THE ULTRA-VIOLET ABSORPTION SPECTRA

OF SOME SULFUR COMPOUNDS

FOUND IN PETROLEUM

THE ULTRA-VIOLET ABSORPTION SPECTRA OF SOME SULFUR COMPOUNDS FOUND IN PETROLEUM

By

MARVIN DUANE LIVINGOOD

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APPROVED:

Paul Arthur

In Charge of Thesis

O C Dermer

In Charge of Thesis

Charles R. Nickalls

In Charge of Thesis

O. M. Smith (C.E.N.)

Head of Department of Chemical Engineering

D. C. W. Intoch

Dean of the Graduate School

128989

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Apparatus belonging to the Engineering Experiment Station was used in the spectrographic analyses made.

This work was done as a part of the Engineering Experiment Station project on ultra-violet absorption studies.

INTRODUCTION

For the past two years, the Engineering Experiment Station of Oklahoma Agricultural and Mechanical College has sponsored a project on the identification of petroleum compounds by means of their ultra-violet absorption spectra. Research has already been completed by Cole (6), on the ultra-violet absorption of crude and topped petroleums, and Mitacek (30), on some aromatic constituents commonly present in crude oil. These studies have revealed the possibilities of this method of analysis for determining origin and composition of crude oil and the various products which are produced from it. The results obtained seemed also to indicate the possibility of using ultra-violet absorption as a tool in determining the efficiency of the various refining and treating processes used in the manufacture of these products.

Since the occurrence of sulfur in various forms in crude and refined petroleums is a problem of major concern to the refiner and user of petroleum products, methods of analysis for elemental sulfur and its compounds in petroleum must be had which are simple and accurate. Although there are many inclusive tests for sulfur compounds (the "doctor"test, copper strip test, and others) no practicable method of analysis for the specific compounds exists.

It was, accordingly, decided to study some of the more commonly occurring sulfur compounds from the standpoint of their ultra-violet absorption spectra in an attempt to work out a method by which individual sulfur compounds could be identified qualitatively, and, if

possible, quantitatively.

The presence of both elemental sulfur and hydrogen sulfide has been confirmed by a number of workers. The following compounds have been definitely identified as occurring in various crudes: isopropyl, isobutyl, ethyl, and isoamyl mercaptans (2), methyl mercaptan (35), methyl, ethyl, ethyl-amyl, n-propyl, n-butyl, isobutyl, amyl, and hexyl sulfides (26), methyl-ethyl, methyl-propyl, and diphenylene sulfides (24). Amyl mercaptan and secondary-hexyl mercaptan have been identified in a 113-155° cut from a Japanese shale oil (21), while methyl sulfide and ethyl mercaptan are found in a cut boiling below 40°. There has also been found cyclic sulfides (26), tetra- and penta-methylene sulfides (40), and, among heterocyclic compounds, thiophene and substituted thiophenes (5, 7, 14, 32, 34, 38). Ellis (12) also states that most of the simpler organic sulfur compounds have been found in petroleums. In addition to the types mentioned above, he adds the disulfides and other polysulfides.

Mercaptans, according to Malisoff (27), are present in petroleum in such proportions that if all of them were recovered, 150 to 200 tons per day of this class of compound alone would be available for chemical purposes. Most "sweetening" processes change the mercaptans to disulfides, which are less offensive in odor and much less corrosive than the corresponding mercaptans. Some treating processes also produce sulfides (thio-ethers) and mixtures of polysulfides, which are found in the products. The thermal decomposition, during cracking or distillation, of sulfur compounds also accounts for the presence of some polysulfides and sulfides. These classes of sulfur compounds make up a major portion of the

sulfur content of any finished refinery products.

Since the lower aliphatic mercaptans, sulfides, and di- and polysulfides are commonly found in crudes and distillates, and are easy to synthesize, they were chosen as the first to be studied in this research. It was decided that as many as possible of the first five normal-alkyl sulfur compounds (methyl, ethyl, n-propyl, n-butyl, and n-amyl mercaptans, sulfides, and disulfides) would be synthesized and studied. This selected list was later narrowed down to the ethyl and n-butyl compounds.

This research was aimed to secure ultra-violet absorption spectra of the selected compounds from at least two samples each, made if possible by entirely different methods, so that false bands due to possible impurities in the samples examined could be detected by the process of elimination. Appropriate synthetic methods were to be selected, and the equipment for purification designed where not available.

APPARATUS

To reduce the chances of contamination of the samples prepared for spectroscopic analysis, it was decided that, wherever possible, all reactions and purifications would be done in all-glass apparatus, and that, wherever rubber connections had to be made, they would be made with tubing or stoppers which had been thoroughly boiled in strong sodium hydroxide solution and washed with distilled water. No lubricant was used on the ground joints; on the stopcocks, where some lubrication was necessary to insure smooth operation, powdered graphite was used as a lubricating medium.

The following units of apparatus were assembled for this work:

I. Reaction apparatus for synthesis.

II. Rough distillation apparatus.

III. Precision fractionator.

IV. Absorption cells.

V. Spectrograph and accessories.

VI. Comparator.

I. Reaction Apparatus.

The reaction apparatus first used was made up of a 1 liter round bottom Pyrex flask to which had been sealed a #19/38 Pyrex ground joint. This flask was connected with a 60 cm. plain reflux condenser with a ground joint at the top, to which was connected a fume line running to the hood. When the need for stirring of the reaction mixture became apparant through low yields and the occurrence

of violent bumping of the liquid when refluxing, an all-glass Grignard apparatus was converted to this use. It consisted of a 1 liter three-necked Pyrex flask provided with ground joints. One side joint was occupied by a dropping funnel with sealed-in fume outlet, controlled by a stopcock; the other carried a 30 cm., five bulb Allihn type reflux condenser. The Allihn condenser was later replaced with a 40 cm. West condenser with #19/38 ground joints. The West condenser was connected by means of a U-tube and ground joints to a trap cooled in dry ice-acetone, and thence to the hood. The center joint was provided with an all glass, mercury sealed motor stirrer. This was made in the usual manner by sealing an inner tube into the male joint to make the mercury trough necessary for the mercury seal. The stirrer was made by sealing a piece of Pyrex capillary tubing through the bottom of a test tube which dipped into the mercury and sealed the vessel from the air. The stirrer was bent at the bottom at an obtuse angle which would just pass in through the ground joint; its length was so adjusted that the bent portion of the stirrer was always submerged. The stirrer was connected by means of a flexible rubber tube to a reduction pulley driven by a 220 volt, fractional horsepower electric motor. In case of an obstruction in the path of the stirrer, the flexible rubber tube would give first, saving the stirrer from breakage and giving notice that something was wrong. The outer cup of the stirrer was cemented in the closely fitting inner race of a ball-bearing which was held in a universal jaw clamp. This held the stirrer so that it ran true and without vibration even at its highest speeds.

The reduction pulleys available made the speed of the stirrer slightly over 100 r. p. m. Although all-glass stirring apparatuses are notably fragile, this one was used for over a year and a half without breakage. It was only necessary to line the stirrer up carefully at the beginning of a run.

As an accessory to the reaction apparatus, it was necessary to set up a train for the purification of the hydrogen sulfide used in the preparation of sodium acid sulfide. At first, hydrogen sulfide was made by the interaction of hydrochloric acid and sodium sulfide; when this method proved too expensive and inconvenient, hydrogen sulfide from a tank was used and passed through a train containing the following units: tube containing iodine suspended on filter astestos, to remove phosphine and arsine (9, 10, 11, 28, 36) ; a Drechsel gas washing bottle containing saturated aqueous sodium sulfide solution to remove entrained iodine; another tube containing calcium chloride or Drierite; and finally a safety bottle to guard against back flow of the reaction mixture. Connections were made of glass tubing insofar as possible, any necessary rubber stoppers being boiled in sodium hydroxide before use. The iodine and hydrogen sulfide in the system evidently reacted with the stoppers; for, after a short time, they became hard and cracked. To avoid this, the apparatus was reassembled, substituting high-form Drechsel gas washing bottles with ground joints for the drying tubes previously used, and making connections by sleeving butt-jointed glass tubes with rubber tubing. No trouble was experienced with leakage from this apparatus.

It was provided with Pyrex stopcocks between units so that the system could be completely closed when not in use. In this manner, once the system was flushed with gas, no contamination was possible. By means of the needle valve on the tank, the pressure of the gas was regulated until 2 or 3 bubbles per second flowed through the sodium sulfide solution.

II. Rough Distillation Apparatus.

The apparatus is shown in Figure 7. It included the distilling flask, of which three sizes were used-- a 1-liter, a 500 ml., and a 125 ml. Pyrex flask, each provided with a #19/38 ground joint. The small flask was provided with a #14/35 side joint for refilling. The stillhead was a plain Pyrex tube 16 cm. long, to which a side arm was sealed at a downward angle. A ground joint connected the sidearm to an ordinary water-cooled condenser, and another joint connected the bottom of the condenser to the receiver. The receiver was made of a 125 ml. distilling flask which was provided with a three-way, 2mm. Pyrex stopcock sealed on as shown. One of the outer arms led to a fume line; the other was left unoccupied for emptying the flask. When it was desired to take a fraction, the receiver was rotated on its joint until the stopcock pointed downward, and the stopcock plug was turned so that the contents drained into a sample bottle through the open arm; the receiver was then returned to its normal position as shown and the stopcock plug turned so that the receiver was connected with the fume line. It was found

unnecessary to interrupt distillation while a fraction was being removed; indeed, the pressure of the system served to force the liquid out. The top of the stillhead was provided with a sealed-in mercury well for the thermometer, as shown. Although this apparatus was intended for rough distillation, it gave a surprising degree of fractionation when run slowly. The use of a closed system was made necessary both by the offensive odor of the compounds being studied, and by the desire to exclude as much air as possible from the system. Pieces of porous clay plate were used to reduce bumping in this apparatus. The flask was heated with a gas burner.

III. Precision Fractionator.

The column (Fig. 5) and stillpot of this apparatus were the same as used by Mitacek (30). Owing to the unsatisfactory performance of the old stillhead in several respects, the column was completely rebuilt from the top of the packed section. The old stillhead provided no opportunity for operation at total reflux and no way to control the reflux ratio other than by the cold finger arrangement formerly used. Tests had shown the desirability of operating under complete reflux until the column had come to equilibrium, in order that the maximum enrichment and separation could be secured; for the same reason, and to give more flexibility in operation, it was found desirable to be able to control the withdrawal of the product accurately. A search of the literature (4, 8, 15, 19, 25, 29, 37, 39) failing to produce any

one stillhead which completely fulfilled these requirements and was simple of operation, the stillhead shown in detail in Fig. 4 and Fig. 6 was designed and built. The stillheads shown in the literature which permitted variable takeoff of product all seemed to give an objectionably high holdup of liquid and consequent lag in composition change. This was reduced to a minimum in this case by making the side arm slant up and by making the downward bend in the side arm on the outside of the stopcock close to the barrel so as to provide a minimum space for entrapped liquid. The ideal arrangement, of course, would be to have the outside arm sealed on to the stopcock barrel at an angle below the horizontal, so that no space at all existed to catch liquid. This was impossible, since the apparatus was assembled from standard parts. The stillhead was connected to the top of the column and the side arm leading to the condenser and receiver with ground joints, as shown in Fig. 4. The column was filled with glass helices as in Mitacek's work. Its operation was as follows: with the stopcock closed, all the vapors passed either directly to the condenser or around past the thermometer bulb, over the "bridge" and to the condenser. When it was desirable to take off product, the stopcock plug was turned so as to connect the stillhead with the side arm. The vapor stream was then divided into two parts--one going to the condenser, and one to the side arm, the relative amounts varying with the stopcock setting. The other arm of the stopcock was connected with a source of nitrogen,[1] so that the side arm could be flushed out each time

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[1] The nitrogen used to flush out the column was purified by passing through a cuprous chloride solution and a drying bulb.

a fraction was taken. The trap on the top of the condenser was arranged so that particles of rubber, etc., from the fume line could not fall into the column. The thermometer dome was provided with a sealed-in platinum wire hook and was adjusted so that the thermometer bulb hung at the level of the side arm, so as to register the proper temperature. Two highly accurate thermometers covering the range of C ° tc 100° and 100° to 200° were used with this apparatus. These thermometers were graduated in divisions of 0.1° and were calibrated by the National Bureau of Standards. With these thermometers and operation of the column at total reflux, the column is in effect a boiling point apparatus, and was used as such. The remainder of the diagram is self-explanatory. For receivers 200 ml. extraction flasks with ground joints were used. The receivers were connected to the fume vent through the stopcock as shown.

IV. Absorption Cells

Preliminary work showed that a thin layer of liquid would be sufficient to produce all the absorption needed for this study. The first absorption cell was made of a 1 cm. length of Pyrex tubing 25 mm. in outside diameter (see Fig. 3) ground flat on both ends, and with a quartz window cemented on one end with crystal clear Testor's Cement. This cell was filled with the liquid to be tested until it overflowed, and the other quartz window was laid carefully on the other end of the cell so that no air bubbles were entrapped. This layer of liquid proved to be too thick, so the second liquid cell was made by drilling a 1.47 cm. hole in a discarded photographic

plate from which the emulsion had been removed. A quartz window was cemented on one side with Testor's cement, and the other window pressed into contact with the other side of the plate after the cell had been filled. It was necessary to clean the rim of the cell and the window carefully to secure a close fit. These precautions were made necessary by the small quantity of liquid the cell contained (0.16 ml.) and the volatility of the hexane used to dilute the samples for study. Even this thin layer of liquid (1 mm.) did not always give satisfactory results, so the vapor cell shown in Fig. 3 was constructed from a 51 cm. length of 25 mm. Pyrex tubing, ground flat on both ends and with quartz windows cemented on both ends. It was provided with two capped ground joints, as shown to facilitate flushing with nitrogen, inserting samples, and cleaning.

V. Spectrograph and Accessories

The spectrograph setup used in this research is found in Fig. 1 and Fig. 2. The spectrograph was a Hilger E37 instrument, with quartz system, 60° Cornu prism, adjustable slit and Hartman diaphragm. The source of ultra-violet light was a hydrogen discharge tube similar to that used by Mitacek (30) with the exception that a smaller reservoir bulb was used to increase ease of flushing air from the tube, and traps were introduced to reduce spraying of the window with aluminum dust. The beam of light passed through a 45° fused quartz prism (which directed the light upward), the liquid cell in its holder, a second 45° quartz prism, and finally through

a quartz lens which focused the beam of light on the spectrograph slit. The entire path of the beam of light was enclosed in a cardboard jacket from the discharge tube to the spectrograph; and provision was made for passing nitrogen gas into this jacket and into the spectrograph to displace the air. This precaution was made necessary by the fact that air absorbs selectively in the ultra-violet below about 2100 Å, while nitrogen does not. When the vapor cell was used, it was placed in the beam of light between the lens and the portion of the jacket surrounding the spectrograph slit; since it was filled with nitrogen and the vapor of the samples, it was not necessary to enclose it in a jacket. The discharge tube was wired as shown in Fig. 2; the power source was two 0.5 K.V.A., 1600 volt transformers wired in parallel in the primary, and in parallel in the secondary. The discharge tube was placed in series with a series-parallel combination of four 3000 ohm resistors having an effective resistance of 3000 ohms and a capacity of 800 watts. An ammeter in the primary circuit served as an indicator of operating conditions within the tube. A standard aluminum spark was supplied by two aluminum electrodes which could be swung into line in the position shown, in a fixed position. A special switch changed the secondary wiring for the aluminum spark to throw the transformer secondaries in series and to place the electrodes in series with an 18000 ohm resistance. In order to increase the intensity of the spark, the spark gap was wired in parallel with two condensers, each of which was made of a 2 liter Pyrex beaker covered inside and out with tinfoil.

VI. Comparator.

The plates were measured and calibrated with the aid of a Gaertner micro-comparator capable of reading with an accuracy of ±0.0001 inch.

SPECTROGRAPH SETUP

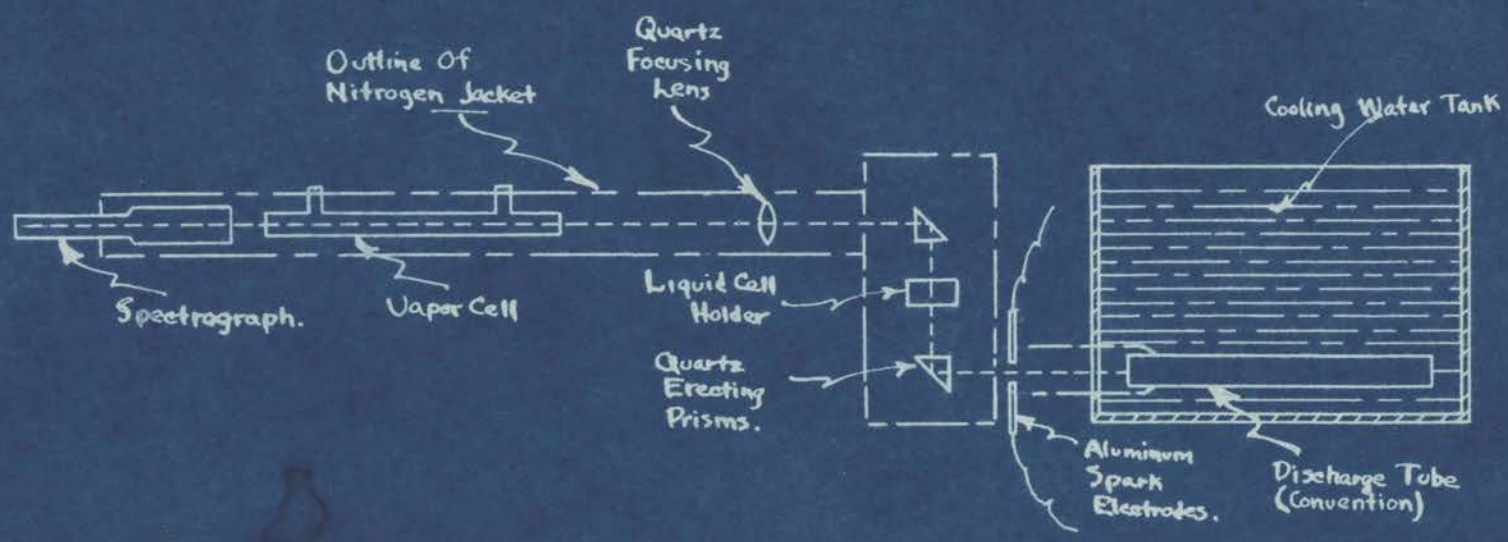


FIGURE 1

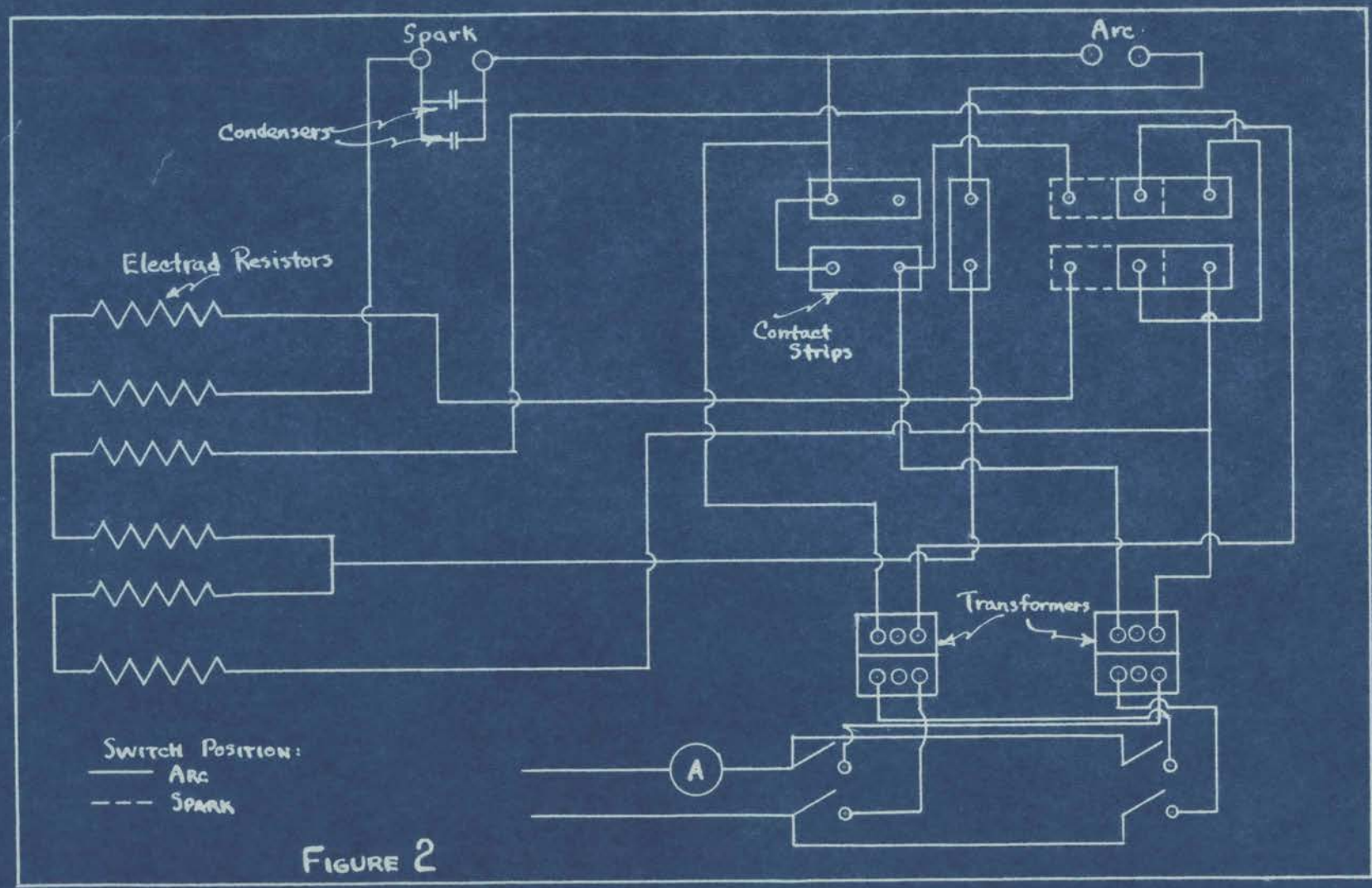

Spark
Arc
Condensers
Electrad Resistors
Contact Strips
Transformers
A
Switch Position:
Arc
Spark

FIGURE 2

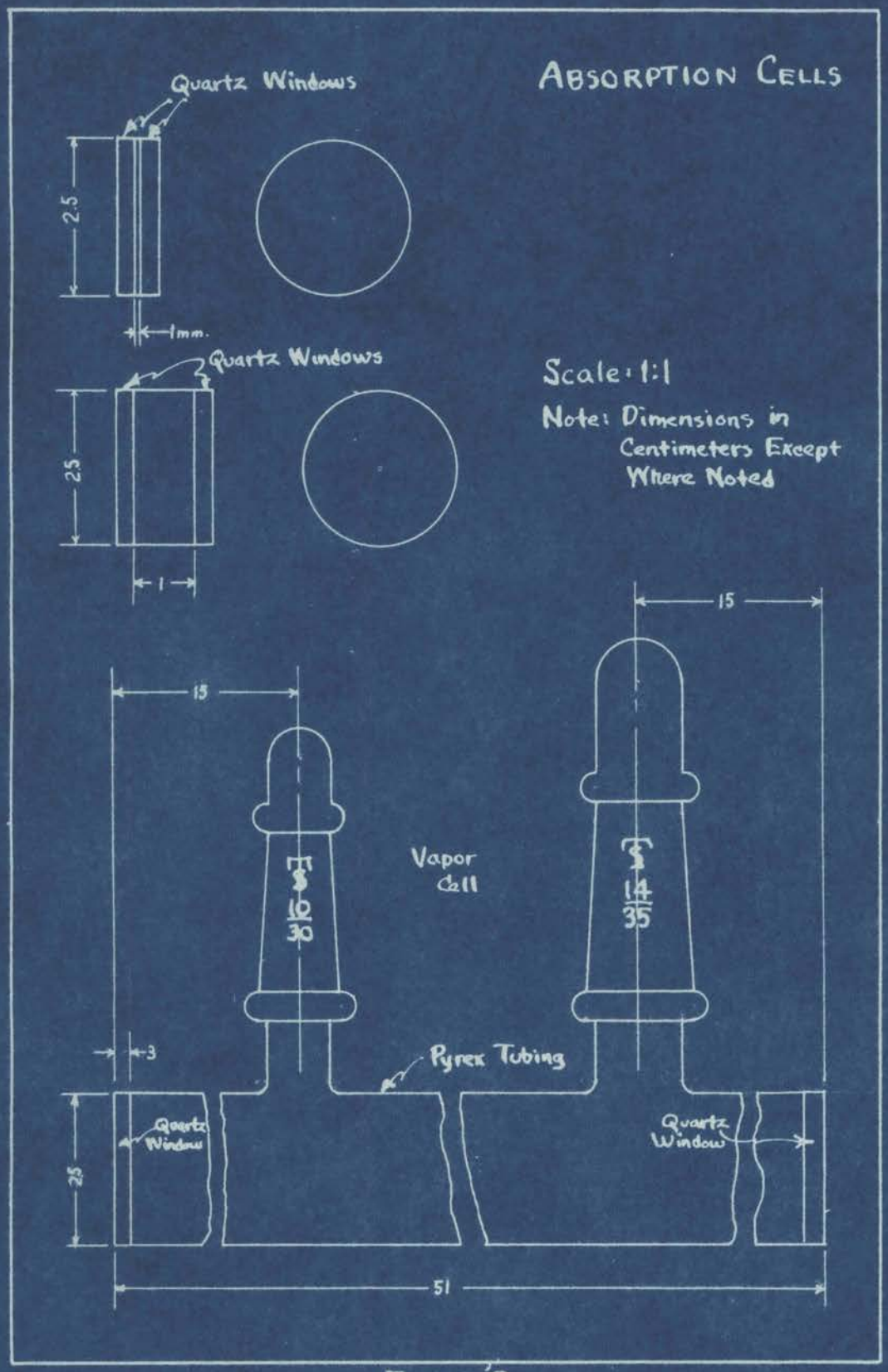

ABSORPTION CELLS
Quartz Windows
2.5
1mm.
Quartz Windows
2.5
1
Scale: 1:1
Note: Dimensions in Centimeters Except Where Noted
15
15
Vapor Cell
10/30
14/35
3
Pyrex Tubing
Quartz Window
Quartz Window
2.5
51

FIGURE 3

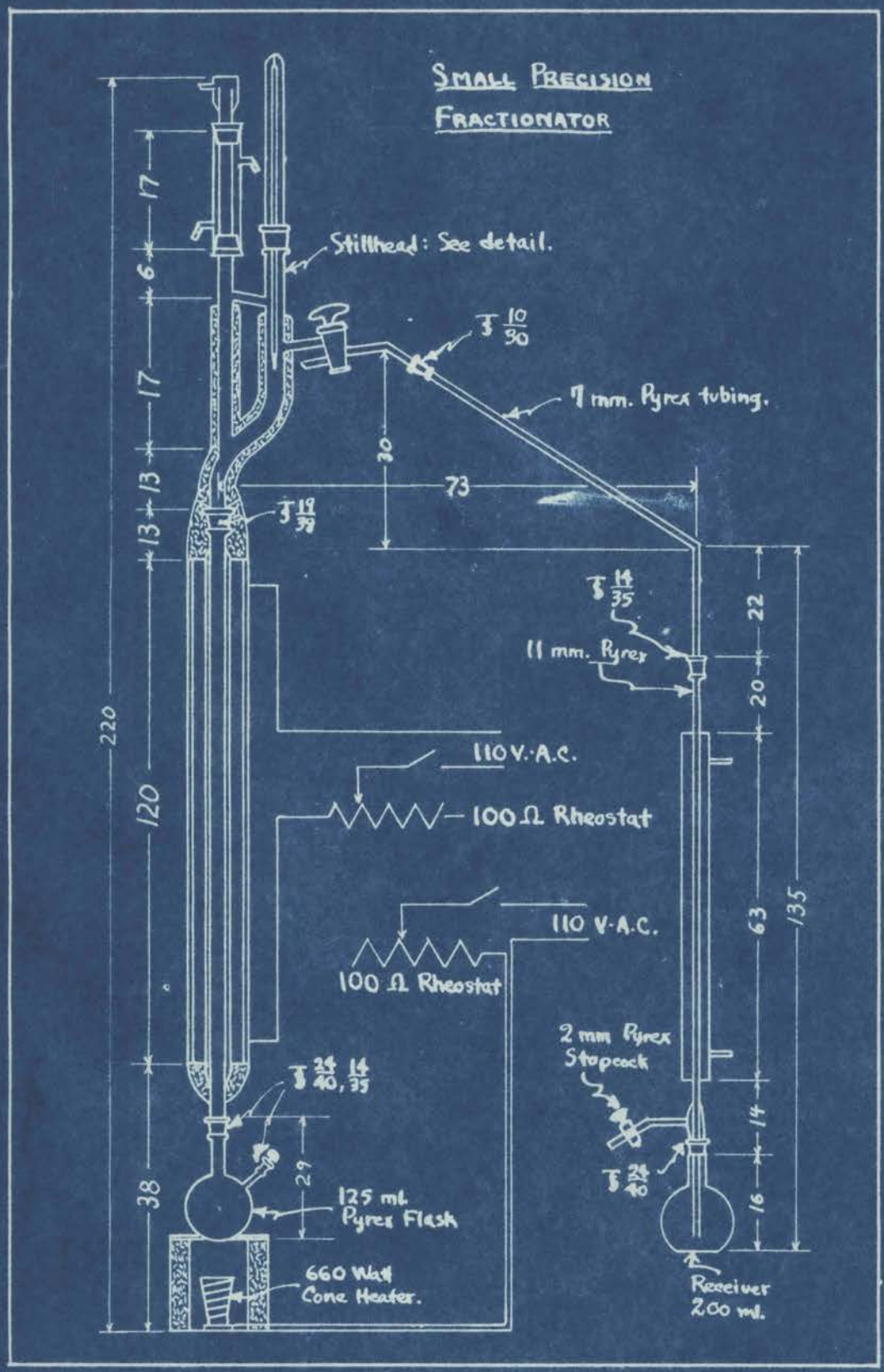
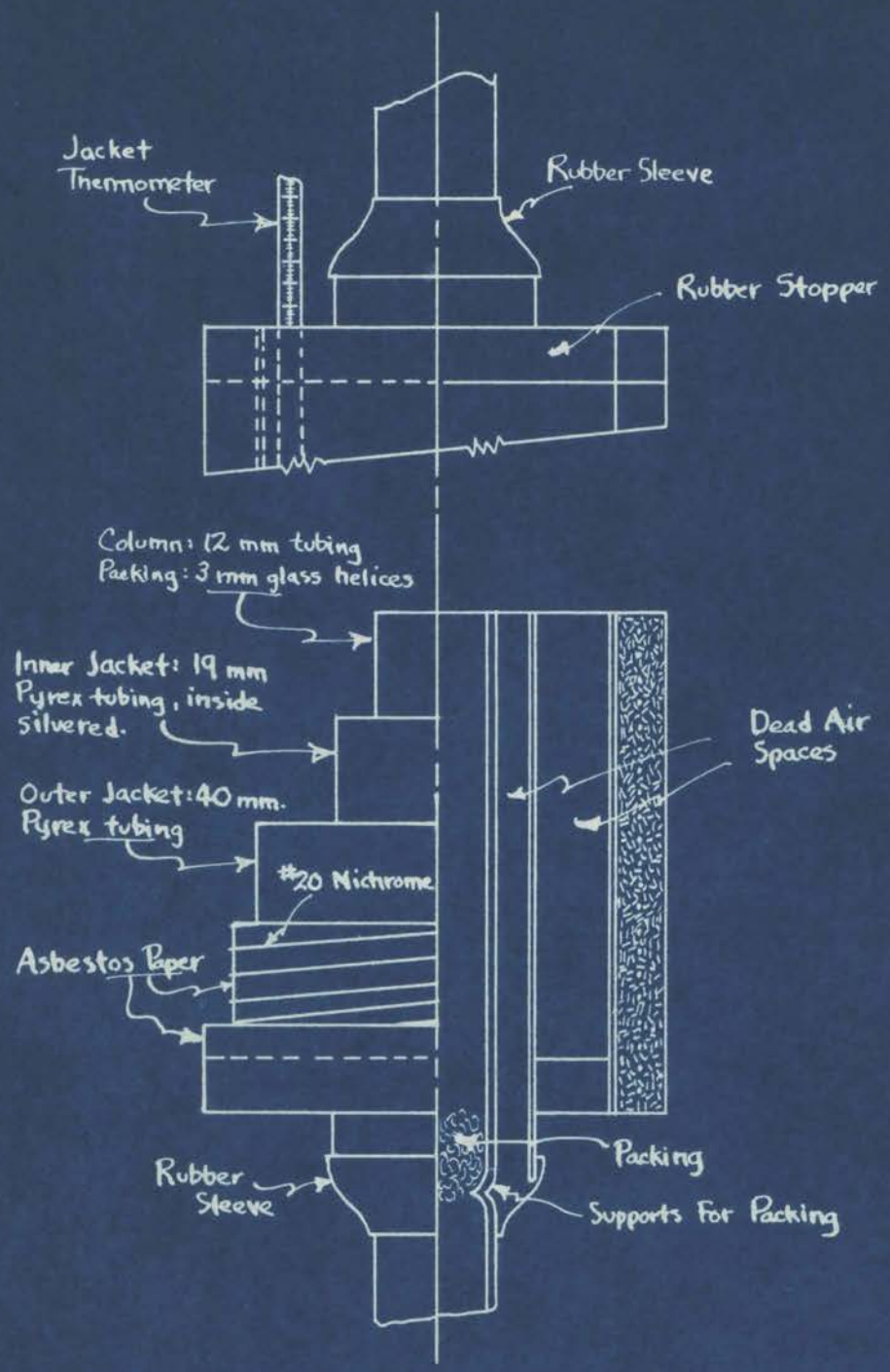
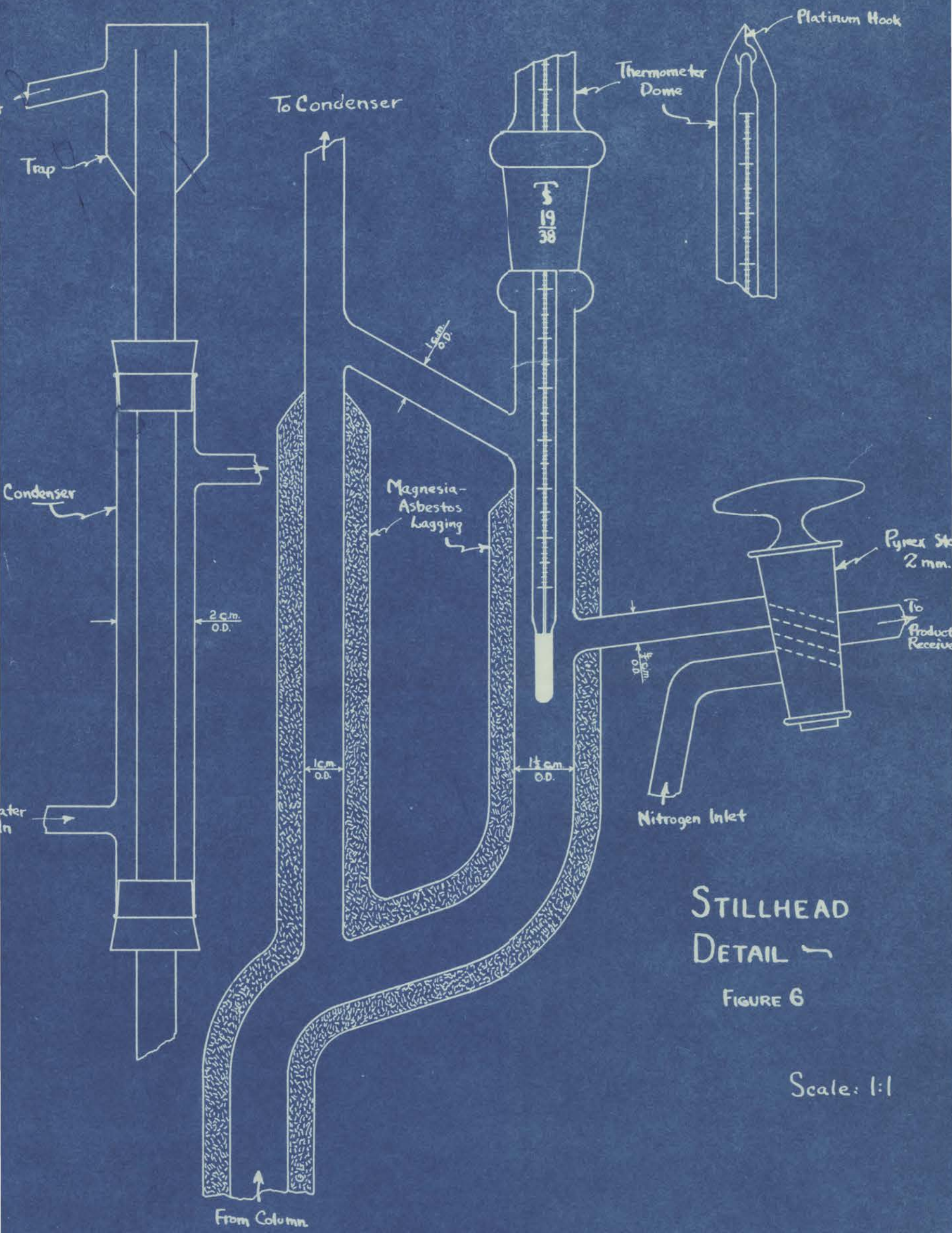

SMALL PRECISION
FRACTIONATOR
Stillhead: See detail.
J 10/30
7 mm. Pyrex tubing.
J 19/38
J 14/35
11 mm. Pyrex
110 V.-A.C.
100 Ω Rheostat
110 V-A.C.
100 Ω Rheostat
2 mm Pyrex
Stopcock
J 24/40, 14/35
J 24/40
125 ml.
Pyrex Flask
660 Watt
Cone Heater.
Receiver
200 ml.
17
6
17
13
13
220
120
38
29
30
73
22
20
63
135
14
16

FIGURE 4



COLUMN DETAIL

FIGURE 5



STILLHEAD DETAIL

FIGURE 6

Scale: 1:1

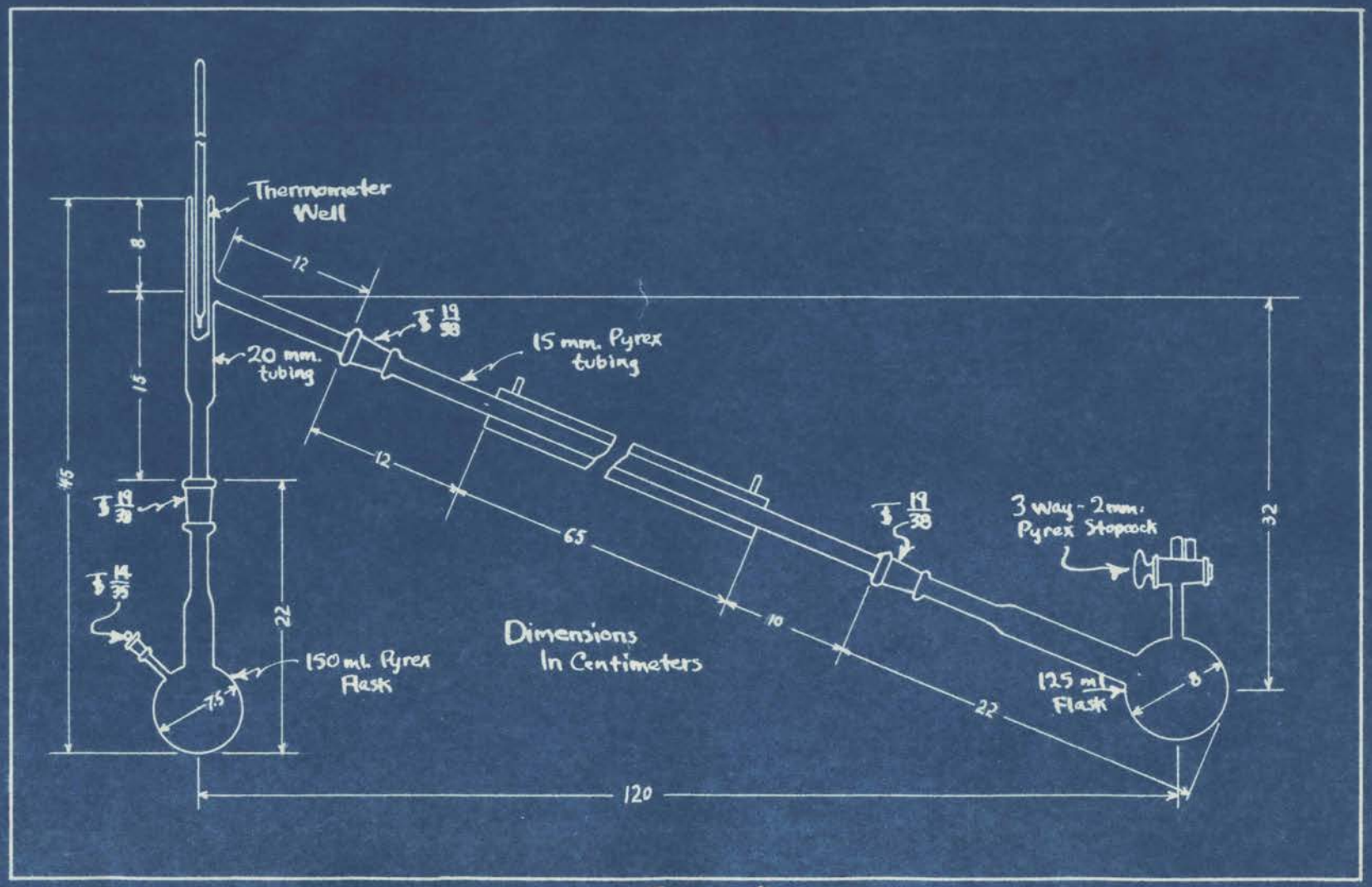

Thermometer Well
12
8
15
45
20 mm. tubing
T 19/38
15 mm. Pyrex tubing
12
65
10
22
T 19/38
T 19/38
T 14/35
22
150 ml. Pyrex Flask
7.5
Dimensions In Centimeters
3 Way - 2mm. Pyrex Stopcock
32
125 ml Flask
8
120

FIGURE 7

MATERIALS

The reagents used in synthesizing the compounds were all of analytical reagent quality unless otherwise noted.

The hexanes used to dilute the standards were purified by the modification of the method of Castille and Henri, reported by Mitacek (30).

Eastman Spectroscopic plates, type 1-O, ultra-violet sensitized and backed, emulsion number 112,939, were used as negative material. These plates were developed in Eastman formula D-72, diluted 1:1, for 3 minutes at 68° F.

Eastman Kodak samples used as check standards were all of the highest purity supplied. Their methods of preparation were ascertained from the Eastman Kodak Laboratories.

EXPERIMENTAL PROCEDURE

1. Synthetic Methods

It was decided that two different procedures would be used in all cases, and, where possible, three procedures. Eastman Kodak reagents were to be used for one sample, and the synthetic method to be used was selected so as to be different insofar as possible, from the methods used in preparing the Eastman Kodak materials. The compounds finally synthesized were n-butyl mercaptan, sulfide, and disulfide, and ethyl mercaptan, sulfide, and disulfide.

The literature revealed a number of methods of preparation. Of these, that apparently the most used was the method of Ellis and Reid (13) for the making of mercaptans by the interaction of an alcoholic solution of KSH (prepared by saturating an alcoholic KOH solution with H_2S) with an alkyl halide or sulfate.

$$KOH + H_2S \longrightarrow KSH + H_2O$$

$$RX + KSH \longrightarrow RSH + KX$$

This same method may be modified (3) by the substitution of K_2S for KSH, in which case the sulfide is produced, or by the substitution of K_2S or Na_2S with the theoretical amount of sulfur added, in order to make the disulfide. The K_2S may be either reagent grade

$$2RX + K_2S \longrightarrow R_2S + 2KX$$

$$2RX + K_2S_2 \longrightarrow R_2S_2 + 2KX$$

K_2S dissolved in 95% alcohol, or may be prepared by the reaction of KSH, prepared as above (by the saturation of KOH solution with H_2S) and an equal portion of KOH. The latter procedure is that recommended by Organic Syntheses and should give purer material. Samples of

C. P. or analytical reagent K_2S and Na_2S are generally not so good as samples of the solution prepared from reagent grade KOH or NaOH and purified H_2S.

The above method is capable of much modification. The substitution of an alkyl chloride or iodide for the bromide is possible, and, in some cases, alkyl sulfonates or alkyl sulfates may be used as the alkylating agent. Sodium or potassium salts are generally used to supply the -SH or -S- groups. Gray and Gutekunst (17) have prepared n-butyl sulfide by the sulfation of butyl alcohol and subsequent treatment with sodium sulfide in aqueous solution. Other workers (13, 22) have substituted dimethyl sulfate and diethyl sulfate in the preparation of methyl and ethyl compounds; with this exception, the alkyl bromides and iodides are the most used. The iodides are somewhat more expensive than the bromides, and, moreover, a supply of student preparations of the alkyl bromides was available. These were purified and used as raw materials in the case of the butyl compounds. For the ethyl compounds, ethyl bromide was first used but yields were so poor that it was found necessary to use Eastman Kodak diethyl sulfate as the reagent in this case.

In an attempt to find a usable third method for making mercaptans in addition to the one just outlined and that used by the Eastman Kodak Company, the catalytic method of Gilfillan (16) was tried. This consists in the reaction of CS_2 or H_2S at elevated temperatures (300°-400°) over catalysts composed of tungsten, titanium or thorium oxides suspended on asbestos. The use of CS_2 was considered

$$ROH + H_2S \xrightarrow[ThO_2]{350^\circ} RSH + H_2O$$

undesirable because this material as an impurity would interfere with the absorption spectra of the other compounds being analyzed for. The method was applied, therefore, by passing H_2S into boiling n-butyl alcohol (a technical grade, redistilled) in such proportion that an equimolar mixture of vapors resulted, and passing the vapors over a thorium oxide-asbestos catalyst (18) heated to 350° C. in an electric tube furnace. The resulting vapors were condensed and cooled in a closed receiver, and were then fractionated. Poor yields of mercaptan were secured by this method, as nearly 90% of the alcohol came through unreacted. Variations of temperature, concentration of catalyst, and rate of throughput failed to better the yields so this method was discarded.

Backer and Stienstra (1) propose the alkylation (methylation) of thiourea and decomposition of the resulting salt of S-methyl isothiourea by refluxing with aqueous sodium hydroxide.

$$S{=}C(NH_2)_2 + R_2SO_4 \longrightarrow \left[HN{=}C\begin{matrix}NH_2\\SR\end{matrix}\right] H_2SO_4$$

$$HN{=}C\begin{matrix}NH_2\\SR\end{matrix} + NaOH \xrightarrow{H_2O} [H_2NCN] + RSNa$$

A small sample of n-butyl mercaptan was made by this method, but the butylation of the thiourea did not proceed readily. This method was used on n-butyl mercaptan only as a trial; it probably would have had more chance of success with ethyl mercaptan.

At this stage, it was decided that only two checks would be run on each compound.

The chosen method, then, for the butyl compounds was the interaction of KSH, K_2S or K_2S_2 with n-butyl bromide which had been redistilled from all-glass apparatus once. Later, to save time by avoiding the intermediate step of the preparation of KSH, reagent

grade sodium sulfide was used in the preparation of the sulfide and disulfide. For the ethyl compounds, KSH and Na_2S or Na_2S_2 were used.

The procedure was as follows: for the mercaptans, 2 moles of reagent grade KOH were dissolved in 500 ml. 95% ethyl alcohol, and the resulting solution saturated with purified H_2S. Saturation usually took place in about six hours, as determined by the gain in weight of the reaction mixture. The mixture was then placed in the 3 neck, 1 liter flask of the reaction apparatus. (See Apparatus). The electric heater was turned on, and 1.5 moles of butyl bromide or ethyl sulfate were placed in the dropping funnel. As soon as the mixture was warm (70°) stirring was commenced and the dropwise addition of the bromide commenced. The rate of addition was such that the mixture barely refluxed. When the bromide had all been added, the stirrer was shut off and the mixture refluxed for three to four hours. In some cases, owing to the voluminous precipitate of potassium bromide, it was necessary to continue stirring throughout the refluxing, to avoid dangerous bumping. The mixture was then allowed to cool. The reaction mixture was made faintly acid with 6N HCl and the upper layer of mercaptan separated. This layer was dried over anhydrous Na_2SO_4 and distilled through a plain all-glass stillhead in a closed system (Fig. 7). It was later refractionated in the small precision fractionator.

For the sulfide, KSH was prepared as before and an equimolar quantity of KOH added to form K_2S. The addition of the bromide was carried out as before; when the reaction mixture had cooled, it was treated with 1 liter of 25% sodium chloride solution to salt out the product. The upper layer of sulfide was separated, dried, and

distilled as before.

For the disulfide, the theoretical quantity of powdered sulfur was added to the K_2S or Na_2S solution and the solution heated for half an hour before the addition of bromide was commenced.

The Eastman Kodak materials were refractionated once in the small precision fractionator, with the exception of ethyl mercaptan and n-butyl disulfide. Ethyl mercaptan boiled too low and n-butyl disulfide required vacuum distillation, to which the fractionator had not been adapted.

Each sample, as it was prepared, was placed in a ground-glass stoppered bottle which was in turn placed in a larger bottle which was tightly stoppered. Both bottles were filled with nitrogen gas to avoid, insofar as possible, the effects of air oxidation. Workers with sulfur compounds have found that this is rather severe in the case of the mercaptans, air oxidation being sufficient to cause disulfides to appear in mercaptan samples. The sulfides and disulfides were apparently more stable.

Table I gives a comparison of the beginning materials used by the Eastman Kodak Laboratories and the beginning materials used in this study in synthesizing the various compounds.

TABLE I

BEGINNING MATERIALS

USED IN SYNTHESES

Compound	Synthetic Material	Eastman Kodak Material
Ethyl mercaptan	Ethyl sulfate, Potassium hydro-sulfide	Ethyl sulfate, Sodium sulfide
Ethyl sulfide	Ethyl sulfate, Na or K sulfide	Ethyl sulfate, Sodium sulfide
Ethyl disulfide	Ethyl sulfate, Na sulfide and Sulfur	Ethyl sulfate, Na sulfide and sulfur.
Butyl mercaptan	Butyl bromide, K hydrosulfide	Butyl sulfate, Na sulfide and Hydrogen sulfide
Butyl sulfide	Butyl bromide, Sodium sulfide	Butyl sulfate, Sodium sulfide
Butyl disulfide	Butyl bromide, Sodium sulfide and Sulfur	Butyl sulfate, Sodium sulfide and Sulfur

2. Operation of Precision Fractionator

The sample to be distilled was placed in the stillpot and the two sections of the column were flushed with purified nitrogen, by leading the gas in through the side arm of the still pot and the nitrogen inlet arm of the stopcock on the stillhead. Condensing water was then started through the stillhead and condenser, and the stillpot heater and jacket heater turned on. The jacket heater was adjusted so that the outside jacket temperature was 5° higher than the boiling point of the liquid being fractionated. The regulator was shut off so that the column would operate at total reflux, and the stillpot heater was adjusted so that the column flooded in about one hour. The heater was then cut until the flow of reflux into the stillpot decreased (usually 3 to 4 minutes) and then turned on again. Usually one flooding was sufficient to warm the column; it was then allowed to operate at constant reflux until the stillhead temperature was constant. The product stopcock was then adjusted so that the desired reflux ratio (about 20:1) was obtained, and product collected until the sample was complete. The product receiver was then changed, the side arm flushed out with nitrogen again, and the procedure of bringing to equilibrium at constant reflux and taking product was repeated until the desired fractions were secured.

The column proved to be very sensitive to drafts. In addition to the lagging shown in the diagram (Fig. 6) it was found necessary to place a sheet of heavy celluloid around the top of the column and stillhead as a draft deflector. The column worked nicely below 150° C., but for work up to 200°, more insulation on the stillhead, a

stillhead heater, or both may be necessary. The stillpot was shielded with two sections of 1" magnesia pipe insulation.

3. Making of Spectrophotograms.

Tests run to determine the optimum conditions of operation for the hydrogen discharge tube showed that the best discharge for this work was secured when a current of 8.0 amperes was flowing through the primary circuit. The tube was flushed out with hydrogen and then pumped down until this reading was obtained on the primary ammeter. Some trouble was had with desorption of gases and moisture from the walls of the discharge tube, and the tube had to be removed from the water jacket and run without cooling until the adsorbed material was driven off. Again, when operating the tube intermittently for short exposures (less than 1 minute) it was necessary to guard against adsorption of hydrogen which made it impossible for a starting current large enough to operate the tube to flow. The best precaution against this was found to be to operate the tube continuously and vary the exposures by a shutter.

For this study, the fixed-thickness liquid cells were first used. With these cells, the concentration of the solution of the compound in hexane had to be varied. The procedure was as follows for a typical plate.

Procedure

1. The desired series of dilutions of the compound in hexane was prepared, and the liquid cell was cleaned.

2. The nitrogen jacket was flushed with nitrogen for five

minutes, with the plate in position.

3. An exposure was made on the empty system, without the cell in place. The plate was then lowered 5 mm.

4. The cell, filled with pure hexane, was placed in position and an exposure made. Plate then lowered 5 mm.

5. The hexane was removed from the cell, and the first dilution in hexane was placed in it. Exposures were made through the series of dilutions, placing each in cell successively. Plate lowered 5 mm. after each exposure. (Note: dilutions generally ranged from pure material to 0.001% solutions.)

6. The cell and collimating lens were removed from the path of the light, and the aluminum spark electrodes swung into position. The switch was changed to place the transformer secondaries in series. Spark placed on plate.

7. Scale placed on plate.

8. Plate developed.

In the use of the vapor cell, the concentration of the vapors in the cell was changed by adding successive accurately measured small portions of the sulfur compound to the cell before each exposure. It was found by trial and error that the addition of successive small portions of the pure sulfur compound produced such high vapor concentrations that absorption was continuous. It was then decided that the pure substances would be diluted with hexane as for the liquid cells and used as above, adding dropwise portions of the solution to the cell and making exposures between each addition. It was assumed that the hexane vapors would not interfere in the region 1900 Å and upward. This assumption was justified in practise.

Considerable experimenting to determine the proper concentrations for both liquid and vapor cell exposures and the proper time of exposures was necessary, and these conditions varied rather widely, according to the region studied. In the low region around 2100-2200 Å, long exposures and weak concentrations were necessary; higher up the scale, shorter exposures and stronger concentrations were used.

The absorption maxima given in Tables III and IV were calculated with the aid of the Hartmann dispersion formula

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

where λ = wavelength of the band being measured in Å and λ_0, B, and D_0 are constants given by the following formaulas and having a given value for any particular plate.

(1) $$D_0 = \frac{\lambda_3 - \lambda_2}{\frac{\lambda_3 - \lambda_1}{d_3} + \frac{\lambda_2 - \lambda_1}{d_2}}$$

(2) $$B = \frac{(\lambda_3 - \lambda_1)(D_0)(D_0 - d_3)}{d_3}$$

(3) $$\lambda_0 = \lambda_1 - \frac{B}{D_0}$$

(4) $\lambda_1, \lambda_2, \lambda_3$ = the wavelength of known lines in the comparison aluminum spark spectrum.

d_2 = distance between λ_2 and λ_1

d_3 = distance between λ_3 and λ_1

d = distance between λ_1 and band in question.

To use the Hartman dispersion formula, it is necessary to identify three lines in the spark spectrum on the plate. These

three lines, which include between them the region covered by any bands to be measured, are measured and the distances and wavelengths thus secured used to compute the constants (1), (2), and (3).

Since all optical parts in the system were fixed in one position, once the plate formula was calculated for one plate the values of the constants for any plate in the same series were known and it was only necessary to measure the distance "d" from the first standard line in order to calculate the wavelength of any absorption band.

EXPERIMENTAL RESULTS

Table II gives the boiling points secured for the samples prepared, and compares them with values found in the literature.

No tests of the new stillhead on the precision fractionator were made. However, the column, operating under the most favorable conditions with the old stillhead and using a binary mixture of benzene and carbon tetrachloride, gave plate efficiencies calculated by the Dodge and Huffman equation of 35 to 40 theoretical plates. It is believed that this efficiency is at least equaled by the new stillhead. Samples of Eastman Kodak materials, having boiling point ranges of 1.0-1.5°, were fractionated to obtain samples with constant boiling points within 0.1°. The highest product rate attained with the new stillhead was 0.25 ml. per minute. The reflux counter in the old stillhead having been removed, the reflux ratio could not be calculated. It may be noted that, with the new stillhead, operation of the column was much simpler and more free from flooding, especially below 125° C. Between 125° and 150° C., some trouble with loss of heat due, in part at least, to insufficient insulation on the stillhead, was experienced.

As stated before, time trials on the operation of the hydrogen discharge tube proved that the best current was from 7 to 8.5 amperes in the primary circuit. With the tube running thus, 15-minute exposures on an empty system (nitrogen filled) gave continuous emission all the way down to approximately 1980 Å; exposures of one hour gave blackening of the plate as far down as 1960 Å, without any air

absorption bands. This showed that a short flushing with nitrogen each time the system was opened was sufficient to keep air absorption below the noticeable minimum.

It has been stated, however (41) that ethyl sulfide has a band at 1850 Å and ethyl mercaptan a band at 1935 Å. Since these bands are below the transparency of the hexane used as solvent in this work (about 2150 Å), they will probably have to be studied in the vapor cell with a more intense source. In order to shorten the time required to a reasonable figure and still produce light in this region, it will probably be necessary to supply more power to the discharge tube than the two transformers now available will handle. A combination of more power and additional condensers would give spark lines of greater intensity and further down in the needed region, for the standard spark spectrum.

The hexane used as solvent in this study apparently is a completely satisfactory solvent down to about 2100-2150 Å.

Tables III and IV show the observed absorption maxima for the samples listed in Table II. Although the data contained in these tables does not bring this out, a careful inspection of the various plates with proper regard for uncertainties in measurement, and the possibility of having seen faint bands where no bands actually existed leads to a fairly certain belief that diethyl sulfide has poorly defined bands at 2182±4 Å and 2240±3 Å, and a somewhat sharper but weak band at 2286±2 Å. None of these bands have been reported in the literature. No definite evidence was obtained for the existence of a band at 2490 Å which was reported by Ley and Arendz (41) though it probably would have been necessary to micro-

Table II

BOILING POINTS OF SAMPLES

Compound	Synthetic Material	Eastman Kodak Material	Literature values (2)
n-Butyl mercaptan	97-97.5°	97.2°	97-98°
n-Butyl sulfide	150° **	186-89°	182-84°
n-Butyl disulfide		100-103°/15mm*	143-44°/83mm
Ethyl mercaptan	35°	34.5-5.5° *	37°
Ethyl sulfide	90-92°	92.05°	93-4°
Ethyl disulfide	151-54°	152-54°	152-4°

* Used as supplied.

** A mixture of high-boiling sulfides, the residue from fractionation of n-Butyl mercaptan syntheses was used for these two samples.

TABLE III

OBSERVED ABSORPTION MAXIMA
Ethyl Compounds

Synthetic Ethyl Mercaptan	Synthetic Ethyl Sulfide	Eastman Kodak Ethyl Sulfide	Eastman Kodak Ethyl Sulfide	Synthetic Ethyl Disulfide	Eastman Kodak Ethyl Disulf.	Literature (41) EtSH	Literature (41) Et_2S
							1890
						1935	
		2182.6	2182.6				
2193.4							
		2218.2					
2228.5			2231.3				
Same band?		2237.5					
2241.7	2243.0						
						2250	
2285.3	2285.4		2286.5				
		2287.3					
				Broad band from about 2370 to 2480			
					Broad band from about 2380 to 2480		2490
				2598.3			

TABLE IV

OBSERVED ABSORPTION MAXIMA
Butyl Compounds

Eastman Kodak Butyl Sulfide	Eastman Kodak Butyl Sulfide	Synthetic Butyl Sulfides	Eastman Kodak Butyl Disulfide
2180.4			
	2187.7	2195.1	2192.9
2228.6			
			2235.4
2242.2		2243.8	
		2250.8	
	2289.7		

No absorption secured in butyl mercaptan plates.

photometer the plate to have observed any such band unless it had been very strong.

Dibutyl sulfide shows bands similar to those obtained from diethyl sulfide. These bands occur at 2191±3, 2235±5, and a doubtful one at 2289±3 Å.

A sample of synthetic ethyl mercaptan gave absorption bands at 2193, 2228, 2241, and 2285 Å. The bands at 2228 and 2241 were probably two measurements of the same band. Eastman Kodak ethyl mercaptan, used without purification, gave no bands whatsoever at the lower vapor concentrations. With higher vapor concentrations, however, some evidence of continuous absorption below 2400 Å was noted. Similar lack of absorption bands was found in the butyl mercaptan plate. It seems probable, therefore, that the bands observed in the sample of synthetic ethyl mercaptan were due to ethyl sulfide formed by air oxidation. The existence of the band reported by Ley and Arendz (41) for ethyl mercaptan at 2250 Å seems to be in great doubt as this is close to the value for the most intense band observed for ethyl sulfide at 2240 Å

The results secured from diethyl disulfide were hard to interpret without new photographs and microphotometer measurements. A general broad band about 100 Å or more wide and centering around 2430 Å was observed in each sample. It is possible that these broad bands may be found to be composed of a number of narrower fuzzy bands; however, additional work will have to be done on this compound to make sure of this. The appearance of the broad bands at least suggests this possibility, however.

Dibutyl disulfide gave a suggestion of a similar wide band,

which was probably no wider than 50 Å, in the same region. A weakness in the sensitivity of the plates used at this point in the spectrum complicated the interpretation of these plates and those of the ethyl disulfide, and makes any interpretation very difficult.

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CONCLUSIONS

It will be necessary to do further synthetic work on all six of the compounds studied. A greater number of methods of synthesis would be desirable in order to get good agreement on absorption maxima; these methods should be aimed to produce material of greater purity than the samples reported in this work. Perhaps a micro-fractionating column would be useful because of the small yields of some of the methods of synthesis.

The mercaptans should be investigated in a region covering the lowest range of the quartz spectrograph (about 1850 Å). Some values cited from literature below 2000 Å and the lack of bands above 2000 Å make this extension of the study necessary. A more intense light source will have to be provided and it may be necessary to eliminate the 45° quartz prisms from the system to conserve the intensity of the light, inasmuch as quartz begins to absorb appreciably in this region.

The weak band due to plate insensitivity made interpretation of the plates on the sulfides and disulfides difficult. Plates with better sensitization should be secured, and the wide bands secured in the disulfides analyzed with a microphotometer. The polysulfides (tri-, tetra-, and higher) should be added to the list requiring observation. It would also be well to run tests on the effect of secondary and tertiary groups on the ultra-violet absorption spectra.

It seems apparent that the analysis of petroleum fractions for these compounds would be difficult and may prove impossible

if even slight interferences enter into the problem, owing to the breadth and weakness of most of the bands.

The detection of the alkyl groups in sulfides seems probably impossible as the difference between ethyl sulfide and butyl sulfide is less than the probable experimental error. The effect of branched chains probably would make no significant difference, but should be tried.

It seems that the higher bands reported in the literature for ethyl mercaptan and ethyl sulfide are probably in error.

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Typed By

Marvin D. Livingood