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ANALYTICAL DETERMINATION OF AROMATIC HYDRO-CARBONS BY ADSORPTION ¹

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ABSTRACT

A simple method is described for determining the amount of aromatic hydrocarbons in a mixture of hydrocarbons, as in the gasoline fraction of petroleum. The mixture to be analyzed is filtered through a column of solid adsorbent. An aromatic-free filtrate is obtained which contains the paraffin, naphthene, or olefin hydrocarbon which was associated in the original solution with the quantity of aromatic hydrocarbon which has been adsorbed. The concentration of an aromatic hydrocarbon which has been adsorbed. The concentration of an aromatic hydrocarbon in an unknown solution is determined by means of a calibration curve, established from experiments on known solutions which show the amount of aromatic-free filtrate produced by the standard adsorbent from solutions of various concentrations of the aromatic hydrocarbon. Results of experiments are given for several concentrations of eight binary solutions of an aromatic hydrocarbon with a paraffin or naphthene hydrocarbon and for three concentrations of a solution consisting of an aromatic hydrocarbon with a paraffin and an olefin. These experiments show that, if the temperature is controlled to within 1° C, the amount of aromatic hydrocarbon can be determined with an accuracy corresponding to 0.10 or less in the percentage by volume. A general procedure is given for determining the aromatic hydrocarbons in a "straight-run" gasoline and in a gasoline containing olefins.

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I. INTRODUCTION

In this paper a simple and precise method is described for determining the amount of aromatic hydrocarbons in a mixture of hydrocarbons as in the gasoline fraction of petroleum. The method involves the process of adsorption, and the analysis is performed without actually separating the aromatic hydrocarbons.³

II. GENERAL DESCRIPTION

At a given temperature the amount of a given aromatic hydrocarbon selectively adsorbed by a "standard" quantity of a "standard" solid adsorbent, from a binary solution of the aromatic hydrocarbon with a given paraffin, naphthene, or olefin hydrocarbon, is a function of the concentration. When a solution containing aromatic, paraffinic, naphthenic, and olefinic hydrocarbons is filtered through a column of adsorbent, the resulting filtrate consists first of (a), material containing no aromatic hydrocarbons, next of (b), a small amount of material intermediate in composition between (a) and the original solution, and finally (c), the original solution. The intermediate part is apportioned (see section IV) between (a) and (c), so that there may be determined the amount of aromatic-free ⁴ material which would have been obtained had the break between (a) and (c) been infinitely sharp, with no intermediate portion. The concentration of the aromatic hydrocarbon in an unknown solution is determined by means of a calibration curve, established from experiments on known solutions which show the amount of aromatic-free filtrate produced by the standard adsorbent from solutions of various concentrations of the aromatic hydrocarbon.

When a solution of an aromatic hydrocarbon with a paraffin, naphthene, or an olefin hydrocarbon is filtered though a column of appropriate solid adsorbent, the first portion of solution comes in contact with successive layers of fresh adsorbent and its aromatic content is progressively reduced to zero. The first, or top, layer of adsorbent comes in contact with successive portions of solution having the initial concentration of aromatic hydrocarbon. This layer of adsorbent soon reaches a state of equilibrium between the aromatic hydrocarbon in the solution of the original concentration and the amount of the aromatic hydrocarbon adsorbed per unit quantity of adsorbent. As the solution progresses down the tube, successive layers of adsorbent come in contact and into equilibrium with solution of the initial concentration, which solution fills the macroscopic interstices of the adsorbent. With continued introduction of solution at the top of the column, the "equilibrium" zone, in which the adsorbed aromatic hydrocarbon is in equilibrium with solution of the initial concentration, extends farther and farther down the tube, forcing the nonaromatic material ahead of it, with a rather sharp region of demarcation between the two zones. Finally the "equilibrium" zone will reach the bottom, or last, layer of adsorbent, and at this point, solution of the original

⁷ ³ For a description of the methods used for separating substances by adsorption, see H. H. Strain, Chroma tographic Adsorption Analysis, (Interscience Publishers, Inc., New York, N. Y., 1942), and L. Zechmeister and L. V. Cholnoky, Principles and Practices of Chromatography, John Wiley & Sons, Inc., New York, N. Y., 1942). With regard to the separation and recovery of aromatic hydrocarbons from petroleum by adsorption, see B. J. Mair and A. F. Forziati, J. Research NBS 32, 165 (1944) RP1583. ⁴ As used in this paper, the term "aromatic-free" refers to the material actually free from aromatic hydrocarbons plus that part of the intermediate portion allocated to it.

composition will just begin to emerge as filtrate from the bottom of the column of adsorbent.

III. APPARATUS AND MATERIAL

An apparatus which may be used for this method of analysis is shown in figure 1.5 This apparatus is made of Pyrex glass and consists of the reservoir A; the main cylindrical section B, holding the bulk of the adsorbent; the filter tube section C, with the porous glass filter D for retaining the adsorbent; the stopcock E; and the graduated receiver F.6

The dimensions of the various parts for three convenient sizes of the apparatus are shown in table 1.

TABLE 1.—Recommended dimensions and capacities for three sizes of the adsorption apparatus

	Sizes		
	1	2	3
Adsorbent, mass of silica gelg	75	37.5	18.75
Reservoir, volumeml	500 13.5	300 10,0	200 8.0
Section Bilongth mm	750	750	650
Section C inside diametermm	10.0	8.0	6.0
(ICHS CHARASSESSESSESSESSESSESSESSESSESSESSESSESSE	80	80	60
(volumeml	20	10	5
Receiver{lengthmm	150	150	150
[graduationsml]	0.2	0.1	0.05

A refractometer is required for measuring the refractive index (usually n_D) of the filtrate, as well as an apparatus for determining the density of the aromatic-free filtrate. The necessary precision in the measurement of refractive index is about 0.0001 and that in the measurement of density about 0.001 g/ml.

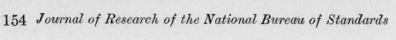
Any suitably prepared solid adsorbent that selectivity adsorbs aromatic hydrocarbons may be used. In the experiments reported here, silica gel, 28 to 200 mesh in size, was used.⁷ It is important to store the adsorbent in a bottle having a tightly fitting screw cap. In weighing the adsorbent, a tolerance of 0.05 percent is satisfactory.

IV. PROPERTIES INVOLVED

The experimental quantity to be determined is the volume or the mass (obtained by means of the density) of the aromatic-free filtrate. The volume of aromatic-free filtrate is determined from observations of the refractive index of the filtrate as a function of its volume. These

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⁶ In the experiments reported here, a simple adsorption tube without receiver was used, the gel was re-tained with a small plug of glass wool, and the filtrate fractions were collected in small bottles and measured in a graduated cylinder. For greater convenienc and possible increased precision; the apparatus shown in figure 1 is recommended. ⁶When operating on fractions containing substantial quantities of very volatile components, such as iso-pentane, it would be desirable to provide the receiver with a refrigerated jacket extending above the capil-lary outlet. ⁷ Silica gel No. 659528-2000, Davison Chemical Corporation, Baltimore, Md.



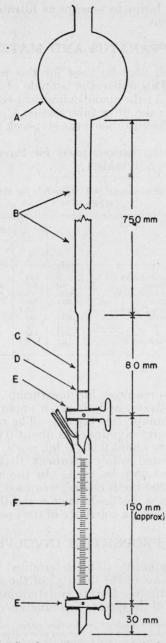


FIGURE 1.—Apparatus for determining aromatic hydrocarbons by adsorption. A, Reservoir; B, main cylindrical section; C, filter section; D, glass filter with large pores; E, stopcock with straight bore, 2 mm in diameter; F, graduated receiver. The dimensions given are those for the size holding 75 g of adsorbent. See table 1 for the other sizes.

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observations will be similar to those shown in figure 2(A), where there appear two plateaus of the refractive index (that of the material containing no aromatic hydrocarbons and that of the original solution) separated by a very small intermediate portion which may be considered as a mixture of these two. The intermediate portion is appropriately divided between the two plateaus (assuming additivity of the

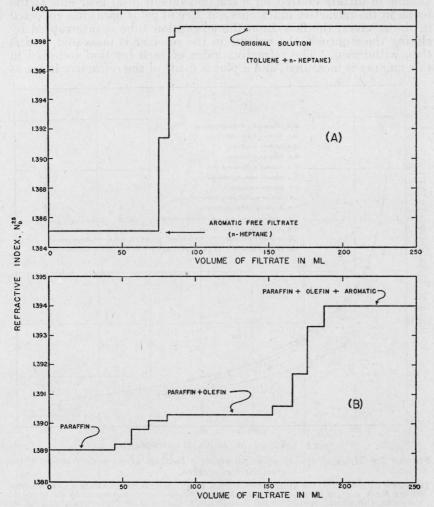


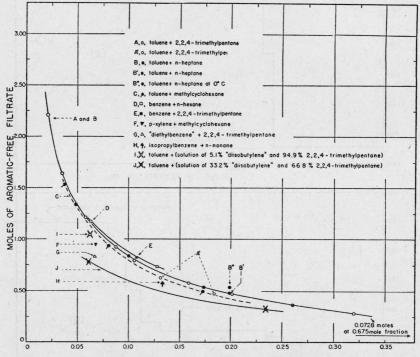
FIGURE 2.—Refractive index of the filtrate as a function of its volume.

The scale of ordinates gives the refractive index, n^{2b}_D of the filtrate, and the scale of abscissas gives the volume of the filtrate in milliliters. The upper plot, 2(A), refers to a solution containing toluene and *n*-heptane. The lower plot, 2(B), refers to a solution containing toluene, "diisobutylene," and 2, 2,4-trimethylpentane.

refractive indices) in such a way as to show the volumes that would have been observed had the break between the two plateaus been infinitely sharp. Where it is desired to know the mass, the density of the portion containing no aromatic hydrocarbons is measured, and the mass computed from this and the measured volume, corrected by the appropriate amount of the intermediate portion.

V. EXPERIMENTAL PROCEDURE AND DATA

A known quantity of silica gel is placed in the adsorption tube (fig. 1), and packed with gentle tapping and it is retained on the porous glass filter. The solution, in whatever amount is required, is introduced into the reservoir at the top of the column. When the volume of filtrate desired for a fraction (about 5 ml near and at the break in the refractive index curve, if 75 g of gel is used) 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 is then withdrawn. The refractive index of each fraction collected in this manner is measured, and a plot is made of the refractive index as



MOLE FRACTION OF AROMATIC HYDROCARBON

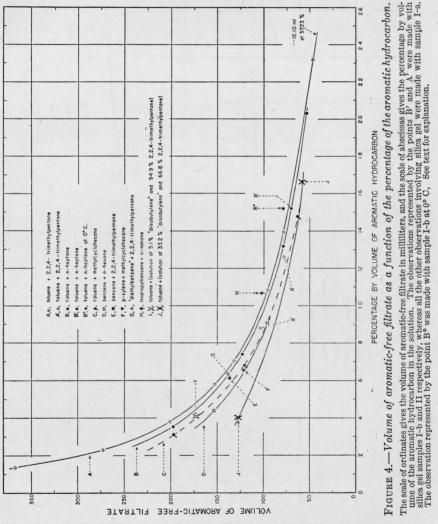
FIGURE 3.—Moles of aromatic-free filtrate as a function of the mole fraction of the aromatic hydrocarbon.

The scale of ordinates gives the moles of aromatic-free filtrate, and the scale of abscissas gives the mole fraction of the aromatic hydrocarbon in the solution. The observations represented by the B' and A' were made with silica gel samples I-b and II, respectively, whereas all the other observations involving silica gel were made with sample I-a. The observation represented by the point B° was made with sample I-b at 0° C. See text for explanation.

a function of the volume of filtrate.⁸ (See fig. 2, A). Where the mass is to be known, the density of the portion actually free from aromatic hydrocarbons is measured. The intermediate portion is properly

⁶ A somewhat different apparatus and modified procedure may be used to obtain a substantially continuous record of refractive index and volume. In this case, in addition to the main receiver, an auxiliary receiver with a known volume of about 0.3 ml is attached to the adsorption tube through a two-way stopcock. This auxiliary receiver is used to collect samples for refractive-index measurements. Readings of the total volume collected are made at the same time that samples are withdrawn for refractive-index measurements.

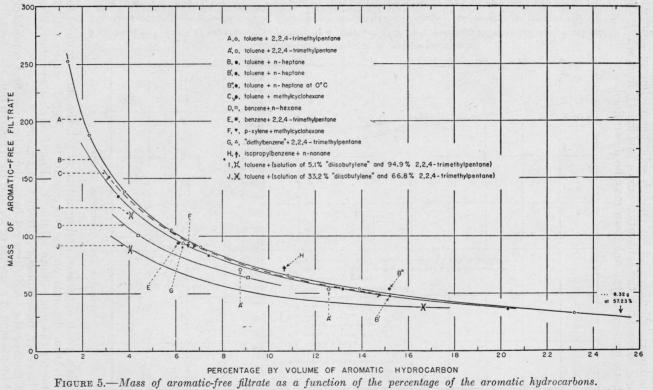
allocated (see section IV) to the two plateaus, and the total volume of aromatic-free filtrate recorded. This experiment is performed on the unknown solution and on enough solutions of known aromatic content to establish the calibration curve (see fig. 4), from which the aromatic content of the unknown may be determined.



With a given apparatus and quantity of gel, the time required for the filtration depends on the volume to be filtered, which will be greater for the more dilute solutions. Practically all such filtrations can, however, be completed in from 1 to 4 hours.

To remove the used silica gel from the tube, it is first completely dried by passage of a stream of air and then poured out.

The results of a number of experiments, plotted in three different ways, are shown in figures 3, 4, and 5, for one or more concentrations of the following solutions:



The scale of ordinates gives the mass of aromatic-free filtrate in milliliters, and the scale of abscissas gives the percentage by volume of the aromatic hydrocarbon in the solution.

The observations represented by the points B' and A' were made with silica gel samples I-b and II respectively, whereas all the other observations involving silica gel were made with sample I-a. The observation represented by the point B° was made with sample I-b at 0° C. See text for explanation.

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A, toluene + 2,2,4-trimethylpentane; A', toluene + 2,2,4-trimethylpentane; B, toluene + n-heptane; B', toluene, + n-heptane; B°, toluene + n-heptane; C, toluene + methylcyclohexane; D, benzene + n-hexane; E, benzene + 2,2,4-trimethylpentane; F, p-xylene + methylcyclohexane; G, "diethylbenzene" + 2,2,4-trimethylpentane; H, isopropylbenzene + n-nonane; I, toluene + (solution of 5.1 percent of "diisobutylene" and 94.9 percent of 2,2,4trimethylpentane); J, toluene + (solution of 33.2 percent of "diisobutylene" and 66.8 percent of 2,2,4-trimethylpentane).

VI. DISCUSSION

1. PRECISION AND SENSITIVITY OF THE METHOD

The observations for solution A fall along the smooth curve marked A, and those for solutions B and C along the curves marked B and C, respectively. In these cases, none of the individual points deviates from their respective lines by an amount which would correspond to more than about 0.1 in the percentage of aromatic hydrocarbon in the mixture.

The sensitivity of the method decreases with increasing aromatic content. At 5 and 20 percent, respectively, a change in the mass of aromatic filtrate of 1 g corresponds to changes of 0.06 and 0.66 in the percentage by volume of aromatic hydrocarbon.

2. EFFECT OF CHANGE IN THE OPERATING TEMPERATURE

With one exception, all the experiments were performed at the prevailing room temperature, which was recorded in each case and found to be within the range 23° to 28° C. To ascertain the effect of temperature on the analysis, one experiment was performed at 0° C. The result for the single experiment at 0° C is marked B° in figures 3, 4, and 5, and is to be compared with the result of an experiment performed at 28° C on the same solution, marked B' in figures 3, 4, and 5. For this solution, which contained 15.23 percent by volume of toluene in *n*-heptane, the masses of aromatic-free filtrate obtained at 28° and 0° C were 47.73 and 53.48 g, respectively. If the temperature of the room stays within a range of about 5° C, the amount of aromatic-free filtrate obtained from this solution will be constant to within 0.46 g, which, for this concentration, corresponds to 0.25 in the volume percentage of aromatic hydrocarbon. For many purposes, this precision will be sufficient, but for the highest precision of which the method is capable, control of the temperature to within 1° C or better is necessary.

3. USE OF DIFFERENT LOTS OF ADSORBENT

Several samples of silica gel,⁹ 28 to 200 mesh, were used. Samples I-a and I-b, although delivered to the laboratory at different times, were from the same manufactured lot. Sample II was from another manufactured lot. The observation represented by point B' was made with sample I-b, whereas the observations for the rest of the B series were made with sample I-a. The point B' falls on the curve

⁶ No. 659528-2000. See footnote 7.

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for the B series and shows that within the limits of these observations samples I-a and I-b have identical adsorptive capacities. The observations represented by the points A' were made with sample II, whereas the rest of the observations for the A series were made with sample I-a. The points A' fall below the curve for the rest of the A series and show that sample II has a lower adsorptive capacity than I-a or I-b. Since different manufactured lots appear to have somewhat different adsorptive capacities, it is necessary to calibrate each different lot of adsorbent with observations on one or two solutions of known concentration. It would appear desirable also to check each lot occasionally in the same manner.

4. VARIATION IN THE COMPOSITION OF THE PARAFFIN AND NAPHTHENE HYDROCARBONS IN THE SOLUTION

When, as in figure 3, the amount of aromatic-free filtrate is expressed in moles and the aromatic content in mole fraction, the curves A and B coincide. These curves represent, respectively, the solutions of toluene plus 2,2,4-trimethylpentane and of toluene plus *n*-heptane. Also the point E, for the solution benzene plus 2,2,4-trimethylpentane, falls on the curve D, which is for solutions of benzene plus *n*-hexane. That is, the amount of aromatic-free filtrate, when expressed in moles (for a given aromatic content expressed in mole fractions) is substantially independent of the particular paraffin which constitutes the nonaromatic portion of the solution. The curve C, in figure 3, for solutions of toluene plus methylcyclohexane, does not coincide with the curves A and B and shows the effect of changing the nonaromatic portion of the solution from a paraffin to a naphthene.

In figure 4, the amount of aromatic-free filtrate is expressed in terms of its volume and the aromatic content in terms of its percentage by volume. When these quantities are expressed in this manner, the curves A, B, and D show that the volume of aromatic-free filtrate (for a given percentage of a given aromatic hydrocarbon) decreases as the molecular weight of the paraffin hydrocarbon in the solution decreases. Curve D was obtained with solutions of benzene in *n*-hexane, and some of the decrease in the amount of the aromatic-free filtrate obtained for this series results from the fact that benzene rather than toluene was used as the aromatic component. However, by a comparison of point E with curve A, the effect of substituting benzene for toluene can be estimated, and it can be seen that a curve for solutions of toluene in *n*-hexane would be approximately as much below B as A is above B. Curve C, when compared with curve B, shows the effect of changing the nonaromatic portion of the solution from a paraffin to a naphthene hydrocarbon having the same number of carbon atoms per molecule. It is apparent that the volume of aromatic-free filtrate is less (for a given percentage of a given aromatic hydrocarbon) when the nonaromatic portion of the solution is a naphthene instead of a paraffin hydrocarbon having the same number of carbon atoms.

In figure 5 the amount of aromatic-free filtrate is expressed in terms of its mass and the aromatic content in terms of its percentage by volume. Curves A, B, and D show that the amount of aromatic-free filtrate decreases as the molecular weight of the paraffin hydrocarbon in the solution decreases. Curve C is in this case closer to curve B and slightly above it. This means that the mass of aromatic-free filtrate, for a given percentage of a given aromatic hydrocarbon, is, within certain limits, approximately independent of the relative amounts of naphthenes and paraffines.

5. VARIATION IN THE COMPOSITION OF THE AROMATIC HYDRO-CARBONS IN THE SOLUTION

The single observations on the solutions E, F, G, and H involve aromatic hydrocarbons other than toluene. The point E, involving benzene, and the point F, involving "diethylbenzene," (a mixture of isomers) should be compared with the curve A, since 2, 2,4-trimethylpentane was the nonaromatic constituent in these cases, while the point G, involving *p*-xylene, should be compared with the curve C, since methylcyclohexane was the nonaromatic constituent in this case. When the results are expressed as in figure 3, it is evident that the number of moles of aromatic-free filtrate varies with the molecular weight of the aromatic hydrocarbon involved. When the results are expressed as in figures 4 and 5, the variations in the mass (or volume) of aromatic-free filtrate, due to changes in the aromatic portion of the solution, are comparatively small, and do not depend much on the molecular weight of the aromatic hydrocarbon involved.

6. EFFECT OF THE PRESENCE OF OLEFIN HYDROCARBONS

The behavior of a solution in which the nonaromatic portion contains an olefin, as well as a paraffin (or naphthene) hydrocarbon, is shown in In this case three plateaus are observed. The first figure 2 (B). plateau represents material free of both olefin and aromatic, the second plateau represents material free of the aromatic hydrocarbon, and the third plateau the original solution. The results of observations on three solutions containing an olefin are shown in figures 3, 4, and 5. In the experiment represented by point G, the nonaromatic portion contains, by volume, 5.14 percent of "diisobutylene" and 94.86 per-cent of 2, 2,4-trimethylpentane. The line through the points J represents solutions in which the nonaromatic portion contains, by volume, 33.2 percent of "diisobutylene" and 66.8 percent by volume of 2, 2,4trimethylpentane. A comparison of the point I and curve J with curve A shows that there is a decrease in the amount of aromatic-free filtrate as the proportion of olefin in the nonaromatic portion is increased. In the region from 5 to 10 percent of aromatic content the amount of aromatic-free filtrate is reduced by an amount which corresponds to about 0.15 in the percentage of aromatics for each percent of olefin in the nonaromatic portion.

VII. RECOMMENDED PROCEDURE FOR ANALYSIS

1. KNOWN AROMATIC HYDROCARBON WITH PARAFFINS AND NAPHTHENES

Owing to the decrease in sensitivity of the method when applied to material of high aromatic content (section VI-1), it is advisable, if the aromatic content is greater than about 20 percent, to dilute the solution by a known amount (with pure paraffin or naphthene or paraffinnaphthene mixture) and to perform the analysis on the diluted mate-

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rial, the concentration of which (in aromatic hydrocarbons) should preferably be in the range of 5 to 10 percent.

For solutions of low aromatic content the volume of material which must be filtered becomes very large. For this reason, if the quantity of material is limited, or if time is an important consideration, it is advisable to increase the aromatic content of solutions containing less than about 1.5 percent of aromatic hydrocarbons by adding a definite quantity of a known aromatic hydrocarbon. The analysis is then performed on the enriched solution.

After the aromatic content of the solution has been brought within the proper range, two filtration experiments are required to determine it accurately.

In the first of these, the larger apparatus with 75 g of silica gel is used. The volume (and density, if necessary) of the aromatic-free filtrate is determined, and an approximate value for the aromatic content is obtained, assuming a probable value for the molecular weight of the nonaromatic portion and using calibration curves similar to those given in figure 4 or 5, according to whether the volume or mass is being measured. A solution of this composition is then prepared, using the known aromatic hydrocarbon as one component and that portion of the filtrate actually free of aromatic hydrocarbon from the first experiment as the second component. In the second filtration experiment, which is performed with this solution, a smaller apparatus and the corresponding amount of silica gel is used. The volume or mass of aromatic-free filtrate is determined and converted to the quantity corresponding to 75 g of adsorbent. (The volume or mass of aromatic-free filtrate is directly proportional to the relative amounts of adsorbent used in the two experiments.) This quantity is now located on the calibration chart and a portion of a new calibration curve is drawn parallel to the others. With this curve and the volume or mass of aromatic-free filtrate obtained in the first experiment, there is determined accurately the percentage of aromatic hydrocarbons.

With this procedure, the naphthene-paraffin portion and the aromatic portion of the solution used for calibration are identical with those portions in the original solution. The accuracy of the determination is therefore the same as the precision, which, with suitable control of temperature, can be made very high, of the order of 0.10 percent or better.

2. KNOWN AROMATIC HYDROCARBON WITH PARAFFINS, NAPHTHENES, AND OLEFINS

The olefin content of the unknown mixture is first determined by an independent method. As pointed out in section VI-6, the olefin content need be known only to within ± 1 percent by volume to obtain the aromatic content to within ± 0.15 percent.

From this point on, the procedure is similar to that described in the preceding section, that is, two adsorption experiments are required. In the first of these, performed with 75 g of silica gel (or more if necessary) the volume or mass of aromatic-free filtrate is determined and an approximate value for the aromatic content obtained using calibration curves similar to those given in figures 4 and 5. The

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solution to be used for calibration in the second experiment is prepared from that part of the filtrate from the first experiment which is free from both aromatic and olefin hydrocarbons, together with the amounts of the appropriate olefin and aromatic hydrocarbon required to give a solution of approximately the same composition as the original solution. From the results of the second experiment, a portion of a calibration curve is prepared, which, together with the results of the first experiment, can be used to ascertain accurately the aromatic content of the unknown.

Some uncertainty will be introduced in this analysis if substantial quantities of diolefins, particularly conjugated ones, are present, because these substances are more strongly adsorbed than monoolefins and, further, may be polymerized by the action of silica gel.

3. AROMATIC HYDROCARBONS IN THE "STRAIGHT-RUN" GASO-LINE FRACTION OF PETROLEUM

The gasoline is first separated by distillation into three fractions, the first of which contains substantially all the benzene, the second all the toluene, and the third the higher-boiling aromatic hydrocarbons.

Each fraction is then analyzed separately for its aromatic content. When analyses of this type are first instituted in a laboratory it is necessary to proceed in the manner described in section VII-1 that is, to use the aromatic-free portion from each fraction, together with the corresponding aromatic hydrocarbon to prepare solutions to be used for calibration. After the analysis of several gasolines, it may be possible to construct a mean calibration curve for each of the three fractions. Since the molecular weight of each fraction will be substantially the same for material from various sources, and since the variation due to change in the relative amount of paraffin and naphthene will be much less than that represented by the pure hydrocarbons methylcyclohexane and n-heptane shown in figure 5, it is evident that deviations from the mean calibration curves will be rather small.

If it is not required to know the amounts of the individual aromatic hydrocarbons, but only the total aromatic content, it is possible to operate on the entire gasoline fraction. In this case, the solution for calibration is prepared from the aromatic-free portion of the gasoline and a suitable aromatic hydrocarbon or mixture of aromatic hydrocarbons. Some uncertainty will be introduced into analyses performed in this manner so far as the aromatic hydrocarbon used in preparing the solution for calibration may not represent the aromatic composition of the unknown, but as already indicated (section VI, 5) the change in the position of the calibration curves (when volume or mass of aromatic-free filtrate is used) caused by substituting one aromatic hydrocarbon for another is not large. If the variation in the boiling-point range of the gasolines to be analyzed is not large (that is, if the mean molecular weights of the various gasolines are substantially the same), a mean calibration curve can be prepared for this fraction.

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4. AROMATIC HYDROCARBONS IN A GASOLINE CONTAINING OLEFINS

The gasoline is first separated by distillation into three fractions. First, the olefin content of each fraction is determined by an independent method. When analyses of this type are first instituted in a laboratory it is necessary to proceed as described in section VII-2, that is, to use the aromatic-free, olefin-free portions from each fraction, together with the corresponding aromatic and olefin hydrocarbons, to prepare solutions to be used for calibration. After the analyses of a sufficient number of gasolines, it may be possible to construct for each of the three fractions a series of calibration curves representing different olefin contents, and thereby make it unnecessary to perform a calibrating experiment for each determination.

WASHINGTON, May 29, 1942.