A STUDY OF THE SEPARATION AND ESTIMATION OF THE

FOUR GENERAL CLASSES OF HYDROCARBONS OCCURRING IN THE

GASOLINE RANGE OF PETROLEUM

By

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INTRODUCTION

In the refining of crude oils and the production
of gasolines, solvent naphthas and paint thinners by pressure
pyrolysis, there has been an ever increasing need for an
accurate and quick method for the analysis of the product
formed. Methods of analysis available in the past were suf-
ficiently rapid because changes in operating conditions were
neither so frequent nor so readily made as today. At present
many investigations are carried out in small units wherein
the operating conditions can be changed at will. This
frequently requires methods of analyses that are accurate and
yet do not cause a delay by being too time consuming.

As in almost all cases where accurate and quick
results are desired, there must be a balance between accuracy
and speed. A rapid method may not always give results which
represent the true composition, but it should give results
which are consistent and bear a definite relationship to a
true composition. When exact analyses are required, methods
may be used that are more extensive and far more time con-
suming. However, some of the more extensive methods may not
always yield results which represent the exact composition
of the material.

In this study existing methods have been investi-
gated and a procedure for the analysis of petroleum fractions
embodying new features and refinements of the existing methods

has been devised.

HISTORICAL

A logical classification of the constituents of petroleum commonly encountered is the division into four general hydrocarbon groups: (a) unsaturated, (b) aromatic, (c) naphthene and (d) paraffin. This classification is not without fault because there exists many hydrocarbons which are in nature both olefinic and aromatic, olefinic and naphthenic, and aromatic and naphthenic, etc. However, the amount of these particular hydrocarbons occurring in gasoline fractions is usually small and may be neglected. If they are thought to be present in large amounts, special methods may be used for their determination.

Olefin Hydrocarbons

The unsaturated hydrocarbons may be determined in
two general ways, that is, either by titration with bromine
or iodine or by chemical absorption with reagents such as
sulfuric acid or sulfur monochloride.

Halogenation Methods.

The sample may be titrated using either bromine or
iodine. The reaction time for iodine is exceedingly large
and this necessitates a large excess of iodine. Reaction
conditions of this nature lead to substitution reactions
which gives incorrect results. The conditions for this
reaction have been standardized but they probably result in
an approximate balance between the unreacted olefins and the
substitution reaction in saturated compounds. When bromine
is used in the place of the iodine, there is a still greater
difficulty in avoiding substitution. Methods have been
devised wherein the hydrogen bromide so formed is measured
but these are unreliable and very cumbersome. There is also
some difficulty in keeping bromine solutions at a uniform
strength, whether the solvent is water or an organic liquid.

Francis (19) however, has devised a method in which
these difficulties may be overcome. In this method a standard
solution of potassium bromate and potassium bromide is used
which, if properly stored, holds its strength indefinitely.

When an acid is added to the bromate-bromide, bromine is generated, the rate depending upon the strength of the acid. By making the solution only slightly acid, the bromine can be generated slowly. The mixture is agitated very vigorously so that the generated bromine is consumed by the double bonds fast enough to keep it at a very low concentration, thus avoiding substitution reactions. Substitution must be kept at a minimum for reliable results.

In this method the reagent is not miscible with the oil. This is not detrimental and may help in avoiding substitution. However, it does make vigorous agitation necessary.

The bromine is generated from an acidified bromate-bromide solution according to the following equation:-

$$KBrO_3 + 5KBr + 3H_2SO_4 \longrightarrow 3K_2SO_4 + 3H_2O + 3Br_2$$

In the titration it is immaterial whether dibromide or bromohydrins are formed, as may be seen from the following equations:-

$$RCH = CHR' + Br_2 + H_2O \nearrow RCHBrCHBrR' + H_2O$$
$$\searrow RCHBrCHOHR' + HBr$$
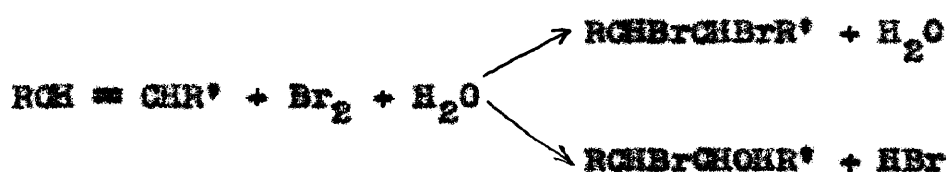
The method is described by Francis as follows:-

"A slight excess (preferably not more than 1cc. as estimated from a trial titration) of the bromide-bromate solution

is measured into a small Erlenmeyer flask,
and the sample of oil, 3 to 50cc., de-
pending upon the unsaturated content, is
pipetted in. The solution is quickly acidi-
fied with about 5cc. of 10% sulfuric acid,
and the flask is stoppered. It is shaken
for one minute as vigorously as may be
necessary to keep the color a pale yellow.
If the color is dark yellow in spite of vio-
lent shaking, too much bromide-bromate has
been added and the analysis should be con-
sidered only a trial titration. In any
case, in order to complete the liberation
of bromine, 15cc. more of acid are added
and the shaking is continued for another
minute. If the solution remains colorless,
a little more bromide-bromate solution is
added. The final color should be light
yellow. One or two cubic centimeters of
saturated potassium iodide are added, and
the iodine liberated is titrated with thio-
sulfate, using vigorous shaking near the
end of the titration to extract the iodine
from the oil layer.

"A few of the results by this
method are shown in Table I. In the
latter part of the table, known mixtures
of a straight-run and a cracked gasoline
were made up and titrated. The "calcu-
lated" figures assumes that the analyses
on the pure gasoline were correct."

TABLE I

Estimation of Unsaturates in Pure Compounds
and Known Gasoline Mixtures

	Found %	Calculated %
Pure trimethylethylene	100.6	100.0
Hexene (containing some pentene)	103.0 103.5	103.0 103.0
Neutral White Oil (Nujol)	0.04	0.0
(A) Straight Run Texas Gasoline	0.90 0.86	
(B) Cracked Gasoline	47.1 47.5	

Known mixtures of A and B

A per cent	B per cent		
22	78	36.9	36.9
36	64	30.7	30.3
59	41	19.5	19.2
74	26	12.73	12.60
81	19	9.17	9.31
85	15	7.29	7.43
85	15	7.32	7.43

The extent of the applicability of the Francis bromide-bromate method has been tested by Cortese (11). Two modifications of the procedure were developed in this work and are given here as they are more detailed and would prove more useful to a person unfamiliar to the method.

Procedure A

"The number of ccs. of the
bromide-bromate solution needed to satu-
rate the sample for analysis is calculated.
This amount and one cc. more are delivered
into a 150cc. glass stoppered Erlenmeyer
flask, which is then set in ice water. One
cc. of the sample, whose temperature and
density are known, is added with a cali-
brated pipette. Five cc. of 10% H_2SO_4 are
run in quickly, the flask stoppered, with-
drawn from the cold bath, shaken until the
color disappears, and returned to the bath.
As the color reappears, the flask is shaken
to destroy it. When the color is persistent,
the contents are shaken for one more minute.
(The total time of the bromine treatment up
to this point varies from 7 to 30 minutes.)
Ten cc. more of 10% H_2SO_4 are added and the
flask is stoppered at once. It is shaken
one minute, one cc. of saturated KI solution
added, and shaken one more minute. The
liberated iodine is titrated with thiosulfate
and starch indicator to the first colorless
end-point, shaking vigorously towards the
end. The starch-iodine color reappears
quite soon in most cases."

Procedure B

"This procedure is useful where
only small amounts of material are avail-
able. The procedure is practically identi-
cal with A. One cc. of sample is diluted
with 10cc. of pure carbon tetrachloride.
Then an aliquot portion of one cc. is taken
for each analysis. Only 0.1 to 0.2cc.
excess bromide-bromate solution is used.
When the carbon tetrachloride assumes a
permanent faint yellow color, the flask
is shaken for 3 minutes, and the analysis
finished as in A. There is usually a small
blank which may or may not be appreciable.

"In the B procedure N/10
bromide-bromate is used in place of N/2."

The results of Cortese are given in Table II.

TABLE II

Substance	No. of double bonds found by procedure		Theoretical double bonds
	A	B	
Pentene (2)	0.99	0.99	1.00
Trimethylethylene	1.00	1.02	1.00
Decene (1)	--	0.84	1.00
Cetene (1)	--	0.94	1.00
Hexadiene (1,5)	1.94	1.98	2.00
Hexadiene (2,4)	1.94	1.94	2.00
2-Methylpentadiene (2,4)	1.90	--	2.00
Dipentene	1.82	--	2.00
Indene	--	0.83	2.00
Furane	--	1.04	2.00
Phenyl butadiene polymer	--	1.00	2.00

It can be seen from this table that aliphatic ole-
fins and aliphatic diolefins, whether conjugated or not, were
accurately shown to contain the required number of double
bonds by employing this method. However, the method at pre-
sent is unreliable for certain ring structures and higher
polymers.

Mulliken and Wakeman (47) modified the procedure

of the Francis method in that all of the sulfuric acid was added at the beginning of the titration. Their results further substantiates those of Cortese and Francis.

Lewis and Bradstreet (37) have proposed a method which eliminates the cooling of the sample during titration. The results for the compounds tested are concordant with those already published; although it would be interesting to see how the method works over a more extensive range of compounds.

If it be desired to make a separate measurement of halogen addition and substitution, the bromine number method of McIlhiney (39) is the most suitable and depends upon the fact that for each atom of hydrogen replaced by bromine, one molecule of hydrogen bromide is formed. By estimation of this free acid as well as the total amount of bromine absorbed, data are obtained for calculating both the bromine taken up by direct addition and the bromine taken up by substitution. Waterman, Spijker and Westen (75) and Waterman and Westen (74) have shown that the method is capable of giving results that agree with the theoretical values.

Various methods and modifications of the methods given may be used to correctly determine the olefin content of an oil, but it is to be recognized that the bromine or iodine values, at the best, only yield the concentration of the double bonds present and not the weight or volume of olefine

present. For example, a diolefin which contains two double bonds would consume twice as much halogen as a mono-olefin. It would necessarily be calculated as a mono-olefin which would result in a value for the olefins twice as large as actually present.

In order to convert the bromine number to the weight basis, a molecular weight for the olefins must be known. When converting to the volume basis, both molecular weight and density of the olefins must either be known or assumed.

Chemical Absorption Methods.

The general chemical method of determining olefins is one of contraction, either on a weight or volume basis. While this contraction is essentially due to chemical combination some contraction will result from physical absorption.

One of the best known methods which is based on contraction is that of Faragher, Morrell and Levine (16). In this method olefins and aromatics are determined simultaneously by using sulfuric acid of 91 and 98% (by weight). Sulfur monochloride is used to remove the olefins from the original sample. The procedure for this method of analysis is as follows:-

> "Step 1 - Shake 100cc. of the
> oil with 3 volumes of 91 per cent sul-
> furic acid for 30 minutes. Withdraw the

acid and note the reduction in volume of
the oil. Distill the oil to a point 5
degrees above the former end-point of the
oil to separate the unchanged oil from
the polymers formed in the acid treatment.
Finally, shake the distillate with 3 volumes
of 98 per cent acid to remove the small
amounts of olefins and aromatic hydrocarbons
that escaped the previous treatment. The
total reduction in volume represents the
olefins and aromatic hydrocarbons in the
oil.

"Step 2 - Add sulfur monochloride
to the oil and allow them to remain in con-
tact over night. Distill the mixture at an
atmospheric pressure for the low boiling por-
tions and then under reduced pressure. This
procedure separates the olefin-sulfur mono-
chloride reaction products from the oil."

The content of aromatic hydrocarbons in the distil-
late is then determined by nitration.

The olefin and aromatic contents are calculated by
means of the formulas

$$U = \frac{100 \ (S - A')}{100 - A'}$$

$$A = S - U$$

Where U and A are the actual percentages of olefin
and aromatic hydrocarbons, respectively, in the oil, S is
the sum of the olefin and aromatic hydrocarbons (Step 1) and
A' is the aromatic content of the olefin free oil (Step 2).

This method is subject to the following criticism.
In the treatment of oils with 91 per cent sulfuric acid,
condensation products as well as polymerization products are

formed. Redistilling to a temperature 5 degrees above the original end-point removes both of these products. Any aromatics that are removed by condensation are, of course, lost from the analysis and will yield results that are low in aromatic content. The reacting time for the sulfur mono-chloride is quite long which is not desirable where quick analyses are needed. The technique required for vacuum distillation is quite involved and not easily performed by routine analysts. Moreover, losses under vacuum distillation may be quite large even when the best of technique is used in the manipulation of the apparatus. There is also some doubt as to the completion of reaction in the case of the higher boiling olefins and also to the stability of these compounds after reaction. It may also be noted that in correcting for polymers by distilling to a temperature 5 degrees above the original end-point it is quite possible for some of the lower boiling dimers and trimers to distill before the end-point of the distillation. This factor could be quite serious in a sample of wide boiling range but probably would not be encountered where the sample was cut into several fractions.

One of the most widely used reagents for absorbing olefins from oils is sulfuric acid. The olefins react with sulfuric acid to give alkyl sulfuric esters, alcohols, paraffins, alkylated cyclo compounds and polymers. It has been shown that in the aliphatic hydrocarbon series the tendency to form alkyl sulfuric esters and alcohols decreases with

increasing molecular weight. In general, the higher boiling olefins are much less reactive (6)(43). Polymerization of some pure olefins using various strengths of sulfuric acid has been studied by Brooks and Humphrey (6). They have shown that the tendency towards polymerization increases with increasing molecular weight. Houghton and Bowman (27) have substantiated this work and also found that polymerization increases with increase in concentration of the acid, the maximum polymerization taking place in the presence of 91 per cent acid. Alkylation of olefins both in absence and presence of aromatics by sulfuric acid has been studied by Ormandy and Craven (51). They state that amylene and heavier olefins occurring in cracked spirits yield large proportions of saturated hydrocarbons of higher boiling point and not olefins polymers as has previously been assumed. In the presence of olefins, aromatics are not entirely removed by sulfuric acid but condense partly with the olefine to form alkylated hydrocarbons.

The formation of saturated hydrocarbons has been observed previously by Maquenne (42) and Remard (52). That paraffin hydrocarbons are formed from the condensation of olefins has been questioned by other workers (43). It was observed by Kramer and Spilker (34) that in the presence of concentrated sulfuric acid, styrene and the xylenes condensed to form styro-xylenes. Condensation of benzene and hexene has been studied by Brooet (5). Several tests were

conducted by Brame (3) using sulfuric acid of strengths
which are generally used for the estimation of olefins. They
found that when 85 per cent acid was used, 30 per cent of the
aromatics originally present in the petrol were removed while
over 50 per cent were removed when 88 per cent acid was em-
ployed. The results of his experiments are not, however,
conclusive for Brame did not determine the absorption of
aromatics alone, using the specified acid strengths. Further
studies on alkylation have been made by Spilker (60). Due to
the fact that aromatics are sulfonated by concentrated sul-
furic acid and that the more deleterious reactions of olefins a
and aromatics are thought to occur at the higher concentrations
of acid, numerous methods have been proposed utilizing acids
of lower strength.

The procedure of Egloff and Morrell (14) is typical
of most of the methods utilizing sulfuric acid. This pro-
cedure is as follows:-

A 500cc. charge of oil is distilled
through a Hempel column containing glass beads until the
temperature of the vapor at the top of the column is 210°C.
The residue is discarded. This temperature is purely arbi-
trary and any other may be employed, providing it is used
throughout the analysis.

The 210°C. fraction is treated with 80 per
cent sulfuric acid, using a ratio of acid to oil of 2 to 1.

The mixture is agitated for 15 minutes, allowed to settle, and the acid layer separated. The volume of the oil layer is measured and the per cent decrease of this volume calculated on the basis of the 210°C. fraction. This calculation gives the percentage of the unsaturated hydrocarbons that have dissolved in the acid layer as reaction products.

The acid-treated oil is washed with water, neutralized with a 10 per cent solution of sodium hydroxide, and then redistilled in the same apparatus until the vapor temperature in the Hempel column reaches 210°C. The volume of the residue of the second fractionation up to 210°C. is calculated as a percentage of the first 210°C. fraction, and is assumed to be the percentage of the olefins that have been polymerized during the acid treatment. This, added to the percentage of the unsaturated hydrocarbons dissolved by the sulfuric acid, gives the total percentage of the unsaturated hydrocarbons in the original 210°C. fraction of the oil.

Towne (66) proposed a method in which 93 per cent acid is used. This method was devised by standardizing the time of contact necessary to remove as great a quantity of the olefins as it is possible to remove using 93 per cent acid. The method of standardization consisted of the absorption of olefins and aromatics followed by the determination of the aromatics as barium salts using barium hydroxide.

In order to correct for these alkylation or con-

densation effects, Towne devised a method wherein the distillation to determine polymerized olefins was applied after treatment with 98 per cent sulfuric acid or after aromatic and olefin removal. The per cent aromatics is given by the difference between the 93 per cent and the 98 per cent sulfuric acid absorption. This gives a partial correction for alkylated products but certain polymerization products are also absorbed by 98 per cent sulfuric acid.

Riesenfeld and Bandte (56) have suggested the use of 94 per cent sulfuric acid but they admit the method is unsuitable when the olefin content exceeds 5 per cent.

Brame and Hunter (4) used a method in which the determination of olefins depended upon the per cent loss to 85 per cent sulfuric acid in a Babcock bottle.

Morrell and Levine (46) devised a method in which 91 and 98 per cent sulfuric acid were used to determine olefins and aromatics. The olefin content is calculated from the weight of residue remaining after distillation of the oil obtained upon treatment with 91 per cent sulfuric acid by the use of empirical formulas developed in this work. It is quite possible that these formulas would not be valid for oils having widely different characteristics than those used in developing the empirical relationships. Numerous other methods have been advanced using sulfuric acid of various strengths with redistillation (49)(38)(22).

There has always been considerable doubt as to the strength of acid necessary to effect the complete removal of olefins. Ormandy and Craven (50) treated oils with sulfuric acid of various strengths and found that the density and refractive index of the residual oil after acid treatment rose until the acid strength reached 88 per cent. At higher strengths acid extraction of aromatic occurred causing a decrease in density and refractive values.

Fisher and Eisner (17), utilizing the idea of Ormandy and Craven (50) have developed a graphic method of characterizing oils, based on changes in volume and physical constants caused by the progressive removal of olefins and aromatics. The density and refractive index rise to maximum values at a point of complete olefin and incipient aromatic removal. Beyond this point the values fall as the aromatics are removed, becoming approximately constant when the residual oil consists of only saturated hydrocarbons. The olefin content is indicated by the volume change to the point of maximum values for the physical constants. It is doubtful whether the maximum value always indicates the olefin content because the residual oil will almost invariably have a definite bromine number indicating that all of the olefins have not been removed.

Moore and Hobson (44) found that 88-90 per cent acid was essential for the complete removal of olefins while Riesenfeld and Bandte (55) state that 92-94 per cent is required. It

is known, however, that sulfuric acid of this strength will react with aromatic hydrocarbons. In fact, according to Reuter (53) m-xylene is soluble in 80 per cent sulfuric acid. It has been proved by Howe (28) that it is impossible to select an acid concentration that will completely remove olefins and yet not react with the aromatics.

A method was suggested by Kattwinkel (32) in which boric acid was used with concentrated sulfuric acid. Indications are that the aromatics are not absorbed but that olefin removal is not complete. It is believed that the boric acid has no inhibiting action upon alkylation.

Aromatic Hydrocarbons

Methods Involving Physical Phenomena.

One of the best known methods used for benzene, toluene and xylenes is that in which percentages are determined by differences in specific gravities. The general procedure for this method is given by Rittman, Towney and Egloff (57). The oil to be tested is distilled into fractions cut at 95°, 120°, and 150°C. These fractions contain benzene, toluene and xylenes respectively. The value of the specific gravity of these three aromatics had previously been determined and the specific gravity of the non-aromatic portions were assumed to be 0.72, 0.73 and 0.76, respectively. The per cent aromatics is given by the following formula:-

$$\% \text{ aromatics} = \frac{\text{Sp.Gr. of fraction-Sp.Gr. Non-aromatics}}{\text{Sp.Gr. pure aromatics-Sp.Gr. Non-aromatics}} \times 100$$

In the method so proposed, the assumed aromatic free bases would not necessarily be of such values as are given. The final specific gravity would depend upon the naphthene and paraffin content and would only be relatively constant for an oil of the same origin and treatment.

Thole (62) modified the above procedure because the expression for the percentage of aromatics is based upon the assumption that the specific gravity-composition curve of mixtures of aromatic and non-aromatic hydrocarbons is a straight line, which is not the case, the specific gravity being

slightly less than that calculated according to the law of mixtures. The deviations were corrected by the construction and use of "a deviation curve".

The results of Thole have been substituted by Colman and Yeoman (10) who also made a more intense study of the "deviation" curve. Refinements to the use of the "deviation" curves are given by Dobryanski and Petrova (13).

Specific gravity methods for determining aromatics are limited to benzene, toluene and xylene because the mixtures containing other aromatics may be so complex that it is impossible to assign a definite accurate value of specific gravity to a mixture of high boiling range because of the variations in specific gravity between individual aromatics present.

Similar methods employing refractive index have been suggested for the determination of the per cent aromatics in oils. The general formula is practically the same as that for specific gravities in which initial indices of refraction are determined and the refraction index of the pure aromatics is known from literature values. These methods suffer the same limitations as specific gravity methods since the refractive indices of the aromatics above the xylenes vary widely.

By using mixtures containing known amounts of toluene and benzene, Karpinski (31) has worked out tables giving

the percentages of toluene and benzene when the refractive index of the mixture is known. Other workers (65)(58) have verified the use of refractive index for quick and accurate measurement of the per cent aromatic in hydrocarbon mixtures. Karpinski (30) and Barker (2) used refractive indices to give indications of the presence or absence of aromatics and was used as a rough estimation of the amount of aromatics present.

Index of refraction was employed by Hoyte (29) for the analysis of aromatic concentration in gasolines. The refractive index of the sample was measured and the aromatics removed by a standard method. The refractive index of this aromatic freed portion was then measured. A known volume of a 50/50 mixture of benzene and toluene was added to a known volume of the aromatic free sample so that the refractive index of the mixture was almost equal to that of the original sample. From these measurements, it is possible to calculate the per cent by volume of aromatics in the original sample.

This method is based on the assumption that a 50 per cent benzene and 50 per cent toluene mixture has a refractive index which is approximately the mean for the aromatics likely to be present in gasolines. From the more recently computed data pertaining to the index of refraction of pure aromatic hydrocarbons, it appears that the assumption made above is quite questionable except for a very limited boiling range.

Schneider, Stanton and Watkins (59) have devsied a

method for the analysis of aromatics using a plot of specific
gravity at 25°C. against refractive index at 20°C. for pure
paraffins, naphthenes and aromatics in the gasoline boiling
range from assembled data, resulting in three curves on one
figure. The sample was fractionated and the volume per cent,
specific gravity, refractive index and bromine number were
determined by bromate-bromide and the specific gravity and
refractive index were corrected for unsaturation by sub-
tracting 0.0254 and 0.028 respectively for each double bond
per mol from the determined values. The calculation is made
by solving three simultaneous equations:

$$nN - aA = m$$
$$n'N - a'A = p$$
$$A - N - P = 1$$

where m = distance from corrected point to paraffin line on
the figure; n = distance from naphthenes of same boiling point
as the cut to paraffin line; a = distance from aromatic com-
pounds of same boiling point as the cut to paraffin line;
P = distance from corrected point to paraffins of same boiling
point as cut; n' = distance from naphthenes of same boiling
point as the cut to paraffin line; a' = distance of aromatics
of same boiling point as the cut to paraffin line; m, n and a
are measured perpendicular, and p', n' and a' parallel to the
paraffin line. The correction for olefins using bromine num-
ber values is questionalbe in view of the fact that the

diolefins and triolefins previously mentioned will affect the correction values which are given for specific gravity and refractive index.

Kurtz and Headington (35) have developed a method for the analysis of petroleum fractions in which a new physical constant called the refractivity intercept is employed. The refractivity intercept is the constant b in the equation:

$$\text{Refractive index} = 0.5 \text{ density} - b$$

This equation is a mathematical expression derived from the fact that when a plot of refractive index against density is made for a given structural type of hydrocarbon, a straight line relationship exists between the refractive index and the density. Hydrocarbon types differ, in this respect, only in the numerical value of b, from which their concentrations can be determined.

The concentration of the aromatic hydrocarbons is determined by treating the fraction under consideration with 98 per cent sulfuric acid. Refractive index and density are measured before and after the absorption of cyclic olefins, non-cyclic olefins and aromatics. The volume contraction is also recorded. From these measurements, a value for the refractivity intercept of the hydrocarbons removed by the acid treatment can be calculated. Using this value in a triangular plot of refractivity intercept against density for

these 3 pure hydrocarbon type, the concentration of the
hydrocarbons contained in the sample may be calculated. From
an inspection of the refractivity values (36) for a specific
hydrocarbon type, such as the paraffins, it can be seen that
these values are not constant, even in narrow boiling ranges.
The deviations are due to the fact that the refractive index-
density relationship is not a strict linear function. These
deviations limit the accuracy of the method. Measurements
of volume contraction and density are also undesirable when
only small samples are available for analysis. Moreover, the
accuracy of the method is further dependent upon the accuracy
of the acid treatment.

Another physical property that is employed for the
estimation of the concentration of aromatics is that of
specific dispersion. The formula that is generally used for
specific dispersion is derived from the Gladstone-Dale
equation for specific refraction as follows:-

$$r_\beta - r_\alpha = \frac{n_\beta - 1}{d} - \frac{n_\alpha - 1}{d} = \frac{n_\beta - n_\alpha}{d} = \frac{\triangle n}{d}$$

where r_β , r_α = specific refraction values

n , n = refractive indices for β and α lines of the
hydrogen spectrum

d = density at temperature at which refractive
indices were measured.

The dispersion values determined by means of the Abbe
refractometer are based on these two spectrum lines. In order

to obtain more convenient values, the specific dispersion is multiplied by 10^4.

It has been observed that the specific dispersion of naphthenes and paraffins is about 100×10^{-4} (12). There is some slight variation between individual naphthenes and paraffins but the average value has been found to follow approximately the value as given. This fact has been further substantiated by other workers (73)(69)(71)(18)(72). The value for the aromatics has been found to be appreciably higher but it is not constant as in the case of paraffins and naphthenes. Generally, the specific dispersion decreases with increase in boiling point. Benzene has the value of 189×10^{-4}. The lowest known specific dispersion value for a benzene homolog is approximately 155×10^{-4}.

This variation in specific dispersion has been the basis of several methods for determining the concentration of aromatics in oils. Von Fuchs and Anderson (18) used it as a means of testing the effect of solvent extraction on the aromaticity of lubricating oils. Vlugter, Waterman and van Weston (70) employed the specific dispersion of aromatic hydrocarbons as a means of examining the ring structure of mineral oils. Mair, Willingham and Streiff (40) also investigated the chemical composition of the extract portion of the lubricant fraction from a mid-continent petroleum using the principle of specific dispersion.

Grosse and Wacker (23) have developed a method in
which specific dispersion is used for the analysis of both
olefins and aromatic hydrocarbons. They found that the in-
crement of specific dispersion due to olefins was equal to
0.16 X bromine number. The weight per cent of aromatics is
given by the following formula:-

$$\% \text{ Aromatics} = \frac{M - 0.16 \text{ X bromine number} - 99}{A - 99} \text{ X } 100$$

where M = specific dispersion of mixtures

A = specific dispersion of pure aromatics

The values of specific dispersion used for pure aromatics are
average values for those aromatics probably occurring in the
various selected cuts. Since these values may vary as much as
20 dispersion units for a single cut, the accuracy of the
method is limited. The value of 0.16 X bromine number for the
specific dispersion increment due to olefins is in error
because the relationship between the olefin increment and the
bromine number is not a strict linear function.

Chavanne and Simon (8) were the first to observe
that the presence of aromatic hydrocarbons lowered the criti-
cal solution temperature of a hydrocarbon mixture in aniline,
and, also that the depression of this temperature was directly
proportional to the weight of aromatics present. Chavanne
and Simon observed that of the four main classes of hydro-
carbons, the paraffins have the highest critical solution

temperature and aromatics the lowest, naphthenes and olefins occupying the intermediate positions. In view of this, they (9) suggested the determination of critical solution temperatures with aniline for the determination of both aromatics and naphthenes in hydrocarbon mixtures.

The method given by Chavanne and Simon is as follows: The sample is fractionated into desirable cuts and the critical solution temperature in aniline of each cut is determined. The maximum temperature of the appearance of turbidity is found by varying the amount of aniline with a given amount of sample. The aromatics are removed from the sample by means of sulfuric acid-nitric acid mixture and the critical solution temperature of the remaining sample is determined. The weight per cent of aromatics is given by the following formula:-

$$A = \alpha \, (T_A - T_B)$$

where A = weight per cent of aromatics

T_A = critical solution temperature after removal of aromatics

T_B = critical solution temperature before removal of aromatics

α = proportionality constant which has a value of 1.14 for benzene; 1.19 for toluene; and 1.24 for xylene.

Tizard and Marshall (67) modified the method of

Chavanne and Simon in that they dispensed with the elaborate and time consuming critical solution temperature determinations and substituted for these, measurements of "Aniline Points". These are defined as temperature at which equal volumes of hydrocarbon mixture and aniline are completely miscible. The treatment of a sample is very similar to that given by Chavanne and Simon except fuming sulfuric acid is used to remove the aromatic hydrocarbons. The same formula is used to calculate the weight per cent of aromatics. Under these new conditions the proportionality constant has a value of 1.19 for benzene; 1.20 for toluene and 1.25 for m-xylene.

Tizard and Marshall have shown that a change in the character of the non-aromatic base will offset the lowering of the aniline point for a given weight of aromatics. This fact has been substantiated by Waterman and Perquin (72). Investigation by various workers (72)(67)(61)(7) has revealed that there are large deviations in the proportionality constant for the higher boiling aromatic hydrocarbons.

Other miscibility reagents such as nitro-benzene (15) and benzyl alcohol (1) have also proposed for the determination of aromatic hydrocarbons.

An objection to all proposed solvents, including aniline, is that the proportionality factor is not the same for all of the aromatic hydrocarbons, particularly for the higher boiling aromatics. Another criticism that applies to

all solvents is that the lowering of the critical solution
temperature depends upon the character of the non-aromatic
base.

One of the most extensively used solvent for the
quantitative extraction of aromatic hydrocarbons from
petroleum distillate is dimethyl sulfate, originally proposed
by Valenta (68), who claims that neither the paraffins nor
the naphthenes are extracted by the solvent. This claim, how-
ever, has been refuted by Graefe (20) and by Harrison and
Perkins (24).

Graefe conducted very complete tests and came to
the conclusion that dimethyl sulfate possesses a very definite
miscibility with saturated hydrocarbons. He also pointed out
that the solubility of an oil in dimethyl sulfate was pro-
portional to the amount of solvent used.

Nitration and Sulfonation Methods.

The concentration of aromatic hydrocarbons in hydro-
carbon mixtures is often determined by nitration. Fuming
nitric acid may be used although the general practice is to
employ a mixture of sulfuric acid and nitric acid. The
nitration method proposed by Hess (25) is based upon the
nitration of the aromatic hydrocarbons to the mono-nitro
compounds which are then dissolved by an added excess of
concentrated sulfuric acid. Hess used a correction of one
cubic centimeter for the solubility of paraffins and naph-

thenes in the nitrating mixture.

Egloff and Morrell (14) proposed a method wherein the nitro-sulfuric acid was so proportioned that the nitro-aromatic compounds were not soluble in it but separated out in a distinct layer. The volume of this layer is measured and a suitable factor is used to convert the volume of nitro-compounds into the per cent of aromatic hydrocarbons.

It has been shown that this method can be used only in the case of limited concentrations of aromatics (54) and that the volume of the nitro layer varies with the particular aromatics present (16).

Manning (41) vaporized a weighed sample of oil and absorbed the vapors in a nitrating mixture. The unsaturated hydrocarbons which were present were oxidized to carbon dioxide and acids. The nitrated aromatics are extracted and weighed, and from the weight obtained the aromatic percentage is calculated.

In this method it is quite possible that some of the olefinic hydrocarbons might be converted to polynitro compounds and thus be included as nitro compounds resulting in high values for the concentration of the aromatics.

Sulfuric acid of various strengths has been widely used for the absorption of aromatic hydrocarbons. The same general procedure is followed in practically all of the

existing methods. The methods differ widely in the strength
of the acid and the ratio of the volume of acid to oil.

Concentrated sulfuric acid (96 per cent) has been
suggested for aromatic removal but is is doubtful whether this
gives complete absorption of the aromatic hydrocarbons,
particularly the lower boiling members such as benzene and
toluene (33). Sulfuric acid of 98 per cent strength has been
used consistently for the removal of aromatic hydrocarbons
(45)(63)(67). One hundred per cent acid has probably been
more widely used (7)(26)(54) .

It has been shown that when 98 or 100 per cent acid
is used, the loss or contraction may be greater than the
actual percentage of aromatic hydrocarbons present (51)(38)(50).
This condition is reported to be caused by reaction of the
acid with naphthenes and paraffins.

Thomas, Block and Hoekstra (64) make use of 25%
fuming sulfuric acid. From their data this acid also has been
shown to remove more than the theoretical amount of aromatic
hydrocarbons.

Kattwinkel (32) has shown that the action of 96%
sulfuric acid upon aromatics may be catalysed by the presence
of phosphorous pentoxide. This reduces the tendency for the
absorption of naphthenes and paraffins.

Essentially, the optimum acid strength appears to

depend upon the concentration of the aromatic hydrocarbons.
Excluding benzene and possibly toluene, equal amounts of high
or low boiling aromatics are removed by sulfuric acid of the
same strength. In order to remove the aromatic hydrocarbons
without action on the naphthenes and paraffins, it appears
that the ratio of acid to oil should be varied rather than
changing the strength of the acid.

Naphthene and Paraffin Hydrocarbons

Chemical methods for determining the concentration of naphthenes and paraffins are limited and not very reliable because these two types of hydrocarbons are relatively inert to the ordinary reagents. Some individual hydrocarbons of both types will react with certain reagents but the reactions are limited and do not proceed to completion for either group as a whole. Because of this chemical stability toward reagents, physical properties of the two types are chiefly used to determine their concentrations.

Aniline Point Methods.

Probably the most common method used for the determination of the concentration of naphthenes and paraffins is the aniline point method. This is an extension of the Tizard and Marshall method for aromatic hydrocarbons (67). In this method the following assumptions are made: (a) all paraffins have an aniline point of $70^{\circ}C.$, (b) all naphthenes boiling up to $95^{\circ}C.$ lower the aniline points of the paraffins with which they are present at a rate of $0.4^{\circ}C.$ per one per cent, for all naphthenes boiling between 95° and $120^{\circ}C.$ the corresponding figure is $0.3^{\circ}C.$, and for all naphthenes of boiling range $120-200^{\circ}C.$ the figure is $0.2^{\circ}C.$

In general practise the mean figure of $0.3^{\circ}C.$ per one per cent is used. If N = per cent naphthenes and T is

the aniline point of the mixture, the value of N is calculated
from the equation

$$N = \frac{70 - T}{0.5}$$

From a study of the physical data of pure paraffins and naph-
thenes, it can be seen that the aniline points increase with
rise in the boiling point of the paraffins and the aniline
points of pure naphthenes are not such as to cause the
lowering of the aniline points to be as assumed.

Griffith (21) recognized the fact that the aniline
points of the paraffin hydrocarbons was dependent upon the
boiling point. In this method the naphthene-paraffin mixture
was stripped of naphthenes by means of fuming sulfuric acid,
and from the remaining paraffins he was able to locate a zero
aniline point curve. It is questionable, however, whether
fuming sulfuric acid will remove all of the naphtheneshydro-
carbons without absorbing some paraffins.

The aniline point method for the determination of
naphthenes and paraffins probably could be made more useful
by using smaller cuts. It would then be more feasible to use
literature values of the critical standard tables of paraffin
and naphthenes occurring in these specified cuts.

Vlugter, Waterman and Van Westen have developed a
method for determining the composition of high boiling oils

from accurately determined molecular weight, density and refractive index values (70). In order to calculate the percentage of paraffins (or paraffin side chains) and naphthenes rings, the specific refraction is calculated from the refractive index and density using the formula of Lorentz-Lorenz:-

$$r = \frac{n^2 - 1}{n^2 - 2} \times \frac{1}{d}$$

A point corresponding to the specific refraction and molecular weight of the unknown sample is located on a prepared chart. On this chart specific refraction is plotted against molecular weight in a series of curves for the classes of hydrocarbons $C_n H_{2n+2}$, $C_n H_{2n}$, $C_n H_{2n-2}$, $C_n H_{2n-4}$ and $C_n H_{2n-6}$. As an example, an oil is found to have a mean molecular weight of 709 and a specific refraction of 0.3279. The specific refraction of a paraffin hydrocarbon of the same molecular weight is 0.3314 and that of a polycylic naphthene with no side chains is 0.3043. The percentage of naphthene rings in the oil therefore is

$$\frac{0.3314 - 0.3279}{0.3314 - 0.3043} \times 100 = 13 \text{ per cent by weight.}$$

In the gasoline range of petroleum fractions the slope of the curve for the $C_n H_{2n+2}$ class of hydrocarbons is rather steep which would necessitate cutting the sample into very small fractions because average molecular weights over a very large cut would not yield the correct analysis of the mixture. In the higher boiling ranges this objection is

minimized because the slopes of the curves are very nearly zero, which allows a wider range for the average molecular weight.

A recent method (64) has been proposed which makes use of index of refraction values. Literature values for the index of refraction of the paraffins are plotted against boiling point. A similar curve for the naphthenes is constructed. The index of refraction for an unknown sample of known boiling point is located between these two curves and from its position the percentage of naphthenes and paraffins may be calculated. The curves as given could probably be improved by data pertaining to paraffins and naphthenes which has been published since the publication of this article.

INTRODUCTION TO EXPERIMENTAL PROCEDURE

There appeared to be certain disadvantages inherent in all of the methods that have been advanced in the field of petroleum analyses. The outstanding objection to some of the more recent methods lies in the time required for their execution, making them too slow and cumbersome for rapid analytical work.

In view of the extensive investigations that have been carried out in the petroleum industry during the past decade, a search for new reagents did not seem desirable. A preliminary study of various special reagents and catalysts for the determination of the four general classes of hydrocarbons was carried out. However, no particular advantages were obtained.

It was thought, however, that a more extensive examination of the best features of several known methods, combined with a new interpretation of data might eliminate the present disadvantages and result in a satisfactory method.

Gasoline samples of widely diversified composition were selected for this study rather than mixtures of pure hydrocarbons in order that the method so developed would be based upon compounds that actually occur. The source and the boil-range of the materials that were used in carrying out the investigations in this study are given in Table I.

TABLE I

Source and Boiling Range of Samples
Employed in Experimental Work

Sample	Boiling Range	Source
A	80 - 200°C	Liquid Phase Cracked Gasoline
B	80 - 200°C	Liquid Phase Cracked Gasoline
C	80 - 200°C	Vapor Phase Cracked Gasoline
D	80 - 200°C	Vapor Phase Cracked Gasoline
	90 - 100°C	Eastman Practical Heptane
F	128 - 140°C	Reformed Pressure Distillate
G	140 - 186°C	Solvent Naphtha
H	186 - 213°C	Solvent Naphtha
J	156 - 204°C	Stoddard Solvent (Varsol)
K	95 - 140°C	Toluol Substitute
L	95 - 140°C	Toluol Substitute
M	85 - 115°C	Reformed Practical Heptane
N	95 - 135°C	Toluol Substitute (Solvesso #1)
P	133 - 178°C	Commercial Solvent Naphtha (Solvesso #2)

The samples A, B, C and D were carefully fractionated into 6 fraction (80-100°C, 100-120°C. etc.). These fractions are identified by a subscript 1 for boiling range 80-100°C. and so forth.

Olefin Hydrocarbons

From the foregoing discussion of the methods which have been suggested for the analysis of olefins, it is evident that no one method appears to give the desired analytical results. When sulfuric acid is used, the problem arises of what acid strength is to be most suitable. If the acid is sufficiently strong to remove all of the olefins, then aromatic hydrocarbons also may be absorbed. On the other hand, if the acid strength is such that the aromatics are not attacked, then removal of the olefins may not be complete.

Because 82% sulfuric acid appeared to have the least effect upon aromatic hydrocarbons, it was selected for determining the more reactive portion of the olefins. It was then necessary to determine any possible absorption of aromatics by this strength acid. It was further necessary to determine the optimum ratio of acid to oil and the time required to give maximum absorption.

It was realized that 82% sulfuric acid may not remove all of the olefins from an oil and it was necessary to determine the concentration of the remaining olefins by other means. Knowing the molecular weight and the density of the olefins, it is possible to determine the olefins remaining after 82% acid treatment by use of the bromine number. Since the determination of molecular weight and density of the ole-

fins remaining in a sample is not feasible, a method using the molecular weight and density for pure mono-olefins was developed. The bromine number was determined by using a standard solution of potassium bromate-potassium bromide.

Treatment with 82% (by weight) sulfuric acid

Five cubic centimeters of the sample were pipetted into a graduated Babcock sulfonation bottle containing 30 cubic centimeters of 82% sulfuric acid. The bottle and acid were chilled in an ice bath before adding the sample. The sample was stoppered and shaken for 30 minutes. It was then removed from the shaking apparatus and fresh 82% acid was added until the volume of the remaining sample could be read from the graduations on the neck of the bottle. The bottle was again stoppered and centrifuged for a period of 10 minutes. It was then removed from the centrifuge and the loss in volume of the oil was recorded.

This loss in volume represents the portion of the olefin hydrocarbons that are soluble in 82% sulfuric acid. The olefins that remain in the sample are determined by a modification of the bromine number which will be discussed later in the procedure.

In the determination of the sulfuric acid-soluble olefin hydrocarbons, it is advantageous to use a ratio of acid to oil that efficiently removes the olefins as economically as possible. It has been found that the ratio of six

volumes of acid to one volume of sample is the most efficient
ratio to use. Ratios above this value do not remove appreciably
any more of the olefins. This ratio was established in the
following manner.

Identical samples of oil were treated with four
different ratios of acid to oil. These ratios were 3 to 1,
6 to 1, 9 to 1 and 12 to 1. The samples were shaken for one-
half hour; the bottles then were filled with acid and centri-
fuged. The degree of unsaturation was determined using the
method of Francis. This unsaturation value is reported as the
number of cubic centimeters of potassium bromate-potassium
bromide solution of half normal concentration per cubic centi-
meters of sample and is hereafter spoken of as the "bromate-
tiber".

Twenty two samples were tested, the results of
which are given in Table II. It can be seen readily that the
bromate titer reaches a minimum approximately 6 volumes of
acid to 1 volume of oil.

In the sulfuric acid treatment it was necessary to
determine the reaction time for maximum absorption. This was
accomplished by treating 6 portions of the same sample for
different periods of time. These time intervals were 5, 10,
15, 20, 25 and 30 minutes. Constancy of the bromate titer
was used as an indication for maximum reaction time.

TABLE II

The Effect of Varying The Ratio of 82% Sulfuric Acid
to Oil on the Bromate Titer

Sample	Original Bromate Titer	3 acid to 1 oil/bromate titer	6 acid to 1 oil/bromate titer	9 acid to 1 oil/bromate titer	12 acid to 1 oil/bromate titer
D_1	16.96	5.72	4.65	4.56	4.55
D_2	15.63	3.29	2.94	2.92	2.88
D_3	13.75	2.81	2.77	2.65	2.64
D_4	10.57	2.34	1.95	1.94	1.92
A_2	20.12	3.73	3.39	3.31	3.04
A_3	16.74	3.88	3.52	3.71	3.72
A_4	11.82	2.89	2.69	2.69	2.62
A_5	8.53	1.99	1.73	1.66	1.59
A_6	5.38	1.37	1.12	1.12	1.17
B_1	15.47	4.89	4.40	4.26	4.20
B_2	14.57	3.57	3.45	3.31	3.23
B_3	13.63	3.40	3.35	3.22	3.21
B_4	11.57	3.18	3.06	3.04	2.96
B_5	9.66	3.12	2.61	2.37	2.33
B_6	7.79	2.34	1.63	1.44	1.43
C_1	30.75	9.05	8.60	8.54	8.52
C_2	24.93	5.81	5.49	4.89	4.62
C_3	19.70	6.62	6.10	6.03	6.02
C_4	18.49	5.64	5.48	5.40	5.37
C_5	16.61	4.28	3.89	3.33	3.02
C_6	12.40	2.78	2.60	2.49	2.50

The procedure for these tests was as follows:

Five cubic centimeters of the sample were pipetted into a graduated Babcock sulfonation bottle containing 30 cubic centimeters of 82% sulfuric acid. The bottle and acid were chilled in an ice bath before adding the sample. The bottle was stoppered and shaken for 5 minutes. It was then removed from the shaking apparatus and sufficient fresh 82% acid was added to bring the oil layer up into the neck of the bottle. The bottle was again stoppered and centrifuged for 10 minutes. It was then removed from the centrifuge and the bromate titer determined.

The results of these tests are given in Table III, and graphically in Figure 1. From the inspection of the data it can be seen that no appreciable absorption takes place after 30 minutes. Thus, the time for the shaking of the samples in the 82% sulfuric acid was set at 30 minutes.

TABLE III

The Effect of Shaking Time on the Bromate Titer
for 82% Sulfuric Acid Treatment of an Oil

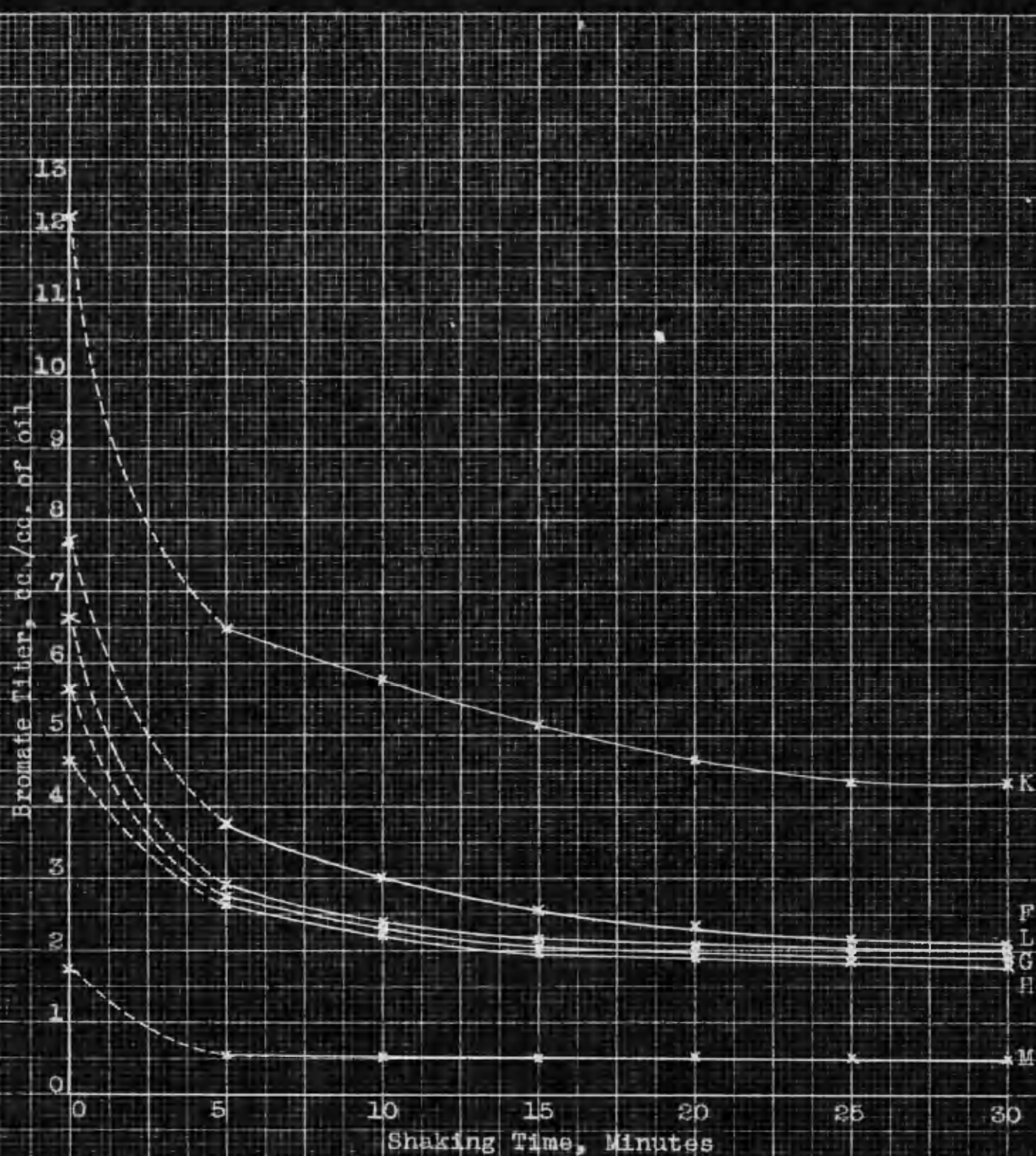| Sample	Original Bromate Titer	Bromate Titer 5 min.	Bromate Titer 10 min.	Bromate Titer 15 min.	Bromate Titer 20 min.	Bromate Titer 25 min.	Bromate Titer 30 min.
M	1.75	0.53	0.51	0.52	0.51	0.50	0.50
H	4.67	2.66	2.20	2.00	1.90	1.85	1.80
G	5.64	2.74	2.39	2.09	2.00	1.94	1.90
L	6.62	2.91	2.40	2.19	2.09	2.04	2.00
F	7.71	3.79	3.02	2.56	2.33	2.19	2.10
K	12.19	6.48	5.77	5.13	4.69	4.36	4.33

Figure 1. The Effect of Shaking Time on the Bromate Titer
for 82% Sulfuric Acid Treatment of an Oil

Method of Determining the Olefin Hydrocarbons
Remaining in the Sample after the Treatment
with 82% Sulfuric Acid

During the treatment of a sample with 82% sulfuric
acid, the tri- and diolefins, which are more reactive than
the mono-olefins, together with some of the mono-olefins are
absorbed.   Some mono-olefins, both of the straight and
branched chain type, remain in the sample. This is shown by
an appreciable bromate titer after acid treatment.

The remaining olefins cannot be removed by absorption
in sulfuric acid of a stronger concentration without the danger
of the absorption of aromatic hydrocarbons. The residual ole-
fins can, however, be determined from the bromate titer if an
assumption is made as to the particular olefins present in
each specified cut.

The olefins assumed to be in each fraction are
given in Table IV. The average values of density, index of
refraction at $25^{o}C$. and the molecular weight of each fraction
from Table IV are given in Table V.

In any specific fraction, it is possible to calcu-
late the bromate titer for the average pure olefin. This
calculation is made in three steps:-

(a) grams of bromine from one cubic centimeter

TABLE IV

Pure Olefins Occurring in Different Boiling Ranges

Boiling Range 80 – 100°C.

Compound	Boiling Point	Molecular Weight	Density 20/4	Refractive Index @ 25°C.
2,4-Dimethylpentene (1)	81	98.11	0.6937	1.3945
2,4-Dimethylpentene (2)	83	98.11	0.6947	1.3995
3-Methylhexene (1)	84	98.11	0.6949	1.3945
2,3-Dimethylpentene (1)	84	98.11	0.7054	1.3997
2-Methylhexene (5)	85	98.11	0.6936	1.3929
2,3-Dimethylpentene (3)	86	98.11	0.7126	1.4027
2-Methylhexene (2)	87	98.11	0.6943	1.3966
3-Methylhexene (5)	87	98.11	0.6969	1.3960
3-Methyl-2-ethylbutene (1)	89	98.11	0.7186	1.4095
2-Methylhexene (1)	91	98.11	0.7000	1.3975
3-Methylhexene (2)	93	98.11	0.7120	1.4055
2-Methylhexene (2)	94	98.11	0.7089	1.4050
2-Ethylpentene (1)	94	98.11	0.7079	1.4025
3-Ethylpentene (2)	95	98.11	0.7172	1.4095
Heptene (1)	95	98.11	0.6993	1.3974
Heptene (3)	96	98.11	0.7016	1.4017
Heptene (2)	98	98.11	0.7034	1.4016
Average 80 – 100°C.		98.11	0.7032	1.4007

TABLE IV (Cont'd)

Boiling Range 100 – 120°C

Compound	Boiling Point	Molecular Weight	Density 20/4	Refractive Index @ 25°C
2,2-Dimethylhexene (3)	100	112.13	0.7048	1.4043
2,4,4-Trimethylpentene(1) (isobutylene) 2	101	112.13	0.7151	1.4057
2,4,4-Trimethylpentene (2)	102	112.13	0.7195	1.4087
3,3-Dimethylhexene (4)	105	112.13	0.7211	1.4133
2,3,3-Trimethylpentene (1)	106	112.13	0.7202	1.4095
2,3,3-Trimethylpentene (3)	108	112.13	0.7363	1.4153
3-Ethylhexene (3)	112	112.13	0.7395	1.4207
4-Methylheptene (3)	119	112.13	0.7318	1.4179
5-Propylpentene (1)	119	112.13	0.7237	1.4145
	119	112.13	0.7255	1.4157
Average 100 – 120°C		112.13	0.7238	1.4126

Boiling Range 120 – 140°C.

Compound	Boiling Point	Molecular Weight	Density 20/4	Refractive Index @ 25°C.
2-Methylheptene (x)	122	112.13	0.7254	1.4144
Octene (1)	124	112.13	0.7155	1.4063
Octene (3)		112.13	0.7248	1.4112
Octene (2)		112.13	0.7197	1.4111
2,3,3,4-Tetramethylpentene (1)	134	126.14	0.7610	1.4380
2,5-Dimethylheptene (2)	137	126.14	0.7420	1.4208
Nonene (1)	139	126.14	0.7433	1.4155
3-Methylheptene (2)		112.13	0.7296	1.4158
4-Methylheptene (2)		112.13	0.7240	1.4125
2,5,5-Trimethylhexene (2)		126.14	0.7340	1.4155
4,5,5-Trimethylhexene (2)		126.14	0.7382	1.4198
4,6-Dimethylheptene (2)		126.14	0.7259	1.4155
4,6-Dimethylheptene (3)		126.14	0.7358	1.4173
4,5-Dimethylheptene (2)		126.14	0.7431	1.4220
3,6-Dimethylheptene (3)		126.14	0.7382	1.4192
4-Methyloctane (2)		126.14	0.7286	1.4158
Average 120 – 140°C		120.88	0.7329	1.4161

TABLE IV (Cont'd)

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Boiling Range 140 - 160°C

Compound	Boiling Point	Molecular Weight	Density 20/4	Refractive Index @ 25°C
2,5-Dimethylheptene (2)	140	126.16	0.7470	1.4255
3-Ethylheptene (3)	142	126.16	0.7414	1.4224
5-Methyloctene (2)	145	126.16	0.7409	1.4222
Nonene (2)		126.16	0.7502	1.4135
2,4,7-Trimethylheptene (3)		140.16	0.7355	1.4135
2,4-Dimethyl Octene (4)		140.16	0.7497	1.4231
2-Methyl-4-ethylheptene (4)	158	140.16	0.7450	1.4246
Average 140 - 160°C		132.16	0.7414	1.4202

Boiling Range 160 - 180°C.

Compound	Boiling Point	Molecular Weight	Density 20/4	Refractive Index @ 25°C
2,7-Dimethyloctene (x)	160	140.16	0.7418	1.4230
4-Propylheptene (3)	161	140.16	0.7502	1.4266
2,6-Dimethyloctene (6)	162	140.16	0.7490	1.4266
3-Ethyloctene (2)		140.16	0.7545	1.4283
Decene (1)	163	140.16	0.7530	1.4276
2,6-Dimethyloctene (x)	164	140.18	0.7558	1.4278
5-Methyldecene (4)		154.18	0.7578	1.4308
(Isobutylene) 3	179	168.19	0.7600	1.4281
Average 160 - 180°C		145.42	0.7528	1.4271

TABLE IV (Cont'd)

Boiling Range 180 - 200°C

Compound	Boiling Point	Molecular Weight	Density 20/4	Refractive Index @ 25°C
2,6-Dimethyl-2-isopropyl-heptene (x)	188	168.19	0.7774	1.4415
2-Methyl-5-propyloctene (x)	192	168.19	0.7609	1.4315
Average 180 - 200°C		168.19	0.7691	1.4365

TABLE V

Average Values for Molecular Weight, Density and Refractive Index for Olefins in Different Boiling Ranges
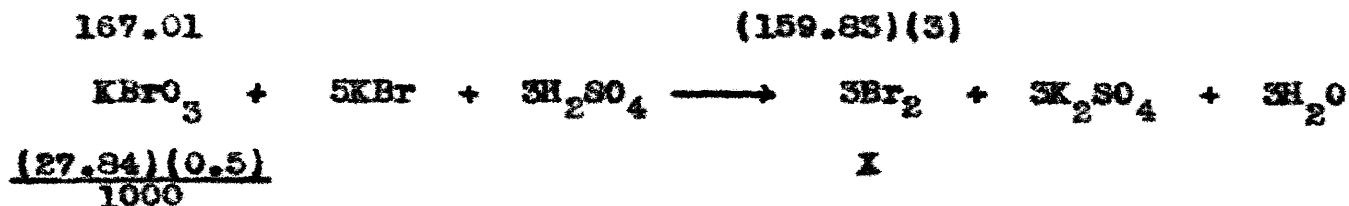
Fraction °C	Average Molecular Weight	Average Density 20/4	Average Index of Refraction @ 25°C
80-100	98.11	0.7032	1.4007
100-120	112.13	0.7238	1.4126
120-140	120.88	0.7329	1.4161
140-160	132.16	0.7414	1.4202
160-180	145.42	0.7588	1.4271
180-200	168.19	0.7691	1.4365

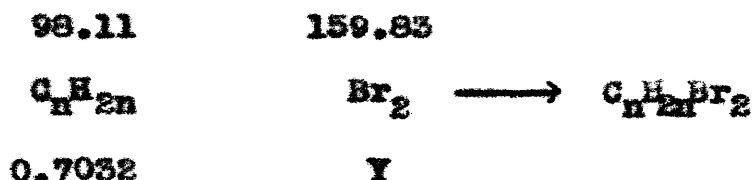of 0.5 N potassium bromate-potassium bromide solution.

(b) grams of bromine required to saturate one cubic centimeter of the average pure olefin of a specified fraction.

(c) the grams of bromine required to saturate the olefin divided by the grams of bromine per cubic centimeter of bromate solution will give the cubic centimeter of 0.5 N potassium bromate-potassium bromide solution per cubic centimeter of pure olefin for a specific fraction.

This is illustrated by a sample calculation of the bromate titer for a pure average olefin of the 80-100°C. fraction.

167.01   (159.83)(3)

$KBrO_3$ + 5KBr + $3H_2SO_4 \longrightarrow 3Br_2$ + $3K_2SO_4$ + $3H_2O$

$\frac{(27.84)(0.5)}{1000}$ X

X = 0.040 gr. Br_2/cc. of 0.5 N $KBrO_3 \cdot KBr$

98.11   159.83

C_nH_{2n} $Br_2 \longrightarrow C_nH_{2n}Br_2$

0.7032   Y

Y = 1.146 grs. Br_2/cc. of pure olefin (80-100°C.)

Then

$\frac{Y}{X} = \frac{1.146}{0.040} = 28.6$ cc. of 0.5 N $KBrO_3KBr$/cc. of pure olefin.

28.6 is the bromate titer for one cubic centimeter of pure average olefin of the 80-100°C. fraction.

From this value and the bromate titer determined after an actual sulfuric acid treatment, the percentage of olefins remaining in the sample may be calculated.

A sample calculation, using the 80-100°C. fraction, will be given to illustrate this:

Volume of sample taken for analysis   5.00 cubic centimeters.

Volume of sample after 82% acid treatment 3.75 cubic centimeters.

% olefins removed by acid treatment $= \dfrac{5.00-3.75}{500}$ (100) $= 25\%$

Bromate titer after acid treatment $= 1.43$

% olefins remaining in acid treated sample $= \dfrac{(1.43)(100)}{28.6} = 5\%$

% olefins remaining in acid treated sample converted to the original sample $= (.5)\dfrac{(100-25)}{100} = 3.75\%$

Thus, from the bromate titer of a treated fraction of definite boiling range and the bromate titer of the pure olefin of the same boiling range, the percentage of olefins remaining in the treated sample may be calculated. Average values for the bromate titer for various boiling ranges are given in Table VI and are represented graphically in Figure 2.

TABLE VI

Average Values for Bromate Titer for Various Boiling Ranges

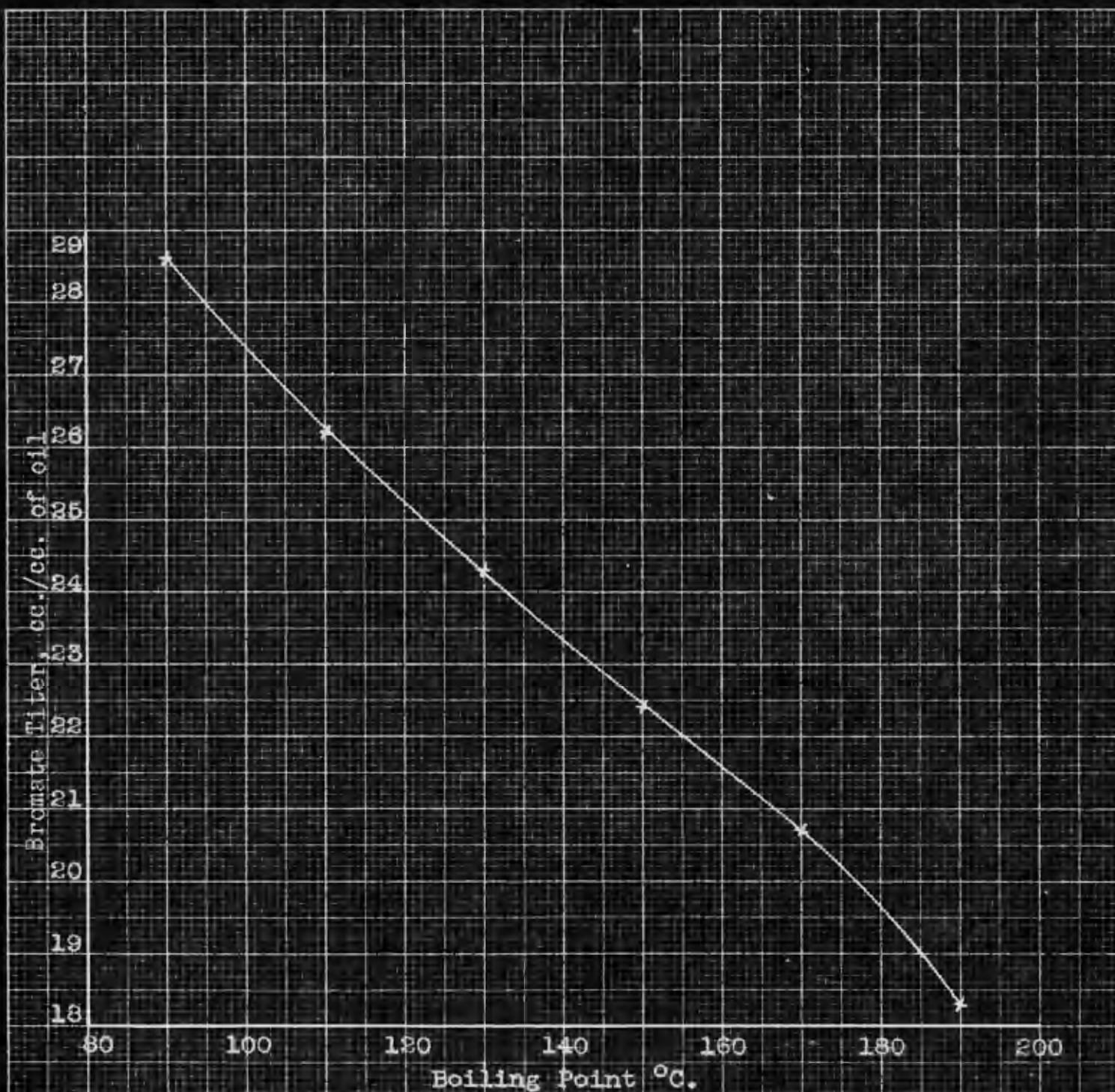| Fraction 0°C	Bromate Titer
80 - 100	28.6
100 - 120	26.2
120 - 140	24.3
140 - 160	22.4
160 - 180	20.7
180 - 200	18.3

Figure 3.   Bromate Titer for representative Mono-olefins
            for various boiling Ranges

Effect of 82 Per Cent Sulfuric Acid
on Aromatic Hydrocarbons

Except in very rare cases, the samples to be anal-
yzed for olefin content will contain some aromatic hydrocarbons.
In order that the contraction due to 82% sulfuric acid be a
true value for the olefins absorbed, it is necessary that the
conditions chosen be such that the aromatic hydrocarbons do
not react with the sulfuric acid.

The effect of 82% acid on various aromatics has been
studied under conditions similar to those used in actual ole-
fin determination. Mixtures of 25 and 75 per cent aromatics
with a heptane base materials were shaken with 82% sulfuric
acid for 30 minutes, the ratio of acid to oil being 6 to 1.

Indications of changes in aromatic content were
determined by changes in index of refraction and compensator
drum reading of an Abbe refractometer. The results of these
tests are given in Table VII.

It can be seen from Table VII that 82% sulfuric acid
has practically no effect on the aromatic hydrocarbons that
were studied. These aromatics are thought to be typical of
those that actually occur in most oil of the gasoline boiling
range. In the case of the 75% pseudo-cumene blend, there was
obviously some absorption of the aromatic hydrocarbon. It is
unlikely that a sample would contain only pseudo-cumene and as
high a percentage of pseudo-cumene as in the synthetic blend

TABLE VII

The Effect of 82% Sulfuric Acid

on Blends of Heptane and Various Aromatics

Sample No	Refractive Index @ 25°C before acid	Refractive Index @ 25°C after acid	Drum Reading before acid	Drum Reading after acid
100% heptane	1.3951	1.3950	41.3	41.3
25% benzene	1.4197	1.4196	39.8	39.8
75% benzene	1.4708	1.4708	36.9	36.9
25% toluene	1.4182	1.4182	39.9	39.9
75% toluene	1.4680	1.4681	37.2	37.2
25% xylene	1.4175	1.4176	40.0	40.0
75% xylene	1.4675	1.4672	37.4	37.4
25% ethylbenzene	1.4181	1.4180	40.0	40.0
75% ethylbenzene	1.4680	1.4680	37.5	37.5
25% cumene	1.4168	1.4167	40.2	40.2
75% cumene	1.4649	1.4649	37.9	37.9
25% pseudo-cumene	1.4193	1.4189	40.1	40.1
75% pseudo-cumene	1.4742	1.4730	37.7	37.8
25% tert-butylbenzene	1.4173	1.4175	40.2	40.2
75% tert-butylbenzene	1.4655	1.4654	38.3	38.3
25% sec-butylbenzene	1.4169	1.4170	40.2	40.2
75% sec-butylbenzene	1.4650	1.4650	38.3	38.3
25% n-butylbenzene	1.4188	1.4189	40.2	40.2
75% n-butylbenzene	1.4702	1.4700	38.1	38.1

* were tested.

Determination of Aromatic Hydrocarbons

It has been shown that nitration and sulfonation methods are frequently unreliable unless carried out with extreme care. Previous methods based upon density, critical solution temperature and index of refraction are all of about the same value but were not considered accurate above the boiling range of the xylenes because the representative physical constants of the aromatics contained in a gasoline above the boiling range of the xylenes have not been determined. It is true that density, critical solution temperature and refractive index values are available for most of the aromatics that occur in the gasoline range of petroleum. However, the actual values that are representative of these aromatics occurring in any specific fraction have not been determined.

Methods employing density, critical solution temperature and index of refraction as a rule are based upon the values of these properties before and after the absorption of the aromatic hydrocarbons. Of these three methods in operation, that of refractive index is by far the simplest. With an Abbe type refractometer, measurements of refractive index may be made on a very small sample (0.2cc.) which means that small samples may be used for the total analysis. This is particularly desirable in studying pilot plant or laboratory scale operations where frequently only small samples are available.

In order to apply determinations of the index of

refraction in the analysis of aromatics, it was necessary to establish values for this property that are truly representative of the aromatics which occur in the gasoline range. It was also necessary to determine the ratio of absorbing reagent to oil for complete removal of the aromatics and the time of reaction to allow for this removal.

From the preliminary investigations, sulfuric acid containing phosphorous pentoxide was chosen (for the absorption of aromatics) because it is easy to maintain at a constant strength and because it is possible to make the determination at room temperature. Fuming sulfuric acid was not used because it slowly loses its strength which necessitates standardization before each determination. Furthermore, it is necessary to absorb aromatics at a temperature near freezing.

Determination of Refractive Index Curve for Pure Aromatics.

Representative refractive index values for the aromatic hydrocarbons occurring in higher boiling fractions were determined using petroleum distillates of widely different characteristics. Samples A, B, C and D from Table I were selected for this study. Fractions A_1, B_1, C_1 and D_1 and fractions A_2, B_2, C_2 and D_2 were omitted because they contain only benzene and toluene, respectively. Representative values for the remaining fractions were determined in the following manner:-

The sample was treated for one-half hour with 80% sulfuric acid, the ratio of acid to oil being 3 to 1. The residue was then treated for one hour with concentrated sulfuric acid, the ratio of acid to oil being 3 to 1.

In the preliminary treatment to remove the olefins from the samples, 80% sulfuric acid was used first in order to keep alkylation at a minimum. Alkylation of the original aromatics by the olefins should be avoided as much as possible because the alkylated aromatics probably would not have the same refractive index values as the original aromatics. As the value of the original aromatics is the property which is desired, obviously any factor tending to change this value should be kept at a minimum.

The remaining olefins were removed with 96% sulfuric acid because it is necessary that there be no contraction in the removal of the aromatic hydrocarbons other than that due to the aromatics themselves. The bromate titer for all of the treated samples was less than 0.02, indicating a negligible olefin content. It is recognized that 96% sulfuric acid absorbs some of the aromatics but if the reaction speeds are approximately equal, the refractive index values will not be seriously affected.

After the complete removal of the olefins, five cubic centimeters of the sample were shaken for one hour with 30 cubic centimeters of sulfuric acid-phosphorous pentoxide

reagent —— (100cc. of 96% sulfuric acid - 30 grams of phos-phorous pentoxide). Treatment with this reagent results in the removal of the aromatic hydrocarbons.

The index of refraction was measured before and after the removal of the aromatics and the percentage of aromatic hydrocarbons was calculated from the measured volume contraction.

The average refractive index value for the aromatics removed was calculated using the following formula:-

$$A = \% \text{ Aromatics} = \frac{X - Y}{Z - Y} (100) \qquad (a)$$

$$Z = \% \text{ Aromatics} = \frac{(X-Y)(100) - AY}{A} \qquad (b)$$

where X = Refractive index of the sample before removal of the aromatics

Y = Refractive index of the sample after removal of the aromatics

Z = Average refractive index of the aromatics occurring in a specific boiling range.

The derivation of this equation is obvious from an inspection of a plot of the refractive index of the aromatics and their respective boiling ranges.
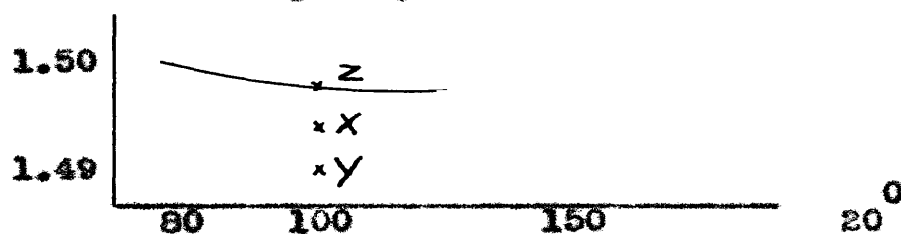
The index of refraction values for the aromatic
hydrocarbons obtained in this manner are given in Table VIII.
Average values for the six specific boiling ranges are
represented graphically in Figure 3. The curve that results
from these data will hereinafter be termed aromatic line.

The pressure distillates subjected to these tests
were produced under widely differing operation conditions.
Obviously, it is essential for precision in this method that
refractive index values for similar fractions of the different
pressure distillates be practically constant. It can be seen
from Table VIII that this condition is fulfilled.

If the refractive index values for the fractions of
the same boiling range from the different pressure distillates
were not constant, it would not be possible to use index of
refraction in an analytical method unless the conditions of
manufacture of the sample to be tested were known. Even if
operating conditions were known, it would be necessary to have
a different aromatic line for every different operation condi-
tion and base stock. It would be impractical to use refractive
indices under these conditions.

However, these conditions were not found to exist
and the use of the refractive index values for the aromatic
hydrocarbons as experimentally determined appears entirely
valid for the analytical determination of aromatic hydrocarbons.

A comparison between the experimentally determined

TABLE VIII

Index of Refraction of Aromatic Hydrocarbons
Occurring in the Fractions of Pressure Distillation

| Sample	Refractive Index Before Acid Treatment	Refractive Index After Acid Treatment	Per Cent Aromatics	Calculated Refractive Index
A_3	1.4399	1.4278	18.37	1.4926
B_3	1.4270	1.4169	13.12	1.4937
C_3	1.4622	1.4271	52.40	1.4941
D_3	1.4345	1.4170	22.75	1.4941
			Average	1.4939
A_4	1.4515	1.4357	26.67	1.4950
B_4	1.4333	1.4224	15.37	1.4942
C_4	1.4675	1.4289	56.60	1.4948
D_4	1.4439	1.4231	29.25	1.4943
			Average	1.4945
A_5	1.4633	1.4438	36.75	1.4969
B_5	1.4412	1.4279	19.60	1.4958
C_5	1.4751	1.4338	65.50	1.4969
D_5	1.4587	1.4318	41.40	1.4968
			Average	1.4966
A_6	1.4719	1.4389	41.05	1.4989
B_6	1.4512	1.4331	27.60	1.4985
C_6	1.4694	1.4381	51.10	1.4993
D_6	1.4704	1.4405	50.95	1.4990
			Average	1.4990
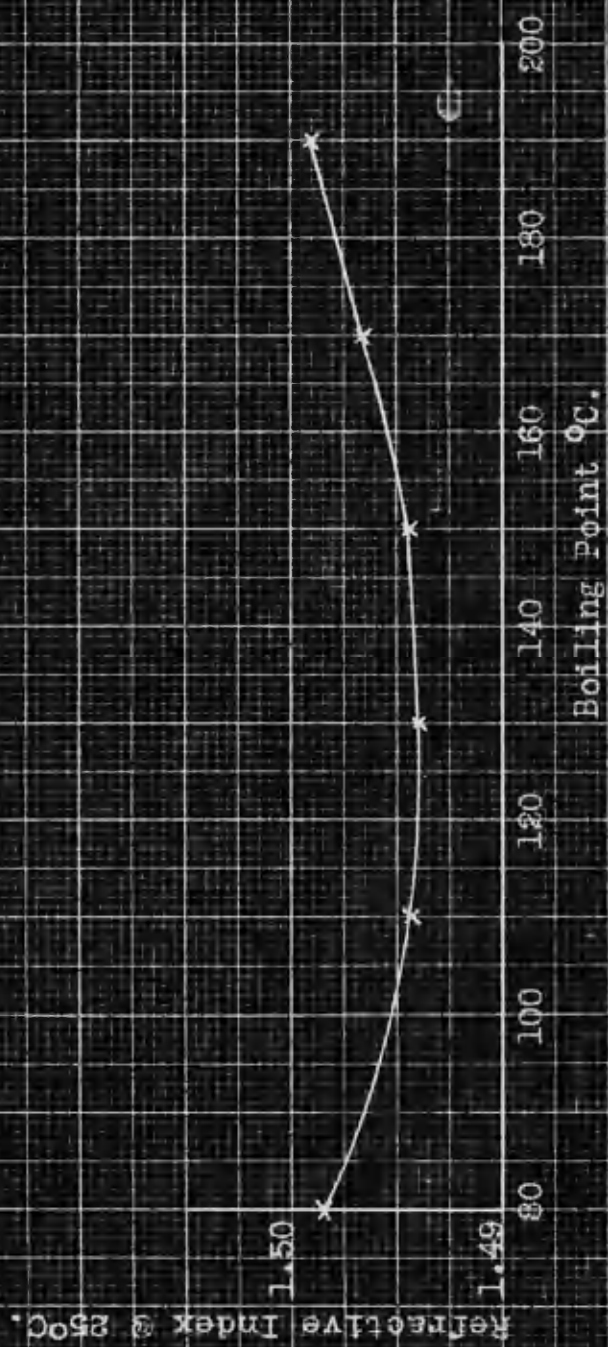
Figure 3.   Experimental Aromatic Line

aromatic line and the theoretical aromatic line is shown in Figure 3A. The theoretical aromatic line was plotted from the literature values for the various hydrocarbons. Agreement between the two curves is very good. The deviation in the higher boiling range is due in part to the fact that polynuclear aromatic hydrocarbons were not plotted on the theoretical curve. These particular aromatics were omitted.from the graph because it is not known just which of these occur in petroleum distillates. However, any that might occur have high refractive indices and would thus cause the theoretical curve to approach more nearly the actual curve.

Optimum Ratios of Acid to Oil in the Aromatic Hydrocarbon Determinations.

In order for any method involving absorption of the aromatics to be accurate, the absorbing reagent must be used in such proportions that the aromatics are completely removed without absorption of naphthenes and paraffins. The methods utilizing sulfuric acid that have been discussed previously did not give any specifications for the ratio of acid to oil to be used for varying amounts of aromatics. A set ratio was defined and this was used regardless of the concentration of the aromatics.

If the same ratio of acid to oil is used a sample containing a small percentage of aromatic will not exhaust the reagent to a point where the naphthenes and paraffins are not

Figure 3A. Comparison of Theoretical and Experimental Aromatic Lines

attacked and conversely a large amount would result in incomplete removal.

It has been shown (73)(69)(18) that the specific dispersion of all naphthenes and paraffins is practically constant at a value of 100×10^{-4}. In the present work this property has been utilized in establishing the optimum ratios of acid to oil for the aromatic hydrocarbons in the following manner.

A sample containing aromatics was treated with various ratios of sulfuric acid-phosphorous pentoxide reagent for one hour. The refractive index was measured before and after the acid treatment and the contraction in volume was measured. The compensator drum reading was recorded for the corresponding final refractive index value. The density of the acid treated sample was measured using a 2 cubic centimeter pycnometer.

The value for the dispersion of the acid treated sample was calculated from the formula given in the table that accompanies the refractometer. The specific dispersion was calculated from the dispersion by dividing by the density.

The samples used in these tests were given a preliminary stripping treatment with 82% sulfuric acid. This was done to minimize any side reactions that would be caused by an excess of olefins. The results of these tests are presented in Tables IX and X and Figures 4, 5 and 6.

It was found that as the ratio of acid to oil was

TABLE IX

Physical Data for Determining
Proper Ratio of Acid to Oil

Ratio of Acid to Oil	Bromate Titer	Refractive Index Corrected for Olefins @ 25°C	Refractive Index before Aromatic Removal @ 25°C	Refractive Index after Aromatic Removal @ 25°C	Compensator Drum Reading	Specific Gravity after Aromatic Removal
			Sample K			
1:1	0.03	1.4131	1.3956	1.3977	43.2	0.727
2:1	0.03	1.4131	1.3950	1.3972	43.4	0.725
3:1	0.03	1.4131	1.3948	1.3968	43.4	0.724
4:1	0.03	1.4131	1.3948	1.3966	43.4	0.724
5:1	0.03	1.4131	1.3946	1.3968	43.4	0.725
			Sample L			
44:1	2.00	1.4475	1.4125	1.4145	43.1	0.754
5:1	2.00	1.4475	1.4102	1.4123	43.3	0.751
6:1	2.00	1.4475	1.4098	1.4118	43.4	0.750
7:1	2.00	1.4475	1.4096	1.4117	43.4	0.750
8:1	2.00	1.4475	1.4095	1.4115	43.4	0.749
			Sample F			
6:1	2.10	1.4756	1.4300	1.4321	42.8	0.780
7:1	2:10	1.4756	1.4270	1.4290	43.2	0.777
8:1	2.10	1.4756	1.4250	1.4271	43.4	0.775
9:1	2.10	1.4756	1.4247	1.4266	43.4	0.774
10:1	2.10	1.4756	1.4245	1.4267	43.4	0.774

TABLE X

Calculated Results for Determining

Proper Ratio of Acid to Oil

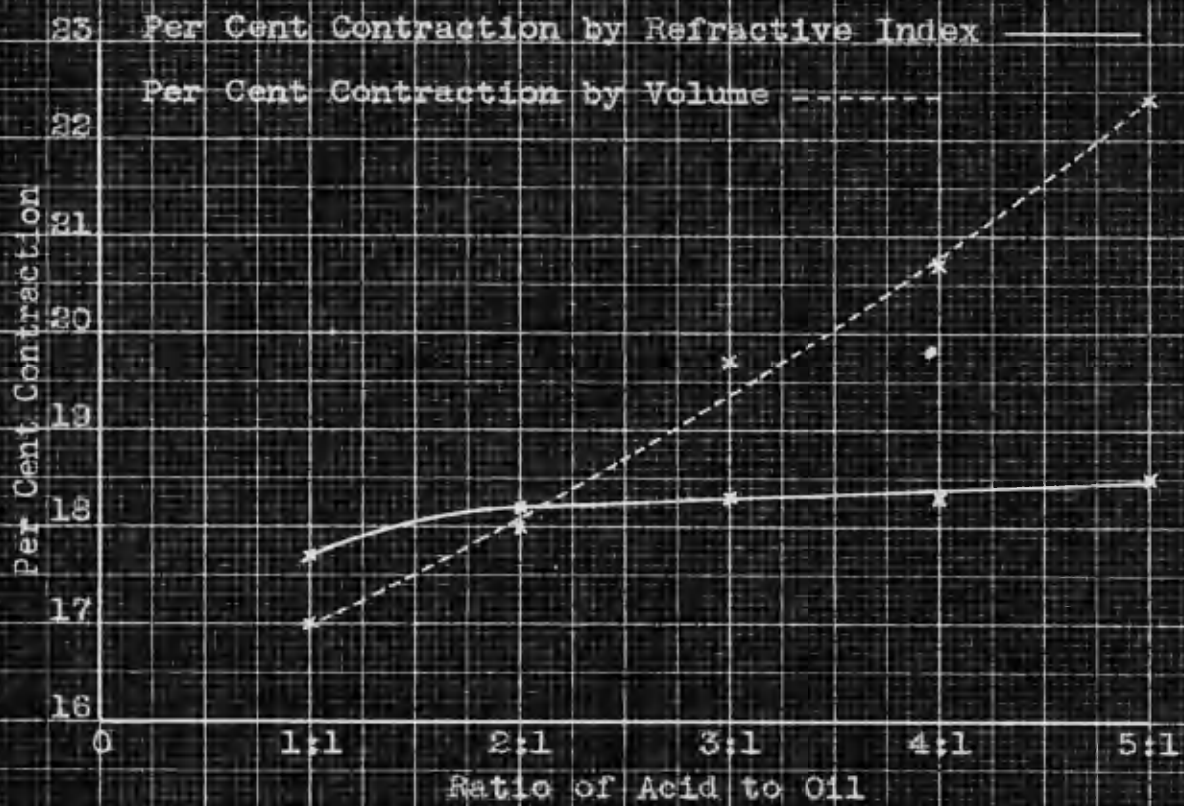| Ratio of Acid to Oil	Percent Olefins from Bromate Titer	Percent Aromatics from Refractive Index	Total Per Cent Aromatics and Olefins from Refractive Index and Bromate Titer	Total Per Cent Aromatics and Olefins from volume contraction	Dispersion X 10⁴	Specific Dispersion X 10⁴
			Sample K			
1:1	0.1	17.6	17.7	17.0	73.8	101.5
2:1	0.1	18.1	18.2	18.0	72.2	99.6
3:1	0.1	18.2	18.3	19.7	72.1	99.5
4:1	0.1	18.2	18.3	20.7	72.0	99.4
5:1	0.1	18.4	18.5	22.4	72.1	99.7
			Sample L			
4:1	8:2	43.0	51.2	49.0	79.6	105.7
5:1	8.2	44.5	52.7	52.0	76.7	102.1
6:1	8.2	44.7	52.9	54.6	75.4	100.6
7:1	8.2	44.9	53.1	55.8	75.3	100.3
8:1	8.2	45.0	53.2	57.6	75.3	100.5
			Sample F			
6:1	8.8	71.2	80.0	77.0	87.2	111.9
7:1	8.8	72.5	81.3	78.9	85.7	107.8
8:1	8.8	73.3	82.1	81.1	78.8	101.8
9:1	8.8	73.5	82.3	84.2	78.7	101.8
10:1	8.8	73.5	82.3	87.3	78.7	101.8

Figure 4.   Relationship between the Ratio of Acid to
              Oil and the Per Cent Contraction
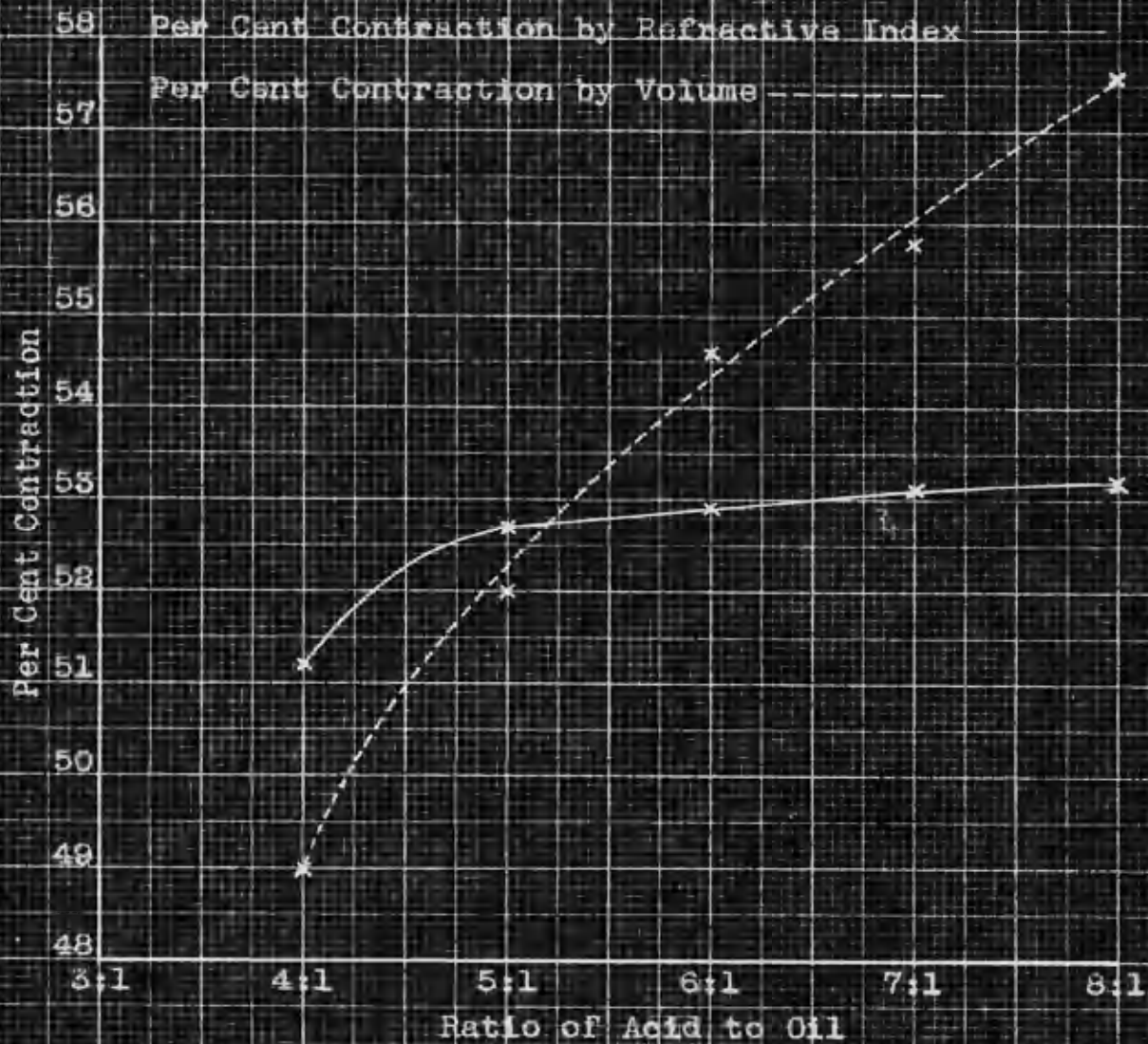
Sample E

Figure 5. Relationship between the Ratio of Acid to Oil and the Per Cent Contraction
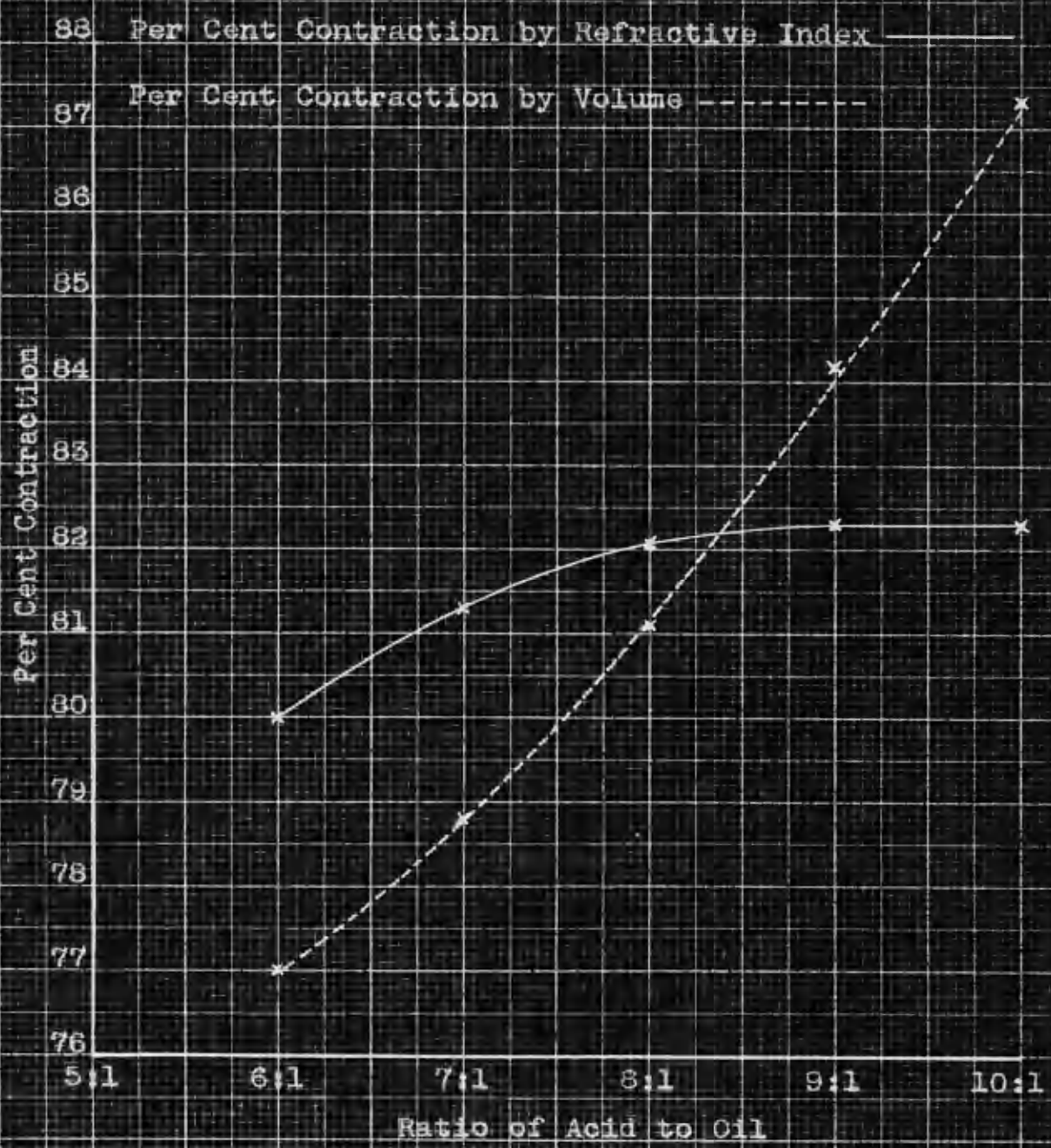
Sample L

Figure 6. Relationship between the Ratio of Acid to Oil and the Per Cent Contraction

Sample F

increased the specific dispersion approached the value of 100 X 10^{-4}. By employing a large number of different ratios of acid to oil, it would be possible to obtain the exact ratio of acid to oil when the specific dispersion just reached the value of 100 X 10^{-4}. However, it was possible to determine this ratio in a simpler manner.

From an inspection of Tables IX and X and Figures 4, 5 and 6, it can be seen that when the ratio of acid to oil is less than the actual ratio required for complete removal of the aromatics, the percentage of aromatics calculated from the refractive index values is greater than the percentage by volume contraction; and that when the ratio is greater than the actual ratio, the percentage calculated from the refractive index values is less than the percentage by volume contraction. It was found that when the ratio of acid to oil was at such a value that the specific dispersion just became constant, the percentages of aromatics by refractive index and by volume contraction became equal. This experimental result is exactly that predicted from theoretical considerations.

In the case where the ratio of acid to oil was greater than that required to remove all of the aromatics, the percentage contraction by volume was greater than that calculated from refractive index. However, the refractive index and volume contraction calculated from it remain practically constant. It appears that the increase in percent contraction by volume

is due to a physical absorption of both paraffins and naphthenes.

In the case where the ratio of acid to oil was less than that required to remove all of the aromatics, the percent contraction by volume theoretically should be equal to that calculated from the refractive index. Actually, however, the percent contraction by volume was found to be less than that by refractive index. It is not certain why this takes place but it is believed to be the result of the alkylation of the aromatics when the sample is treated with the Kattwinkel reagent. This results in the formation of benzene homologs with chains longer than the parent aromatics. These alkylated aromatics have refractive index values that are different from the parent aromatics. It is this difference that is believed to cause the discrepancy between the two contraction values. When all the aromatics are removed by using the proper ratio of acid to oil, this discrepancy is no longer observed because the drop in index of refraction is due to the aromatics originally present and is unaffected by intermediate compounds that may be formed during the absorption.

It was mentioned above that the percent contraction by refractive index calculation remains practically constant after the proper ratio of acid to oil has been reached. This can be seen from Figures 4, 5 and 6. This is important because it shows than an excess of reagent may be used without seriously affecting the results.

It   ay u.   con-
tion   a increa   ratio   oil
the be   complete   tle removal. Figure 7
              etwe   reat contraction d the
              oil   lete   arb   ytrocarbon
and   initial refracti   ass   assumed value for the
refractive index fter sulfuric acid-phosphorous pentoxide
treatme t,   rough estimation of   r cent   tics can be
made. From this estimation the correct ratio   o oil
      be obtained from Figure 7. In using this figure it
      s bored   t t   rcent contraction includes the
      aining aft   sulfuric acid treatm t   ell
tics.

Calculation of efractive Index Value before Removal of Aromatics

      In   alcula   ontent by
refractive index,   necessary to   values bef r
      ovel   tics.   bove st
      ive index v   after   ov l of aromatics
atisfactory. If olefi   s   resent, however,
   lue representi   e before   tic removal may
   siderable error.   e value obtained after treatment
      furic acid is not satisfactory because alkylation
olymerization or abnormal shift in refractive index
recover, if olefins   ent, be   for the ori
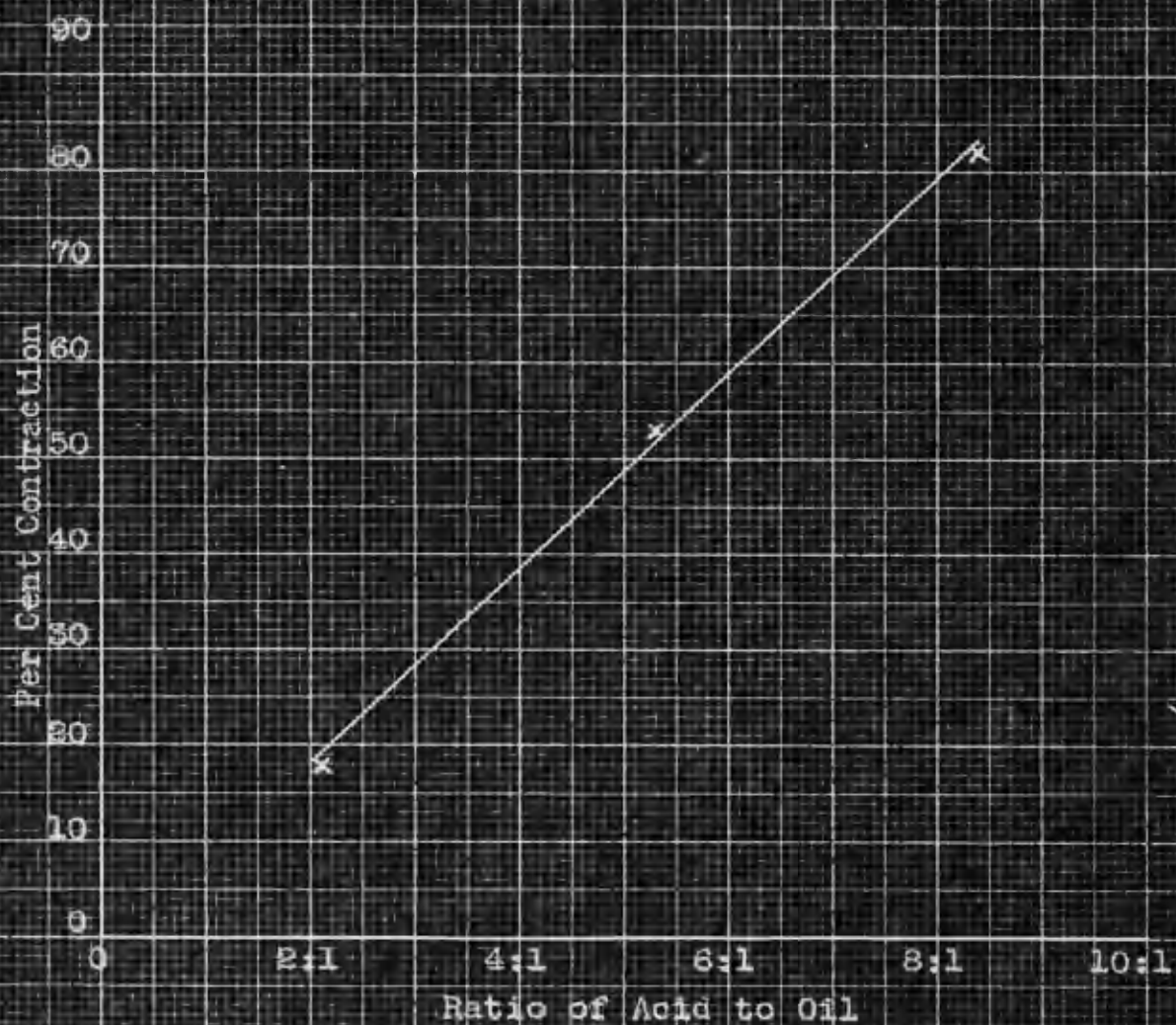   could not be   en been   refractive i

Figure 7.   Relationship Between Proper Ratio of Acid to
Oil and the Assumed Per Cent Contraction for
Aromatic Determination

for the olefins would probably be different than the refractive index of the sample were all of the olefins to be absent.

A correction for the original refractive index is obtained by assuming that the olefins are chiefly of the mon- and diolefin classes. Cyclic olefins and unsaturated benzene homologs are known to be present but in proportions small enough so that they may be neglected without appreciable error. The converted original refractive index value is obtained in the following manner:

The olefins in the sample are determined by the bromate titer and the per cent is calculated as though all the olefins were mono-olefins. It follows from this that:

$$B = M + 2D \quad (1)$$

where B = per cent olefins from the bromate titer, calculated as mono-olefins

M = per cent mono-olefins that are actually present

D = per cent diolefins

It has been shown on Page 53 that:

$$O = M + D \quad (2)$$

where O = per cent of olefins (actual)

Therefore:

$$B = O + D \quad (3)$$

and $$F = \frac{D}{O} \quad (4)$$

where F = fraction of diolefins in the olefin mixture.

Therefore:

$$F = \frac{B - O}{O} \quad (5)$$

$$N_{DM} = (1 - F)N_M + FN_D \quad (6)$$

where N_{DM} = refractive index of mono-olefin, diolefin mixture

N_M = refractive index of mono-olefins

N_D = refractive index of diolefins

$$N_{DM} = N_M + F (N_D - N_M) \quad (7)$$

$$N_D - N_M = C \quad (8)$$

where C = difference in refractive index values between mono-olefins and diolefins

$$N_{DM} = N_M - FC \quad (9)$$

$$N_S = \frac{(100 - O)N_A - ON_{DM}}{100} \quad (10)$$

where N_S = original refractive index

N_A = refractive index corrected for mon-olefins and diolefins

$$N_A = \frac{100N_S - ON_{DM}}{100 - O} \quad (11)$$

Substituting equation (9) in equation (11)

$$N_A = \frac{100N_S - ON_M - OFC}{100 - O} \quad (12)$$

Substituting equation (5) in equation (12)

$$N_A = \frac{100N_S - ON_M - (O)\frac{(B-O)}{O}(C)}{100 - O} \quad (13)$$

$$N_A = \frac{100N_S - ON_M - (B-O)C}{100 - O} \quad (14)$$

Values for N_M and C are given for different boiling ranges in Table XI and are represented graphically in Figure 8.

The per cent aromatics on the whole sample is calculated from the following formula which was derived from equation (a) on Page 61.

$$\% \text{ Aromatics} = \frac{N_A - N_Y}{N_Z - N_Y}(100 - O) \quad (15)$$

where N_Y = refractive index after $H_2SO_4 \cdot P_2O_5$

N_Z = refractive index from aromatic line for the specified boiling range

N_A = corrected refractive index, Equation 14

This method for determining the corrected original refractive index value to be used for obtaining the per cent aromatics was verified the following manner in using samples A_2, A_3, D_2 and D_3.

TABLE XI

Average Values for Refractive Index of
Mono-olefins and Diolefins for Different Boiling Ranges

Fraction ^{o} Centigrade	Refractive Index of Mono-Olefins @ 25°C N_D	Refractive Index of Diolefins @ 25°C N_M	$N_D - N_M$ C
80 - 100	1.4007	1.4226	0.0259
100 - 120	1.4126	1.4360	0.0234
120 - 140	1.4161	1.4382	0.0221
140 - 160	1.4202	1.4455	0.0253
160 - 180	1.4271	1.4476	0.0205
180 - 200	1.4365	1.4546	0.0181
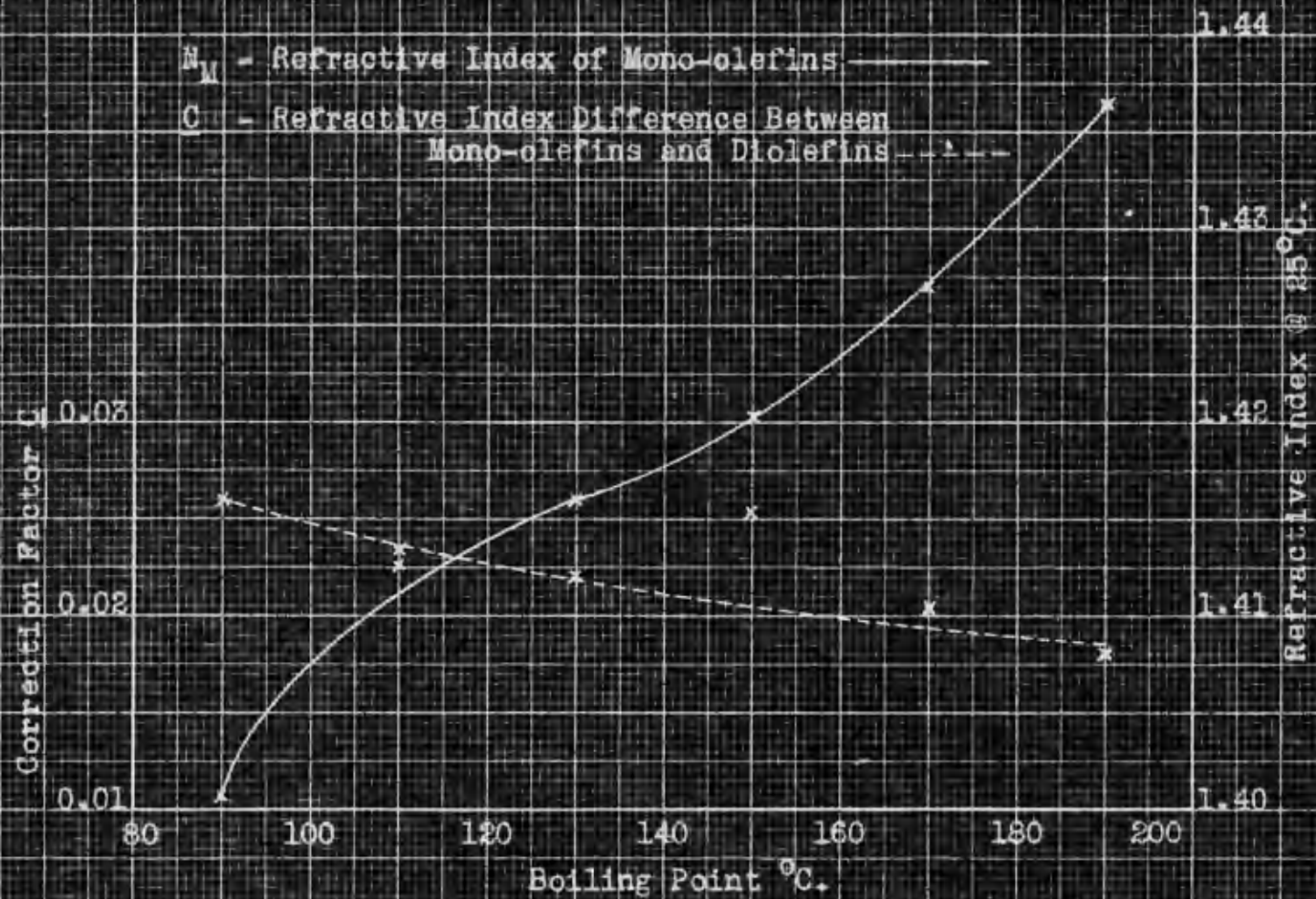
Figure 8. Variations of N_M and C with Change in Boiling Point for Use in Equation 14

The per cent aromatics was determined by hydrogenating the samples until most of the olefins were converted into saturated hydrocarbons. The bromate titer and refractive index were then measured. The refractive index after removal of the aromatics was obtained by stripping with sulfuric acid and phosphorous pentoxide reagent.

The aromatic content of these same samples were then determined by using the original and final refractive index, initial bromate titer and bromate titer after 82% sulfuric acid treatment.

A comparison of the per cent aromatics calculated from Equations 14 and 15 and the per cent calculated from the hydrogenation data is given in Table XII. The values for the per cent aromatics by the two methods are in good agreement which gives verification for the use of Equation 14.

Reaction Time for Removal of Aromatics

The optimum reaction time for the complete absorption of aromatics was established by treating portions of the same sample for six different periods of time. The selected time intervals varied from 10 minutes to one hour. Completeness of the reaction was determined by the constancy of the refractive index. The proper ratio of acid to oil as indicated by Figure 7 was employed. Samples containing a low, medium and high concentration of aromatics were tested.

TABLE XII

Comparison of the Per Cent Aromatics Calculated

by the Use of the Correction Factor $\underline{C}$ and the

Per Cent Aromatics Calculated from the Hydrogenation Data

	A_2	HA_2 *	A_3	HA_3
Original Bromate Titer	20.63	0.06	17.18	0.71
N_S	1.4369	1.4238	1.4482	1.4378
B	78.7	0.2	70.7	2.9
% Olefins by 82% Sulfuric Acid	26.0	not meas.	25.0	not meas.
Bromate Titer after 82% H_2SO_4	3.39	not meas.	3.80	not meas.
N_M	1.4126	1.4126	1.4163	1.4163
C	0.0235	---	0.022	---
Olefins on Whole Sample Corresponding to Bromate Titer after 82% H_2SO_4	9.5	---	11.7	---
O	35.5	---	36.7	---
N_A	1.4346	1.4237	1.4549	1.4384
N_P	1.4141	1.4091	1.4290	1.4180
Per Cent Aromatic in Whole Sample	16.5	17.1	25.4	26.5

*HA_2 signifies hydrogenated sample. In these samples B = 0

TABLE XII (Cont'd)

	D_2	HD_2	D_3	HD_3
Original Bromate Titer	16.03	1.20	14.10	2.84
N_0	1.4239	1.4130	1.4331	1.4240
B	61.2	4.6	58.0	11.7
% Olefins by 82% Sulfuric Acid	20	not meas.	21.3	not meas.
Bromate Titer after 82% H_2SO_4	3.39	not meas.	3.80	not meas.
N_M	1.4126	1.4126	1.4163	1.4163
C	0.0235	—	0.022	—
Olefins on Whole Sample Corresponding to Bromate Titer after 82% H_2SO_4	9.2	—	8.8	—
O	29.2	—	30.1	—
N_A	1.4179	1.4130	1.4330	1.4250
N_P	1.4058	1.4039	1.4180	1.4120
Per Cent Aromatic in Whole Sample	9.6	9.6	13.9	14.1

The results of this study appear in Table XIII and are shown graphically in Figure 9. From these curves it can be seen that the refractive index is practically constant after 30 minutes of acid treatment. The time of reaction for the complete absorption of aromatics was thus set at 30 minutes.

TABLE XIII

Determination of Optimum Reaction Time

for Complete Aromatic Removal

Sample	Original Refractive Index @ 25°C.	N_D^{25} after 10 min.	N_D^{25} after 20 min.	N_D^{25} after 30 min.	N_D^{25} after 40 min.	N_D^{25} after 50 min.	N_D^{25} after 60 min.
K	1.4132	1.3955	1.3952	1.3950	1.3939	1.3946	1.3946
L	1.4415	1.4125	1.4100	1.4098	1.4097	1.4097	1.4098
F	1.4705	1.4345	1.4300	1.4280	1.4278	1.4279	1.4278
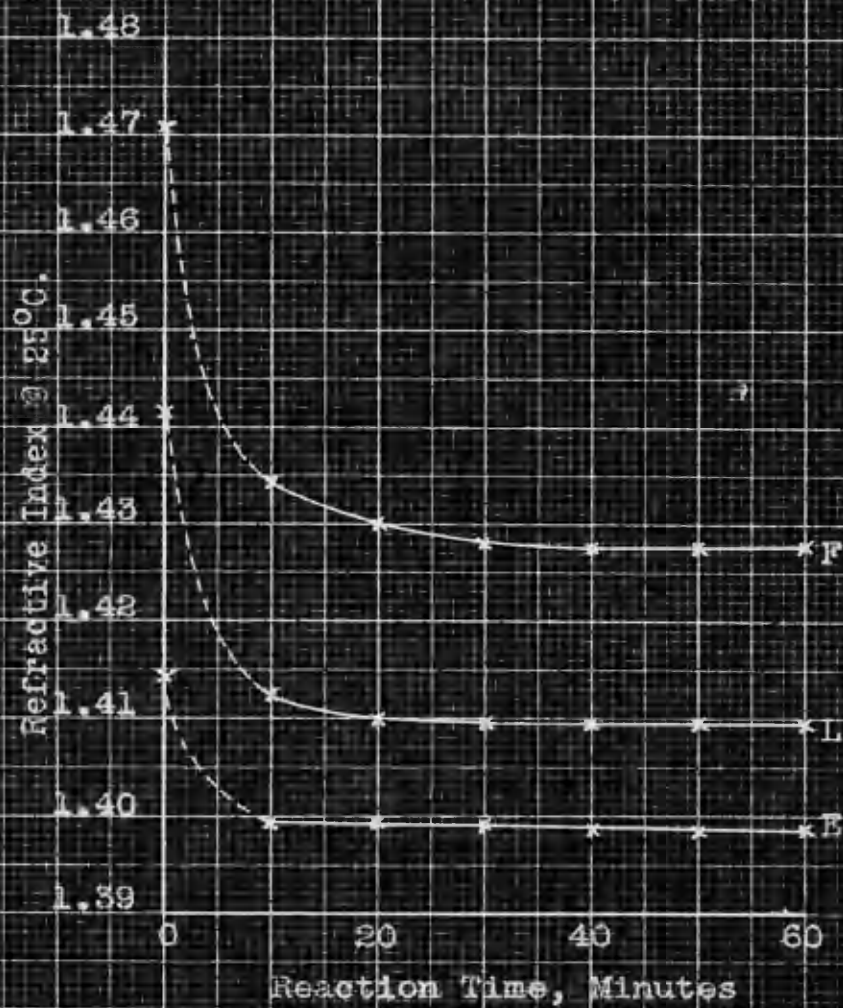
Figure 9. Determination of Optimum Reaction Time for Complete Aromatic Removal

Determination of Naphthene and Paraffin Hydrocarbons

It is well known that naphthenes and paraffins are relatively inert to most chemical reagents. However, upon treatment with strong fuming sulfuric acid, there is a reaction but it is slow and very selective. Only a few naphthenes and highly branched paraffins react. Contraction in volume will be given in most cases but this has been proven not to be preferential but to be a substantially equal absorption of both paraffins and naphthenes.

Dehydrogenation has been used to convert the homologs of cyclohexane to those of benzene structure. These benzene compounds are then absorbed by sulfuric or nitric acid. The contraction in volume will give the homologs of cyclohexane but the method does not take into account cyclopentanes and other saturated ring structures. Therefore, it does not give a satisfactory measure of the concentration of the naphthene hydrocarbons.

It was thought that the most satisfactory methods for the determination of naphthene and paraffin hydrocarbons were those based upon refractive index and critical solution temperatures with aniline. Both of these methods have been discussed previously.

Refractive Index Method.

In this method the refractive index of pure naph-

thenes and paraffins are plotted against boiling point.
Average curves are first drawn through these points.

In testing a sample of known boiling range, the
refractive index is measured and its position between the two
curves is determined. By a simple proportion of the distance
between the two curves and the distance of the point from the
paraffin curve, the percentage of naphthenes can be determined.
The per cent of naphthenes can be calculated from Equation 16.
The per cent of paraffins is given by Equation 17.

$$\text{Per cent Naphthenes, } N = \frac{N_Y - N_P}{N_N - N_P}\left[100 - (0 + A)\right] \quad (16)$$

where N_Y = Refractive index after $H_2SO_4 \cdot P_2O_5$

N_P = Refractive index for paraffins, Figure 12

N_N = Refractive index for naphthenes, Figure 12

0 = Per cent olefins

A = Per cent aromatics

Per cent Paraffins, $P = 100 - (0 + A + N)$ (17)

The paraffin and naphthene curves for refractive
index are shown in Figures 10 and 11. The naphthene curve is
dotted beyond 170°C. because refractive indices for naphthenes
above this temperature are very meagre and it is necessary to
assume representative values. The curves of Figures 10 and 11
are repeated in Figure 12, eliminating the individual values
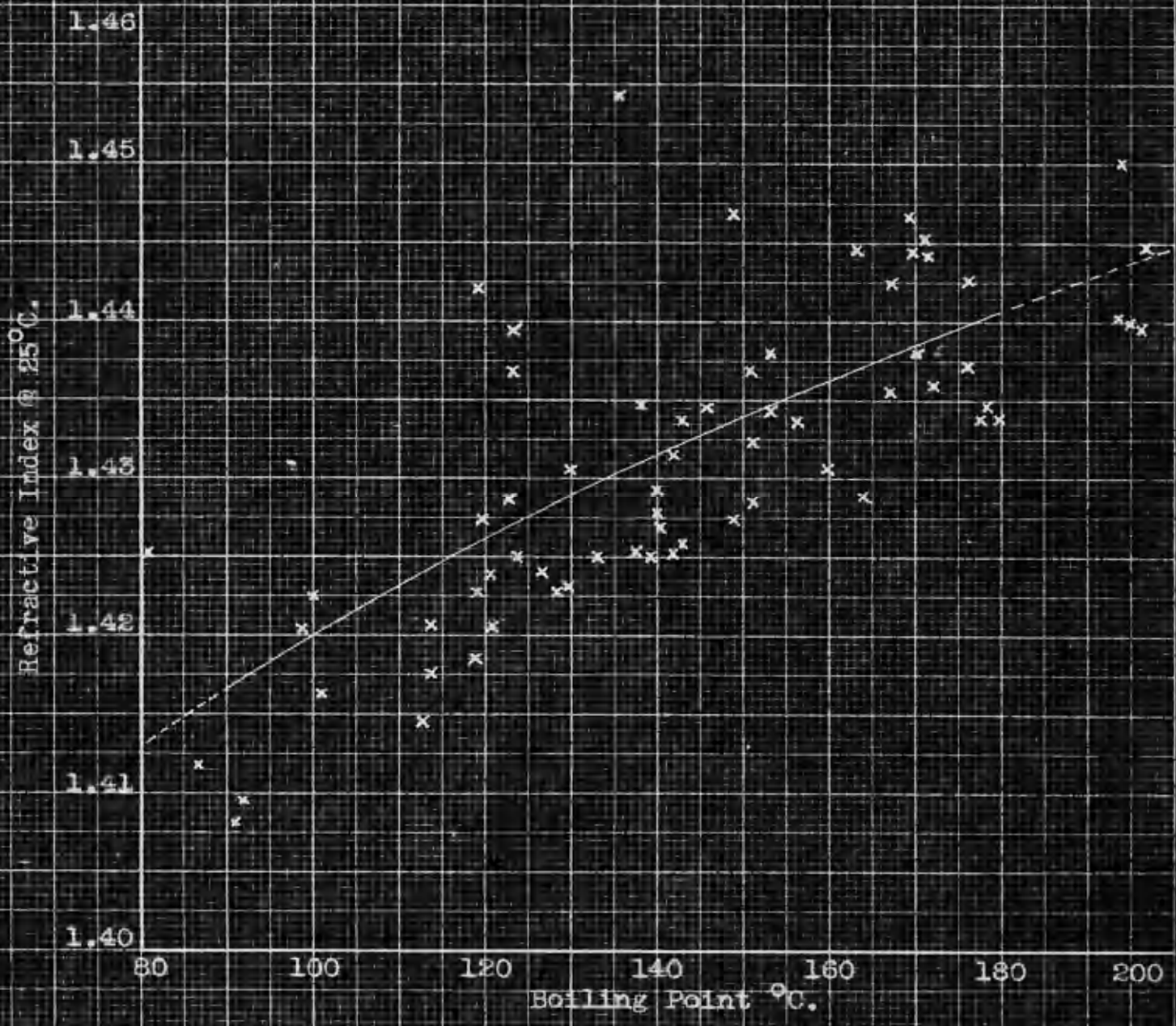used to determine them in order that they will be less

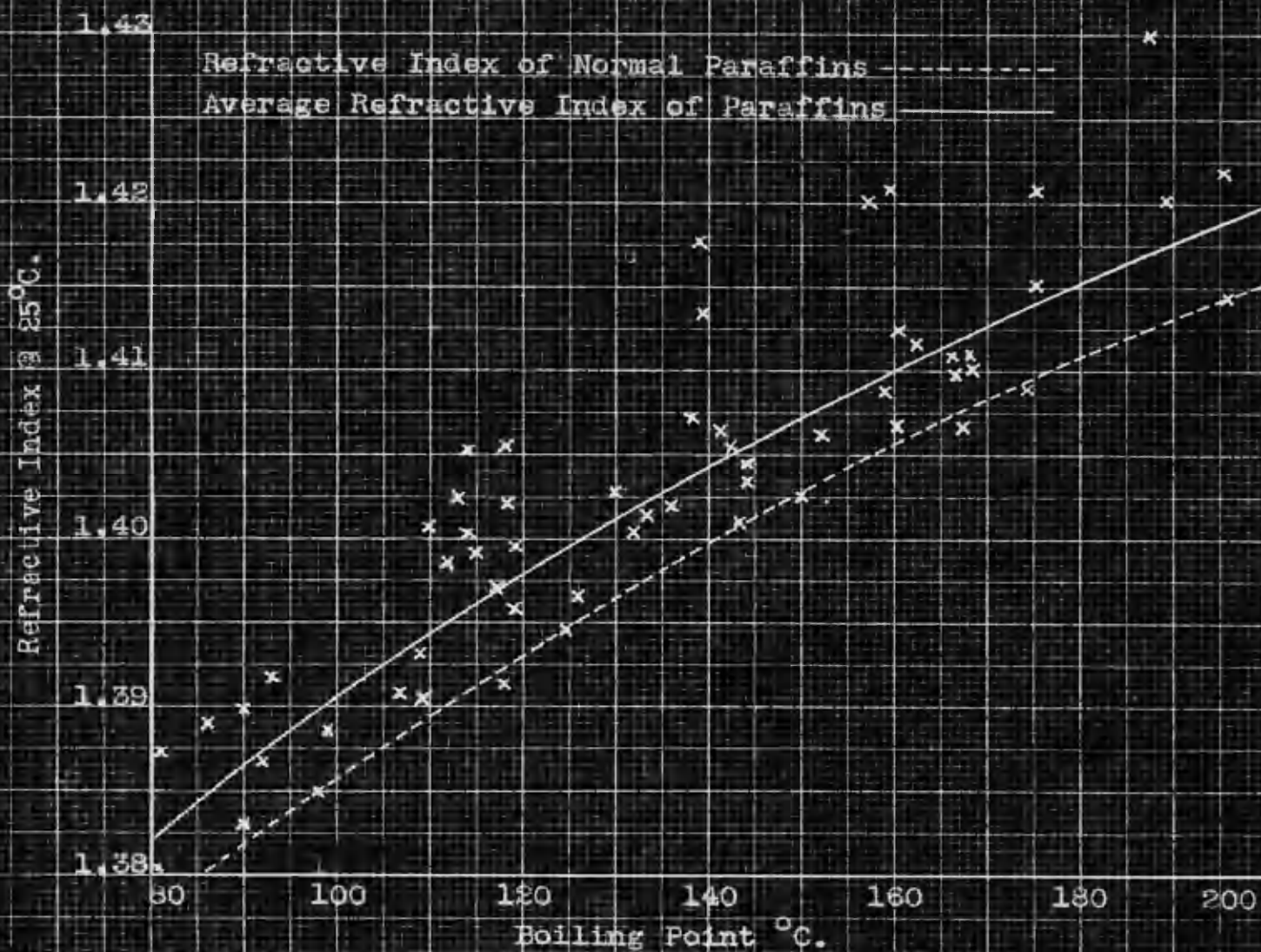Figure 10. Refractive Index for Naphthene Hydrocarbons

Figure 11.   Refractive Index of Paraffin Hydrocarbons

Figure 12. Refractive Index of Naphthenes and Paraffins

confusing when used in analytical methods.

Aniline Number Method.

Critical solution temperatures of naphthenes and paraffins with aniline have been used quite widely for their determination. In this work the critical solution temperature with aniline is termed the aniline number. In this method the aniline numbers of the pure naphthenes and paraffins are plotted against boiling point. Smooth curves are constructed through these points, using the method of averages.

The determination by aniline number is carried out in a manner similar to that of refractive index. By a simple proportion of the distance between the two curves and the distance of the point from the paraffin curve the percentage of naphthenes can be determined. The percentage of paraffins is obtained from Equation 17.

The paraffin and naphthene curves are shown in Figure 13. Both paraffin and naphthene curves are dotted beyond 170°C. because aniline number data above this are very meagre and it becomes necessary to assume representative values. Figure 14 is obtained in the same manner as Figure 12.

In the construction of the naphthene curve for aniline number and for refractive index only those hydrocarbons likely to occur in petroleum were used. This excludes all cyclopropane and cyclobutane homologs.
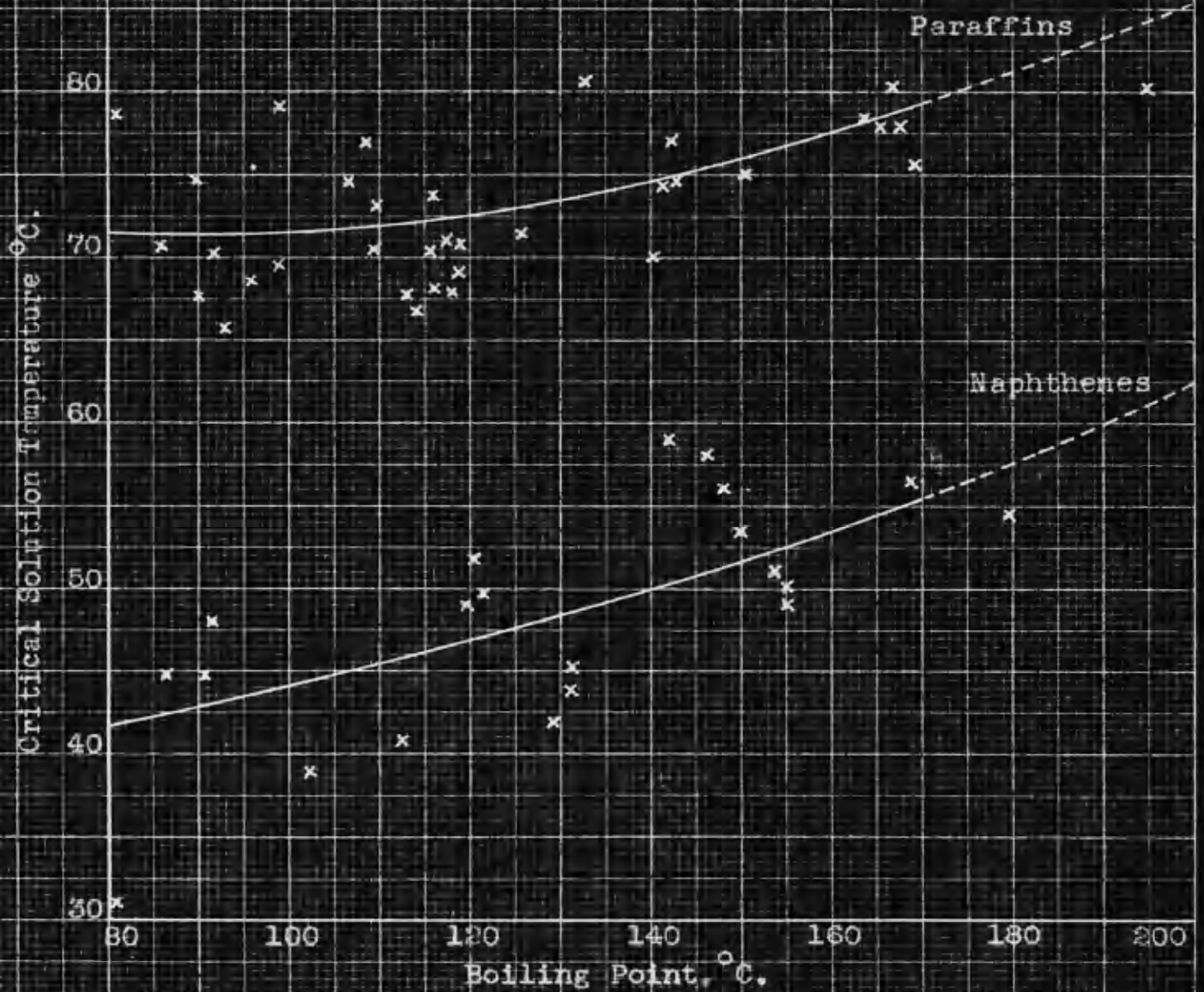
Figure 13.   Critical Solution Temperatures with Aniline of
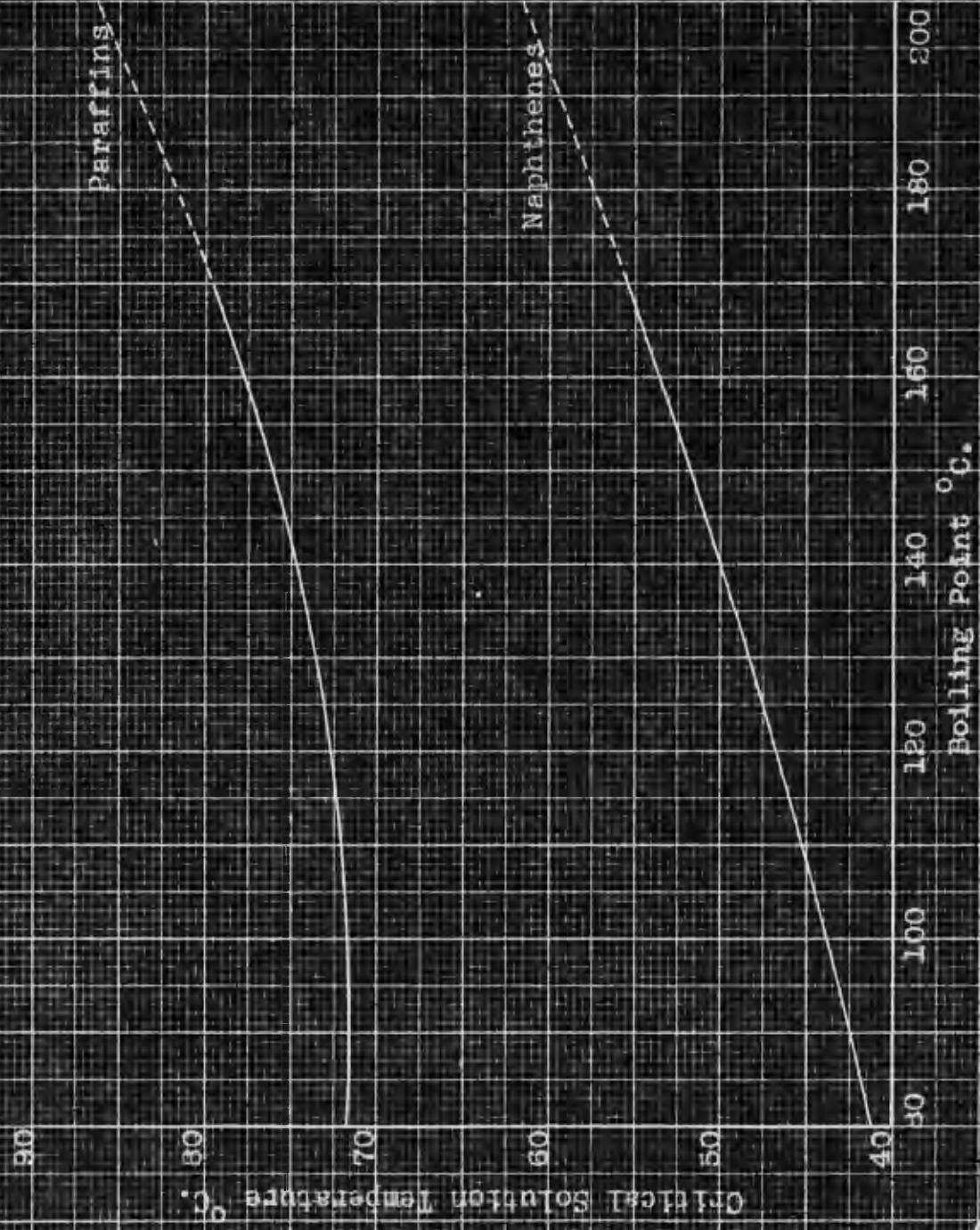Naphthene and Paraffin Hydrocarbons

Figure 14.   Critical Solution Temperatures with Aniline of
Naphthene and Paraffin Hydrocarbons.

The concentration of naphthenes and paraffins was determined for several samples, using the refractive index method and the aniline number method. The results of these tests are given in Table XIV. It is observed that in most cases the agreement between the values for the two methods is good.

TABLE XIV

Comparison of Critical Solution Temperature and
Refractive Index Methods for
Naphthene and Paraffin Determination

Sample	N_D^{25}	CST	Refractive Index		Aniline Number	
			% naphthene	% paraffin	% naphthene	% paraffin
B_1	1.3980	61.6	40.8	59.2	34.5	65.5
B_2	1.4050	63.8	35.6	64.4	30.6	69.4
B_3	1.4117	65.3	36.1	63.9	32.5	67.5
B_4	1.4182	67.0	39.2	60.8	36.8	63.2
B_5	1.4260	68.3	51.1	48.9	46.4	53.6
B_6	1.4327	71.0	61.4	38.6	54.5	45.5
D_1	1.3993	60.8	45.5	54.5	37.2	62.8
D_2	1.4058	61.4	38.4	61.6	39.6	60.4
D_3	1.4138	63.0	43.9	56.1	41.6	58.4
D_4	1.4215	65.0	51.9	48.1	45.0	55.0
D_5	1.4263	67.0	52.4	47.6	51.9	48.1

RESULTS AND CONCLUSIONS

An outline of the method which has been developed in this study of the analysis of hydrocarbon mixtures is presented below:

(1) Fractionate the sample into 20 degree cuts from 80 to 200°C.

(2) Determine the original bromate titer of each fraction.

(3) Determine the original refractive index of each fraction.

(4) Treat 5 cubic centimeters of the fraction with 30 cubic centimeters of 82 per cent sulfuric acid for 30 minutes. Measure the contraction and the bromate titer.

From the contraction due to 82 per cent sulfuric acid and the bromate titer, calculate the per cent olefins in the sample. This calculation has been shown on page 53.

(5) Estimate the percentage of aromatics in the acid treated fraction and then determine the proper ratio of acid to oil from Figure 7.

(6) Treat the oil residue from Step 4 with sulfuric acid-phosphorous pentoxide reagent for 30 minutes using the proper ratio of acid to oil.

(7) Determine the refractive index after this treatment.

(8) From Equation 14 calculate the refractive index to be used as the initial value for determining the per cent

aromatics.

(9) From Equation 15 on page 73, calculate the per cent aromatics.

(10) Using the refractive index value after treatment with sulfuric acid-phosphorous pentoxide reagent calculate the per cent naphthenes and paraffins from Equations 16 and 17 on page 83.

When the percent of olefins as calculated from the original bromate titer is less than five per cent, treatment with 82 per cent sulfuric acid may be omitted. The rest of the method is followed as outlined.

In order to reduce manual labor in the acid treatments, mechanical shakers can be used providing there is complete emulsification of the acid and oil for the duration of the treatment.

Discussion of the Method

The determination of olefins by the bromine number is not claimed to be entirely new but in previous methods it was necessary to have a knowledge of the average density and molecular weight of the olefins before it was possible to calculate their concentration. In the method developed these factors have been approximated by assuming certain mono-olefins to be present. It is true that certain samples may or may not contain some of the olefins assumed to be present but the absence or presence of these olefins will not materially affect the bromate titer of each specified boiling range.

The constant C of Equation 14 was developed by obtaining the difference in refractive index of mono-olefins and diolefins which were assumed to occur in petroleum. Here again, certain samples may or may not contain some of the compounds which are assumed to be present. However, since C was obtained by using a large number of compounds, the absence or presence of some of these will not materially effect its value.

The use of Equation 14 for determining the initial refractive index for the calculation of the per cent aromatics gives values which approach more nearly to the true value. Methods that use the value after treatment with sulfuric acid are in error due to reactions such as polymerization and alkylation. A more complete knowledge of the physical data for the mono-olefins and diolefins would aid in further establishing the validity of Equation 14.

The use of refractive index for determining the concentration of aromatic hydrocarbons is quick and accurate. It has not been used hitherto because representative values for the refractive index of aromatics occurring in specific boiling ranges were not known. Values determined for widely diversified distillates have been found to be in good agreement for each boiling range and in fair agreement with average values taken from the literature.

It is possible that the aromatic line could be established also by hydrogenating the olefins and then following the method that was employed in the sulfuric acid treatment. This would give still another check on the aromatics line established in this work.

The use of the refractive index for determining the concentration of naphthenes and paraffins should become more certain as more complete information regarding the physical constants of naphthenes and paraffins actually occurring in petroleum becomes available.

The determination of naphthenes and paraffins by the refractive index is preferred over critical solution temperatures because data relative to refractive index is more complete and because the operation is very simple.

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James Grant Hayden, Jr., Doctor of Philosophy, 1941
Chemical Engineering

A Study of the Separation and Estimation of the Four General
Classes of Hydrocarbons Occurring in the Gasoline Range of
Petroleum

Directed by Dr. Wilbert J. Huff and Dr. Donald T. Bonney

Pages in Thesis   103   Words in Abstract   358

ABSTRACT

A method of analysis has been devised for the
quantitative separation of the olefin, aromatic, naphthene
and paraffin hydrocarbons which occur in the gasoline fract-
ion of petroleum. The method involves new features and new
manipulation of the existing data.

Triolefins, diolefins and some of the mono-olefins
are absorbed in 82 per cent sulfuric acid. The olefins re-
maining after the acid treatment are determined with the acid
of an empirical relationship based upon the bromine number
obtained by an acidified standard solution of potassium bro-
mate and potassium bromide. The total per cent of olefins is
calculated from this relationship and the contraction due to
sulfuric acid. The optimum time of reaction for the 82 per
cent sulfuric acid treatment was established.

After the removal of the olefins, aromatic hydro-
carbons are determined by the difference in refractive index
before and after removal of the aromatics. These compounds
are removed by absorption in the Kattwinkel reagent (concen-
trated sulfuric acid plus phosphorous pentoxide). In order
to employ the refractometer in the determination of aromatics

it was necessary to develop a factor for correcting the original refractive index for the olefins that were present. It was also necessary to determine representative values for the aromatic hydrocarbons boiling above the xylenes. The per cent of aromatic hydrocarbons is calculated from the corrected original refractive index, the refractive index after acid treatment and the representative refractive index of the pure aromatics. Optimum reaction time for the complete removal of the aromatics by the Kattwinkel reagent was established.

Naphthene and paraffin hydrocarbons are also determined by using the refractometer. Curves for the refractive indices and boiling points of the naphthene and paraffin hydrocarbons were constructed using the most recent values for these compounds as given in the literature. The value of the refractive index for a specific sample after removal of the olefins and aromatics lies somewhere between the naphthene and paraffin curves. By a simple proportion, the distance of the point from the paraffin curve and the total distance between the two curves are used to compute the per cent of naphthene hydrocarbons. The per cent of paraffin hydrocarbons is obtained by difference from 100.

VITA

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