



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

ENGINEERING EXPERIMENT STATION
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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

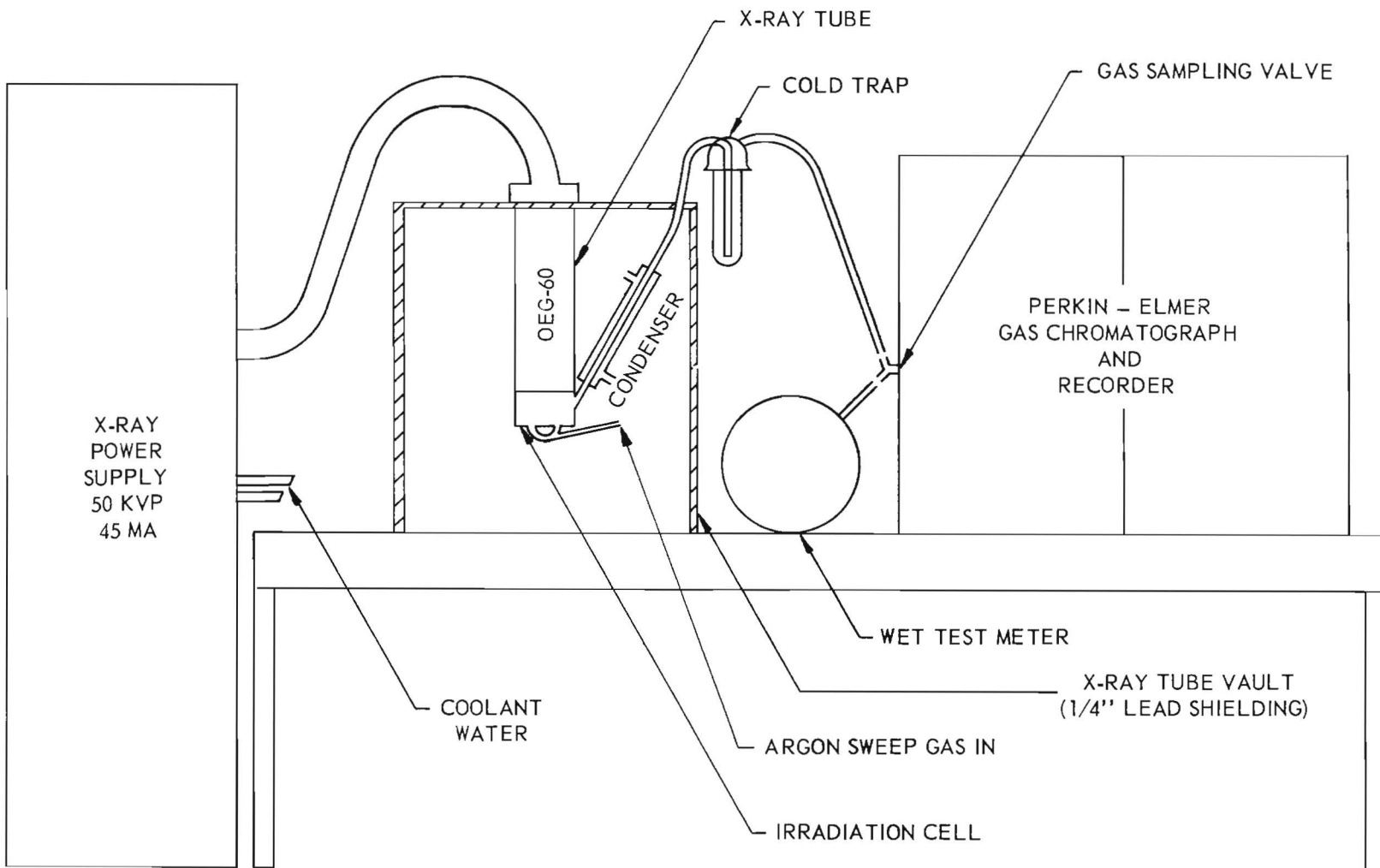


Figure 1. Equipment Arrangement for Irradiations.

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.

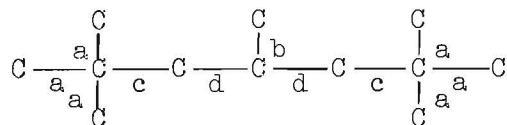
The G values for hydrogen and methane from the two irradiations of nitric acid-saturated PMH are in good agreement and also from the two irradiations of PMH in contact with 4 M. nitric acid. These G values are the

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,

✓ James A. Knight, Jr.
Project Director

Approved:

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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.