A STUDY OF THE SEPARATION OF PETROLEUM
INTO FRACTIONS AND THEIR IDENTIFICATION
BY ULTRA-VIOLET ABSORPTION

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A STUDY OF THE SEPARATION OF PETROLEUM INTO FRACTIONS AND THEIR IDENTIFICATION BY ULTRA-VIOLET ABSORPTION

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Submitted to the Department of Chemical Engineering
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In Partial Fulfillment of the Requirements
For the degree of
MASTER OF SCIENCE
1939

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OCT 27 1939

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ACKNOWLEDGMENT

The author wished to express his sincere appreciation for the constructive criticism and valuable advice which was so generously given by Dr. Paul Arthur, Dr. C. L. Nickolls, and Dr. Otis C. Dermer.

He also wishes to express his gratitude to the Engineering Experimenting Station, the Chemical Engineering and Chemistry Departments of Oklahoma Agricultural and Mechanical College for the research assistantship making this work possible.

He is further indebted to Harold M. Smith of the Bureau of Mines Station at Bartlesville, Oklahoma, for the samples of crude oil used in this research.

A STUDY OF THE SEPARATION OF PETROLEUM INTO FRACTIONS AND THEIR IDENTIFICATION BY ULTRA-VIOLET ABSORPTION

INTRODUCTION

In recent years there has developed an increasing need for a means of identifying individual components of petroleum. The refinery engineer would like to and should know more about the composition of his product. Certain treating processes can be studied more thoroughly if a means of identifying individual components can be developed. Petroleum contains many compounds other than those in fuel and lubricants which may be of great value, but not much progress can be made in that direction until the identification of those compounds can be simplified.

As there never has been a satisfactory method for analyzing petroleum from the standpoint of rapidly determining its detailed composition, the Engineering Experimenting Station decided to sponsor the study of the ultra-violet absorption spectra of petroleum with the purpose of establishing a method for determining at least certain constituents of petroleum fractions. In accordance with the plan adopted, equipment was to be designed from the standpoint of making it possible to run analyses in as short a time as possible without loss of accuracy.

Although there is some data available on ultra-violet absorption spectra for some of the compounds found in petroleum, due to the disagreement in published results it was decided the absorption spectrum would be redetermined for every compound for which analytical methods were to be developed. Each compound was to be prepared more than one way in order to remove any possibility that impurities might lead to inaccuracies in determining the absorption spectrum of the pure compound.

This particular research problem deals with the qualitative analysis of some of the aromatic hydrocarbons found in Mid-Continent petroleums, and the methods and apparatus used. Only those aromatic hydrocarbons having boiling points below 150° C. were to be considered because more work has been done on the identification of these hydrocarbons by different methods, and the possibilities of correlating results and thoroughly testing the spectroscopic methods were greater.

Since paraffins and cyclo-paraffins do not give selective absorption down as far as 2000 Å (6), it was realized from the first that ultra-violet absorption methods could not be readily applied to such compounds. This apparent weakness in the proposed procedure, however, was offset by the fact that such compounds could not interfere with the analysis for other compounds--- a distinct advantage over most other analytical methods. Nitrogen, sulfur and oxygen compounds and the aromatic hydrocarbons, however, absorb in the region 3500 Å to 1900 Å. All of these types of compounds have been reported as present in Mid-Continent petroleums (7).

In order to prevent the spreading of effort over too great a territory, it was decided to restrict the present investigation to a few of those aromatic hydrocarbons having boiling points below 150° C. which have been identified in petroleum from different parts of the world. These are benzene (1, 12, 23, 29, 41, 49), toluene (12, 23, 29, 41, 49), ethylbenzene (41, 49), o-, m-, and p-xylene (49), o- and p-xylene (41), and m-xylene (23, 29).

The absorption spectra of the compounds listed above are given in Table I.

Some work in this direction was done by earlier workers. Gex and Vlex (19) found that certain absorption bands of gasoline samples they were examining weakened during the various stages of refinement. Cole (8) observed that the ultra-violet absorption spectra of samples of different crude oils were very much alike and none of them gave much evidence of selectivity. He found that the spectra obtained with different gasolines, though very sharp and distinctive, were too complex to permit analysis in terms of the components which produced them until much more was known about the spectra of the pure components. Cole further concluded that in order for the ultra-violet absorption spectra of crude oil to be used successfully, the petroleum must be separated into fractions and the fractions analyzed. It seemed best also to follow a similar procedure in regard to gasoline.

Since the method to be used consisted of examining separate distillation fractions of the petroleum, it was necessary to design a fractionating column to accomplish this separation sufficiently accurate to prevent interference from compounds having similar spectra.

LITERATURE ON
FRACTIONATING COLUMNS

Column

Fenske (47) got as high as 100 theoretical plates with a 20 mm. column 2.82 meters long. The vaporization rate he used was 1.26 liters per hour and the column was tested under total reflux. With another column 51 mm. in diameter and 2.59 meters long (14) he got 45 theoretical plates when the column was tested at a vaporization rate of 10 liters per hour. Palkin (33) has made a column which can be operated under vacuum, consisting of a series of glass traps hung in wire gauze plates giving a small liquid holdup and consequently a small pressure difference between stillhead and stillpot. Bruun (3) has developed a corrosion-resistant column which was constructed completely of glass. He obtained low H. E. T. P. values with this column which was of the bubble-cap type. Fenske, Tongberg and Quiggle (15) have found that the degree of separation increased logarithmically, not linearly, with the number of theoretical plates. Marshall and Sutherland (28) have compared lagged and unlagged columns operating at the same distillation rates and they have found that a lagged column is 2.4 to 41.5 times as effective as the same column operating unlagged under the same conditions. Hill and Ferris (20) obtained an almost adiabatic column by placing a dead air jacket around the column and a heated air jacket outside of that. Podbielniak (37) devised a vacuum-jacketed column, using quartz for the inner tube and a Pyrex tube as a jacket around the inner tube. With this type of vacuum jacket there was no breakage due to thermal expansion or contraction.

TABLE I

Compound	References	Band Maxima Expressed in Å												
Benzene	44	2338	2347	2381	2391	2433	2492	2553	2614	2688				
Benzene	17	1980	2040	2070	2276	2350	2376	2440	2480	2560	2610	2695		
Benzene	18	1980	2040	2070	2276	2337	2376	2439	2510	2526	2610	2695		
Benzene	43	2040	2070	2276	2350	2380	2437	2485	2520	2560	2613	2700		
Benzene	4	1980	2040	2280	2344	2370	2480	2550	2600	2695				
Average for Benzene		1980	2040	2070	2278	2337	2347	2375	2436	2483	2523	2555	2612	2694
Toluene	44	2450	2489	2531	2550	2580	2592	2618	2643	2682				
Toluene	21, 25	2425	2440	2452	2458	2470	2494	2506	2526	2532	2565	2585	2598	2624
		2660	2684	2704										
Average for Toluene		2425	2440	2451	2458	2492	2526	2531	2560	2583	2595	2621	2660	2683
		2704												
Ethylbenzene	44	2522	2581	2595	2608	2640	2672							
O-Xylene	22, 26	2083	2500	2524	2563	2624	2712							
M-Xylene	22, 26	2151	2440	2500	2565	2598	2620	2649	2690	2727				
P-Xylene	7, 8	2133	2446	2469	2495	2516	2549	2591	2649	2670	2704	2742		

Tongberg and Fenske (45) used brass rings 6x6 mm. as packing for a column 8 feet long and 3/4" in diameter. Fenske, Tongberg, Quiggle and Cryder (16) used a 40-45 foot nickel fractionating column packed with one-turn nickel wire helices and obtained values of 100 theoretical plates. A packing of glass beads coated with carborundum was used by Midgley (30). He found that the efficiency of the column was increased by using beads coated with carborundum rather than using uncoated beads. Farnum (13) confirmed Midgley's observations. He also used lumps of carborundum as the packing material and obtained a column having a good throughput. Schicktanz (42) found that a double jack-chain packing increased the efficiency of the column, while a single jack-chain was not as efficient. A spiral of no. 20 wire with 6 or 7 turns per inch was used by Podbielniak (36) to pack a 3.8 mm. column, while Mair, Schicktanz and Rose (25) used a 2 mm. column packed with no. 8 copper wire spirals. Rose (40) compared the column efficiency obtained by using single turn wire helices and spiral packing and he found that the single turn wire helices gave the smaller H. E. T. P. for the same operating conditions. Glass helices were used to pack a column made by Wilson (50) and he found that a low H. E. T. P. value could be obtained with a column packed with this material.

Peters and Baker (33) used a jacket around which a heater of resistance wire had been wrapped and circulated hot air through the jacket. Tongberg, Quiggle and Fenske (47) jacketed a small column and passed hot vapors from the still around the column itself. They also used a column around which resistance wire was wrapped in sections, each section being independently controlled.

Stillpot Heater

For heating laboratory column stillpots, gas and electric heaters and various heated baths have been used. Marshall and Sutherland (28) insulated a 1000 ml. glass stillpot with asbestos and used an internal electric heater. External electric heaters were used more than internal electric heaters when petroleum was fractionated.

Stillhead

Peters and Baker (34) obtained a better separation with a partial condenser than with a total condenser. With a total condenser a small holdup of distillate in the reflux regulator decreased the separation because the liquid holdup blended with the later distillate before collection. Podbielniak (38) confirmed the work of Peters and Baker and found that the partial condenser method of regulating reflux gave good results when the charge in the stillpot was small while the total condenser method of regulating reflux gave good results when the charge in the stillpot was large. Leslie and Geniesse (24) used both types of condensers and obtained satisfactory results.

APPARATUS

After a survey of the literature on fractionating columns has been completed it was decided that glass helices would be used for packing material and that partial condensation would be used for controlling the reflux ratio. Glass helices were favored over other packing materials because they were easier to clean and were corrosion resistant. Partial condensation was favored over total condensation because in total condensation there is a blending of components due to liquid holdup in the proportioning device.

The essential apparatus for the qualitative analysis of petroleum fractions by ultra-violet absorption spectra consisted of:

I. Fractionating columns.

II. Hydrogen discharge tube.

III. Baly tube for an absorption cell.

IV. Iron spark for use in calibrating the absorption spectrum plates.

V. Spectrograph.

VI. Comparator.

I. Fractionating Columns

A. Large Fractionating Column.

<u>Stillpot:</u> The stillpot consisted of a 2000 ml. round-bottom Pyrex flask provided with a side tube. This side tube was used to sweep nitrogen gas through the flask and column before any distillate was collected. The flask was lagged with a one-inch thickness of 85% magnesia-asbestos as shown in Figure 3. A ₷ 34/45 Pyrex ground glass joint was used to connect the stillpot to the column.

Stillpot Heater: The stillpot heater was made from a box 12 inches square and 6 inches high. The box was filled with powdered magnesia-asbestos, which was moistened with water and moulded to form a depression shaped to fit the bottom of the stillpot. The heating element consisted of 25 feet of no. 20 nichrome wire wound into a spiral and this in turn wound spirally on the curved surface of the depression in the magnesia-asbestos. The clearance between the stillpot and heating element was one-half inch and a 30 ohm rheostat with a current capacity of 6 amperes was used to control the temperature of the heater.

Column: The column consisted of a 170 cm. length of 20 mm. Pyrex tubing packed with single-turn glass helices. The ratio of the diameter of the column to the diameter of the packing was 3 to 1. Lumps of carborundum were used first to pack the column but the column flooded too easily, although the ratio of the diameter of column to the size of the carborundum lumps was also 3 to 1. The column was equipped with a Pyrex glass jacket 170 cm. long and 40 mm. in diameter. Rubber stoppers were used to support the jacket around the column, the stoppers acting as shock absorbers as well as serving the purpose of sealing the space between the jacket and column. This provided a dead air space which aided in insulating the column. The column was tested at this point and it was found that no distillate from substances boiling over 100° C. would come over. Two layers of asbestos paper were therefore wrapped on the outside of the jacket and then 85 turns of no. 20 nichrome wire spaced three-fourths of an inch apart, were wound aroung the jacket. A 100 ohm variable rheostat with a current capacity of 3 amperes was used to control the jacket temperature.

A one inch thickness of 85% magnesia-asbestos was then plastered over the jacket heater, leaving two open spaces 2" in length to serve as windows to permit observation of the column packing whenever a fractionation was being performed. Two thermometer wells were inserted through the insulating material to permit a determination of the jacket temperature. These were spaced so that one thermometer would show the jacket temperature at the top while the other would show the temperature midway between the top and bottom of the column. Since the turns of wire comprising the heating element were equally spaced along the jacket, every portion of the jacket was equally heated.

Stillhead: The stillhead was designed as shown in Figure 3. A layer of asbestos paper and then five turns of hollow tin tubing was wrapped around the stillhead as shown in Figure 3. Connections were arranged so that air or water could be passed through the tin tube at varying rates of flow, thus controlling the reflux ratio. The stillhead was covered by a one-inch layer of magnesia-asbestos lagging. The insulation on the stillhead was necessary because without it no distillate could be collected due to the fact that all of the vapors condensed on the stillhead walls. The proper thickness of the insulation around the stillhead was determined by the trial and error method. A thickness was determined which allowed just enough heat to be dissipated to permit a reflux ratio of 20 to 1 for the light hydrocarbon fractions.

B. Small Precision Fractionator.

Stillpot Heater: The stillpot heater consisted of a 660 watt cone-type heating element mounted inside a 4" steel pipe which was lagged with one inch of magnesia-asbestos. The heater was controlled by a 50 ohm variable rheostat having a current capacity of 5 amperes.

Column: The column was designed as shown in Figure 4. It consisted of a 12 mm. tube which was packed with 3 mm. single turn glass helices. Two tubes were placed concentrically around the column, one 19 mm. in diameter and the other 40 mm. The 19 mm. tube was silvered on the outside to prevent the loss of heat by radiation from the column. Rubber spacing and supporting sleeves served to make a dead air space between the column and the first tube and at the same time to support both tubes. The column was packed for a height of 112 cm.

The column was tested before the jacket heater was placed around the column. It was determined that a jacket heater was necessary because no distillate came over under these conditions. Two layers of asbestos paper were wrapped around the outside of the outer jacket and then 60 turns of no. 26 nichrome wire were wound around the entire length of the packed section. Two layers of asbestos paper were finally wrapped around the jacket heater. A 100 ohm variable rheostat with a current capacity of 3 amperes was used to control the jacket temperature. A thermometer was placed at the top of the packed section between the inner and outer jacket.

Stillhead: The stillhead was designed as shown in Figure 4. Six turns of hollow tin tubing were wrapped around the stillhead and one end was attached to a pipe through which hot air from an air heater was forced by means of a blower. The temperature of the air was regulated by means of a 30 ohm variable rheostat. The column was tested without lagging around the stillhead and it was found that the time necessary for the column to reach equilibrium condition was greater than the time necessary to run the rest of the distillation. Lagging was then used around the stillhead. The column then reached equilibrium condition within an hour when lagging was used.

II. Hydrogen Discharge Tube

The hydrogen discharge tube was designed as shown in Figure 2. The inside of the tube connecting the electrode chambers was coated with silver to reduce the atomic hydrogen spectrum, by dissolving silver hydroxide in ammonium hydroxide, wetting the inside surface of the tube with the solution, and passing the tube through a hot flame.

The arrangement of electrodes used in this apparatus gave a minimum of the fogging effect often caused by aluminum dust collecting on the quartz window. A 3 mm. fused quartz window was cemented to the discharge tube with picein cement. Mercury was used in the stopcock on the hydrogen inlet side because no stopcock grease could be used due to the fact that small traces of stopcock grease on the inside of the hydrogen discharge tube would cause undesirable hydrocarbon emission lines to show.

The entire discharge tube was cooled by immersion in a water bath. An A. C. ammeter placed in the primary circuit of the 1 K.V.A. transformer combination was used to indicate the power at which the tube was operating. Since the current flowing in the secondary circuit when the discharge tube was operating varied with the pressure, it was possible by trial and error to determine the best operating conditions using the ammeter in the primary as the indicator.

Two 0.5 K.V.A. transformers with primaries connected in parallel and having a combined output of 3200 volts were connected in series on the secondary side with a 2000 ohm resistor circuit and the discharge tube. A single switch of the design shown in Figure 1 was placed in the circuit enabling instantaneous change from the discharge tube circuit to a second circuit in which the secondaries of the transformers were thrown in series and connected through an118000 ohm resistance to the iron spark.

A Cenco Megavac pump was used to evacuate the discharge tube. A direct current generator supplied the current for generating hydrogen gas by the electrolysis of a 15% solution of sodium hydroxide. The hydrogen was dried by passing it through two baths of cold concentrated sulfuric acid and an 18 inch tower filled with glass wool. A tower filled with anhydrous calcium oxide was first used in the drying system but the porous material contained a large amount of adsorbed air and this added to the hydrogen small quantities of air as an impurity.

III. Absorption Cell

The absorption cell was constructed similar to a Baly tube with the exception that brass was used for the cylinders. The outer cylinder was 4" long and had an inside diameter of 1 1/8". The inside cylinder was 4" long and had an outside diameter of 1 7/64" and an inside diameter of 1 5/16". Fused quartz windows were cemented to the inside and outside cylinders by a cellulose acetate cement. A scale attached to the stationary outside tube and a pointer attached to the movable inside cylinder made it possible to set the cell for any desired thickness up to a maximum of 40 mm.

IV. Iron Spark

Two welding rods served as the material for producing the iron spark. These rods were mounted in a frame which could be changed in position to allow the hydrogen arc to be used after the plate was exposed to the iron spark. With this arrangement it was possible to always set the iron electrodes to the same position every time. It was necessary to operate the iron spark with the two transformers in series in the secondary circuit and with an 18000 ohm resistor in series with the spark.

V. Spectrograph

A Hilger E 37 quartz spectrograph equipped with a 60° Cornu prism and an internal wavelength scale was used to photograph the absorption spectra of the pure compounds and of the petroleum fractions.

VI. Comparator

A Gaertner Comparator capable of measurements accurate to plus or minus 0.0001 inch was used for measuring the plates. Using known lines of the iron comparison spectrum as standards, the wavelength of the band maxima were calculated by substituting the measurements obtained in the Hartmann dispersion formula.

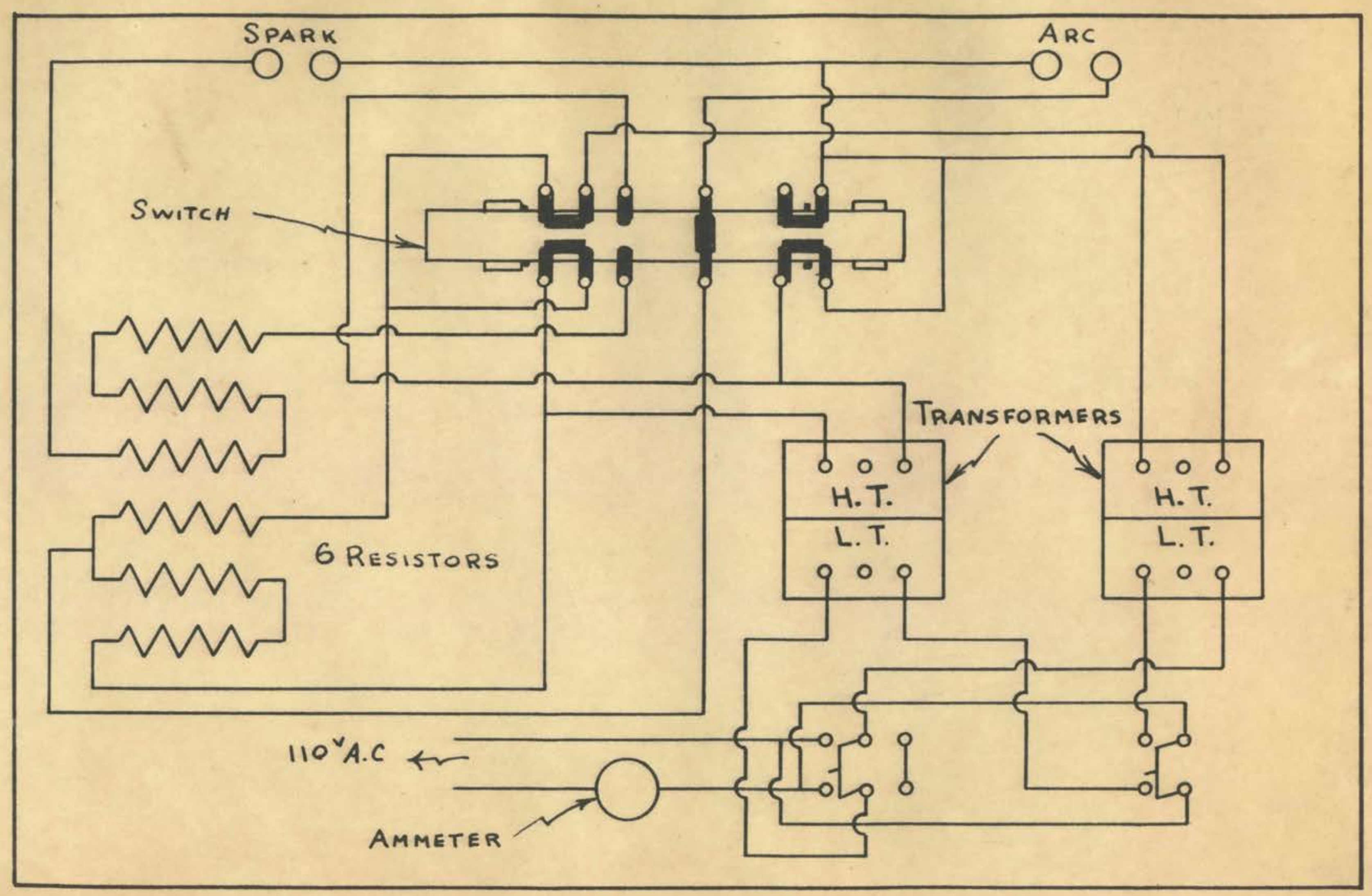

SPARK
ARC
SWITCH
6 RESISTORS
TRANSFORMERS
H.T.
L.T.
H.T.
L.T.
110V A.C
AMMETER

FIGURE No. 1

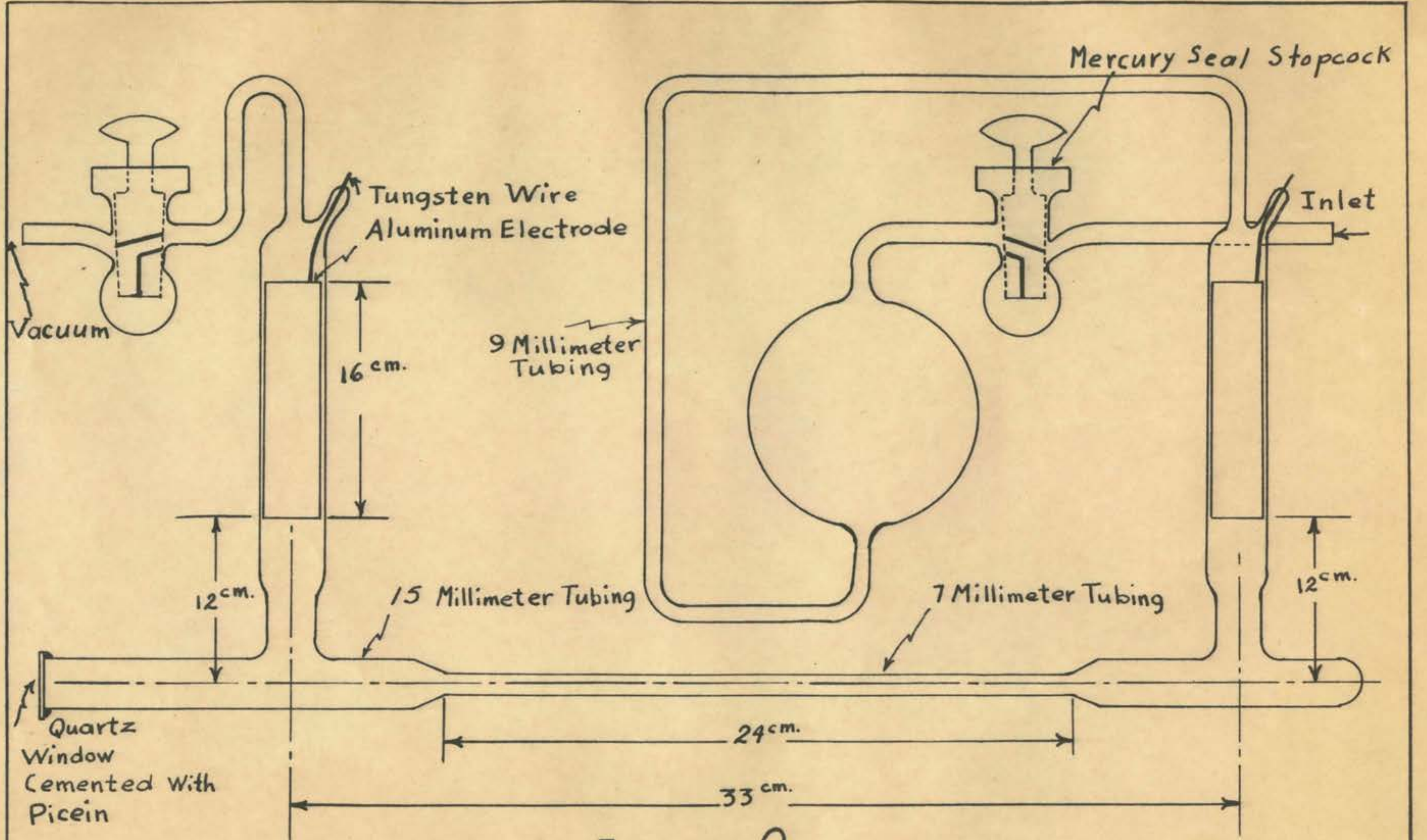
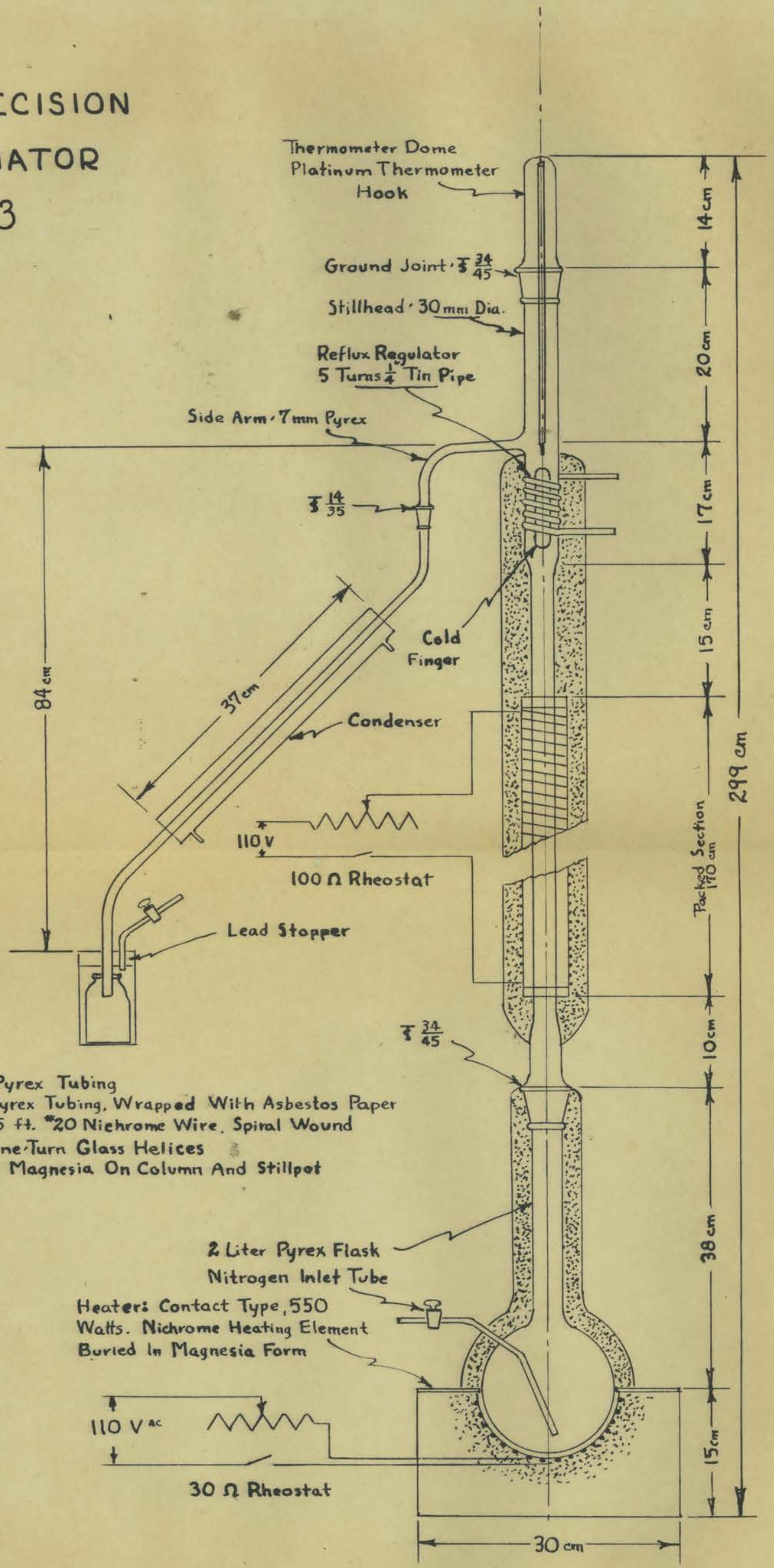

Mercury Seal Stopcock
Tungsten Wire
Aluminum Electrode
Inlet
Vacuum
16 cm.
9 Millimeter Tubing
12 cm.
15 Millimeter Tubing
7 Millimeter Tubing
12 cm.
Quartz Window Cemented With Picein
24 cm.
33 cm.

FIGURE 2

LARGE PRECISION FRACTIONATOR

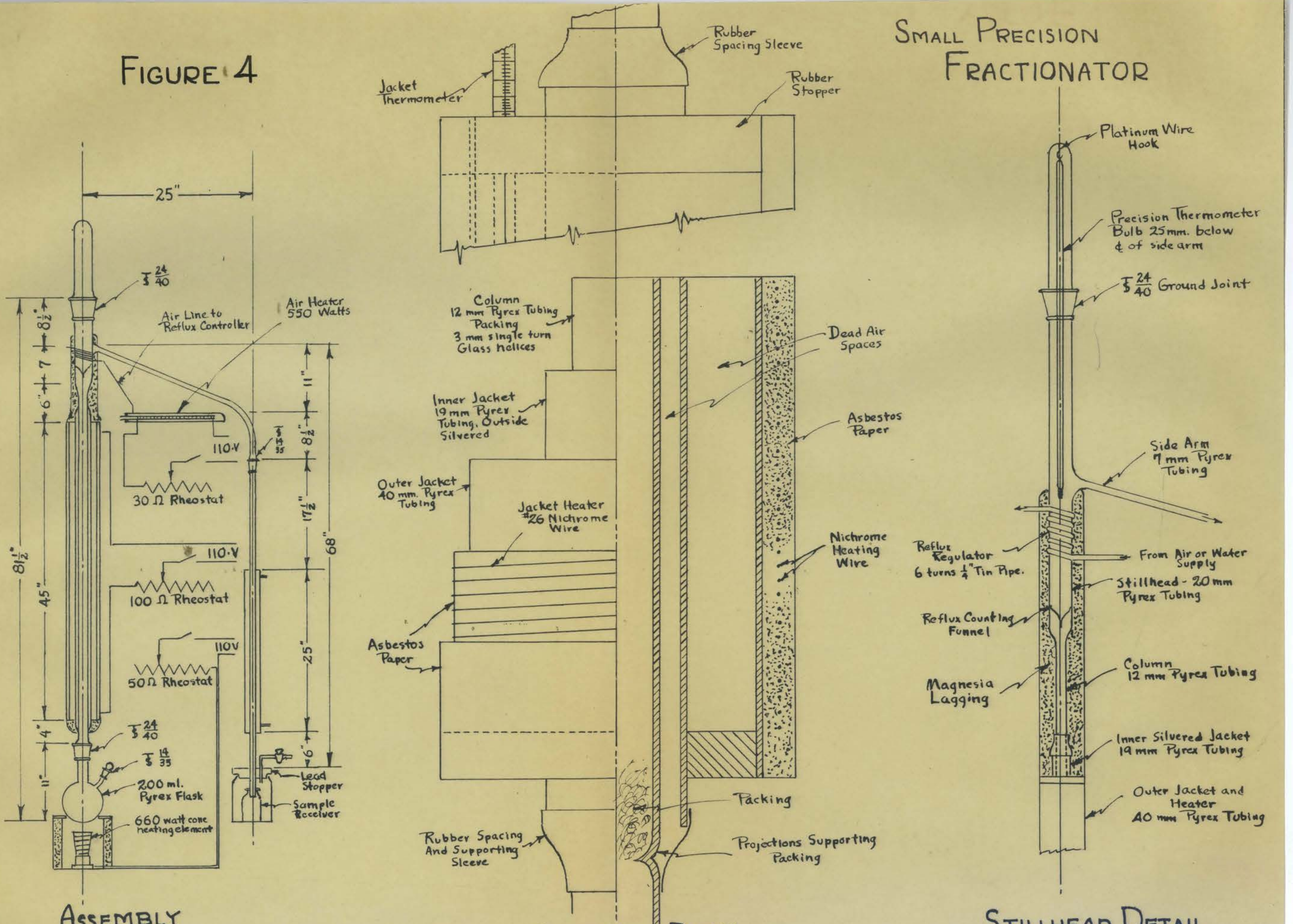
FIGURE 3



Column: 20 mm. Pyrex Tubing
Jacket: 40 mm. Pyrex Tubing, Wrapped With Asbestos Paper
Jacket Heater: 45 ft. #20 Nichrome Wire, Spiral Wound
Packing: 6 mm. One-Turn Glass Helices
Lagging: 1" 85% Magnesia On Column And Stillpot

FIGURE 4

SMALL PRECISION FRACTIONATOR



ASSEMBLY

COLUMN DETAIL

STILLHEAD DETAIL

MATERIALS

Mixed hexanes purified by a modification of the method of Castille and Henri (5) were used. The method used consisted of shaking two liters of the mixed hexanes with one-half pound of 15% fuming sulfuric acid for a 16 hour period, decanting, and repeating until the acid was not colored when added to the hexane. The hexane was then washed with distilled water, decanted and shaken for 30 minutes with a 10% solution of sodium hydroxide. It was then treated with a 1 N solution of alkaline potassium permanganate, decanted, and then treated with 1 N acid potassium permanganate. The hexane was then decanted and washed with several portions of distilled water. The hexane was dried with anhydrous calcium chloride and the portion boiling between 60-67° C. was used as its transmission ranged down as far as 2150 Å.

The photographic plates used were Eastman Spectroscopic Plate, Type 1-O, Ultra-violet sensitized and backed.

The sample of crude oil was obtained from the Bureau of Mines Station located at Bartlesville, Oklahoma. It was Sample No. 38160 from Continental Oil Company's C.S.O. Hill Well No. 13, Sec. 8, Twp. 25 North, Range 2 East.

Table II shows the compound, method of preparation, index of refraction at 20° C., and boiling point for the compounds prepared as standards.

TABLE II

Compound	Method of Preparation	Method of Purification	n_D @ 20° C By Dipping Refractometer	Accepted Value For n_D @ 20° (11)	Boiling Point At 760 mm. (11)
Benzene	Pyrolysis of Sodium Benzoate	Method A	1.50120	1.50123	80.102
Benzene	Merck's C. P.	Method A	1.50126	1.50123	80.102
Ethylbenzene	Eastman Kodak	Method B	1.49555	1.49587	136.150
Ethylbenzene	Friedel-Crafts Benzene, EtBr	Method B	1.49571	1.49587	136.150
Ethylbenzene	Clemmensen Reduction of Acetophenone	Method B	1.49586	1.49587	136.150

Purification Method A (39)

1. Product fractionally crystallized by allowing one-half of the product to crystallize and saving that portion which crystallized.

2. Product once again fractionally crystallized.

3. Product shaken with mercury for fifteen minutes.

4. Decanted and washed with water followed by shaking with cold concentrated sulfuric acid for 2½ hours.

5. Decanted and repeated shaking with sulfuric acid until there was no discoloration of the acid.

6. Decanted and washed with a 10% solution of sodium hydroxide for 2½ hours.

7. Decanted and washed with several separate portions of water.

8. Decanted and again shaken with mercury for fifteen minutes.

9. Decanted and washed with water, then decanted and dried with anhydrous calcium chloride.

10. Fractionated in a 35-plate fractionating column and the middle fraction saved.

11. This middle fraction again fractionally crystallized twice.

12. Product preserved in ground-glass stoppered bottle and tin foil placed over stopper to keep dust from collecting on the stopper and mouth of the bottle.

Purification Method B (39)

Same as method A except no fractional crystallization was used and two repeated fractional distillations were substituted for the repeated fractional crystallization

PROCEDURE

One liter of crude oil, Sample No. 38160, was placed in an ordinary two liter distilling flask provided with a tube for blowing nitrogen gas into the flask. The nitrogen was allowed to sweep through the flask until distillate started to collect. At this point the velocity of the vapors rising from the distilling flask were great enough to keep air from entering the flask. Distillate was collected up to a temperature of 200° C. Similarly, another liter of crude oil was topped and the distillates from both were poured into the stillpot of the large fractionating column.

The stillpot heater and the jacket heater of the large fractionating column were turned on and regulated so that the stillpot heater was at a slightly higher temperature than necessary to operate the column without flooding. The jacket heater was adjusted to give a column temperature of 50° C. and cold water was allowed to circulate through the hollow tin tube located on the stillhead. After two hours the column flooded and the stillpot heater was then regulated so that the vaporization rate was just sufficient to keep the column just below the point of flooding. The rate of flow of water through the tin tube on the stillhead was regulated so that a reflux ratio of 20 to 1 was obtained and distillate was collected at the rate of 2 cc. per minute.

By a simple adjustment of the variable rheostat controlling the jacket heater it was possible to gradually step up the jacket temperature and still maintain an almost adiabatic column. For instance, when collecting distillate between 93 and 103° C., the column jacket temperature was adjusted to 98° C. and maintained there until it was time to collect a new fraction.

Partial condensation was not controlled by rate of flow of water through the tin tube on the stillhead, after the stillhead temperature had reached 90° C. The lagging around the stillhead was of such a thickness, determined by trial and error, that the hollow tin pipe absorbed enough heat and dissipated it fast enough to allow just enough temperature difference between the stillhead walls and vapors so that it was an easy matter to keep the reflux ratio practically constant at a distillation rate of 2 cc. per minute. The column was operated until fractions had been collected up to 160° C. The total time to collect each fraction varied with the quantity of constituents having boiling points in that range, but on an average, it took two hours to collect each 10° C. fraction. After a sample had been collected it was labelled and the absorption spectra taken. It was found possible to completely analyze one fraction before the next fraction had been completely collected.

The following procedure was used in taking the absorption spectra of each fraction:

Preliminary: The pressure in the hydrogen discharge tube was adjusted by allowing hydrogen to flow in through the inlet stopcock, then evacuating until the ammeter placed in the primary circuit showed that 5 amperes were flowing through the primary circuit. This was equivalent to about 0.5 ampere flowing through the secondary side. Although by further evacuation it was possible to get 10 amperes flowing through the primary, by trial and error it was noted that when the discharge tube was evacuated just so that the ammeter showed 5 amperes in the primary, the most intense and continuous spectrum was obtained. At lower pressures the atomic line spectrum of hydrogen became more pronounced. This is much less suitable for absorption work, particularly when narrow bands are to be observed.

Procedure	Time
1. A 2 to 5% solution of the fraction in hexane was prepared.	120 sec.
2. Switch was then changed to place transformers in series.	5 sec.
3. Iron electrodes placed in position for exposing the plate to the iron spark.	15 sec.
4. Plate exposed to iron spark for 45 sec.	45 sec.
5. Scale placed on plate.	20 sec.
6. Iron electrodes removed from this position and switch changed to place transformers in parallel. Slit height was adjusted to 3 mm. Plate holder was lowered 3 mm.	10 sec.
7. Cell placed in position, filled with pure hexane to the maximum thickness of 40 mm. and exposed to ultra-violet light for 5 sec. Plate holder then lowered 3 mm.	25 sec.
8. Cell removed from its position, hexane removed, cell placed back in position, and plate exposed for 5 seconds with arc through cell windows touching. Plate holder then lowered 3 mm.	45 sec.
9. Solution of petroleum fraction in hexane placed in cell and the following thicknesses used: 0.5, 1, 2, 5, 10, 15, 20, 30, and 40 mm. Plate ex-	

Procedure (Cont'd)	Time
posed for 5 seconds for each thickness and plate holder lowered 3 mm. after each exposure.	150 sec.
10. Plate developed and dried.	60 min.
11. Plate calibrated	30 min.
Total time for each analysis:	Approximately 100 min.

A 5% solution of each fraction below 100° C. was exposed for a maximum time of 5 seconds to obtain the most satisfactory results. For those fractions above 100° C. a 2% solution of the fractions in hexane was used, with the same maximum exposure.

The small fractionating column was used in the fractionation of the aromatic hydrocarbons which were to be used as standards. Since this column was designed to operate at the rate of 10-15 cc. of distillate per hour, it was a little more difficult to adjust. The method used to bring the column to equilibrium was to first have the stillpot temperature high enough so that the vapor velocity in the jacketed section was just enough to cause the column to flood. When the column flooded for the first time, the variable rheostat controlling the stillpot heater was adjusted so that the column operated just below flooding. The jacket temperature was adjusted to be equal to the boiling point of the pure product. The column was designed so that the stillhead dissipated heat fast enough to maintain a reflux ratio of 20 to 1 and a distillation rate of 10 cc. per hour. For compounds boiling above 100° C. it was necessary to blow hot air through the hollow tube on the stillhead. The rate of flow of hot air was adjusted to give the proper temperature gradient between stillhead and column vapors and thereby a constant reflux ratio was maintained.

EXPERIMENTAL RESULTS

The large fractionating column was tested with a binary mixture of benzene and carbon tetrachloride. The mol percent of each component was determined with an Abbe refractometer. The vaporization rate was determined by operating the stillpot under the same conditions used when the column was tested, and the volume of distillate per unit time was measured. To allow for the return of hot reflux to the stillpot, an amount of hot liquid having approximately the same composition as the distillate and equal in volume to the distillate collected per unit time, was returned to the stillpot by means of the side tube of the stillpot.

The vaporization rate had to be determined by this method because the column was designed for the purpose of fractionating petroleum and was not to be used as a column in which various operating variables were to be tested as to their effect upon separation and H. E. T. P.

The small fractionating column was tested with a binary mixture of benzene and carbon tetrachloride. The mol percent of each constituent was measured by means of an Abbe refractometer. The reflux ratio was determined by counting drops from the product line and from the reflux counter funnel located in the stillhead.

Table III gives the results of the test on the large and small columns.

The absorption maxima listed in Tables IV and V were calculated with the aid of Hartmann's dispersion formula:

$$\lambda = \lambda_0 + \frac{B}{D_0 - d}$$

where λ = wavelength in Å of the band in question, and λ_0, B, and D_0

are constants having a particular value for a given plate.

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

(2) $$B = \frac{(\lambda_3 - \lambda_1)(D_o)(D_o - d_3)}{d_3}$$

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

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

d_2 = distance between λ_1 and λ_2

d_3 = distance between λ_1 and λ_3

d = distance between λ_1 and band in question.

The distance d was measured with a Gaertner comparator capable of measurements to plus or minus 0.0001 inch.

TABLE III

Run No.	Column	Vaporization Rate cc./min.	Product Rate cc./min.	Reflux Ratio	Mol % CCl_4 In Distillate	Mol % CCl_4 In Residue	Rel.Vol-atility	No. Theo.* Plates	H.E.T.P. cm.
1	Large	10	1	10-1	0.890	0.595	1.135	40.5	4.20
2	Large	40	2	20-1	0.900	0.610	1.135	17.7	9.61
3	Small	3	.2	15-1	0.790	0.380	1.135	30.0	3.80
4	Small	6	.3	20-1	0.830	0.400	1.135	23.5	4.85
5	Small	1.5	.15	10-1	0.840	0.510	1.135	36.8	3.10

* Number of Theoretical Plates were calculated by means of the equation of Dodge and Huffman (10).

TABLE IV

Compound	Method of Preparation	Band Maxima Expressed in Å							
Benzene	Merck's C. P.	2680	2600	2540	2480	2427	2375	2340	
Benzene	Pyrolysis of Sodium Benzoate	2677	2598	2537	2480	2430	2377	2340	
Average for Benzene		2678±2	2599±1	2538±2	2480±0	2428±2	2376±1	2340±0	
Ethylbenzene	Eastman Kodak	2670	2639	2598	2578	2546	2532	2473	2420
Ethylbenzene	Friedel-Crafts	2669	2640	2600	2576	2543	2523	2473	2418
Ethylbenzene	Clemmenson Reduction	2667	2638	2602	2576	2543	2527	2472	2417
Average for Ethylbenzene		2668±2	2639±1	2600±2	2577±1	2544±2	2527±4	2473±1	2418±2

TABLE V

Boiling Point Of Fraction	Band Maxima Expressed in Å													
39-76° C.	2680	2601	2542	2483	2431	2377								
76-93° C.	2678	2601	2542	2485	2428	2379								
93-103° C.	2683	2671	2657	2637	2620	2609	2577	2554	2544	2536	2525	2479	2463	2423	2414
103-113° C.	2678	2615	2599	2587	2565	2537	2480	2435							
113-123° C.	2736	2718	2678	2645	2613	2595	2583	2546	2483						
123-133° C.	2733	2704	2668	2644	2613	2566	2523	2504							
133-143° C.	2738	2723	2685	2661	2638	2600	2575	2549	2516	2474					
143-153° C.	2712	2674	2643	2609	2588										

DISCUSSION

In Tables VI to XIV a comparison between the absorption maxima determined for fractions 39° C. to 153° C., respectively, and the absorption maxima for the aromatic hydrocarbons are shown. Although benzene and ethylbenzene are the only aromatic hydrocarbons which were prepared for this research work, the absorption maxima for toluene and the xylenes are also included. The agreements between the values of absorption maxima for benzene and ethylbenzene as determined in this research and from the literature was satisfactory and therefore it was assumed that the absorption band maxima data for toluene and the xylenes as found in the literature would suffice to show that by fractionation and ultra-violet absorption spectra, it was possible to identify these constituents found in crude oil.

The absorption band spectra for fractions boiling up to 123° C. showed benzene was present. The fact that benzene showed up in all other fractions was not the fault of the fractionating column. Benzene exhibits a very strong absorption characteristic and therefore a thousandth of one per cent of benzene would probably show up in the absorption spectra for fractions which contained that amount or more.

It was the purpose of this research to show that while petroleum must be fractionated to obtain the best ultra-violet absorption data, an overlapping of one or two compounds in the next fraction would not interfere with the identification of constituents by ultra-violet absorption spectra. The results of this research show that while petroleum must be fractionated for the purpose of separating components which may be more easily identified, the separation need not be absolutely complete because in this research the separation was not complete and no intereference due to overlapping of absorption bands was experienced.

Benzene was identified in the fraction 39-76° C. (Table VII) because all 6 absorption bands of that fraction coincided with 6 bands of the benzene standard. Benzene was also identified in fraction 76-93° C. (Table VIII) when a similar comparison was made. The absorption maxima for fraction 93-103° C. (Table IX) when compared with benzene and ethylbenzene standards showed benzene and ethylbenzene as constituents of that fraction. The toluene absorption maxima from literature data, when compared with this fraction, showed toluene to be present.

Fraction 103-113° C. (Table X) when compared with a benzene standard and toluene absorption maxima data, showed benzene and toluene to be present in this fraction. The number of benzene bands was less than in the two previous fractions. Toluene bands seemed to be the strongest for this fraction.

Table XI shows that for fraction 113-123° C. that benzene, toluene, o-xylene and p-xylene were present. Three bands of the benzene standard coincided with three bands of this fraction. One band of o-xylene had the same wavelength as that band determined for this fraction. Three bands in this fraction were identical with three bands for p-xylene absorption maxima. Three bands for toluene when compared to the absorption bands for this fraction showed toluene to be present. Therefore all bands were accounted for and benzene, toluene, and o- and p-xylene were present in this fraction.

The absorption maxima for fraction 123-133° C. (Table XII) when compared with ethylbenzene, toluene, and m-xylene absorption data, showed that ethylbenzene, toluene, and m-xylene were present in this fraction.

Fraction 133-143° C. (Table XIII) contained ethylbenzene, toluene, m- and p-xylene. Ethylbenzene bands showed up the strongest.

Fraction 143-153° C. (Table XIV) contained o- and p-xylene.

It may be definitely said that benzene and ethylbenzene were present in this sample of crude oil. Toluene and the xylenes were found to be present in this same sample. It was decided that standards would be prepared for every compound analyzed and therefore while comparisons were made to show that toluene and the xylenes were present, these comparisons were made to bring out the fact that the separation of petroleum into 10° C. fractions was satisfactory from the standpoint of determining composition by ultra-violet absorption spectra.

The results of this research show that qualitative analysis may be run by taking ultra-violet absorption spectra and that it would be possible to run a quantitative analysis because by using 10° C. fractions the absorption spectra so obtained were spread over a wide range of bands and there was no general absorption.

The time to run a qualitative analysis by fractionation and ultra-violet absorption analysis was much less than any other method used. The time to run such an analysis may be reduced by further experimentation along the lines of developing a method for more rapid plate calibration, a faster plate development, possibly a greater rate of distillation, and a less precise distillation.

TABLE VI

COMPARISON BETWEEN LITERATURE DATA AND VALUES OBTAINED FOR ABSORPTION BAND MAXIMA AS DETERMINED IN THIS RESEARCH

Benzene* Standard	Benzene** Literature Values	Ethylbenzene Standard*	Ethylbenzene Literature Values**
	1980	2418±2	
	2040	2473±1	
	2070	2527±4	2522
	2278±2	2544±1	
2340	2337	2577±1	2581
	2347±3	2600±2	2595
2376±1	2375±5		2608
2428±2	2436±4	2639±1	2640
2480	2483±3	2668±2	2672
2538±2	2523±3		
	2555±5		
2599±1			
	2612±2		
2678±2			
	2694±6		

* Standard values taken from Table IV.

** Literature values taken from Table I.

TABLE VII

FRACTION 39-76° C.
ABSORPTION MAXIMA EXPRESSED IN Å

Fraction	Benzene Standard
2680	2678±2
2601	2599±1
2542	2538±2
2483	2480
2431	2428±2
2377	2376±1

TABLE VIII

FRACTION 76-93° C.
ABSORPTION MAXIMA EXPRESSED IN Å

Fraction	Benzene Standard
2678	2678±2
2601	2599±1
2542	2538±2
2485	2480
2428	2428±2
2379	2376±1

TABLE IX

FRACTION 93-103° C.
ABSORPTION MAXIMA EXPRESSED IN Å

Fraction	Benzene Standard	Ethyl-Benzene Standard	Toluene
2683	2678±2		2683±1
2671		2668±2	
2657			2660
2637		2639±1	
2620			2621±3
2609		2600±2	
2577		2577±1	
2554			2560±5
2544		2544±2	
2536	2538±2		2531
2525		2527±4	2526
2479	2480±0	2473±1	
2463			2458
2423	2428±2		2425
2414		2418±2	

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TABLE X

FRACTION 103-113° C.
ABSORPTION MAXIMA EXPRESSED IN Å

Fraction	Benzene Standard	Ethyl-Benzene Standard	Toluene
2678	2678±2		
2615			2621±3
2599	2599±1	2600±2	2595±3
2587			2583±3
2565			2560±1
2537			2531
2480	2480	2473±1	
2435			2440

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TABLE XI

FRACTION 113-123° C.
ABSORPTION MAXIMA EXPRESSED IN Å

Fraction	Benzene	Ethyl-Benzene Standard	Toluene	o-Xylene	p-Xylene	m-Xylene
2736					2742	2727
2718				2712		
2678	2678±2					
2645		2639±1			2649	2644
2613			2621±3			2620
2595	2599±1	2600±2	2595±3			2598
2583			2583±3			
2546		2544±2			2544	
2483	2480					

TABLE XII

FRACTION 123-133° C.
ABSORPTION MAXIMA EXPRESSED IN Å

Fraction	Ethyl-Benzene Standard	Toluene	o-Xylene	p-Xylene	m-Xylene
2733					2727
2704		2704		2704	
2668	2668±2			2670	
2644	2639±1			2649	2649
2613					2620
2566		2560±5	2563		2565
2523	2527±4		2524		
2504			2500		2500

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TABLE XIII

FRACTION 133-143° C.
ABSORPTION MAXIMA EXPRESSED IN Å

Fraction	Ethyl-Benzene Standard	Toluene	o-Xylene	p-Xylene	m-Xylene
2738				2742	
2723			2712		2727
2685		2683			2690
2661		2660			
2638	2639±1				
2600	2600±2	2595±3			2598
2575	2577±1				
2549	2544±2				
2516			2524	2516	
2474	2473±1				

TABLE XIV

FRACTION 143-153° C.
ABSORPTION MAXIMA EXPRESSED IN Å

Fraction	o-Xylene	p-Xylene	m-Xylene
2712	2712		
2674		2670	
2643		2649	2649
2609			
2588		2591	

SUMMARY

1. A review of the literature concerning work done on ultra-violet absorption of petroleums and petroleum fractions is presented.

2. A review of the literature concerning fractionating columns, their design, advantages and disadvantages, is presented.

3. Diagrams and descriptions of the apparatus used are given.

4. The materials used in this research are given.

5. The procedure used in running an analysis of crude oil is given.

6. Absorption maxima found for the aromatic hydrocarbons which were prepared, have been tabulated.

7. The absorption maxima found for every fraction have been tabulated.

8. The comparisons between fractions and the aromatic hydrocarbons concerning absorption band maxima have been tabulated.

9. The comparison between the absorption maxima for some of the hydrocarbons studied as found in the literature and between the maxima found in this research have been tabulated.

10. The future possibility of using ultra-violet absorption as a tool for determining composition of crude oils has been suggested.

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