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GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION
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To: F. L. Culler

From: R. G. Wymer

Subject: Semiannual Report on Subcontract No. 1082
under W-7405-eng-26

INTRODUCTION

The objectives of the project reported below are to provide more information regarding solvent radiation damage for the Thorex program and permissible irradiation levels for solvents used in processing power reactor fuels.

Amsco 125-82 has been selected for use in the initial studies. It is a diluent typical of the types commonly used in fuel processing and raw materials processing, so any information regarding the number and kinds of its constituents and their physical and chemical properties should be of general usefulness. It was decided that the Amsco 125-82 should be fractionated into its pure components, both major and minor, and that these pure components should be investigated individually. In this way the nature of the Amsco will be more closely defined, and unnecessary complexity in the interpretation of irradiation results will be avoided. The major components will be studied first, with work on the minor ones following as time permits.

The project should be considered on a time basis as consisting of three periods. The first period is the interval from January 1, 1957 to June 15. Period 2 is the interval from June 16 to September 15. Period 3 is the interval from September 16 to December 31, 1957. On the basis of the scheduling of manpower to the project, approximately 25 per cent of the effort was expended during period 1; 50 per cent will be expended during period 2; the remaining 25 per cent will be expended during period 3. The high concentration of effort during period 2 is attributable to the fact that a senior scientist and a

student assistant are working full time, and the project director one-quarter time, during this period, which includes the three summer months.

This report summarizes the accomplishments of period 1 of the project.

DISCUSSION

The accomplishments of period 1 include acquiring x-ray equipment with which to perform the irradiations; setting up the x-ray unit and building a shielded box in which to house the high-intensity x-ray tube; measuring the x-ray tube output; and constructing a distillation column and fractionating several liters of Amsco 125-82 diluent, which was chosen as the first material to be studied.

X-ray Equipment

A GE x-ray diffraction unit power supply, model XRD-5 and accessories was chosen for the project work because of the high continuous power output of the unit. The x-ray tube is a shielded Machett OEG-60 end-window tube capable of operating continuously at 50 KVP and 50 Ma, and giving an estimated dose rate of 2×10^6 r/min. The XRD-5 unit will operate continuously at the 2500 KVA required by the tube for maximum output.

Irradiation Set-up

A lead-lined $1/4$ in. thick box having internal dimensions of $17 \frac{1}{2}$ in. x $17 \frac{1}{2}$ in. at the bottom, and $23 \frac{1}{2}$ inches in height was fabricated and modified to hold the x-ray tube in a vertical position, with the end-window pointing down. Holes with off-set shielding were provided for experimental lines. Approximately half of the shielded x-ray tube protrudes from the top of the box, thus leaving ample space inside the box for experimental equipment.

X-ray Tube Output

The x-ray output is 0.24 watt. The output has been measured using both a ferrous ammonium sulfate-sulfuric acid dosimeter and a ceric ammonium sulfate-sulfuric acid dosimeter. A direct calorimetric measurement of the output is planned, but will not be charged to this project, since it is felt that agreement between the two chemical dosimeters gives reasonable assurance of the accuracy of the tube output measurement.

A G value of 14.8 was used for the iron dosimeter, and of 3.2 for the cerium dosimeter. The accepted G value for the iron dosimeter using air- or oxygen-saturated solutions is 15.5. However, work done by Dr. E. L. Alexander[†] using four Machlett OEG-60 tubes has shown that a value of 14.8 is the correct one under the conditions employed, namely, stirring in the presence of air. The G value rises to the accepted value of 15.5 when oxygen is bubbled through the solution during the irradiation. There is considerable disagreement among workers as to the correct G value to use for the cerium dosimeter, but the mode seems to be about 3.2. This value is in agreement with the value obtained by Dr. Alexander, who has made a direct calorimetric measurement.

Fractionating Amsco 125-82

A distillation column having a 4 feet high, 3/4 in. i.d. rectifying section packed with glass helices, and a three liter still pot was constructed for this part of the work. A careful distillation at atmospheric pressure of two liters of Amsco 125-82 failed to separate its thirteen or so components into any less than five or six components in each fraction. Vacuum distillation was shown by Mr. W. Baldwin, ORNL Chemistry Division, to effect more complete separation. Distillation of another two liters of Amsco at 48 mm Hg pressure produced fractions containing only two or three components, with one major component in most cases. These fractions are currently being redistilled to effect their further separation into pure components.

CONCLUSION

The objective of the first period of the project has been to finish those jobs which would assure that optimum use of time during the large summer period would be achieved. This objective has been met. Progress made during the summer months will be reported as requested under the contract.

[†]Dr. Alexander, formerly of Knolls Atomic Power Laboratory, is now with Georgia Tech, and consults daily on this project.



ANNUAL REPORT NO. 1

PROJECT NO. A-323

RADIATION CHEMISTRY OF ORGANIC SUBSTANCES

By

RAYMOND G. WYMER

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SUBCONTRACT NO. 1082

UNDER W-7405 eng-26

- o - o - o - o - o -

1 JANUARY 1957 TO 31 DECEMBER 1957

PUBLISHED 31 MARCH 1958

PLACED WITH THE CHEMICAL TECHNOLOGY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE



Engineering Experiment Station
Georgia Institute of Technology

Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
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I. INTRODUCTION

The objectives of this project are to provide more information regarding solvent radiation damage for the Thorex program and permissible irradiation levels for solvents used in processing power reactor fuels.

Amsco 125-82 has been selected for use in the initial studies. It is a diluent typical of the types commonly used for extractants employed in fuel processing and raw materials processing. It has also been used as a heat exchange fluid in equipment exposed to high radiation fields. Therefore, any information regarding the number and kinds of its constituents and their physical and chemical properties, especially with regard to the effects of irradiation, should be of general usefulness.

It was decided that the Amsco 125-82 should be fractionated as nearly as is practicable into its pure components, both major and minor, and that these pure components should be investigated individually. In this way the nature of the Amsco will be more closely defined, and unnecessary complexity in the interpretation of irradiation results is avoided.

II. EQUIPMENT

The principal pieces of equipment employed in this research have been the x-ray apparatus, a gas chromatograph and several distillation set-ups. Some special apparatus has been fabricated to fill special needs. These pieces include a brass irradiation cell and a glass cold trap for volatile radiolysis products. Finally, general analytical equipment such as infra-red and ultra-violet spectrometers has been used more or less routinely.

A. X-ray Apparatus

A GE x-ray diffraction unit power supply, model XRD-5 and accessories, was chosen for the project work because of the high continuous power output of the unit. The x-ray tube is a shielded Machlett OEG-60 end-window tube capable of operating continuously at 50 KVP and 50 Ma, and giving an estimated dose rate of 2×10^6 r/min. The XRD-5 power supply will operate continuously at the 2500 KVA required by the tube for maximum output.

A box lined with 1/4 inch thick lead and having internal dimensions of 17 1/2 inches x 17 1/2 inches at the bottom and 23 1/2 inches in height was fabricated and modified to hold the x-ray tube in a vertical position, with the end-window pointing down. Holes with off-set shielding were provided for experimental lines. Approximately one-fourth of the shielded x-ray tube protrudes from the top of the box, thus leaving ample space inside the box for experimental equipment. Figure 1 shows the x-ray power supply and the lead-lined box containing the x-ray tube. The gas chromatograph is shown on the right-hand side of the photograph. Figure 2 is a close-up shot of the inside of the box showing the x-ray tube entering from the top of the box. The irradiation cell is shown held in its normal position. The micro-switch which shuts off the power to the tube whenever the door to the

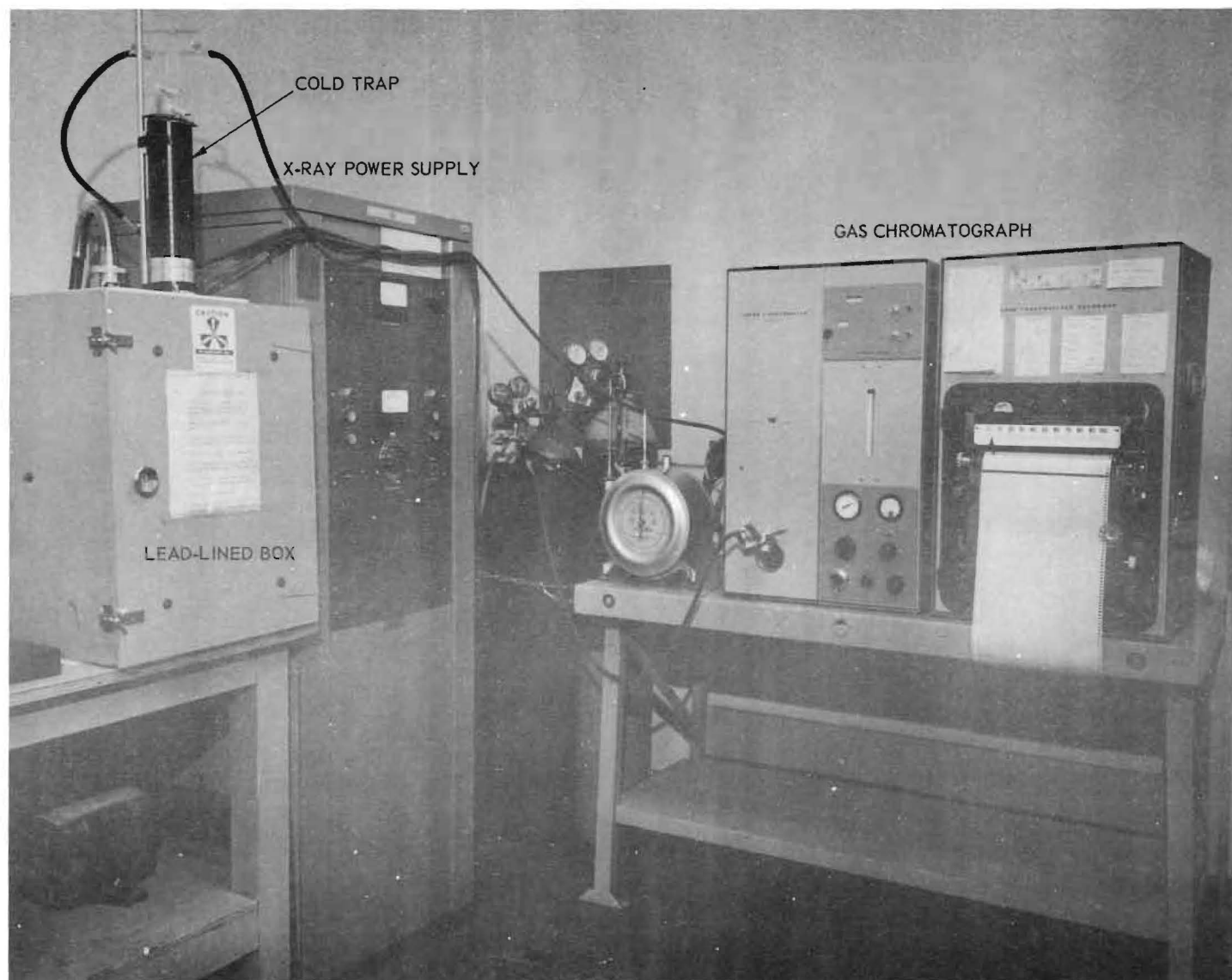


Figure 1. Irradiation Set-up.

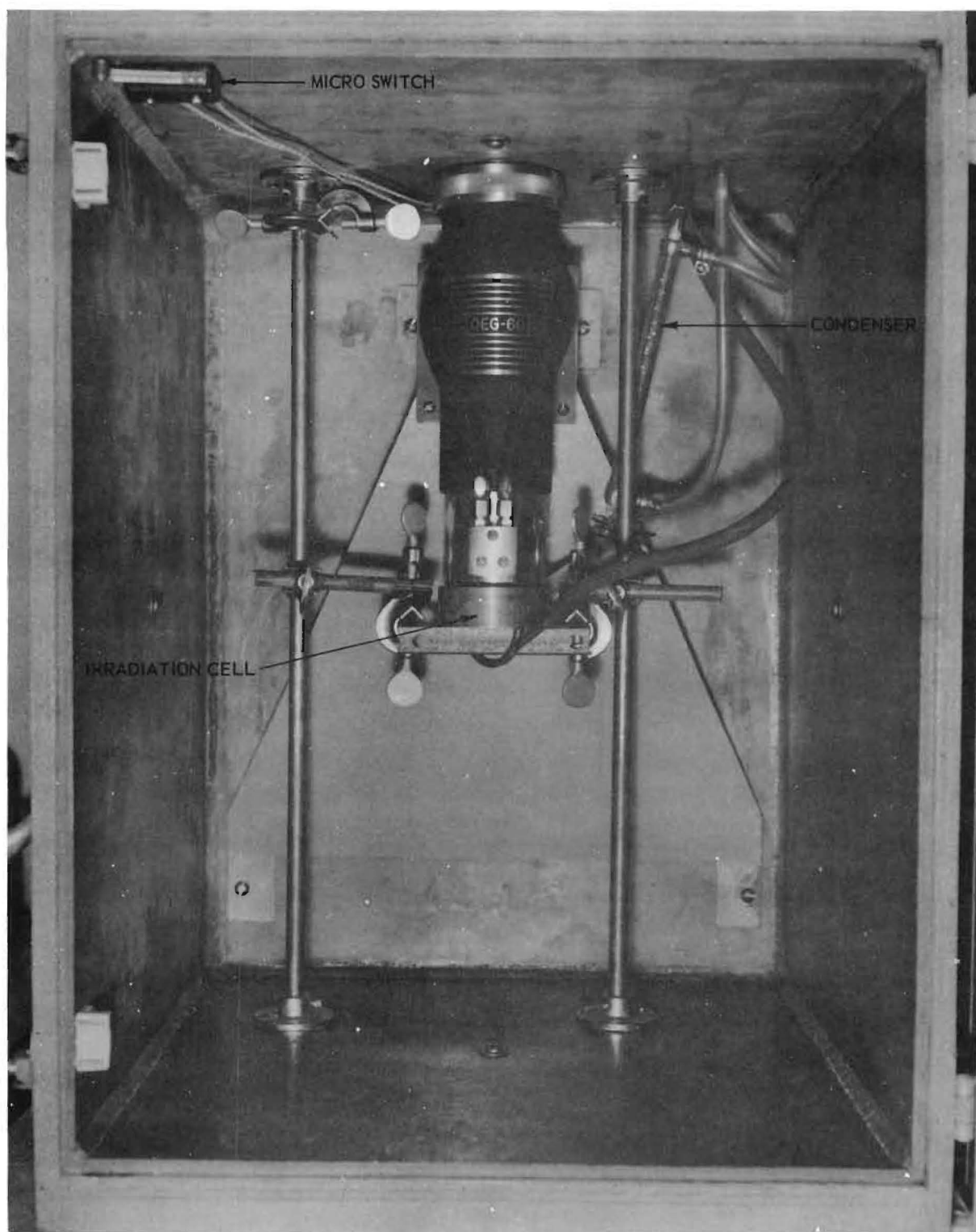


Figure 2. Interior of Lead-Lined Box.

shielded box is opened is shown in the upper left-hand corner of the picture. The pieces of light-colored tubing supply water to the small glass condenser which returns condensable vapor to the irradiation cell during irradiations. The condenser is needed because the temperature of the end of the x-ray tube reaches an estimated 60 to 70°C. At this temperature the vapor pressures of the liquids being irradiated are not negligible.

B. Gas Chromatograph

The primary analytical tool used for identification of the components in both the sample of Amsco 125-82 and in the radiolysis products obtained by irradiating purified cuts of Amsco 125-82 has been a Perkin-Elmer model 154-B Vapor Fractometer. In this instrument a sample mixture of gases or liquids is introduced into a carrier gas stream which transports the sample into a column. Each component appears at the column exit at a different time where it is detected by a sensitive thermal conductivity gage. Recording the detector output provides a series of peaks, the area of each being proportional to the concentration of the component producing it. The "retention volume" (time multiplied by carrier gas flow rate) serves to identify the component.

The principal variables in the use of the gas chromatograph are the type of column packing and the temperature of the columns. The carrier gas flow rate is a variable of secondary importance. Degree of response of the thermal conductivity gage is directly related to the difference between the thermal conductivities of the carrier gas and the component being analyzed for: the larger the difference, the greater the response for a given amount of the component. Table I lists the thermal conductivities of some representative substances.

TABLE I
THERMAL CONDUCTIVITIES[†]

Substance	Conductivity, (BTU/ft. ² .sec) for (1° F/in.) temp. gradient	
	0°C	100°C
Benzene	2.08	4.12
Hexene	2.44	4.36
iso-pentane	2.88	5.08
n-hexane	2.88	----
n-pentane	2.96	----
Ethyl ether	3.08	5.24
n-butane	3.12	5.40
iso-butane	3.20	5.56
Carbon dioxide	3.40	5.32
Propane	3.48	6.04
Argon	3.88	5.09
Ethene	4.04	6.44
Ethane	4.24	7.00
Ethyne	4.40	----
Nitrogen	5.60	7.20
Oxygen	5.68	7.40
Methane	7.00	(9.7 extrapolated)
Helium	33.6	39.9
Hydrogen	40.00	54.6
Cyclohexane	----	3.80
n-heptane	----	4.12
Ethyl alcohol	----	4.96
Water vapor	----	6.36

Note: Conversion Factor: 1.24 X English System = Metric System.

[†] Obtained from Ch. E. Handbook, 3rd. Ed., pp. 461.

From this table it is apparent that helium is a good carrier gas for almost any gas but hydrogen. When hydrogen is the substance being analyzed for, it is desirable to use argon gas as a carrier. The inert gases make good carriers because of their relatively slight affinity for the stationary phase in the columns.

The columns used are typically made of 1/4 inch tubing and are about two meters long. Column packings are generally of two types: vapor-liquid partition

and vapor-solid partition. Didecylphthalate-coated crushed firebrick exemplifies the first type; molecular sieve, the second. The former is useful for separating fairly high molecular weight hydrocarbons; the latter, for separating light gases such as hydrogen, oxygen, carbon dioxide, methane, nitrogen, et. al.

In the work done to date molecular sieve columns have been used to separate and analyze for hydrogen and methane using argon carrier gas. All other hydrocarbons are analyzed for using an appropriate vapor-liquid partitioning column with helium carrier gas to increase the response for these substances of moderate thermal conductivity.

It was found that when gas samples of greater than about 10 ml (STP) were introduced into a four-meter molecular sieve column (two 2-meter columns in series) the resulting peaks were not symmetrical, but were badly skewed and often had flat tops, making identification by time of peak emergence impossible. This problem was surmounted by modifying the column so that entering gas samples passed first into an enlarged section of column about 4 1/2 inches long and 5/8 inch in diameter before entering the main body of the 1/4 inch diameter column. Using this column modification no trouble was experienced using a nominal 25 ml sampler, which was the largest gas sampler available.

At small gas sample volumes (volumes less than about 1 ml) a problem of another sort arose. The method of construction of the gas sampling attachment is such that the system contains a dead volume which is filled with gas during every sampling operation. This volume must be added to the volume of the calibrated (see page 27) gas sampling loops if accurately known gas volumes are to be obtained.

Liquid samples may be obtained and analyzed reproducibly by using the Perkin-Elmer Micro-Dipper Sample Introduction System. The liquid sample is drawn into a glass capillary dipper of the desired size by capillary action, and then forced into the sample introduction attachment and the instrument system by a stream of carrier gas at a slightly higher pressure than that in the instrument.

C. Special Apparatus

Two important pieces of equipment had to be fabricated for this research. These pieces are an irradiation cell and a cold trap for collecting volatile radiolysis products.

The x-ray beam is composed to a large extent of low energy photons (10-30 KV) which do not penetrate a liquid sample deeply. It was desirable, therefore, to design an irradiation cell which would provide continual stirring during irradiation. In addition, since gaseous radiolysis products were known to be formed it was necessary to provide an outlet for them to prevent pressure build-up and to make it possible to trap and analyze them. The x-ray tube, as shown in Fig. 2, is mounted with the beam coming vertically down into the irradiation cell. To prevent loss of gaseous products around the end of the x-ray tube, and to prevent air from leaking in, a fairly large pressure must be exerted on the irradiation cell to hold it up tightly against the tube. This pressure was sufficient to crack a glass cell which was otherwise satisfactory. A brass cell has been fabricated which meets the requirements mentioned above but which must be coated with polyethylene to prevent dezincification whenever acidic dosimetry solutions are put into it. Despite this shortcoming, the cell has been used for the work reported here, and has proven to be satisfactory. It is likely that this brass cell is not the final answer, however, and a stainless steel irradiation cell is being considered.

During all irradiations to date, a stream of argon gas has been continuously bubbled through the irradiation cell. The argon is introduced through an arm of a gas lift-pump fastened to the bottom of the irradiation cell. In this way continuous stirring of the liquid being irradiated is assured. Flow rates of argon of 2 to 5 ml per minute have been used. Flow rates are kept low to keep down argon dilution of the volatile radiolysis products (especially hydrogen and methane). Figure 3 gives dimensions of the cell, and clearly shows the lift-pump arrangement.

As the argon moves out of the irradiation cell it carries with it a steady-state amount of radiolysis products as well as a very little of the high-boiling organic liquid sample. All gases which liquify at the temperature of tap water are returned to the irradiation cell by the packed condenser shown in Fig. 2. The remaining gases pass out of the lead-lined box into the glass cold trap shown in Fig. 4. The cold trap is normally held at the salt-ice mixture temperature (about -20°C). Four or 5 ml of the liquid being irradiated are placed in the cold trap and the gases bubbled through it to ensure that gases condensable at -20°C are actually cooled to that temperature. In addition to providing good thermal contact with the gases and a cold reservoir for heat uptake, the liquid in the trap also provides a non-reactive solvent for the gases, reducing their vapor pressures by a colligative as well as a thermal action. Finally, sampling the cold-trapped compounds is an easy matter, and an almost unlimited number of samples for the gas chromatograph may be taken from 4 ml of solution: (An order-of-magnitude calculation serves to show that no significant radiolysis product will be missed because of excessive dilution by 4 ml of diluent: the beam output caught in the sample is about 8×10^{17} e.v./sec.; in 25 hours a total of

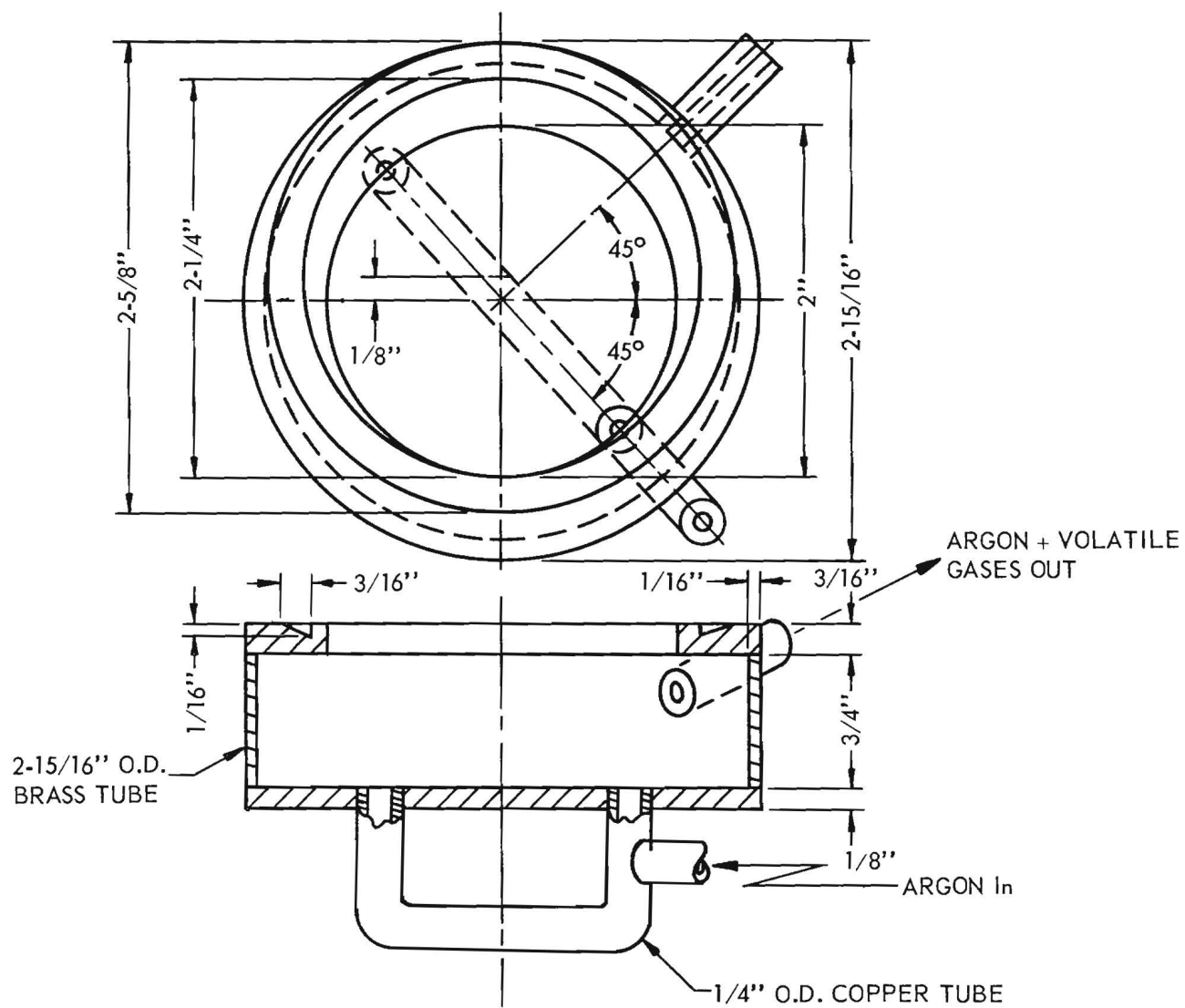


Figure 3. Irradiation Cell.

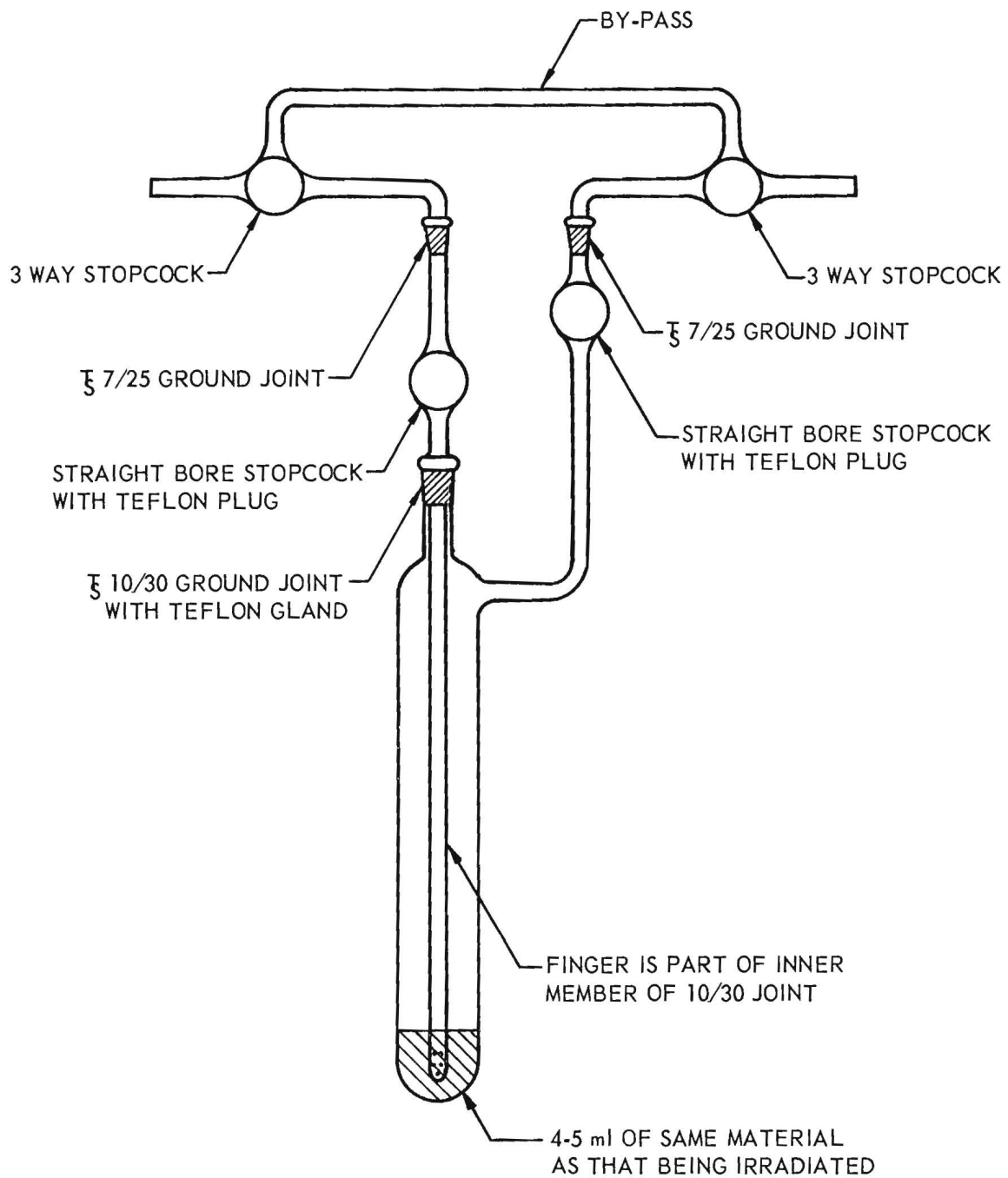


Figure 4. Cold Trap.

7.2×10^{22} e.v. will have been absorbed, so any radiolysis product with a G value of 0.01 or greater will be present in the cold trap liquid at a concentration of about $7.2 \times 10^{22} \times 10^{-2} \times 10^{-2} \times \frac{1000}{4} \times \frac{1}{6 \times 10^{23}} = 0.003 \text{ M}$. On a mole fraction basis this amounts to about 0.0006 mole fraction, or around 60 parts per hundred thousand. The gas chromatograph has a limiting sensitivity of around 1 part per hundred thousand).

D. Still Description

The general method of attack in separating the components of Amsco 125-82 has been distillation and then redistillation of selected cuts of the initial distillation. Four large-scale distillations (1.5 liters) of Amsco 125-82 have been run. The cuts from those four distillations which were richest in the component desired to be separated were combined and redistilled. The large-scale distillations were carried out in a 5/8 inch diameter column. The small-scale distillations of the combined cuts (150-300 ml) were carried out in a 1/2 inch diameter column. The smaller column, of course, reduces the hold-up as well as the through-put. The major components of the distillation set-up are the stand and support, the column and heat jackets, the reflux head, the heat control system, and the vacuum system.

The stand and support for the column and accessory equipment are constructed of half inch iron pipe in a lattice pattern.

The column itself is shown in Fig. 5. It is constructed of three concentric pyrex glass tubes of successively larger diameters. The inner tube serves as the distillation column and contains the packing. The next tube serves as the heating element support and provides a dead air space between the heating element and the distilling column. The outer tube provides a

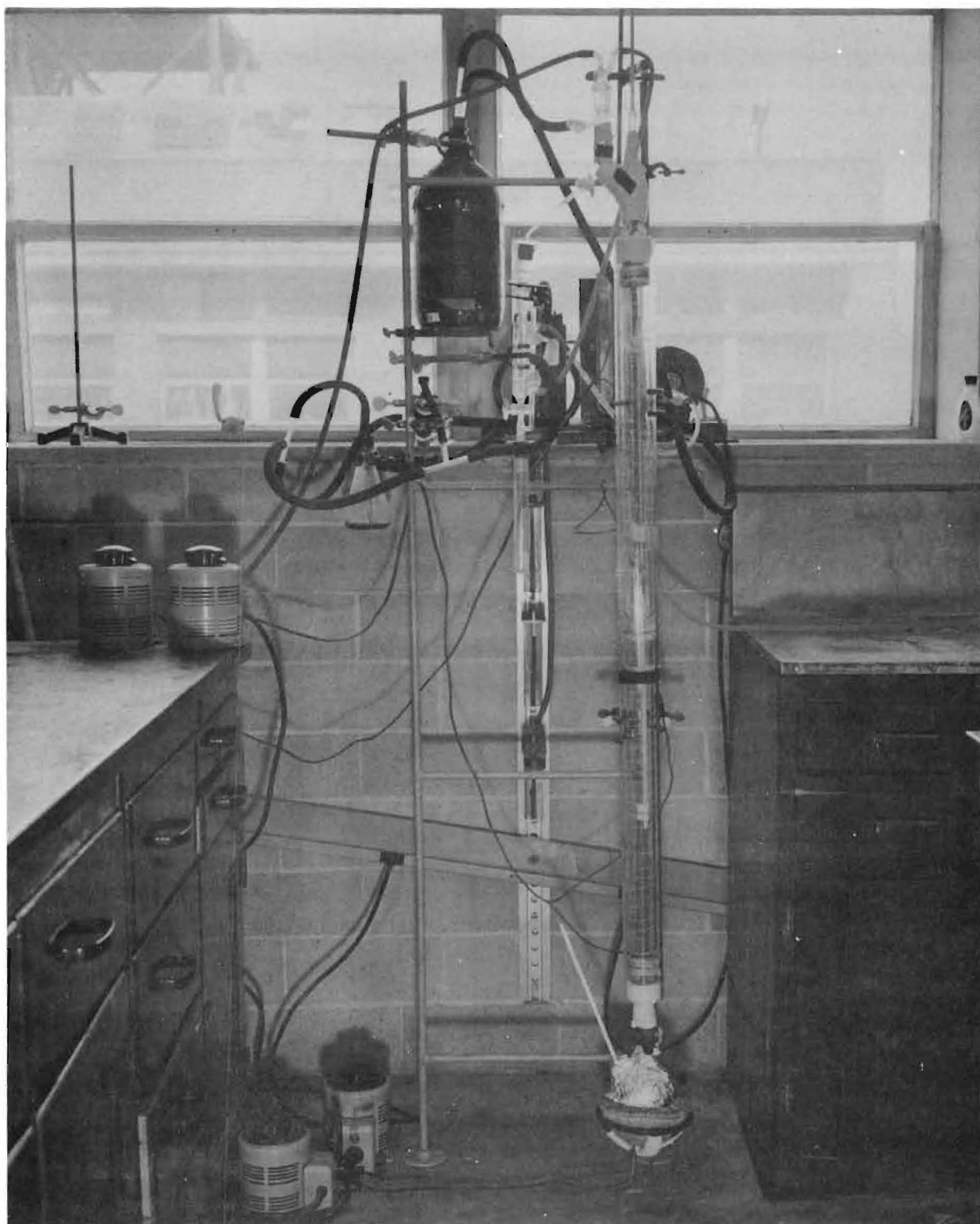


Figure 5. Distillation Column.

protective cover for the other tubes and the heating element and provides a dead air space between the heating element and the column surroundings. The three tubes are held together as a unit by packing asbestos tape between the tubes at each end. This also serves to make the dead air space more effective by preventing air circulation. Small holes are provided in the outer tube to allow entrance and exit of the column heating element leads. The inner tube is provided with projections on the inner surface near the lower end to support the packing.

Several columns of this general design have been used in this work. The only variations have been in dimensions and packing. All of the inner tubes are constructed with ground glass joints at each end for the attachment of the still pot and the distilling head.

The different column packings that have been used are case-hardened 3/16 inch single turn pyrex glass helicies and #2116 and #2117 nichrome, Podbielniak Heli-Pak packing. The glass helicies were used until the more efficient Heli-Pak packing was obtained. Although the Heli-Pak packing seems to be much more efficient, it presents greater operating problems. Flooding is particularly hard to prevent.

The reflux head is composed of a "cold finger" condensing surface which drips directly over a take-off stopcock. There is also a standard taper joint by which a thermometer with a standard taper plug may be introduced a few inches above the packing just before the condenser. The distilling head is fitted to the inner tube of the column by means of a standard taper joint. The plug in the take-off stopcock is of teflon and has been modified for accurate control by notching. This teflon plug has the advantage of requiring no lubricant. Ordinary stopcock greases are somewhat soluble in hot Amsco.

The reflux ratio is measured by counting the drops of liquid condensing off of the "cold finger" condenser tip per minute and the drops of liquid from the take-off arm per minute. It has been determined empirically that 20 drops of hydrocarbon is equal to approximately 0.6 to 0.7 ml. The reflux ratio is determined for a given through-put by carefully adjusting the take-off stopcock until the desired ratio is obtained. The reflux ratio that has been used is ~ 30 to 1.

The heat input to the column is through two sets of nichrome wire windings around the intermediate glass tubing. Each set of windings covers two feet of the packed column and contains approximately 25 turns with a total resistance of 45 ohms for each set. The voltage to each winding is controlled by a separate variable transformer. The purpose of these column heating coils is to balance the heat losses from the inner distillation tube and make it effectively adiabatic.

A careful distillation at atmospheric pressure of two liters of Amsco 125-82 failed to separate its seventeen or so components into any less than five or six components in each fraction. Vacuum distillation was shown by Mr. W. Baldwin, ORNL Chemistry Division, to effect more complete separation.

Qualitatively, as has been noted, the cuts from the preliminary distillation of Amsco 125-82 at atmospheric pressure did not contain less than five components per cut. However, distillations at a pressure of 16 mm Hg produced cuts from the initial distillation of about three components per cut. Due to the better results obtained at 16 mm Hg pressure, all subsequent distillations have been run at this reduced pressure.

The vacuum system used consists of a Cenco Presovac 4 pump, a Todd type pressure regulator, a standard U-tube mercury manometer, a surge tank, and an oil trap.

The Todd pressure regulator using mercury has a range of 2-50 mm Hg with a sensitivity reported by the manufacturer of ± 0.01 mm Hg. The fraction cutter is maintained at a pressure slightly below the column. This makes the take-off rate control somewhat easier to set at very low flow-rates.

There is an optimum through-put rate at which the column operates smoothly. If the heat input to the still is increased slightly the column floods; if the heat input is reduced there is practically no reflux. The through-put is determined by counting the drops from the "cold finger" condenser per minute and converting to ml/minute by the conversion factor above. The through-put rate on the large column (5/8 inch x 4 feet) is approximately 5 ml/minute and the through-put on the small column (1/2 inch x 4 feet) is approximately 0.5 ml/minute. Both of the above are for Podbeilniak #2117 packing. It is realized that the above types of determinations are not extremely accurate, due mainly to internal reflux and condensation other than on the "cold finger". However, they do give operating parameters with which to work.

The basic control for the whole column for a given take-off and pressure is, of course, the heat input. It is desirable to make the column as adiabatic as possible; that is to put just enough heat into the jacket surrounding the distillation column to balance the losses by radiation and convection. An estimate of the heat input necessary to accomplish this can be made fairly accurately.

Heat is put into the apparatus in two places: the still pot and the column. The heating elements that have been used for the various still pot sizes are glass-cloth heating mantles. The voltage control into the still pot mantle is provided by two variable voltage transformers in series. The transformers are hooked in series in order to get a fine voltage adjustment to the still pot heating mantle.

Since little is known about the individual components of Amsco 125-82 no calculations can be made concerning the various column efficiencies. It is possible however, to infer from the results that the columns used are quite efficient, even though nothing quantitative can be said about their efficiency. As a general rule, components boiling within one to two degrees centigrade of each other will require approximately 100 theoretical plates to effect a 95 percent separation of the high boiling component.

E. General Analytical Equipment

In the identification of a saturated hydrocarbon having a molecular weight of the order of 170 to 194 (C_{12} to C_{14}) about the most useful property is the infra-red and near-infra-red absorption spectrum. The information provided by the absorption spectrum, along with an accurate molecular weight determination, may be sufficient to reduce the number of possible structures to an isomer ^{or} ~~of~~ two in favorable cases. The lack of functional groups makes other standard identifying tests of very little value. Time of emergence from the gas chromatograph has considerable value for identification purposes at low molecular weights, where isomerization is not so extensive, but great caution must be used when the chance for many very similar compounds to be present exists. It is quite possible, for example, for a straight chain compound to emerge coincident with a highly branched compound which has two methylene groups greater molecular weight.

In this work a Perkin-Elmer model 21 recording spectrophotometer equipped with sodium chloride optics and prism has been used fairly extensively. Sodium chloride sample cells with a nominal 0.022 mm sample thickness have been used.

In addition to the infra-red spectra a Beckman model DK-2 automatic recording spectrophotometer has been used to record the ultra-violet absorption spectra of the hydrocarbons both before and after their irradiation. In

running these absorption spectra matched quartz cells having a 1 cm path length have been used for sample and blank. Iso-octane has been used for a reference liquid as well as for an inert solvent for the hydrocarbons, which are too optically dense in the ultra-violet region to be analyzed undiluted. Concentrations of between 20 and 200 grams of sample per liter of iso-octane have been used successfully.

III. LIKELY COMPONENTS OF AMSCO 125-82

It was stated by J. H. Goode in a Progress Report on "Extraction Reagent Performance", for the period from October 1956 to January 1957, that Amsco 125-82 is made from the polymerization of butenes and pentenes. Using this information, a number of inferences can be drawn about the products which might be formed. These are given below. Additional information has been requested from the American Mineral Spirits Company to enable more accurate conclusions to be drawn about relative amounts of components which are probably formed.

A. Assumptions

- 1) The composition of the mixture of butenes and pentenes was not reported. It was assumed that all possible isomers of both butene and pentene were present, and that the polymerization was acid-catalyzed.
- 2) Of the possible carbonium ions from a mixture of the isomeric butenes and pentenes, the most stable and the most reactive would be the tertiary butyl and the tertiary amyl carbonium ions.

References: (i) Whitmore, "Chem. and Eng. News", 26 668 (1948). (ii) Ipatieff and Schaad, "Ind. Eng. Chem.", 37, 362 (1945).

In the copolymerization of isobutylene with propene in the presence of phosphoric acid, no more than a trace of the product (2,4-dimethylpentene) which would be formed by the addition of the isopropyl carbonium ion to isobutylene was found. The products (2,2-and 2,3-dimethyl-x-pentene) found were formed by the addition of the t-butyl carbonium ion to propene.

(iii) Whitmore, et al, JACS, 63, 756 (1941).

In the copolymerization of isobutylene with 2-butene, in which equimolar quantities of tertiary butyl and sec-butyl alcohols at 64° in 75 per cent sulfuric acid were used, the formation of the products found could be explained on the basis of the addition of the t-butyl carbonium ion to either isobutylene or 2-butene. None of the products which would be expected by the addition of sec-butyl carbonium ion to iso-butylene or 2-butene were obtained.

- 3) The addition of a carbonium ion to an ethylenic double bond would follow the Markownikoff rule. That is, the carbonium ion would add to that carbon of a carbon-carbon double bond which has the greater number of hydrogen atoms.

Reference: Royals, "Advanced Organic Chemistry", Prentice-Hall, Inc., p. 214.

- 4) A number of olefins were eliminated as intermediates on the basis that the addition of a t-butyl cation or t-amyl cation to the olefin would be unlikely because of steric hindrance.

Reference: (i) Whitmore, et al, 63, 2035 (1941).

Of the isomers present in triisobutylene, no product was found which would have been formed by the addition of a t-butyl cation to 2,4,4-trimethyl-2-pentene ($\text{c}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\text{c}=\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\text{c}$), which is formed in about twenty per cent yield in the dimerization of isobutylene.

(ii) Whitmore and Meunier, JACS, 63, 2197 (1941).

In the dimerization of tetramethylethylene in the presence of eighty per cent sulfuric acid, none of the products found correspond to the simple addition of a carbonium ion formed from the tetramethylethylene to another molecule of the tetramethylethylene.

- 5) None of the possible carbonium ions from the octenes, nonenes, and decenes were used in predicting possible addition reactions with the isomeric butenes and pentenes as it seems that the yields would be quite low.

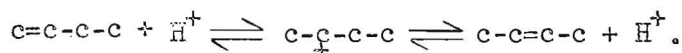
Reference: (1) Whitmore, et al, 63, 2035 (1941).

Of the products present in triisobutylene, ninety per cent of the products (two dodecenes) can be accounted for by the addition of t-butyl cation to 2,4,4-trimethyl-1-pentene. The other ten per cent can be accounted for by the addition of the tertiary carbonium ion $(\text{c}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\text{c}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}})$, formed by the addition of a proton to 2,4,4-trimethyl-1-pentene or 2,4,4-trimethyl-2-pentene, to isobutylene.

- 6) Some intermediates, which would be formed by the addition of t-butyl or t-amyl cation to 1-butene or 1-pentene, were eliminated as it seems likely that the yields would be low.

Reference: (1) Brooks, "Ind. Eng. Chem.", 41, 1694 (1949).

In the copolymerization of isobutene with 1-butene, 32.7 per cent of the products could be accounted for by the addition of the t-butyl cation to 1-butene whereas 56.3 per cent of the products could be accounted for by the addition to 2-butene, which could be formed as follows:



- 7) The presence of isomeric decanes in large amounts in Amsco 125-82 does not seem likely as the initial boiling point in the fractionation of Amsco at atmospheric pressure is 167°. Only one (3,3-dimethyl-4-ethylhexane) of the decanes most likely to be present has a boiling

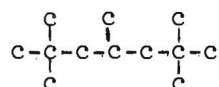
point (170°) higher than 167°. Two other decanes, 3,4-dimethyloctane and 2-methyl-3-ethylheptane, have the same boiling point, 166°. Also, the molecular weight determinations of the first large fraction (#2-5) give an average value of 173.4, whereas the decanes have a molecular weight of 142.

- 8) The presence of isomeric undecanes does not seem likely as it is not possible to form an eleven carbon hydrocarbon by any combination of any of the isomers present in a mixture of isomeric butenes and pentenes.

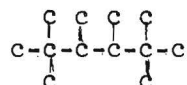
B. Probable Components

1) C₁₂ hydrocarbons

(i) 2,2,4,6,6-pentamethylheptane

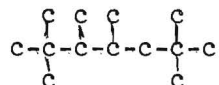


(ii) 2,2,3,4,5,5-hexamethylhexane

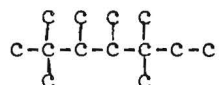


2) C₁₃ hydrocarbons

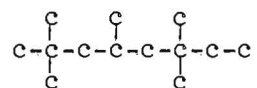
(i) 2,2,3,4,6,6,-hexamethylheptane



(ii) 2,2,3,4,5,5,-hexamethylheptane

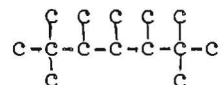


(iii) 2,2,4,6,6-pentamethyloctane

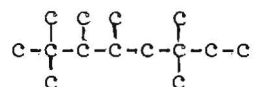


3) C₁₄ hydrocarbons

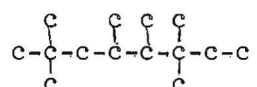
(1) 2,2,3,4,5,6,6-heptamethylheptane



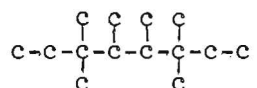
(ii) 2,2,3,4,6,6-hexamethyloctane



(iii) 2,2,4,5,6,6-hexamethyloctane



(iiii) 3,3,4,5,6,6-hexamethyloctane



IV. EXPERIMENTAL

The experimental work has been largely in the three areas of calibrating the x-ray and gas chromatographic equipment, analyzing the Amsco 125-82, and performing irradiations of purified representative hydrocarbons.

A. X-ray Dosimetry

The basis for all the dosimetry work reported here is the series of calorimetric determinations of the energy output of a Machlett OEG-60 tungsten target end window tube made by Dr. E. L. Alexander. In his determinations a known fraction of the tube output was absorbed in either water or o-xylene. Using standard calorimetric procedures he was able to show that the accepted G value of 15.5 for the oxygen-saturated ferrous sulfate-sulfuric acid dosimeter was valid to within a possible error of 10% for the radiation from that tube. It was important to establish that this was so because a large fraction of the photons from the Machlett OEG-60 x-ray tube are of energies lower than those for which the G value of 15.5 had been demonstrated to be valid. Further experiments have shown that a G value of 15.2 is the correct one to use when the dosimeter solution is air-saturated rather than oxygen-saturated.

Calibrations of the brass irradiation cell were made using the ferrous ion dosimeter. Since these experiments were made under air-saturation conditions the G value of 15.2 was employed in the calculations. The presence of sulfuric acid in the dosimeter solution made it necessary to coat the brass irradiation cell with polyethylene to prevent acid attack (dezincification). The volume of hydrocarbon used in this work has customarily been an accurately measured 30 ml. For this reason 30 ml of dosimeter solution was chosen. This procedure ensured a constant depth of solution in the irradiation cell. (It was recognized

that for the soft, non-homogeneous radiation from the x-ray tube used a given depth of aqueous solution does not absorb the same fraction of the x-ray beam as the same depth of organic liquids. A correction based on electron density and on measured fractional beam absorption in various thicknesses of dosimeter solution has been made and is presented in section IV. D. below.)

The total x-ray tube beam power was found to be 0.25 watt by irradiating a volume of dosimeter solution which was so large that an increase in either depth or diameter caused no measureable increase in the equivalents of iron oxidized in a given time. Thirty ml of dosimeter solution in the irradiation cell was then shown to absorb energy at a rate of 0.12 watt. From this it is evident that about 50% of the total x-ray beam is absorbed in the irradiation cell. That part of the beam which is not absorbed is primarily from the high energy portion of the beam and so a disproportionately large fractional increase in dosimeter solution volume would be required to contain, say, 75 per cent of the beam. Because obtaining useful volumes of purified hydrocarbons is one of the major problems in this work, increased beam absorption at the cost of considerably increased sample size did not seem profitable and was not pursued.

From the foregoing it is seen that the dose received by dosimeter solution in the irradiation cell cannot exceed $\frac{0.12}{0.030} = 4$ beta watt-hours per liter in one hour. The dose received by the same volume of organic liquids is somewhat less because of a lower electron density.

B. Gas Chromatograph Calibrations

The gas chromatograph is a quantitative analytical device if it is calibrated under carefully controlled conditions for each substance for which it is used. Variations in response caused by changing carrier gases are so pronounced

that calibrations are valid only for a specific carrier gas. (This follows qualitatively from the fact that response is related directly to the difference in thermal conductivities of the substance being analyzed for and the carrier gas.) Small changes in column temperature or in flow rate of carrier gas are intolerable because they alter the time of emergence of the substances passing through the instrument and so make identification based on time of emergence impossible. In addition, calibrations must be made using sample sizes not very different from those to be used during the actual analysis.

Although the gas chromatograph is supplied with gas and liquid samplers made by Perkin-Elmer, it was soon found that the nominal gas sampler volumes were considerably different from their true volumes as determined by weighing the amount of mercury each would hold and then dividing by the density of mercury. Table II lists the nominal and the true volumes of the gas samplers. The dead volume in the sampling attachment (see page 7) and the volumes of two homemade samplers are given for completeness.

The gas sampling attachment of the gas chromatograph is used primarily for taking periodic hydrogen and methane samples during the course of an irradiation. For this reason, the instrument has been carefully calibrated for these two gases. The necessary calibrations required that each gas be sampled using several of the gas samplers, and that these samples be run against argon carrier gas, which is used as sweep-gas during irradiations. The conditions of temperature, pressure, and flow rate were chosen to produce a large signal from the thermal conductivity gage and to permit a sample to be run in 5 to 10 minutes. Temperature and pressure corrections were made on the sample volumes so that the number of moles of gas which produced a given instrument response could

TABLE II
GAS SAMPLER CALIBRATIONS

Description	Volume [†] (cc)
Dead volume	0.099
P-E nominal 0.25 cc	0.294
Homemade nominal 0.50 cc	0.603
Homemade nominal 1.00 cc	1.031
P-E nominal 1.00 cc	1.487
P-E nominal 5.00 cc	5.272
P-E nominal 25.00 cc	23.31
[†] At room temperature.	

be calculated. From these data it was possible to plot a graph of instrument response (expressed as the area under the curves produced by using the output from the thermal conductivity gage to drive a recorder) versus moles of gas.

The column packing used for these calibrations was molecular sieve. Because the 25 cc (nominal) sampler is used routinely to take gas samples during irradiations it is necessary to use the modified molecular sieve column to prevent peak distortion. (See page 7) For this reason the calibrations were also made using that column.

The hydrogen calibration curve, along with the conditions of analysis listed according to the convention adopted in this work, is given in Figure 6. The calibration curve for methane is shown in Figure 7.

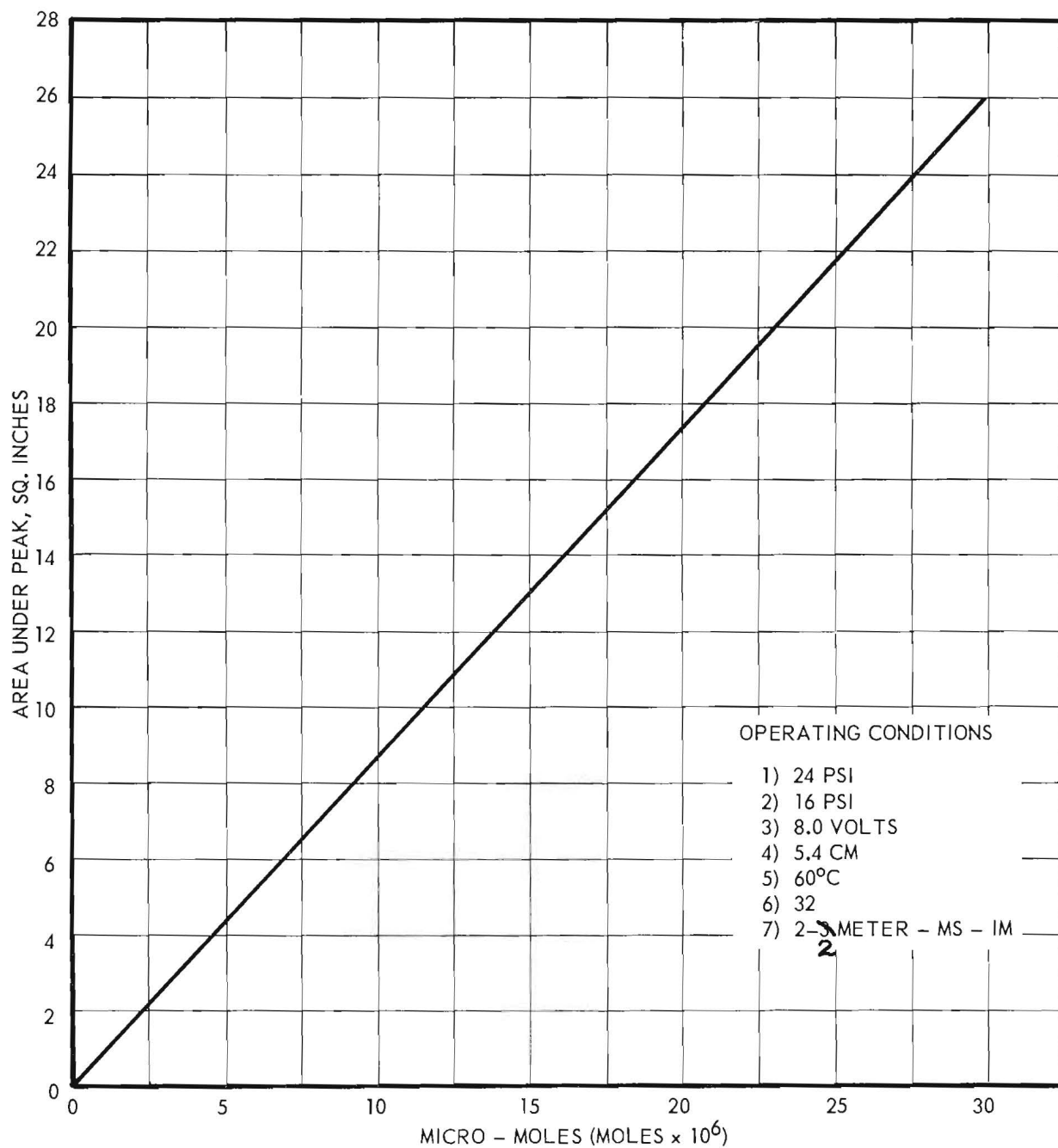


Figure 6. Hydrogen Calibration.

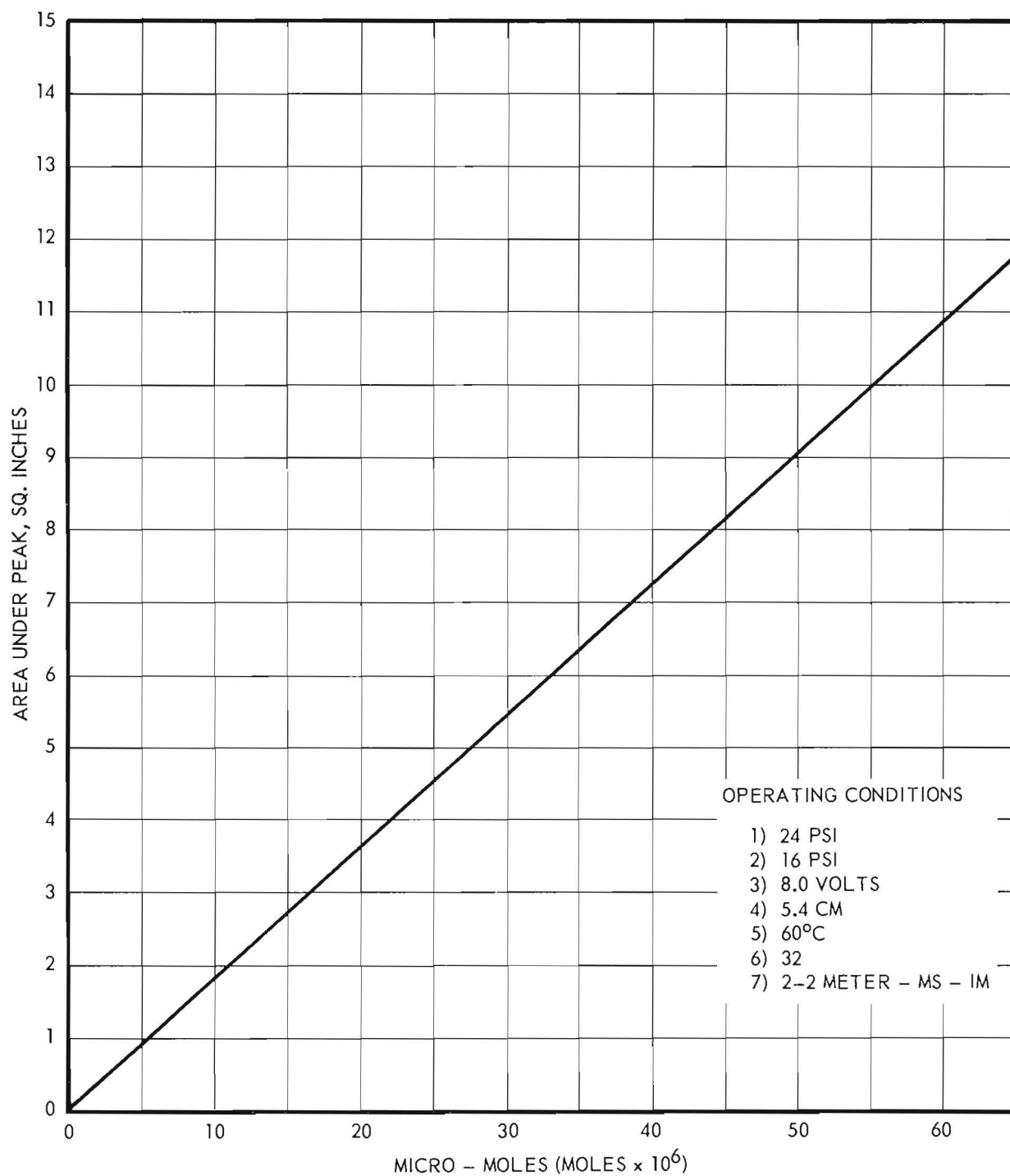


Figure 7. Methane Calibration.

The convention for listing column operating conditions is as follows:

- 1) Carrier gas tank pressure
- 2) Column pressure
- 3) Conductivity gage voltage
- 4) Flow meter reading, in cm
- 5) Column temperature
- 6) Temperature setting scale
- 7) Column description.

The column description, item 7, is given by listing first the number of columns used (the instrument will accommodate either one or two columns), second the length of a column, third a letter indicating the column packing, and fourth, special modifications, if any. Thus, "2-2 meter-MS-1M" means that two molecular sieve columns each of 2 meters length, and embodying one modification were used.

At present the gas chromatograph is being calibrated for use with liquid unknowns in the five-carbon to eight-carbon atom range. Studies made so far in this work indicate that most of the light radiolysis products other than hydrogen and methane will be in this range.

C. Characterization of Amsco 125-82

There are at least seventeen components in Amsco 125-82. These components give the average properties shown in Table III.

1. Density

The density was determined by pipetting 25 ml of the Amsco 125-82 into a tared weighing bottle at 24.2° C.

2. Boiling Range

The range obtained during distillations at atmospheric pressure has been used here.

TABLE III
PROPERTIES OF AMSCO 125-82

-
1. Density: 0.7468 g/cm^3 24.2° C.
 2. Boiling Range: 165 to 210° C. (atmospheric pressure)
 3. U. V. Absorption: Considerable absorption between 300 and $220 \text{ m}\mu$
 4. Bromine Test for Unsaturation: Positive
 5. Potassium Permanganate Test for Unsaturation: Negative
 6. Average Molecular Weight: 184 (this value is probably about five units low)
 7. Hydrogenation Test for Unsaturation: 0.76 mole per cent unsaturation; based on Avg. Mol. wt. of 184
 8. Formation of Urea Adducts: Negative, indicating a high degree of branching
 9. Iodine Number (Hanus Method): $2.4 \text{ gI}_2/100\text{g Amsco 125-82}$
 10. Refractive Index: 1.41767 at 30° C. using Na D line
-

3. U. V. Absorption

Ten ml samples of Amsco 125-82 dissolved in 25 ml of iso-octane run against an iso-octane blank gave high absorption from about $300 \text{ m}\mu$ to $220 \text{ m}\mu$, going to nearly complete absorption at $220 \text{ m}\mu$.

4. Bromine Test

Tests with a two per cent bromine solution in carbon tetrachloride indicated a small amount of unsaturation.

5. Permanganate Test

Tests with a 0.5 per cent aqueous solution of potassium permanganate were negative for unsaturation.

6. Molecular Weight Determinations

Molecular weight determinations by the freezing point lowering method were made on the Amsco 125-82, and on known samples of iso-octane and 1-dodecene as checks on the method. Both benzene and cyclohexane were used as solvents. Cyclohexane gave better results on the known samples. Therefore, the molecular weights given below were determined using cyclohexane. Iso-octane gave a value of 111 as compared with the calculated molecular weight of 114, and 1-dodecene (Matheson, Coleman and Bell) gave a value of 163 as compared with the calculated molecular weight of 168. Molecular weight determinations on Amsco 125-82 gave a value of 184. This value may be four or five units low, indicating strongly that at least one fourteen-carbon-atom component is present.

7. Hydrogenation

The determination of the amount of unsaturation in Amsco 125-82 by measuring the amount of hydrogen absorbed, using PtO_2 as a catalyst, by a sample of Amsco, gave a value of 0.76 mole per cent unsaturation using a molecular weight of 184 for Amsco.

8. Urea Adducts

The treatment of Amsco 125-82 with a saturated urea-methanol solution does not yield a urea-hydrocarbon adduct, which indicates that the hydrocarbons present in Amsco are highly branched.

9. Iodine Number

Iodine numbers were determined by the ~~Hanus~~ Method, which is based on the reactivity of an iodine-bromine species rather than the iodine-chlorine species which is used in the Wijs Methods. An average value of 2.4 was obtained.

10. Refractive Index

A refractive index value of 1.4167 was obtained using the sodium D line in a refractometer thermostated at 30° C. Refractive indices taken on impure cuts from the distillations ranged from 1.4134 to 1.4207. These measurements seem to provide a sensitive parameter for distinguishing between hydrocarbons.

A gas chromatograph of Amsco 125-82 is shown in Figure 8. The envelope (indicated by the heavy line) which the instrument draws has been resolved into the individual peaks shown by assuming the peaks to be symmetrical. This assumption is valid to a very good approximation. Figure 9 is an infra-red spectrum of Amsco 125-82.

D. Irradiation of 2,2,4,6,6-Pentamethylheptane

On the basis of conclusions drawn in section III (beginning on page 7) of this report a likely component of Amsco 125-82 is 2,2,4,6,6-pentamethylheptane (to be referred to hereafter as PMH). This compound can be made in good yield by catalytic hydrogenation of commercially available triisobutylene. Even if PMH itself is not present in Amsco 125-82, it must be so similar to the constituents of Amsco that a study of its radiation chemistry should be directly useful to this work.

Several hundred milliliters of triisobutylene were hydrogenated and fractionally distilled to obtain about 100 ml of PMH of greater than 95% purity (purity was estimated using peak areas obtained using the gas chromatograph and assuming mole per cent to be proportional to peak area). The time of emergence of the PMH coincided with that of one of the peaks of the Amsco which, along with the inferences of section III, lead to the tentative assignment of the

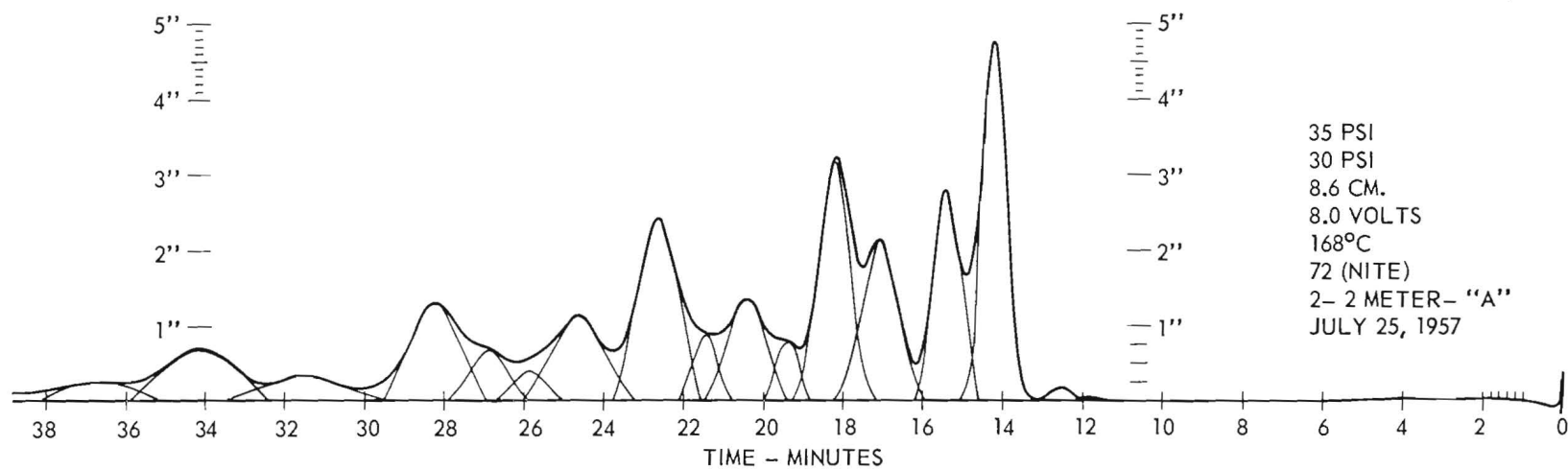


Figure 8. Gas Chromatograph of Amsco 125-82. (0.005 ml sample; sensitivity: x2).

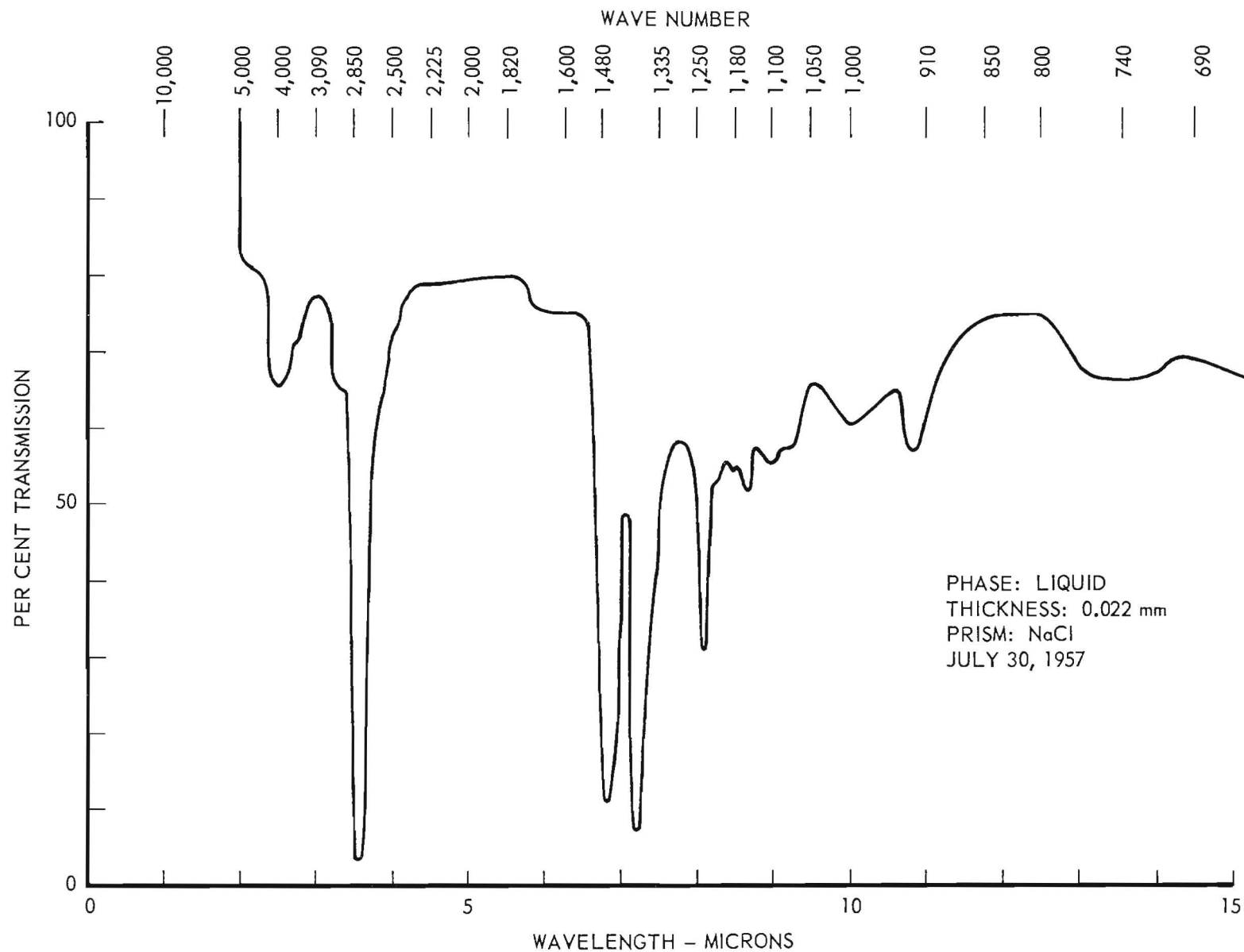


Figure 9. Infra-red Spectrum of Amsco 125-82.

formula of PMH to the Amsco constituent in question. Further work with infra-red analyses have not confirmed this tentative assignment, however, and the identification of the unknown Amsco peak is in question.

Four irradiations of PMH have been made to date. Two of these irradiations have been for about 25 hours. The other two were for shorter periods. These irradiations have yielded data from which G values of 1.15 have been determined for H_2 production and 0.78 for CH_4 production. Volatile radiolysis products have been cold-trapped and analyzed with the gas chromatograph. Iodine number, ultra-violet light absorption, infra-red energy absorption, and refractive index have been determined, and all have been found to increase upon irradiation of PMH, with the exception of infra-red absorption.

The G value determinations are based on the calibrated response of the gas chromatograph to hydrogen and methane, and the energy absorption correction required to convert from energy absorbed by aqueous dosimeter solution to energy absorbed by an equal thickness of PMH. The assumption which must be made to apply the energy absorption correction is that the electron density of a substance is the primary determinant of x-ray stopping power.

To illustrate the method of determination of G values the following example, chosen from the third irradiation, is cited.

Example of G Value Determinations

Conditions: 50 KVP, 45 Ma; argon sweep-gas flow rate 2.46 ml/min;
duration of irradiation 195 min (3 hrs and 15 min);
30 ml sample of 6.5 mm depth; brass irradiation cell;
744.3 mm Hg barometric pressure; 26-27° C.

Procedure: The x-ray is turned on and the timer is started.
After 30 to 60 minutes the rates of hydrogen and

methane evolution reach their steady state values. This is verified by analyzing for H_2 and CH_4 in the argon sweep-gas every few minutes. When several successive sweep-gas samples show the same H_2 and CH_4 peak heights, the areas under the peaks may be measured (generally with a planimeter), and the moles of H_2 and CH_4 present in the sample determined by reference to Figures 6 and 7.

Calculations:

Hydrogen Production

- a) Area under H_2 peak = 6.3 sq. in.; from Figure 6, moles $H_2 = 7.23 \times 10^{-6}$; calibrated volume of gas sampler = 23.3 cc.
- b) Volume of argon sweep-gas through cell during irradiation = 0.0175 cu. ft. as measured with wet test meter; this becomes 478 ml of argon when corrected for the vapor pressure of water.
- c) Argon flow rate through irradiation cell and gas sampler = $478 \text{ ml} / 195 \text{ min} = 2.46 \text{ ml/min}$
- d) Rate of H_2 evolution = $7.23 \times 10^{-6} \times 2.46 / 23.3 = 7.66 \times 10^{-7} \text{ mole/min.}$ or $7.66 \times 10^{-7} \times 6.02 \times 10^{23} = 4.62 \times 10^{17} \text{ molecules } H_2/\text{min}$
- e) Rate of energy absorption by 30 ml (6.5 mm deep) of dosimeter solution as determined by Fe^{+2} equivalents oxidized = $4.36 \times 10^{19} \text{ e.v./min.}$
- f) Electron density of PMH = $\frac{740 \text{ g/l}}{170 \text{ g/mole}} \times 98 \frac{\text{electrons}}{\text{molecule}} \times 6.02 \times 10^{23} \frac{\text{molecules}}{\text{mole}} = 2.56 \times 10^{26} \frac{\text{electrons}}{\text{liter}}$
- g) Electron density of dosimeter solution = $3.38 \times 10^{26} \text{ electrons/liter}$
- h) Electron density ratio = $\frac{2.56 \times 10^{26}}{3.38 \times 10^{26}} = 0.76$

This means that a one cm depth of PMH has the same x-ray beam absorption as 0.76 cm of dosimeter

solution. From this it follows that the 6.5 mm PMH sample depth would absorb the same fraction of the beam energy as $0.76 \times 6.5 = 4.95$ mm of dosimeter solution.

- i) Figure 10 shows how energy absorption, as measured by ferrous ion oxidation, varies with depth of dosimeter solution. Values from the curve show that 6.5 mm gives 10.6×10^{-4} equivalent Fe^{+2} oxidized per hour, while 4.95 mm gives 9.7×10^{-4} equivalent Fe^{+2} oxidized per hour. Therefore, the fraction of the beam absorbed by 6.5 mm of PMH is only $\frac{9.7 \times 10^{-4}}{10.6 \times 10^{-4}} = 0.92$
- j) The rate of energy absorption by 6.5 mm of dosimeter solution is 4.36×10^{19} e.v./min; the rate of absorption by 6.5 mm of PMH is $0.92 \times 4.36 \times 10^{19} = 4.0 \times 10^{19}$ e.v./min.
- k) G value for $\text{H}_2 = \frac{4.6 \times 10^{17} \text{ molecules/min.} \times 100}{4.0 \times 10^{19} \text{ e.v./min}} = 1.15$

Methane Production

- a) Area under CH_4 peak = 0.90 sq. in.; from Figure 7, moles $\text{CH}_4 = 4.91 \times 10^{-6}$
- b) Rate of CH_4 evolution = $4.9 \times 10^{-6} \times \frac{2.46}{23.3} = 5.2 \times 10^{-7}$ mole/min. or $5.2 \times 10^{-7} \times 6.02 \times 10^{23} = 3.12 \times 10^{17}$ molecules/min.
- (combines steps b, c and d above)
- c) Rate of energy absorbed in PMH = 4.0×10^{19} e.v./min.
(taken from value obtained in steps e, f, g, h, i, and j above)
- d) G value for $\text{CH}_4 = \frac{3.13 \times 10^{17} \text{ molecules/min.} \times 100}{4.0 \times 10^{19} \text{ e.v./min}} = 0.78$

Volatile radiolysis products have been cold-trapped using a glass spiral immersed in a dry ice-alcohol bath. A small amount of liquid was trapped using this method. A gas chromatograph was run on the liquid, and the result

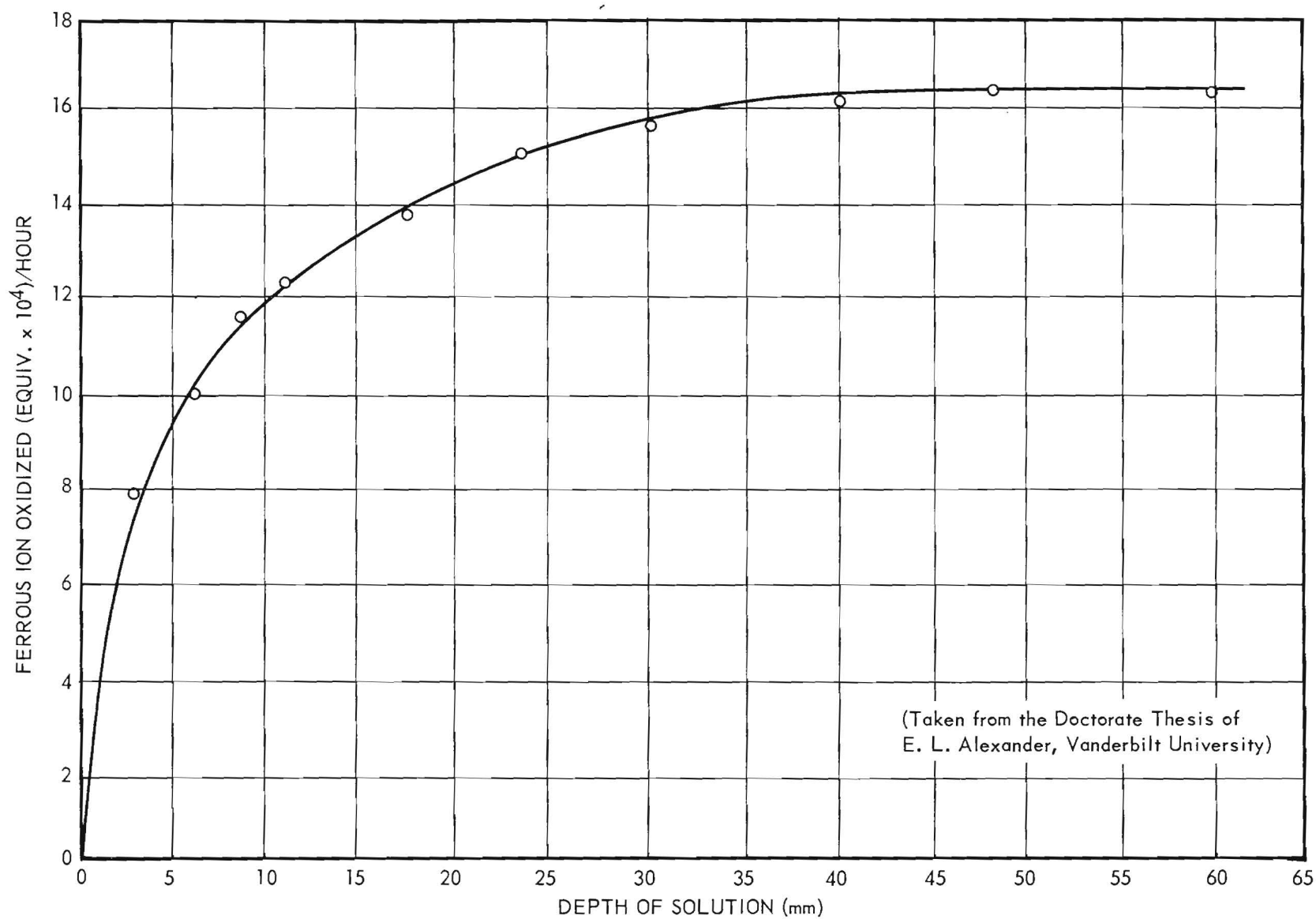


Figure 10. X-ray Energy Absorption vs. Depth of Dosimeter Solution.

is shown in Figure 11. From this curve it appears that a significant amount of the PMH is vaporized from the irradiation cell and carried off with the argon sweep-gas. In addition to the PMH peak, which emerges at 11.5 minutes, there is a smaller peak which comes through after only 4.1 minutes under the conditions shown. This peak has not yet been identified, but it seems likely that it represents a hydrocarbon molecule of less than eight carbon atoms. In addition to the small peak at 4.1 minutes, there are minor peaks at still shorter times which suggest radiolysis products which are even smaller than eight-carbon atom compounds. (These statements as to the approximate size of the radiolysis products are based on data obtained subsequent to December 30, 1957, and so do not properly belong in this report. The data will appear shortly in the first quarterly report for the contract period January 1, 1958 to December 31, 1958. As a matter of fact, use of the new cold trap discussed in section II. C. has made possible the trapping of nearly 20 radiolysis products, and present work is directed toward their identification.)

Iodine numbers are a useful measure of unsaturation in a compound. It must be recognized, however, that their first use was in the empirical comparison of unsaturated fats. Their adaptation to the quantitative measurement of unsaturation is an extension of their original use which must be considered carefully for each class of compounds for which the adaptation is to be used. In the simplest, ideal case the iodine number may be converted directly to number of double bonds per molecule of pure unsaturated compound, or number of double bonds created by irradiating a pure saturated hydrocarbon of known molecular weight, in cases where only a small fraction of the hydrocarbon molecules are affected. The basis for calculating number of double

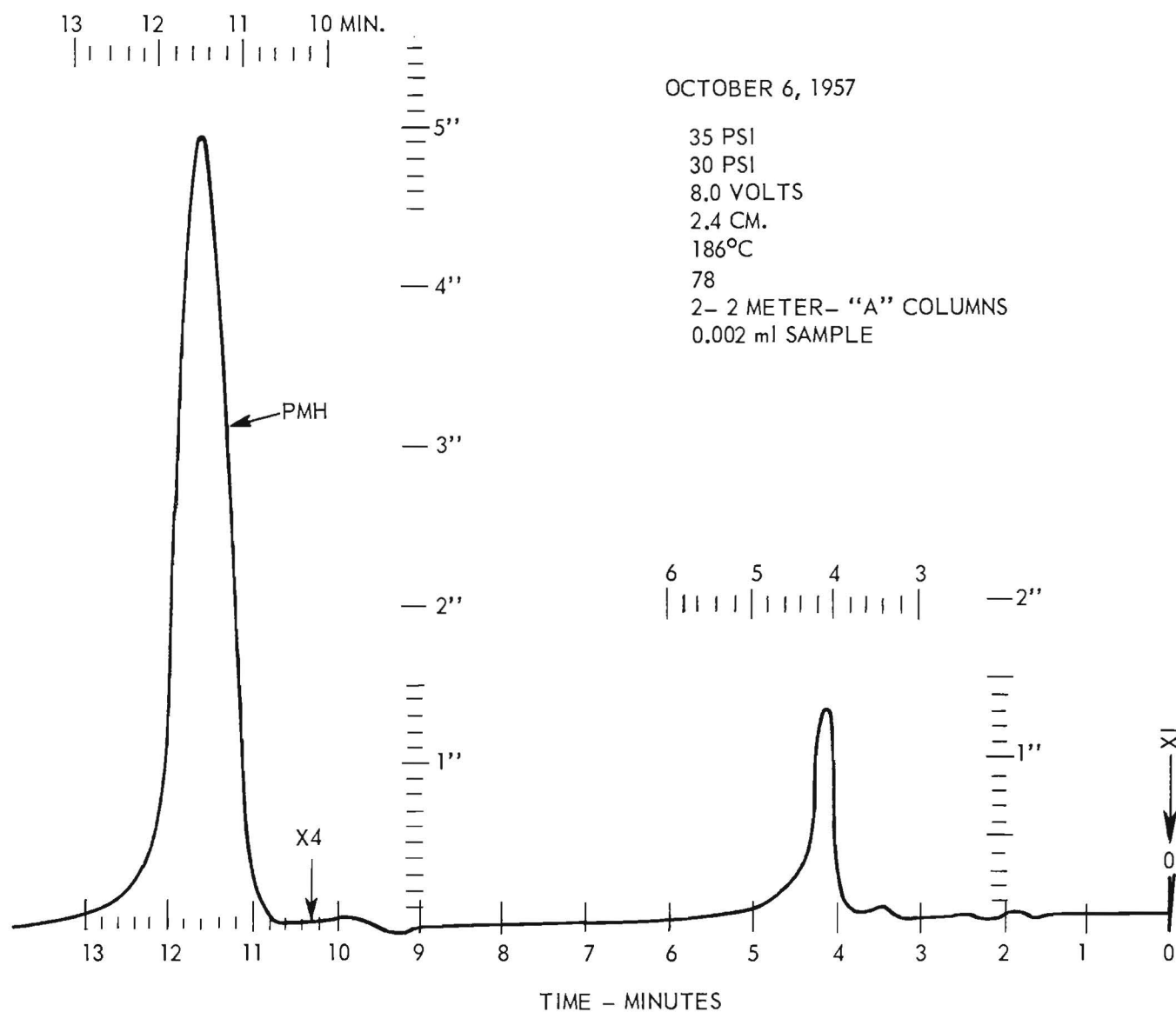


Figure 11. Gas Chromatograph of Cold-Trapped Liquid.

bonds from iodine numbers is the assumption that one I_2 molecule (or its equivalent) adds to each double bond. Thus, heptene-1 (molecular weight = 98) has an iodine number of $(254 \times \frac{100}{98} =)$ 260. Table IV shows how the iodine number of PMH (which has no unsaturation) changes upon irradiation for 25 hours. The iodine numbers were run using the Hanus Method which uses the halogenating properties of IBr.

Values of the refractive indices before and after irradiation are also included in Table IV.

TABLE IV
IODINE NUMBERS AND REFRACTIVE INDICES OF PMH

	<u>Iodine No.</u> ($gI_2/100g$)	<u>Refractive Index</u>
Before Irrad.	1.98	$n_D^{30} = 1.41478$
After Irrad.	5.51	$n_D^{30} = 1.41566$

The fact that fully-saturated PMH does appear to react with the Hanus solution to yield an iodine number, even though small, illustrates the shortcomings of the use of iodine numbers for quantitative unsaturation measurements. Iodine numbers should be substantiated by direct measurement of H_2 uptake in the presence of a catalyst in order to determine the bias in the Hanus method. These direct H_2 uptake measurements will be run as soon as the equipment can be assembled and set up.

The increase in ultra-violet light absorption is shown clearly in Figure 12. Such absorption strongly suggests double bond formation. The lack of distinctive absorption peaks precludes drawing any specific conclusions about the nature of the strongly absorptive radiolysis product.

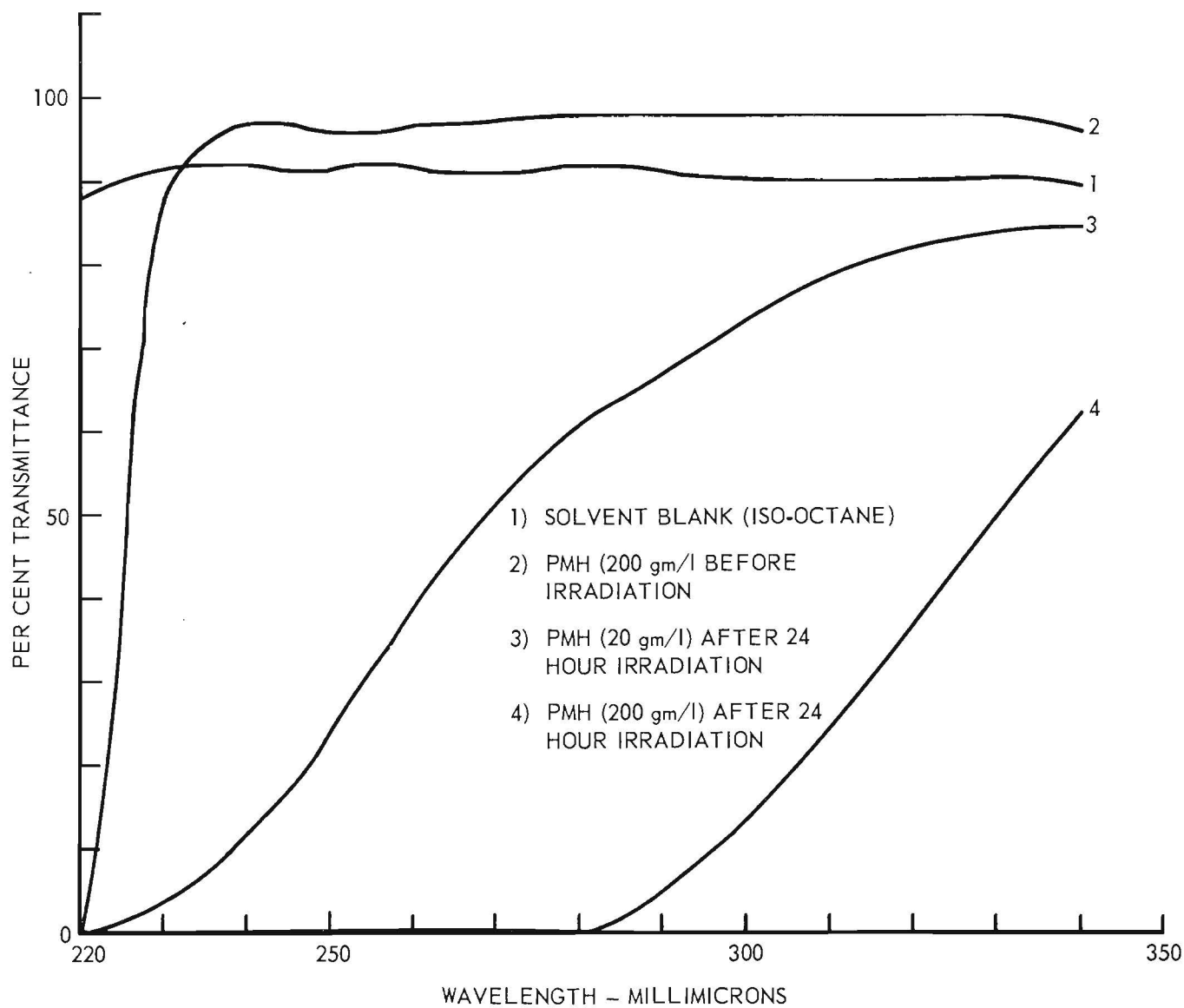


Figure 12. Ultra-violet Absorption Spectra of Unirradiated and Irradiated PMH.

Figure 13 is the infra-red spectrum of PMH before irradiation. There are no new peaks produced by irradiation so the spectrum taken after irradiation has not been included in this report.

E. Simulated Thorex Extraction Experiment

Cobalt-60 irradiations have been made of aqueous and organic solutions adjusted to Thorex Process conditions. Results indicate that irradiation of Thorex feed solutions prior to contacting with TBP-Amsco solvent results in decontamination factors (D.F.'s) only about $1/3$ as large as those found when irradiations are made with the organic phase present.

Chemical attack of nitrous acid on the organic solvent has been suggested as a possible cause of poor D.F.'s through the formation of organic phase-soluble complexing agents. The known reaction of amines with nitrous acid suggested the use of the very rapidly reacting amino acid glycine as a means of reducing nitrous acid concentration, and thereby preventing chemical attack. However, glycine in concentrations up to 0.1 M in the feed solution produced no clearly recognizable improvement in the D.F.'s.

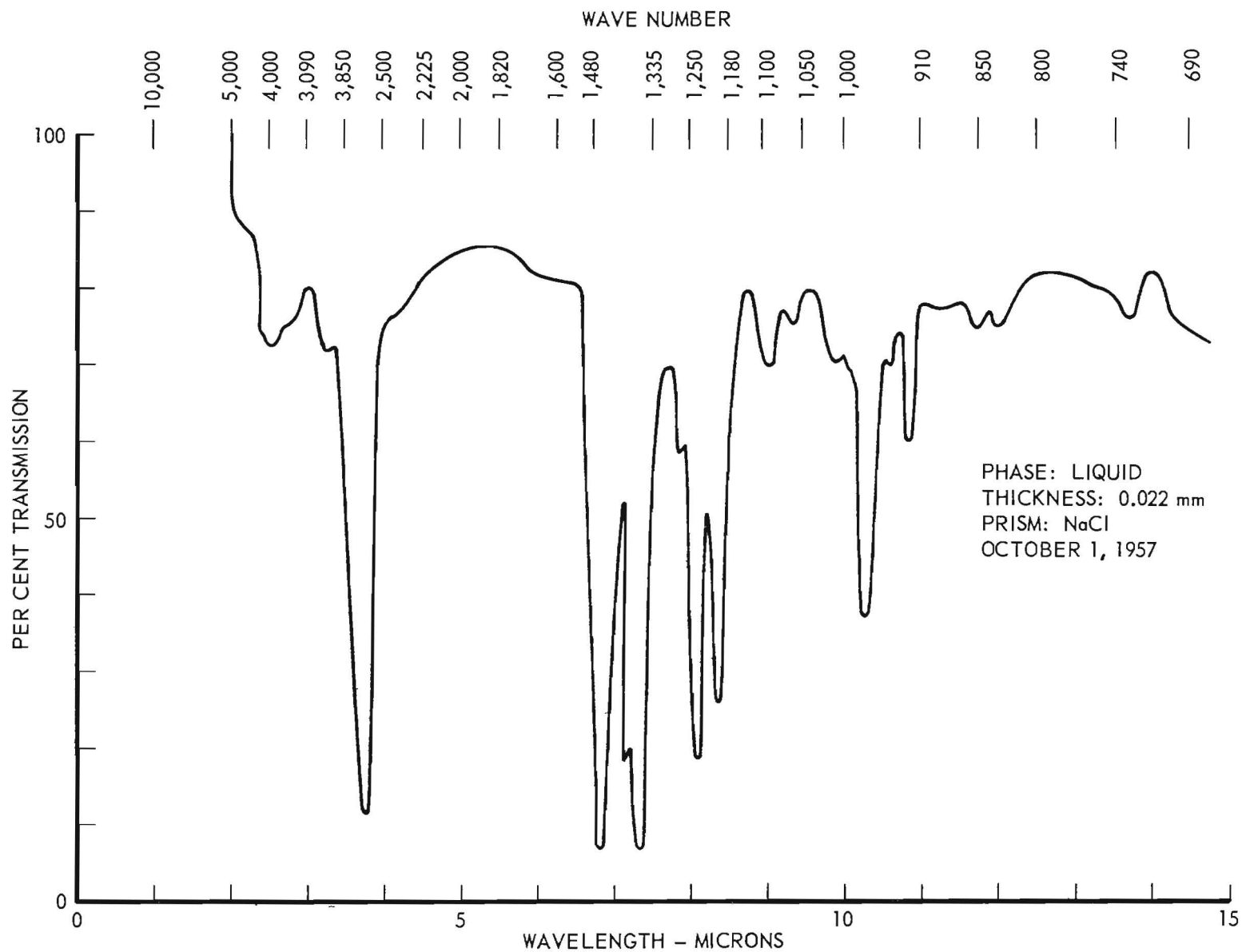


Figure 13. Infra-red Spectrum of Unirradiated PMH.

V. DISCUSSION

The year's work described above has been, in large part, devoted to obtaining and calibrating equipment. Enough experimental information has been obtained to rather closely define the properties of Amsco 125-82, but it cannot be said with certainty that the exact structure of any constituent is known. An intensive program of irradiations has been started, but analyses are just now underway.

Irradiations of 2,2,4,6,6-pentamethylheptane, which is either identical with one of the constituents of Amsco 125-82, or very similar to one or more of the constituents, have shown the G values of 1.15 for hydrogen and 0.78 for methane obtained for PMH to be quite different from the respective values of 2.10 to 2.77 for hydrogen and 0.56 to 0.62 for methane obtained at Stanford Research Institute from irradiations of Amsco 125-82 (SRI Semi-Annual Report No. 1, Report for Period January 1 to June 30, 1957, dated September 3, 1957). The difference observed is probably caused by a combination of factors. Two factors which seem particularly likely are: first, that Amsco 125-82 may contain a larger proportion of nearly straight chain hydrocarbon constituents than have been inferred from the assumed method of synthesis; second, that the high dose rates obtained with the SRI resonance transformer may cause radiation degradation of the primary radiolysis products before they leave the irradiation cell. If the latter factor were an important one, a larger number of unsaturated compounds, probably of lower molecular weight, should be obtained with the SRI resonance transformer than with the Georgia Tech x-ray. It is not possible at present to make a comparison of the number and kinds of unsaturates found at SRI with those found at Georgia Tech, but it should be possible in the near future.

Work done on analyzing cold-trapped volatile radiolysis products has shown that radiolysis products above ethane in molecular weight are indeed very soluble in PMH itself. In the work done on this project the continuous sparging action of the stream of argon bubbling slowly through the irradiation cell during irradiations helps to keep the volatile radiolysis products flushed out of the liquid being irradiated, and removes them to the cold trap. In the work done at SRI it appears that the gaseous products are removed by having the system evacuated by connecting with two evacuated metal bulbs. The difference between the methods could easily result in the differences observed in products formed.

It is worth noting that the irradiation set-up used in this research is unique in that it permits analyses for hydrogen and methane and for cold-trapped products at convenient intervals during the irradiation. Further, these analyses are representative of the instantaneous amounts of products present rather than cumulative amounts. Therefore, if there are any products whose amounts depend strongly on whether they remain in the x-ray beam for extended intervals of time, or which exhibit unusual growth patterns with time, these will be recognized in the normal course of operation.

VI. FUTURE WORK

The separation of and attempts to identify the five principal components of Amsco 125-82 will be continued.

The work to the present time has provided samples of radiolysis products which are currently being analyzed. The results of these analyses will permit a quite detailed discussion of the nature of the degradative processes involved in the irradiation of 2,2,4,6,6-pentamethylheptane, and so too of the degradative processes of similar saturated hydrocarbon molecules.

Some gas chromatograph calibrations for low-boiling liquids remain to be done, but for the most part all the necessary equipment for this research has been obtained and calibrated.

An attempt to learn more about the yields and nature of polymers formed by irradiating PMH will be made by room temperature vacuum-distillation removal of PMH and light radiolysis products from irradiated PMH samples. The polymer residue will be dissolved, if feasible, in a suitable solvent for average molecular weight determination; and absorption spectra, refractive index, and iodine number will be determined, if possible.

Further irradiations of purified PMH and of water-saturated, and perhaps nitric acid-saturated, PMH will be performed to see if the radiolysis products differ significantly among these cases. These results should help determine the value of the work done on water-free systems insofar as applications to solvent extraction systems are concerned.

Approved:

Respectfully submitted:

Wyatt C. Whitley, Chief
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Central Files
Proj. A-323

To: F. R. Bruce

From: R. G. Wymer

Subject: July Report on Subcontract No. 1082 under W-7405-eng-26

I. SUMMARY

Work done during the month of July has consisted primarily of isolating and characterizing pure components of Amsco 125-82, and of determining what compounds are most likely to be in it, based on results of other workers. At the time of this writing irradiation of the first purified fraction is in progress. Applied experiments based on ruthenium extraction under simulated Thorex conditions have been planned.

II. DISCUSSION

A. Isolation of Components

Batches of Amsco 125-82 are being distilled on a continuous basis to provide cuts for further distillation. The initial rough classifying distillations are performed using the four feet high column described previously. The final distillations made on combined selected cuts from the rough distillation are performed on a smaller column. Both columns are operated under the reduced pressure of 16 mm Hg and contain Podbielniak packing. There are seventeen components in our batch of Amsco 125-82, according to analysis by gas chromatography. Five of these have been selected for isolation. The selection was based on abundance, and boiling point. The components selected are among the most abundant in the Amsco 125-82, and cover almost the entire boiling range of 165 to 210° C., at atmospheric pressure.

Procurement of a Perkin-Elmer Vapor Fractometer for this work has greatly simplified the job of analyzing cuts from the distillation column, and makes possible nearly continuous control of the distillations. This results in a great saving of time.

B. Characterization of Amsco 125-82 and Its Purified Components

There are at least seventeen components in Amsco 125-82. These components give the average properties shown in the table below.

TABLE I

PROPERTIES OF AMSCO 125-82

1. Density: 0.7468 @ 24.2° C.
2. Boiling Range: 165 to 210° C.
3. U. V. Absorption: Considerable absorption between 300 and 220 $m\mu$
4. Bromine Test for Unsaturation: Positive
5. Potassium Permanganate Test for Unsaturation: Negative
6. Average Molecular Weight: 184 (this value is probably about five units low)
7. Hydrogenation Test for Unsaturation: 0.76 mole per cent unsaturation; based on Avg. Mol. wt. of 184
8. Formation of Urea Adducts: Negative, indicating a high degree of branching
9. Iodine Number (Hanus Method): 2.4 $gI_2/100g$ Amsco 125-82
10. Refractive Index: 1.41767 @ 30° C. using Na D line

1. Density

The density was determined by pipetting 25 ml of the Amsco 125-82 into a tared weighing bottle at 24.2° C.

2. Boiling Range

The range obtained during distillations at atmospheric pressure has been used here.

3. U. V. Absorption

Ten ml samples of Amsco 125-82 dissolved in 25 ml of iso-octane run against an iso-octane blank gave high absorption from about 300 $m\mu$ to 220 $m\mu$, going to nearly complete absorption at 220 $m\mu$

4. Bromine Test

Tests with a two per cent bromine solution in carbon tetrachloride indicated a small amount of unsaturation.

5. Permanganate Test

Tests with a 0.5 per cent aqueous solution of potassium permanganate were negative for unsaturation.

6. Molecular Weight Determinations

Molecular weight determinations by the freezing point lowering method were made on the Amsco 125-82, and on known samples of iso-octane and 1-dodecene as checks on the method. Both benzene and cyclohexane were used as solvents. Cyclohexane gave much better results on the known samples. Therefore, the molecular weights given below were determined using cyclohexane. Iso-octane gave a value of 111 as compared with the calculated molecular weight of 114, and 1-dodecene (Matheson, Coleman and Bell) gave a value of 163 as compared with the calculated molecular weight of 168. Molecular weight determinations on Amsco 125-82 gave a value of 184. This value may be four or five units low, indicating strongly that at least one fourteen-carbon-atom component is present.

7. Hydrogenation

The determination of the amount of unsaturation in Amsco 125-82 by measuring the amount of hydrogen absorbed, using PtO_2 as a catalyst, by a sample of Amsco, gave a value of 0.76 per cent (mole) unsaturation using a molecular weight of 184 for Amsco.

8. Urea Adducts

The treatment of Amsco 125-82 with a saturated urea-methanol solution does not yield a urea-hydrocarbon adduct, which indicates that the hydrocarbons present in Amsco are highly branched.

9. Iodine Number

Iodine numbers were determined by the Hanus Method, which is based on the reactivity of an iodine-bromine species rather than the iodine-chlorine species which is used in the Wijs Method. An average value of 2.4 was obtained.

10. Refractive Index

A refractive index value of 1.4167 was obtained using the sodium D line in a refractometer thermostated at 30° C. Refractive indices taken on impure cuts from the distillations ranged from 1.4134 to 1.4207. These measurements seem to provide a sensitive parameter for distinguishing between hydrocarbons.

C. Determination of Likely Compounds

It was stated by J. H. Goode in a Progress Report on "Extraction Reagent Performance", for the period from October 1956 to January 1957, that Amsco 125-82 is made from the polymerization of butenes and pentenes. Using this information, a number of conclusions can be drawn about the products which might be formed. These are given below. Additional information has been requested from the American Mineral Spirits Company to enable more accurate conclusions to be drawn about relative amounts of components which are probably formed.

1. Assumptions

- a) The composition of the mixture of butenes and pentenes was not reported. It was assumed that all possible isomers of both butene and pentene were present, and that the polymerization was acid-catalyzed.
- b) Of the possible carbonium ions from a mixture of the isomeric butenes and pentenes, the most stable and the most reactive would be the tertiary butyl and the tertiary amyl carbonium ions.

References: (i) Whitmore, "Chem. and Eng. News", 26, 668(1948).
(ii) Ipatieff and Schaad, "Ind. Eng. Chem.", 37, 362 (1945).

In the copolymerization of isobutylene with propene in the presence of phosphoric acid, no more than a trace of the product (2,4-dimethylpentene) which would be formed by the addition of the isopropyl carbonium ion to isobutylene was found. The products (2,2-and 2,3-dimethyl-x-pentene) found were formed by the addition of the t-butyl carbonium ion to propene.

(iii) Whitmore, et al, J. A. C. S., 63, 756 (1941)

In the copolymerization of isobutylene with 2-butene in which equimolar quantities of tertiary butyl and sec-butyl alcohols at 64° in 75 per cent sulfuric acid were used, the formation of the products found could be explained on the basis of the addition of the t-butyl carbonium ion to either isobutylene or 2-butene. None of the products which would be expected by the addition of sec-butyl carbonium ion to iso-butylene or 2-butene were obtained.

- c) The addition of a carbonium ion to an ethylenic double bond would follow the Markownikoff rule. That is the carbonium ion would add to that carbon of a carbon-carbon double bond which has the greater number of hydrogen atoms.

Reference: Royals, "Advanced Organic Chemistry", Prentice-Hall, Inc., p. 214.

- d) A number of olefins were eliminated as intermediates on the basis that the addition of a t-butyl cation or t-amyl cation to the olefin would be unlikely because of steric hindrance.

Reference: (i) Whitmore, et al, 63, 2035 (1941).

Of the isomers present in triisobutylene, no product was found which would have been formed by the addition of a

t-butyl cation to 2,4,4-trimethyl-2-pentene ($\text{c}-\overset{\text{q}}{\underset{\text{c}}{\text{q}}}-\text{c}=\overset{\text{q}}{\text{c}}-\text{c}$), which is formed in about twenty per cent yield in the dimerization of isobutylene.

(ii) Whitmore and Meunier, J. A. C. S., 63, 2197 (1941)

In the dimerization of tetramethylethylene in the presence of eighty per cent sulfuric acid, none of the products found corresponded to the simple addition of a carbonium ion formed from the tetramethylethylene to another molecule of the tetramethylethylene.

- e) None of the possible carbonium ions from the octenes, nonenes, and decenes were used in predicting possible addition reactions with the isomeric butenes and pentenes as it seems that the yields would be quite low.

Reference: (i) Whitmore, et al, 63, 2035 (1941)

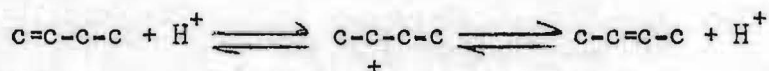
Of the products present in triisobutylene, ninety per cent of the products (two decenes) can be accounted for by the addition of t-butyl cation to 2,4,4-trimethyl-1-pentene. The other ten per cent can be accounted for by the addition of the tertiary carbonium ion ($\text{c}-\overset{\text{q}}{\underset{\text{c}}{\text{q}}}-\text{c}-\overset{\text{q}}{\underset{\text{c}}{\text{q}}}+$), formed by the addition of a proton to 2,4,4-trimethyl-1-pentene or 2,4,4-trimethyl-2-pentene, to isobutylene.

- f) Some intermediates, which would be formed by the addition of t-butyl or t-amyl cation to 1-butene or 1-pentene, were eliminated as it seems likely that the yields would be low.

Reference: (i) Brooks, "Ind. Eng. Chem.", 41, 1694 (1949)

In the copolymerization of isobutene with 1-butene, 32.7 per cent of the products could be accounted for by the

addition of the t-butyl cation to 1-butene whereas 56.3 per cent of the products could be accounted for by the addition to 2-butene, which could be formed as follows:

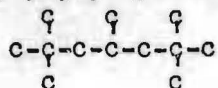


- g) The presence of isomeric decanes in large amounts in Amsco 125-82 does not seem likely as the initial boiling point in the fractionation of Amsco at atmospheric pressure is 167° . Only one (3,3-dimethyl-4-ethylhexane) of the decanes most likely to be present has a boiling point (170°) higher than 167° . Two other decanes, 3,4-dimethyloctane and 2-methyl-3-ethylheptane, have the same boiling point, 166° . Also, the molecular weight determinations of the first large fraction (#2-5) give an average value of 173.4, whereas the decanes have a molecular weight of 142.
- h) The presence of isomeric undecanes does not seem likely as it is not possible to form an eleven carbon hydrocarbon by any combination of any of the isomers present in a mixture of isomeric butenes and pentenes.

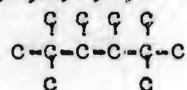
2. Most Probable Components in Amsco 125-82

a) C_{12} hydrocarbons

(i) 2,2,4,6,6-pentamethylheptane

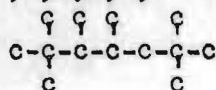


(ii) 2,2,3,4,5,5-hexamethylhexane

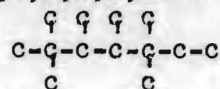


b) C_{13} hydrocarbons

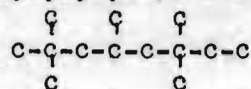
(i) 2,2,3,4,6,6-hexamethylheptane



(ii) 2,2,3,4,5,5-hexamethylheptane

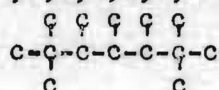


(iii) 2,2,4,6,6-pentamethyloctane

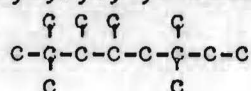


c) C₁₄ hydrocarbons

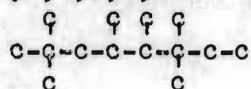
(i) 2,2,3,4,5,6,6-heptamethylheptane



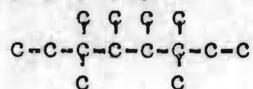
(ii) 2,2,3,4,6,6-hexamethyloctane



(iii) 2,2,4,5,6,6-hexamethyloctane



(iiii) 3,3,4,5,6,6-hexamethyloctane

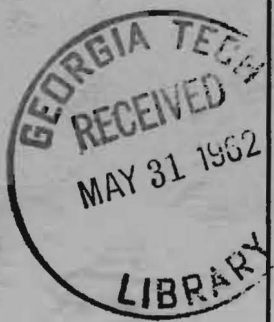


III. PLANNED RUTHENIUM EXTRACTIONS

It is planned to combine irradiated pure fractions of the Amsco 125-82 with TBP and make extractions under Thorex conditions, using Ru D.F.'s as a measure of the effect of irradiation on extraction reagent performance. Ruthenium tracer has been ordered for this work, and the necessary equipment and supplies are on hand. This phase of the work will be discussed more fully at a later time.

IV. CONCLUSION

Work has progressed to the point where irradiations have been started on the first pure major fraction from Amsco 125-82. This phase of the work will consume the bulk of the remaining time on the contract.



SEMIANNUAL REPORT

PROJECT NO. A-323

RADIATION CHEMISTRY OF ORGANIC SUBSTANCES

By

JAMES A. KNIGHT, JR.

- o - o - o - o - o - o -

SUB CONTRACT NO. 1082
UNDER W-7405 eng-26

- o - o - o - o - o - o -

1 JANUARY 1958 TO 30 JUNE 1958

PUBLISHED AUGUST 15, 1958

PLACED WITH THE CHEMICAL TECHNOLOGY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE



Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
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I. INTRODUCTION

The objectives of this project are to provide more information regarding radiation damage to solvents which are used as diluents in the Thorex program.

As stated in Annual Report No. 1, there are at least 17 components in Amsco 125-82. Also, it seems most likely that the components of Amsco 125-82 are highly branched saturated hydrocarbons. FMH (2,2,4,6,6-pentamethylheptane) has been used in the irradiation studies to date because of the similarity of FMH to some of the most likely components in Amsco 125-82. Therefore, a study of the radiation chemistry of FMH should be directly useful and informative to this work. FMH can be made in good yield by the catalytic hydrogenation of commercially available triisobutylene.

Several irradiations of FMH under varying conditions were made during the period January 1 to June 30, 1958, and the results are included in this report.

II. EQUIPMENT

The principal pieces of equipment and special apparatus employed in this research are described in detail in Annual Report No. 1, 1957, for this project. Special apparatus fabricated for use in the past 6 months includes a stainless steel irradiation cell and a distillation setup for the isolation of polymeric material formed during irradiation.

A. Stainless Steel Irradiation Cell

The stainless steel irradiation cell shown in Figure 1 is of the same design as the brass irradiation cell, which is described in Annual Report No. 1, 1957. A modification on the stainless steel cell is a side arm arrangement which contains a rubber septum. This modification permits liquid samples to be removed with a syringe during an irradiation without the necessity of opening the irradiation cell to the atmosphere. The removal of liquid samples during an irradiation without exposing the liquid to the atmosphere is of special importance when an irradiation is being conducted in an inert atmosphere.

B. Distillation Apparatus for Isolation of Polymeric Material

Figure 2 shows the experimental setup for the apparatus for the isolation of polymeric material from the irradiated PMH. The procedure for the isolation of the polymeric material is described in Chapter III.

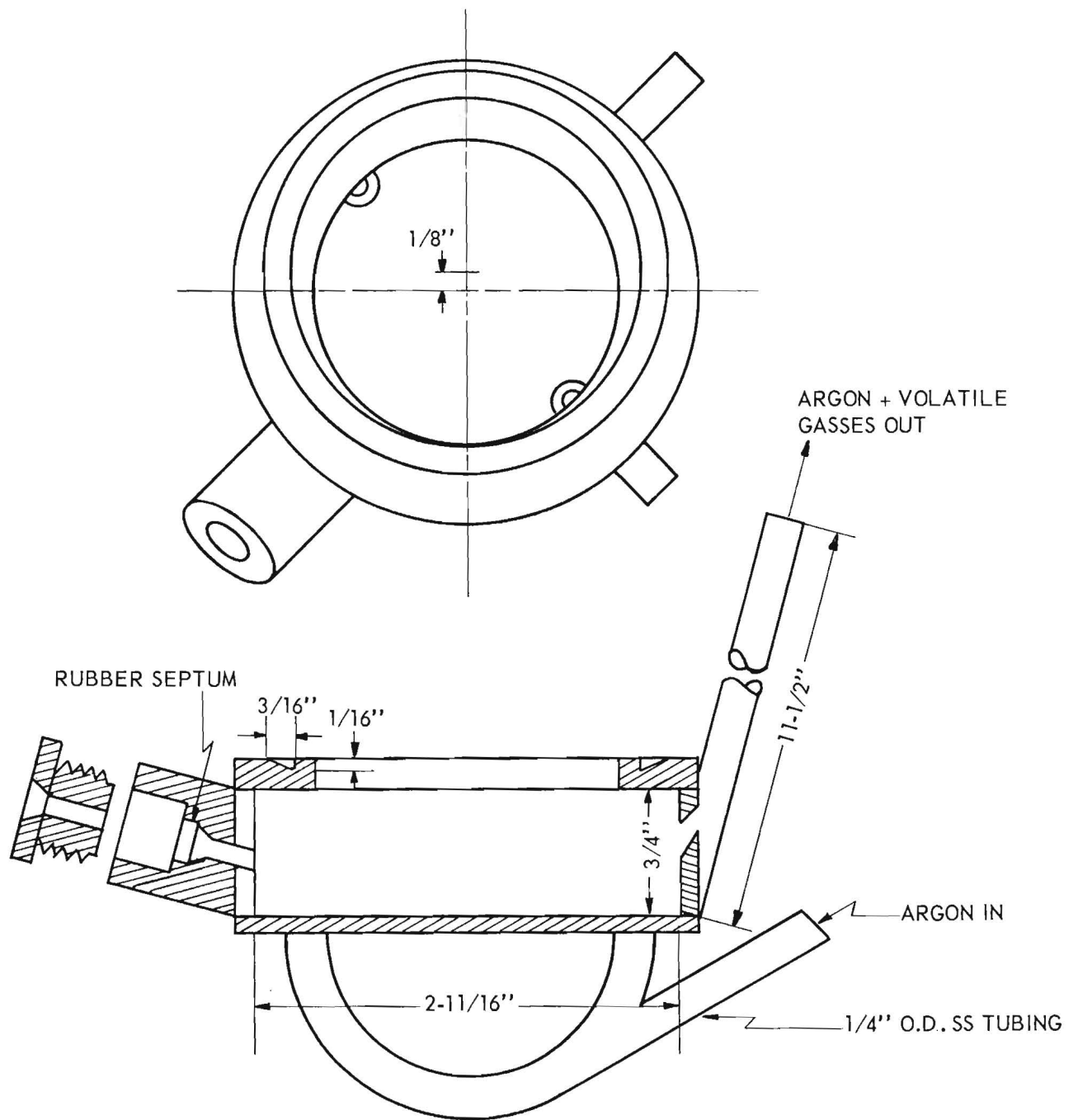


Figure 1. Stainless Steel Irradiation Cell.

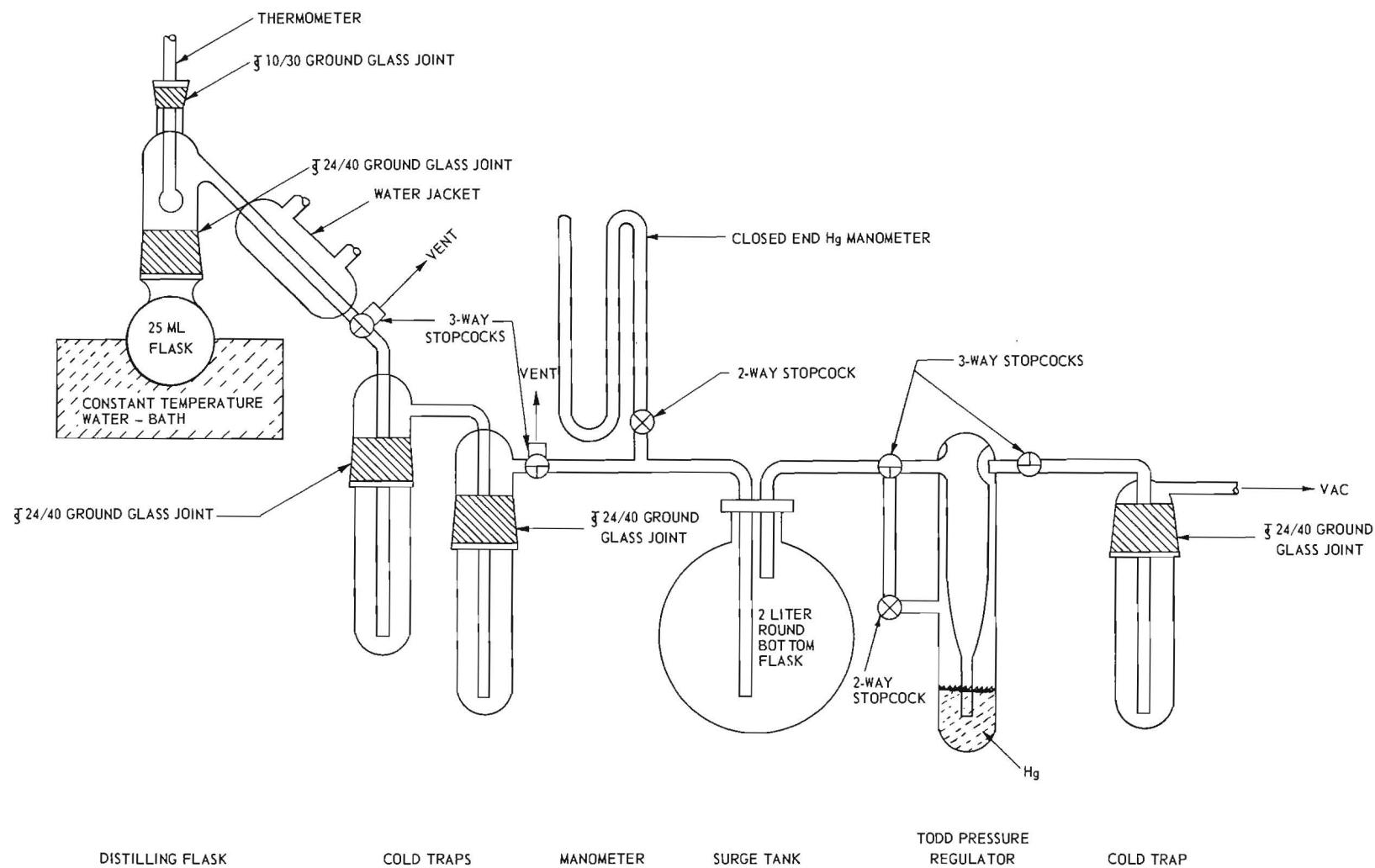


Figure 2. Vacuum Distillation Apparatus for Isolation of the Polymeric Material.

III. EXPERIMENTAL

A. X-Ray Dosimetry

The ferrous sulfate-sulfuric acid dosimeter was used to calibrate the stainless steel cell. As explained in Annual Report No. 1, a G value of 15.2 should be used when the dosimeter solution is air-saturated rather than oxygen-saturated.

Thirty ml of dosimeter solution was used in these calibrations as in our previous calibrations and irradiation work. The 30 ml of dosimeter solution in the stainless steel irradiation cell was shown to absorb energy at a rate of 0.125 watt. In order to check the calibration of the stainless steel cell, a glass cell having essentially the same dimensions as the stainless steel cell was fabricated. The 30 ml of dosimeter solution in the glass cell was shown to absorb energy at a rate of 0.128 watt.

From the foregoing it is seen that the dose received by the dosimeter solution in the stainless steel irradiation cell cannot exceed $\frac{0.125}{0.030} = 4.17$ beta watt-hours per liter in one hour. The dose received by the same volume of PMH is somewhat less because of a lower electron density.

B. Isolation and Molecular Weight Determination of Polymeric Material

The procedure for isolating the polymeric material from the irradiated PMH was as follows: a weighed sample of the irradiated PMH was introduced into the distilling flask and the pressure reduced to approximately 2 mm at room temperature; the apparatus was held at these conditions for approximately 8 hours in order to remove the low boiling material; the temperature was then raised to 70° C by use of a constant temperature bath; and the bath was maintained at this temperature until the weight of the polymeric material became constant.

A 10.00-g sample of dry irradiated PMH (brass cell irradiation) gave 0.168 g of polymer. The G value for polymer formation (expressed as molecules of PMH converted to polymer) is 2.1. The calculation of the G value is as follows:

- a) Weight of polymer = 0.168 g
- b) Weight of irradiated sample = 10.00 g
- c) Dose rate (brass cell) = 4×10^{19} ev/min
- d) Time of irradiation = 25.5 hr
- e) Weight of polymer formed in total sample (30-ml) of irradiated PMH = $\frac{0.168}{10.00} \times 30 \times 0.74 = 0.37$ g polymer/30 ml PMH
- f) Moles PMH converted to polymer = $\frac{0.37}{170} = 2.18 \times 10^{-3}$
- g) Molecules PMH converted to polymer = $2.18 \times 10^{-3} \times 6.02 \times 10^{23} = 1.31 \times 10^{21}$
- h) G (Molecules PMH converted to polymer/100 ev) = $\frac{1.31 \times 10^{21} \times 10^2}{4 \times 10^{19} \times 1530} = 2.1$

A 7.37-g sample from a later irradiation of dry PMH in the stainless steel cell yielded 0.279 g of polymer. The G value for polymer formation expressed as molecules of PMH converted to polymer is 4.6. The calculation of the G value was made in the same manner as above. A 3.688-g sample from the irradiation of water-saturated PMH in the stainless steel cell yielded 0.0532 g of polymeric material, corresponding to a G value of 1.8 for polymer formation. The above G value of 4.6 appears to be high and will be checked.

A viscosity average molecular weight of the polymeric material obtained from the dry PMH irradiated in the stainless steel cell was determined from

viscosity measurements; viz., the method of Harris¹. Viscosities were measured in xylene solution at 75° C using an Ostwald-Cannon-Fenske viscosimeter. The concentration units were grams per liter. The specific viscosity* ($n_{sp} = n_{rel} - 1$) was determined at several concentrations and the values of n_{sp}/c plotted against c (concentration). The graph is given in Figure 3. The results give a straight line in agreement with the equation $n_{sp}/c = [\eta] - k'[\eta]^2 c$. The intrinsic viscosity is evaluated from the intercept at $c=0$ obtained by a linear extrapolation. \bar{M} , the viscosity average molecular weight, is calculated from the following equation, in which the constants were evaluated by Harris:²

$$[\eta] = 1.35 \times 10^{-4} \bar{M}^{0.63}$$

From the intrinsic viscosity obtained by linear extrapolation of the straight line from Figure 3, the viscosity average molecular weight of the polymer was calculated to be 981. This value indicates that there is approximately an average of six molecules of PMH per average molecule of polymer.

¹Harris, J. of Polymer Science 8, 353-364, (1952).

*Relative viscosity (n_{rel}) is defined as the ratio of the viscosity of the solution to viscosity of the solvent, i.e.,

$$n_{rel} = \frac{n_{solution}}{n_{solvent}}$$

Specific viscosity is defined as follows:

$$n_{sp} = \frac{n_{solution} - n_{solvent}}{n_{solvent}} = (n_{rel} - 1)$$

This use for the term "specific viscosity" is not to be confused with another use of the term, which applies to the ratio of the absolute viscosity of a material to that of water at the same temperature. Intrinsic viscosity is defined as follows:

$$\text{Intrinsic viscosity} = [\eta] \equiv \lim_{c \rightarrow 0} \left(\frac{n_{sp}}{c} \right)$$

These definitions are from Weissberger, Physical Methods of Organic Chemistry, 2nd ed., Part 1, Page 330.

²Harris, loc. cit.

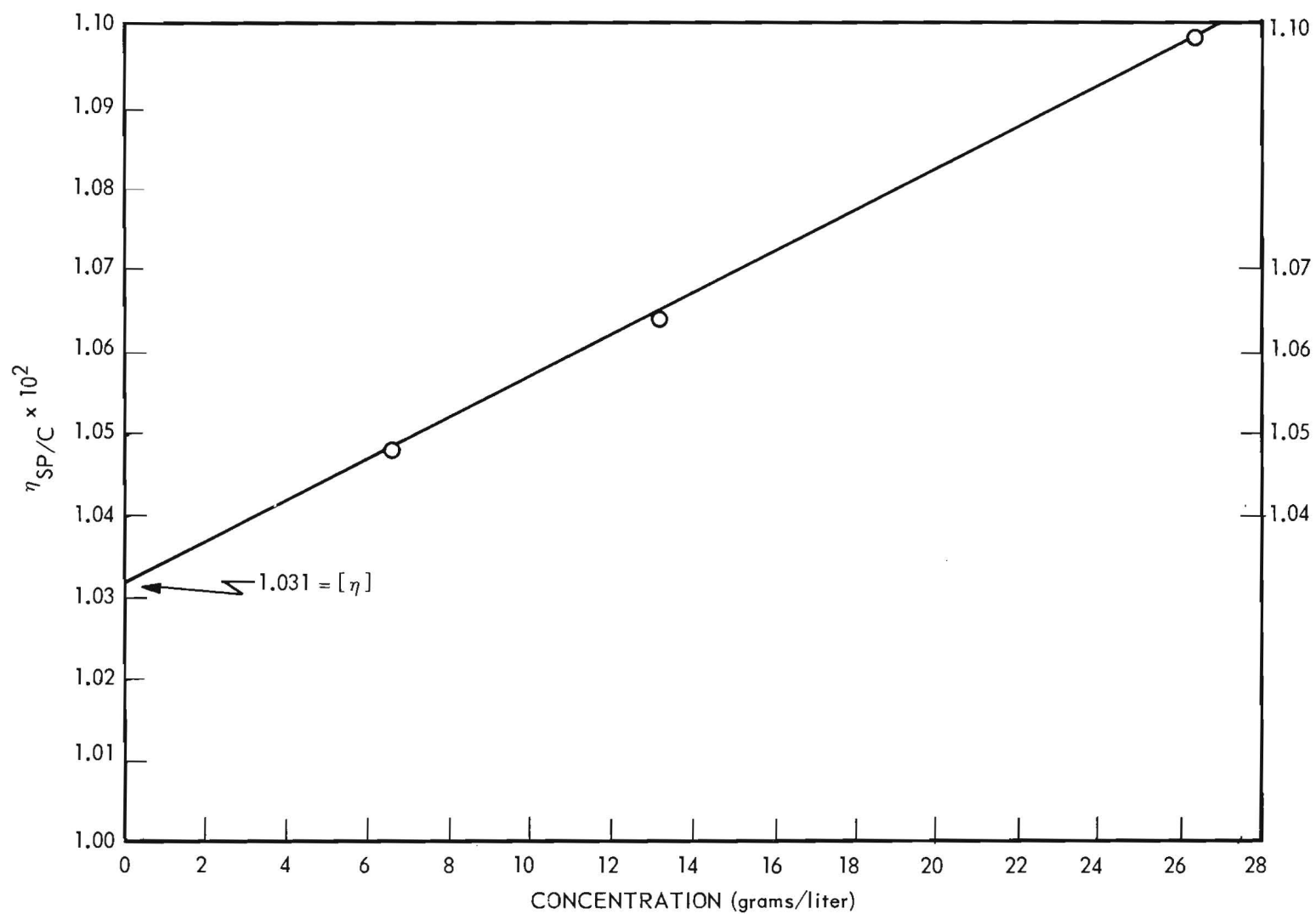


Figure 3. Determination of Intrinsic Viscosity for Calculating the Viscosity Average Molecular Weight of the Polymer.

C. Ultraviolet Spectra

The ultraviolet light absorption curves for the polymeric material isolated from the irradiated dry PMH (stainless steel cell) and for PMH before and after irradiation are shown in Figure 4. Table I gives the concentration of each solution. The samples were dissolved in iso-octane.

TABLE I
ULTRAVIOLET ABSORPTION CURVES

<u>Curve No.</u>	<u>Material</u>	<u>Concentration</u> (g/l.)
1	PMH before irradiation	200
2	Isolated polymeric material	0.24
3	Isolated polymeric material	0.48
4	Isolated polymeric material	0.96
5	Isolated polymeric material	1.92
6	PMH after irradiation	200

Such absorption as shown by Curves 2, 3, 4, 5, and 6 indicates a high degree of unsaturation, such as carbon-carbon double bonds. The high degree of absorption shown by the isolated polymeric material at the relatively low concentrations strongly suggests that the polymeric material accounts for a considerable portion of the unsaturation in the irradiated PMH.

D. Iodine Numbers and Unsaturation

The iodine numbers for the various irradiations are given in Table II. G values for double bond formation based on the iodine values are included in the table also.

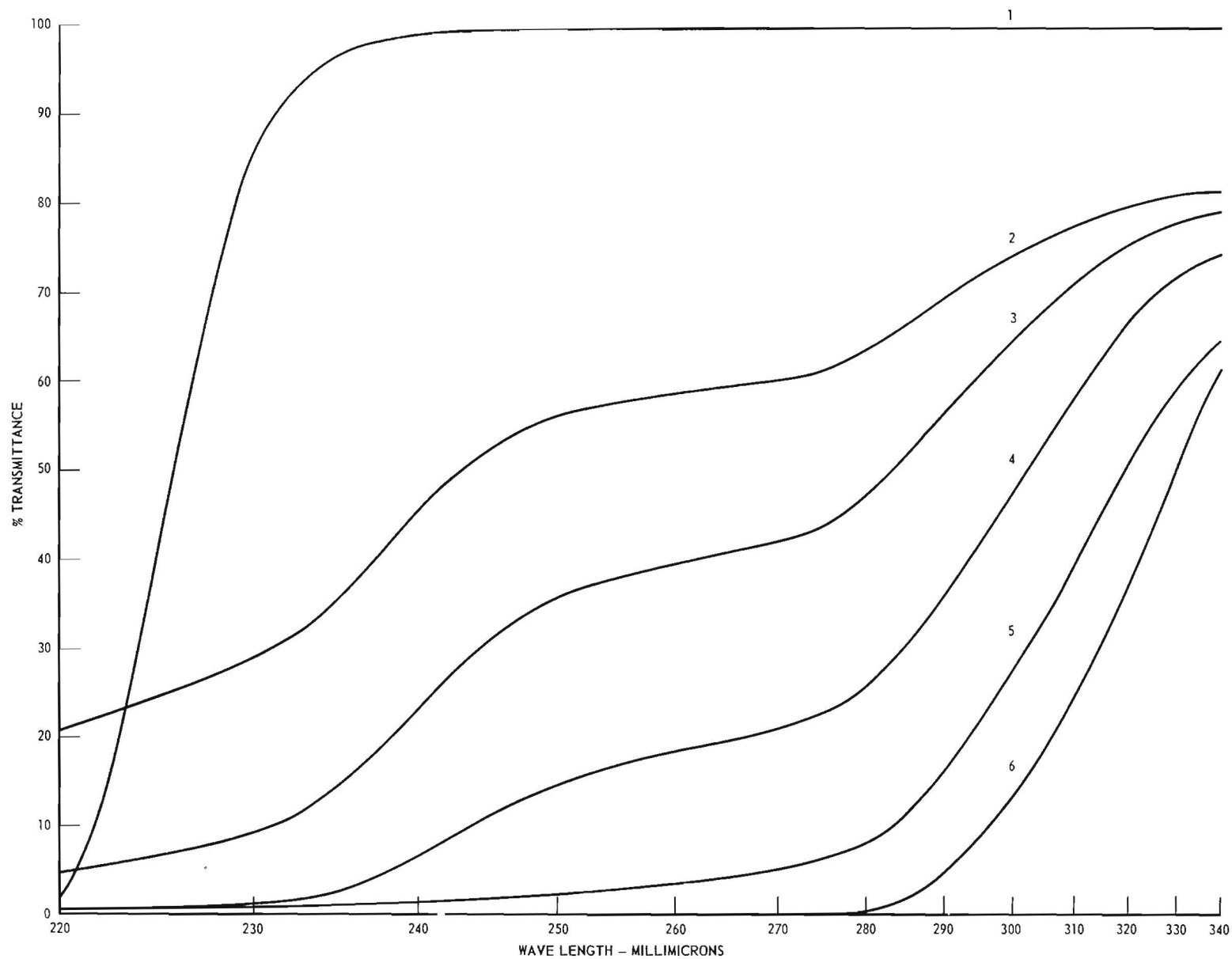


Figure 4. Ultra-violet Absorption Spectra of Unirradiated and Irradiated PMH and Polymer from Irradiated PMH.

TABLE II
IODINE NUMBERS FOR VARIOUS IRRADIATIONS

<u>Irradiation Type</u>	<u>Iodine No.[†]</u>	<u>Time of Irradiation (hr)</u>	<u>Dose Rate (ev/min)</u>	<u>G Value for Double Bond Formation</u>
PMH before irradiation	1.98	----	----	----
Irradiation of dry PMH in brass cell	5.51	25.5	4.0×10^{19}	3.0
Irradiation of dry PMH in stainless steel cell	11.17	25	4.3×10^{19}	8.0
Irradiation of water- saturated PMH in stainless steel cell	8.81	25	4.3×10^{19}	5.5

[†]Iodine No. = grams of iodine per 100 g of sample; average of two determinations.

The calculations for the G value for double bond formation, **based on iodine** numbers as a measure of unsaturation, are shown below for the irradiation of dry PMH in the brass cell. The other G values for double bond formation were calculated in the same manner, i.e.

a) Increase in iodine value = $5.51 - 1.98 = 3.53 \text{ g I}_2/100 \text{ g sample}$

b) Dose rate (brass cell) = $4 \times 10^{19} \text{ ev/min}$

c) Time of irradiation = 25.5 hr

d) Number of moles iodine taken up per mole PMH = $\frac{\frac{3.53}{254} \text{ moles I}_2}{\frac{100}{170} \text{ moles PMH}} = 2.36 \times 10^{-2}$

e) The assumption is made that one mole of iodine absorbed is equivalent to one mole of carbon-carbon "double bonds."

f) Double bonds/ molecule FMH = 2.36×10^{-2}

g) Double bonds formed in 30 ml FMH = $2.36 \times 10^{-2} \times \frac{0.740 \times 30}{170} \times 6.02 \times 10^{23}$

h) G (double bond formation) = $\frac{1.86 \times 10^{21} \times 10^2}{4.0 \times 10^{19} \times 1530} = 3.0$

E. Acid Number of Irradiated Water-Saturated FMH

Since the possibility for the formation of acidic components existed in the irradiation of water-saturated FMH, the irradiated material was checked for acid number by titration with 0.01-N sodium hydroxide in absolute alcohol with a pH meter. The results gave an upper limit of 0.025 for the acid number, expressed as grams of sodium hydroxide required to neutralize a 100-g organic sample. The method was checked for accuracy with a sample of octanoic acid (Eastman white label grade). The results show that the presence of the small amount of water in water-saturated FMH did not lead to the formation of any significant amount of acidic components during the irradiation.

F. G Values for Hydrogen and Methane

The G values for hydrogen and methane, Table III, were calculated by the method outlined in Annual Report No. 1, 1957, pp. 36-38.

G. Gas Chromatogram of Products in Cold Trap

The procedure for irradiations in which a stream of argon gas is continuously bubbled through the irradiation cell is described in Annual Report No. 1 page 9. The exit argon gas from the irradiation cell is passed through a water-cooled condenser which should return to the irradiation cell most of the high-boiling constituents. The argon stream with the volatile radiolysis product is then bubbled through 5 ml of FMH in a cold trap immersed in a salt-ice bath. This procedure traps essentially all of the volatile products except hydrogen and methane.

TABLE III
G VALUES FOR HYDROGEN AND METHANE

Irradiation Type	G Values		Time of Irradiation (hr)	Dose Rate (ev/min)
	H_2	CH_4		
Irradiation of dry PMH in brass cell	1.15	0.78	3.25	4.0×10^{19}
Irradiation of dry PMH in brass cell	1.14	0.81	25.5	4.0×10^{19}
Irradiation of dry PMH in stainless steel cell	1.30	0.85	25	4.3×10^{19}
Irradiation of water- saturated stainless steel cell	1.92	1.38	25	4.3×10^{19}

A gas chromatogram of the cold-trapped radiolysis products is shown in Figure 5. Samples of known gaseous and liquid hydrocarbons were run in the gas chromatograph under the same conditions as the sample of cold-trapped products. The times of emergence of the known samples are shown at the top of the gas chromatogram in Figure 5.

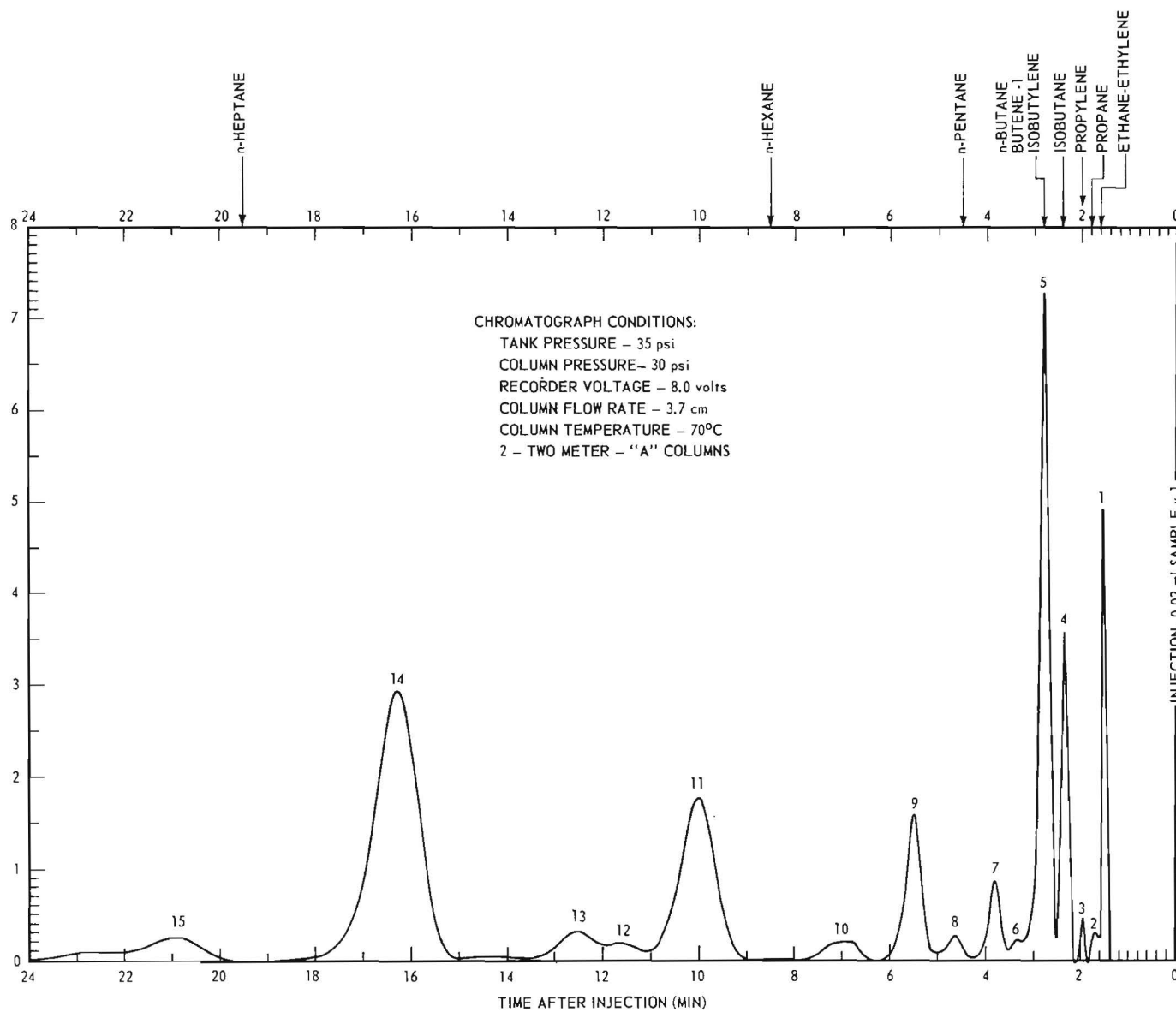


Figure 5. Gas Chromatogram of Cold Trapped Liquid.

IV. DISCUSSION

A. Dosimetry

The calibrations of the stainless steel irradiation cell were made with the ferrous ion dosimeter. Thirty ml of the dosimeter solution was found to absorb energy at the rate of 4.68×10^{19} ev/min or 0.125 watt. Calibrations were made using a glass cell having essentially the same dimensions as the stainless steel cell. Thirty ml of the dosimeter solution in the glass cell was found to absorb energy at the rate of 4.80×10^{19} ev/min or 0.128 watt. The close agreement of the calibrations indicates that the calibrations for the stainless steel cell are reliable and reasonably accurate.

As pointed out in Annual Report No. 1, the dose absorbed by 30 ml of PMH is somewhat less than the dose absorbed by 30 ml of dosimeter solution because of the lower electron density of PMH. In order to correct for this, the dose rate in the dosimeter solution is multiplied by 0.92 (see page 37, Annual Report No. 1, for details concerning this correction factor). This gives a value of 4.3×10^{19} ev/min, which is the dose rate used for calculations involving the stainless steel cell.

B. G Values for Hydrogen and Methane

The G values for hydrogen and methane from the several irradiations of PMH are given in Table III. There is good agreement among the G values for both hydrogen and methane for the irradiation of dry PMH in the brass cell at the two different time lengths of irradiation. The G values for hydrogen and methane for the irradiation of dry PMH in the stainless steel cell are only slightly higher than in the case of the brass cell. The G values for the irradiation of water-saturated PMH in the stainless steel cell are somewhat higher than for the irradiation of dry PMH in either the brass or stainless

steel cell. These results indicate that the presence of a very small amount of water in PMH has a pronounced effect on the formation of hydrogen and methane during irradiation. It should be pointed out that the solubility of water in the PMH would be very small.

C. Isolation and Characterization of Polymeric Material

Since the nature and amount of polymeric material formed during an irradiation are of considerable interest, the isolation and characterization of the polymer is desirable. The apparatus for the isolation of the polymeric material is shown in Figure 2. One of the difficulties encountered in the isolation of the polymeric material from the irradiated PMH is the removal of the last traces of PMH. This point must be taken into consideration in interpreting the results of the work on the polymeric material. The polymeric material isolated from the irradiated PMH (brass cell, 25.5-hr) was a viscous material with a yellowish tinge. A 10.0-g sample of irradiated PMH (brass cell) gave 0.168 g of polymer. Using this result, a G value for polymer formation (expressed as molecules of PMH converted to polymer) of 2.1 is obtained.

Polymeric material was isolated from a 7.37-g sample of irradiated dry PMH (stainless steel cell, 25-hr). This sample gave 0.279 g of polymeric material (3.84 per cent polymer) and a G value for polymer formation of 4.6, expressed as molecules of PMH converted to polymer. The G value for polymer formation for the irradiation of water-saturated PMH in the stainless steel cell is 1.8. The G value for polymer formation in the irradiation of dry PMH in the stainless steel cell is higher than the G values obtained for polymer formation in the irradiation of dry PMH in the brass cell or water-saturated PMH in the stainless steel cell. The increase in G value for polymer formation is outside the limits of experimental error.

Attempts to determine the molecular weight of the polymeric material, isolated from PMH irradiated in the brass cell, by the freezing point lowering method with cyclohexane as a solvent, gave inconclusive results. Viscosity measurements are used as a means of determining molecular weights of polymeric materials. This method was used with the polymeric material isolated from irradiated PMH (stainless steel cell, 25-hr). A viscosity average molecular weight of 981 was obtained by the method of Harris³. This value indicates that there is approximately an average of six molecules of PMH per molecule of polymer. Additional work on the isolation and determination of the molecular weight of the polymeric material is planned.

D. Unsaturation

The iodine numbers, which are used as a measure of unsaturation, for the irradiated PMH are given in Table II. The values show a considerable increase for irradiated PMH (either dry or water-saturated) in the stainless steel cell over the value for PMH in the brass cell. G values for double bond formation (number of double bonds formed per 100 ev) were calculated from the differences between the iodine number of PMH before irradiation and after irradiation. These calculations are based on the assumption that for every mole of iodine absorbed, one mole of carbon-carbon double bonds are present in the organic

³Harris, loc. cit.

material. In the irradiation of water-saturated PMH in the stainless steel cell, the presence of water evidently decreases the amount of unsaturation as compared with the amount of unsaturation from the irradiation of dry PMH. It would be of interest to determine the effect that water as a second phase would have on the irradiation of PMH.

Since it seems likely that the presence of water in the water-saturated PMH could lead to the formation of acidic compounds during the irradiation, an acid number determination was made on the irradiated PMH. The results show that acidic material is not formed in an amount which can be determined by titration with 0.01 N sodium hydroxide. It would be of interest to determine if any appreciable amount of acidic material is formed during the irradiation of PMH in the presence of water as a second phase.

The curves for ultraviolet absorption spectra are given in Figure 4. Examination of the curves shows that unirradiated PMH has little absorption in the ultraviolet region whereas the irradiated PMH and the isolated polymeric material have considerable absorption. A comparison of the curves of different concentrations of the polymeric material with the curve for irradiated PMH shows that the polymeric material is strongly absorptive. This indicates the presence of unsaturation (such as carbon-carbon double bonds) in both the irradiated PMH and the polymeric material. The polymeric material in the irradiated PMH is responsible for a considerable amount of the absorption in the ultraviolet region.

E. Cold-Trapped Products

The gas chromatogram of the cold-trapped products is shown in Figure 5. The volatile radiolysis products, other than hydrogen and methane, seem to fall in the range of C_2 to C_7 compounds. Some of the cold-trapped radiolysis products are tentatively identified. Additional work is planned on the identification of these radiolysis products ~~with~~ different column packings in the gas chromatograph.

F. Stainless Steel Cell

The use of a stainless steel cell for irradiations has lead to some differences in the results obtained. For example, the iodine number for PMH irradiated in the stainless steel cell is slightly more than twice the value obtained for PMH irradiated in the brass cell. Also, the amount of polymeric material isolated from one irradiation of PMH in the stainless steel cell is considerably more than the polymeric material isolated from the PMH irradiated in the brass cell. The amount of polymeric material isolated from the irradiated PMH (stainless steel cell) is 3.84 per cent as compared with 1.68 per cent for polymeric material from irradiated PMH (brass cell). This difference will be investigated and checked more thoroughly. However, there is good agreement in the case of G values for hydrogen and methane, for irradiations carried out on dry PMH in either the stainless steel cell or the brass cell.

V. FUTURE WORK

Irradiations of nitric-acid-saturated PMH, PMH in presence of water and PMH in presence of nitric acid solution are being planned and will be carried out in the near future. The stainless steel cell will be used for these irradiations.

Additional work involving the isolation and characterization of the polymeric material formed during an irradiation is in progress. Molecular weight determinations will be tried using other methods in addition to the viscosity method.

The work on the identification of the cold-trapped radiolysis products will be continued.

Respectfully submitted:

✓ James A. Knight, Jr. ✓
Project Director

Approved: ✓

✓ Wyatt C. Whitley, Chief
Chemical Sciences Division ✓



FINAL REPORT

PROJECT NO. A-323

RADIATION CHEMISTRY OF ORGANIC SUBSTANCES

By

JAMES A. KNIGHT, JR.

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SUB CONTRACT NO. 1082
UNDER W-7405 eng-26

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1 JANUARY 1957 to 31 JANUARY 1959

PUBLISHED JANUARY 31, 1959

PLACED WITH THE CHEMICAL TECHNOLOGY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE



Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

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This report contains 35 pages.

I. INTRODUCTION

The chemical processing of reactor fuels involves the use of organic substances as extracting agents and as diluents. When most organic substances are exposed to reactor fuels, radiation damage occurs. Some of the radiation damage effects are: formation of gaseous products, such as hydrogen and methane; formation of liquid substances more volatile than the original material; formation of substances of greater molecular weight than the original material; and formation of unsaturated substances.

The objectives of this project were to provide more information regarding radiation damage to hydrocarbon solvents which are similar to those used as diluents in the Thorex program and to determine if the radiation-damaged diluent has a pronounced deleterious effect upon the extraction process.

Amsco 125-82 is used as a diluent in the Thorex process. As stated in Annual Report No. 1, there are at least seventeen components in Amsco 125-82. Also, it seems most likely that the components of Amsco 125-82 are highly branched, saturated hydrocarbons. The hydrocarbon, 2,2,4,6,6-pentamethylheptane (PMH), has been used in the irradiation studies to date because of the similarity of PMH to some of the most likely components in Amsco 125-82. Therefore, the results of a study of the radiation chemistry of PMH should be directly useful and informative for the extraction process. PMH can be prepared in good yield by the catalytic hydrogenation of commercially available triisobutylene.

PMH has been irradiated as a pure compound, water-saturated, nitric acid-saturated, in contact with water and in contact with 4 M. nitric acid. Radiolysis products, including those of higher molecular weight than PMH, have been isolated and studied. The effects of irradiated Amsco 125-82 on the extraction characteristics of the Amsco-tributyl phosphate (TBP) mixture were studied.

II. EQUIPMENT

The source of radiation employed in this research has been an x-ray apparatus. The primary analytical tool has been a gas chromatographic unit. Other apparatus, such as irradiation cells, have been fabricated to fill special needs.

A. X-Ray Apparatus

A GE x-ray diffraction unit power supply, model XRD-5 and accessories, was chosen for the project work because of the high continuous power output of the unit. The x-ray tube is a shielded Machlett OEG-60 end-window tube capable of operating continuously at 50 KVP and 50 Ma, and giving an estimated dose rate of 2×10^6 r/min. The XRD-5 power supply will operate continuously at the 2.5 KVA required by the tube for maximum output.

A box lined with 1/4 inch thick lead and having internal dimensions of 17-1/2 inches x 17-1/2 inches at the bottom and 23-1/2 inches in height was fabricated and modified to hold the x-ray tube in a vertical position. Holes with off-set shielding were provided for experimental lines. Approximately one-fourth of the shielded x-ray tube protrudes from the top of the box, thus leaving ample space inside the box for experimental equipment. Figure 1 of the Annual Report No. 1, 1957, shows the x-ray power supply and the lead-lined box containing the x-ray tube.

B. Irradiation Cells

The x-ray beam is composed to a large extent of low energy photons (10-30 KV) which do not penetrate a liquid sample deeply. It was desirable, therefore, to design an irradiation cell which would allow continuous stirring

during irradiation. In addition, since gaseous radiolysis products were known to be formed, it was necessary to provide an outlet for them to prevent pressure buildup and to make it possible to trap and analyze them. The x-ray tube is mounted with the beam coming vertically down into the irradiation cell. To prevent loss of gaseous products around the end of the x-ray tube, and to prevent air from leaking in, a fairly large pressure must be exerted on the irradiation cell to hold it up tightly against the tube. This pressure was sufficient to crack a glass cell which was otherwise satisfactory. A brass cell was fabricated which met the requirements mentioned above but which had to be coated with polyethylene to prevent dezincification whenever acidic dosimetry solutions were put into it. Despite this shortcoming, the cell was used for the initial phases of the work reported here. A diagram of the brass cell can be found in Annual Report No. 1, Figure 3.

A stainless steel cell was fabricated for use during the irradiations of hydrocarbon solvents in contact with nitric acid. A modification on the stainless steel cell is a side arm arrangement which contains a rubber septum. This modification permits liquid samples to be removed with a syringe during an irradiation without the necessity of opening the irradiation cell to the atmosphere. The removal of liquid samples during an irradiation without exposing the liquid to the atmosphere is of special importance when an irradiation is being conducted in an inert atmosphere. A diagram of the stainless steel cell is shown in the Semiannual Report, 1958, Figure 1, p. 3.

C. Gas Chromatograph

The primary analytical tool used in this work for identification of the radiolysis products obtained by irradiating hydrocarbon solvents was a Perkin-

Elmer model 154-B Vapor Fractometer. In this instrument a sample mixture of gases or liquids is introduced into a carrier gas stream which transports the sample into a packed column. Each component of the mixture appears at the column exit at a different time where it is detected by a sensitive thermal conductivity gage. Recording the detector output provides a series of peaks, the area of each being proportional to the concentration of the component producing it. The "retention volume" (time of emergence multiplied by carrier gas flow rate) serves to identify the component.

The principal variables in the use of the gas chromatograph are the type of column packing and the temperature of the columns. The carrier gas flow rate is a variable of secondary importance. Degree of response of the thermal conductivity gage is directly related to the difference between the thermal conductivities of the carrier gas and the component being analyzed for; the larger the difference, the greater the response for a given amount of the component.

The columns used are typically made of 1/4 inch tubing and are about two meters long. Column packings are generally of two types: vapor-liquid partition and vapor-solid partition. Didecylphthalate-coated crushed firebrick exemplifies the first type; molecular sieve, the second. The former is useful for separating fairly high molecular weight hydrocarbons; the latter, for separating light gases such as hydrogen, oxygen, carbon dioxide, methane, nitrogen, et.al.

In this work molecular sieve columns with argon carrier gas have been used to separate and analyze for hydrogen and methane. All other hydrocarbons were analyzed with an appropriate vapor-liquid partitioning column and helium carrier gas to increase the response for these substances of moderate thermal conductivities.

It was found that when gas samples of greater than about 10 ml (STP) were introduced into a four-meter molecular sieve column (two 2-meter columns in series) the resulting peaks were not symmetrical, but were badly skewed and often had flat tops, which made identification by time of peak emergence impossible. This problem was surmounted by modifying the column so that entering gas samples passed first into an enlarged section of column about 4-1/2 inches long and 5/8 inch in diameter before entering the main body of the 1/4 inch diameter column. With this column modification no trouble was experienced using a nominal 25 ml sampler, the largest gas sampler available.

D. Distillation Apparatus for Isolation of Polymeric Material

Figure 2 of the Semiannual Report, 1958, shows the experimental setup of the apparatus for the isolation of polymeric material from the irradiated PMH. The procedure for the isolation of the polymeric material is described in Chapter III, Semiannual Report, 1958.

E. Freezing Point Apparatus for Determination of Molecular Weights

In the determination of molecular weights with the usual apparatus by the freezing point lowering method, relatively large samples of solutes are required. In this research it was desirable to determine the molecular weight of the polymeric material formed during an irradiation. As the quantity of polymeric material formed during an irradiation is very small (0.03 - 0.10g), the ordinary techniques were not applicable. A procedure using a thermistor as the temperature sensing component and a 10 mv recorder was developed for measuring the freezing point lowering of the solvent (benzene) in the molecular weight determinations. With this apparatus the amount of solution required is about 0.5 ml.

III. EXPERIMENTAL

A. Irradiations of Organic Substances

1. Irradiation Technique

The technique employed during an irradiation in this research provided for the constant removal of gaseous and volatile radiolysis products. The irradiation cells, described on page 2, were designed so that a constant stream of an inert gas could be bubbled through the cell during an irradiation. The stream of inert gas, bubbling through the liquid being irradiated, served two purposes: first, it provided continuous stirring of the liquid; and second, it allowed for the removal of volatile radiolysis products during an irradiation.

During all irradiations in this research, a stream of argon gas was continuously bubbled through the irradiation cell. The argon was introduced through an arm of a gas lift-pump fastened to the bottom of the irradiation cell. Low flow rates of argon (2 to 5 ml per minute) were used to maintain low dilution of the volatile radiolysis products (especially hydrogen and methane) by argon.

As the argon moved out of the irradiation cell it carried with it a steady state amount of radiolysis products as well as a very little of the high-boiling organic liquid sample. All substances which liquify at the temperature of tap water were returned to the irradiation cell by the condenser. The remaining gases passed out of the condenser into a glass cold trap, which was maintained at a temperature of about -20°C or less. Three to five ml of the liquid being irradiated was placed in the cold trap and the gases bubbled through it to ensure that gases condensable at -20°C or less are actually cooled to that temperature. In addition to providing good thermal contact with the gases

and a cold reservoir for heat uptake, the liquid in the trap also provided a non-reactive solvent for the gases, reducing their vapor pressures by a colligative as well as a thermal action.

The argon sweep gas passed from the cold trap directly to the gas sampling loop of the gas chromatographic unit. The method allowed for periodic sampling during an irradiation of the sweep gas for hydrogen and methane.

A schematic diagram of the experimental set-up is shown in Figure 1.

2. Irradiations of 2,2,4,6,6-Pentamethylheptane (PMH)

Irradiations of PMH were performed using dry PMH, water-saturated PMH, nitric acid-saturated PMH, a two phase liquid system of PMH and water, and a two phase liquid system of PMH and 4 M. nitric acid. In all irradiations, a total volume 30 ml of liquid was used. In the two phase liquid systems, 25 ml of PMH and 5 ml of either water or 4 M. nitric acid were used. Two irradiations of raw Amsco 125-82 were made. All of the irradiations were made in the manner described above with argon as the sweep gas. In the irradiations of nitric acid-saturated PMH and of PMH in contact with 4 M. nitric acid, the beryllium window of the x-ray tube was covered with a sheet of mica (6 mg/cm^2) to protect the beryllium window from any possible attack by the nitric acid. The irradiations included in this report are given in Table I.

B. G Values for Hydrogen and Methane

The argon sweep gas, after passing through the cold trap, passed through the gas sampling loop of the gas chromatographic unit. This procedure allowed for the periodic sampling for hydrogen and methane during an irradiation. In analyzing for hydrogen and methane, Linde "Molecular Sieve" was used as

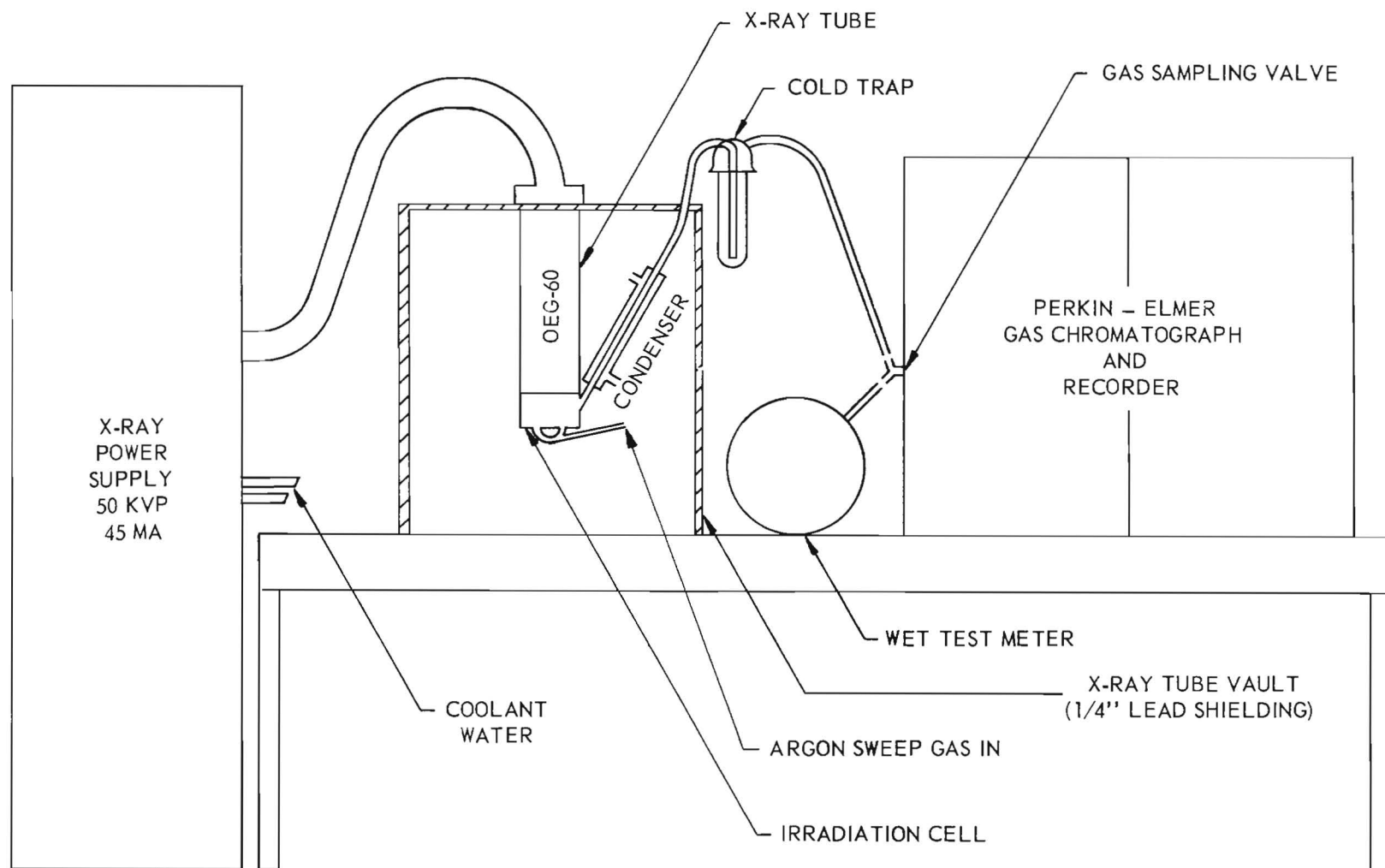


Figure 1. Equipment Arrangement for Irradiations.

TABLE I
SUMMARY OF IRRADIATIONS

<u>Irradiation Number</u>	<u>Liquid Irradiated</u>	<u>Cell</u>	<u>Length of Time (Hr)</u>	<u>Dose Rate (Ev/Min)</u>
1	PMH (dry)	Brass	3.25	4.0×10^{19}
2	PMH (dry)	Brass	25.5	4.0×10^{19}
3	PMH (dry)	Stainless Steel	25	4.3×10^{19}
4	PMH (dry)	"	25	4.3×10^{19}
5	Water-saturated PMH	"	25	4.3×10^{19}
6	Nitric Acid- saturated PMH	"	25	4.0×10^{19}
7	Nitric Acid- saturated PMH	"	25	4.0×10^{19}
8	PMH in contact with 5 ml water	"	25	4.3×10^{19}
9	PMH in contact with 5 ml water	"	25	4.3×10^{19}
10	PMH in contact with 5 ml 4 M HNO_3	"	25	4.0×10^{19}
11	PMH in contact with 5 ml 4 M HNO_3	"	25	4.0×10^{19}
12	Amsco 125-82	"	25	4.3×10^{19}
13	Amsco 125-82	"	100	4.3×10^{19}

packing in the chromatographic column. A more complete discussion of the gas chromatographic apparatus and of the calibrations of the instrument for hydrogen and methane is given in Annual Report No. 1, 1957, pp. 25-30.

The G values for hydrogen and methane for the irradiations are given in Table II. The G values were calculated according to the method outlined in Annual Report No. 1, 1957, pp. 36-38.

TABLE II
G VALUES FOR HYDROGEN AND METHANE

<u>Irradiation Number</u>	<u>Liquid Irradiated</u>	<u>H₂</u>	<u>CH₄</u>	<u>Cell</u>
1	PMH (dry)	1.15	0.78	Brass
2	PMH (dry)	1.14	0.81	Brass
3	PMH (dry)	1.30	0.85	Stainless Steel
4	PMH (dry)	1.24	0.81	"
5	Water-saturated PMH	1.92	1.38	"
6	Nitric Acid- saturated PMH	0.98	0.76	"
7	Nitric Acid- saturated PMH	0.99	0.65	"
8	PMH in contact with 5 ml water	1.16	0.74	"
9	PMH in contact with 5 ml water	1.20	0.79	"
10	PMH in contact with 5 ml 4 M HNO ₃	0.96	0.45	"
11	PMH in contact with 5 ml 4 M HNO ₃	0.96	0.37	"
12	Amsco 125-82	1.90	0.57	"
13	Amsco 125-82	1.56	0.55	"

C. Iodine Numbers and Unsaturation

Iodine numbers are a useful measure of unsaturation in an organic compound. The iodine number is defined as the grams of iodine taken up by 100 g of the organic sample. It must be recognized, however, that their first use was in the empirical comparison of unsaturated fats. Their adaptation to the

quantitative measurement of unsaturation is an extension of their original use which must be considered carefully for each class of compounds for which the adaptation is to be used. In the simplest, ideal case the iodine number may be converted directly to number of double bonds per molecule of pure unsaturated compound, or number of double bonds created by irradiating a pure saturated hydrocarbon of known molecular weight, in cases where only a small fraction of the hydrocarbon molecules are affected. The basis for calculating number of double bonds from iodine numbers is the assumption that one iodine molecule (or its equivalent) adds to each double bond. Thus, heptene-1 (molecular weight = 98) has an iodine number of $(254 \times \frac{100}{98} =) 260$. The iodine numbers were run using the Hanus Method which uses the halogenating properties of IBr in glacial acetic acid.

Fully saturated PMH, when treated with the Hanus solution, gave an iodine number of 1.98. Amsco 125-82 gave an iodine number of 2.4. This illustrates one of the shortcomings of the use of iodine numbers for quantitative unsaturation measurements.

The iodine numbers for the various irradiations are given in Table III. G values for double bond formation based on the difference in iodine numbers of the irradiated and non-irradiated liquid are included in the table also. The method for calculating G values for double bond formation can be found in the Semiannual Report, 1958, pp. 11-12.

D. Isolation and Molecular Weight Determinations of Polymeric Material

The term polymeric material in this report refers to that substance formed during an irradiation which has a molecular weight greater than the original substance. The apparatus used for isolating the polymeric material

TABLE III
IODINE NUMBERS AND G VALUES FOR DOUBLE BOND FORMATION

<u>Irradiation Number</u>	<u>Liquid Irradiated</u>	<u>Iodine Number</u>	<u>G Value for Double Bond Formation</u>
2	PMH (dry) Brass cell	5.51	3.0
3	PMH (dry) Stainless steel cell	11.17	7.5
4	PMH (dry)	11.41	7.7
5	Water-saturated PMH	8.81	5.5
6	Nitric Acid- saturated PMH	5.58	3.1
7	Nitric Acid - saturated PMH	3.83	1.6
8	PMH in contact with 5 ml of water	7.33	3.6
10	PMH in contact with 5 ml 4 M HNO ₃	Nil	---
11	PMH in contact with 5 ml 4 M HNO ₃	Nil	---
12	Amsco 125-82 (25 hr. irradiation)	7.1	3.9
13	Amsco 125-82 (100 hr. irradiation)	11.3	1.8

is shown in Figure 2, p. 4, Semiannual Report, 1958. The procedure used in the isolation of the polymeric material from the irradiated PMH is discussed in the Semiannual Report, 1958, p. 5.

From the amount of polymeric material isolated, G values for polymer formation (expressed as molecules of PMH converted to polymer) were calculated. Details of the calculations are given in Semiannual Report, 1958, p. 6.

Molecular weight determinations were made on some samples of the polymeric material. In the Semiannual Report, 1958, pp. 6-7, the determination of a viscosity average molecular weight of a polymeric sample using viscosity measurements was discussed. Due to the difficulty in obtaining reproducible and meaningful results using viscosity measurements, a technique employing small samples and the freezing point lowering method was developed.

The results of the work on the polymeric material are summarized in Table IV.

E. Chromatographic Analyses of the Cold-Trapped Products and of the Irradiated Cell Liquid

The gas chromatographic apparatus was the main analytical tool used in analysing the radiolysis products in the cold trap and in the irradiated cell liquid. In the initial phases of this research, the main objective was qualitative analysis and identification of the products from the cold trap. In the latter phases of the work, some quantitative results (G values) have been obtained by making use of an internal standard as described below.

The chromatographic columns used in the identification of the radiolysis products, other than hydrogen and methane, were of the vapor-liquid partition type. Column packings used in this work consisted of: didecylphthalate-coated

TABLE IV
POLYMERIC MATERIAL

Irradiation Number	Liquid Irradiated	Polymeric Material Per Cent (Weight % of Organic Phase)	G Values for Polymer Formation (Expressed as Molecules of PMH Converted to Polymer)	Molecular ^a Weight of Polymeric Material
2	PMH (dry) Brass Cell	1.68	2.1	---
3	PMH (dry) Stainless steel cell	3.79 ^b	4.6	981
4	PMH (dry) Stainless steel cell	1.95	2.4	464
5	Water-saturated PMH Stainless steel cell	1.44	1.8	---
6	Nitric Acid- saturated PMH Stainless steel cell	1.23	1.6	296
7	Nitric Acid- saturated PMH Stainless steel cell	0.43	0.56	331
8	PMH in contact with 5 ml of water Stainless steel cell	1.34	1.31	323
10	PMH in contact with 5 ml 4 M HNO ₃ Stainless steel cell	0.36	0.39	438
11	PMH in contact with 5 ml 4 M HNO ₃ Stainless steel cell	0.19	0.21	---

^a All of the molecular weights were determined by the freezing point lowering method, with the exception of the value of 981, irradiation number 3. This value was determined from viscosity measurements.

^b As mentioned in Semiannual Report, 1958, this figure appears to be high.

crushed firebrick, tri-m-cresyl phosphate-coated crushed firebrick, and dimethylsulfolane-coated crushed firebrick. The carrier gas was helium.

Qualitative identification of substances with the gas chromatographic apparatus is accomplished by comparing times of emergence or "retention volumes" (time of emergence multiplied by carrier gas flow rate) of the unknown substances with known substances. By using the same column at different temperatures or by using two different columns, more definite identification of substances can be made. A typical chromatogram of the cold-trapped radiolysis products is shown in Figure 5, p. 14, of the Semiannual Report, 1958. The results of the qualitative analyses of the radiolysis products for dry PMH and water-saturated PMH are given in Table V.

TABLE V
PRODUCTS FROM COLD TRAP

<u>Irradiation No. 3</u> <u>PMH (dry).</u> <u>Stainless steel cell.</u> <u>Identified Cold-Trapped Products</u>	<u>Irradiation No. 5</u> <u>Water-saturated PMH.</u> <u>Stainless steel cell.</u> <u>Identified Cold-Trapped Products</u>
Ethane-ethylene (trace)	Ethane-ethylene (trace)
Propane (trace)	Propane (trace)
Isobutane	Isobutane
Isobutylene	Isobutylene
Neopentane	Neopentane
2,2,4-Trimethylpentane	2,2,4 Trimethylpentane

In addition to the peaks in the chromatogram which were identified as being due to the substances listed in Table V, there were five other peaks which are most likely C₆ saturated hydrocarbons or C₅ unsaturated hydrocarbons.

Samples of the irradiated cell liquid in addition to giving a peak for PMH gave three other peaks. One of these peaks was due to 2,2,4-trimethylpentane and the other two appear just before the PMH peak. Therefore, these peaks are most likely C_9 and C_{11} hydrocarbons.

Quantitative results (G values) have been obtained by making use of an internal standard. According to Ray¹ and Hausdorff², the weight per cent of any one component in a mixture is equal to the fractional value of the area of that component as compared to the sum of the areas due to all the components in the mixture. This has been verified for molecules having a weight in excess of 50 mass units (C_4 hydrocarbons). Therefore an internal standard may be added to a sample, and peak areas of all other components compared to the peak area of the standard.

Since there were no peaks in the chromatograms of the cold trap material or of the cell liquid which had a retention time corresponding to n-hexane, this compound was selected as the internal standard. Hexane (0.033 g) was added to the 3 ml of the PMH, which contained the radiolysis products absorbed in the cold trap. A 20 lambda sample of this mixture was then injected into the gas chromatographic unit. From the resulting chromatogram, the areas of all the peaks were determined. The following is a sample calculation for the 2,2,4-trimethylpentane found in the cold trap of irradiation number 8.

- | | |
|--|-------|
| a) Peak area of 2,2,4-trimethylpentane = | 19.66 |
| b) Peak area of n-hexane = | 33.00 |

¹Ray, J. App. Chem., 4, 21(1954).

²Hausdorff, Presented at Symposium, Inst. Soc. of America, Los Angeles, (September, 1955).

- c) Weight of 2,2,4-trimethylpentane =
$$\frac{\text{Area of 2,2,4-trimethylpentane} \times \text{weight of n-hexane}}{\text{Area of n-hexane}}$$
- d) Weight of 2,2,4-trimethylpentane =
$$\frac{19.66}{33.00} \times 0.033 \text{ g.}$$
- e) Weight of 2,2,4-trimethylpentane = 0.0197 g.
- f) No. of moles of 2,2,4-trimethylpentane =
$$\frac{\text{Weight}}{\text{g - mol. weight}}$$
- g) No. of moles of 2,2,4-trimethylpentane =
$$\frac{0.0197}{114.2}$$
- h) No. of moles of 2,2,4-trimethylpentane = 0.000172 moles
- i) Energy absorbed =
$$6.45 \times 10^{22} \text{ ev/25 hours.}$$
- j) $G(2,2,4\text{-trimethylpentane}) = \frac{\text{Number of moles} \times \text{Avogadro's No.} \times 100}{\text{Energy absorbed}}$
- k) $G(2,2,4\text{-trimethylpentane}) = \frac{0.000172 \times 6.02 \times 10^{23} \times 100}{6.45 \times 10^{22}}$
- l) $G = 0.16 \text{ molecules of 2,2,4-trimethylpentane/100 ev.}$

To a 3 ml aliquot of the cell liquid, 0.033 g of hexane was added. A 20 lambda sample of the mixture was then injected into the gas chromatographic unit. The calculations for G values are the same as those described above for the cold-trapped radiolysis products with the following exception: the weight of any radiolysis product in the cell liquid is given by the following expression - Wt. of Product =

$$\frac{\text{Area of product}}{\text{Area of n-hexane}} \times \text{Wt of n-hexane} \times \frac{\text{Total volume of cell liquid}}{3 \text{ ml aliquot}}$$

Some of the radiolysis products from the cold trap have been identified, and the G values determined. Other products in the cold trap have not been definitely identified. It is possible, however, to assume a certain carbon content for them by comparing the times of emergence of these products with times of emergence of known compounds, and therefore, calculate G values for

them. The same procedure has been used with radiolysis products found in the cell liquid. The results are summarized in Table VI.

F. X-Ray Dosimetry

The basis for all the dosimetry work reported here is the series of calorimetric determinations made by Dr. E. L. Alexander of the energy output of a Machlett OEG-60 tungsten target end-window tube. In his determinations a known fraction of the tube output was absorbed in either water or o-xylene. Using standard calorimetric procedures he was able to show that the accepted G value of 15.5 for the oxygen-saturated ferrous sulfate-sulfuric acid dosimeter was valid to within a possible error of 10% for the radiation from that tube. It was important to establish that this was so because a large fraction of the photons from the Machlett OEG-60 x-ray tube are of energies lower than those for which the G value of 15.5 had been demonstrated to be valid. Further experiments have shown that a G value of 15.2 is the correct one to use when the dosimeter solution is air-saturated rather than oxygen-saturated.

Calibrations of the brass irradiation cell were made using the ferrous ion dosimeter. Since these experiments were made under air-saturated conditions, the G value of 15.2 was employed in the calculations. The presence of sulfuric acid in the dosimeter solution made it necessary to coat the brass irradiation cell with polyethylene to prevent acid attack (dezincification). The volume of sample used in this work was 30 ml. For this reason 30 ml of dosimeter solution was chosen. This procedure ensured a constant depth of solution in the irradiation cell.

The total x-ray tube beam power was found to be 0.25 watt by irradiating a volume of dosimeter solution which was so large that an increase in either

TABLE VI
G VALUES FOR RADIOLYSIS PRODUCTS

Irradiation No. 7 Nitric Acid-saturated PMH (a) Products from Cold Trap		Irradiation No. 8 PMH in contact with water (a) Products from Cold Trap		Irradiation No. 10 PMH in contact with 4 M HNO ₃ (a) Products from Cold Trap	
Product	G Value	Product	G Value	Product	G Value
Isobutane	0.043	Isobutane	0.010	Isobutane	0.026
Neopentane	0.091	Neopentane	0.015	Neopentane	0.043
Isobutylene	0.110	Isobutylene	0.015	Isobutylene	0.11
Isopentane	0.016	Isopentane	0.0066	Isopentane	0.003
2,2,4-Trimethylpentane	0.067	Neohexane	0.012	Neohexane	0.015
Neohexane	0.019	2,2,4-Trimethylpentane	0.16	2,3-Dimethylpentane	0.002
C ₅ Hydrocarbon (1 peak)	0.004	C ₆ Hydrocarbons (3 peaks)	0.0075	2,4-Dimethylpentane	0.016
C ₆ Hydrocarbon (2 peaks)	0.022	C ₇ Hydrocarbons (4 peaks)	0.036	2,2,4-Trimethylpentane	0.08
C ₇ Hydrocarbon (4 peaks)	0.072			C ₄ Hydrocarbon (1 peak)	0.005
				C ₅ Hydrocarbon (1 peak)	0.004
				C ₆ Hydrocarbon (1 peak)	0.005
				C ₇ Hydrocarbon (2 peaks)	0.041
(b) Products in Cell Liquid		(b) Products in Cell Liquid		(b) Products in Cell Liquid	
Product	G Value	Product	G Value	Product	G Value
2,2,4-Trimethylpentane	0.51	2,2,4-Trimethylpentane	0.47	2,2,4-Trimethylpentane	0.30
C ₉ Hydrocarbons (1 peak)	0.16	C ₉ Hydrocarbons (1 peak)	0.021	C ₉ Hydrocarbons (1 peak)	0.059
C ₁₁ Hydrocarbons (1 peak)	0.28	C ₁₁ Hydrocarbons (1 peak)	0.016	C ₁₁ Hydrocarbons (1 peak)	0.080

depth or diameter caused no measureable increase in the equivalents of iron oxidized in a given time. Thirty ml of dosimeter solution in the irradiation cell was then shown to absorb energy at a rate of 0.12 watt. From this it is evident that about 50% of the total x-ray beam is absorbed in the irradiation cell. That part of the beam which is not absorbed is primarily from the high energy portion of the beam and so a disproportionately large fractional increase in dosimeter solution volume would be required to contain even 75 per cent of the beam. Because obtaining useful volumes of purified hydrocarbons was one of the major problems in this work, increased beam absorption at the cost of considerably increased sample size did not seem profitable and was not pursued.

The ferrous ion dosimeter was used to calibrate the stainless steel cell. The 30 ml of dosimeter solution in the stainless steel irradiation cell was shown to absorb energy at a rate of 0.125 watt. In order to check the calibration of the metal cells, a glass cell having essentially the same dimensions as the metal cells was fabricated. The 30 ml of dosimeter solution in the glass cell was shown to absorb energy at a rate of 0.128 watt.

IV. DISCUSSION

A. Results of the Irradiations

The conditions for the irradiations in this research are given in Table I. PMH has been irradiated as a pure, dry substance; water-saturated substance; nitric acid-saturated substance; in contact with water; and in contact with 4 M. nitric acid. In all irradiations, except two, the stainless steel irradiation cell was used.

1. G Values for Hydrogen and Methane

The G values for hydrogen and methane are given in Table II. There is good agreement among the G values for both hydrogen and methane for the irradiation of dry PMH in the brass cell at the two different time lengths of irradiation. The G values for hydrogen and methane for the two irradiations of dry PMH in the stainless steel cell are in good agreement and are only slightly higher than in the case of the brass cell.

The irradiation of water-saturated PMH in the stainless steel cell gave the highest G values for hydrogen and methane. These results indicate that the presence of a very small amount of water in PMH has a pronounced effect on the formation of hydrogen and methane during an irradiation. It should be pointed out that the solubility of water in PMH is very small. In the irradiations of 25 ml PMH in contact with 5 ml water, the G values for hydrogen and methane fall in range for the G values from the irradiations of dry PMH.

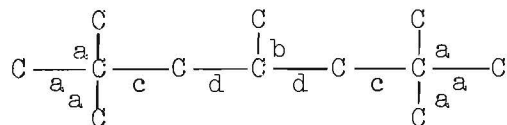
The G values for hydrogen and methane from the two irradiations of nitric acid-saturated PMH are in good agreement and also from the two irradiations of PMH in contact with 4 M. nitric acid. These G values are the

lowest obtained for hydrogen and methane from any of the irradiations of PMH. Although in the case of hydrogen the decrease in the G value is not large, there is a definite decrease. In the irradiation of PMH in contact with 4 M. nitric acid, the G value for methane is about one-half that of the other irradiations with the exceptions of the water-saturated PMH.

2. Radiolysis Products Found in the Cold Trap and in the Irradiated Cell Liquid

During an irradiation the stream of argon sweep gas carried with it the volatile radiolysis products. All of the volatile radiolysis products except hydrogen and methane were condensed in the cold trap. At the end of an irradiation, samples from the cold trap liquid were analysed as quickly as possible on the gas chromatographic unit. Also samples of the cell liquid were analysed in the gas chromatographic unit to determine if any radiolysis products were present in the cell liquid. In some of the irradiations, G values were obtained for these products. These results are summarized in Tables V and VI.

An examination of the carbon skeleton of PMH,



would lead one to expect certain radiolysis products from the rupture of the various carbon to carbon bonds. Rupture of either carbon bond a or b would lead to a methyl group and an eleven carbon skeleton. The methyl group, by extracting a hydrogen from an adjacent molecule, would form methane. G values for methane are given in Table II, p. 10. Evidence for C₁₁ compounds was found in the chromatograms of the cell liquid. Samples of the

cell liquid gave chromatograms with peaks which appeared just before the peak for PMH (C_{12} hydrocarbon). Although no definite identification could be made for these peaks, it seems that they are most likely due to C_{11} compounds based on a comparison of emergence times of PMH and some other known compounds.

Rupture of carbon to carbon bond c would lead to an isobutane carbon skeleton and a carbon skeleton corresponding to 2,2,4-trimethylpentane. Isobutane and isobutylene were both identified as products from the cold trap for the various irradiations of PMH. 2,2,4-Trimethylpentane was identified as a product from both the cold trap and the cell liquid. The total G values for 2,2,4-trimethylpentane are: 0.63 for irradiation of PMH in contact with water; 0.58 for irradiation of nitric acid-saturated PMH; and 0.38 for irradiation of PMH in contact with 4 M. nitric acid.

Rupture of carbon to carbon bond d would lead to a neopentane carbon skeleton and a 2,2-dimethylpentane carbon skeleton. Neopentane was identified a product for the various irradiations of PMH. The presence of 2,2-dimethylpentane could not be definitely established because a sample of known 2,2-dimethylpentane was not available for purposes of comparison.

Other products which were identified cannot be accounted for on the basis of primary bond rupture in PMH, but are possibly due to a combination of radiolysis fragments or a rupture of carbon to carbon bonds in some of the primary radiolysis products. Other peaks which appeared on the chromatograms were not identified but were assigned a certain carbon content based on a comparison of the times of emergence of these peaks with known substances available in this study.

3. Polymeric Material

In the irradiation of an organic substance, there is usually formed a substance with a higher molecular weight than the original substance. In this report, this higher molecular weight substance is referred to as the polymeric material. The isolation of the polymeric material is discussed on p. 5. From the quantity of polymeric material isolated from a sample of irradiated PMH, the percent polymeric material was determined and also the G value (expressed as molecules of PMH converted to polymeric material) for polymer formation. In some cases, molecular weight determinations were made on the polymeric material. These results are summarized in Table IV, p. 14.

The amount of polymeric material isolated from two of the irradiations of dry PMH are in fair agreement, 1.68 % and 1.95%. The amount of polymeric material, 3.7%, obtained from the other irradiation of dry PMH appears to be high and inconsistent with the other results.

The other irradiations of PMH, in which PMH had been saturated with either water or nitric acid or was in contact with water or 4 M. nitric acid, gave smaller amounts of polymeric material. The results show that the presence of a second and/or third component, either dissolved in the PMH or as a second phase, has the effect of decreasing the amount of polymeric material formed. In the case of the irradiation of PMH in contact with nitric acid this decreased the amount of polymeric material to less than 0.4%.

The molecular weight determinations of the polymeric material were made using the freezing point lowering method with the exception of the polymeric material from irradiation no. 3. In this case, the molecular weight was determined from viscosity measurements as reported in the Semiannual Report,

1958. The value 981 appears to be too high when compared with the other values, which were determined by the freezing point lowering method. This method employed a thermistor as the temperature sensing component and a 10 mv recorder. With this method, a molecular weight of 112 (theoretical value, 114) was obtained for 2,2,4-trimethylpentane and a molecular weight of 388 (theoretical value, 411) was obtained for 90% pure squalene ($C_{30}H_{50}$). From the molecular weights, it appears that the polymeric material was formed by dimerization of two molecules of PMH or by reaction of a PMH molecule with a C_{11} fragment. These reactions would give products in the 312 to 340 molecular weight range.

Some samples of polymeric material were run on the gas chromatographic unit at a column temperature of 200° C. The chromatogram showed five peaks having retention volumes which correspond to C_{22} to C_{25} hydrocarbons. No identification work was possible because of the lack of any samples of hydrocarbons that could be used for identification. Before complete characterization of the polymeric material can be made, a great deal more study would have to be devoted to the polymeric material. One of the difficulties involved is the small amount of material available from an irradiation for experimental purposes.

4. Unsaturation

The iodine numbers, which are used as a measure of unsaturation in an organic substance, for the irradiated PMH are given in Table III. G values for double bond formation (number of double bonds formed per 100 ev) were calculated from the differences between the iodine number of PMH before irradiation (1.98) and after irradiation. These calculations are based on the

assumption that for every mole of iodine absorbed, one mole of carbon-carbon double bonds is present in the organic material.

The iodine numbers show a considerable increase for irradiated dry PMH in the stainless steel cell over the iodine number for PMH in the brass cell. It is not clear just why there should be an increase. An examination of the iodine numbers shows that the addition of either water or nitric acid to the PMH decreases the amount of unsaturation produced during irradiation. In the case of PMH in contact with 4 M. nitric acid, the unsaturation is nil based on the fact that the irradiated PMH gave no iodine number. These results show that the presence of a second and/or third component in the PMH during irradiation has a pronounced effect on the amount of unsaturation produced.

The iodine numbers for the irradiated raw Amsco 125-82 are in the same range as for irradiated dry PMH. It seems reasonable to assume that if Amsco 125-82 were irradiated under the varying conditions that PMH was irradiated, it would show similar results with respect to unsaturation.

5. Irradiations of PMH Involving Nitric Acid

Two irradiations of nitric acid-saturated PMH and two irradiations of PMH in contact with 4 M. nitric acid were made. The conditions for the irradiations were the same as for the other irradiations with the exception that the beryllium end window of the x-ray tube was covered with a sheet of mica (6 mg/sq cm). The mica window reduced the dose rate from 4.3×10^{19} ev/min to 4.0×10^{19} ev/min. All of the irradiations involving nitric acid were made in the stainless steel cell.

The G values for hydrogen and methane from the four irradiations of PMH involving nitric acid were the lowest obtained. This indicates that

some competing reactions are taking place during an irradiation when nitric acid is present which decreases the amounts of hydrogen and methane produced.

The amount of unsaturation produced during the irradiation of nitric acid-saturated PMH is decreased by about one-half as compared with the irradiation of dry PMH in the stainless steel cell. In the case of PMH in contact with 4 M. nitric acid, the results of the iodine numbers show that the unsaturation is negligible. These results indicate that the nitric acid or some fragment produced from nitric acid is reacting with the position in PMH which would ordinarily lead to unsaturation.

The smallest amount of polymeric material isolated from irradiated PMH was from the PMH in contact with 4 M. nitric acid. This polymeric material had a brownish color whereas the polymeric material from the other irradiations had a light cream color. The molecular weight of 438 for this polymeric material indicates that the substance is composed of dimers and trimers of PMH.

During the irradiation of PMH in contact with 4 M. nitric acid, it seems likely that radiolysis products would be formed which would contain nitrogen and/or oxygen. It seems reasonable to expect products which would contain the nitro group, although the formation of other nitrogen-containing compounds is not impossible. The gas chromatograms of the cold trap products and of the cell liquid did not give any peaks which would be due to nitromethane, nitroethane, 1-nitropropane and 2-nitropropane. Nitromethane has a boiling point of 101°, and if formed during the irradiation, most of it should remain in the cell liquid. The other nitro compounds if formed should be in the cell liquid. A sample of the cell liquid was analysed³ for carbon, hydrogen and

³Analyses by Weiber and Strauss Microanalytical Laboratory, 164 Banbury Road, Oxford, England.

nitrogen with the following results:

% carbon, 84.42; % hydrogen, 15.3; no nitrogen found.

The calculated percentages for carbon and hydrogen are 84.7 and 15.3, respectively, for PMH. There was not sufficient polymeric material for an elemental analysis. The results of the work indicate that if nitrogen and/or oxygen containing compounds were formed during the irradiations of PMH in contact with nitric acid, they were not formed in sufficient quantities to be detectable.

B. Dosimetry

The calibrations of the stainless steel irradiation cell were made with the ferrous ion dosimeter. Thirty ml of the dosimeter solution was found to absorb energy at the rate of 4.68×10^{19} ev/min or 0.125 watt. Calibrations were made using a glass cell having essentially the same dimensions as the stainless steel cell. Thirty ml of the dosimeter solution in the glass cell was found to absorb energy at the rate of 4.80×10^{19} ev/min or 0.128 watt. The close agreement of the calibrations indicates that the calibrations for the stainless steel cell are reliable and reasonably accurate.

As pointed out in Annual Report No. 1, the dose absorbed by 30 ml of PMH is somewhat less than the dose absorbed by 30 ml of dosimeter solution because of the lower electron density of PMH. In order to correct for this, the dose rate in the dosimeter solution is multiplied by 0.92 (see page 37, Annual Report No. 1, for details concerning this correction factor). This gives a value of 4.3×10^{19} ev/min, which is the dose rate used for calculations involving the stainless steel cell.

In the irradiation of PMH involving nitric acid, the beryllium end-window of the x-ray tube was covered with a sheet of mica (6 mg/sq cm). The dose rate with this modification was found to be 4.0×10^{19} ev/min., and this value was used in the calculations of results from the irradiations of PMH involving nitric acid.

VI. SUMMARY

The irradiations of the PMH and Amsco 125-82 in this research have been carried out so that the volatile radiolysis products were constantly removed from the irradiation cell by a stream of argon gas. With the exception of hydrogen and methane, the volatile radiolysis products were caught in a cold trap. The argon gas stream was analysed periodically for hydrogen and methane with the gas chromatographic apparatus. The products in the cold trap and cell liquid were also analysed with the gas chromatographic apparatus. Unsaturation was determined from the iodine numbers of the cell liquid. Polymeric material was isolated from the cell liquid, and molecular weight determinations were made on this material. Irradiations were performed on the following: pure, dry PMH; water-saturated PMH; nitric acid-saturated PMH; PMH in contact with water; PMH in contact with 4 M. nitric acid; and raw Amsco 125-82.

The G values for hydrogen for PMH vary from a high of 1.92 for the water-saturated PMH to a low of 0.96 for PMH in contact with 4 M. nitric acid. The G values for methane for PMH vary from a high of 1.38 for the water-saturated PMH to a low of 0.37 for PMH in contact with 4 M. nitric acid. These variations in G values for hydrogen and methane for irradiation of PMH under different conditions shows the effects of a second and/or third component on quantity of a radiolysis product. The G values for hydrogen from two different irradiations of pure dry PMH in the stainless steel are 1.24 and 1.30 and for methane, 0.81 and 0.85. Dewhurst⁴ reported G values for hydrogen and methane of 4.9 and 0.05, respectively, for dodecane ($C_{12}H_{26}$) which

⁴Dewhurst, Radiation Chemistry of Organic Compounds, J. of Phy. Chem., 61, 1466(1957).

is a straight chain hydrocarbon and is isomeric with PMH. Since PMH is highly branched with methyl groups, it is reasonable to expect a greater yield of methane and a lower yield of hydrogen than from dodecane. Amsco 125-82, irradiated 25 hours, gave G values of 1.9 and 0.57 for hydrogen and methane respectively.

In addition to hydrogen and methane, other radiolysis products (which would be expected to be formed by rupture of the different carbon to carbon bonds in the PMH) were identified in the cold trap and cell liquid. These products include isobutylene, isobutane, neopentane, and 2,2,4-trimethylpentane. Other products were identified which cannot be accounted for by carbon to carbon bond rupture in the PMH molecule, and must be due to a combination of radiolysis fragments and/or further carbon to carbon bond rupture in some of the radiolysis fragments. Complete identification of all of the radiolysis products would involve a considerable amount of effort. One of the difficulties involved is the small quantity of radiolysis products formed.

The iodine numbers, which are used as a measure of the amount of unsaturation in organic substances, varied from a high of 11.41 for the irradiated dry PMH to a low of zero for PMH irradiated in contact with 4 M. nitric acid. The iodine numbers for the irradiated PMH decrease in the following order: dry PMH, 11.17 and 11.41; water-saturated PMH, 8.81; PMH in contact with 5 ml. water, 7.33; nitric acid-saturated PMH, 3.83 and 5.58; PMH in contact with 5 ml 4 M nitric acid, zero. The order in which the iodine numbers decrease demonstrates the effect of the second and/or third component on the amount of unsaturation produced during an irradiation. The fact that PMH irradiated in contact with 4 M. nitric acid had an iodine number of zero indicated that the nitric acid, or some fragment formed from nitric acid during irradiation,

is reacting with those positions of the PMH molecule where the unsaturation is produced during the irradiation of dry PMH. No concrete evidence, however, could be found for the presence of nitrogen and/or oxygen containing compounds in either the volatile radiolysis products or the cell liquid.

The amount of polymeric material isolated from the irradiated PMH varied from a high of 1.95 per cent for dry PMH to a low of 0.19 per cent for PMH in contact with 4 M. nitric acid. This indicates that the presence of a second and/or third component during an irradiation has a pronounced effect on the amount of polymeric material formed. The molecular weights for the polymeric material falls in the range of molecular weights of dimers and trimers formed from PMH. A gas chromatogram of a sample of polymeric material gave five peaks, which demonstrates that the polymeric material is a mixture.

VII. ACKNOWLEDGEMENTS

During the course of this research, a number of persons have contributed to the project. The project was initiated under the direction of Dr. Raymond G. Wymer, who continued as project director until June 30, 1958. During that time Dr. E. L. Alexander was consulted frequently on the project. Since July 1, 1958, Dr. R. G. Palmer has carried out a number of the irradiations. Dr. Fred Sicilio has been consulted frequently on the project since July 1, 1958. Others who have contributed to various phases of the irradiations and laboratory work are Messers. Randall Carter, Bert Wilkins, Keith Davis, Herschel Godbee, and William Van Willis.

Respectfully submitted,

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VIII. SUPPLEMENT: EXTRACTION STUDIES ON AMSCO-TRIBUTYL PHOSPHATE MIXTURES[†]

A. Objective

The object of these studies was to determine the effects of irradiated Amsco 125-82 on the extraction characteristics of the Amsco-tributyl phosphate (TBP) mixture.

B. Background

In the Thorex Process a mixture of Amsco-TBP is used to extract uranium and thorium from an acid deficient feed solution containing fission products. The decontamination factor (DF) is then used as a measure of the increase in product purity attained in the overall process or in any one of its steps. This is generally calculated as the ratio of the amount of contaminant per unit weight of product before and after the process. When the solvent is regenerated, however, it is found that the DF's for fission products have decreased due to the radiation damage to the solvent.

C. Experimental Method

1. Solutions

The following solutions were prepared for the study:

- (1) TBP plus unirradiated Amsco (42.5 : 57.5).
- (2) TBP plus raw Amsco irradiated to 8.16×10^{22} ev (42.5 : 57.5).
- (3) TBP plus raw Amsco irradiated to 2.58×10^{23} ev (42.5 : 57.5).
- (4) Thorex feed solution prepared as follows:
350 grams of thorium per liter
0.55 M $\text{Al}(\text{NO}_3)_3$
0.2 M acid deficient,
 5.44×10^4 alpha counts per 10 min. per ml

[†]This supplement was prepared by Richard C. Palmer.

- (5) Ru-106 spike solution prepared by boiling Ru-106 in nitric acid for 48 hours, taking to dryness, and diluting to 2 ml with 0.01 nitric acid. Beta, gamma count was 6.3×10^6 c/10 min.-ml

2. Extraction Process

One ml samples of Thorex feed solution which had been spiked with Ru-106 were extracted with 5 ml aliquots of each of the TBP-Amsco Mixtures. Duplicate samples were run. The mixtures were shaken for 5 minutes and then allowed to stand for 1.5 hours.

3. Counting Procedure

0.1 cc samples of the organic phase were transferred to small watch glasses. One drop of dilute collodion solution was added. The watch glasses were placed on small aluminum rings and dried for 2 hours on a hot plate. Beta, gamma count was then obtained with an end-window geiger tube. Alpha count was obtained with an alpha scintillation counter.

D. Results

- (1) TBP plus unirradiated Amsco; DF is 52.
- (2) TBP plus Amsco (8.16×10^{22} ev); DF is 50.
- (3) TBP plus Amsco (2.58×10^{23} ev); DF is 47.

These results indicate that irradiation of Amsco has no effect on the Ru-106 decontamination factor. It must be remembered, however, that the low boiling materials are no longer present due to the irradiation set-up.