phenylmethane in any of the methods that have been employed for that purpose.

It has been stated in one of the preceding paragraphs that not only phenoxytriphenylmethane but also hydroxytetraphenylmethane was obtained on some occasions when triphenylchloromethane was condensed with sodium phenolate. The formation of this second product under these conditions of experiment could not be ascribed to an intramolecular rearrangement of the first, such a rearrangement as has been assumed by Gomberg and Jickling.[1] for the formation of di-*p*-hydroxytetraphenylmethane from diphenoxydiphenylmethane through the agency of acids. Upon further examination we found that, in addition to phenoxytriphenylmethane, some hydroxytetraphenylmethane is always formed when not all the metallic sodium has gone into solution in the phenol previously to the addition of triphenylchloromethane. Under these circumstances some triphenylmethyl must be formed through the action of the metallic sodium upon triphenylchloromethane, and the triphenylmethyl unites, in its turn, with phenol.[2]

$$2(C_6H_5)_3C + C_6H_5OH = (C_6H_5)_3C.C_6H_4OH + (C_6H_5)_3CH.$$

This, we believe, offers a satisfactory explanation for the occasional formation of hydroxytetraphenylmethane in the above condensation.

Summary.

1. It has been shown that triphenylchloromethane gives, with phenyl magnesium bromide at 150–200°, yields of 10–12% of tetraphenylmethane, as compared with 3–5% that have been previously obtained at lower temperatures.

2. The methyl and ethyl ethers of triphenylcarbinol give, with phenyl magnesium bromide, yields of 10–12% of tetraphenylmethane; the phenyl ether, however, gives 20%.

3. Triphenylcarbinol and the carbinol chloride condense with phenol in the presence of very small quantities of acid and give almost quantitatively *p*-hydroxytetraphenylmethane.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE.]

THE RELATIONS IN COMPOSITION OF THE DIFFERENT FORMS OF NATURAL BITUMENS.

BY CHARLES F. MABERY.

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There has long been much discussion concerning the numerous varieties of bitumen as to their formation, composition, and their relation

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[1] THIS JOURNAL, 37, 2358 (1915).

[2] Schmidlin, *Ber.*, 45, 3180 (1912); Gomberg and Cone, *Ibid.*, 37, 2040 (1904).

in origin, but in comparison with the opportunities for actual study of their ultimate composition on an adequate scale, the results on record are extremely limited. The products of the destructive distillation of coal, especially in coal tar, have been quite thoroughly examined. Several attempts on a laboratory scale to avoid decomposition of the coal substance by distillation under diminished pressure, have yielded further information concerning its decomposition products. But the distillation of at least 1000 lb. lots *in vacuo* under carefully regulated conditions is greatly to be desired both for the larger quantities needed for precise identification, and the detection of constituents present in minute proportions, that escape observation in the laboratory manipulation of smaller charges.

In an examination of British coals, Jones and Wheeler,[1] and Brooks and Humphries,[2] carried on distillations of small amounts very slowly, prolonging each distillation through five weeks. The distillates condensed at low temperatures contained methane, ethane and their homologs, besides less volatile liquid hydrocarbons of the same series, but in too limited yields for identification of the individual hydrocarbons. Pictet and Bouvier[3] distilled Loire coal *in vacuo* and identified two hydrocarbons, $C_{10}H_{20}$ and $C_{11}H_{22}$, that had been recognized previously in Canadian petroleum. Solid paraffin was observed in the distillation from the British coals, and elsewhere in flue dust.

In the comprehensive study of asphalts, especially of the deposit at Trinidad by Clifford Richardson,[4] a similarity in composition was shown between some of the hydrocarbon constituents of the asphalts and those of the heavy asphaltic varieties of petroleum. The sulfur derivatives of the hydrocarbons which are characteristic of most of the heavy varieties of petroleum appeared even more prominently in the asphalts. Intermediate in composition and properties between petroleum and the natural asphalts is the class of bitumens known in this country as Grahamite, Gilsonite, and a number of other allied substances found in Colorado and Utah, concerning which little is known except that they yield black paints and varnishes of superior quality. Under the title,[5] W. C. Day has described an examination of Gilsonite which included its chemical and physical nature, but the composition of distillates collected under atmospheric pressure within limits of 30° was not ascertained. The presence of nitrogen derivatives was recognized by their peculiar odor, which was described as that of pyridine or chinoline, but nothing further was done toward their identification.

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[1] *J. Chem. Soc.*, **105**, 2562 (1914).

[2] *Ibid.*, 393 (1915).

[3] *Ber.*, **46**, 3342 (1913).

[4] *J. Soc. Chem. Ind.*, 1898; *The Modern Asphalt Pavement*, 1908.

[5] "Investigation of Utah Gilsonite, a variety of asphalt" (Franklin Institute, 1895).

Ohio Bituminous Coal.—While studying the petroleum area on the Mahoning river in Milton township, Ohio, five years ago, I observed a thick outcropping partly weathered seam of coal that proved on analysis to contain more than 50% of carbonaceous matter. This coal appeared to be an outcrop of a seam in the Palmyra district that has yielded some of the best coal in the state; one-half mile farther to the north, at a depth of 150 feet below the level of the river, it forms what is known as the Deerfield coal. The near proximity of this seam of coal to the oil area and the similar depth of the oil strata led me to procure a barrel of the coal for examination. Approximate analysis of this coal gave:

Volatile matter 38.43%, coke 58.29%, ash 2.31%, and by combustion 81.10% C, and 5.78% H, 0.68% S, 0.05% N.

Three years ago a part of this coal was distilled in an iron electric still *in vacuo*, and recently the fractionated distillates have been examined. Each distillation occupied a day of eight hours and the yield of first distillate was 5.6% of the weight of coal taken. The British coals distilled more slowly, gave 7% of distillate. The large evolution of gas that preceded the run of oil indicated the breaking down of the coal substance, and it continued to some extent throughout the run. It appears doubtful that the hydrocarbons collected in distillation, except possibly those of high molecular weight and the solid paraffins, are contained as such in this coal. In a representative run a charge of two kilos gave 85 g., —1.7% water, —5.7% oil distillate, with a residue of 1545 g. The distillate was composed of a thick tar heavier than water, and a smaller amount lighter than water. For the separation of the constituents of the lighter oil, a kilo was collected in 10° distillates, then each was dissolved in light gasoline, and refined, first with common sulfuric acid, then with the fuming acid, and with sodium carbonate. After distilling off the gasoline, the remaining oils were fractionated under 20 mm. pressure, collecting at first within 5° and then within 2°. On account of the limited amounts of the distillates it cannot be assumed that they were completely separated, but the analytical values and molecular weights were sufficiently close to indicate the presence of several hydrocarbons.

The following table gives a summary of the data on which were calculated the symbols of the hydrocarbons separated:

Fractions. At. pres.	Sp. gr. at 20°.	Determinations.				Required.		
		Mol. wt.	C.	H.	For.	Mol. wt.	C.	H'.
194–196°	0.8018	165	85.65	13.87	$C_{12}H_{24}$	168	85.70	14.30
20 mm.								
83–85°	0.8030	143	85.65	14.50	$C_{10}H_{20}$	140	85.70	14.30
151–153°	0.8682	214	87.12	12.74	$C_{16}H_{28}$	218	87.28	12.72
183–185°	0.8706	240	86.80	12.50	$C_{17}H_{30}$	234	87.18	12.82
193–195°	0.8734	247	87.04	12.64	$C_{18}H_{32}$	248	87.10	12.90
228–230°	0.8816	270	86.74	13.22	$C_{20}H_{36}$	276	86.95	13.05

Calculated on the basis, C 12, H 1.

The fractions above 225°, 20 mm., became solid with paraffin. After pressing in filter press what collected at 270–300°, it was crystallized several times from ether-alcohol, then several times from ether and again thoroughly pressed. It melted sharply at 60°, the melting point of the hydrocarbon, $C_{30}H_{62}$.

A combustion gave: C 85.53, H 14.60. Required for $C_{30}H_{62}$: C 85.31, H 14.69.

The partly solid distillates collected at 225–270° indicated the presence of other solid paraffin hydrocarbons. Much ammonium acetate was contained in the water of the first distillate, and the light oil gave the pungent odor and characteristic reactions of acetic aldehyde which has always been observed in the light distillates from Mahone petroleum. A violet-colored deposit appeared in the lighter distillates on standing. From the sodium carbonate solution used in refining distillates by the addition of acids, naphthene acids were set free. When extracted with ether the residue of evaporation had the peculiar sharp odor of these acids; it dissolved readily in alkalies, reprecipitated with acids, decomposed insoluble carbonates with the formation of salts, and showed the strong emulsifying power of these acids in alkaline solution on the petroleum hydrocarbons. Since little attention has been given to these acids in American petroleum, I have procured refinery emulsions and other by-products for their further study.

The first distillates differed essentially in their behavior with bromine and other reagents. With bromine some were hardly attacked and gave off no hydrobromic acid; others containing unsaturated hydrocarbons absorbed bromine with little acid evolution, giving heavy addition products; still others evolved the acid copiously and the heavy addition products had the peculiar piney odor of aliphatic bromine derivatives. With potassium permanganate similar differences were observed; the fractions containing unsaturated hydrocarbons quickly bleached the solution. The pungent odor of the aromatic hydroxyl derivatives in the light tar distillates remained persistently even after refining. On standing over sodium colored precipitates appeared in some of the distillates, various shades of blue and violet, which dissolved in acids but were reprecipitated by alkalies with return of the colors. These substances were probably formed by the action of acetic aldehyde on hydroxyl derivatives in the presence of the sodium.

Besides the solid paraffins no other hydrocarbons of the series C_nH_{2n+2} were recognized; since the former appear quite generally in the distillation of organic matter such as fats, oils and vegetable substances, it is not surprising that they are formed in the distillation of coal. But under the conditions of the original distillation, the decomposition of the coal substance with the large evolution of gases evidently included also the elimination of hydrogen with the formation of lower unsaturated hydrocarbons. In more prolonged distillations such as those of the British coals, mentioned above, the slower decomposition of the coal substance may cause less cracking and evolve saturated bodies. Then, no doubt the hydrocarbons formed by distillation depend to some extent on the composition of the coal.

There is a marked similarity between some of the hydrocarbons in the distillates from Deerfield coal and those from the larger part of the adjacent Mahone petroleum. Those of the series C_nH_{2n-4} form a large part of the coal distillates as they do of the distillates from the petroleum.[1] While no members of the series C_nH_{2n-2} were found in the coal distillates, they form a considerable part of the petroleum, and the series C_nH_{2n}, not found in this petroleum but generally in Russian, Japanese and American petroleum had the members $C_{10}H_{20}$ and $C_{12}H_{24}$ in the lower coal distillates; but it is quite probable that distillations on a larger scale should reveal constituents present in smaller proportions. Under any conditions of operation, however, with or without air, the distillation of coal is a destructive decomposition of the coal substance, which, as has been shown, may be partially avoided by extending the time, but the gradual changes that proceed under natural conditions of moderate temperatures and long periods of time, it is impossible to repeat. As mentioned in the paper referred to above, Mahone oil is found at a depth of 150 feet in a section of loose fine-grained quartz sand with an overlying impervious shale. The Deerfoot coal forms a seam four feet thick inclosed in loose sandstone and shale. In the near vicinity of the oil sands there are other seams of coal that have not been uncovered.

The products evolved in its distillation indicate that this coal is an intermediary state of decomposition between vegetable substance and petroleum. Although different in composition, it evidently retains the inert character of its vegetable source. In the bituminous varieties the composition of the coal substance is of great interest but not easy of solution. Its constituents are not readily affected by solvents as many attempts to extract it have shown. While a close relationship of coal to petroleum is not always evident, and with some varieties of petroleum never existed with others it seems extremely probable, as in this instance, that the oil came though the coal, or simultaneously with the coal from the vegetable substance.

It is asserted by David White[2] that "in most petroliferous regions of the world the oil pools lie in or near (often beneath) formations carrying coal," and that "if we examine the oils of the United States, we find that those formations and regions in which the carbonaceous detrital deposits

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[1] Mahone, "Petroleum," *J. Ind. Eng. Chem.*, **6**, 201 (1914).

[2] "Some Relations in Origin between Coal and Petroleum," *J. Wash. Acad. Sci.*, **5**, 203 (1915).

(coals) are but little altered by dynamic influences that the oils are of high gravity." That Deerfield coal and Mahone petroleum afford a typical example of this relation is borne out by the similarity of the hydrocarbons that compose the petroleum to those that are evolved by the distillation of the coal. The coal has not been altered by dynamic influence, and the oil is a typical non-paraffin heavy petroleum composed of comparatively few hydrocarbons.

Utah Gilsonite has recently been described by Richardson[1] as to its geological occurrence and its relations in origin to the neighboring deposits of Grahamite. Richardson is of the opinion that both were derived from petroleum and that Gilsonite is the intermediate product. Although the recently recognized valuable qualities of Gilsonite indicate its peculiar composition, no attempts have been made toward identifying the hydrocarbons of which it is composed. In Day's examination[2] the only reference to the constituent hydrocarbons was the statement that the chemical inertness of the distillate obtained under atmospheric pressure after treatment with sulfuric acid indicated that it was composed of the paraffin hydrocarbons, but there was no further experimental evidence in its support. But the result of the examination to be described in this paper and the nature of the material render it improbable that it contains members of the series C_nH_{2n+2} lower than the solid paraffins.

My examination has not included analysis of a sufficient number of samples to show whether the natural product is homogeneous in composition, but it appears from a comparison with the percentages in Day's analysis that there is some variation.

Day's analysis: C 88.30, H 9.96, S 1.32%. My sample: C 87.83, H 11.27, S 0.02 N 1.05%.

Then a variation in specific gravity found by Richardson in four samples of Utah Gilsonite from 1.011 to 1.057 probably indicates some variation in composition. I am unable to understand Day's failure to determine sulfur by combustion, since it is, certainly, the most accurate and expeditious method for this determination in all varieties of petroleum, asphalts and products obtained from them, even gasoline. But the method used by Day which included oxidation with nitric acid in an open dish, and treating the unoxidized material by the Escha method is open to serious objections. In his analysis nitrogen was not determined, but it formed with oxygen an estimated difference of 0.32%. In all specimens of Gilsonite I have seen, the nitrogen compounds are considerable in amount much larger in fact than this small proportion of nitrogen would indicate.

The material used in this examination was for the most part in lumps up to five lbs. in weight, homogeneous in appearance, having a bright

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[1] *J. Ind. Eng. Chem.*, 8 (1916).

[2] *Loc. cit.*

vitreous luster, conchoidal fracture and very brittle. It melted at 180° and its flash point was 295°, which indicated a harder substance than those described by Richardson, of which the softest flowed at 140°, and the hardest with a flow point at 175°.

The distillations were made in a still of steel pipe 30 inches long and four inches interior diameter, wound with two lengths of iron wire and insulated with sheets of asbestos. A current of 6 to 8 amperes was sufficient for the maximum temperature; in the beginning it had to be carefully controlled to prevent frothing, caused by the brisk evolution of gases that could not be entirely prevented even with the utmost care. Whether the gases were evolved from unstable constituents, or whether the asphaltic substance must undergo complete disintegration before the hydrocarbons appear was not ascertained, but it seems probable that a great part of the distillate is the result of decomposition, as in the distillation of coal. On account of the frothing, the charges were limited to 500 to 800 g. and even then under the most careful control, five hours was the shortest time for a single run. Four distillations of 800 g. each gave 1600 g. of distillate, a yield of 50%; with smaller charges, 56% was obtained. This same yield was obtained by Day under atmospheric pressure. The temperature at which the distillate came over was 200°; at the rear of the still it was 300° to 400°.

Since it contained little, if any, of the aromatic compounds, the odor of the first distillate was quite unlike that of the coal distillate rather resembling the odor of the unsaturated hydrocarbons; it was quite thin in consistency, flowing readily. For the separation of its constituents, it was distilled within 10° under 20 mm. pressure, giving a total of 800 g. with 200 g. of asphaltic residue. Each of these fractions was then agitated thoroughly with common concentrated sulfuric acid, and washed with a solution of sodium carbonate. Upon diluting the acid solution another oil was precipitated, and by the addition of sodium carbonate to the diluted acid still another oil was thrown down, consisting of the basic nitrogen compounds. Three classes of products were therefore separated from the distillates, the first refined with acid and sodium carbonate, the second oil, separated by diluting the acid used in refining the first oil, and a third oil, precipitation by sodium carbonate form the diluted acid. The identification of these products will be described.

After drying the first refined distillates with calcium chloride and sodium they were subjected to further distillation within 5° and 2°, under atmospheric pressure to 190°, and higher under 20 mm. Distillates began to collect at 110° but in too small amounts for examination. Increasing above 130°, at 158° or higher and at 735 mm. the presence of individual hydrocarbons was indicated by the larger amounts distilling within definite limits, and confirmed by molecular weight determinations and analyses as shown in the following table:

Fractions.	Sp. gr.	Found.				Calculated.		
At. pres.	at 20°.	Mol. wt.	C.	H.	For.	Mol. wt.	C.	H.
158–160°	0.7922	145	85.49%	14.14%	$C_{10}H_{20}$	140	85.70%	14.30%
193–195°	0.8021	162	85.74	14.34	$C_{12}H_{24}$	166	85.70	14.30
20 mm.								
116–117°	0.8273	205	86.58	13.63	$C_{15}H_{28}$	208	86.53	13.47
148–150°	0.8500	224	86.46	13.22	$C_{16}H_{30}$	222	86.49	13.51
162–164°	0.8506	248	86.84	12.86	$C_{18}H_{34}$	250	86.40	13.60
184–186°	0.8564	268	87.02	12.82	$C_{19}H_{36}$	264	86.36	13.64

The hydrocarbon 158–160° appears to be identical with α-dekanaphthene, b. p. 162–164°, separated by Markownikoff and Ogloblin[1] from Apscheron naphtha, sp. gr. 0.7936, and by Mabery and Takano[2] from Japanese petroleum, sp. gr. 0.7902, and by Mabery and Hudson[3] from California petroleum.

When exposed to the vapor of bromine for several days this hydrocarbon combined with an equivalent in weight of two atoms and gave off large volumes of hydrobromic acid. Crystals of the bromine derivative that appeared in the oil after a little evaporation formed fine needles from carbon disulfide quite soluble in hot water, less so in cold, quite sparingly soluble in carbon tetrachloride from which it is best purified. Melting point, 170°. The quantity obtained was not sufficient for analysis.

A close agreement is to be noted between the hydrocarbon collected at 193–195° in specific gravity and molecular weight with dodecane separated by Markownikoff and Ogloblin from Balachany petroleum, sp. gr. 0.8055. But the hydrocarbon found in American petroleum with this boiling point was undecane, $C_{11}H_{22}$. Although the formulas of the next four hydrocarbons are supported by analysis and molecular weights, their specific gravity and boiling points are lower than the hydrocarbons with these formulas separated from the heavy petroleum of various sources. On account of the limited amounts of these fractions, evidently complete separation of their constituents was not possible.

The composition of Gilsonite, therefore, resembles that of the heavy varieties of petroleum. While, as mentioned above, there is considerable decomposition in the initial distillation, it seems probable that the heavier saturated hydrocarbons and the solid paraffins form a considerable part of the natural bitumen. It needs distillation on a larger scale than is possible in the laboratory to separate the hydrocarbons in sufficient amounts for complete identification.

Unsaturated Hydrocarbons.—The portions of the 10° distillates men-

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[1] *Ber.*, **16**, 1983 (1873).

[2] *J. Soc. Chem. Ind.*, **29**, 614 (1900).

[3] *Proc. Am. Acad. Arts Sci.*, **35** (1900).

tioned above as precipitated by dilution of the acid used in treatment, in their properties and reactions were quite unlike the residual oils. They were collected in several distillations within 2° at 20 mm. pressure and the fractions examined for their individual constituents. When freshly distilled all the fractions were colorless, but on standing even in corked containers they became deeply colored, first on the surface, and the color gradually extended until the entire mass of the oil became very dark; on long standing a viscous solid was deposited on the inside of the container. A similar coloration and deposit has been observed in distillates that have stood several years, especially in oils extracted by sulfuric acid, such as unsaturated sulfur-free oils that have accompanied the sulfur oils. This coloration is evidently caused by the absorption of atmospheric oxygen. In combustions of freshly prepared distillates the total percentages of carbon and hydrogen approached closely to 100%, but in the colored oils there was a material deficiency. Even in containers where the color had extended only part way down, the uncolored portion gave percentages excluding oxygen, but the colored portions showed its presence. It has hitherto been assumed that the principal influence of oxygen on the petroleum hydrocarbons was exerted in the removal of hydrogen. but its ready absorption by the unsaturated hydrocarbons doubtless explains the coloration of distillates on standing, and it is probably one of the chief causes of the deep color in crude petroleum. I have never observed the unsaturated hydrocarbons in the light-colored varieties, such as the Berea Grit or West Virginia crudes.

On the oils refined with sulfuric acid, nitric acid has no action in the cold and it is not vigorous when warmed. But the oils soluble in the acid are immediately attacked and with explosive violence when warmed, with the formation of extremely stable nitro-products that require prolonged boiling with sodium to decompose completely. All these hydrocarbons showed the characteristic reactions with potassium permanganate, bleaching a dilute solution with great readiness. Some of the oils fractionated within 2° at 20 mm. pressure were examined for their individual constituents with the following results:

Fractions. 20 mm.	Sp. gr. at 20°.	Found.				Calculated.		
		Mol. wt.	C.	H.	For.	Mol. wt.	C.	H.
58–60°	0.7711	131	85.54	14.38	C_9H_{18}	126	85.70	14.30
80–82°	0.7977	154	85.34	14.74	$C_{11}H_{22}$	154	85.70	14.30
100–102°	0.8095	181	86.08	13.88	$C_{13}H_{26}$	182	85.70	14.30

The hydrocarbon C_9H_{18} may be the same nonylene that Mabery and Quayle found in Canadian petroleum. There is no doubt that most varieties of petroleum contain these hydrocarbons in small proportions and that they are readily extracted by sulfuric acid. Their peculiar odor is always present in diluted acid sludge.

The effect of prolonged exposure to the air on these unsaturated hydrocarbons, as mentioned above, appeared in the higher specific gravity and changes in composition. A distillate collected at 148-150°, sp. gr. at 20°, 0.9063 gave C 86.56%, H 11.94%. Another collected at 168-170°, sp. gr. 0.8956, gave C 85.98%, H 11.87%. A third, collected at 180-182°, sp. gr. 0.9118, gave C 85.69%, H 11.24%.

An excess of sodium carbonate added to the diluted acid after the separation of the unsaturated hydrocarbons precipitated the nitrogen derivatives in part as an oil and in part as a crystalline solid from the higher distillates. These substances were precisely similar in odor and reactions to the nitrogen oils that have been separated in this laboratory from many varieties of petroleum. Analyses now in progress here indicate their presence in variable proportions in all petroleum and this peculiarity appears in a comprehensive study of their structure now in progress. Such a large proportion of the nitrogen compounds in Gilsonite is interesting as a proof of a common origin with petroleum, and as additional evidence of the close relationship that is brought out by the similarity of the hydrocarbons common to both.

Grahamite.—Since, so far as it appears from published records, no attempts have been made to determine the composition of Grahamite, it seemed of interest to ascertain the nature of the hydrocarbons it yields by distillation, for comparison with those from Gilsonite. Through the courtesy of the Barber Asphalt Company, 50 lbs. of the natural product, which was assumed to represent its average composition, were obtained for this examination.

Grahamite differs materially in its appearance and composition from Gilsonite, lacking its highly vitreous luster, conchoidal fracture and hardness. In its duller luster, hardness and general appearance, it rather resembles the Deerfield coal described above. The difference in composition is manifest in the following proximate analyses:

	Gilsonite	Grahamite.	Coal.
Volatile matter	56%	44.52%	38.43%
Fixed carbon	54	38.99	58.29
Ash	0.02	5.54	2.31
Sulfur	...	2.07	0.69
Nitrogen	1.05	...	0.05

In the first distillations in an iron still heated by gas lamps under 30 mm. pressure there was no violent frothing such as interfered with the continuous distillations of Gilsonite, but care was necessary in the beginning to avoid clogging the exit tube by fine powder that came over with the first oil. At 140° the first oil appeared, and the last came over at 240°. A charge of 1500 g. gave 200 g. of oil, or 13.5% with sp. gr. 0.85 at 20°. This oil has a specific gravity considerably higher than that of the first distillate from Gilsonite. Its odor, quite unlike that of the other, resembled closely that of petroleum distillates. No odor of nitrogen derivatives, plainly evident in the Gilsonite oil, could be detected in the first distillate from Grahamite, although it appeared in some of the higher 2° distillates. The residue was a hard brittle solid. To separate the hydrocarbons in the first distillate it was fractionated at 10°, 5° and 2°, under atmospheric pressure; it began to come over at 150°, and continued to 285°, and from there on under 20 mm. to 260°. From the distillate collected at 215° atmospheric pressure, on cooling to 15°, solid hydrocarbons began to separate in increasing amounts, until the fractions distilled at 200° and 20 mm. pressure became nearly solid. In their stability, during distillation, and behavior with reagents, these distillates were essentially different from those obtained from coal and Gilsonite. For identification of the individual hydrocarbons each fraction was agitated with concentrated sulfuric acid and then with sodium carbonate and after washing was dried over sodium. The acid had very little effect on the lower distillates. The odor of sulfur dioxide, which is always evident in refining petroleum distillates, was absent here, except in the higher fractions where there was some previous decomposition. On diluting the acid sludge scarcely any oil separated. Sodium hydroxide caused so much emulsion of the oil that could not be used; even sodium carbonate gave some milky emulsion. The following table gives a summary of the hydrocarbons that were separated:

Fractions. Atmos. pres.	Sp. gr. at 20°.	Found.				Calculated.		
		Mol. wt.	C.	H.	For.	Mol. wt.	C.	H.
143–145°	0.8730	124	86.07%	13.88%	C_9H_{18}	126	85.70%	14.30%
170–172°	0.7874	138	86.19	13.78	$C_{10}H_{20}$	140	85.70	14.30
194–196°	0.8019	164	85.31	14.69	$C_{12}H_{24}$	168	85.70	14.30
206–208°	0.8132	182	85.83	13.93	$C_{13}H_{26}$	182	85.70	14.30
222–224°	0.8301	210	86.34	13.24	$C_{15}H_{28}$	208	86.53	13.27
250–252°	0.8405	227	86.47	13.38	$C_{16}H_{30}$	222	86.49	13.51
280–282°	0.8512	271	86.50	13.44	$C_{19}H_{36}$	264	86.40	13.60
200 mm.								
208–210°	0.8585	286	86.22	13.45	$C_{21}H_{40}$	292	86.30	13.70

The refined hydrocarbons in the lower distillates were not affected by potassium permanganate; on diluting the acid sludge from refining them a very small amount of thin oil separated that bleached the permanganate solution. But the proportion of unsaturated hydrocarbons in these distillates were only a trace as compared with the Gilsonite fractions. With nitric acid their behavior was similar to that of the petroleum hydrocarbons, also with bromine, hydrobromic acid was evolved and substitution products heavier than water were formed with the characteristic odor of the aliphatic bromine substitution products. These crystallized well from CS_2. From the fractions 255–260° the solid paraffin was filtered, pressed in filter paper and crystallized from alcohol-ether, and then from ether. It formed white pearly scales, m. p. 66°, the melting point of the paraffin hydrocarbon $C_{31}H_{64}$.

By combustion it gave: C, 65.09; H, 15.00%. Calc. for $C_{31}H_{64}$: C, 85.32; H, 14.68.

From the next lower fractions, a solid was separated and purified that melted at 64°, the m. p. of the hydrocarbon $C_{29}H_{60}$. There is, therefore, no doubt that these distillates contained a series of solid paraffin hydrocarbons corresponding to those in petroleum. The high values for carbon and low values for hydrogen in the table above indicate that the hydrocarbons were not fully purified, which was evidently not possible with the limited amounts of the fractions. Yet the values for specific gravity and composition agree very well with those of hydrocarbons that have been separated from American, Russian and Japanese petroleum. In fact they show the close relationship of Grahamite to the heavy varieties of petroleum; and since these hydrocarbons may be extracted by naphtha, it seems probable that they are contained in the natural bitumen and are not products of decomposition. The resemblance of the hydrocarbons in Grahamite to those in Gilsonite suggest a common origin. A closer relationship of Gilsonite to petroleum is indicated by the large percentage of nitrogen compounds it contains, which appear only as a trace in Grahamite. If Grahamite were formed directly from Gilsonite it should contain the same or a larger proportion of these nitrogen bases. The proportion of unsaturated hydrocarbons, soluble in sulfuric acid, is larger in Gilsonite, or rather in its vacuum distillates, than in any petroleum I have examined. In a direct change of Gilsonite into Grahamite it would seem that these bodies should accompany the saturated hydrocarbons for the latter contains as volatile constituents as the former. The interesting study of these forms of bitumen as to their geologic occurrence by Clifford Richardson,[1] leads him to the belief that Gilsonite is formed direct from petroleum and Grahamite from Gilsonite. Their appearance and physical properties alone would support this opinion; but his observation that they contain only very small amounts of hydrocarbons not affected by sulfuric acid does not apply to the material from which the hydrocarbons described in this paper were separated. Gilsonite yields 56% of volatile constituents and certainly more than half was represented by the hydrocarbons described in this paper. But there can be no question, as Richardson asserts, that petroleum and these bitumens are closely related as to their origin. That they all contain complex nitrogen derivatives which may, perhaps, be synthesized by circuitous processes in the laboratory, but in nature only through the agency of organic growth, renders it certain that organic matter, most probably of vegetable nature, is to be regarded as their origin.

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[1] "Gilsonite and Grahamite; the Result of the Metamorphism of Petroleum under a Particular Environment," *J. Ind. Eng. Chem.*, 8, 493 (1916).

Summary.

1. Deerfield bituminous coal yields, by vacuum distillation, a number of hydrocarbons, mostly of the series C_nH_{2n-4}, resembling the hydrocarbons that compose the neighboring Mahone petroleum.

2. Utah Gilsonite gives members of the series, C_nH_{2n} and C_nH_{2n-2} that resemble the same hydrocarbons in petroleum, also a series of unsaturated hydrocarbons. It contains in large proportion the nitrogen compounds that are found in all petroleum, which demonstrates its organic origin.

3. Grahamite gives a series of hydrocarbons resembling those from Gilsonite.

4. As above mentioned, there is a no more urgent and promising field of investigation than the composition of the natural bitumens on an adequate scale with a sufficient outlay of expense and expert labor.

[CONTRIBUTION FROM LABORATORY OF THE OFFICE OF SOIL FERTILITY, THE BUREAU OF PLANT INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE.]

THE POSSIBILITIES AND LIMITATIONS OF THE DUCLAUX METHOD FOR THE ESTIMATION OF VOLATILE ACIDS.

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Introduction.

The different members of the volatile fatty acid series differ in properties only in slight gradations and the separation of the individual acids occurring in a mixture must be effected by some method of fractionation. The procedures which have been employed with a certain degree of success are: (*a*) Fractional distillation; (*b*) fractional precipitation of their salts; (*c*) fractional liberation from their salts; (*d*) fractional crystallization of their salts; and (*e*) fractional extraction of the barium salts with alcohol. All of these procedures are very laborious and give at best only partial satisfaction.

Many of the fatty acids are natural products occurring either in the free state or as esters and are of great theoretical and technical importance. The value therefore of a rapid and accurate method for their detection and estimation is patent. The method which has yielded the most satisfactory results is the one devised by Duclaux,[6] which is an indirect method based upon the behavior of the acids during distillation from dilute aqueous solution. He used this method in estimating the volatile fatty acids in wines and various fermentations and other biological products.

The method has since been used extensively by numerous investigators with more or less success. Only a few will be mentioned. Jensen[11] Suzuki, Hastings and Hart[17] and Currie[3] have used this method in es-