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## SEPARATION AND DETERMINATION OF AROMATIC AND MONOOLEFIN HYDROCARBONS IN MIXTURES WITH PARAFFINS AND NAPHTHENES BY ADSORPTION<sup>1</sup>

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### ABSTRACT

A new method is described for separating and determining aromatic and monoolefin hydrocarbons in mixtures with paraffins and naphthenes by adsorption. The mixture to be analysed is introduced into the top of a column of silica gel and, when the liquid level just reaches the top of the silica gel, a suitable desorbing liquid, such as ethyl alcohol, is added. The desorbing liquid forces the hydrocarbon portion down the column, during which passage the hydrocarbon portion is fractionated according to the adsorbability of the various components. These components issue from the bottom of the column in the following order: Paraffin plus naphthene, monoolefin, and aromatic hydrocarbons. The analysis is made by determining the fraction of the total volume constituted by each of these classes.

Results of the analyses of five solutions containing aromatic and paraffin hydrocarbons, and three solutions containing aromatic, monoolefin, and paraffin hydrocarbons are given. A procedure is outlined for determining the aromatic content of a straight-run petroleum distillate, as in the gasoline or kerosine fractions

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<sup>1</sup> This investigation was performed jointly with the American Petroleum Institute Research Project 6 at the National Bureau of Standards on the "Analysis, Purification, and Properties of Petroleum Hydrocarbons."

## I. INTRODUCTION

This report describes a new method for separating and determining aromatic and monoolefin hydrocarbons in mixtures with paraffins and naphthenes by absorption. In comparison with the method previously reported for the determination of aromatic hydrocarbons by adsorption [1]\*, the method described here is simpler and more accurate because it involves no calibration of the adsorbents with the hydrocarbons involved.

## II. GENERAL DESCRIPTION

This method is a development of the Tswett or chromatographic method of analysis [2, 3]. The sample to be analysed (a mixture of aromatic, monoolefin, and paraffin plus naphthene hydrocarbons) is introduced into a reservoir at the top of a column of silica gel. When the sample has completely entered the adsorbent, an appropriate desorbing liquid, such as ethyl alcohol, is added to the reservoir. The desorbing liquid forces the hydrocarbon portion down the column, during which passage the hydrocarbon portion is fractionated and separated into three contiguous zones according to the adsorbability of the components. The lowest zone contains the naphthenes and paraffins, the middle zone the monoolefins, and the top zone the aromatic hydrocarbons. The liquid issuing from the bottom of the column is collected in appropriate small fractions, with the experiment being terminated as soon as substantially pure desorbing liquid issues. The volumes and refractive indices of the fractions of filtrate are determined, and a plot of the refractive index of the filtrate as a function of its volume is made. From this plot, the volume and percentage by volume of each of the three groups of hydrocarbons, (a) paraffins plus naphthenes, (b) monoolefins, and (c) aromatic hydrocarbons, are determined.

## III. APPARATUS AND MATERIAL

An apparatus which may be used for this method of analysis is shown in figure 1. The apparatus, made of Pyrex glass, consists essentially of the reservoir, *E*, sealed to the column proper, which itself consists of a section, *F*, sealed to a section of smaller diameter, *I*. At the bottom of section *I* is sealed a sintered glass plate, *J*, of medium or fine porosity, which serves to retain the silica gel, *G*. Below *J* is stopcock *K* and the ground joint, *L* (standard taper 19/38), through which the graduated receiver *O* is attached. The diameter of the bore of the stopcock plugs, *K* and *P*, is 2 mm. The outside diameter of the outlet, *N*, is 6 mm. *M* is a capillary vent. The volume of the tube between the sintered plate, *J*, and stopcock *K* is 2.0 ml.<sup>2</sup>

It is desirable to have two receivers, one with a capacity of 1.1 ml, graduated to 0.01 ml with 0.001 ml estimated, the other with a capacity of 11 ml, graduated to 0.1 ml with 0.01 ml estimated. To

\* Figures in brackets indicate the literature references at the end of this paper.

<sup>2</sup> When stopcock *K* is closed for the measurement and withdrawal of a fraction, liquid and noncondensable gas collects in this space and the pressure produced may cause leakage of the stopcock if this space is too small. On the other hand, this space should not be too large, as this increases the hold-up. It is necessary also that the plug of the stopcock be held firmly in its shell with spring clamps or other device.

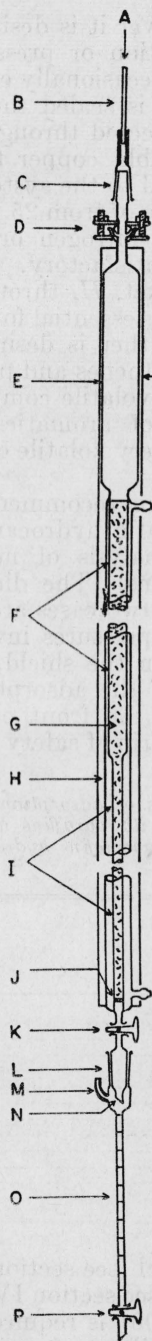


FIGURE 1.—Apparatus for the analysis by adsorption of mixtures containing aromatic and monoolefin hydrocarbons with paraffins and naphthenes.

See the text for the significance of the letters, and see table 1 for the dimensions of the various parts.

the vent, *M*, of the 1.1-ml receiver it is desirable to attach a rubber tube through which gentle suction or pressure may be applied to dislodge gas bubbles, which are occasionally entrapped in the receiver. To the top of the reservoir, *E*, is sealed the spherical ground joint (18/9), *D*, which is in turn connected through the soldered metal-to-glass joint *C* [4], with the flexible copper tubing ( $\frac{1}{8}$  in. o. d.), *B*, through which pressure is applied to the system. It is also necessary that a source of inert gas pressure of from 25 to 50 lb/in.<sup>2</sup> be available. For this purpose a cylinder of nitrogen or carbon dioxide with a pressure regulating valve is satisfactory. The column shown in figure 1 is provided with a jacket, *H*, through which cooling water may be passed. This provision is essential for the analysis of mixtures containing monoolefins, and further is desirable for the analysis of mixtures of aromatics with naphthenes and paraffins if these mixtures contain appreciable amounts of volatile components such as pentane or isopentane. For mixtures of aromatics with naphthenes and paraffins, and in the absence of very volatile components, refrigeration is unnecessary.

The dimensions of the column recommended for the analysis of mixtures containing only aromatic hydrocarbons are different from those recommended for the analysis of mixtures containing substantial quantities of monoolefins. The dimensions of the various parts of the apparatus for these two cases are given in table 1. As a safety measure, because of the pressures involved, it is desirable to mount the adsorption column in the shield, *Q*. This shield should surround the front and sides of the adsorption column, and should provide for the observation of the front of the column. A satisfactory shield may consist of a strip of safety glass in a suitable frame.

TABLE 1.—*Dimensions and capacities of adsorption apparatus for (A) mixtures containing aromatic hydrocarbons with paraffins and naphthenes and (B) mixtures containing aromatic and monoolefin hydrocarbons with paraffins and naphthenes*

	Mixture	
	A	B
Approximate mass of adsorbent (silica gel)..... g.....	160	150
Volume of reservoir..... ml.....	200	200
Section F, inside diameter..... mm.....	22	15
Section F, inside length..... mm.....	600	750
Section I, inside diameter..... mm.....	10	10
Section I, inside length..... mm.....	750	1000
Receiver 1, volume..... ml.....	1.1	1.1
Receiver 1, length..... mm.....	200	200
Receiver 1, graduations..... ml.....	0.01	0.01
Receiver 2, volume..... ml.....	11	-----
Receiver 2, length..... mm.....	200	-----
Receiver 2, graduations..... ml.....	0.1	-----

The adsorbent used is silica gel (see section IV-1, c). The desorbing liquid may be ethyl alcohol (see section IV-1, e). A refractometer having a precision of about 0.0001 is required for the determination of the refractive indices of the filtrate fractions. The refractometer preferably should be equipped with a slot to permit the introduction of volatile fractions without opening the prisms.

## IV. METHOD AND RESULTS

## 1. AROMATIC HYDROCARBONS IN MIXTURES WITH PARAFFINS AND NAPHTHENES

## (a) PROCEDURE

The appropriate adsorption column (see table 1) is filled with silica gel and packed by tapping throughout its length with a rubber-covered wooden rod. The packing and filling is continued until the level of silica gel decreases less than 5 mm in 5 minutes of packing and the final height of the silica gel is about 2 to 5 cm below the bottom of the reservoir. The time required to pack a column is about 20 minutes. If the column is not to be used immediately, the silica gel is closed off from the moisture of the atmosphere. The column is then mounted in the shield,  $Q$ , and the receiver attached.

For the concentration range 0 to 80 percent by volume of aromatic hydrocarbon, a volume of solution sufficient to contain about 20 ml of aromatic hydrocarbon is used for each analysis, except that not less than 30 ml nor more than 125 ml of solution is used. For the concentration range 80 to 100 percent by volume of aromatic hydrocarbon, the solution preferably should be diluted with one-fifth its volume of an aromatic-free paraffin, naphthene, or paraffin-naphthene mixture, and a 30-ml portion of this diluted solution used.<sup>3</sup> The volume selected for the analysis is introduced into the reservoir. The smaller volumes may be introduced with a pipette, which can be inserted through the neck of the reservoir, care being taken not to wet the upper portion of the reservoir. Pressure of 5 to 10 lb/in.<sup>2</sup> is then applied. When the sample has completely entered the silica gel (which should take about 10 to 20 minutes for the 30- to 50-ml portions), the pressure is reduced, the reservoir opened, and a layer of 1 to 2 cm of silica gel added. The reservoir is then filled with ethyl alcohol and the necessary pressure applied, which is 15 to 50 lb/in.<sup>2</sup>, depending on the particle size of the silica gel and the viscosity of the hydrocarbon portion and desorbing liquid (sections IV-1, c and 1, d). When a fraction has collected in the receiver, the flow from the adsorption tube is interrupted by closing the stopcock. The volume in the receiver is measured and the fraction withdrawn. A standard procedure should be adopted for measuring and withdrawing fractions. About 40 seconds should be allowed for the upper parts of the receiver to drain before the volume is read and an equal interval allowed for drainage after the withdrawal of the bulk of the fraction before the stopcock on the receiver is closed.<sup>4</sup>

In cases where from 30 to 50 ml is used for the analysis, a receiver of 1.1-ml capacity is sufficient, and all the fractions may be taken approximately equal to 1 ml. For the more dilute solutions, where more than 50 ml is used for the analysis, the collection of so many fractions is tedious and an 11-ml receiver may be used to collect fractions until close to the point where it is estimated that aromatic

<sup>3</sup> For solutions containing appreciably more than 80 percent by volume of aromatic hydrocarbon, the volume intermediate between the aromatic and nonaromatic portions is more than the 1 to 2 ml customarily obtained with more dilute solutions and with the appropriate silica gel (sections IV-1, c and 1, d). In this instance, the liquid front is a very short distance from the boundary between the aromatic and nonaromatic portions, and the heat of wetting is not dissipated before that boundary reaches the warm region. It may be that convection produced by the thermal gradient is responsible for this lack of sharpness in the "break" with very concentrated solutions. In some cases no fraction completely free from aromatic material is produced, and it is for this reason that concentrated solutions should be diluted before analysis.

<sup>4</sup> If stopcock  $K$  is opened too rapidly, gas bubbles may be trapped in the 1.1 ml receiver. In this event, the stopcock may be closed temporarily and the bubbles displaced by applying suction to the rubber tube attached to  $M$ .

material will appear in the filtrate. At this point, it is necessary to change to a 1.1-ml receiver.<sup>5</sup> When a sufficient amount of the desorbing liquid has collected the experiment can be discontinued.<sup>6</sup> It is not necessary to determine the refractive index of every fraction, only the refractive indices of those fractions required to locate the plateaus (see fig. 3), and the breaks between them need be determined. The volumes of the components are then determined and the volume percentage computed by using for the total volume the volume of material actually recovered.

During the experiment the pressure should be adjusted so that the rate of flow of filtrate from the column does not exceed about 40 ml/hr when the 11 ml-receiver is used and about 20 ml/hr when the 1.1-ml receiver is used. Rates of flow much higher than these values do not leave adequate time for drainage and the precise determination of the volume of the filtrate fractions. As the rate of flow decreases as the experiment progresses and ethyl alcohol substitutes itself for the original hydrocarbon portion (section IV-1, d), a constant pressure throughout the experiment will give (for solutions of low aromatic content) rates of flow of about 30 to 40 ml/hr at the beginning of the experiment and of about 20 ml/hr toward the end of the experiment. The total time required for an experiment varies from about 3 hours for solutions of high aromatic content to about 6 hours for solutions of low aromatic content. Of this time, about 1½ to 2 hours is required for the liquid to reach the bottom of the column and about 1½ to 4 hours for the collection of the fractions of filtrate.

After an experiment, the adsorbent is found to be tightly packed in the column and cannot be removed by simple tapping. Flushing with water will, however, readily remove the adsorbent. To do this, the column is placed in a reclining position with the top slightly lower than the bottom. A metal tube, which is flexibly connected to the water main and from which a stream of water is issuing, is then inserted in the column and gently forced throughout its length. The silica gel is displaced and flows with the water out of the column.

In future work, it is intended to reactivate the silica gel in the adsorption column. This will save the time required for packing and unpacking the column and will have the further advantage that the silica gel will not come in contact with the moisture of the atmosphere during the filling operation. Reactivation of the silica gel is accomplished by heating it to 180° to 200° C in a slow stream of inert gas.

#### (b) DIMENSIONS OF THE ADSORPTION COLUMN

A number of adsorption columns of different dimensions were tried in preliminary experiments with lot II of silica gel (see section IV-1, c). These included long narrow columns (260 cm long, 0.9 cm inside diameter) and short wide columns (76 cm long, 2.2 cm inside diameter). Satisfactory results were obtained with the long, narrow columns, the volume of material intermediate between the nonaromatic and the aromatic portions being small and amounting to about 1 to 2 ml. However, this length of column is cumbersome to handle (particularly

<sup>5</sup> Where only one receiver is used and where approximately the same size of fraction is withdrawn throughout, it is not necessary to know the absolute volume of the receiver. Where two receivers are used it is necessary to know the volume of one in terms of the other.

<sup>6</sup> As stated in section IV-1, e, it is possible to see the boundary between the desorbing liquid and the hydrocarbon portion. About 3 ml should be collected after this boundary has passed out of the column.

in removing the silica gel), and a considerable time is required for the hydrocarbon portion to reach the bottom of the column. With the short, wide column the volume of material intermediate between the nonaromatic and the aromatic portion is comparatively large, and a pure aromatic portion is not obtained. The column finally selected for this method of analysis consists of two sections sealed together, the upper section being 50 cm long and 2.2 cm inside diameter and the lower section being 75 cm long and 1.0 cm inside diameter (see table 1). This column, when used with silica gel of proper particle size, has a capacity and fractionating length sufficient to separate about 20 ml of aromatic hydrocarbon from mixtures with aromatic contents from 20 to 100 percent by volume and somewhat less than 20 ml for lower concentrations. Under these conditions, the volume of material intermediate between the aromatic and nonaromatic portion is usually from 1 to 2 ml for solutions containing less than 80 percent by volume of aromatic hydrocarbon.<sup>7</sup>

(c) EFFECT OF PARTICLE SIZE OF THE ADSORBENT

Experiments were performed with four lots of silica gel. Three of these lots were used as received from the manufacturer. The number given by the manufacturer to designate the type of silica gel, together with the particle size are recorded below for these three lots. The fourth lot was prepared in this laboratory by further treatment of lot III.

Lot	Manufacturer's designation	Particle size <sup>9</sup> (U. S. Standard Sieve)
I -----	659528—2000	No. 28 to No. 200.
II -----	6595150—	100% through No. 150, 41% through No. 325.
III -----	6595150—	100% through No. 150, 0% through No. 325.

Experiments with lot I showed that this material, with the natural rate of flow obtained with no external pressure, was too coarse to give satisfactory results. The break between the aromatic and the nonaromatic portion was not sharp, and the aromatic portion was not free from nonaromatic material. Lots II and III differed considerably in the distribution of their particle size, as indicated. The second lot of adsorbent was satisfactory at all rates of flow tested (see section IV-1, d), the volume intermediate between the nonaromatic and the aromatic portion amounting usually to not more than 1 or 2 ml. The third lot of silica gel was not satisfactory at any rate of flow tested (see section IV-1, d); the break between the aromatic and nonaromatic portions was not sharp and the aromatic portion contained some nonaromatic material. That the unsatisfactory behavior of lot III was due entirely to its lack of very fine material was established by determining first that the adsorptive capacity of lots II and III were essentially the same, and then by grinding some of lot III, reactivating the ground material,<sup>10</sup> and thereby preparing lot IV, which proved to be as satisfactory as lot III.<sup>11</sup>

<sup>7</sup> See footnote 3.

<sup>8</sup> Davison Chemical Corporation, Baltimore, Md.

<sup>9</sup> The values for the No. 150 sieve are the manufacturer's specifications, whereas the values for the No 325 sieve were determined by the Bureau's Cement and Concreting Materials Section.

<sup>10</sup> Necessary only to remove moisture adsorbed during the grinding process.

<sup>11</sup> Silica gel with satisfactory characteristics may be obtained from the Davison Chemical Corporation, Baltimore, Md., under the number "6595150—50% through No. 325."

## (d) EFFECT OF RATE OF FLOW

The rate of flow depends on the particle size of the adsorbent, the density of packing of the column, the viscosity of the hydrocarbon sample, the viscosity of the desorbing liquid, and the pressure applied to the column. When lot II of silica gel (section IV-1, c), was used, with hydrocarbons of the gasoline range and the natural rate of flow obtained with a head of 15 cm of desorbing liquid (dimethyl furane), the average rate at which the front of liquid travelled down the column was about 5 cm/hr, being higher than this value in the upper portion of the column and lower than this value toward the bottom of the column. With a gage pressure of 20 lb/in.<sup>2</sup> and ethyl alcohol as the desorbing liquid, the average rate at which the front of liquid travelled down the column was about 80 cm/hr, being substantially higher than this value in the upper portion, and decreasing toward the bottom of the column.<sup>12</sup> The results obtained for these diverse rates of flow were not significantly different, in both cases the volume intermediate between the nonaromatic and the aromatic portions being about 1 to 2 ml. With lot III of silica gel (section IV-1, c) and a gage pressure of 20 lb/in.<sup>2</sup> the average rate at which the front of liquid travelled down the column was about 240 cm/hr. For this lot of silica gel, at average rates of flow of 240, 100, and 25 cm/hr, the results were unsatisfactory, the volume intermediate between the nonaromatic and aromatic portions amounting to 5 to 8 ml and the aromatic portion containing some nonaromatic material. When lot IV of silica gel and a gage pressure of 45 lb/in.<sup>2</sup> was used, the average rate at which the front travelled down the column was 90 cm/hr, the volume intermediate between the nonaromatic and the aromatic portions being 1 to 2 ml.

From the above experiments, it is evident that the sharpness of the separation does not depend significantly on the rate of flow within the range investigated. The upper limit at which it is satisfactory to operate depends instead in the time required for the precise determination of the volume of the filtrate fractions (section IV-1, a) and is about 20 ml/hr during the collection of the aromatic portion toward the end of the analysis. For each lot of silica gel which is sufficiently fine (but not so fine that excessively high pressures are required), the pressure required to give a rate of flow of 20 ml of filtrate per hour toward the end of the experiment can be determined and used in subsequent analyses.

## (e) DESORBING LIQUID

Experiments were performed with the following desorbing liquids: Methyl alcohol, ethyl alcohol, propyl alcohol, acetone, methyl ethyl ketone, diethyl ether, and dimethyl furane. With the exception of dimethyl furane, the boundary between the desorbing liquid and the hydrocarbon portion is plainly visible.<sup>13</sup> In the case of diethyl ether, acetone, and methyl ethyl ketone the boundaries between the desorbing liquid and the hydrocarbon portion are not normal to the walls of

<sup>12</sup> As filtrate issues from the column, and ethyl alcohol replaces the original hydrocarbon portion, the rate of flow decreases because ethyl alcohol has a higher viscosity than the average for hydrocarbons of the gasoline range. On the other hand, with higher boiling fractions, such as kerosine, etc., the rate of flow may be expected to stay constant or increase slightly as ethyl alcohol replaces the original hydrocarbon portion. As each milliliter of liquid occupies a length of about 2 cm in the packed section with 1.0 cm inside diameter, a rate of movement of the liquid front of 40 cm/hr corresponds to a rate of flow of filtrate of about 20 ml/hr.

<sup>13</sup> In many experiments it is also possible to see the boundary between the aromatic and the nonaromatic portion.



the column but are irregular and frequently extend over a length of 5 to 10 cm. In the case of methyl alcohol two phases are present in one or more fractions toward the end of the experiment.<sup>14</sup> The occurrence of two phases makes difficult if not impossible the accurate determination of the volume of aromatic hydrocarbon. With ethyl alcohol and propyl alcohol, the boundaries between the desorbing liquid and the hydrocarbon portion are substantially normal to the walls of the column and only one phase occurs, at least with hydrocarbons of the gasoline range.<sup>15</sup> Owing to its higher viscosity, the rate of filtration with propyl alcohol for a given applied pressure is much slower than with ethyl alcohol. Fairly satisfactory results were obtained with dimethyl furane.

#### (f) EXPERIMENTAL RESULTS

The result of an experiment<sup>16</sup> with a solution containing a paraffin hydrocarbon (2,2,4-trimethylpentane) and a naphthene hydrocarbon (methylcyclohexane) is shown in figure 2. It is apparent that the

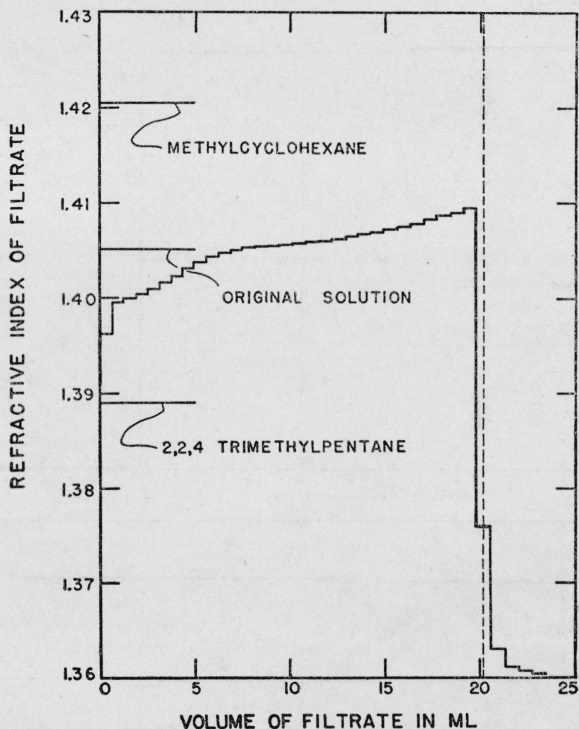


FIGURE 2.—Experiment with a paraffin and a naphthene hydrocarbon.

The scale of ordinates gives the refractive index,  $n_D^{25}$ , of the filtrate, and the scale of abscissas gives the volume of the filtrate in milliliters. The plot refers to an experiment in which 20 ml of solution containing equal volumes of 2,2,4-trimethylpentane and methylcyclohexane was used.

<sup>14</sup> Since aromatic hydrocarbons of the gasoline range are completely soluble in methyl alcohol, it is evident that sufficient water has been displaced from the silica gel by the methyl alcohol to cause the appearance of two phases. This behavior has been observed previously [5].

<sup>15</sup> Ethyl alcohol was used as the desorbing liquid in two experiments with material from the kerosine range. In one case with material containing substantially no aromatic hydrocarbons two phases were observed, whereas in the other case with material of relatively high aromatic content (15 percent) only one phase was produced. The appearance of two phases in the first case is doubtless due to the limited solubility of paraffins and naphthenes of the kerosine region in ethyl alcohol.

<sup>16</sup> This experiment, together with two of the analyses given in table 2 were made by A. J. Streiff.

separation of paraffins from naphthenes with the apparatus and procedure in question is small enough to permit these two classes to be grouped together in the results from an analysis.

The results of analyses that are typical are shown for two solutions of known aromatic content in figure 3, *A* and *B*. The refractive indices of the fractions in the plateaus agree with the refractive indices of the pure components within 0.0001. The volume intermediate between substantially nonaromatic and substantially aromatic material is about 1 to 2 ml, and the volume intermediate between substantially aromatic material and the desorbing liquid (ethyl alcohol) is about the same. The accuracy obtainable when this method is applied to synthetic mixtures is indicated by the data in table 2.

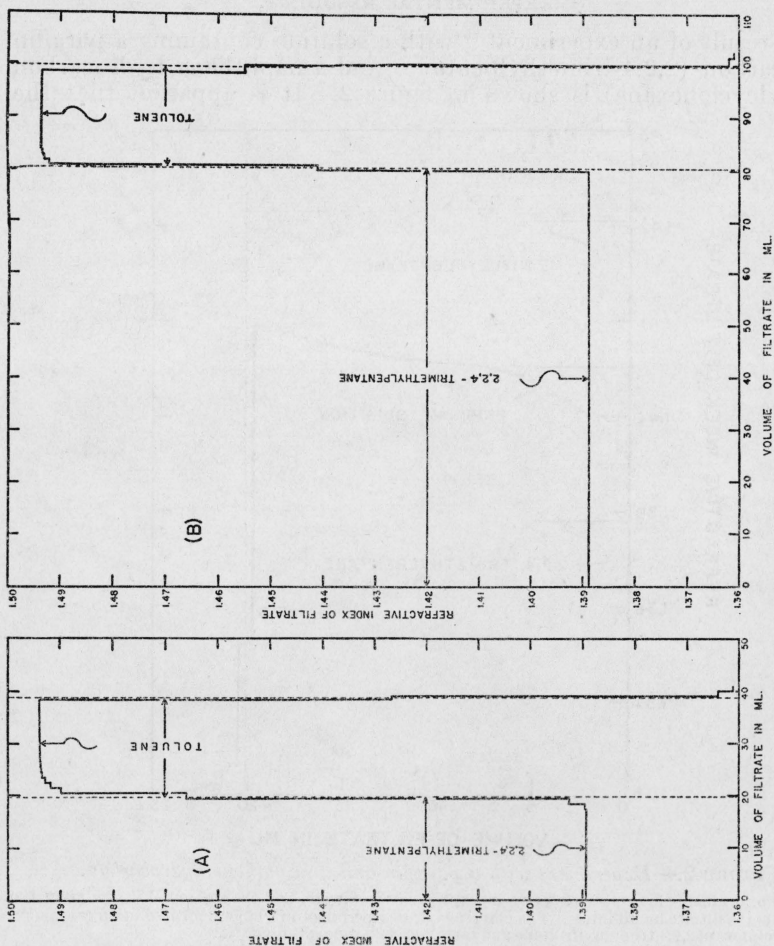


FIGURE 3.—Analyses of mixtures containing aromatic and paraffin hydrocarbons.

The scale of ordinates gives the refractive index,  $n_D^{25}$ , of the filtrate, and the scale of abscissas gives the volume of the filtrate in milliliters. *A*, an analysis in which approximately 40 ml of a solution containing 49 and 51 percent by volume of toluene and 2,2,4-trimethylpentane, respectively, was used; *B*, an analysis in which approximately 100 ml of a solution containing 19.6 and 80.4 percent by volume of toluene and 2,2,4-trimethylpentane, respectively, was used.

TABLE 2.—Comparison of values for the composition of five solutions, as given by synthesis and as determined analytically

Solution	Components	Composition by—	
		Synthesis	Analysis
1	Toluene.....	% by volume 3.996	% by volume 4.053
	(2,3,4-trimethylpentane.....)	96.00	95.95
2	Toluene.....	22.20	22.45
	(2,2,4-trimethylpentane.....)	77.80	77.55
3	Toluene.....	49.95	49.92
	(2,2,4-trimethylpentane.....)	50.05	50.08
4	Toluene.....	79.91	79.89
	(2,2,4-trimethylpentane.....)	20.09	20.11
5	Toluene.....	92.49	92.45
	(2,2,4-trimethylpentane.....)	7.51	7.55

The result of the analysis of an aviation gasoline containing approximately 16 percent by volume of aromatic hydrocarbons is shown in figure 4. The small fluctuations in the refractive indices of the naphthene-paraffin portion are due principally to the loss of volatile compounds during the collection of the fractions and the measurement of the refractive indices. The result of the analysis of material from the kerosine range (bp 166 to 290° C at 1 atm), containing approximately 15 percent by volume of aromatic material, is shown in figure 5.

## 2. AROMATIC AND MONOOLEFIN HYDROCARBONS IN MIXTURES WITH PARAFFINS AND NAPHTHENES

### (a) PROCEDURE

The appropriate adsorption column (see table 1) is prepared as described in section IV-1, a. Ice water is allowed to flow through the jacket of the column for 10 minutes before the introduction of the sample.<sup>17</sup> A measured 5-ml portion of a paraffin, a naphthene, or a paraffin-naphthene mixture is then added from a pipette to the top of the adsorption column. When nearly all of this material has entered the silica gel, the sample to be analysed is introduced from a pipette. The remainder of the analysis is similar to that described in section IV-1, a. In this case, however, the rate of flow for a given gage pressure is substantially less than the rate of flow obtained in the analysis of aromatic hydrocarbons. This is due in part to the higher viscosity of the liquids at the lower temperature and in part to the decrease in rate of filtration with increase in the length of the column (section IV-1, d). Thus, with a gage pressure of 30 to 35 lb/in.<sup>2</sup>, when lot II of silica gel was used (section IV-1, c), it was found that 4 to 5 hours were required for the liquid to reach the bottom of the column, the rate of flow of the filtrate being about 10 ml/hr. The column recommended for this analysis is longer than that recommended for aromatics in mixtures with paraffins and naphthenes. The additional length appears to be necessary to effect the separation of paraffin-naphthene material from monoolefins, and of monoolefins from aromatics. This column will separate about 10 ml of mo-

<sup>17</sup> If brine or any other refrigerating fluid at -10° to -20° C is available, it should preferably be used.

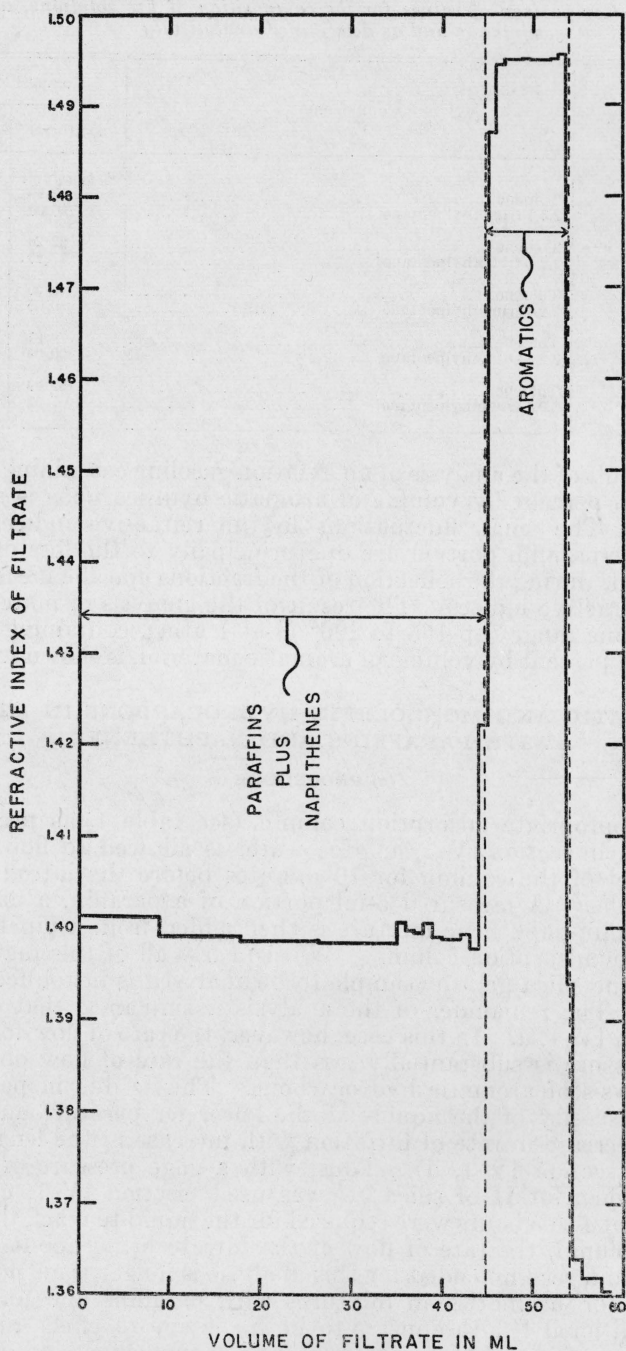


FIGURE 4.—*Analysis of an aviation gasoline.*

The scale of ordinates gives the refractive index,  $n_D^{25}$ , of the filtrate, and the scale of abscissas gives the volume of the filtrate in milliliters. The plot refers to an analysis in which approximately 55 ml of an aviation gasoline was used.

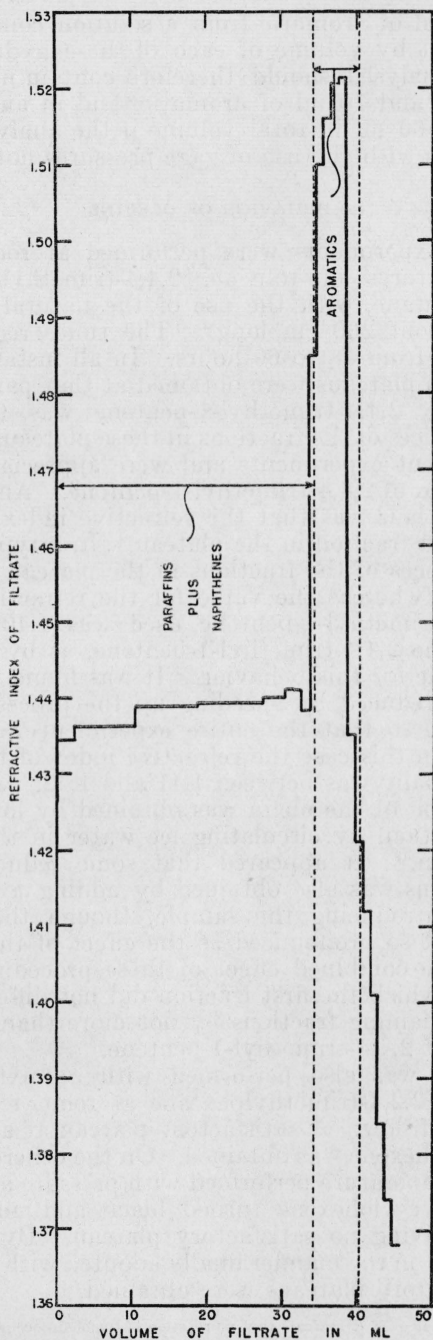


FIGURE 5. Analysis of a kerosine fraction.

The scale of ordinates gives the refractive index,  $n_D^{25}$ , of the filtrate, and the scale of abscissas gives the volume of the filtrate in milliliters. The plot refers to an analysis in which approximately 40 ml of a kerosine sample (bp, 166° to 290° C) was used.

noolefin and 10 ml of aromatic from a solution containing approximately 30 percent by volume of each of these hydrocarbons. The solution to be analysed should therefore contain not more than 10 ml of monoolefin and 10 ml of aromatic, and in any event should not exceed 50 to 60 ml in total volume if the analysis is to be performed in 9 hours with the use of gage pressures not in excess of 50 lb/in<sup>2</sup>.

(b) BEHAVIOR OF OLEFINS

A number of experiments were performed at room temperature with known mixtures of toluene, 2,4,4-trimethyl-1-pentene, and 2,2,4-trimethylpentane, with the use of the natural rate of flow in long columns (about 260 cm long). The times required for these experiments were from 48 to 60 hours. In all instances plateaus or approximations to plateaus were obtained at that part in the volume of filtrate where 2,4,4-trimethyl-1-pentene was to be expected. The refractive indices of the fractions in these plateaus were, however, different in different experiments and were appreciably higher than the refractive index of 2,4,4-trimethyl-1-pentene. Another characteristic of these plateaus was that the refractive index decreased from the first to the last fraction in the plateau. In a typical experiment, the refractive indices of the fractions in the plateau decreased from 1.4324 to 1.4217, whereas the value for the refractive index of the sample of 2,4,4-trimethyl-1-pentene used was 1.4063. It appears that reaction of the 2,4,4-trimethyl-1-pentene, as by polymerization, may be responsible for this behavior. It was found that this "polymerization" was reduced by speeding up the process by the application of pressure so that the entire experiment was performed in about 6 hours. In this case the refractive index of the first fraction in the plateau usually was between 1.41 and 1.42. A further reduction in the reaction of the olefin was obtained by lowering the temperature of operation, by circulating ice water in the jacket of the adsorption column.<sup>18</sup> It appeared that some reduction in the reaction of the olefins was also obtained by adding a 5-ml portion of paraffin before introducing the sample, though the effect of this procedure was not so pronounced as the effect of the two foregoing procedures.<sup>19</sup> The combined effect of these procedures was to produce plateaus in which the first fraction did not differ by more than 0.004 and the remaining fractions by not more than 0.003 from the refractive index of 2,4,4-trimethyl-1-pentene.

An experiment was also performed with a mixture of toluene, cyclohexene, and 2,2,4-trimethylpentane at room temperature with the natural rate of flow. A satisfactory plateau at about the refractive index of cyclohexene was obtained. On the other hand, in experiments at room temperature performed with pressure and a more rapid rate of flow, the cyclohexene turned black and mingled with the toluene portion giving no satisfactory plateau. By operating near 0° C with pressure, in the manner finally adopted with 2,4,4-trimethyl-1-pentene, satisfactory plateaus were obtained.

<sup>18</sup> Small scale tests made at -76° C indicate that no reaction of the olefin occurs at this temperature in 24 hours.

<sup>19</sup> When the front of hydrocarbon comes in contact with fresh silica gel, a substantial rise in temperature takes place. The introduction of the paraffin hydrocarbon before the sample allows time for this heat of wetting to be dissipated before the olefin reaches that portion of silica gel. The paraffin hydrocarbon also displaces a substantial part of the air from the tube and may in this way help to reduce the reaction of the olefins. Removal of oxygen by evacuation of the column would also serve to reduce the reaction of olefins. However, the complete evacuation of the column described here is a slow process and appears impracticable.

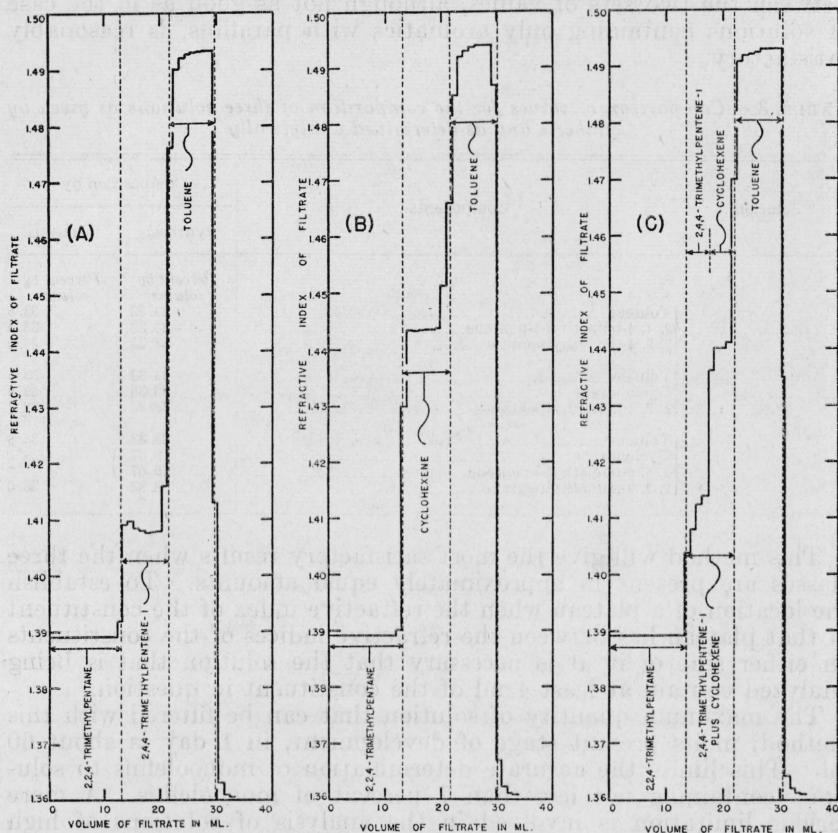


FIGURE 6.—Analyses of solutions containing aromatic, monoolefin, and paraffin hydrocarbons.

The scale of ordinates gives the refractive index,  $n_D^{25}$ , of the filtrate, and the scale of abscissas gives the volume of the filtrate in milliliters. *A*, an analysis in which approximately 25 ml of a solution containing equal volumes of toluene, 2,4,4-trimethyl-1-pentene, and 2,2,4-trimethylpentane was used; *B*, an analysis in which approximately 25 ml of a solution containing equal volumes of toluene, cyclohexene, and 2,2,4-trimethylpentane was used; *C*, an analysis in which approximately 25 ml of a solution containing one-third toluene, one-sixth cyclohexene, one-sixth 2,4,4-trimethyl-1-pentene, and one-third 2,2,4-trimethylpentane was used. In all three analyses 5 ml of 2,2,4-trimethylpentane was introduced into the adsorption column prior to the introduction of the solution.

#### (c) EXPERIMENTAL RESULTS

The results of the analyses of three solutions are shown in figure 6 *A*, *B*, and *C*. It is evident from these that the separation of each of the three classes of hydrocarbons from one another is reasonably sharp. The characteristic decrease in the refractive index at the 2,4,4-trimethyl-1-pentene plateau (section IV-2, b) is noticeable (*A*). The cyclohexene plateau, however, does not show this behavior (*B*). It is interesting to observe (*C*) that there was a separation of 2,4,4-trimethyl-1-pentene and cyclohexene and that the relative amounts of these two substances in a mixture can be estimated from an experiment of this type. The values for the amounts of the constituents of these solutions as given by synthesis and as determined analytically are given in table 3. It will be seen that the agreement

between the two sets of values, although not as good as in the case of solutions containing only aromatics with paraffins, is reasonably satisfactory.

TABLE 3.—*Comparison of values for the composition of three solutions as given by synthesis and as determined analytically*

Solution	Components	Composition by—	
		Synthesis	Analysis
		<i>Percent by volume</i>	<i>Percent by volume</i>
1.....	{Toluene.....	33.33	33.5
	{2, 4, 4-trimethyl-1-pentene.....	33.33	33.5
	{2, 2, 4-trimethylpentane.....	33.33	33.0
2.....	{Toluene.....	33.33	33.5
	{Cyclohexene.....	33.33	33.8
	{2, 2, 4-trimethylpentane.....	33.33	32.7
3.....	{Toluene.....	33.33	33.8
	{Cyclohexene.....	16.67	} 33.2
	{2, 4, 4-trimethyl-1-pentene.....	16.67	
	{2, 2, 4-trimethylpentane.....	33.33	33.0

This method will give the most satisfactory results when the three classes are present in approximately equal amounts. To establish the location of a plateau when the refractive index of the constituent in that plateau lies between the refractive indices of the constituents on either side of it, it is necessary that the solution that is being analyzed contain at least 4 ml of the constituent in question.

The maximum quantity of solution that can be filtered with this method, in its present stage of development, in 1 day is about 60 ml. This limits the accurate determination of monoolefins to solutions containing not less than 7 percent of monoolefins. A more serious limitation is involved in the analysis of solutions of high aromatic content. As the maximum quantity of aromatic that can be separated from solutions containing olefins is of the order of 15 to 20 ml, it is not possible to use more than about 20 ml of sample of high aromatic content for an experiment. In order that 4 ml of monoolefin be obtained such a sample must contain 20 percent of monoolefin. Where possible, the composition of the solution to be analyzed should be brought to approximately the optimum composition by adding to it known amounts of hydrocarbons from the requisite classes.

## V. RECOMMENDED PROCEDURE FOR THE DETERMINATION OF THE AROMATIC CONTENT OF A STRAIGHT-RUN PETROLEUM DISTILLATE

The aromatic content of the sample to be analyzed is estimated roughly. In the absence of information as to the source of the material, this estimate may be made from a consideration of the refractive index of the sample or from the results of a preliminary experiment (which requires only 10 to 15 minutes) in which a few milliliters of sample is filtered through a few grams of silica gel (No. 28 to No. 200 U. S. Standard Sieve) and the difference between the refractive index of the first drop of filtrate (which should be aromatic free)



and the refractive index of the original sample obtained [6]. The size of the sample to be used in the analysis is then decided upon (section IV-1, a) and the adsorption column selected (table 1). If the sample contains significant quantities of pentane or isopentane, it is necessary to use a jacketed column for operation near 0° C. The procedure for the analysis is the same as that described in section IV-1, a.

If the petroleum distillate contains nonhydrocarbon substances such as sulfur, oxygen, or nitrogen compounds, or dyes which have been added for coloring purposes, these materials are displaced by ethyl alcohol and appear in the filtrate principally in the region of the junction of the aromatic portion with ethyl alcohol. Where a significant amount of nonhydrocarbon material is present, the analysis should be corrected if possible, and if not possible, the uncertainty introduced from this source should be recognized. If the nonhydrocarbon material has the same refractive index as the aromatic hydrocarbons, the analysis will give the sum of aromatic hydrocarbons plus the nonhydrocarbon material; whereas if the nonhydrocarbon material has the same refractive index as ethyl alcohol, the analysis will give only the aromatic content. For the gasoline fraction, average values of 1.496 and 1.482 may be assumed for the refractive indices of the aromatic hydrocarbons and the sulfur compounds, respectively. When compared with the value 1.360 for the refractive index of ethyl alcohol, it is evident that each milliliter of sulfur compound present will have an effect on the analysis equivalent to 0.9 ml of aromatic hydrocarbon. For the gasoline fraction, the correction for sulfur compounds may be made by determining the percentage by weight of sulfur, multiplying the value obtained<sup>20</sup> by 3.7 to convert to percentage by volume of sulfur compounds and deducting 0.9 times the percentage by volume of sulfur compounds from the uncorrected value for the aromatic content.

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<sup>20</sup> This factor is obtained by assuming that each sulfur compound had 1 atom of sulfur per molecule, that the average molecule weight of the sulfur compounds is 130, and that the average density of the sulfur compounds is 0.83.