

RESEARCH PAPER RP809

Part of Journal of Research of the National Bureau of Standards, Volume 15,
July 1935

SEPARATION OF PETROLEUM HYDROCARBONS WITH SILICA GEL¹

By Beveridge J. Mair and Joseph D. White²

ABSTRACT

The fractionation, by filtration through columns of silica gel, of a number of binary mixtures of pure hydrocarbons boiling from 80 to 175° C is reported.

The results of these experiments show that (a) the aromatic and olefin hydrocarbons could be completely removed from the paraffin and naphthene hydrocarbons, but the capacity of the gel as an adsorbent of the one olefin ("diamylene") investigated was only one-third of its capacity as an adsorbent of the aromatic hydrocarbons; (b) the capacity of silica gel as an adsorbent of the aromatic hydrocarbons was found to depend on the concentration of the solution and also, to some extent, on the components of the solution from which the aromatic hydrocarbon is being adsorbed, the amount of *o*-xylene, for example, adsorbed from a 10 percent solution of that aromatic in *n*-nonane being about 12 to 13 ml per 100 g of gel and approximately the same for gel of different grain size; (c) a small but definite separation of naphthene from paraffin hydrocarbons occurred, the naphthenes tending to be adsorbed by the gel in preference to the paraffins; (d) a slight separation of normal paraffin hydrocarbons of different molecular weights occurred, the paraffin of low molecular weight being adsorbed in preference to that of high molecular weight; and (e) under conditions of these experiments, silica gel did not crack or otherwise attack aromatic, naphthene, or paraffin hydrocarbons.

A simple laboratory method for the complete removal of aromatic from naphthene or paraffin hydrocarbons by adsorption on silica gel, with a recovery of 98 percent or better, is described. The method is very useful for investigating the composition of petroleum distillates containing less than 15 percent of aromatic hydrocarbon. If the concentration of aromatics is higher than this a preliminary extraction with sulphur dioxide may be advantageous.

CONTENTS

	Page
I. Introduction.....	52
II. Apparatus and materials.....	52
III. Adsorption experiments with mixtures of an aromatic and a naphthene or a paraffin hydrocarbon.....	53
IV. Experiments to determine the capacity of silica gel as an adsorbent of aromatic and olefin hydrocarbons.....	55
V. Adsorption experiments with mixtures of a naphthene and a paraffin hydrocarbon.....	57
VI. An adsorption experiment with a mixture of normal paraffin hydrocarbons of different molecular weights.....	58
VII. Experiments to ascertain whether silica gel decomposes a mixture of hydrocarbons.....	58
VIII. Application of silica gel adsorption to the fractionation of a distillate of petroleum boiling between 140 and 145.5° C.....	59
IX. Literature references.....	62

¹ Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

² Research Associates at the National Bureau of Standards representing the American Petroleum Institute.

I. INTRODUCTION

In an investigation in progress at this Bureau on the isolation, identification, and determination of the hydrocarbons in petroleum, a simple method by which the aromatics may be separated completely from the naphthenes and paraffins is needed. The method should preferably be a physical one, and should permit nearly quantitative recovery of unchanged hydrocarbons.

Extraction with liquid sulphur dioxide at low temperatures may be employed to advantage with fractions rich in aromatics, but the complete removal of aromatic hydrocarbons by this solvent is not practical. Two chemical methods, nitration or sulphonation, may also be used for removal of aromatics. With nitration the aromatics cannot easily be regenerated, while with sulphonation the aromatics can usually be recovered by hydrolysis of the sulphonic acids. Both methods involve the use of a strong oxidizing agent for a considerable period of time, and there is consequently danger that any nonaromatic hydrocarbons present may also be attacked. With these methods it is difficult to remove completely the last trace of nitro compounds or sulphonic acids from the unattacked oil.

The use of adsorbents in petroleum refining for the removal of compounds containing sulphur and oxygen and of hydrocarbons with a low ratio of hydrogen to carbon is well known. Most investigations on the separation by adsorbents of the hydrocarbons in petroleum have been made with such complex mixtures that little definite information is available. Day and coworkers (1)³ in 1911 found that when a solution of benzene and a paraffin oil is allowed to diffuse upward through a tube packed with fuller's earth, the benzene tends to collect in the lower sections and the paraffin oil in the upper sections of the tube. Tarasov (2) in 1927 reported that all the aromatics could be removed from the naphthenes and paraffins by adsorption if sufficient silica gel was used. More recently, Hofmeier and Meiner (3) studied the action of five silica gels on the naphtha fraction of petroleum and found that with the best gel the aromatic content could be reduced by only 50 percent. Neither of these investigators found any separation of paraffins and naphthenes. Hofmeier and Meiner did not obtain a satisfactory recovery of oil.

In this paper are presented the results of experiments on the adsorption by silica gel of binary mixtures of hydrocarbons of different types and molecular weights. In particular, a simple method is described which should find extensive use in removing aromatic hydrocarbons from petroleum distillates. This method is considered superior to nitration or sulphonation in simplicity, completeness of removal of aromatics, and total recovery of oil. It is superior to extraction with sulphur dioxide in simplicity and completeness of removal. The method is scarcely practical for mixtures containing more than 15 percent of aromatics because of the small volume of aromatic-free oil recovered from such concentrated mixtures. In this case a preliminary extraction with sulphur dioxide is recommended.

II. APPARATUS AND MATERIALS

The apparatus is very simple, consisting of glass tubes mounted vertically and filled with silica gel. One of these tubes is shown in

³ The figures in parentheses throughout this paper refer to the numbered references listed on page 62.

figure 1. At the top is sealed a glass bulb as a reservoir for the hydrocarbon mixture. To the top of this reservoir may be attached a rubber tube through which air pressure can be applied during filtration. At the bottom of the adsorption tube is sealed a smaller tube which extends into a stoppered graduated cylinder. A small plug of glass cotton at the bottom of the adsorption tube suffices to hold the silica gel in place. The adsorption tubes used in these experiments were 40 cm long and had an inside diameter of 1.5 to 1.7 cm.

Two grades of silica gel obtained from the Silica Gel Corporation, Baltimore, Md., were used. These were grade "150-F-850" (40- to 200-mesh) and "Intermediate" (200-mesh and finer). These grades will be referred to throughout the rest of this paper as coarse and fine, respectively. The gel, after use and after displacement of the oil with water, was reactivated by transferring it while wet to a Pyrex-glass tube, sucking it as dry as possible and placing it in an oven, where it was heated for 24 hours at a temperature of 300 to 350° C, while air was aspirated through it. Both the original gel and the reactivated gel were stored in moistureproof containers.

All the hydrocarbons used in this work, except those mentioned below, were isolated from petroleum, or prepared synthetically or purified in this laboratory. The samples were not of the highest purity, but they were sufficiently pure for the purpose of these experiments. Their refractive indices differed by only a few units in the fourth decimal place from those of the best material prepared by us. The *n*-heptane of Jeffrey pine origin and the 2,2,4-trimethylpentane were commercial materials of high purity. The *n*-tetradecane was an Eastman product. Its treatment before use is described in a later section of this paper. The diamylene was a mixture of 3,5,5-trimethylheptene-2 and 3,4,5,5-tetramethylhexene-2. This sample was obtained through the courtesy of W. L. Drake (4), who has described the analysis of the mixture.

III. ADSORPTION EXPERIMENTS WITH MIXTURES OF AN AROMATIC AND A NAPHTHENE OR A PARAFFIN HYDROCARBON

These experiments were designed principally to show the degree of separation obtained when an aromatic hydrocarbon mixed with a naphthene or a paraff

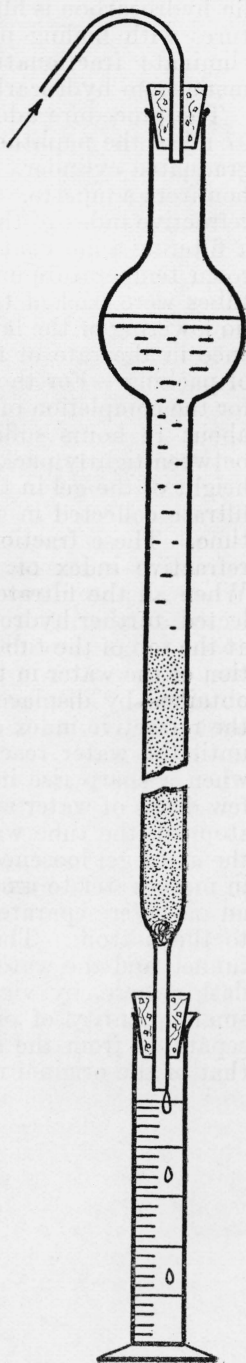


FIGURE 1.—Adsorption tube.

fin hydrocarbon is filtered through silica gel. A series of binary mixtures with boiling points from about 80 to 175° C was used. To eliminate fractionation by evaporation, each binary mixture was made from hydrocarbons with approximately the same boiling point.

The procedure adopted for these experiments was to measure out 97 ml of the naphthene or paraffin hydrocarbon in a glass-stoppered graduated cylinder. To this was added 5 ml of aromatic hydrocarbon from a pipette. The cylinder was stoppered and shaken, and the refractive index of the mixture observed. It was then transferred to a filtering tube containing 50 g of fine gel and allowed to filter at room temperature under air pressure of about 4 lb/in². Some of the tubes were packed tightly with silica gel by tapping the tube until no lowering of the level of the gel could be observed. A great difference in the rate of filtration was noticed, depending on the degree of packing. For those packed tightly, about 48 hours was required for the completion of an experiment, while with those loosely packed, about 16 hours sufficed. No significant difference in effectiveness between tightly packed and loosely packed tubes was observed. The height of the gel in the tubes varied from 36 to 40 cm. Fractions of filtrate collected in graduated cylinders were removed from time to time. These fractions all had the same refractive index, i. e., the refractive index of the pure paraffin or naphthene used initially. When all the filtrate which would drain of its own accord had collected, further hydrocarbon fractions were displaced by adding water at the top of the tube. A sharp line of demarcation showed the position of the water in the tube. The refractive indices of the fractions obtained by displacement with water usually remained constant at the refractive index of the pure paraffin or naphthene in the mixture until the water reached about 3 cm from the bottom of the tube, when a sharp rise in the refractive index occurred. After the first few drops of water appeared in the graduated cylinder, filtration was stopped, the tube was disconnected, the bottom end stoppered, and the silica gel loosened with a reamer and transferred as a suspension in more water to a 500-ml erlenmeyer flask. During this treatment, an oil layer separated on top of the water and the silica gel settled to the bottom. The oil and water were poured into a separatory funnel, and the water run again onto the silica gel in the erlenmeyer flask, where, by vigorous shaking, it was possible to get a second small quantity of oil to separate. The refractive index of the oil separated from the silica gel in this manner was much higher than that of the original mixture.

TABLE 1.—Data showing the separation of aromatic from naphthene or paraffin hydrocarbons by adsorption on 50 grams of fine silica gel

Hydrocarbons	Vol- ume of hy- dro- car- bons	Refractive indices of		Volume and refractive indices of fractions after passage through silica gel								
		Hy- dro- car- bons	Mix- tures	Filtrate		Main por- tion of fil- trate dis- placed by water	Last por- tion of fil- trate dis- placed by water	Adsorbed material shaken out with water		Total vol- ume recov- ered		
				ml	n_D^{25}			ml	n_D^{25}		ml	n_D^{25}
Mesitylene.....	5	1.4972	} 1.4139	62	1.4096	32.5	1.4096	3	1.4496	4.4	1.4683	101.9
<i>n</i> -Decane ¹	97	1.4098										
<i>m</i> -Xylene.....	5	1.4949	} 1.4000	63	1.3950	29.2	1.3950	3.5	1.4068	4.2	1.4677	99.9
<i>n</i> -Octane ¹	97	1.3952										
Toluene.....	5	1.4940	} 1.4237	61.7	1.4202	{15.1 17}	{1.4202 1.4225}	3	1.4522	2.5	1.4687	99.3
Methylcyclohexane.....	97	1.4205										
Benzene.....	5	1.4977	} 1.4105	65.5	1.4069	28	1.4094	3.5	1.4209	1.8	1.4610	98.8
Methylcyclopentane.....	97	1.4069										

¹ These hydrocarbons had refractive indices a little higher than the values obtained on the best samples isolated from petroleum in this laboratory. They evidently contained traces of aromatics or unsaturated hydrocarbons. After the mixture had run through silica gel, the values of the filtrate approached more nearly the values for the pure hydrocarbons.

The results of these experiments are shown in table 1, in which are tabulated the refractive indices and volumes of the starting material, the various fractions of filtrate, the filtrate displaced by water, and the adsorbed material shaken out of the silica gel with water. It is evident from the refractive index that the aromatic hydrocarbons were removed from the filtrate, and that in two cases (mesitylene with *n*-decane and *m*-xylene with *n*-octane) the first portion of the filtrate displaced by water was also free from them. For the other two cases, toluene with methylcyclohexane and benzene with methylcyclopentane, a rise in the refractive index of the filtrate displaced by water was noticed. This may have been due to allowing the water to come too close to the bottom of the tube before withdrawing the fraction, or to the fact that the gel had reached its capacity at this stage. The recovery for this series averaged about 98 percent. From an initial solution of 102 ml, made from 97 ml of a paraffin and 5 ml of an aromatic hydrocarbon, more than 90 ml of pure paraffin hydrocarbon and 5 to 8 ml of aromatic concentrate were obtained.

IV. EXPERIMENTS TO DETERMINE THE CAPACITY OF SILICA GEL AS AN ADSORBENT OF AROMATIC AND OLEFIN HYDROCARBONS

In table 2 are recorded the results of experiments to determine the capacity of a fine gel, a reactivated fine gel, and a coarse gel, with respect to aromatic hydrocarbons, and of a fine gel with respect to olefin hydrocarbons. When the saturation capacity of fine silica gel is reached, the refractive index of the filtrate rises rapidly, during the passage of a few milliliters, from that of the pure paraffin hydrocarbon to that of the mixture employed.

TABLE 2.—Data showing the capacity of certain silica gels as adsorbents of aromatic and olefin hydrocarbons

Gel		Hydrocarbons	Volume of hydrocarbon	Refractive indices of:		Volumes and refractive indices of fractions after passage through silica gel								Total volume recovered
Wt.	Condition			Hydrocarbon	Mixtures	Filtrate ¹	Main portion of filtrate displaced by water	Last portion of filtrate displaced by water	Adsorbed material shaken out with water					
		ml	n_D^{25}	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	ml	
50	Fine	<i>o</i> -Xylene <i>n</i> -Nonane	10 92	1.5030 1.4039	1.4132	61.5 7.0 99.8	1.4039 1.4094 1.4039	22.7	1.4132	4.0	1.4533	3.2	1.4922	98.4
50	do	<i>o</i> -Xylene <i>n</i> -Nonane	10 194	1.5030 1.4039	1.4084	7.2 4.0 54.5	1.4040 1.4083 1.4084	24	1.4084	7.5	1.4197	6.8	1.4584	203.8
50	do	Toluene <i>n</i> -Heptane	10 92	1.4939 1.3850	1.3953	55.5 7.2	1.3850 1.3894	4.8 22	1.3950 1.3953	6.0	1.4207	4.7	1.4620	100.2
50	Fine, reactivated	<i>o</i> -Xylene <i>n</i> -Nonane	10 92	1.5030 1.4039	1.4132	55.3	1.4039	9.5 24	1.4061 1.4132	5.0	1.4390	6.4	1.4761	100.2
50	Coarse	<i>o</i> -Xylene <i>n</i> -Nonane	10 92	1.4039 1.5030	1.4132	45 12 12.6	1.4039 1.4049 1.4104	9.5 8.0	1.4130 1.4131	4.0	1.4548	4.7	1.4828	99.8
50	Fine	Diamylene <i>n</i> -Decane	5 97	1.4330 1.4096	1.4107	40.5 14	1.4096 1.4105	31	1.4105	3.6 2.0	1.4108 1.4141	7.0	1.4146	98.3

¹ Small fractions of filtrate were removed from time to time. The total volume of those with the same refractive index is recorded here.

The capacity of silica gel as an adsorbent of aromatic hydrocarbons depends on the concentration of the solution and also to some extent on the components of the solution from which the aromatic hydrocarbon is being adsorbed. In the first experiment with fine gel, 61.5 ml of filtrate free from *o*-xylene was obtained and the *o*-xylene content of a further 7 ml was reduced by an amount corresponding to its complete removal from 2.9 ml. Thus, 50 g of fine gel was capable of adsorbing 6.4 ml of *o*-xylene from a 10-percent solution of that aromatic hydrocarbon in *n*-nonane. In the second experiment, in which a 5-percent solution of *o*-xylene in *n*-nonane was used, the *o*-xylene was removed from 107 ml, so that 50 g of fine gel adsorbed about 5.35 ml of *o*-xylene from a solution of this concentration. In experiment 3, the adsorption capacity of 50 g of fine gel with respect to a different aromatic hydrocarbon, namely toluene, is shown. In this case, 55.5 ml of filtrate free from toluene was obtained and the toluene content of a further 7.2 ml reduced by an amount corresponding to 4.1 ml, so that about 5.96 ml of toluene was adsorbed from a 10-percent solution of that aromatic hydrocarbon in *n*-heptane.

The reactivated fine gel is, within the limits of the experiments, as good as the original, because when used with a 10-percent solution of *o*-xylene in *n*-nonane, 55.3 ml of filtrate free from *o*-xylene was obtained and the *o*-xylene content of 9.5 ml was reduced by an amount corresponding to 7.2 ml. A 50-g portion of this gel therefore adsorbed about 6.3 ml of *o*-xylene. The coarse gel removed completely the *o*-xylene from only 45 ml, and the rise in the refractive index to that of the original mixture did not occur within so small a volume as with the fine gel. The capacity of the coarse gel does not seem to be much less than that of fine gel, about 6.0 ml of *o*-xylene being adsorbed from a 10-percent solution in *n*-nonane by 50 g of gel. Channeling was apparent with the coarse gel and probably accounts for the less effective separation. However, the speed of filtration is much more rapid than with the fine gel and so, for some purposes, it may be preferable. The experiment with diamylene and *n*-decane shows that

silica gel removed completely the olefin hydrocarbon from its mixture with a paraffin. For a solution containing 5 ml of diamylene and 97 ml of *n*-decane, 40.5 ml of filtrate was obtained free from the olefin hydrocarbon, when 50 g of gel was used. Thus, 50 g of gel adsorbed about 2 ml of diamylene, which volume is approximately one-third that of the aromatic which can be adsorbed by the same quantity of gel. This interesting fact may be associated with the number of double bonds in the molecule, *o*-xylene having three and diamylene one.

V. ADSORPTION EXPERIMENTS WITH MIXTURES OF A NAPHTHENE AND A PARAFFIN HYDROCARBON

These experiments were designed to show the separation obtained when a naphthene hydrocarbon mixed with a paraffin hydrocarbon is filtered through silica gel. As with the preceding experiments, each mixture was made from hydrocarbons with approximately the same boiling point. Naphthenes with both 5- and 6-membered rings and both normal and branched-chain paraffins were used. Since the presence of small traces of such an impurity as an aromatic or unsaturated hydrocarbon would render the results of these experiments unreliable, it was first established that the individual hydrocarbons did not fractionate when passed through silica gel. The results of the experiment are shown in table 3. A small but quite definite separation occurred in every case, the naphthene tending to be adsorbed by the gel. The first 6 ml of filtrate had a definitely lower refractive index than the original mixture, the first 1 or 2 ml having an index lower than the original by 2 to 3 parts in the third decimal place, which corresponds to a reduction of the naphthene content, from the original 10, to 2 or 3 percent. The adsorbed material had a definitely higher refractive index than the original. The separation is disappointingly small. Nevertheless, the separation of naphthenes from paraffins is frequently so difficult that a method which gives any separation whatsoever is worthy of consideration as a research tool.

TABLE 3.—Data showing the separation of naphthene from paraffin or isoparaffin hydrocarbons by adsorption on 50 grams of fine silica gel

Hydrocarbons	Volume of hydrocarbons		Refractive indices of:		Volume and refractive indices of fractions after passage through silica gel							
	ml	Hydrocarbons	Mixtures	Filtrate ¹		Main portion of filtrate displaced by water	Last portion of filtrate displaced by water		Adsorbed material shaken out with water		Total volume recovered	
				ml	n_D^{25}		ml	n_D^{25}	ml	n_D^{25}		ml
<i>n</i> -Heptane.....	92	1.3850	} 1.3885	1	1.3861	24.6	1.3886	-----	7.6	1.3893	98.9	
Methylcyclohexane.....	10	1.4202										3
2,2,4-trimethylpentane..	92	1.3890	} 1.3922	4	1.3910	7	1.3922	} 1.5	1.3932	3.2	1.3930	100.9
Methylcyclohexane.....	10	1.4202										
<i>n</i> -Octane.....	50	1.3950	} 1.3980	2.0	1.3978	27.5	1.3980	-----	8.5	1.3987	53.2	
Nonanaphthene (a cyclopentane).	5	1.4273										11.5

¹ Small fractions of filtrate were removed from time to time. The total volume of those with the same refractive index is recorded here.

VI. AN ADSORPTION EXPERIMENT WITH A MIXTURE OF NORMAL PARAFFIN HYDROCARBONS OF DIFFERENT MOLECULAR WEIGHTS

This experiment was performed to determine whether any separation occurred when a mixture of normal paraffin hydrocarbons of different molecular weights was filtered through silica gel. To minimize fractionation by evaporation, hydrocarbons with relatively high boiling points (*n*-nonane and *n*-tetradecane) were chosen. The *n*-tetradecane was an Eastman product with refractive index $n_D^{25} = 1.4270$. This material had an odor of cracked compounds so it was filtered twice through silica gel, and yielded a filtrate with refractive index $n_D^{25} = 1.4266$. The *n*-nonane from petroleum was also given a preliminary filtration through silica gel. The results of these experiments are shown in table 4. The first 6 ml of filtrate is definitely higher in refractive index than the original mixture and the adsorbed material is definitely lower in refractive index. These results show that the hydrocarbon of low molecular weight was adsorbed in preference to that of high molecular weight. These results are in contrast to what is stated to happen with the lubricating oil fraction of petroleum in which, according to Kalichevsky and Stagner (5), paraffins of high molecular weight are more readily adsorbed than those of low molecular weight.

TABLE 4.—Data showing the separation of normal paraffin hydrocarbons of different molecular weights by adsorption on 40 grams of fine silica gel

Hydrocarbons	Volume of hydrocarbons	Refractive indices of:		Volume and refractive indices of fractions after passage through silica gel								
		Hydrocarbons	Mixtures	Filtrate ¹		Main portion of filtrate displaced by water		Last portion of filtrate displaced by water		Adsorbed material shaken out with water		Total volume recovered
				ml	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	ml	n_D^{25}	
<i>n</i> -Tetradecane.....	25	1.4266	} 1.4156	1.5	1.4196	} 21.5	} 1.4158	} 4.0	} 1.4152	} 6.0	} 1.4124	} 47.8
<i>n</i> -Nonane.....	25	1.4039		2.3	1.4179							
			2.3	1.4158								
			10.2	1.4156								

¹ Small fractions of filtrate were removed from time to time. The total volume of those with the same refractive index is recorded here.

VII. EXPERIMENTS TO ASCERTAIN WHETHER SILICA GEL DECOMPOSES A MIXTURE OF HYDROCARBONS

Silica gel is believed to act as a cracking catalyst under certain conditions. Several experiments were performed to determine whether, under the conditions employed here, the gel had any deleterious effect on the oil. Since the filtrates were found to have the same refractive indices as the pure hydrocarbons, it is evident that the gel had no harmful effect on them. The composition of the adsorbed material was also tested. A volume of 8.5 ml of the adsorbed material ($n_D^{25} = 1.4810$), from the previous experiments on the mixtures of *o*-xylene with *n*-nonane, was sulphonated with concen-

trated sulphuric acid. From this was obtained 1.8 ml of unattacked oil with refractive index $n_D^{25}=1.4043$, which is only slightly higher than that of *n*-nonane. The sulphonated material was then transferred to a flask for hydrolysis and steam passed through at 110° C. to remove any traces of unattacked oil. No measurable quantity was collected at this temperature. The temperature was then raised. Hydrolysis began at 155° C. From 155 to 165° C, 3.5 ml with the same refractive index as *o*-xylene ($n_D^{25}=1.5030$) was collected. From 165 to 170° C, 0.3 ml more was collected, with a refractive index $n_D^{25}=1.5038$.

The results show that *n*-nonane and *o*-xylene can be recovered unchanged from the adsorbed material rich in aromatics. Further evidence that silica gel has no harmful effect on these hydrocarbons was obtained from an experiment with a mixture of pseudocumene and *n*-decane in which the filtrate and the adsorbed material were carefully recombined. In this experiment, the filtrate was collected as one fraction in the graduated cylinder in which the hydrocarbons were mixed. Contrary to the usual practice of shaking the adsorbed material out of the silica gel with water in an erlenmeyer flask, the silica gel and adsorbed material were transferred directly to a distilling flask as a suspension in water and the adsorbed material was distilled over with steam. Its refractive index was then observed and it was recombined with the filtrate. The volumes and refractive indices of the original mixture, the filtrate, the adsorbed material, and the recombined fractions are shown in table 5. It can be seen that only 0.6 ml was lost in this procedure. The greater part of this loss probably occurred in the adsorbed material of high refractive index, which underwent more operations than the filtrate. The slightly lower refractive index of the recombined material (only 3 parts in the fourth decimal place) is attributable to the proportionately greater loss of adsorbed material. It is evident that no appreciable harm, if any, was done to the oil.

TABLE 5.—Data of an experiment to ascertain whether silica gel decomposes a mixture of *n*-decane and pseudocumene

Material	Volume	n_D^{25}
	ml	
Mixture.....	98	1.4182
Filtrate.....	88	1.4122
Adsorbed material steamed out of gel.....	9.4	1.4765
Recombined fractions.....	97.4	1.4179

VIII. APPLICATION OF SILICA GEL ADSORPTION TO THE FRACTIONATION OF A DISTILLATE OF PETROLEUM BOILING BETWEEN 140 AND 145.5° C

Adsorption on silica gel has been used in this laboratory to remove aromatic hydrocarbons from a 17-liter fraction of petroleum distillate boiling normally between 140 and 145.5° C. It consisted chiefly of a mixture of isononanes and some naphthenes, but it also contained a small amount of aromatic constituents. The last named were originally present in large quantities, and although an interlocking process of extraction with liquid sulphur dioxide and fractional dis-

tillation had been used to remove the greater part of them (6), some still remained. In a final distillation the portion immiscible with sulphur dioxide had been separated into 0.5° C cuts. The material boiling near 140° C and near 145° C smelled faintly of aromatic hydrocarbons. Samples of these fractions also yielded upon nitration a small amount of nitro product in the form of a red oil. In the material boiling between 142 and 144° C, where the bulk of paraffin constituents had concentrated, only a little aromatic material could be detected. Nitration tests showed that the average aromatic content of the whole distillate was about 2 percent.

In addition to the constituents mentioned, the distillate contained some "cracked" material. After distillation, it had been stored in glass bottles for three years. When the present work was begun, it was observed to have deposited a thin ring of gum where the oil surface wet the bottle. Likewise, a film of sludge was observed at the bottom of the oil, notably in the bottles containing distillation residues. The residues were also consistently yellow in color and possessed an unpleasant odor. To ascertain if the color, odor, and gum could be removed by adsorption, a sample of residue was filtered through a column of silica gel. As more and more oil passed through the gel, the top layer became colored—at first a light amber, later an amber red. (This coloration likewise had been observed when the olefin, diamylene, was passed through gel.) Some of the coloration produced on the gel was attributed to the polymerization or oxidation of unsaturated hydrocarbons arising from the cracking of the oil during distillation. The filtered oil was colorless and had no unpleasant odor, which was taken to mean that gum had been removed completely by the gel. Once the gum was removed, the oil remained stable with further filtration as evidenced by the fact that no further coloration was produced.

To remove both aromatic hydrocarbons and gum from the distillate, it was filtered through silica gel in essentially the same manner as were the synthetic mixtures of hydrocarbons. Oil was recovered from the spent gel in a similar way.

In this operation, it was obvious that, since the capacity of the gel to adsorb aromatic hydrocarbons varied with their concentration in the oil being filtered, some aromatic material adsorbed from more concentrated solutions would be dislodged from the gel when oil with a lower aromatic concentration was filtered through. To prevent this occurring all of the distillate was blended, before filtering, into three fractions corresponding approximately to constant-boiling mixtures. These are listed in table 6 according to their boiling range.

TABLE 6.—Volumes and refractive indices of fractions of petroleum distillate before and after filtering through silica gel

Boiling range 760 mm before filtering	Volume				Refractive index		
	Before filtering	After filtering		Lost by filtering	Before filtering	After filtering	
		Filtrate	Adsorbed			Filtrate	Adsorbed
<i>Degrees C</i>	ml	ml	ml	ml	n_D^{25}	n_D^{25}	n_D^{25}
140 to 142.5.....	5, 230	4, 905	210	115	1.415	1.4125	1.445
142.5 to 144.....	5, 850	5, 380	360	110	1.4125	1.4115	1.425
144 to 145.5.....	5, 660	5, 150	460	50	1.418	1.416	1.438

In practice, coarse gel was used for the most part because of the decidedly shorter time required to filter 17 liters of oil. Although its effectiveness in removing aromatic constituents was somewhat less than that for fine gel, because of channeling, the difference was minimized by using columns no greater than 3 cm in diameter. When channeling had obviously occurred, the oil was refiltered through fresh columns of gel. The columns were about 50 cm long. One measuring 2 by 50 cm held about 100 g of gel; one measuring 3 by 50 cm held 200 g. The time required for oil to flow from top to bottom of the column, under a hydrostatic head of 10 cm of oil, was about 20 minutes. Longer columns were not used because it was more difficult to remove the gel.

The procedure adopted for the systematic filtration was as follows. A portion of the blended distillate was filtered through the columns of gel. Portions of filtrate were removed until the first rise in refractive index was observed and were stored as being free of aromatics. This procedure was followed since it had been shown with the synthetic mixtures of hydrocarbons that the filtrate was free of aromatic material until a rise in refractive index was noted. As a comparison it was found that material purified by the silica gel was lower in refractive index by 0.0001 than the raffinate from treatment with a nitrating mixture. Further fractions of filtrate were collected until the refractive index attained that of the oil being filtered, at which time the gel had become saturated. This material was refiltered.

The columns of saturated gel were allowed to drain until oil ceased to flow, after which adhering oil was displaced by the addition of water at the top. The gel was then removed from its tube and the adsorbed oil recovered by shaking with water or distilling with steam.

In table 6 are listed the volumes and refractive indices of the fractions of petroleum distillate before and after filtering them through silica gel. The volumes listed for the fractions of adsorbed material are large in proportion to the aromatic content of the original distillate because some of the oil adhering to the gel was mixed with the fraction adsorbed. This caused a correspondingly lower refractive index for the combined fraction than that for the adsorbed material alone.

This experiment with one petroleum fraction shows that silica gel adsorption should prove to be a useful tool in the investigation of the composition of petroleum distillates.

IX. LITERATURE REFERENCES

- (1) D. T. Day, J. E. Gilpin, and M. P. Cram, Bull. 365, U. S. Geological Survey (1908); J. E. Gilpin and O. E. Bransky, Bull. 475, U. S. Geological Survey (1911).
- (2) B. Tarasov, *Azerbaidzhanskoe Neftyanoe Khozyaistvo* **1**, no. 10, 47-50 (1926).
- (3) H. Hofmeier and H. Meiner, *Z. angew. Chem.* **46**, 229 (1933).
- (4) N. L. Drake, G. M. Kline, and W. G. Rose, *J. Am. Chem. Soc.* **56**, 2,076 (1934)
- (5) Kalichevsky and Stagner, *Chemical Refining of Petroleum*, p. 182. (The Chemical Catalog Co., 1933.)
- (6) J. D. White and F. W. Rose, Jr., *BS J. Research* **9**, 714 (1932) RP501.

WASHINGTON March 4, 1935.