

THE SEPARATION OF OLIMPINES AND AROMATICS  
FROM HYDROCARBON MIXTURES

by

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## INTRODUCTION

Much attention has been devoted to the determination of the chemical nature of hydrocarbon mixtures since the beginning of the petroleum industry. Little progress has been made however, in the development of reliable analytical methods for the determination of the constituents of complex mixtures, although much valuable work has been done on the subject.

Since petroleum products are very complex mixtures of hydrocarbons which exhibit a wide range of chemical and physical properties, the difficulties encountered in their analysis are very great. The problem is further augmented by the fact that the chemistry of pure hydrocarbons, with possibly the exception of the aromatics, is a neglected chapter in organic chemistry. Information available on the behavior of pure hydrocarbons has largely been obtained on substances of doubtful purity, and as a result much contradictory information has been published.

It is quite important to the petroleum industry

that reliable and accurate analytical methods for the determination of the constituents of hydrocarbon mixtures be developed. Such methods might be used to evaluate motor fuels, although their evaluation by means of the knock motor is quite successful, and their application to products of the cracking process would give a clearer picture of what actually happens when an oil is cracked. Very few crudes originally contain unsaturated or olefinic hydrocarbons, and those few in very small amounts; but after being subjected to the temperature and pressure of the cracking process, the resulting products may contain very high percentages of both aromatic and unsaturated compounds. Analytical procedures should be available for the study of this process. Such procedures would also lend material assistance in the manufacture of synthetic hydrocarbons from petroleum derivatives, both in research work and process control.

In the estimation of motor fuel and light oil constituents, it is usually sufficient to determine the relative proportions of unsaturated, aromatic, naphthenic, and paraffinic hydrocarbons. These are classified

as follows (21):

- (a) Unsaturated hydrocarbons.--Those containing olefinic double bonds, i.e., mono- and diolefines, acetylenes, di- and tetra-hydrobenzene and their homologues and aromatic and naphthenic hydrocarbons containing olefinic double bonds in their side chains.
- (b) Aromatic hydrocarbons.--Benzene, naphthalene, anthracene and their homologues.
- (c) Naphthenic hydrocarbons.--Saturated cyclic hydrocarbons or poly-methylenes and their homologues, having the general formula  $C_nH_{2n}$ .
- (d) Paraffinic hydrocarbons.--Saturated straight or branched chain hydrocarbons of the general formula  $C_nH_{2n+2}$ .

Methods of analysis used for the estimation of these four main classes of hydrocarbons are basically physical or chemical, or combinations of both. When chemical methods are used the olefines, which are the most reactive, are usually first removed and estimated, then the aromatics, naphthenes, and paraffins. Alternatively the aromatics and olefines may be estimated as a combined class, and the olefines estimated separately.

The purpose of this investigation was to collect data on some of the proposed analytical methods, using synthetic mixtures of known composition as samples, and by correlation of this information to obtain a procedure which would give approximately correct results.

#### THEORETICAL DISCUSSION

In all of the proposed methods for hydrocarbon analysis the method is primarily based on some chemical or physical characteristic which is shared by the fairly common compounds of that particular series. Experimental work is carried out on a synthetic mixture of known composition, and the method adjusted to give correct results on this mixture, or an empirical correction made to adjust the results found. While such attempts are the best available, there is often no assurance that the method devised in this manner will give correct results on other hydrocarbon mixtures. In many cases failure to control all possible variables, combined with differences in operating technique, leads to very contradictory results.

Very little is known in regard to the reactions in-

volved in most of the analytical methods which have been proposed from time to time, or their possibilities and limitations. For the purpose of reviewing the more important methods, they are grouped according to the hydrocarbon series on which they have been used.

### Estimation of Unsaturated Hydrocarbons

When chemically estimating constituents of hydrocarbon mixtures it is necessary to first separate unsaturated compounds from the mixture before other constituents can be determined as the olefines are the most reactive. Determination of the amount of olefines present may or may not be made at the same time, depending upon the method used. The following methods are used for the separation of olefines:

- (a) Solution in sulfuric acid.
- (b) Halogen absorption.
- (c) Reactions with mercury salts.
- (d) Reaction with ozone.
- (e) Oxidation with perbenzoic acid.
- (f) Reaction with sulfur monochloride.
- (g) Nitration.
- (h) Solution in sulfuric acid with catalysis.

Sulfuric acid reacts with olefines in hydrocarbon mixtures to give five types of products: (a) alcohols (b) esters (c) polymers (d) oxidation products (e) saturated hydrocarbons by reduction. The extent to which each of these five reactions take place is a function of the molecular weight and the structure of the olefine and the acid concentration (1). Sulfuric acid would be a good reagent for removing olefines were it not for the fact that it dissolves or reacts with aromatics also, the amount going into solution depending on the concentration of the acid used, and the length of time of contact (6). Consequently this method is not accurate, although it is rapid and convenient.

Halogen absorption methods include Hubl and Wijs iodine numbers, and Hanus, Francis, and McIlhiney bromine numbers (18). These are useful in the examination of animal and vegetable oils but are not very applicable to mineral oil due to the complexity of the oil and the necessity of using a mean molecular weight in the conversion of the halogen number to per cent olefines.

Unsaturated hydrocarbons react with certain mercury salts either forming complex addition compounds or



becoming oxidized. However, the reaction is uncertain, depending on the hydrocarbons present, and is not suited to general analytical use (13).

Ozone reacts with unsaturated hydrocarbons to form ozonides, which easily decompose forming water soluble compounds. The accuracy of the ozone method is doubtful because very little reliable data exists regarding the action of ozone on other hydrocarbons, however, action is very probably positive (21). Use of perbenzoic acid involves a very tedious procedure, and gives as a result an "oxygen value" of the oil, corresponding to an "iodine number" in halogen absorption, and having the same objections.

Sulfur monochloride reacts vigorously with unsaturated hydrocarbons and also, at a moderate rate, with saturated hydrocarbons, the reaction in the latter case probably being a chlorination (16). A direct determination of per cent olefines cannot be made with this reagent. Olefines and aromatics together are first determined by treatment with sulfuric acid, olefines are removed from another sample by treatment with sulfur monochloride, and aromatics are determined on the

olefine-free oil by a nitration method (6). The olefine and aromatic contents are then calculated.

Nitric acid is far too vigorous in its action for the selective removal of olefines as it attacks hydrocarbons of other series. However, a method for the quantitative absorption of both olefines and aromatics using fuming nitric acid at  $-10^{\circ}\text{C}$ . has been proposed (9).

Sulfuric acid (gravity 1.84) containing boric acid has been recommended for the determination of olefines (15), the boric acid preventing the action of sulfuric acid on aromatics.

#### Estimation of Aromatic Hydrocarbons

There are two important methods for the estimation of aromatics and olefines together; sulfonation and nitration. Other than these two, all methods of estimating aromatics are applicable only with olefine-free oils. The most important chemical methods are:

- (a) Concentrated sulfuric acid treatment.
- (b) Sulfuric acid with catalysis.
- (c) Critical solution temperature (C.S.T.) measurements with various solvents.

(d) Treatment with nitric acid or some form of nitration mixture.

(e) Solvent extraction.

Concentrated sulfuric acid (98-100 per cent by weight) has been used for some time for the determination of aromatics. The reaction involved is sulfonation, the aromatic sulfonic acids formed dissolving in the acid sludge, and percentage aromatics measured by volume loss calculations. Much controversy exists in regard to the acid concentration which should be used. Sulfuric acid containing free  $\text{SO}_3$  has a pronounced action on straight chain and naphthenic hydrocarbons, so the concentration must be less than 100 per cent. However, certain workers (21) have found free  $\text{SO}_3$  necessary to extract all of the aromatics present in kerosene. The standard method adopted by the Institution of Petroleum Technologists consists of treating the oil to be examined with twice its volume of 98 $\pm$ 1 per cent sulfuric acid for fifteen minutes, preferably in a mechanical shaker. The acid layer is then withdrawn and the acid treatment repeated for two further periods of fifteen minutes each, using in each of these cases one volume of acid. The aromatic content is then determined by difference in "aniline point" before and after treatment.

The "aniline point" method is an application of the C. S. T. of an oil with aniline, and will be discussed later under those methods.

Sulfuric acid (gravity 1.84) containing phosphorus pentoxide has been recommended for extraction of aromatics (15). The action of sulfuric acid upon aromatics is catalysed by the presence of  $P_2O_5$ , and the percentage of aromatics is determined from the volume loss. This method is similar to the method for removal of olefines using sulfuric acid containing boric acid.

The presence of aromatic hydrocarbons decreases the C. S. T. of a hydrocarbon mixture with aniline, nitrobenzene, and various other solvents, the depression being proportional to the weight of aromatics present (21). Since a C. S. T. determination is tedious and time consuming, resort is usually made to the use of "aniline point" determinations. An "aniline point" may be defined as the temperature at which equal volumes of a hydrocarbon mixture and aniline are just completely miscible. It is very important that the aniline be dry and freshly distilled as the presence of water introduces a large error in an "aniline point" determination. The aniline and oil (10 cc. of each) are poured into a test tube, fitted with

a stirring device and a thermometer, and air-jacketed by a larger test tube. Constantly stirring, the mixture is heated or cooled to the temperature of complete miscibility which is the "aniline point". This is a standard method of the American Society of Testing Materials. It is usually necessary to apply a correction factor in the determination of aromatics by "aniline points", taken before and after extraction with concentrated sulfuric acid. By application of C. S. T. determinations with two solvents, as aniline and nitrobenzene, assuming C. S. T. curves when plotted against percentage aromatics follow a straight line, and double interpolation between the two sets of curves, it is possible to estimate the amount of aromatics present without extraction (21). This method is wrong, however, in its basic assumption that the "aniline points" of all aromatics are the same.

Treatment with nitric acid, measuring volume loss, is a nitration reaction, and is usually carried out using fuming nitric acid. Aromatic hydrocarbons may be easily nitrated; but the nitro-aromatic compounds are not completely soluble in the acid sludge, each nitrated hydrocarbon giving a different volume change and a different volume of nitrated products, hence the method is not

accurate. These errors are not corrected by dissolving out the nitro-aromatics with sulfuric acid, due to a change in total volume when this is done. More reliable results are obtained by the use of a nitrating mixture containing 25 per cent nitric acid, 58 per cent sulfuric acid, and 17 per cent water. This nitrating mixture does not appreciably dissolve the nitro-compounds, and they usually separate out in a distinct layer, the volume of which is proportional to the aromatic content of the oil. The aromatic content can be empirically calculated from this volume, or the nitro-compounds extracted with concentrated sulfuric acid, and the remaining volume used as a basis of calculation. However, the volume of nitro-compounds formed varies with the particular aromatic hydrocarbons reacting (6), and factors must be introduced to compensate for this defect, which leads to inaccuracy.

Certain solvents show a preferential action on aromatic hydrocarbons, and their use has been applied to the quantitative determination of aromatics. Sulfur dioxide, dimethyl sulfate and diethyl sulfate have been used in a number of cases. Since the solubility of an oil is proportional to the amount of solvent used this method is not in favor at the present time.

Physical methods, based on specific gravity and refractive index measurements, show a great deal of promise in the determination of aromatics, which have the highest refractive indices and specific gravities of the four main classes of hydrocarbons. Most of these methods require the extraction of the aromatics, and do not compensate for variations from the above rule with resulting inaccuracies.

#### Estimation of Naphthene and Paraffin Hydrocarbons

This is the most difficult step in the analysis of hydrocarbon mixtures, and as yet no method giving more than approximate results has been proposed. The only direct method is an empirical calculation from "aniline point" determinations, in which erroneous assumptions must be made.

### EXPERIMENTAL PROCEDURE

#### Apparatus

A distillation apparatus was built, consisting of a



200 cc. round-bottom short-neck Pyrex balloon flask, surmounted by an insulated Hempel column six inches high and containing four inches of glass beads. This apparatus is shown in Plate I. The side-arm of the Hempel column was connected to a vertical copper tube condenser fourteen inches in length, glass-jacketed, with suitable connections for cooling water. This apparatus was mounted on a single ring-stand in order to give maximum stability. An insulated metal jacket with observation windows of mica was placed around the balloon flask, and was enclosed on the bottom by a transite plate with a one and one-quarter inch hole in the center in which the flask rested, and on the top by a split plate of transite with a hole of sufficient size to accommodate the neck of the balloon flask.

The Hempel column was constructed of Pyrex glass tubing, three-fourths of an inch in diameter, tapering to three-eighths of an inch in diameter one and one-half inches from the bottom, and with a one-fourth inch side-arm five inches long. The column was insulated with three layers of small asbestos cord with the exception of a portion three-fourths of an inch wide just below the side-arm, which was left bare. A piece of glass tubing of greater diameter was fitted over the asbestos winding, air-



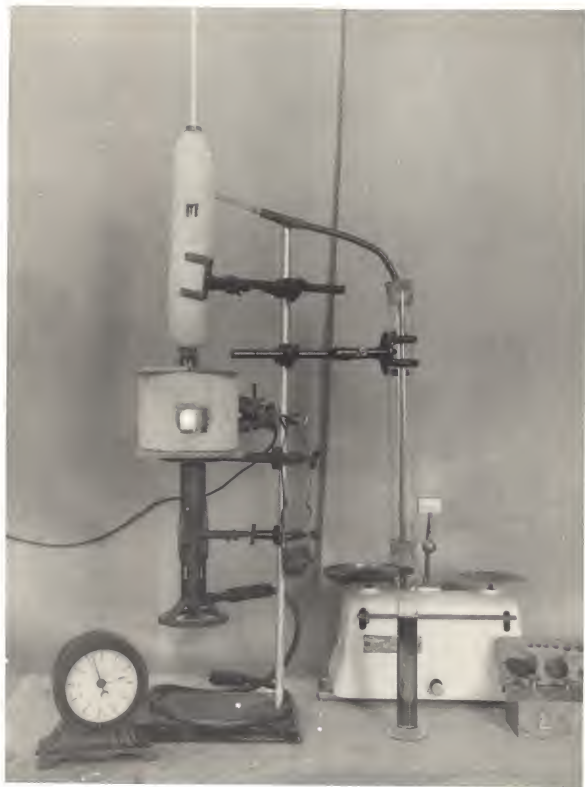
jacketing the bare portion of the column, and extending a short distance over the asbestos winding thus holding it in place. The column was then insulated with three-eighths of an inch of shredded asbestos mixed with a small amount of Portland cement as a binder, leaving very small windows on opposite sides of the column,  $90^{\circ}$  from the side-arm, and on a level with the top of the packing. These windows were provided for observation of the operation and to allow heat loss for condensation of vapor for reflux, so that the column could be operated just short of priming. Cork connections between the column and the flask held the thermometer in the top of the column. These were lacquered with clear lacquer and replaced after each distillation to prevent loss of volatile material and destructive distillation of the cork. The rubber tube connection between the side-arm and condenser inlet was lacquered on the inside, and was replaced on noticeable swelling.

A metal lined wooden box was used for a constant temperature bath, with the manual addition of hot water or ice as needed to maintain the temperature desired.

The nitration tube used was of the two-bulb separatory funnel type. It was glass-stoppered at the top, and had a glass stop-cock at the bottom, with a graduated column of 35 cc. capacity between the bulbs.

Explanation of Plate I.

The Distillation Apparatus.



### Reagents and Samples

Various concentrations of sulfuric acid from 30 per cent to 98 per cent by weight were prepared, and adjusted by titration to within one-tenth of one per cent of the concentration desired.

A nitration mixture consisting of 25 per cent by weight  $\text{HNO}_3$ , 58 per cent  $\text{H}_2\text{SO}_4$ , and 17 per cent  $\text{H}_2\text{O}$ , was prepared for the determination of aromatics (6), and two solutions of sulfuric acid, one containing 5 gms. boric acid per 100 cc. acid (gravity 1.84), and the other containing 30 gms. phosphorus pentoxide per 100 cc. acid, for the determination of olefines and aromatics, respectively (15).

A sample of highly cracked gas oil (gravity  $25^\circ$  API) was used in preliminary work. Most of the work was done on samples of four synthetic mixtures of the compositions shown in Table I.

The "aniline points" given in Table I are the results of determinations made during the preparation of the synthetic mixtures, and hence may be used as a measure of the completeness of separation of the mixtures during analysis. Total paraffins is denoted by P, which in all cases con-

sisted only of heptane. N and A denote naphthenes and aromatics respectively. Since mixture No. 2 contained no olefines the "aniline point" of the original oil is the same as that of total paraffins, naphthenes, and aromatics.

Table I  
"Aniline Points" of Representative Hydrocarbons.

No.	Hydrocarbon	Vol. %	Aniline Points			Oil
			P	P+N	P+N+A	
1.	Heptane (normal)	60	142.2			
	Cyclohexane	5		139.0		
	Benzene	15			79.0	
	Toluene	15				77.5
	Octylene	5				
2.	Heptane	60	142.2			
	Cyclohexane	10		138.5		
	Phenyl cyclohexane	10		110.0	110.0	
	Benzene	20			75.6	75.6
3.	Heptane	60	142.2	142.2		
	Iso-propyl benzene	15				
	Toluene	15			75.5	
	Octylene	10				83.8
4.	Heptane	60	142.2			
	Cyclohexane	10		132.2		
	Benzene	20			89.8	
	Cyclohexane	4				
	Octylene	4				85.0
	Diallyl	2				

## Methods

Effect of Varying Concentration of Sulfuric Acid on Solution and Polymerization Losses in Gas Oil. The oil was cooled to 60°F. and 50 cc. measured into a tared graduate cylinder and weighed ( $V_1$  and  $W_1$ ). In subsequent determinations the samples were weighed, obviating the necessity of cooling to 60°F. each time. The oil was placed in a 200 cc. separatory funnel, allowing several minutes for draining, cooled to 35-40°F. in an ice-water bath, and shaken with two volumes of sulfuric acid for ten minutes. The acid was also previously cooled, and was added in approximately 50 cc. portions, shaking and cooling after each addition. After total acid addition the mixture was shaken for ten minutes in two-minute periods, cooling for two minutes between each period.

The acid sludge was separated into the lower layer by centrifuging, drawn off and discarded. The remaining oil was washed once with one volume of water, once with one volume of 5 per cent sodium hydroxide solution, and finally with one volume of water, drawn off into the original graduate, weighed, and the volume of the oil recorded after ad-

justing the temperature to 60°F. ( $W_2$  and  $V_2$ ). The loss by solution in the acid sludge ( $L_1$ ) was found by volume change:

$$L_1 = V_1 - V_2 \quad (1)$$

The next step was the separation by distillation of the unchanged oil from polymers and olefine-aromatic condensation products by fractional distillation. In order to compensate for distillation losses this was carried out in the following manner:

The oil remaining from the above acid treatment was transferred to a weighed 200 cc. balloon flask in the distilling apparatus previously described. Distillation was carried out at a rate of about two drops a second to the end point of the oil, which in all cases was less than that of the original oil. The distillate was collected in the original graduate, which, after distillation, was weighed ( $W_3$ ), stoppered, cooled to 60°F. and the volume read ( $V_3$ ). The volume loss in this case was due to polymerization losses ( $P$ ), or the difference in weight of the distillation flask before and after distillation, and to evaporation or non-recovery ( $L_w$ ), where:

$$L_w = W_2 - (W_3 + P) \quad (2)$$

Since  $l_w$  is a weight loss and the other losses (as  $L_1$ ) were volume losses,  $l_w$  was converted to a volume loss ( $l_v$ ) by the assumption that evaporation loss had the same specific gravity as the distillate, and division of  $l_w$  by that specific gravity, as determined by a hydrometer. Loss in volume ( $L_2$ ) was found by the following computation:

$$\frac{l_w}{\text{sp. g. of dist.}} = l_v \quad (3)$$

$$L_2 = V_2 - (V_3 + l_v) \quad (4)$$

And finding the total volume loss ( $L$ ):

$$L = L_1 + L_2 \quad (5)$$

Method of Faragher, Morrell, and Levine (6). Olefines and some aromatics were removed by treating with 90-92 per cent by weight sulfuric acid, with subsequent distillation for removal of polymers. Remaining aromatics were then removed by treating with 98 per cent sulfuric acid, and the



total volume loss was taken as sum of olefines and aromatics. Olefines were removed from a second sample by treatment with sulfur monochloride, and the aromatic content of the olefine-free oil determined by a nitration method.

Before the actual analysis of the synthetic mixtures a study was made of the effect of varying reaction temperature, time of contact, and the relative acid volume used in the second acid treatment. This work was done on mixture No. 1, and the mildest conditions which gave approximately correct results were adopted for the analysis of the other three mixtures.

In the determination of total olefines and aromatics together, 50 cc. of the hydrocarbon mixture was shaken with two volumes of 90-92 per cent sulfuric acid, and the procedure carried through exactly as in the work on gas oil, where a volume ( $V_3$ ) was recovered from the distillation for removal of polymers. In working with the synthetic mixtures this oil was transferred to a 200 cc. separatory funnel, cooled to 35-40°F., and shaken with three volumes of 98 per cent sulfuric acid for ten minutes, shaking two minutes and cooling two minutes as in the primary acid treatment.

The acid sludge was settled or centrifuged out, drawn off, and discarded. The remaining oil was drawn off into the original graduate, cooled to 60°F., and volume ( $V_4$ ) read. The volume loss due to solution of remaining aromatics in the acid sludge ( $L_3$ ) was found by volume change:

$$L_3 = V_3 - V_4 \quad (6)$$

The total volume loss, equivalent to the sum of the olefinic and aromatic content of the oil, was found by adding the three volume losses. Since this total loss was expressed in cubic centimeters, multiplication by two converted the loss to per cent loss. A form for the recorded data is given below:

Table II  
Data Form of Aromatic and Olefine Analysis.

Sample			91% $H_2SO_4$ Treat.			Distillation				
No.	$W_1$	$V_1$	$V_2$	$W_2$	$(V_1 - V_2)$	P	$W_3$	$W_2 - (W_3 + P)$	$l_v$	$V_3$
					$L_1$			$l_w$		

Dist.	98% $H_2SO_4$		Results			
$V_2 - (V_3 + l_v)$		$V_3 - V_4$	Total	Correct	%	A.P.
$L_2$	$V_4$	$L_3$	L	L	L	OF.

A blank determination was made in all cases to compensate for errors introduced through manipulation. Although they were the best obtainable, the heptane and naphthenic compounds were of doubtful purity, so correction was also made for their solubility in the acid.

After finding the sum of the olefines and aromatics, the next step involved separation of olefines by treating with sulfur monochloride, and the determination of aromatics on the olefine-free sample.

A sample of 100 cc. of the synthetic mixture was measured into a 500 cc. round-bottom short-neck flask, fitted with a reflux condenser and a dropping funnel. The flask was immersed in a pan of cold water, and 30 cc. of sulfur monochloride added through the dropping funnel. This operation was carried out under a hood, due to the very disagreeable odor of sulfur monochloride. After standing overnight the mixture was cooled by the addition of ice, and washed four times with 10 per cent alkali and finally with water in a separatory funnel. At the completion of the washing there was no appreciable odor of  $\text{HCl}$ . The oil was dried over  $\text{CaCl}_2$ , filtered, distilled to  $120^\circ\text{C}$ . at atmospheric pressure, allowed to cool to room temperature

and distilled in partial vacuum until decomposition of residue was shown by red color of oil condensing on flask walls.

The distillates were combined, washed once with alkali, once with water, and dried over  $\text{CaCl}_2$ . At this stage the oil was approximately olefine-free.

Due to the excessively large mechanical loss in the sulfur monochloride treatment the volume loss could not be taken directly as the amount of olefines present. This was the procedure used in the determination of olefines and aromatics together. A sample of 20 cc. of the olefine-free oil was poured into a nitration tube, placed in a constant temperature bath for ten minutes, and the volume read. Fifty cubic centimeters of acid mixture (25 per cent by weight  $\text{HNO}_3$ , 58 per cent  $\text{H}_2\text{SO}_4$ , and 17 per cent  $\text{H}_2\text{O}$ ) was added in 5 cc. portions, shaking under tap water to total addition. Shaking was continued for five minutes under the tap and five minutes in air. After standing for thirty minutes the acid mixture was withdrawn, and the oil washed with 50 cc.  $\text{H}_2\text{SO}_4$  (sp. g. 1.84), adding in 10 cc. portions, and shaking vigorously under tap water to total addition--about one minute. The acid sludge was withdrawn after settling, the oil displaced into graduated portion by in-

roducing water through the stop-cock, and the tube placed in the constant temperature bath in a vertical position. Volume loss was read after thirty minutes, and the amount of olefines and aromatics calculated, correcting for the sample being olefine-free in the above nitration.

As an alternate method for determination of aromatics, 20 cc. of olefine-free oil was treated in a nitration tube with three volumes of 98 per cent sulfuric acid, shaking for five minutes under tap water, and ten minutes in air.

For the calculation of results from sulfur monochloride treatment and subsequent treatment with either the nitration mixture or sulfuric acid the following formulas were used:

$$U = \frac{100(S - A')}{100 - A'} \quad (7)$$

$$A = S - U \quad (8)$$

where:  $U$  &  $A$  = actual per cent olefines and aromatics.  
 $S$  = sum of olefines and aromatics.  
 $A'$  = aromatic content of olefine-free oil.

Method of Kattwinkel (15). Olefines were removed with sulfuric acid (sp. g. 1.84) containing 5 gms. boric acid per 100 cc. acid, and aromatics with sulfuric acid containing 30 gms. phosphorus pentoxide per 100 cc. acid, treating the olefine-free oil from the olefine determination.

Volume losses were taken directly in both cases and converted to percentages.

A sample of 20 cc. of oil was poured into a nitration tube, placed in a constant temperature bath for ten minutes, and the volume read. The tube was placed in an ice-water bath at 35°F. for ten minutes, one volume of the boric acid mixture, also cooled, added, and the mixture shaken vigorously in the ice-water bath. The effect of varying time of shaking was studied.

A sample of 10 cc. of the oil from the above treatment was shaken with three volumes of the  $P_2O_5$  acid mixture, using the same procedure as in the boric acid treatment.

#### PRINCIPAL RESULTS

In treatment of oil with various concentrations of sulfuric acid, polymerization increases with increase in acid strength, to a concentration of 90-92 per cent sulfuric acid by weight, and is also a function of the time of contact, temperature, and acid ratio. Figure 1 shows polymerization loss obtained on gas oil with an acid ratio of 3:1, a time of contact of ten minutes, and at 35-40°F. When the

time of contact was decreased to two minutes the polymerization loss was almost constant for acid concentrations from 60 per cent to 98 per cent by weight sulfuric acid.

Solution loss on sulfuric acid treatment increases with concentration increase, time of contact increase, acid ratio increase, and increase in temperature, as would be expected.

After preliminary treatment with 90-92 per cent sulfuric acid and distillation to remove polymers, the removal of remaining aromatics was obtained most satisfactorily using 98 per cent sulfuric acid, shaking for fifteen minutes at 35-40°F., and using a relative acid ratio of 3:1. These conditions were the least severe which gave approximately correct results, as shown in Table III.

Loss on treatment with 90-92 per cent sulfuric acid ( $L_1$ ) was constant within experimental accuracy, as was the polymerization loss on distillation (P). This work was done on synthetic mixture No. 1. Results given in the table are uncorrected with the exception of the total per cent loss (L) and the "aniline point". Other results are subject to the blank determination run given last.

Using the procedure determined by the above work, the results shown in Table IV were obtained for total olefines and aromatics.



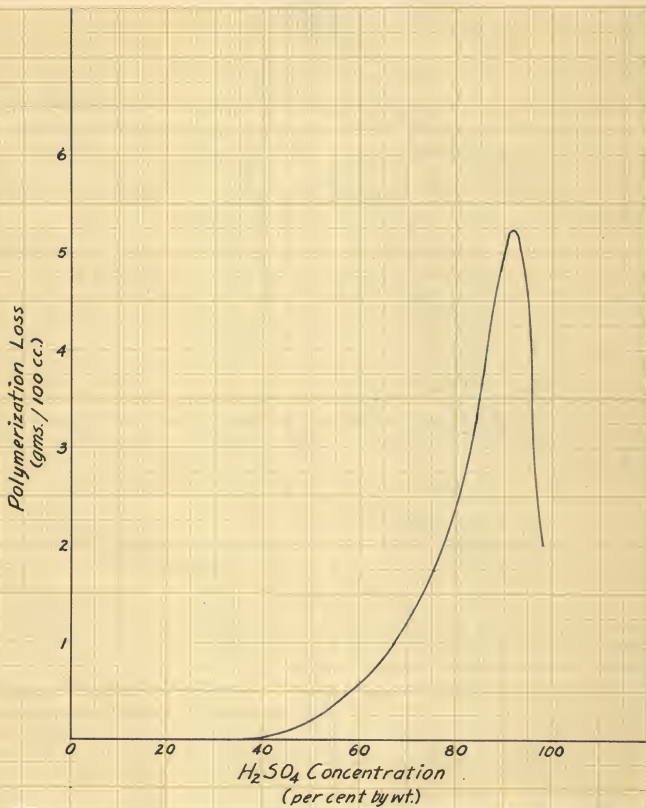


Figure 1. Effect of Acid Concentration on Polymerization Loss.



Table III

Temp. °F.	Sulfuric Acid Removal of Aromatics.							A. P. °F.
	Time Min.	Acid Vol.	cc. L <sub>1</sub>	Gas. P	cc. L <sub>2</sub>	cc. L <sub>3</sub>	g. L	
35	5	1	6.5	3.3	4.2	3.1	21	110.6
35	5	2	6.6	3.2	4.1	4.9	24	116.4
35	5	3	6.5	3.3	4.2	5.4	25	118.6
35	10	1	6.7	3.1	4.0	7.7	30	129.0
35	10	2	6.5	3.3	4.2	8.7	32	130.2
35	10	3	6.5	3.3	4.2	9.3	33	139.0
35	15	1	6.6	3.2	4.1	8.9	32	131.0
35	15	2	6.7	3.1	4.0	9.9	34	138.0
35	15	3	6.8	3.0	3.9	10.0	34	139.2
75	5	1	6.6	3.2	4.1	7.7	30	129.2
75	5	2	6.7	3.1	4.0	9.9	34	137.2
75	5	3	6.6	3.2	4.1	10.3	35	139.8
75	10	1	6.5	3.2	4.1	8.9	32	135.0
75	10	2	6.4	3.2	4.1	10.1	34	137.6
75	10	3	6.5	3.2	4.1	10.8	36	139.8
75	15	1	6.7	3.1	4.0	8.9	32	136.2
75	15	2	6.7	3.1	4.0	10.4	35	139.2
75	15	3	6.8	3.0	3.9	10.8	36	139.2
Blank Determination								
35	15	3	0.7	1.7	2.1	0.7	7	77.5

Table IV

Olefines and Aromatics Analyses.

<u>Syn. Mix.</u> <u>No.</u>	<u>cc.</u> <u>L<sub>1</sub></u>	<u>gms.</u> <u>P.</u>	<u>cc.</u> <u>L<sub>2</sub></u>	<u>cc.</u> <u>L<sub>3</sub></u>	<u>°</u> <u>L</u>	<u>A.P.</u> <u>°F.</u>
1	6.1	1.4	1.9	8.8	34	137.8
	6.0	1.4	1.9	8.9	34	138.4
2.	2.5	0	0	9.9	25	134.6
	2.5	0	0	10.0	25	135.0
3.	8.1	3.7	4.5	7.0	39	142.8
	8.1	3.7	4.4	7.0	39	143.2
4.	7.9	3.8	4.6	2.1	29	131.0
	7.8	3.9	4.7	2.2	29	129.8
Gas Oil	16.0	2.6	2.9	10.1	58	163.0
	16.2	2.6	2.9	9.8	58	162.4

The foregoing values are corrected for blank determinations. Referring back to composition and "aniline points" given for the synthetic mixtures the above results agree very well with the actual values with the exception of mixture No. 2. In this case the phenyl cyclohexane molecule is evidently split by the acid treatment into its equivalent aromatic and naphthenic parts.

In the removal of olefines by treatment with sulfur monochloride separation was approximately quantitative, as shown by the "aniline points" of the products of the treatments in the table below:

Table V

Sulfur Monochloride Analysis.

Synthetic Mixture No.	1	2	3	4
Product Aniline Point	84.8	79.3	78.8	92.6
Actual A. P.	79.0	75.6	83.8	85.0

The presence of small amounts of reaction product in the oil from the sulfur monochloride removal of olefines affects "aniline point" determinations sufficiently to cause errors as large as those above. The actual "an-

iline points" shown were determined when the mixtures were made up, and have been given previously. Sulfur monochloride separation was not made on the gas oil due to the stubborn emulsion formed in the treatment.

Results obtained on nitration of olefine-free oil from the sulfur monochloride treatment in all cases exceeded the sum of olefines and aromatics, making impossible the calculation of olefines and aromatics separately from this determination. No reliable results were obtained. The determination on mixture No. 2 showed approximately a 15 per cent error, while that on mixture No. 3 showed only 1 per cent.

The determination of aromatics on the olefins-free oil from sulfur monochloride treatment was made by shaking with 98 per cent sulfuric acid, and gave reliable results on mixture No. 1 as shown below:

Table VI  
Determination of Aromatic Hydrocarbons.

Loss cc.	A'	S	U	A	A. P.
6.1	30.5	34	5	29	139.4

Time did not permit further work on this method.

In treatment with sulfuric acid containing boric acid for determination of olefines the results were not reliable. Results in all cases were too high. Mixture No. 2 which contained no unsaturated compounds showed a 6 per cent loss. However, the presence of boric acid retarded the action of the sulfuric acid as determined by the same treatment with pure sulfuric acid.

Determination of aromatics on either the oil from the boric acid treatment or the original oil also gave unreliable results. Changing the time of contact, temperature, and relative volume of acid did not materially adjust the accuracy of the method.

#### CONCLUSIONS

From this investigation the author feels that none of the methods used give reliable results. The use of sulfuric acid for the determination of total olefines and aromatics gave reliable results, and shows the most possibilities for the determination of aromatics after the olefine separation by use of sulfur monochloride. A method of analysis with an accuracy of less than five per cent could very probably be worked out using those reagents.

In the analysis of known synthetic mixtures the accuracy of such a method could probably be increased to approximately two per cent. However, no synthetic mixture can approach the complexity of the fuels obtained from the cracking process, and as the complexity of the oil increases the accuracy of any method, whether chemical or physical, will decrease accordingly. The apparent splitting of the phenyl cyclohexane molecule in mixture No. 2 illustrates this point. In complex mixtures the presence of a large number of such compounds is assured, even though they are in small amounts. Whether these compounds will split or separate with the parent molecule or the side chain is a function of the particular compound involved and its chemical and physical properties. The author feels that there is no method, either physical or chemical, known today, that will give accurate results.

A tremendous amount of work on the physical and chemical properties of pure hydrocarbons would materially simplify the problem of analysis, but until the results of such work are available resort must be made to simple methods of estimation. In the author's opinion the most suitable method available is the one based on reaction

with sulfuric acid. This method gives approximate results on synthetic mixtures as shown by determination of per cent aromatics and olefines, and also "aniline points" of the resulting oils.

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## BIBLIOGRAPHY

- (1) Brooks, B. T., and Humphrey, Irwin.  
The action of concentrated sulphuric acid on  
olefins . . . petroleum distillates. J. Am.  
Chem. Soc., 40: 822-856. 1918.
- (2) Carpenter, J. A.  
The composition of petroleum fractions. J.  
Inst. Petr. Tech., 14: 446-476. 1928.
- (3) Cross, Roy.  
A handbook of petroleum, asphalt, and natural  
gas. Kansas City, Mo. Kansas City Testing  
Laboratory. 864 p. 1931.
- (4) De Kok, W. J. C., Waterman, H. I., and van Westen, H.A.  
The hydrogen value as a means for measuring un-  
saturateds. J. Soc. Chem. Ind., 55: 225T-231T. 1936.
- (5) Erskine, A. M.  
The precise determination of aromatic hydro-  
carbons in gasoline. Ind. Engr. Chem., 18:  
294-298. 1926.
- (6) Faragher, W. F., Morrell, J. C., and Levine, I. M.  
Determination of olefin and aromatic hydro-  
carbons. Ind. Engr. Chem. (Anal.) 2: 18-24.
- (7) Ferris, S. W., Birkhimer, F. R., and Henderson, L. M.  
Solvent extraction of lubricating oils.  
Engr. Chem., 23: 753-761. 1931.
- (8) Francis, A. W.  
Estimation of unsaturated content of petroleum  
products. Ind. Engr. Chem., 18: 821-822. 1926.
- (9) Garner, F. H.  
The analysis of cracked spirits. J. Inst.  
Petr. Tech., 14: 695-732. 1928.



- (10) Griffith, R. H., and Hollings, H.  
Analysis of Hydrocarbon Oils. J. Inst. Petr.  
Tech., 19: 701-712. 1933.
- (11) Griffith, R. H.  
The valuation and cracking of gas oils.  
J. Soc. Chem. Ind., 48: 252T-263T. 1929.
- (12) Griffith, R. H.  
The analysis of gas oils and hydrocarbon oils  
from tars. J. Soc. Chem. Ind., 47: 21T-24T.  
1928.
- (13) Howes, D. A.  
The chemical examination of gasolines and light  
mineral oils. J. Inst. Petr. Tech., 16: 54-58.  
1930.
- (14) Kalichevsky, Vladimir A., and Stagner, Bert Allen.  
Chemical refining of petroleum. New York.  
Chemical Catalog Company. p. 450. 1933.
- (15) Kattwinkel, R.  
Determination of aromatic and unsaturated hy-  
drocarbons in benzene by means of sulphuric  
acid. Chem. Abstracts, 22: 3039. 1928.  
(Original - - Brennstoff-Chem., 8: 353-358. 1927.)
- (16) Lorand, Eugene.  
Action of sulfur monochloride on petroleum  
hydrocarbons. Ind. Engr. Chem., 19: 733-735.  
1927.
- (17) Meigs, J. V.  
Observations on the action of sulfur monochloride  
on bituminous and tarry substances and hydrocarbon  
oils. Ind. Engr. Chem., 9: 655-661. 1917.
- (18) McIlhiney, P. C.  
The determination of the bromine absorption of  
oils. J. Am. Chem. Soc., 21: 1084-1089. 1899.

- (19) Morrell, Jacques C., and Egloff, Gustav.  
Unsaturated, aromatic, naphthene, and paraffin hydrocarbons in motor fuels and their auto-motive equivalents. Ind. Engr. Chem., 18: 354-356. 1926.
- (20) Morrell, Jacques C., and Egloff, Gustav.  
Sulphuric acid absorption and iodine values of various petroleum products and cracked distillates obtained therefrom. Ind. Engr. Chem., 17: 1259-1261. 1925.
- (21) Nash, Alfred W., and Howes, Donald A.  
Principles of motor fuel preparation and application. The hydrocarbon analysis of motor fuels. New York. John Wiley and Sons, 926 p. 1935.
- (22) Tizard, E. T., and Marshall, A. G.  
The determination of aromatic hydrocarbons in mixtures of hydrocarbons. J. Soc. Chem. Ind., 40: 20T-25T. 1921.
- (23) Vlugter, J. C.  
Determination of aromatic content in cracked gasoline. J. Inst. Petr. Tech., 21: 316-319. 1935.

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