

ULTRA-VIOLET ABSORPTION OF PETROLEUMS AND PETROLEUM FRACTIONS

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ULTRA-VIOLET ABSORPTION OF PETROLEUMS AND PETROLEUM FRACTIONS

By

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## PREFACE

This research was undertaken with the idea, chiefly, of determining whether the study of the ultra-violet absorption of petroleum and its fractions might serve as a useful tool by means of which problems of composition or origin might be studied. More specifically, it was planned to study petroleums from different sections of the country to see whether or not there would be any characteristic differences in absorption by means of which the origin of unknown samples might be determined. It was also planned to study various gasolines to see if their spectra were of such nature as to permit using their ultra-violet absorption in the study of the numerous possible problems relative to their composition or that of the petroleum from which they were obtained.

## INTRODUCTION

In recent years because of the public demand for petroleum products of a more nearly uniform nature, and to the ever changing design of combustion engines, much interest has been directed to specialized fields of research in petroleum. The finding of new uses for petroleum products has also done much toward this stimulation.

The general method of classifying petroleum and its different fractions according to the percentages of paraffins, aromatics, naphthenes, olefins, asphaltic material, sulfur, nitrogen and oxygen compounds, is gradually being replaced by the more specific method of isolating and identifying the individual components.

Mabery (57d, 57c) believed petroleum to consist of a complex mixture of members of a few homologous series of hydrocarbons with small percentages of N, S, and O compounds. Marcasson (59) partially verified this when he found a high boiling mineral oil to contain paraffins, olefins, naphthenes, and polynaphthenes. Brunn (19) also agrees since his work has proved that petroleum and its products contain a complex mixture of aliphatic, cyclic, and aromatic compounds. Another author (77) classifies petroleum products as: (1) methane (paraffins), (2) naphthene, (3) methane naphthene, (4) aromatics, (5) methane-naphthene-aromatic, (6) naphthene-aromatic.

Burrell (22) in summarizing the field of research in 1928, states that Eastern gasolines are predominantly paraffinic, Mid-continent ones not so much so, while Californian and Gulf Coast gasolines are naphthenic, with considerable quantities of aromatics in the Californian.

## Paraffinic Hydrocarbons

2-Methylhexane (29) together with small quantities of isomeric secondary heptanes and dimethylcyclopentanes have been found in a fraction of Colibasi petroleum. By fractional distillation Schorlemmer (88) in 1873 isolated n-heptane from a Pennsylvania crude. By the same method in 1883 iso- and n-pentane, along with isohexane, were separated from a Galacian petroleum fraction (52) and in the same year Mendeleff separated similar fractions from a Russian and a Pennsylvania crude (89).

Young and Thomas (104) by fractional distillation have isolated isopentane, n-pentane, isohexane, n-hexane, isoheptane and n-octane from an American petroleum. Isopentane (3), hexane (60), isobutane, isohexane, and methylpentane (77) have been found in Baku petroleum, Caucasian Naphthas, and a Colibasi petroleum.

Commercial straight run gasoline from Cabin Creek Field, West Virginia (18) was systematically fractionated (a) in a column 18 feet high, packed with modified Raschig rings one-half inch in diameter (b), in a similar column 10 feet high containing one-fourth inch rings, and (c) in a glass column 5 feet high packed with one-eighth inch rings. By refractionating some of the fractions a number of times, the number depending on the substance isolated, isopentane, n-pentane, isohexane, n-hexane, n-heptane, iso-octane, n-octane, and n-nonane were isolated.

In fractionating a natural gasoline from Pennsylvania, Anderson and Erskine (1) found isopentane, n-pentane, 2-methylpentane, n-hexane, 2-methylhexane, n-heptane, propane and n-butane.



In reviewing the work of the A. P. I. Project 6, Rossini (84) states that by distillation, crystallization, extraction, and absorption and combination of these, 45 pure hydrocarbons have been isolated and identified in a Midcontinent petroleum fraction normally boiling below 180°C. In addition to the above mentioned paraffins the following are included: methane, ethane, isobutane, 2,3-dimethylbutane, 3-methylpentane, 2,2-dimethylpentane, 3-methylhexane, 2-methylheptane, n-octane, 2,6-dimethylheptane, iso-nonane, 2-, 3-, and 4-methyloctane, n-nonane, and n-decane. Thus Panyutin and Firsanove (71) were justified in their belief that a Surakhansk gasoline contained n-heptane and 2,2-dimethylpentane. Tongberg and Fenske (100) have recently isolated a number of the above mentioned hydrocarbons from a number of virgin naphthas from different fields in various parts of the world.

Paraffin, slop wax, and rod wax have been separated into a series of paraffin hydrocarbons ranging from  $C_{18}H_{38}$  to  $C_{43}H_{88}$  (20); however, no attempt was made to name these compounds, the authors having based their conclusions only on physical properties and crystalline structures. Tridecane ( $C_{13}H_{28}$ ), tetradecane ( $C_{14}H_{30}$ ), pentadecane ( $C_{15}H_{32}$ ), hexadecane ( $C_{16}H_{34}$ ) and heptadecane ( $C_{17}H_{36}$ ) were found in a Pennsylvanian petroleum fraction boiling above 216°C. (57b).

The lubricating fraction appears to increase in complexity almost geometrically with increase in molecular weight or size of molecule. On an average the lubricating oil fraction contains four or five times as many atoms per molecule as those of gasoline. The lubricating portion has been separated into 3 broad fractions: "extract", "wax", and "water white" oils. The water white oil was further subdivided by distillation into 600 fractions. Rossini has synthesized a number of high molecular

weight hydrocarbons which he is using to aid in the classification of the above mentioned fractions (84). Mikeska (65) believes the higher boiling fractions of lubricating oils to contain the same type of compound that Marcusson found in high boiling mineral oils. It is thought by Bestuchew (11) that the aromatics and naphthenes of any given fraction contain the same number of rings in the molecule. He considers the lower fractions as derivatives of benzene and naphthalene on the one hand, and cyclohexane and decalin on the other. The higher boiling fractions are regarded as derivatives of anthracene and the other higher polycyclic derivatives. A method proposed for approximating the relative amounts of each type of hydrocarbon present depends on determining the critical solution temperature of the oil in aniline (85).

#### Aromatic Hydrocarbons

Schorlemmer (88) as early as 1863 stated that he found small quantities of aromatic hydrocarbons in American petroleum. In 1882 diethyl toluene (the exact isomer was not given) and pseudocumene were identified in a Caucasian product (60), and one year later benzene, naphthalene, and anthracene were isolated from a Baku naphtha residue (53). It has been proved that Ohio and Canadian crudes contain small amounts of benzene, toluene, m- and p-xylenes (57b) and that other American petroleum contain toluene (104).

Markownikoff (60), who found benzene present in a Grosny naphtha, was followed by Poni (77) who isolated not only benzene from a Colibasi petroleum fraction, but also m-xylene and mesitylene.

By various methods, such as fractional distillation and then nitration, sulfonation, formation of picrates, and extraction, the

following aromatic hydrocarbons, some of which have already been mentioned, have been identified in petroleum fractions from different sections of the world: toluene (18, 32, 51, 62, 66, 83, 84, 96, 99, 100), benzene (17, 18, 32, 51, 62, 66, 81, 84, 99, 100), o-, m- and p-xylenes (83, 96, 100), o- and p-xylene (66, 84), m-xylene (32, 62), naphthalene (28, 51, 66, 83), mesitylene (51, 62, 84), pseudocumene (51, 84), hemimellitene (51, 84) cumene and cymene (62), ethylbenzene (66, 84, 100), isopropyl benzene (13) beta-methyl naphthalene (12) and beta-isomyl naphthalene (8).

#### Naphthenic Hydrocarbons

Markownikoff (60) by distillation and dephlegnation isolated cyclohexane, methylcyclopentane, and cyclopentane from a Russian petroleum, and later cyclohexane from a Caucasian naphtha. Dimethylcyclopentane has been isolated from a Colibasi petroleum (29).

Panyutin and Firsanova (71) by catalytic dehydrogenation with platinum-impregnated coal, found that most of the Surakhansk gasoline consists of methylcyclohexane, cyclohexane, dimethylcyclohexanes, methyl and dimethylcyclopentanes, ethyl- and trimethylcyclopentanes, and propylcyclopentane. In addition to the above compounds, the following naphthenic hydrocarbons have been isolated from a Midcontinent fraction: 1,1-dimethylcyclopentane, 1,3- and 1,2-dimethylcyclohexane, ethylcyclohexane, octanaphthene, and two nonanaphthenes (84). Others have reported finding: cyclopentane (104), methylcyclopentane (3, 77, 104), cyclohexane (35, 104), dimethylcyclopentane (102) methylcyclohexane (77, 104), and ethylcyclohexane (77) in petroleum from many different countries.

#### Olefinic Hydrocarbons

According to Burrell (22), olefins have only once been identified in

crude petroleum. This was in Mabery's work on a Canadian crude which showed traces of hexylene, heptylene, octylene and nonylene (57f). No polyenes or acetylenes have been reported present in crude petroleum; however, ethylene, propene, butadiene, butenes, pentadiene and higher conjugated dienes have been formed in cracking petroleum and its products (2, 15).

### Sulfur Compounds

It is commonly agreed that sulfur in petroleum and its products is present in three forms: (a) sulfur, (b) hydrogen sulfide, (c) organic sulfur compounds (14).

Girard and Colt (36), Thiele (97), Richardson and Wallace (82), Peckam (77), and a number of others have confirmed the presence of free sulfur in petroleum.

Hydrogen sulfide has been reported by Mabery (57b), Richardson and Wallace (82), Brooks and Humphrey (17) and many others.

The following organic sulfur compounds have been identified in petroleum and its products; carbon disulfide (38, 41), isopropyl and isobutyl mercaptans (13), ethyl and isoamyl mercaptans (13), *n*-tolyl mercaptan (no specific one named) (90) and methyl mercaptan (90). The following sulfides: dimethyl, diethyl, ethylamyl, di-*n*-propyl, di-*n*-butyl, di-isobutyl, diamyl, and dihexyl (57b), methyl ethyl, methyl propyl (98) and diphenylene sulfides (50). Cyclic sulfides of the general formula  $(CH_2)_xS$  where  $x = 6, 7, 8, 9, 10, 11, 14, 16, 18$  (57b); tetra and pentamethylene sulfides (88). The heterocyclic compounds: thiophene (27, 32, 64, 74),  $\alpha$ -methyl-(2-methyl) thiophene (27, 31, 64, 74),

$\alpha$ -,  $\beta$ -dimethyl-(2,3-dimethyl) thiophene (27, 31),  $\alpha$ -ethyl-(27) and  $\beta$ -methylthiophene (64) n-propyl-3-, isopropyl-2-, n-butyl thiophenes (102), and pentiophene (87).

#### Nitrogen Compounds

In an extended examination of the basic oil extracted from Californian petroleum, one series of bases separated appeared to be derivatives of methyl quinoline (57a). A similar basic fraction, along with what was believed to be pyridine and its derivatives, was also separated from a Japanese petroleum (57c). Later Mabery (57e) proved nitrogen bases to be present in petroleum from all sections of the United States.

The belief of earlier investigators concerning the nitrogen compounds found in different fractions has been justified by Bailey and associates (6), who by their cumulative extraction methods (60) and amplified distillation (6b) have isolated from kero bases extracted from oleum residues of a Californian petroleum: 2,4-, 2,5-, 2,6-, and 3,5-dimethylpyridines; 2,4,6-trimethylpyridine, quinoline, quinaldine, 2,4,8-, and 2,3,8-trimethylquinolines, 2,3-, 2,4-, and 2,8-dimethylquinolines, and two kero bases of the formulas  $C_{16}H_{25}N$  and  $C_{16}H_{31}N$ .

Von Braun (16) believed nitrogen compounds existed in the form of albumins in the original petroleum.

#### Oxygen Compounds

Naphthenic and fatty acids, along with aromatic hydroxy compounds, principally phenols, are the principal oxygen-containing compounds of petroleum that have received particular attention.

In considering the naphthenic acids that have been separated from Roumanian, Californian, German and Galician petroleums it has been found

that the  $C_6$  and  $C_7$  compounds were paraffinic, the  $C_8$  to  $C_{12}$  monocyclic, and those of high molecular weight to at least  $C_{22}$  were bicyclic. Due to the fact that the  $C_6$  and  $C_7$  compounds were absent from the crude oil, and to the slight variances in the composition of the acids in the distillate, Von Braun (16) concludes that these compounds are not primary constituents, but result from oxidation during distillation.

Phyala (76) has made and studied hepta-, octa-, nona-, deca-, undeca-, penta-, eicosan-, and pentacosan-naphthenic acids. He believes these to be present in petroleum distillates. Bestuchew (10) also made several naphthenic acids and compared these to different fractions derived from petroleum.

The fatty acids; palmitic, stearic, myristic and arachidic, have been isolated from a gas oil distillate of Ishikari petroleum and the presence of higher and lower weight acids was suggested (95). Similar fatty acids occur in variable quantities in many Japanese, Californian and Borneo oils, including what was believed to be butyric, valeric, and caproic acids (93). These same acids have been identified in light lubricating oils of Boryslav petroleum (47).

Of the phenols extracted from a Japanese petroleum, approximately 50% was p-cresol, 30% m-cresol, 15% o-cresol, 4% 2,4-xyleneol, and the remainder 2,3-xyleneol, diethylphenols and triethylphenols (94). Story and Snow (93), separated phenols in small amounts from both cracked and straight run petroleum distillates. The larger quantity present in the cracked distillate indicated that they were produced largely in the cracking process. All three cresols were found to be present. O-, m- and p-cresols along with 1,3,5-, 1,2,4-, and 1,3,4-xyleneols, beta-naphthol

and a mesitol were found in a Boryslav light oil distillate (34).

The doubtful question as to whether cholesterol is a constituent of petroleum was reviewed by Rakuzin in 1928 (31).

#### Ultra-Violet Absorption

Ultra-violet light has been used in the petroleum industry chiefly to accelerate changes in artificial aging tests (7), and in some cases to distinguish crude oil from refined oil (9). In 1925 it was used in determining the composition of petroleum and some of its derivatives. Gex and Vles (37), studying the ultra-violet absorption of petroleum and its derivatives, found five principal characteristic zones of absorption, in the form of bands or groups of bands with maxima near 3000, 2800, 2650, 2420 and 2410 Å. Although they made no attempt to determine the constituents responsible for each of the bands, they were of the opinion that the saturated acyclic carbon compounds had a preponderant part in the formation of the band at 2400 Å, and also that carbon rings, saturated or not, played a role in the general absorption.

In order to coordinate the ultra-violet absorption studies made on petroleum and its different fractions with those of pure hydrocarbons and other compounds found in petroleum, the following table has been prepared.

TABLE I

ABSORPTION MAXIMA OF COMPOUNDS FOUND IN PETROLEUM  
(Between the limits 2000 - 3500<sup>0</sup>Å)

Compound	References	Band Maxima Expressed in Å									
<u>Paraffins</u>		No absorption in region 6000 - 1965 <sup>0</sup> Å									
Methane	23, 24, 48										
Ethane	23, 24, 48										
Butane	23, 24, 48										
Heptane	23, 24, 48										
Hexane	23, 24, 48										
Octane	23, 24, 48										
<u>Naphthenic (Cycloparaffins)</u>		No absorption as far down as 2000 <sup>0</sup> Å									
Cyclopropane	43										
Cyclohexane	43										
Methylcyclohexane	101										
<u>Aromatic</u>											
Anthracene*	25, 61, 70										
Benzene	33, 49, 58	2702	2679±5	2631	2610±2	2598	2578±4	2548±4	2526	2513	
		2486±2	2440±3	2385±5	2340±1	2286±2	2073	2039±2	1976±5		
Ethylbenzene*	39, 101										
Propylbenzene*	39, 44, 73										
Allylbenzene*	39, 44, 73										
Butylbenzene*	73										
Amylbenzene*	73										
Triethylbenzene*	73										
Mesitylene*	8, 79, 91										
Pseudocumene*	91										
Hemimellitene*	91										
Cumene*	5										



TABLE I (Cont'd)

Compound	References	Band Maxima Expressed in $\text{\AA}$							
<u>Aromatic (Cont'd)</u>									
Naphthalene	30, 33, 67	3204 $\pm$ 1	3145 $\pm$ 3	3106 $\pm$ 4	3066 $\pm$ 2	3040 $\pm$ 5	3017 $\pm$ 3	2997 $\pm$ 1	2972 $\pm$ 2
		2925	2889	2860 $\pm$ 5	2831 $\pm$ 4	2784	2752 $\pm$ 2	2740	2720 $\pm$ 2
		2710	2680	2657 $\pm$ 3	2644	2636	2618 $\pm$ 5	2590	2565
		2221	2210 $\pm$ 1	2175					
$\beta$ -Methylnaphthalene	30	3225	3177	3135	3081	3033	2987	2933	2888
		2819	2704						
$\alpha$ -Methylnaphthalene	30	3250	3183	3142	3101	3051	2996	2978	2819
		2741	2660						
2,6-Dimethylnaphthalene	58	3220	3147	3075	2800				
1,6-Dimethylnaphthalene	58	3240	3170	3103	2737				
Toluene	47, 58	2704	2684	2660	2624 $\pm$ 2	2598	2585	2565	2532
		2526	2506	2494	2470	2458	2452	2440	2425
o-Xylene	49, 58	2712 $\pm$ 4	2624	2563	2524	2500	2083		
m-Xylene	49, 58	2727 $\pm$ 4	2690	2649 $\pm$ 5	2620	2598	2565	2500	2440
		2151							
p-Xylene	49, 58	2742 $\pm$ 2	2704	2670	2649	2591	2549	2516	2495
		2469	2446	2133					
<u>Sulfur Compounds</u>									
Hydrogen Sulfide*	56, 78								
Carbon Disulfide*	69, 68, 103								
Ethyl Sulfide	56	2490	1850						
Ethyl Mercaptan	56	2250	1935						
Thionaphthene	58	3332	2966	2890	2578	2266	(in alc.)		
Thiophene	39, 63	2719	2426	2359	2174				
<u>Nitrogen Compounds</u>									
Pyridine	33, 35, 63, 67	2889	2841 $\pm$ 2	2807	2760	2724 $\pm$ 3	2628	2567	2517 $\pm$ 5
		2510							
Pyridine (in EtOH)	33	2889	2839 $\pm$ 2	2803 $\pm$ 5	2763 $\pm$ 3	2723 $\pm$ 5			

TABLE I (Cont'd)

Compound	References	Band Maxima Expressed in Å							
<u>Nitrogen Compounds (Cont'd)</u>									
$\alpha$ -Methylpyridine	67, 79	2880	2861	2859	2856	2853	2846	2834	2819
		2814	2809	2785	2685	2620	2560		
$\beta$ -Methylpyridine	46, 67	2690	2620	2555					
iso-Quinoline(EtOH)	33, 67	3175	3125	3097 $\pm$ 5	3061	3046	3033	2986 $\pm$ 1	2904 $\pm$ 4
		2847 $\pm$ 4	2620	2272	2153 $\pm$ 2				
iso-Quinoline (in EtOH)	58	3136	3136	3048	2660				
Quinoline	33, 67	3112 $\pm$ 4	3057 $\pm$ 1	2993 $\pm$ 3	2932 $\pm$ 5	2871 $\pm$ 5	2753		
Quinoline (in EtOH)	33	3116	3056	2996	2936	2876			
<u>Oxygen Compounds</u>									
o-Cresol	49	2780	2716	2704	2668	2649			
m-Cresol	79	2796	2778	2771	2766	2754	2732 to 2691	2684	
		2644	2638	2633	2630	2623	2618		
p-Cresol	49, 79	2854 $\pm$ 4	2841	2840	2828	2823	2807 to 2794	2775 to	
		2760	2733	2728	2709 to 2702				
m-Xylenol*	55								
p-Xylenol*	55								
$\alpha$ -Naphthol	30	3309	3281	3237	3206	3140	3103	3069	3004
		2834	2722	2626	2525				
$\beta$ -Naphthol	30	3216	3175	3138	3103	3079	3013	2975	2929
		2879	2799						
Cholesterol	45	Absorbs generally							
Palmitic Acid*	12, 52, 77								
Stearic Acid*	21, 52, 77								
Myristic Acid*	21, 52, 77								
Arachidic Acid*	21, 52, 77								

\*The incompleteness of the table can be attributed to the lack of reference material containing the original articles. However, to make the table as complete as possible the references found in abstracting journals and other sources have been listed.

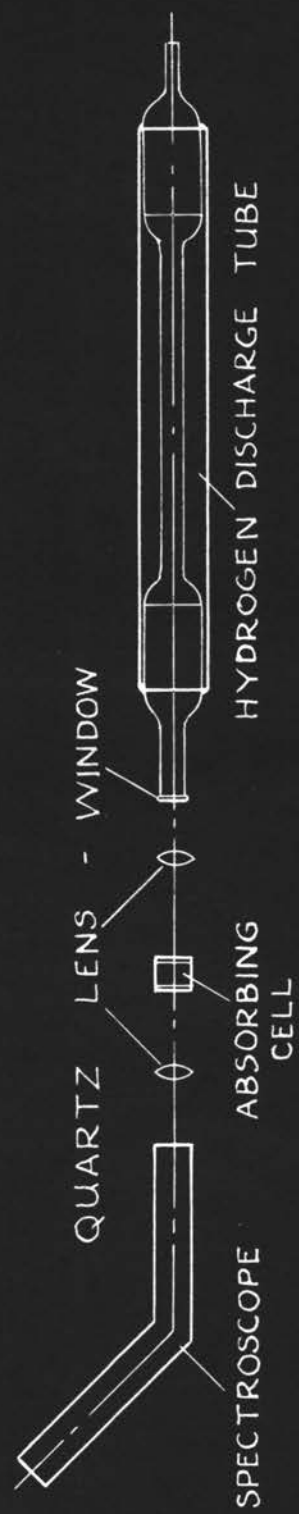


Fig. 1

### Apparatus and Materials

The absorption spectra were photographed with a Hilger E37 quartz spectrograph equipped with a Cornu prism and internal wave length scale, and having a dispersion of 85 mm. from  $1850\text{\AA}$  to  $8000\text{\AA}$  (Fig. 1).

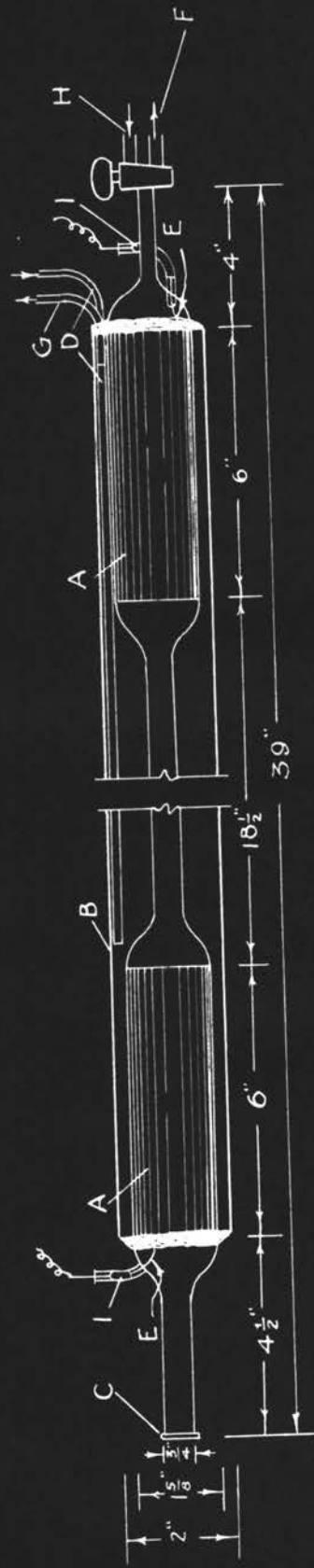
For some of the preliminary work Eastman Number 40 plates were used. In order to sensitize the plates to the shorter wave lengths, the emulsion sides were bathed in a solution of transformer oil in carbon tetrachloride. After exposure the plates were washed free of the oil with carbon tetrachloride before developing. It was found that this procedure left the plates somewhat mottled, making them difficult to read.

This difficulty was remedied by changing to Eastman Type 1-0 plates, which contain as a sensitizer a special organic compound that can be washed off with acetone after exposure without leaving the plates mottled in any manner.

As a source of ultra-violet light a hydrogen discharge tube was designed and constructed as illustrated in Figure 2. The cylindrical aluminum electrodes (A) were of such size that they just fitted into the enlarged ends of the discharge tube, with the tungsten lead-in wires sealed through the wall of the glass tube. A fused quartz window (C), 2.5 cm. in diameter, and 3 mm. in thickness, was sealed on the end of the tube with picein. The tube was sealed inside the water jacket with cotton backed with picein.

The electrolytic hydrogen generator, which operated on a principle somewhat similar to that of a Kipp generator, was made by supporting a 3 foot length of 2 inch O.D. glass tubing inside a larger and somewhat shorter glass cylinder, with the lower and open end of the inner tubing resting on the closed bottom of the larger cylinder. The electrodes,

# HYDROGEN DISCHARGE TUBE



- A - ALUMINUM ELECTRODES
- B - WATER JACKET
- C - QUARTZ WINDOW
- D - WATER INLET
- I - MERCURY

- E - TUNGSTEN WIRE
- F - VACUUM LINE
- G - WATER OUTLET
- H - HYDROGEN INLET

Fig. 2

which were made by rolling 8 inch lengths of sheet nickel into a cylindrical shape, were of such diameter that one would fit just inside and the other just outside the central glass tube. The inside or negative electrode was placed at the bottom of the glass tubing and the height of the outside, or positive electrode, was regulated so as to minimize the possibility of oxygen escaping into the inner, or hydrogen compartment. The generator was filled two-thirds full of a 10% solution of sodium hydroxide in water as an electrolyte, and the hydrogen compartment was attached to a drying setup and all connections carefully sealed with picein. The oxygen compartment was left open to the atmosphere.

The hydrogen was dried by passing it through two baths of concentrated sulfuric acid, a 10 inch tower filled with glass beads covered with phosphorus pentoxide, and an 18 inch tower filled with glass wool. To reduce the possibility that air might leak into the hydrogen compartment and drying apparatus the gas in the system was kept above atmospheric pressure. This was accomplished by keeping an Edison battery attached to the generator at all times.

Foreign gases were removed as much as possible by flushing out the entire setup several times with the dried hydrogen.

The power for the arc was furnished by two 110 volt transformers with a combined output of 6000 volts. These were wired (Fig. 3) in such manner as to give only 3300 volts but to increase the power output to about two-thirds KVA under operating conditions. As the transformers used were one-half KVA transformers with very light primary windings it was necessary to put a resistance of 4500 ohms in the secondary to hold the primary current down to 10 amperes. The resistance used consisted of two units connected in parallel, each unit being made of three 3000 ohm,

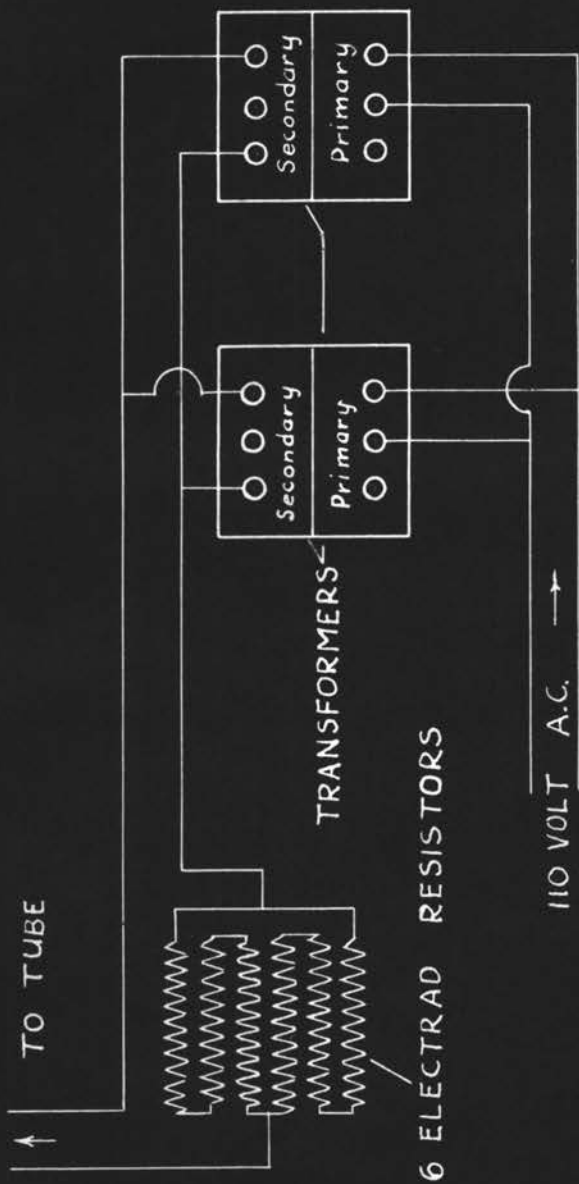


Fig. 3

then an acid solution of the permanganate and washing the product with sulfuric acid and finally water. After the product was dried and distilled over sodium it transmitted ultra-violet light as far down as  $2300\text{\AA}$ .

Since this transmission was not sufficiently complete, mixed hexanes secured from the Phillips Petroleum Company were used as a solvent. A modified form of the method used by Castille and Henri (26) was used in purification. Their method consists of shaking the hexane with 15% fuming sulfuric acid during a 12 hour period, repeating this twice and following by a 12 hour period of shaking with concentrated sulfuric acid. This product is washed twice with distilled water, decanted and shaken 12 hours with 10% sodium hydroxide in water solution; subsequently it is treated for 12 hours with a 1 N solution of alkaline potassium permanganate and finally the same length of time with acid potassium permanganate. The hexane is then decanted, washed repeatedly with distilled water, dried over sodium and fractionated through a Vigreux column. The method used in this research differed from theirs in that the contact periods with each of the wash solutions were longer, except the wash with concentrated sulfuric acid, which was only for about 30 minutes. The 12 hour wash period with 10% sodium hydroxide solution was omitted, a short scrubbing with sodium hydroxide solution being substituted, this serving to neutralize the acids in the hexane before the addition of the alkaline potassium permanganate. Instead of sodium, Baker's C.P. anhydrous calcium chloride was used for drying the hexanes. According to Castille and Henri, the hexanes purified by their method transmitted ultra-violet light to  $1900\text{\AA}$ . Ours transmitted to approximately  $2050\text{\AA}$ .

Since minute traces of some impurities give absorption spectra, the greatest of care was exercised at all times after purification in



preventing contamination of the solvent.

The samples of crude petroleum and different fractions of crudes were furnished by oil companies from different sections of the United States. The following samples with their physical constants were received from the oil companies indicated.

PHILLIPS PETROLEUM COMPANY, BARTLESVILLE, OKLAHOMA

Sample No. 5: Straight run untreated gasoline. Source of crude from which the gasoline was made is unknown. Properties are listed in Table 2.

Sample No. 6: Natural untreated gasoline. From Natural gasoline plant located at Lep, Oklahoma. Properties are listed in Table 2.

Crude Petroleum

Sample No. 7: From Russell County, Kansas. Production from siliceous lime. Depth 3364-3369 ft.

Sample No. 8: From Hutchinson County, Texas. Production from brown dolomite. Depth 3260 ft.

Sample No. 9: From Union County, Arkansas. Production from Wilcox formation. Depth 3260 ft.

Sample No. 10: From Lincoln County, Oklahoma. Production from Travis Peak sand. Depth 3544-3559 ft.

THE HANCOCK OIL COMPANY OF LONG BEACH, CALIFORNIA

Sample No. 1: Crude oil from Hancock Well No. 16, Stanley Ave. and 23rd St., Depth 4400 ft.

Sample No. 2: Pressure distillate from Hancock liquid phase cracking process.

Sample No. 3: Primary cut from straight run untreated gasoline.

Sample No. 4: Straight run gasoline blended with 40% of cracked gasoline.

Sample No. 5: Casinghead gasoline.

## ANDERSON-PRICHARD OIL CORPORATION, OKLAHOMA CITY, OKLAHOMA

Sample No. 3611: Crude oil of 36.7 A.P.I. gravity from Magnolia's No. 1 Henley SE1/4 - Sec. 35 - Twp 6N, R10W, Caddo County, Oklahoma. Production from sand at 3270 ft. to 3370 ft., bottom of Hale.

Sample No. 3612: Gasoline. Properties listed in Table 2.

## THE PENNZOIL COMPANY, ROUSEVILLE, PENNSYLVANIA

Sample No. 1: "Eureka" Crude from West Virginia.

Sample No. 2: "Bradford" Crude from Bradford, Pennsylvania.

Sample No. 3: "Local" Crude oil from region about Oil City, Pennsylvania.

Sample No. 4: "Franklin" Crude oil from region near Franklin, Pennsylvania.

Sample No. 5: Raw untreated gasoline--origin of crude from which it came unknown, other than it was from West Virginia or Pennsylvania.

Sample No. 6: Raw, untreated gasoline with a 65.4 A.P.I. gravity and 365°F. E.P. (From Bradford Crude)

TABLE II  
PHYSICAL DATA ON GASOLINE SAMPLES

	<u>PHILLIPS</u>		<u>ANDERSON-PRICHARD</u>
	Sample No. 5 Okmulgee Refinery	Sample No. 6 DeNoya Plant	Sample No. 3612
Gravity A.P.I.	56.8	81.6	58.3
I. B. P.	120	82	106
5%	160	90	146
10%	183	94	170
20%	220	100	204
30%	245	108	226
40%	270	118	240
50%	295	132	258
60%	320	144	274
70%	345	162	292
80%	370	190	310
90%	395	220	331
95%		256	347
E. P.	426	318	374
Rm. Temp.		82	
V.P. at 100°F.		18.2	
Color	30	30+	
Odor		Sour	30
Doctor	Pos.	Pos.	
Corrosion	Pos.	Neg.	
% Rec. at 100°F.		20	
Evap. at 212°F.	19.0		
Rec.	97.5%	98	98
Res.	1.0%	0.40%	
Dist. Loss	1.5%	1.6	

## EXPERIMENTAL

With the fixed cell used in this work it was found necessary to study the ultra-violet absorption of the Pennsylvania crudes using concentrations between the limits 0.0001% and 1.00% with the intermediate concentrations of 0.001%, 0.007%, 0.010%, 0.015%, 0.020%, 0.030% and 0.10%. The same order of concentrations were used in studying the Midcontinent and Californian crudes, the only difference being in the limits that were needed to give the desired absorption details, those for the Midcontinent being between 0.0001% and 0.10% and for the Californian between 0.0001% and 0.030%. The gasoline samples were examined at concentrations of 0.010%, 0.50%, 1.00%, 3.00%, 5.00%, 10.00%, 50.00%, and 100.00%.

Exposures of exactly one minute were used in every case when the backed, special sensitized Type 1-0 plates were used. In order to check results two plates were made of each sample.

All the crudes gave general absorption except the Bradford, Local and Eureka samples from Pennsylvania, and the sample of Hancock crude from California. The Bradford, Local, and Eureka crudes gave two broad, diffuse bands as indicated in Table 3. However, owing to the diffuse nature and breadth of the bands, and the lack of contrast between them and the general absorption region, it was practically impossible to determine, with an accuracy greater than  $\pm 5\text{\AA}$ , the absorption maxima of the bands. The Hancock crudes gave two slightly narrower diffuse bands in the region indicated in Table 3.

The absorption spectra of the gasolines were quite different in appearance from those of the crudes. (Fig. 4a, b, c, d). In every case,

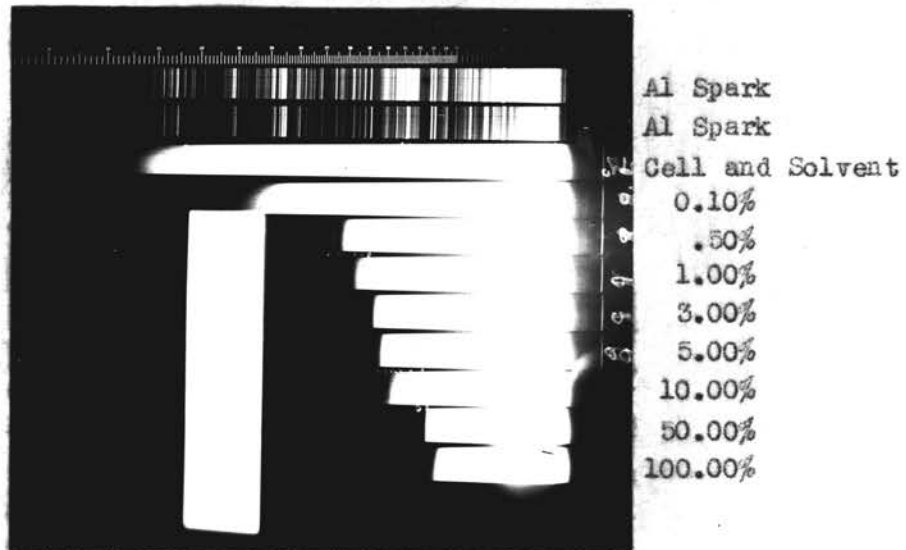


Figure 4a. Hancock No. 4. Straight Run Gasoline  
Blended with 40% Cracked Gasoline

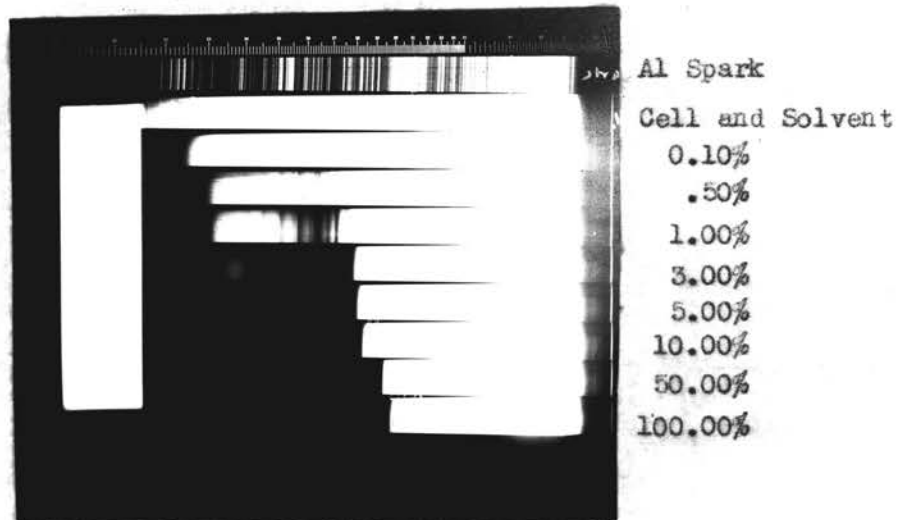


Figure 4b. Hancock No. 3. Primary Cut Gasoline

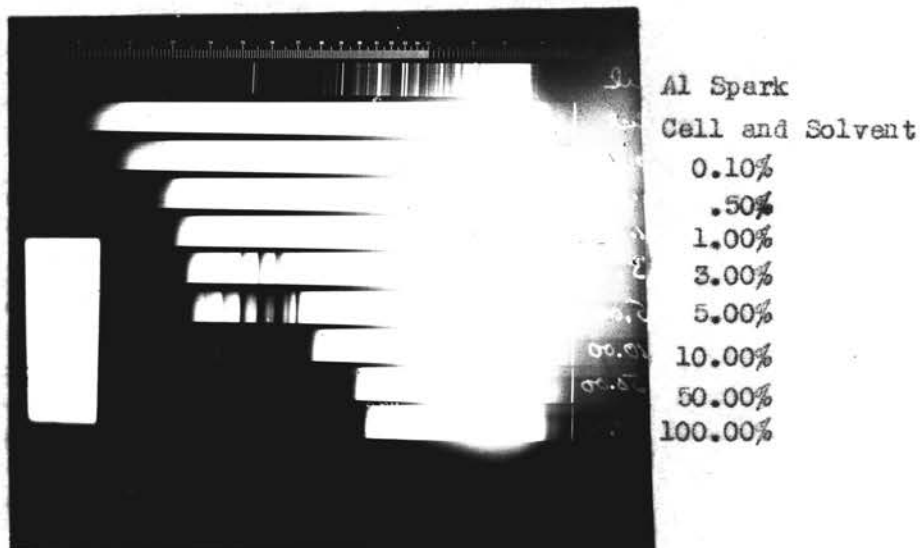


Figure 4c. Phillips No. 6. Raw Untreated Gasoline

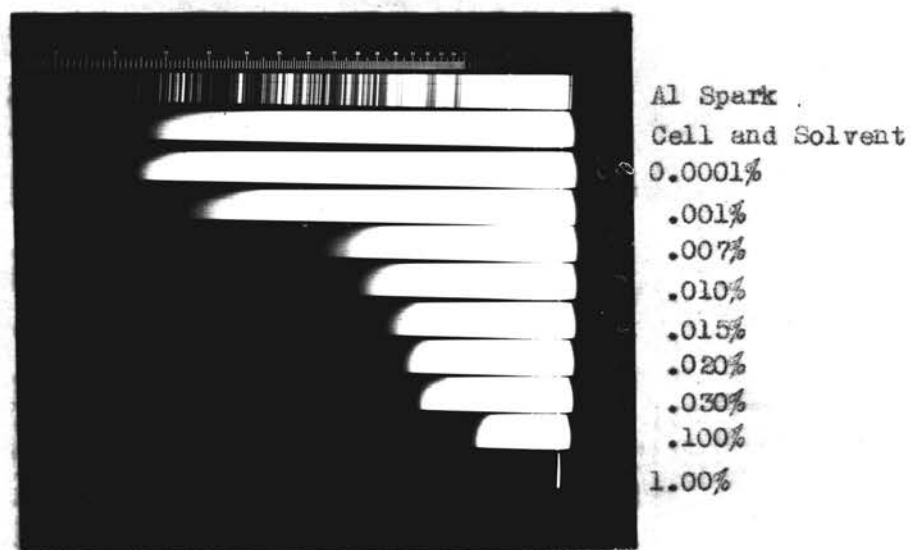


Figure 4d. Pennsylvania Type Crude No. 3. "Local".

a number of very narrow, well-defined bands were obtained, covering approximately the same spectral region as that covered by the general absorption observed for the crudes. In all cases, evidence of the existence of six or more faint absorption bands between 3000 $\text{\AA}$  and 3500 $\text{\AA}$  was seen. Due to limitations of the instruments available, however, it was found impractical to confirm the presence of these bands, or to obtain their probable maxima with any degree of assurance. The bands between 2300 $\text{\AA}$  and 3000 $\text{\AA}$ , however, were measured with an accuracy of  $\pm 5\text{\AA}$  or better (See Table 3). At those concentrations at which these bands were most readily observed, their breadths ranged between 3 $\text{\AA}$  and 20 $\text{\AA}$ . There was also some evidence of a faint, finer structure in some of these bands.

The absorption maxima listed in Table 3 were calculated with the aid of Hartman's dispersion formula:

$$\lambda = \lambda_0 + \frac{B}{D - d}$$

Where  $\lambda$  = wavelength in  $\text{\AA}$  of the band in question, and  $\lambda_0$ , B and D are constants having a particular value for a given plate.

$$(1) \quad D = \frac{\lambda_3 - \lambda_2}{d_3} - \frac{\lambda_2 - \lambda_1}{d_2}$$

$$(2) \quad B = \frac{(\lambda_3 - \lambda_1)D^2}{d_3} - (\lambda_3 - \lambda_1)D = \frac{(\lambda_3 - \lambda_1)D(D - d_3)}{d_3}$$

$$(3) \quad \lambda_0 = \lambda_1 - \frac{B}{D}$$

(4)  $\lambda_{1,2,3}$  = wavelengths of known lines in the aluminum spark spectrum.

$d_2$  = distance between  $\lambda_1$  and  $\lambda_2$

$d_3$  = distance between  $\lambda_1$  and  $\lambda_3$

$d$  = distance between band in question and  $\lambda_1$ .

The distance "d" was measured with a Gaertner comparator graduated in 0.01 mm. divisions, covering a total range of 50 mm.



TABLE III

## ABSORPTION MAXIMA FOUND IN CRUDES AND GASOLINES

<u>CRUDES</u>			<u>GASOLINES</u>									
Pennsylvania			Calif.	Midcontinent			Pennsylvania		Pacific Coast			
<u>No. 1</u>	<u>No. 2</u>	<u>No. 3</u>	<u>No. 1</u>	<u>No. 5</u>	<u>No. 6</u>	Phillips	Anderson Prichard	<u>No. 5</u>	<u>No. 6</u>	<u>No. 3</u>	<u>No. 4</u>	<u>No. 2</u>
								2308±9				
								2328				
						2346		2359		2350		
						2396		2394		2392		2400±25
				2433		2421	2429±4	2432	2430	2435		
						2450						
				2485			2487±3	2490	2485	2493(a)		
						2511(b)						
								2523	2522			
									2535			
				2544			2541±8	2550	2551±5(b)	2555(a)		
2586±5	2605±5	2589±5						2579(b)	2584	2587		
						2574(a)	2588	2600(b)	2597(b)	2610		
				2616		2611	2614	2622(a)	2623(b)	2623(a)		
			2626±5			2632(b)						
						2652(b)	2649(b)	2650(a)	2658(a)	2657(a)	2652(a)	
						2690(b)	2677	2686±1(a)	2685(a)	2689(a)	2698(a)	2672(a)
						2717	2718	2722(b)	2718			2717(a)
						2733(a)				2738		
2763±5							2744		2745		2741±5(a)	
	2746±5	2762±5					2755		2763			
							2764					
				2785		2776	2783	2781(b)		2797		2789
				2838		2828						
												2851
				2888		2897				2880(b)		

TABLE III (Cont'd)

<u>CRUDES</u>						<u>GASOLINES</u>						
Pennsylvania			Calif.	Midcontinent			Pennsylvania			Pacific Coast		
				Phillips	Anderson		Pennzoil					
						Prichard						
<u>No. 1</u>	<u>No. 2</u>	<u>No. 3</u>	<u>No. 1</u>	<u>No. 5</u>	<u>No. 6</u>	<u>No. 3612</u>	<u>No. 5</u>	<u>No. 6</u>	<u>No. 3</u>	<u>No. 4</u>	<u>No. 2</u>	
				2928						2935		
					2964					2965		
				2987								
				3061						3045		
			3101							3104		
				3128								

(a) These are the strongest measurable bands found in the sample mentioned (Note: where two or more bands are given the same designation it means they are approximately of equal intensity)

(b) Weaker than bands marked (a) but still quite strong.

## DISCUSSION

In considering the ultra-violet absorption spectra of the various samples studied in this research it was found that the Eureka, Local, and Bradford crudes of the Pennsylvania area were very much alike while each of the samples of crude from Arkansas and from California stood very much alone. The Oklahoma, Texas and Kansas samples appeared to show similar characteristics and resembled the Franklin crude from Pennsylvania.

There is a possibility that with careful work and more accurate instruments definite maxima might be found in all the crudes, since the change in spectra with change in concentration gave evidence to support the belief that the intensity of absorption throughout the region studied did not change in any regular fashion. The plates were traced by a microphotometer but no new data were obtained from the curves.

It is quite evident on the basis of present experimental work that ultra-violet absorption in the region studied does not offer any easy method of determining the origin of petroleum.

The five characteristic bands found in a Pechelbronn crude by Gex and Vles did not correspond to any bands found in the samples studied in this research. However, the strongest band reported by Gex and Vles at 2650<sup>0</sup>Å corresponds roughly to the most intense band found in the four American crudes for which definite maxima have been reported in Table 3.

In studying the gasolines it was found that the most intense groupings of bands seemed to fall in approximately the same spectral regions as did the maxima observed in the absorption by the crudes. This occurrence may be entirely fortuitous. In any case it points to a need for further investigation along these lines, as the different bands in

the crudes might well be due to overlapping of numerous unresolved bands from their components.\*

The spectra obtained from the gasoline samples were too complex to permit their analysis in terms of the components which produced them. However, investigation of fractions taken between narrower temperature limits might be expected to yield more comprehensible results.

In view of the fact that paraffins and cycloparaffins do not absorb in this region the bands observed must come from compounds of other types. However, the presence of these bands is not surprising in view of the large number of aromatics and unsaturated hydrocarbons, and sulfur, nitrogen, and oxygen compounds that have been reported present in petroleum.

In conclusion, it seems highly probably that, in spite of the reported complexity of petroleum, the ultra-violet absorption of petroleum and its fractions may yield a large amount of fairly definite information regarding its composition. This conclusion is based, to a large extent, on the fact that the paraffins and cycloparaffins present do not interfere with ultra-violet studies in this region, whereas they do interfere with actual separations.

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\* Gex and Vles found that the absorption bands of their gasoline samples weakened during the various stages in refinement. However, as they do not report their method of refinement, it is impossible to make any definite statements in regard to this angle of the problem at the present time.

## SUMMARY

1. A review of the literature concerning (a) the compounds that have been isolated from petroleum, and (b) those that have been studied for ultra-violet absorption is presented.
2. Diagrams and descriptions of the apparatus used are given. The apparatus is adequate for studies in the region between 2100<sup>0</sup>Å and 3500<sup>0</sup>Å.
3. The procedure and technique used in studying ultra-violet absorption of petroleum and gasoline have been given, with a discussion of the results.
4. Absorption maxima found have been tabulated.
5. Photographs of some of the more typical spectra are included.
6. Ultra-violet absorption as a tool in studying petroleum and its products has been evaluated and the lines along which further research might be undertaken have been suggested.

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## AUTOBIOGRAPHY

I, Ralph C. Cole was born near Alma, Arkansas, December 6, 1909. My elementary and high school training were received at Mulberry, Arkansas.

Two years of my undergraduate work were completed at Arkansas Polytechnic College, Russellville, Arkansas during the years 1931-1933. The following year I entered Oklahoma Agricultural and Mechanical College and received the degree of Bachelor of Science in Chemistry from this school in May, 1936. The following two years, while being employed by the Department of Chemistry as a graduate assistant, I have been pursuing courses leading toward the degree of Master of Science in Chemistry.

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