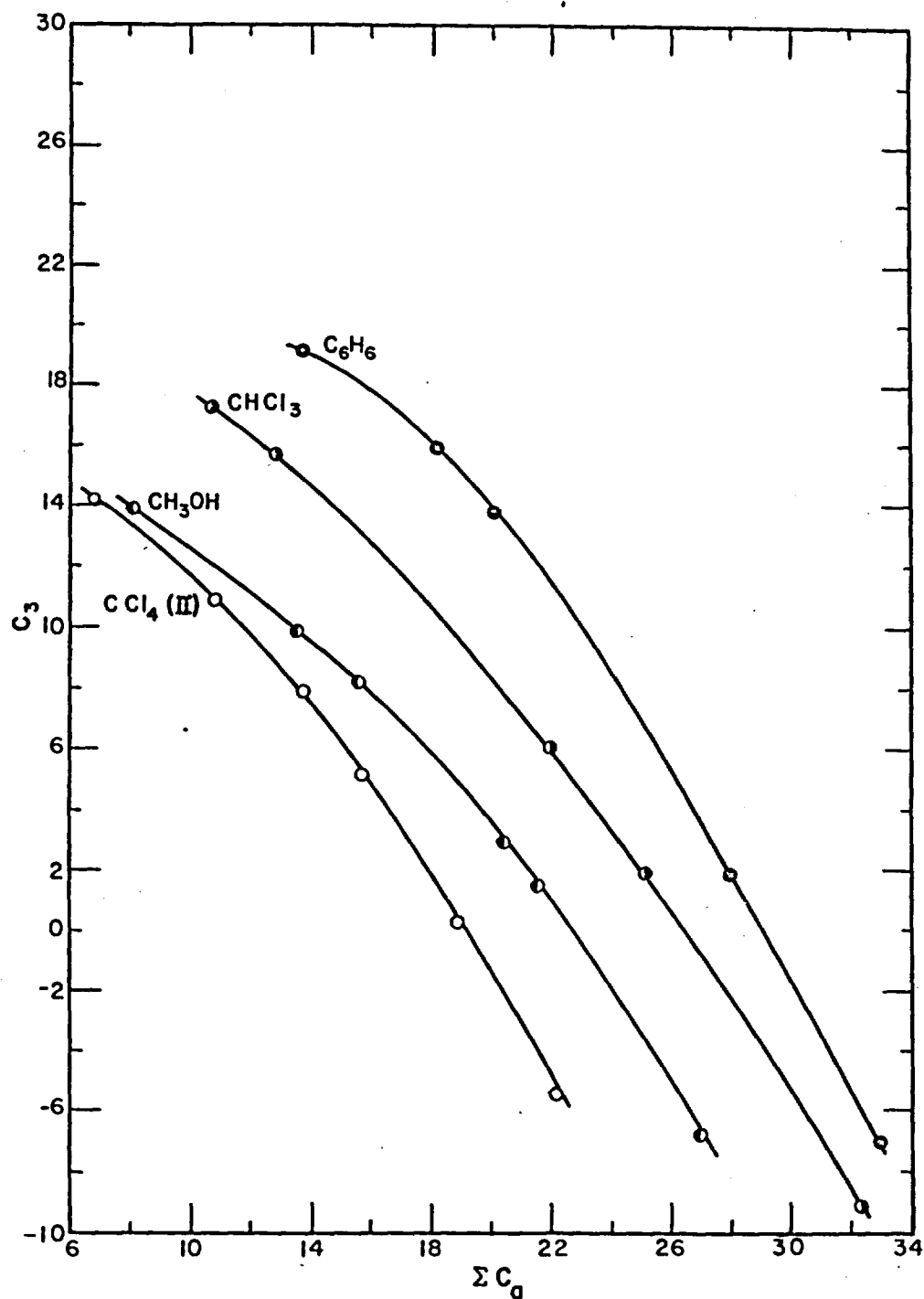


Figure 14. Results of the Montgomery-Boyd analysis (Scheme MB1) of the resins.  $C_3$  versus  $\Sigma C_a$ .

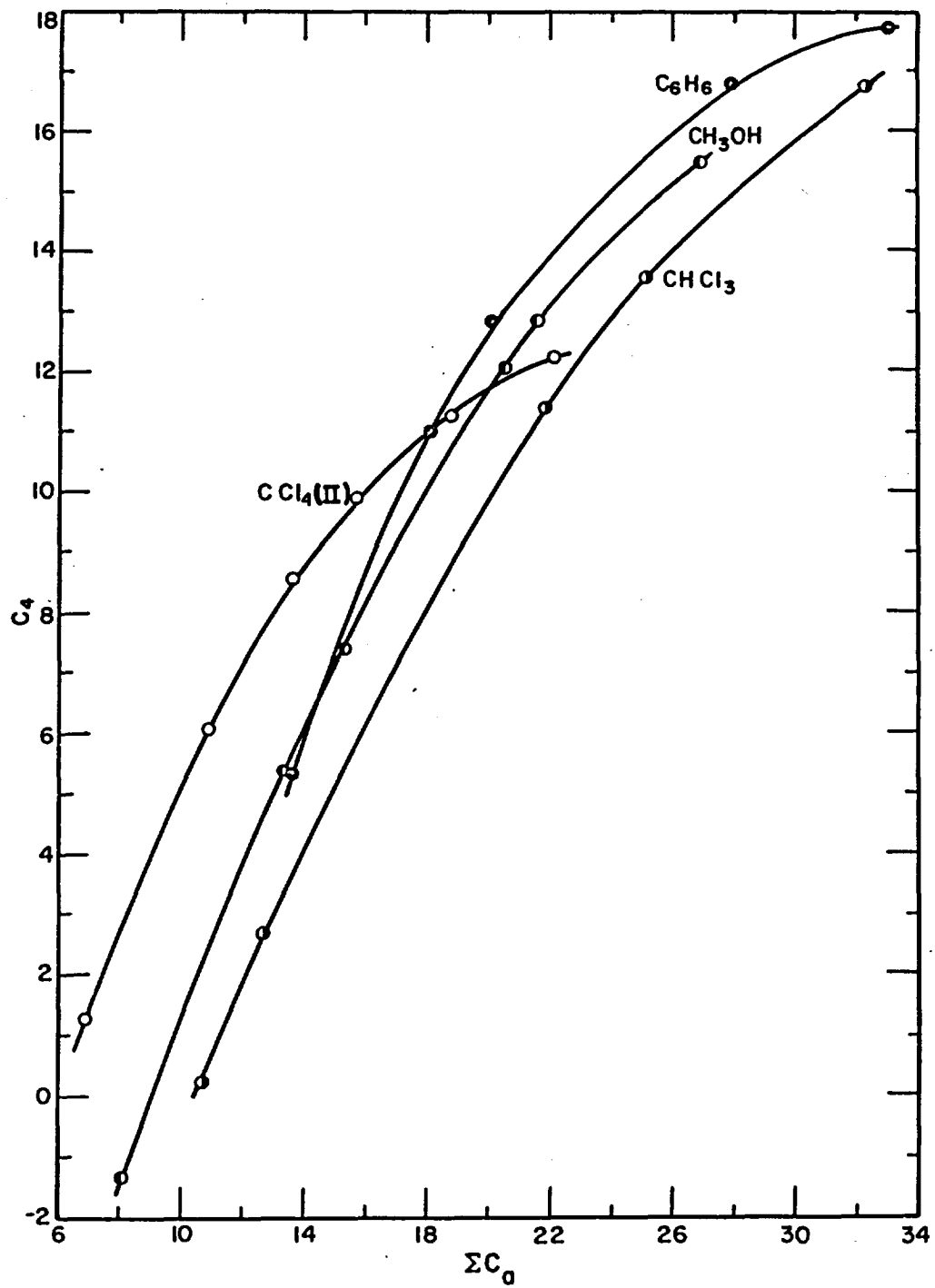


Figure 15. Results of the Montgomery-Boyd analysis (Scheme MB1) of the resins.  $C_4$  versus  $\Sigma C_a$ .

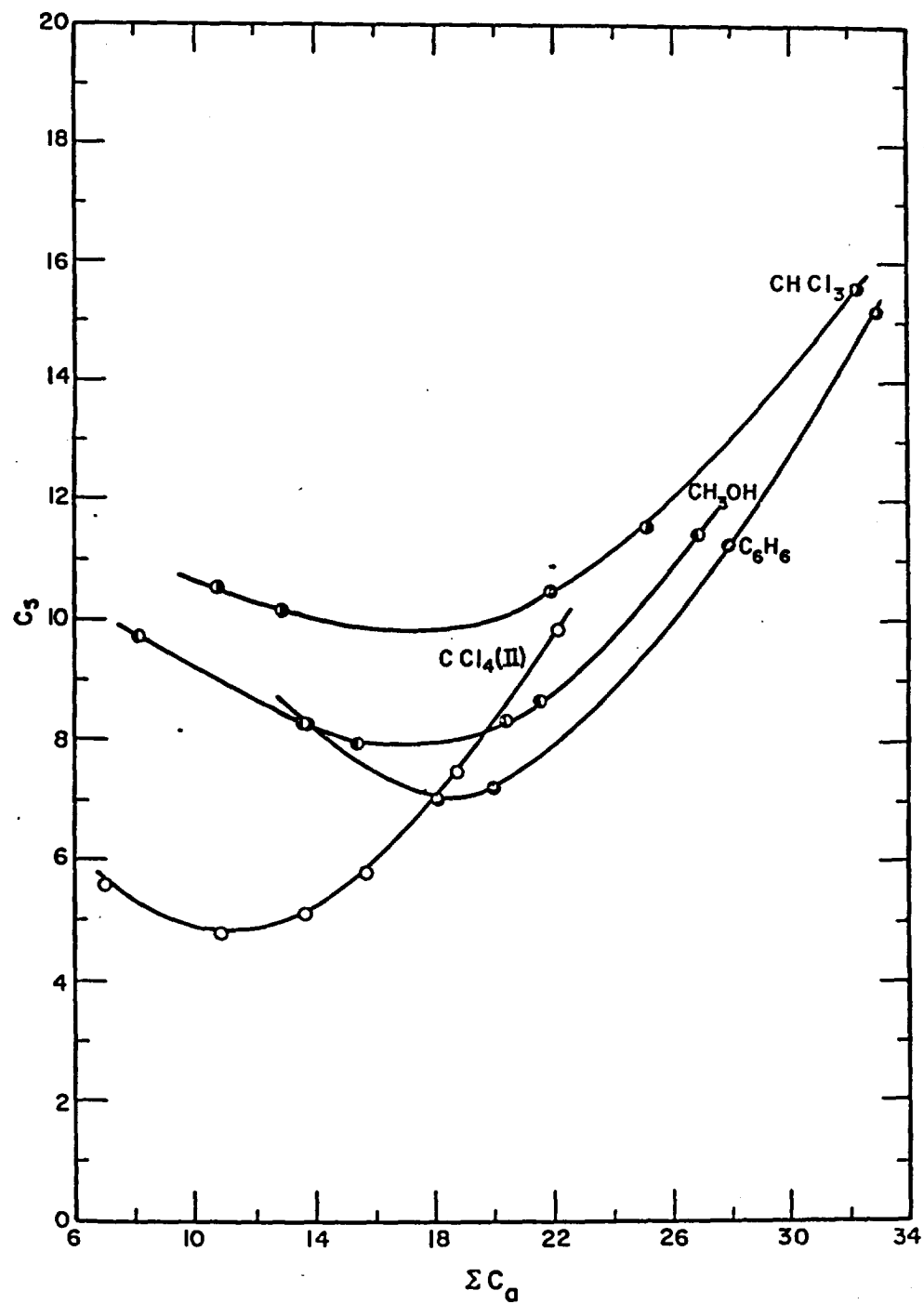


Figure 16. Results of the Montgomery-Boyd analysis (Scheme MB1) of the resins.  $C_5$  versus  $\Sigma C_a$ .

Application of the Modified Montgomery-Boyd Structural  
Group Analysis Method (Scheme MB2)

The original structural group analysis (Scheme MB1) developed by the authors has been modified to analyze material in which  $C_3$  was zero,  $C_2$  was small, and both fused and non-fused aromatic rings were present. If there was some "a priori" knowledge that  $C_3$  was zero, this then permitted the addition of another parameter. For the present case, the parameter added was  $C_7$ , the number of junction carbon atoms per molecule in non-fused aromatic rings. Use was made of molar volume and molar refraction equations which had been developed by the authors to fit non-fused aromatic compounds.<sup>(38)</sup> This modified structural analysis system consisted of the solution of a second set of five equations, which represented the identical properties as the first set but which were set up in terms of a second set of parameters,  $C_1$ ,  $C_2$ ,  $C_4$ ,  $C_5$  and  $C_7$ . This method has a further qualification:  $C_2$  must be present only in small quantities. This was required because, in the development of the molar volume and molar refraction equations<sup>(38)</sup> to fit hydrocarbons containing both fused and non-fused aromatic rings, it was found necessary to omit a  $C_2$  "correction term" on  $C_4$ , which had been used in the equations of the original system. For convenience this second set of five equations is tabulated below:

$$(25) \quad C_1 + C_2 + C_4 + C_5 + C_7 = \Sigma C$$

$$(26) \quad 2C_1 + 2C_2 + C_4 = \Sigma H$$

$$(27) \quad C_4 + C_5 + C_7 = \Sigma C_a$$

$$(28) \quad C_1 \left( 16.38 + \frac{30.61}{\Sigma C} \right) + C_2 \left( 13.20 + \frac{28.48}{\Sigma C} \right) +$$

$$C_4 \left( 12.406 + \frac{14.042}{\Sigma C} - 1.96 \frac{C_1}{\Sigma C} \right) + C_5 \left( 5.124 - \frac{5.238}{\Sigma C} \right) +$$

$$C_7 \left( 7.04 + \frac{16.53}{\Sigma C} \right) = \text{M.V.}$$

20°C,  
1 atmos. press.

$$(29) \quad C_1 \left( 4.623 + \frac{2.314}{\Sigma C} \right) + C_2 \left( 4.468 + \frac{0.868}{\Sigma C} - 0.245 \frac{C_1}{\Sigma C} \right) +$$

$$C_4 \left( 4.5445 - \frac{1.021}{\Sigma C} - 0.396 \frac{C_1}{\Sigma C} \right) + C_5 \left( 5.734 - \frac{14.333}{\Sigma C} \right) +$$

$$C_7 \left( 2.872 + \frac{5.405}{\Sigma C} \right) = \text{M.R.}$$

20°C,  
1 atmos. press.

To obtain an estimate of how the aromatic atoms were divided between fused and non-fused rings consistent with this choice of parameters, this second analysis scheme was applied to each of the resin fractions. The value of  $\Sigma C_a$  used for each fraction was that value which corresponded to a zero value of  $C_3$  in the results of the original Montgomery-Boyd method (Scheme MB1). These values were read directly from the graph shown in Figure 14. The results of this application are tabulated in Table 10.



TABLE 10

Application of Modified Montgomery-Boyd Analysis

Resin Fraction	$\Sigma C_a$	$C_1$	$C_2$	$C_4$	$C_5$	$C_7$	$C_5/C_7$
C Cl <sub>4</sub> (II)	19.1	17.5	3.8	11.7	3.0	4.4	0.68
Benzene	29.0	22.1	3.7	17.0	6.1	5.9	1.03
Chloroform	26.4	32.2	5.7	14.7	7.4	4.7	1.57
Methanol	22.6	28.6	2.6	13.6	6.5	2.5	2.60

## DISCUSSION

The results of the structural group analyses are discussed from two viewpoints: 1) to learn as much as possible about the structure of each individual fraction; and 2) to compare the compositions of the fractions in an attempt to determine the differences between them and to discover on what basis the chromatographic separation took place.

All the methods of structural analysis that have been applied here have two assumptions in common. First, all involve the additivity of the molar volume (and the molar refraction) in the liquid state, and, secondly, all double bonds present are in aromatic rings. The resin fractions exhibited all the normal properties of fluids at the temperature at which measurements were taken (20°C), so that the properties measured here may be considered to be equilibrium properties of the fractions being studied. Regarding the

nature of the unsaturation in the resin fractions, the infra-red spectra did not reveal the presence of any olefinic-type linkage, as evidenced by the absence of a  $6.1\mu$  side band on the  $6.2\mu$  aromatic absorption band. There are undoubtedly small amounts of other types of unsaturation present which probably account for the polymerization in air and the colour. The standard chemical tests for unsaturation yielded somewhat inconclusive results when applied to material of this type.

Attention is drawn to the fact that the chromatography of  $C Cl_4$  (I) fraction (Figure 7) on silica gel yielded only a very small amount of saturated compounds (3.25%). This was considered to be important from the point of view of applying hydrocarbon structural analysis schemes. If extreme types such as saturates and aromatics did not exist as a mechanical mixture in the resin fractions, there would be much less contraction due to the interaction of these types, and the errors involved in employing the structural analysis system would be reduced. It follows that the  $C_1$  and  $C_2$  groups found are attached by chemical bonds to the aromatic portion of the molecule. An additional reason for attempting to eliminate as much of the saturated material as possible is that the hydrogen balance equation in the Montgomery-Boyd method is not valid for normal or branched paraffins. On the basis of the chromatography of  $C Cl_4$  (I), it was assumed that the remainder of the resin fractions eluted with more polar solvents were essentially free of

saturates. These fractions can be considered as approximately homogeneous as to chemical type, and therefore should be particularly suitable for the application of these structural analysis systems. The presence of a mechanical mixture of different chemical types would tend to obscure the statistical interpretation of the results.

In van Krevelen's methods of estimating  $R/C$  and  $f_a$ , it was assumed that the density was not a function of the state of strain of the sample but was an equilibrium property of the liquid which could be expressed in terms of the sum of atomic increments and structural factors. Method I, which is van Krevelen's densimetric method,<sup>(30)</sup> gave  $f_a$  values of 0.34 for  $C Cl_4$  (II), 0.33 for the benzene fraction, 0.17 for the chloroform fraction, and 0.25 for the methanol fraction. This method regarded all structural contributions to the molar volume as due to rings, and this structural factor was determined to be a linear function of the  $H/C$  ratio based on the following model substances: cellulose, polystyrene, and graphite. The  $f_a$  values from Method II were slightly higher than those from I (the difference ranging from 3% to 5%), although this did not affect the relative differences between the resin fractions themselves. These differences were the results of using the experimental molecular weight in Method II and, as a result, being able to make use of a more accurate form of the  $f_a - R/C - H/C$  equation (equation 4 instead of equation 2). Method III,

van Krevelen's Graphical Densimetric method, (31) yielded considerably higher values of  $f_a$  and also altered the relative position between the resin fractions. This method gave  $f_a$  values varying between 0.39 and 0.51 for these fractions, with the benzene fraction having the highest value and the chloroform fraction having the lowest. By this method, the chloroform and methanol fractions have  $f_a$  values differing only by 1%, and the  $C Cl_4$  (II) and benzene fractions have values 8 to 11% higher. It must be borne in mind that this particular method was based on the relationship between  $\frac{Mc}{d}$ ,  $\frac{H}{C}$  and  $f_a$  for pure aromatic hydrocarbons. This method will be discussed in conjunction with the Montgomery-Boyd results, since both methods are based on pure hydrocarbons. Recent controversies concerning the upper and lower ends of the  $f_a$  scale (39, 40, 41) do not affect the present case, since the resin fractions like the asphaltenes would appear to lie well away from these areas of the  $f_a$  scale. Similarly, these fractions would not be affected by the limitations of this method pertaining to the relative proportions of aromatic and naphthenic carbon atoms (if naphthenic groups are present, then  $f_a$  must be greater than 0.25).

Since, in considering any possible structure, the number of rings per molecule is of particular importance, it is of some interest to note the corresponding values of R (the number of rings per molecule) for the various values of  $f_a$  obtained by

van Krevelen's methods. The densimetric method predicted 6.4 rings/molecule for  $C Cl_4$  (II), 11.5 for the benzene fraction, 13.9 for the chloroform fraction, and 9.1 for the methanol fraction, whereas the graphical densimetric method resulted in somewhat lower values: 3.8 for  $C Cl_4$  (II), 6.6 for the benzene, 6.7 for the chloroform, and 5.1 for the methanol fractions. The fourth set of structural information based on van Krevelen's methods was that obtained by the application of his 4-type carbon group analysis, (33) (Method IV). This method is based on the probability of the occurrence of a  $CH_2$  group as a function of  $H/C$  (equation 12) for a number of macromolecular model structures. In equations 13 and 14, the values of  $f_a$  and  $R/C$  from the densimetric method were used. The resulting values for  $C_1$  (paraffinic and naphthenic  $CH_2$ ) varied from 38 to 49%, with the benzene fraction having the lowest value and the chloroform and methanol fractions both containing 49%. Values for  $C_2$  (naphthenic fused ring junctions) varied from 22% for the  $C Cl_4$  (II) fraction to 35% for the chloroform fraction. The lowest value for  $C_3$  (aromatic  $CH$ ), 8%, belonged to the chloroform fraction and the highest, 24%, to the  $C Cl_4$  (II) fraction. The values for  $C_4$  (fused aromatic ring junctions) remained fairly constant, varying only 5% for all resins (8-13%).

The results from Method IV cannot be given the same weight as those from Methods I, II and III, owing to the doubtful basis of equation 12, which was recognized by van Krevelen, and also

due to the fact that this method involved  $f_a$  and R/C from Method I. Values for  $f_a$  from Method III are considered more realistic than the original densimetric method (Methods I and II). Method IV has been included herein as a matter of historical interest.

It should be noted that the structural parameters obtained from van Krevelen's methods, R/C and  $f_a$ , were obtained from two physical properties only -- the density and the H/C ratio. In effect, van Krevelen showed the type of structural information that could be obtained from these two properties. His methods were designed especially for coal, whose structure was considered to be largely condensed aromatic rings. However, in the case of the bitumen, more experimentally determined properties were available than was the case for coal. Consequently, the structural analysis system developed by the authors was intended to yield the maximum amount of chemical structural information from the five properties available. Van Krevelen's parameters did not yield any information about the saturated carbon portion of the molecule, knowledge of which was considered desirable for the bitumen resin fractions. The structural parameters in the Montgomery-Boyd method were chosen to cover a wider range of possible structures than the van Krevelen methods. The van Krevelen methods were applied to the resin fractions for the specific purpose of obtaining an estimate of  $f_a$ , since this property was required to apply the Montgomery-Boyd method.

The results of the structural analysis method developed by the authors<sup>(36)</sup> will now be considered. This system (MB1) consisted of five property equations that were capable of simultaneous solution. The significance attached to these results should be regarded in the light of the fact that the molar volume and molar refraction equations, which form a part of the system of five equations, were designed especially to fit the hydrocarbons of API project 42. The accuracy with which the method is capable of analyzing these hydrocarbons ( $C_{10} - C_{50}$ ) has already been determined.<sup>(36)</sup> If, as is the case here, the input data fed into the system refer to mixtures of compounds, the solutions obtained will be the structure of the equivalent pure compound; that is to say, the pure compound which would possess the same density, refractive index, average molecular weight, number of carbon atoms, hydrogen atoms and aromatic carbon atoms. As has already been referred to, this method was applied to each resin fraction over a considerable range of  $\Sigma C_a$  values due to the fact that no reliable method of determining  $\Sigma C_a$  experimentally existed for this type of material. The range arbitrarily chosen was intended to cover all possible values obtained from the infra-red spectra and also calculated by van Krevelen's methods. The various sets of results were then critically assessed on the basis of certain algebraic and chemical criteria (for details, see pages 76-84). The net effect of applying these criteria was to confine the aromaticity to

certain limits, and hence the various structural groups. These criteria may be briefly summarized as follows: (1) All physically impossible answers were eliminated (i. e. negative solutions) and thus a range of possible  $\Sigma C_a$  values was established. (2) van Krevelen's Ring Balance equation (which in terms of the present parameters could be written  $C_3 + C_5 = 2R - 2$ ) was applied to all sets of results to give a value of R for each case, and, from this, the number of cyclic carbon groups per ring which was equal to  $\frac{C_2 + C_3 + C_4 + C_5}{R}$  was determined. The values of  $C_R/R$  were compared with those of possible model structures. It is obvious that for a particular value of  $C_R/R$ , a unique solution exists. (3) An indirect determination of  $\Sigma C_a$  was made from the quantitative estimation of methyl and methylene groups from the infrared spectra (Table 3). This value permitted another unique solution. The object of the application of these criteria was to show that they permitted the structure of each resin fraction to be defined within a reasonably narrow range.

The additional structural data required for the application of these criteria are tabulated in Table 11 and depicted graphically in Figures 17-26. Table 12 contains the analysis expressed in terms of fractions of the total carbon, and is included here as a convenience because, in comparing the compositions of the various fractions with one another and also in comparing the various methods with one another, it is found more convenient to do so on a percentage basis.



TABLE 11

Structural Characteristics of the Resins from the  
Montgomery-Boyd Analysis

Fraction	$\Sigma C_a$	$C_2/C_3$	$C_4/C_5$	R	$C_R/R$	$(C_1+C_2)$
C Cl <sub>4</sub> (II)	6.83 <sup>c</sup>	-0.04	0.23	10.83	1.87	19.25
	10.85	0.063	1.27	8.82	2.54	18.47
	13.63 <sup>a</sup>	0.28	1.68	7.44	3.17	18.79
	15.68 <sup>b</sup>	0.72	1.70	6.41	3.80	19.50
	18.77 <sup>d</sup>	25.8	1.51	4.86	5.18	21.19
	22.10	-1.70	1.24	3.20	8.09	23.55
Benzene	13.70 <sup>c</sup>	-0.13	0.66	14.65	2.06	22.07
	18.07 <sup>a</sup>	-0.073	1.56	12.46	2.63	20.87
	20.01 <sup>b</sup>	-0.002	1.79	11.50	2.94	20.97
	27.95 <sup>d</sup>	3.80	1.49	7.52	4.89	25.01
	32.90	-1.73	1.16	5.05	7.54	29.00
Chloroform	10.74 <sup>a</sup>	0.07	0.02	14.88	1.96	36.31
	12.80 <sup>b</sup>	0.10	0.26	13.85	2.16	35.96
	21.09 <sup>c</sup>	0.94	1.09	9.30	3.63	36.28
	25.09 <sup>d</sup>	4.31	1.17	7.70	4.54	37.36
	32.20	-1.55	1.07	4.15	8.99	41.32
Methanol	8.07	-0.04	-0.17	12.76	1.67	31.92
	13.55 <sup>a</sup>	0.009	0.64	10.02	2.34	30.47
	15.43 <sup>b</sup>	0.071	0.93	9.08	2.66	30.18
	20.40 <sup>c</sup>	0.99	1.45	6.60	3.96	30.51
	21.50 <sup>d</sup>	2.44	1.49	6.05	4.38	30.84
	26.90	-1.18	1.35	3.35	8.39	33.63

a - van Krevelen Method I.

b - van Krevelen Method II.

c - infra-red, 6.25 $\mu$  band compared to methyl naphthalenes (12 compounds).

d - van Krevelen Method III.

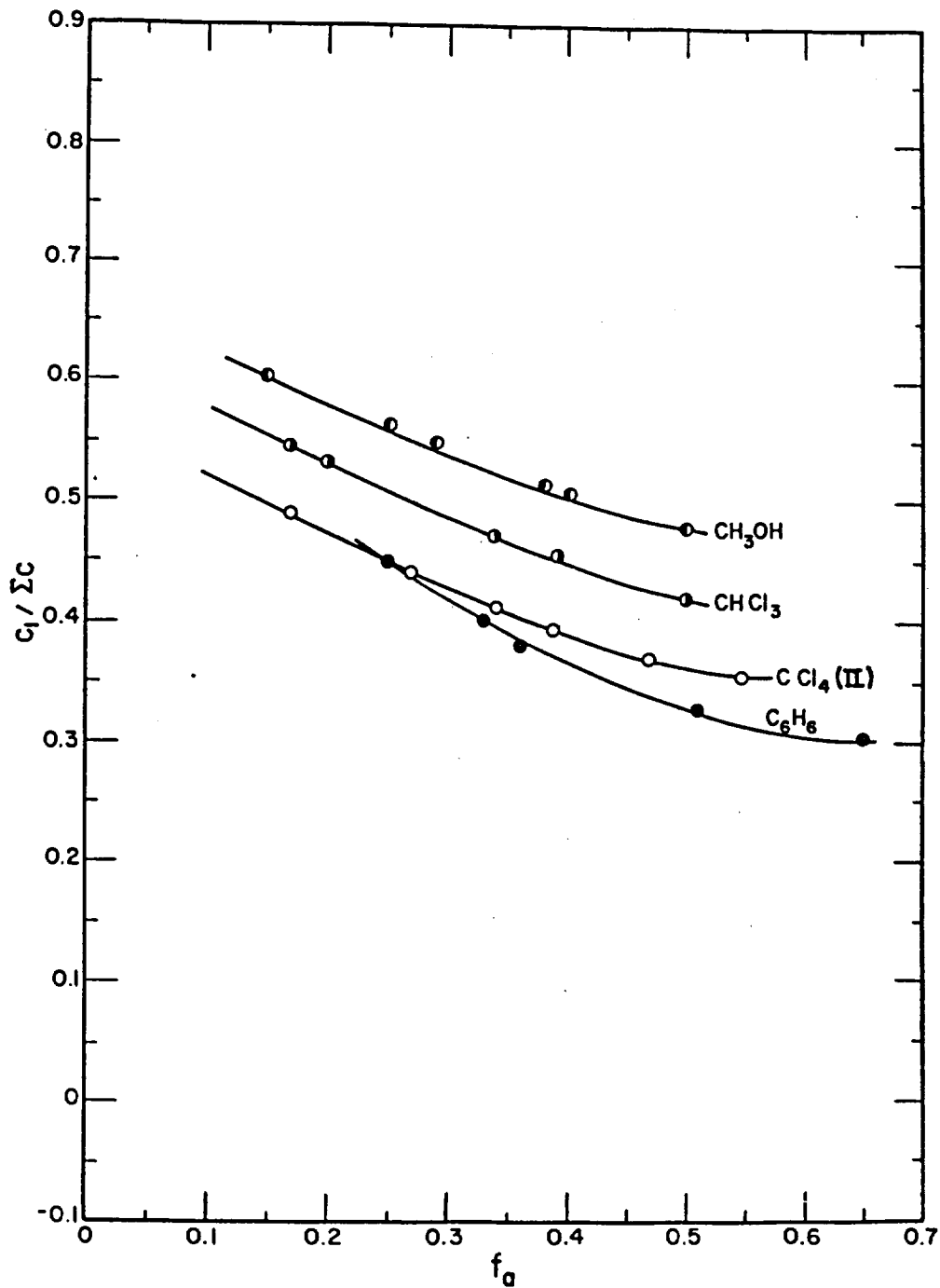


Figure 17. Results of the Montgomery-Boyd analysis (Scheme MBI) of the resins, expressed as fractions of the total carbon.  $C_1/\Sigma C$  versus  $f_a$ .

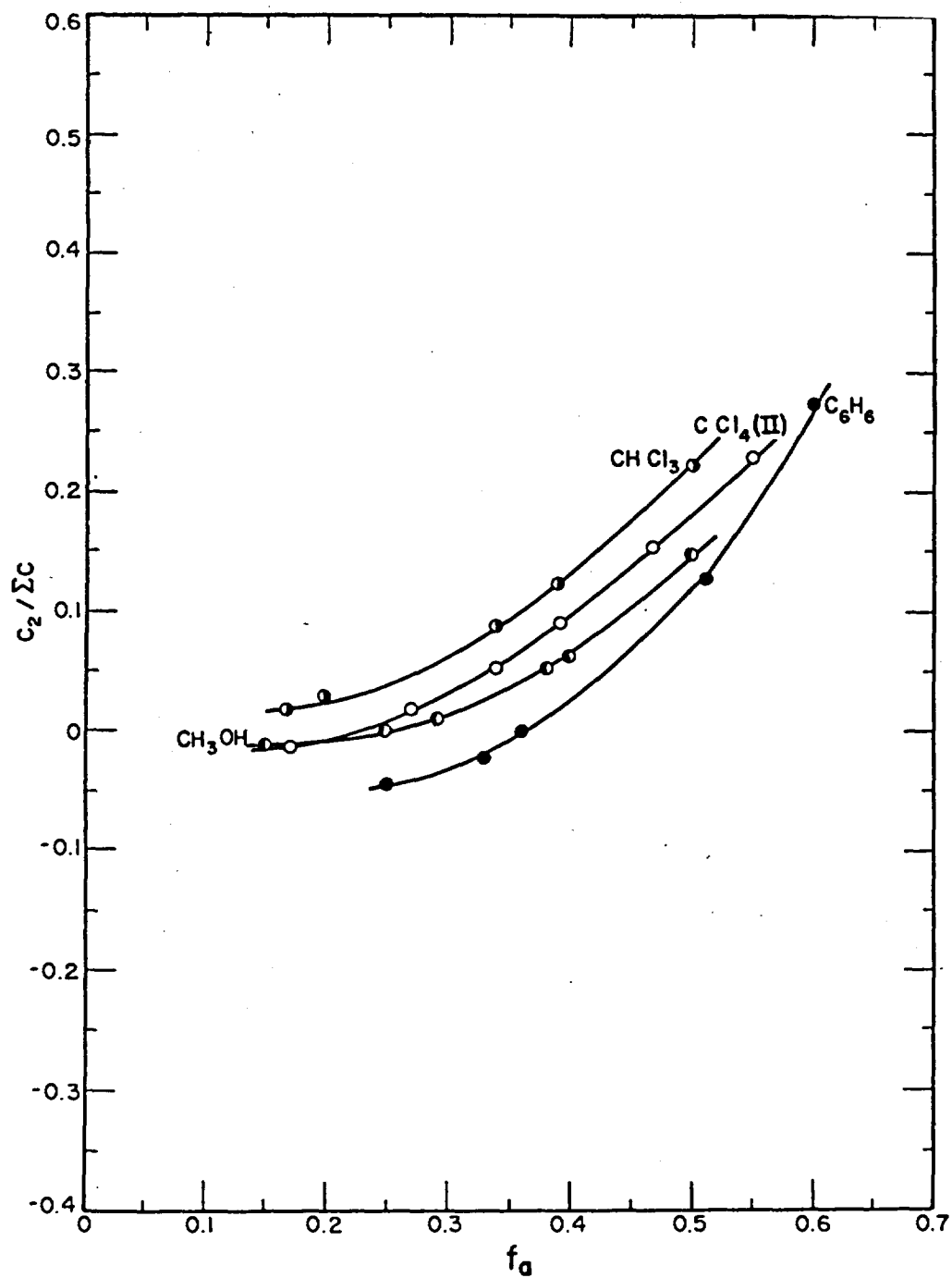


Figure 18. Results of the Montgomery-Boyd analysis (Scheme MB1) of the resins, expressed as fractions of the total carbon.  $C_2/\Sigma C$  versus  $f_a$ .

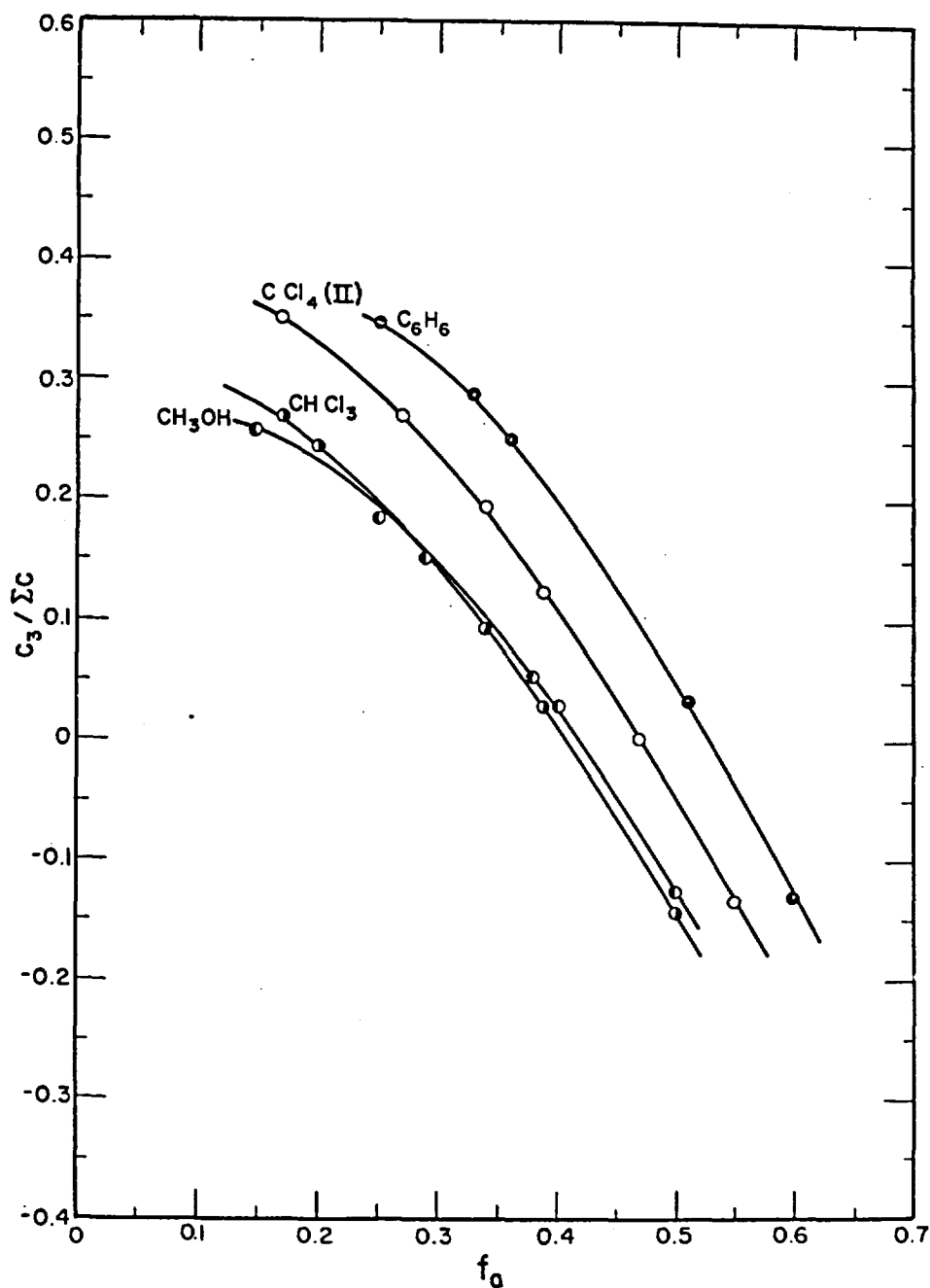


Figure 19. Results of the Montgomery-Boyd analysis (Scheme MB1) of the resins, expressed as fractions of the total carbon.  $C_3/\Sigma C$  versus  $f_a$ .

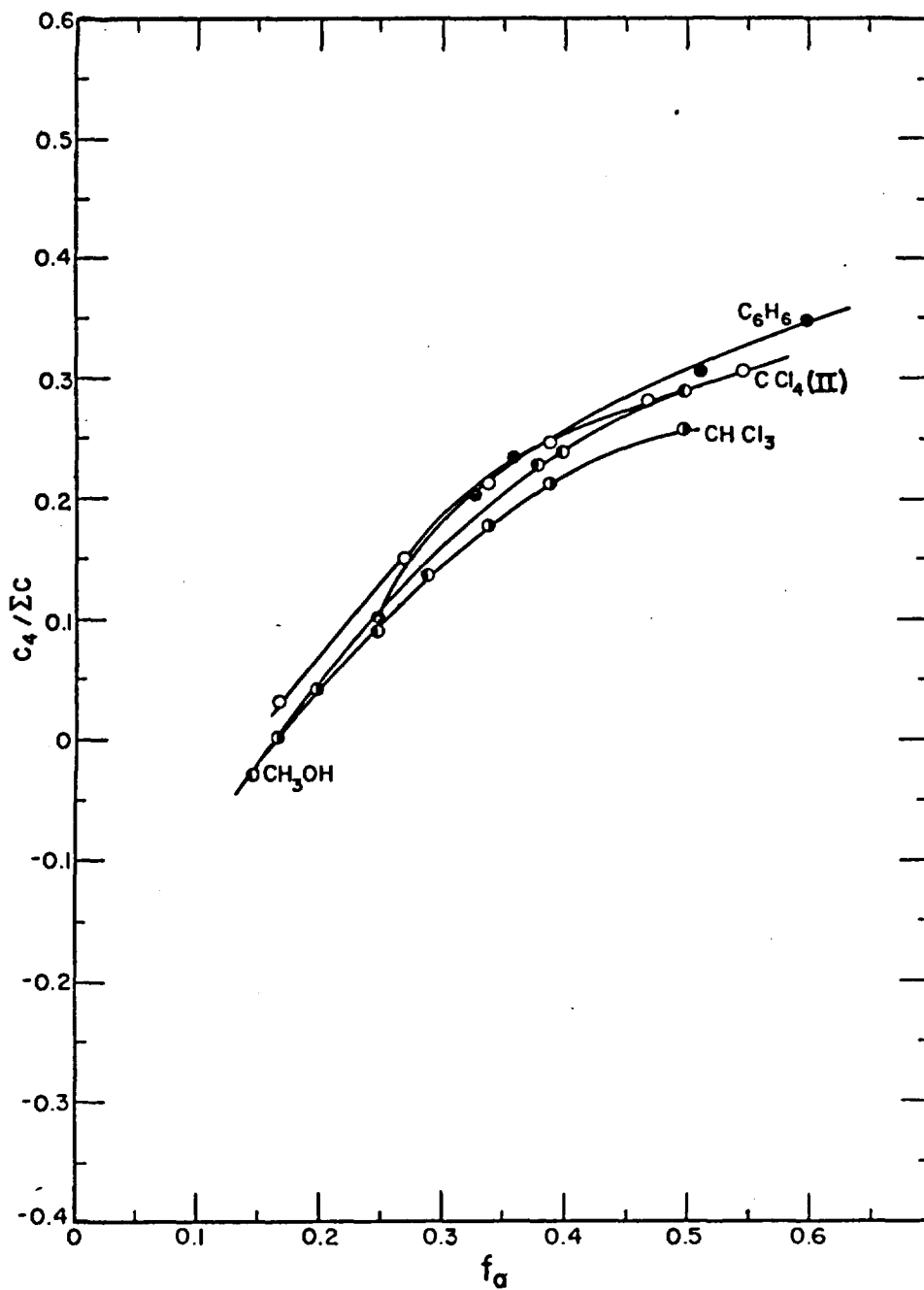


Figure 20. Results of the Montgomery-Boyd analysis (Scheme MB1) of the resins, expressed as fractions of the total carbon.  $C_4/\Sigma C$  versus  $f_a$ .

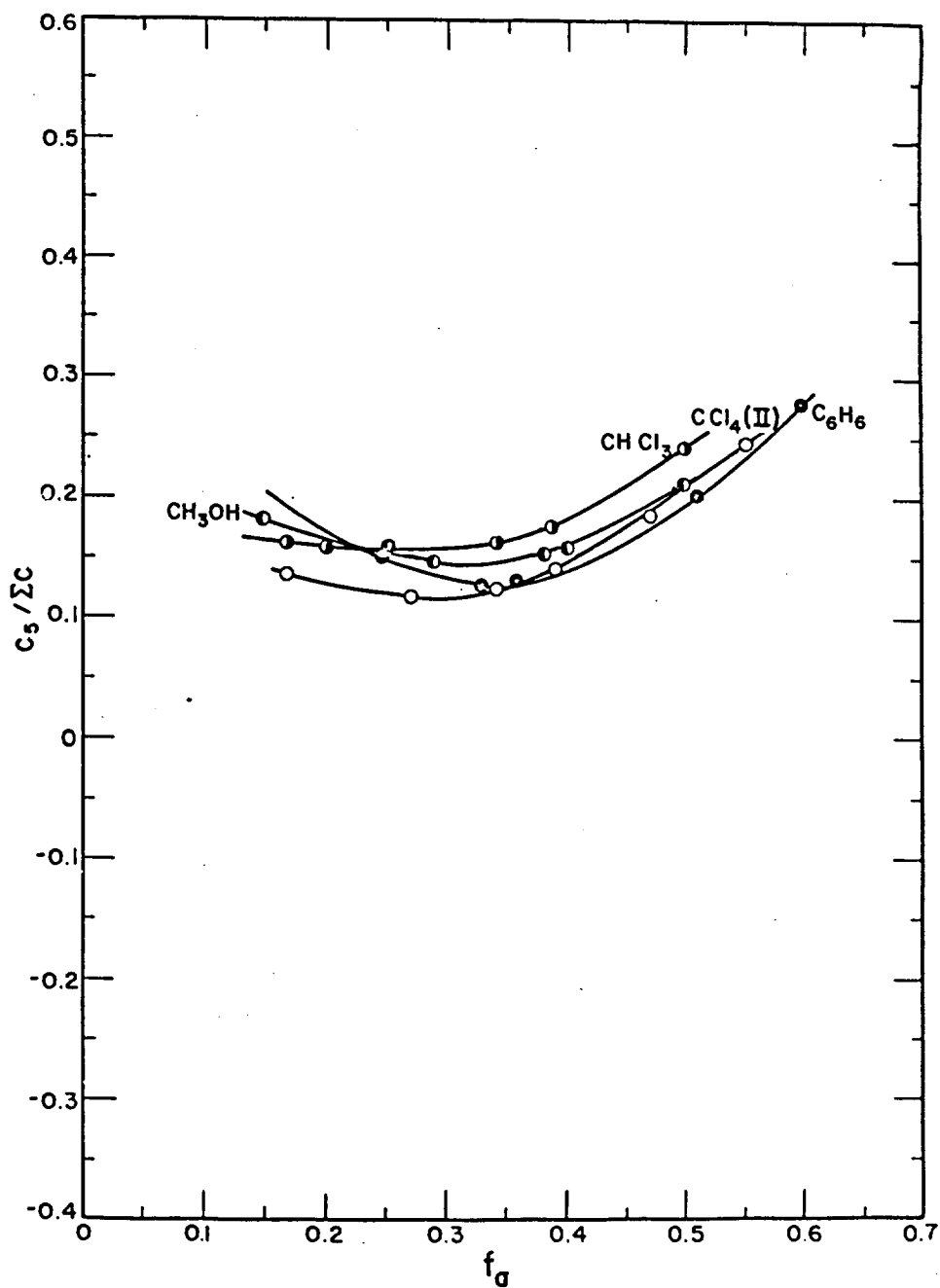


Figure 21. Results of the Montgomery-Boyd analysis (Scheme MB1) of the resins, expressed as fractions of the total carbon.  $C_5/\Sigma C$  versus  $f_a$ .

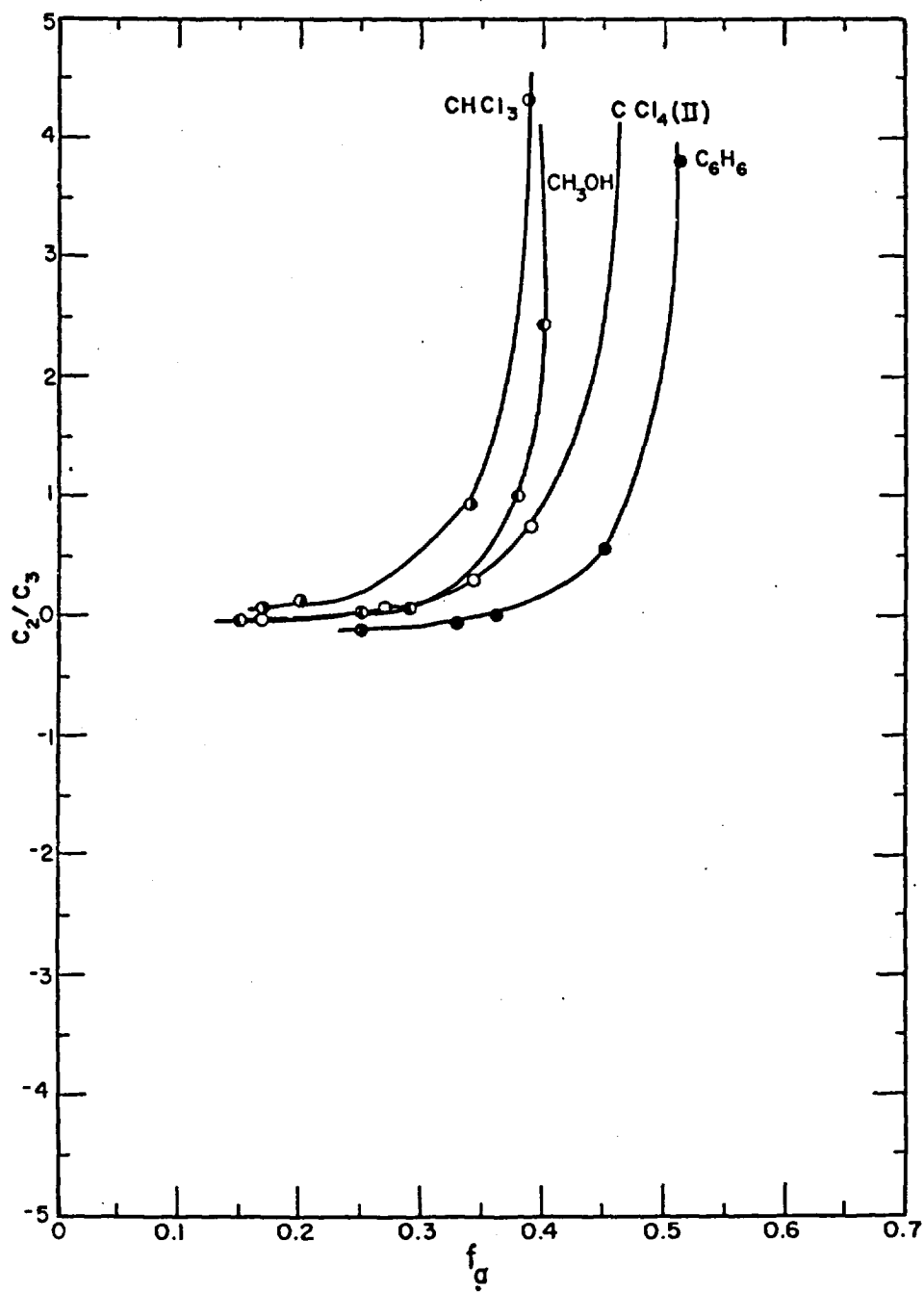


Figure 22. Variation of  $C_2/C_3$  with  $f_a$  for the Montgomery-Boyd analysis of the resins (Scheme MB1).

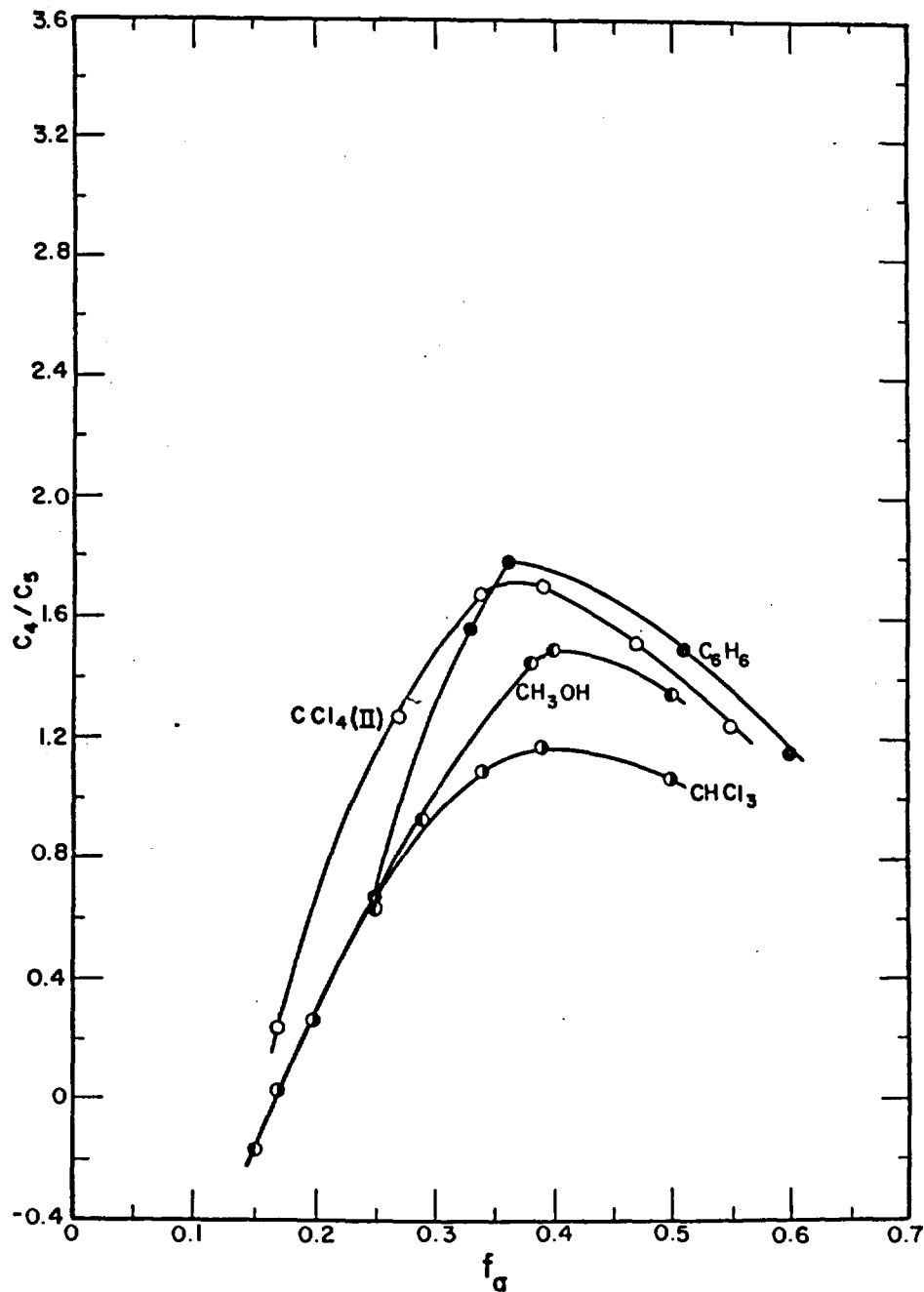


Figure 23. Variation of  $C_4/C_5$  with  $f_a$  for the Montgomery-Boyd analysis of the resins (Scheme MB1).



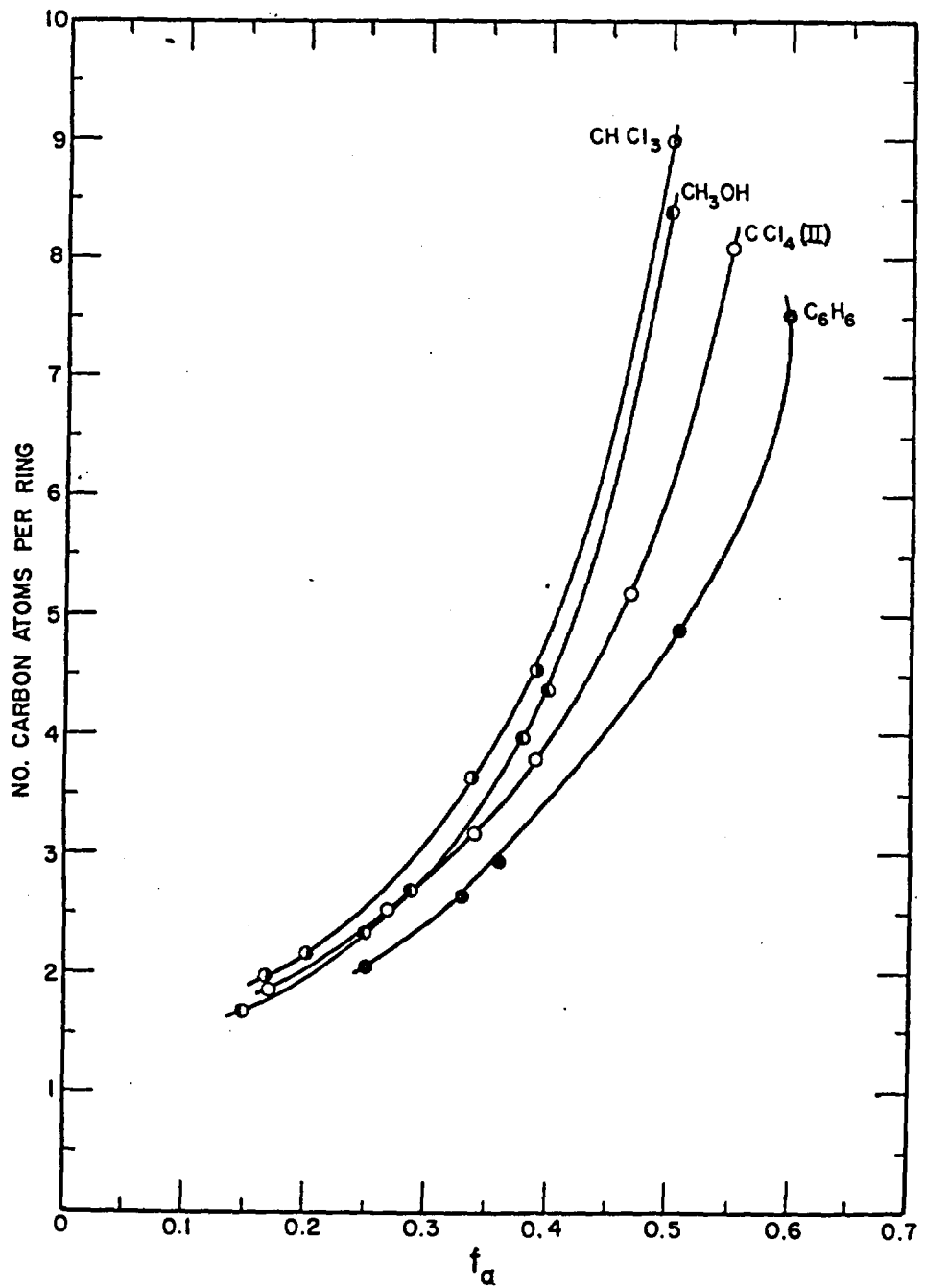


Figure 24. The number of carbon atoms per ring versus  $f_a$  for the Montgomery-Boyd analysis of the resins (Scheme MB1).

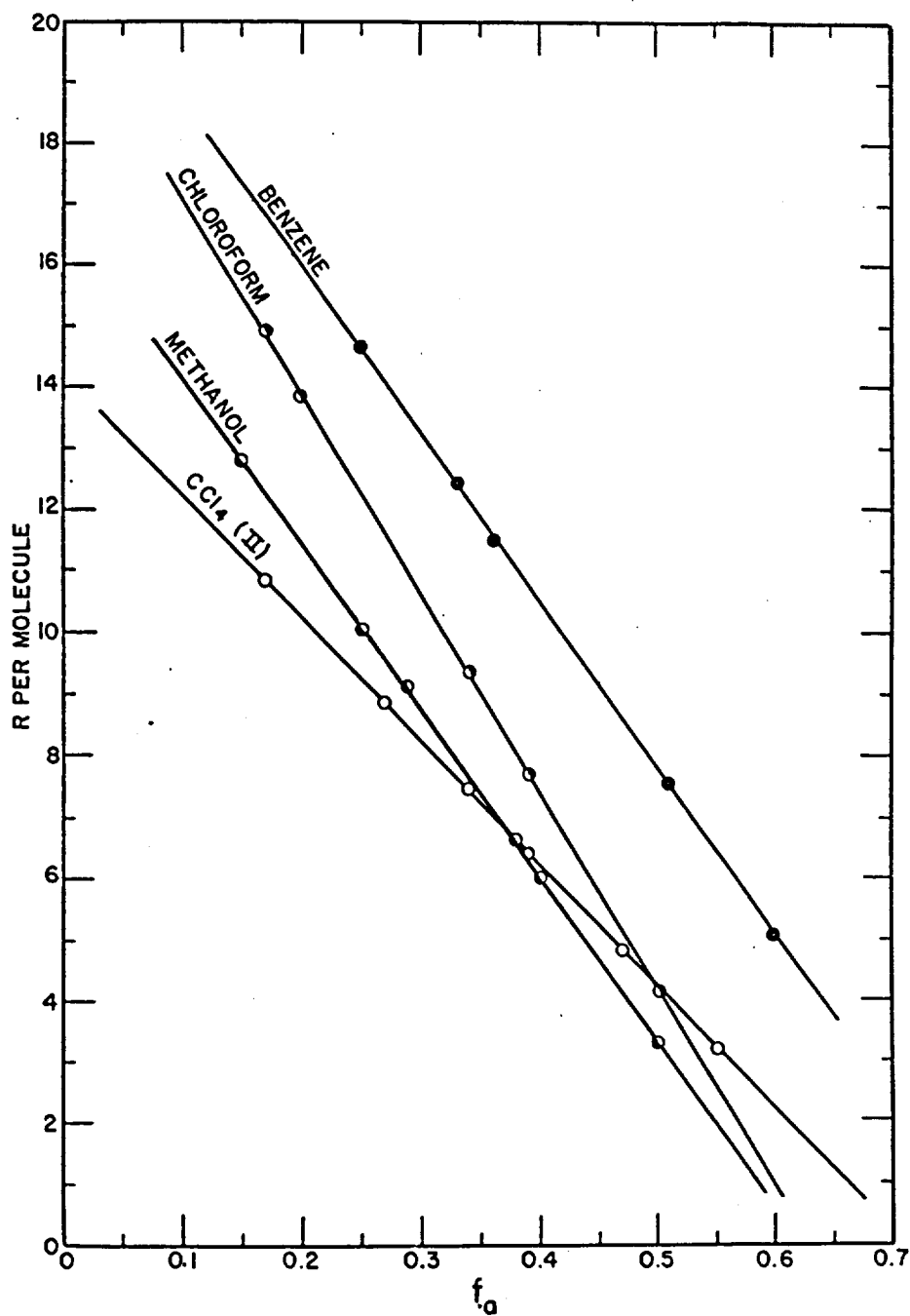


Figure 25. Rings/molecule versus  $f_a$  for the Montgomery-Boyd analysis of the resins (Scheme MB1).

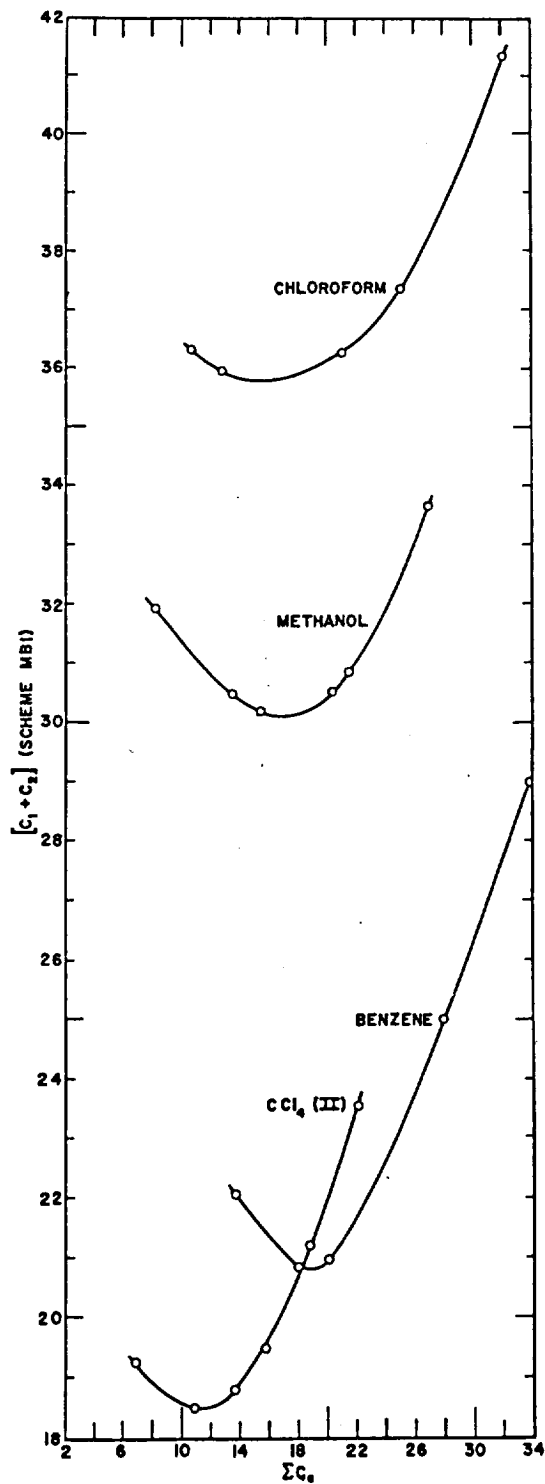


Figure 26.  $(C_1 + C_2)$  versus  $\Sigma C_a$  for the Montgomery-Boyd analysis of the resins (Scheme MB1).

TABLE 12

Montgomery-Boyd Analysis (MB1) of the Resins Expressed  
as Fractions of the Total Carbon

Fraction	$f_a$	$C_1 / \Sigma C$	$C_2 / \Sigma C$	$C_3 / \Sigma C$	$C_4 / \Sigma C$	$C_5 / \Sigma C$
C Cl <sub>4</sub> (II)	0.17 <sup>c</sup>	0.492	-0.0129	0.351	0.0318	0.138
	0.27	0.442	0.0169	0.270	0.151	0.119
	0.34 <sup>a</sup>	0.413	0.0547	0.194	0.213	0.126
	0.39 <sup>b</sup>	0.395	0.0905	0.125	0.246	0.144
	0.47 <sup>d</sup>	0.373	0.154	0.006	0.281	0.186
	0.55	0.356	0.230	-0.135	0.305	0.245
Benzene	0.25 <sup>c</sup>	0.449	-0.0465	0.347	0.099	0.151
	0.33 <sup>a</sup>	0.402	-0.0212	0.289	0.201	0.129
	0.36 <sup>b</sup>	0.383	-0.0005	0.252	0.234	0.131
	0.51 <sup>d</sup>	0.329	0.128	0.034	0.305	0.204
	0.60	0.305	0.224	-0.130	0.323	0.277
Chloroform	0.17 <sup>a</sup>	0.546	0.0179	0.268	0.00357	0.163
	0.20 <sup>b</sup>	0.534	0.0255	0.242	0.0410	0.158
	0.34 <sup>c</sup>	0.475	0.0891	0.0952	0.178	0.163
	0.39 <sup>d</sup>	0.456	0.124	0.0289	0.211	0.180
	0.50	0.420	0.223	-0.143	0.259	0.241
Methanol	0.15	0.604	-0.0111	0.257	-0.0307	0.181
	0.25 <sup>a</sup>	0.565	0.00167	0.182	0.0981	0.154
	0.29 <sup>b</sup>	0.550	0.0108	0.152	0.138	0.148
	0.38 <sup>c</sup>	0.514	0.0532	0.0537	0.225	0.154
	0.40 <sup>d</sup>	0.507	0.0664	0.0271	0.239	0.160
	0.50	0.477	0.148	-0.125	0.288	0.212

- a - van Krevelen Method I.  
 b - van Krevelen Method II.  
 c - infra-red, 6.25 $\mu$  band compared to  
 methyl naphthalenes (12 compounds).  
 d - van Krevelen Method III.

### Application of Criterion I

A review of the graphs in Figures 12-16 revealed that a considerable number of physically impossible solutions existed. It was found 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  $C_2 = 0$ . It is 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  $C_2$  became negative. It was noted also that at a very much lower value of  $\Sigma C_a$ ,  $C_4$  also became negative. These limiting values of  $\Sigma C_a$ , and the carbon-type composition corresponding to them, are listed below in Table 13 for the four resin fractions.

TABLE 13

Limiting Compositions of Resin Fractions by Criterion I

Fraction	$f_a$	$\Sigma C_a$	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$
C Cl <sub>4</sub> (II)	0.47	19.1	14.7	6.5	0.0	11.4	7.7
	0.225	9.2	18.5	0.0	12.2	4.1	4.95
Benzene	0.53	29.0	17.35	8.1	0.0	17.05	12.05
	0.36	20.3	21.0	0.0	13.4	13.0	7.3
Chloroform	0.41	26.4	28.8	8.65	0.0	14.3	12.15
	0.16*	10.6*	35.2	1.2	17.3	0.0	10.5
Methanol	0.423	22.6	26.9	4.4	0.0	13.5	9.0
	0.245	13.8	30.1	0.0	9.6	5.9	8.2

\* This limit corresponds to the value where  $C_4$  became negative. For this fraction,  $C_2$  did not become negative as in the other cases.

It was noted that the above upper limit for  $f_a$  corresponded very closely for each fraction to the value calculated by van Krevelen's graphical densimetric analysis. (The latter values were 0 to 2% lower.)

Application of Criterion II

As has already been stated, this criterion involves a consideration of the possible values of  $C_R/R$  calculated from the Ring Balance equation. A unique solution may be obtained by the

introduction of the following assumptions. It was assumed that, on the average, the resin fractions are composed of six-membered rings; that the ring balance equation  $C_3 + C_5 = 2R - 2$  is valid; and that, on the average,  $C_R/R = 4$ . This would then permit a unique solution. The significance of selecting  $C_R/R = 4$  has the following basis: The limiting value with increasing molecular weight for pericondensed six-membered rings is three and that for kata-condensed rings is 4, while the value corresponding to the lowest member of the kata-condensed series is 5. The value of  $C_R/R$  must be between these extremes of 3 and 5 unless a higher degree of condensation than pericondensation is envisaged.

Attention is drawn to the fact that the Waterman system of structural analysis for oils used this assumption of kata-condensed, six-membered rings. (42) Consequently, from Figure 24 ( $C_R/R$  vs  $f_a$ ) the value of  $f_a$  was read off corresponding to  $C_R/R = 4$  for each fraction. The unique set of values of  $C_1$  to  $C_5$  corresponding to this value of  $f_a$  were then read off the graphs in Figures 12-16 for each fraction. This procedure gave the set of compositions for the resin fractions, tabulated in Table 14.

TABLE 14

Composition of Resin Fractions by Criterion II ( $C_R/R = 4$ )

Fraction	$f_a$	$\Sigma C_a$	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$
C Cl <sub>4</sub> (II)	0.405	16.3	15.6	4.2	4.1	10.2	6.1
Benzene	0.446	24.4	19.1	3.5	7.4	15.45	9.0
Chloroform	0.365	23.5	29.8	6.6	4.0	12.5	10.95
Methanol	0.380	20.4	27.6	3.0	2.9	12.0	8.3

It is of interest to compare the results from the application of this criterion with the results in Table 13 from the application of the first criterion. In terms of the aromaticity, this second set of results essentially reduced the range of possible  $f_a$  values. The difference between the upper limit set in Table 13 and the values obtained in Table 14 was 6.5% for the C Cl<sub>4</sub> (II) fraction, 8.4% for the benzene fraction, 4.5% for the chloroform fraction, and 4.3% for the methanol fraction. It should be noted that the  $f_a$  values obtained by van Krevelen's graphical densimetric technique fell within this range; in fact, in most cases, the value fell almost at the midway point of this range.

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

The quantitative estimation of methyl and methylene groups from infra-red data was tabulated in Table 3. These data were used to estimate the aromaticity quantitatively in the following



manner: It was assumed that, to a first approximation, the sum of the methyl and methylene groups could be considered equal to  $(C_1 + C_2)$  in the present structural analysis system. The data in Table 3 thus permitted two estimates of  $(C_1 + C_2)$  to be made, one based on the 7.28 and 3.42  $\mu$  bands and the second based on the 3.50  $\mu$  band. Figure 26 is a plot of  $(C_1 + C_2)$  vs  $\Sigma C_a$  for the structural group analysis.  $\Sigma C_a$  values were read off this graph corresponding to the two values of  $(C_1 + C_2)$  from the infra-red data. These values of  $\Sigma C_a$  thus obtained have been tabulated in Table 15.

TABLE 15

Indirect Determination of the Aromaticity from Infra-red Data

Fraction	$(C_1 + C_2)$		$\Sigma C_a$ (Figure 26)	
	7.28 $\mu$ + 3.42 $\mu$	3.50 $\mu$	7.28 $\mu$ + 3.42 $\mu$	3.50 $\mu$
C Cl <sub>4</sub> (II)	20.3	17.2	17.3	-
Benzene	26.5	21.0	30.2	20.2
Chloroform	36.4	32.0	21.8	-
Methanol	28.1	25.4	-	-

It should be noted that in Table 15 no value was given for the methanol fraction from either absorption band, nor for the C Cl<sub>4</sub> (II) and chloroform fractions from the 3.50 $\mu$  band. For these cases the values of  $(C_1 + C_2)$  from the infra-red fell below the minimum value of  $(C_1 + C_2)$  allowable under the structural

analysis system (Figure 26). The values obtained from the absorption bands at  $7.28\mu$  and  $3.42\mu$  were considered to be more reliable than those obtained from the band at  $3.50\mu$ . The absorption band at  $3.50\mu$  was not nearly as well defined as those at  $7.28\mu$  and  $3.42\mu$ . For the purposes of the structural analysis use will be made only of the  $\Sigma C_a$  values derived from the  $7.28$  and  $3.42\mu$  bands.

Another estimate of  $\Sigma C_a$  was made from this same infrared data by the use of a further assumption. This second estimate of  $\Sigma C_a$  was made because of the failure of the first estimate to give a value of  $\Sigma C_a$  for the methanol fraction. In this second estimate, the sum of the methyl and methylene groups obtained from the  $7.28\mu$  and  $3.42\mu$  bands was considered the sum of all saturated carbon atoms in the molecule (i. e.  $C_1 + C_2 + C_3$ ). It was felt that this was justified by the small numerical values of  $C_3$  given in Table 13 (upper limit of  $\Sigma C_a$ ), and the fact that the  $\Sigma C_a$  values in Table 14 were only 4 to 8% lower than those in Table 13. In view of these facts, in this second estimate  $\Sigma C_a$  was taken as the difference between the total number of carbon atoms and the sum of the methyl and methylene groups (from the  $7.28 + 3.42\mu$  bands). These values are tabulated in Table 16. For convenience in making a comparison,  $\Sigma C_a$  values obtained by Criteria I and II are also tabulated here.

TABLE 16

Second Indirect Estimate of Aromaticity from Infra-red Data

Fraction	$\text{CH}_3 + \text{CH}_2$ (7.28 + 3.42 $\mu$ )	$\Sigma C_a = \Sigma C -$ ( $\text{CH}_3 + \text{CH}_2$ )	$\Sigma C_a$ Upper limit by Criterion I	$\Sigma C_a$ Criterion II
C Cl <sub>4</sub> (II)	20.3	19.9	19.1	16.3
Benzene	26.5	28.3	29.0	24.4
Chloroform	36.4	27.9	26.4	23.5
Methanol	28.1	25.7	22.6	20.4

Since  $\Sigma C_a$  values obtained from  $\Sigma C - (\text{CH}_3 + \text{CH}_2)$  will tend to be a high estimate by virtue of the approximations made, the figures obtained by this method would tend to support the values obtained by Criterion I (upper limit). The fact that the values from Criterion II were somewhat lower is probably evidence that the value of  $C_R/R$  for this type of material is slightly greater than 4.

To give a unique set of solutions of the structural analysis based on infra-red data,  $\Sigma C_a$  values for C Cl<sub>4</sub>(II), benzene and chloroform fractions were taken from Table 15 (7.28 $\mu$  + 3.42 $\mu$  values), and, for the methanol fraction, from Table 16. This set of compositions is tabulated in Table 17.

TABLE 17

Composition of Resin Fractions by Criterion III

Fraction	$\Sigma C_a$	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$
C Cl <sub>4</sub> (II)	17.3	15.3	5.0	2.8	10.6	6.6
Benzene	30.2*	17.4	9.3	-2.0	17.3	13.0
Chloroform	21.8	30.6	5.6	6.2	11.3	10.4
Methanol	25.7*	26.1	6.9	-4.5	15.0	10.7

\* These values are slightly higher than the upper limit set by the appearance of negative numbers. These values were hence considered as supporting evidence for this upper limit.

A summary of the compositions thus obtained is given in Table 18. This constituted defining the limits of the structure of these fractions.

By reviewing the compositions which have been given in Tables 13, 14, and 17, it was possible to define the limits of the structure of each fraction as determined by the various conditions. Criterion I set an upper and a lower limit, and these covered a considerable range. The results of Criteria II and III were very much closer to the upper limit than the lower from I, and for this reason the lower limit from Criterion I 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 18. The upper limit in each case corresponded to the

upper limit set by Criterion I. The lower limit for the  $C Cl_4$  (II), benzene and methanol fractions was set by Criterion II and for the chloroform fraction by Criterion III.

TABLE 18

Summary of Results by Scheme MB1

Fraction	$f_a$	$\Sigma C_a$	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$
$C Cl_4$ (II)	0.47-0.40	19.1-16.3	14.7-15.6	6.5-4.2	0.0-4.1	11.4-10.2	7.7 - 6.1
Benzene	0.53-0.45	29.0-24.4	17.3-19.1	8.1-3.5	0.0-7.4	17.0-15.4	12.0 - 9.0
Chloroform	0.41-0.34	26.4-21.8	28.8-30.6	8.6-5.6	0.0-6.2	14.3-11.3	12.2-10.4
Methanol	0.42-0.38	22.6-20.4	26.9-27.6	4.4-3.0	0.0-2.9	13.5-12.0	9.0 - 8.3

It is of interest to note the variation of the secondary structural parameters for the limiting structures whose compositions are summarized in Table 18. This information is given in Table 19.

TABLE 19

Structural Characteristics of the Resins for the  
Limiting Composition Range

Fraction	$f_a$	R	$C_R/R$	$C_4/C_5$	$C_2/C_3$
$C Cl_4$ (II)	0.47-0.40	4.8-6.3	5.2-3.93	1.40-1.68	$\infty$ - 0.9
Benzene	0.53-0.45	7.0-9.1	5.3-4.05	1.43-1.66	$\infty$ - 0.6
Chloroform	0.41-0.34	7.0-9.3	5.05-3.65	1.16-1.08	$\infty$ - 0.95
Methanol	0.42-0.38	5.4-6.6	4.94-4.0	1.48-1.45	$\infty$ - 1.0

One particularly striking fact about the preceding carbon-type compositions was the large proportion of the saturated carbon atoms which were present in linear and branched chains. If one considers the average of the two limiting compositions in each case, as representative of the average composition, then the C Cl<sub>4</sub>(II) fraction contained 36.6% linear and branched carbon chains and 18.4% cyclic saturated carbons; or, in other words, 66.5% of the saturated atoms are in linear and branched chains. Similarly, the benzene fraction contained 33.2% linear and branched carbons and 17.3% cyclic saturated carbons; that is, 65.0% of the saturated carbons occurred in linear and branched chains. In the chloroform fraction, 46.2% of the carbon atoms were in linear and branched form and 15.9% in the saturated cyclic form; that is, 74.4% of the saturated portion was linear and branched. For the methanol fraction, 50.6% of the total carbon atoms were linear and branched and only 9.5% were saturated cyclic; that is, 84.2% of the saturated atoms were linear and branched. In this discussion of the linear and branched portion of the molecule, it is of interest to take into consideration the quantitative estimates of terminal methyl groups which were made from the infra-red spectra (Table 3). In terms of the number of CH<sub>3</sub> groups per molecule, this quantity amounted to 7.0 for C Cl<sub>4</sub>(II), 10.0 for the benzene fraction, 12.2 for the chloroform fraction, and 10.8 for the methanol fraction. It was considered

that these values for  $\text{CH}_3$  represented the maximum number of linear chains possible. Consequently, it was possible to estimate the average chain length. This was calculated as  $C_1/\text{CH}_3$ . This quantity was 2.16 for the  $\text{C Cl}_4$  (II) fraction, 1.82 for the benzene fraction, 2.43 for the chloroform fraction, and 2.52 for the methanol fraction.

The results of the Montgomery-Boyd analysis (MB1) have indicated that the proportion of the saturated carbon atoms present in rings was comparatively small (9 to 19%) and that the upper limit of  $f_a$  predicted by this system corresponded to a carbon-type analysis in which  $C_3$  was zero. This suggested that the modified Montgomery-Boyd analysis (MB2) could be applied in this case (i. e., for the value of  $\Sigma C_a$  in which  $C_3$  is zero), since this system was especially designed for materials where  $C_3$  was known to be zero and  $C_2$  small. The results of this application were given in Table 10. This second structural analysis scheme was intended to illustrate the effects of changing the parameters of the system and to give some indication how the aromatic carbon atoms were distributed between fused and non-fused rings. The ratio  $C_5/C_7$  which was given in Table 10 may be taken as an indication of the relative proportion of fused aromatic rings to non-fused aromatic rings. This ratio was a convenient basis upon which to compare the fractions. It was

noted that  $\frac{C_5}{C_7}$  increased in passing from C Cl<sub>4</sub> (II), which had a value of 0.68, to a value of 2.60 for the methanol fraction.

This indicated that as one passed from C Cl<sub>4</sub> (II) fraction → benzene fraction → chloroform fraction → methanol fraction, the proportion of fused aromatic rings was increasing in relation to the number of non-fused rings. In other words, C Cl<sub>4</sub> (II) fraction would have the highest relative proportion of non-fused aromatic rings and the methanol fraction the lowest. The results of this second analysis would seem to provide a very logical basis for the chromatographic separation, since it is entirely reasonable that the higher the degree of condensation the more tightly the material would adhere to the adsorbent.

It should be noted that this second structural analysis (MB2) scheme did not predict the same distribution between C<sub>1</sub> and C<sub>2</sub> as did the first system (MB1). The second scheme predicted a much higher proportion of C<sub>1</sub>'s. This is probably due to the inherent assumptions in the second system. At the present time, there are few data available fulfilling the structural requirements of the second system on which to test its accuracy. On the other hand, the accuracy of the MB1 scheme on API42 compounds is known, but it is not known whether the substances being analyzed are of this type, so that assessment of accuracy in an absolute sense is a difficult matter.



The results of the second analysis which pertain to the degree of condensation are further substantiated by the infra-red spectra, in particular from the  $f_a$  values calculated from the  $6.25\mu$  absorption band. The range of  $f_a$  values given in Table 18 were compared with the  $f_a$  values in Table 4 (calculated from the  $6.25\mu$  absorption band). On this basis of comparison, the C Cl<sub>4</sub> (II) and the benzene fractions resemble the non-fused aromatic class and the chloroform and methanol fractions correspond to fused aromatics with side chains. In this respect, therefore, the infra-red results are in essential agreement with the structural analysis results.

Another interesting structural feature is the ratio  $R_A/S$ , the number of aromatic rings per sulphur atom, which gives some indication of the manner in which the sulphur is associated with the aromatic ring structure. This ratio was calculated for the solution of the MBI system corresponding to the  $\Sigma C_a$  value which gave  $C_3 = 0$ . These results are given in Table 20.

TABLE 20

Determination of  $R_A/S$  for the Resin Fractions

Fraction	$\Sigma S$	$R_A$ [MBI system] $C_3 = 0$	$R_A/S$
C Cl <sub>4</sub> (II)	1.28	4.7	3.67
Benzene	1.76	7.0	3.98
Chloroform	2.05	7.0	3.41
Methanol	1.81	5.5	3.04

It is rather noteworthy that the ratio changes only very slightly over the entire range of the resin fractions. This would suggest that the sulphur atom probably occurs associated with the aromatic rings in some repetitive fashion in the resin molecules.

Conclusions Concerning the Structure  
of the Resin Fractions

1. Van Krevelen's densimetric analysis predicted the C Cl<sub>4</sub> (II) fraction to have 39% aromatic carbon atoms and 6.4 rings per molecule, the benzene fraction to have 36% aromatic carbon atoms and 11.5 rings per molecule, the chloroform fraction to have 20% aromatic carbon atoms and 13.9 rings per molecule, and the methanol fraction to have 29% aromatic carbon atoms and 9.1 rings per molecule.

2. Van Krevelen's "Graphical Densimetric Method" resulted in the C Cl<sub>4</sub> (II) fraction having 47% aromatic carbon atoms and 3.8 rings per molecule, the benzene fraction, 51% aromatic carbon atoms and 6.6 rings per molecule, the chloroform fraction, 39% aromatic carbon atoms and 6.8 rings per molecule, and the methanol fraction, 40% aromatic carbon atoms and 5.1 rings per molecule.
3. The Montgomery-Boyd "five-parameter" structural analysis system MB1, designed for fused-ring systems in conjunction with infra-red data and certain assumptions pertaining to C<sub>R</sub>/R, has defined the aromaticity and the carbon-type composition for each of the resin fractions, within the following limits:

Fraction	% $\Sigma C_a$	% C <sub>1</sub>	% C <sub>2</sub>	% C <sub>3</sub>	% C <sub>4</sub>	% C <sub>5</sub>
C Cl <sub>4</sub> (II)	47-40	36.6-38.8	16.2-10.4	0-10.2	28.4-25.4	19.2-15.2
Benzene	53-45	31.6-34.8	14.8- 6.4	0-13.5	31.0-28.1	21.9-16.4
Chloroform	41-34	44.8-47.6	13.4- 8.7	0- 9.6	22.2-17.6	19.0-16.2
Methanol	42-38	50.0-51.3	8.2- 5.6	0- 5.4	25.1-22.3	16.7-15.4

4. To illustrate the effect of changing the parameters, a second five-parameter system was applied to the resin fractions. This gave an estimate of the number of aromatic fused-ring junction carbon atoms (C<sub>5</sub>) as compared to aromatic non-fused-ring junction carbon atoms: C<sub>5</sub>/C<sub>7</sub> was determined to be 0.68 for the C Cl<sub>4</sub> (II) fraction, 1.03 for the benzene fraction, 1.57 for the

chloroform fraction, and 2.60 for the methanol fraction. This system gave the following compositions for each fraction:

Fraction	% C <sub>1</sub>	% C <sub>2</sub>	% C <sub>4</sub>	% C <sub>5</sub>	% C <sub>7</sub>
C Cl <sub>4</sub> (II)	43.5	9.5	29.1	7.5	10.9
Benzene	40.3	6.8	31.0	11.1	10.8
Chloroform	50.1	8.9	22.9	11.5	7.3
Methanol	53.1	4.8	25.3	12.1	4.6

- The average side chain length was estimated to be 2.16 for the C Cl<sub>4</sub> (II) fraction, 1.82 for the benzene fraction, 2.43 for the chloroform fraction, and 2.52 for the methanol fraction.
- The ratio  $R_A/S$  was found to be essentially constant for all the fractions. The average value was 3.5.

#### ACKNOWLEDGMENTS

The authors wish to express their thanks to Miss F. E. Goodspeed for the spectral measurements, to Dr. L. H. King for the refractive index and density measurements, and to Mr. M. P. Pleet for technical assistance.

## REFERENCES

- (1) Boyd, M. L. and Montgomery, D. S., Mines Branch Research Report R78, Dept. Mines and Technical Surveys, Ottawa, Canada, November 1961.
- (2) Boyd, M. L. and Montgomery, D. S., Internal Report, Fuels Division, Mines Branch, Dept. Mines and Technical Surveys, Ottawa, Canada, June 1951.
- (3) Mair, B. J., J. Res. Natl. Bur. Stds. 34, 435 (1945).
- (4) Smit, W. M., Chromatographic Analysis; Discussions of the Faraday Society, No. 7, 248 (1949).
- (5) Marcusson, J., Z. angew. Chemie 29, 346, 349 (1916)
- (6) Grader, R., Oel u Kohle 38, 867 (1942).
- (7) Hubbard, R. L. and Stanfield, K. E., Anal. Chem. 20, 460 (1948).
- (8) Kriehle, V. K. and Seyer, W. F., J. Am. Chem. Soc. 43, 1337 (1921).
- (9) Katz, M., Can. J. Res. 10, 435 (1934).
- (10) Pasternack, D. S. and Clark, K. A., Report #58, Alberta Research Council, Edmonton, Canada, 1951.
- (11) Streiter, O. G., J. Res. Natl. Bur. Stds. 26, 415 (1941).
- (12) Gishler, P. E. and Matchen, B., Report #C51-51S, National Research Council of Canada, Ottawa, June 1951.
- (13) Weil-Malherbe, H., J. Chem. Soc. p. 303 (1943)
- (14) LeRosen, A. L., J. Am. Chem. Soc. 69, 87 (1947).
- (15) Dickey, F. H., Proc. Natl. Acad. Sciences 35, 227 (1949).  
Pauling, L., J. Am. Chem. Soc. 62, 2643 (1940).
- (16) Trappe, W., Biochem. Z. 307, 97 (1940).

- (17) Pfeiffer, J. Ph., *The Properties of Asphaltic Bitumen* (Elsevier Publishing Co., New York, 1950).
- (18) Brockmann, H. and Schodder, H., *Ber.* 74, 73 (1941)
- (19) Reference 1, Table 4, Experiment 2, p. 23.
- (20) Karr, C. Jr., private communication.
- (21) Friedel, R. A. and Orchin, M., *Ultraviolet Spectra of Aromatic Compounds* (John Wiley and Sons, Inc., New York, 1951).
- (22) Goodspeed, F. E., Internal Report FMP-60/170-RBS, Fuels and Mining Practice Division, Mines Branch, Dept. Mines and Technical Surveys, Ottawa, Canada, 1960.
- (23) Triebs, A., *Liebig's Ann. der Chemie* 509, 103 (1934); 510, 43, 50 (1934); 517, 172 (1935); and 520, 144 (1935).
- (24) Skinner, D. A., *Ind. Eng. Chem.* 44, 1159 (1952).
- (25) Burdett, R. A., Taylor, L. W. and Jones, L. C. Jr., *Molecular Spectroscopy; Report of a Conference Organized by the Spectroscopic Panel of the Hydrocarbon Research Group of the Institute of Petroleum, London, Oct. 28-29, 1954.*
- (26) Brandes, G., *Erdöl u Kohle* 11, 700 (1958).
- (27) Maule, C., *Beiträge wiss. Bot.* 4, 166 (1900).
- (28) Krevelen, van, D. W., *Fuel* 29, 269 (1950).
- (29) Krevelen, van, D. W. and Schuyer, J., *Coal Science* (Elsevier, New York, 1957), chapter VII.
- (30) *Ibid*, pp. 156-158.
- (31) *Ibid*, p. 160.
- (32) Krevelen, van, D. W. and Chermin, H. A. G., *Fuel* 33, 338 (1954).
- (33) Krevelen, van, D. W., *Brennstoffe-Chemie* 33, 260 (1952).

- (34) Varga, J., Hesp. V. and Haidegger, E., Brennstoffe-Chemie 37, 363 (1956).
- (35) Padovani, C., Berti, V. and Prinetti, A., Paper 21, Section V, Fifth World Petroleum Congress, New York (1959).
- (36) Montgomery, D.S. and Boyd, M.L., Anal. Chem. 31, 1290 (1959).
- (37) Krevelen, van, D.W., Brennstoffe-Chemie 34, 167 (1953).
- (38) Boyd, M.L. and Montgomery, D.S., J. Inst. Petr. 45, 345-72 (1959).
- (39) Mazumber, B.K., Chakrabarty, S.K. and Lahiri, A., Fuel 38, 115 (1959).
- (40) Krevelen, van, D.W., Goldkoop, M.L. and Palmer, P.H.G., Fuel 38, 256 (1959).
- (41) Rona, V., Fuel 39, 187 (1960).
- (42) Vlugter, J.C., Waterman, H.I. and van Westen, H.A., J. Inst. Petr. Tech. 21, 661-76 (1935).
- =====  
 (26) Krevelen, van, D.W., Fuel 39, 187 (1960).  
 (27) Mante, C., Beitrage wiss. Bot. 4, 166 (1900).  
 (28) Krevelen, van, D.W., Fuel 39, 269 (1960).  
 (29) Krevelen, van, D.W., Fuel 39, 269 (1960).  
 (30) Ibid, pp. 156-158.  
 (31) Ibid, p. 160.  
 (32) Dickey, F.H., Proc. Natl. Acad. Sciences 35, 222 (1949).  
 (33) Krevelen, van, D.W., Brennstoffe-Chemie 33, 280 (1952).

MLB:DSM:(PES)PH