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FINAL REPORT

PROJECT NO. A-428

DISTILLATIONAL PURIFICATION OF IRRADIATED TRIBUTYL PHOSPHATE IN KEROSENE-TYPE DILUENT

By

FRED SICILIO, T. H. GOODGAME, AND BERT WILKINS, JR.

SUBCONTRACT NO. 1374
UNDER W-7405-eng-26

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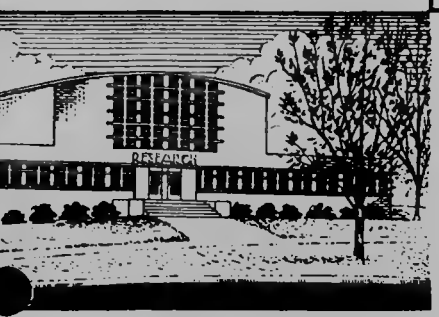
PLACED WITH THE CHEMICAL TECHNOLOGY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE



Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

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

A. Background

1. Tributyl Phosphate and Amsco 125-82

In the Purex Process for the separation of uranium and thorium from fission products and reactor element materials, a mixture of tributyl phosphate (TBP) and paraffinic hydrocarbons (Amsco 125-82) is used to extract the fissionable materials. Amsco 125-82, a mixture of highly branched, saturated hydrocarbons, reportedly prepared commercially by the polymerization and subsequent hydrogenation of olefins, consists of about 17 components in the C_{12} to C_{14} range.[1]

2. Radiation Damage to Purex Process Solvent

In the Purex Process, the solvent is subjected to a considerable amount of radiation damage. This results in emulsion formation, deposition of solids at the interface, and in lower decontamination factors for the fission products. In addition, it becomes more difficult to strip the fissionable materials from the process solvent.

At the present time, knowledge of the amount and the nature of the degradation products is limited. It is known that the tributyl phosphate degrades to give mono- and dibutyl phosphates and probably phosphoric acid. The diluent probably degrades through bond rupture at the branching positions to give lighter fractions and some polymerized products. It has been found in this laboratory that irradiation of the diluent alone to a dose of 8.16×10^{22} ev yields 26 detectable products. Solutions of tributyl phosphate and the

[1] Raymond G. Wymer, "Radiation Chemistry of Organic Substances," Annual Report No. 1, Project No. A-323, Engineering Experiment Station, Georgia Institute of Technology, March 31, 1958.

diluent which have been equilibrated with nitric acid prior to irradiation can be expected to yield a considerably larger number of products upon irradiation.

Several investigators have reported on the effect of radiation damage on TBP-hydrocarbon extraction solvents.[2,3] In particular, it has been found that the TBP--Amsco 125-82 system is noticeably affected by radiation doses of 2 watt-hours/liter.

The TBP--Amsco 125-82 solvent is affected in a number of ways which are immediately noticeable. In the operation of an extraction column, the increased tendency for emulsion formation and the build-up of "crud" in the column are evident. Another effect that is noticed is the deterioration of desirable extraction characteristics, in that fission product extraction is enhanced. Also, once extracted, the fission products are difficult to wash out. The extraction of fuel such as uranium does not seem to be affected very much, but once extracted, it is very difficult to back extract it out of the solvent. These factors lead to poor recoveries with low decontamination factors, even if emulsion formation does not completely prohibit the operation.

3. Radiation Chemistry of TBP and Amsco 125-82

A number of authors have reported on the radiolysis products of TBP and Amsco 125-82. Among these are: Cathers,[4] Wymer,[5] Goode,[6] Burger

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[2] G. I. Cathers, "Radiation Damage to Radiochemical Processing Reagents," Progress in Nuclear Energy, Vol. III, Process Chemistry, Bruce, et al., McGraw-Hill (1957).

[3] Fred Sicilio, The Stability of Some Solvents to X-rays. Ph.D. Thesis, Vanderbilt University (1956).

[4] Cathers, loc. cit.

[5] Wymer, loc. cit.

[6] J. H. Goode, Nucleonics 15, No. 2 (1957).

and McClanahan,[7] and Knight.[8] The radiolysis of TBP yields various light hydrocarbon gases as well as hydrogen, dibutyl phosphate, monobutyl phosphate, butyl alcohol, and polymer. The irradiation of Amsco 125-82, and pure compounds believed to be very similar to it, yields a number of lighter hydrocarbons, hydrogen, and a polymer. It is not clear, as yet, how radiation affects a mixture of these solvents in contact with an aqueous phase under actual extraction conditions.

Dibutyl phosphate, monbutyl phosphate and butanol have been shown to have an effect on the solvent-extraction characteristics of the solvents. However, the possibility exists that nitrated organics are also formed, and these products could also contribute to the alteration of characteristics. Also of interest is the polymer detected in radiolysis work.

B. Purification of Radiation-Damaged Solvent

Due to the increased use of nuclear fuels and the reprocessing of these fuels, it will be necessary to develop a process for the removal of those products which give rise to undesirable properties in the solvent. Fractionation and/or chemical treatment are the most obvious means of recovering the solvent.

The purpose of this work is to determine the feasibility of fractionation, or a combination of fractionation and washing, as means of purifying radiation-damaged Purex Process solvent. Purex-type solvent which had been subjected to simulated Purex Process conditions was used in this work.

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[7] L. L. Burger and E. D. McClanahan, "Tributylphosphate and Its Diluent Systems," Industrial and Engineering Chemistry, 50, No. 2, (1958).

[8] James A. Knight, "Radiation Chemistry of Organic Substances," Final Report, Project No. A-323, Engineering Experiment Station, Georgia Institute of Technology, January 31, 1959.

II. DESCRIPTION OF MATERIAL AND EQUIPMENT

A. Description of Solvent

1. Purex Process Solvent

Purex Process solvent is composed of a mixture of tributyl phosphate and Amsco 125-82. Properties of these materials are given in Tables I and II.

TABLE I

PROPERTIES OF TRIBUTYL PHOSPHATE[9]

Chemical Formula	$(C_4H_9)_3PO_4$
Molecular Weight	266
Color	Water White
Odor	Mildly Sweet
Refractive Index at 20° C	1.4245
Viscosity at 25° C	3.41 centipoises
85° C	0.8 Centipoises
Boiling Point at 760 mm Hg	289° C
15 mm Hg	173° C
1 mm Hg	121° C
Specific Gravity at 25° C	0.973
Freezing Point	80° C
Flash Point, Cleveland Open Cup	145° C
Dielectric Constant at 30° C	7.97
Solubility in Water at 25° C	0.6 vol %
Solubility of Water in TBP at 25° C	7 vol %

[9] J. R. Flannary, "Solvent Extraction of Uranium and Plutonium from Fission Products by Means of Tributyl Phosphate," Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. 9, p. 531, United Nations, New York, 1956.

TABLE II

PROPERTIES OF AMSCO 125-82[10]

Density at 24.2° C	0.7468 gm/cm^3
Boiling Range at 760 mm Hg	165-210° C
U. V. Absorption	300-220 mμ
Bromine Test for Unsaturation	Positive
Potassium Permanganate Test for Unsaturation	Negative
Hydrogen Uptake Test for Unsaturation	0.76 mole %
Average Molecular Weight	184
Formation of Urea Adducts	Negative
Iodine Number (Hanus Method)	2.4
Refractive Index at 30° (Na D line)	1.41767

Several liters of fresh stock TBP and Amsco 125-82 were supplied by the Oak Ridge National Laboratory. These solvents, as supplied, were used as control samples during these studies.

2. Irradiated Solvent (Simulated Purex-Type)

The sample of irradiated solvent used in these studies was prepared by the Oak Ridge National Laboratory. A solution containing 30 per cent by volume of TBP was made up from pretreated TBP and Amsco 125-82. This solvent solution was then contacted with an aqueous solution containing the following concentrations before contact: 1.30M natural uranium and 1.84N nitric acid. The two phases, in contact, were irradiated in a cobalt-60 gamma source to a dose of 121 watt-hours/liter to the organic phase. The organic phase was then stripped by successive contacting with aqueous solutions of 0.01N nitric acid. Four strips were performed with a volume ratio (aqueous/organic) of 0.32 and four with a volume ratio of 0.80. The last aqueous strip solution contained 0.68 gm/liter natural uranium. The analysis of the organic phase is given in Table III.

[10] Wymer, loc. cit.

TABLE III

COMPOSITE ANALYSIS
OF STRIPPED IRRADIATED TBP--AMSCO 125-82[11]

Natural Uranium	3.29 gm/liter	[TBP]	32.1% by volume
$[H^+]$	0.01 molar	$[H_2O]$	2.1 gm/liter
	Specific Gravity	0.825 at 25.5° C	

3. Aqueous Stock Solution for Contact Studies

The following aqueous solutions were prepared for use in the solvent-extraction equilibration studies:

Solution A: 40 mg/liter U^{233}; 40 mc/liter Ru^{106}-Rh^{106}; 4.86N HNO_3

Solution B: 15 mg/liter U^{233}; 15 mc/liter Ru^{106}-Rh^{106}; 4.47N HNO_3

B. Rapid Volatilization Apparatus

The setup for the rapid volatilization work is shown in Figure 1. It consisted of either a 1- or 3-liter round bottom distilling flask with a 35/25 ball and socket connector and a thermometer well. The condenser and distillation head consisted of one piece so that the vapor and condensate came in contact with only glass from the time that they left the distilling head until they were in the distillate receiver. The distillation head contained a thermometer well located in the vapor stream to measure the temperature of the distilling vapor. A Cenco Hy-Vac pump was used to produce the necessary low

[11] Wallace Davis, Jr., Private Communication. The guide for establishing conditions of the simulated aqueous feed and contact was taken from "The Purex Process-A Solvent Extraction Reprocessing Method for Irradiated Uranium," by E. R. Irish and W. H. Reas, Symposium on The Reprocessing of Irradiated Fuels, Book 1, Session I, p. 83, Brussels, Belgium, May 20-25, 1957 (TID-7534).

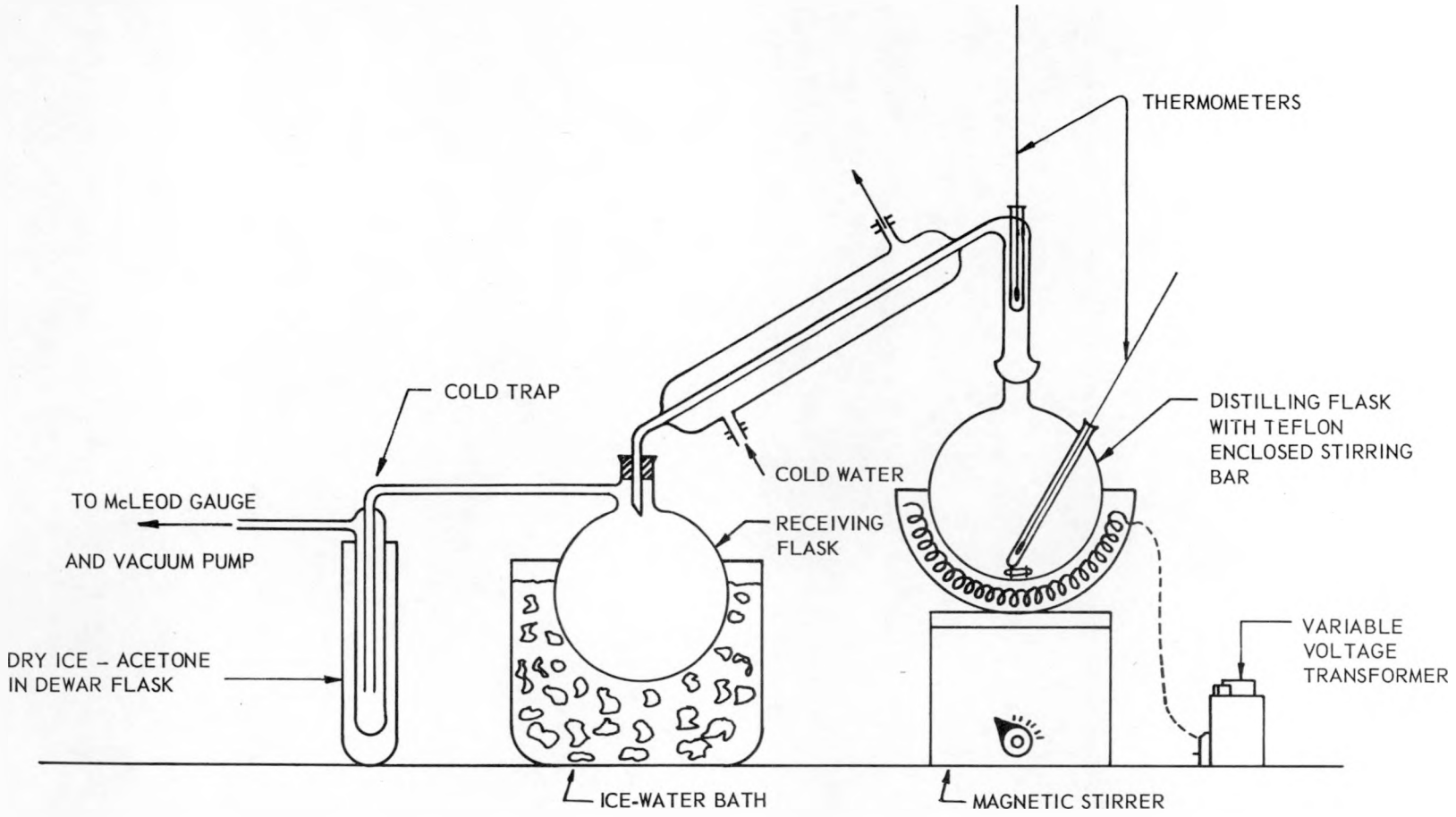

Figure 1. Apparatus for Rapid Volatilization.

pressures and it was protected by a cold trap immersed in a bath of dry ice and acetone. A McLeod gauge was used to measure the pressure. The pressure in the system was regulated manually by a screw clamp on the vacuum line to ± 0.1 mm mercury. A laboratory heating mantel and a variable voltage transformer were used to supply the heat for distilling. To prevent bumping and to provide a high rate of volatilization, a one-inch stirring bar in the distillation flask was stirred magnetically. Tap water was used as coolant for the condenser, but an ice bath was maintained around the distillate receiver.

C. Fractional Distillation Apparatus

The fractional distillation apparatus, shown in Figure 2, was designed and constructed with the following principles in mind:

1. That it be capable of operating from atmospheric to low pressure (on the order of 10 mm).
2. That contact of the distillate with extraneous soluble materials such as stopcock grease be kept at a minimum, if not eliminated completely.
3. That reflux, boil-up, and pressure be maintained and controlled accurately and automatically for extended periods of time.
4. That the efficiency of the column be high even at reduced pressure, e.g., low pressure drops at high through-puts.
5. That the hold-up in the column be kept low in relation to the charge.

The fractional distillation column was constructed from 1-, 1-5/8-, and 2-1/4- inch-diameter concentrically arranged pyrex glass tubes of 4-foot lengths. The inner one-inch tube contained the packing and was the actual distillation

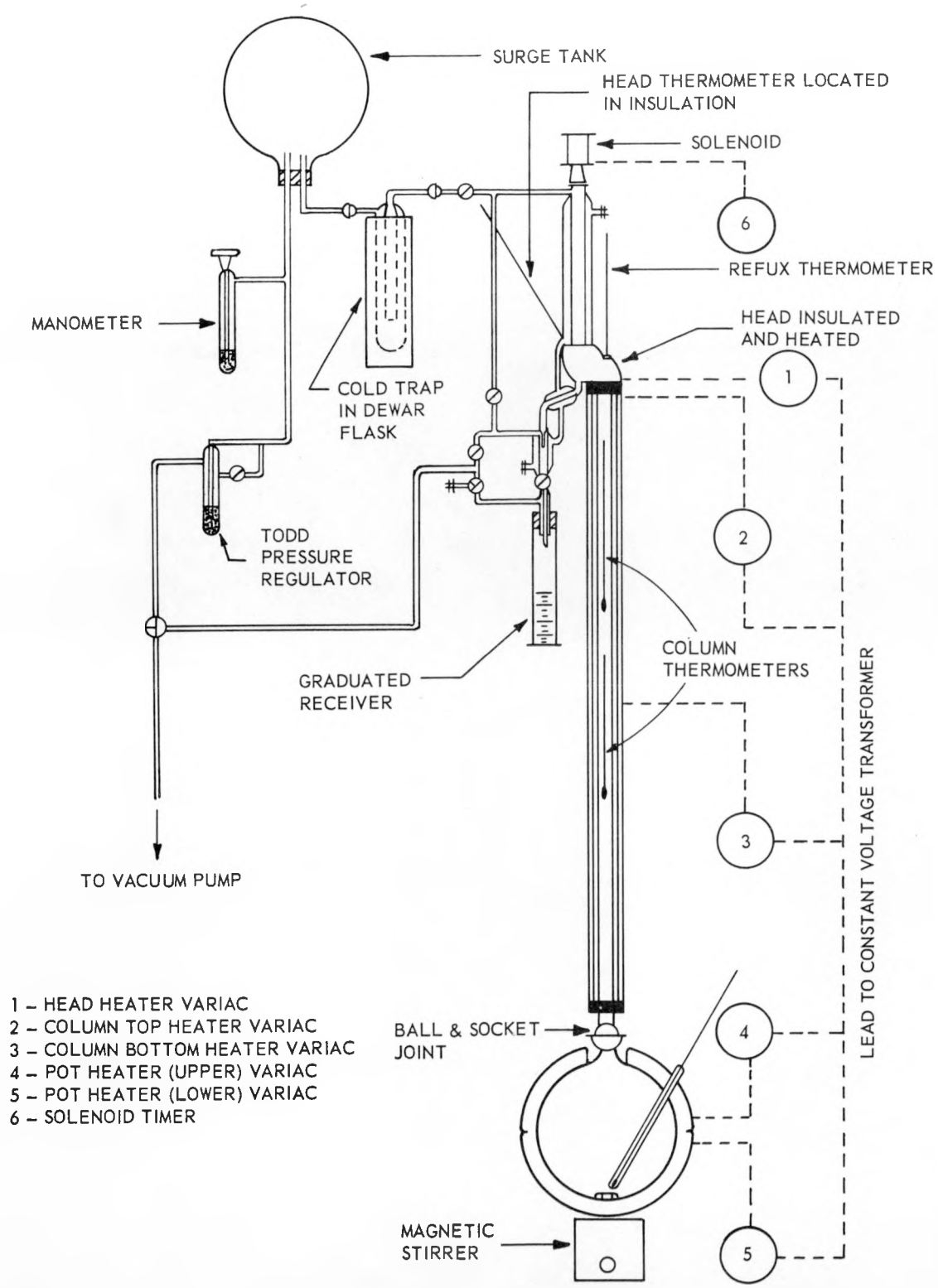

Figure 2. Fractional Distillation Column.

column. The second tube provided an air bath and supported the nichrome wire heating elements which were wrapped around its outside. The outside tube provided another air bath for thermal insulation and protected the heating elements. The all-glass construction permitted complete observation of the packed section during operation. The inner tube supported two total immersion thermometers located such that they indicated the temperature one-third of the way from the top and the bottom of the column. Each heating element consisted of approximately 45 turns of nichrome wire; the total resistance at 25° C was 18 ohms in each section. Each heating element was controlled independently and covered 2 feet of the column. The inner tube was glass welded directly to the distillation head at the top and was connected at the distilling pot by a 35/25 ball joint. The packing was supported by a stainless steel or nichrome packing support.

The distillation head, shown in Figure 3, was designed and constructed such that the only surfaces that came in contact with the distillate were of glass or teflon and such that all valves through which the distillate flowed were "greaseless." The design of the head is essentially that of Kieselbach,[12] with several modifications to achieve the above mentioned conditions.

The distillate temperature was measured to ± 0.10° C by a thermometer mounted in a well which protruded into the vapor stream. To insure accurate readings, the well was made of thin glass with a diameter just large enough to allow free entrance for the thermometer. Several drops of dibutyl phthalate were added to the well to act as a heat transfer medium. In order to obtain an accurate reading in the measured reflux ratio, the lower section of the

[12] R. Kieselbach, Analytical Chemistry, 19, No. 10, 815 (1947).

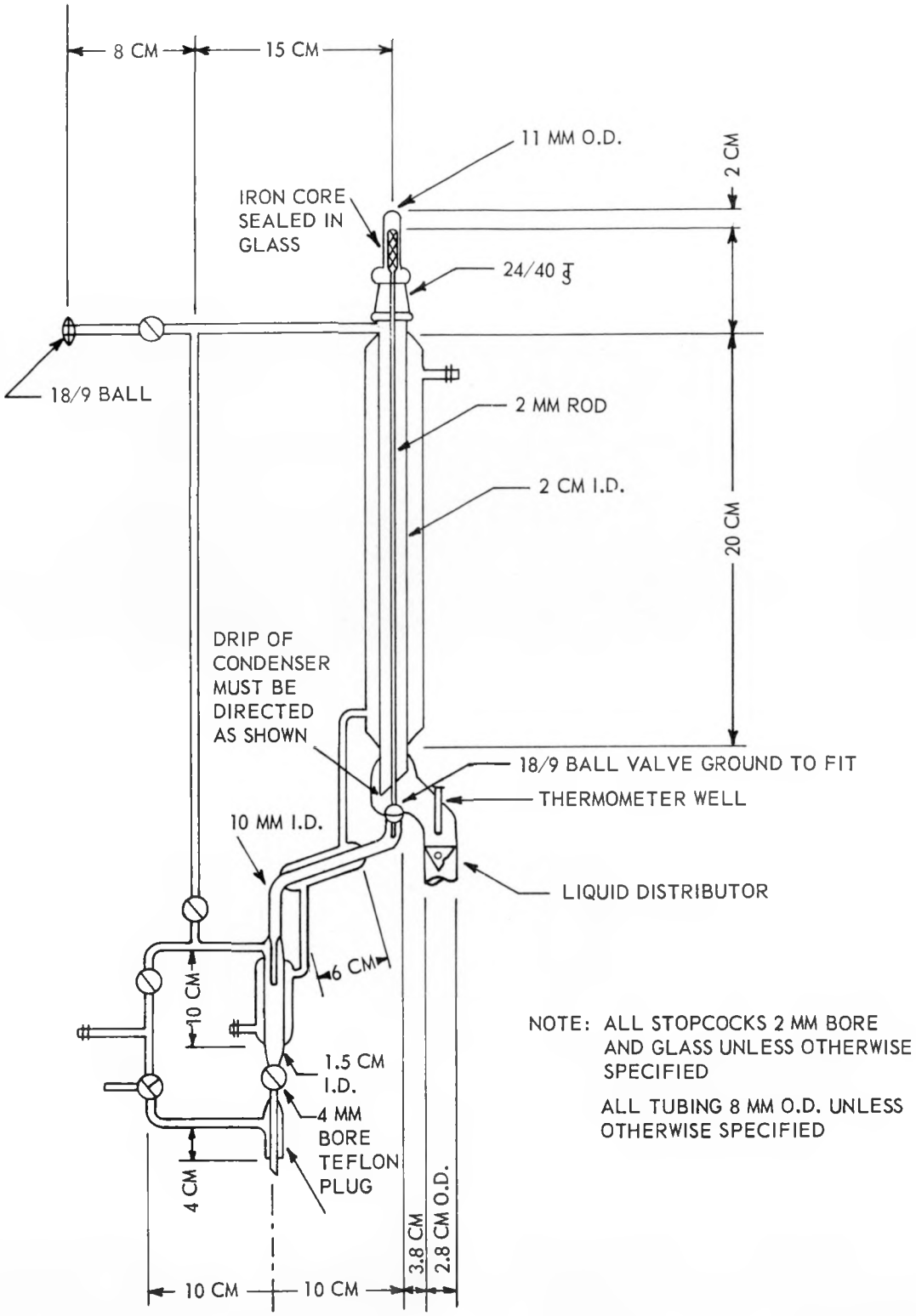

Figure 3. Fractional Distillation Column Head.

distillation head was insulated with fiberglas and equipped with a small nichrome wire heater. A thermometer was located at the outside wall of the vapor head but inside the heater and the insulation. The distillation head was equipped with a solenoid-operated ball valve which served as the take-off valve. The valve was located so that, when open, all reflux from the condenser flowed out through it; when closed, all reflux from the condenser flowed around it and back to the packed section of the column. The solenoid was actuated by a General Electric variable timer, Model No. 3TSA14AP30A. The total cycle of the timer was 30 seconds, with an adjustable on-or-off interval from 1 to 99 per cent of the total cycle.

The reflux head was also equipped with a system of stopcock valving to permit taking of cuts without disturbing either the reflux ratio or the pressure in the distilling head and column.

A Todd pressure regulator, designed to operate between 2 and 50 mm mercury with a sensitivity of ± 0.05 mm, was used. The pressure was measured with a closed-end mercury manometer with an accuracy of 0.5 mm mercury. The cold trap was cooled by a dry ice--acetone bath. The cold trap served to protect the pump and catch very volatile distillate; it could handle approximately 50 ml of material without becoming obstructed.

Standard Pyrex glass distilling flasks equipped with 35/25 socket joints and a thermometer well were used as still pots. Laboratory heating mantels were used as still pot heaters.

Electrical voltage to the entire system was regulated by a General Electric constant voltage transformer. The solenoid voltage and the heater voltage were controlled by heat input at the pot. Constant boil-up for any heat input was insured by regulating the system voltage and by regulating the room temperature (the laboratory was air-conditioned).

The column packing used for this work was Podbielniak Heli-Pak No. 2117 stainless steel distillation packing, of very high efficiency and low pressure drop characteristics. The packing was poured into the column and then "tamped" until no change in height was noticed, since the manufacturer reports a marked increase in column efficiency for "tamped" packing over "untamped" packing.

D. Counting Equipment

An end-window Geiger-mueller detector and scaler was used to count beta-gamma radiation. A zinc sulfide (silver activated) scintillation detector with photomultiplier, preamplifier, and scaling circuit was used to count alpha radiation.

E. Other Equipment

Solvent extraction equilibrations were performed in 3-milliliter vials with ground glass stoppers. All transfers were made with glass pippettes. Samples were taken from the equilibration vials with micropipettes attached to hypodermic syringes.

The gas chromatograph used in this work was a Fisher Model No. 300. The chromatographic column was prepared by packing two 6-foot lengths of 1/4-inch copper tubing with Fisher Scientific 30- to 60-mesh, acid-washed firebrick coated with Dow Corning No. 200 silicone oil (25 weight per cent silicone oil). The density of packing was 5.1 gm/ft of tubing. The packing material was prepared by dissolving the silicone oil in iso-octane and making a slurry of this solution and the firebrick. The iso-octane was then evaporated over a steam bath with constant stirring. When apparent dryness was attained the packing was dried for 12 hours in an oven at 120° C.

III. EXPERIMENTAL PROCEDURES

A. Rapid Volatilization

The rapid volatilization evaporations were performed by charging a 2-liter flask with 500 to 700 ml of Amsco-TBP solvent. The apparatus described in Chapter II B was set up and the stirring motor turned on. The pressure was reduced to approximately 0.5 mm mercury and controlled by hand. After very light materials were distilled, the temperature of the pot was gradually increased until a rapid efflux from the condenser was noticed. When all the Amsco diluent had evaporated, as noted by a dropping head temperature and an increasing pot temperature, the pot was cooled and the pressure brought back to atmospheric pressure. The processes were repeated with additional portions of Amsco-TBP solvent until the desired volume had been processed. The Amsco fractions were then combined to be fractionally distilled. The pot residues were combined and charged to the rapid volatilization apparatus and in a similar manner the TBP was volatilized. The evaporated TBP was then ready to be fractionally distilled.

B. Fractional Distillation

All fractional distillations were carried out in the column described in Chapter II C. The material was charged to either a 1- or 2-liter distillation flask which was then attached to the distillation column. The pressure was reduced to the desired operating pressure and the pressure regulator was set. The pot and column heaters were then turned on and the column and pot temperatures were gradually increased. In order for the column to equilibrate quickly and attain its maximum efficiency, the column was preflooded. The voltage

settings were then reduced to approximate operating values and the column was allowed to equilibrate for 4 hours at total reflux. After the column had equilibrated, the reflux timer was set for the desired reflux ratio, and distillate take-off was started. The boil-up rate was determined by recording the time taken to collect 10 ml of distillate at a given reflux ratio. The through-put was then calculated from the following:

$$\frac{(\text{Reflux Ratio} + 1)\ \ (10)}{(\text{Time to Collect 10 Ml})} = \text{Volumetric Through-put}$$

Small adjustments of the pot heater necessary to bring the through-put to the proper value were then made. The column heaters were adjusted, so that nearly adiabatic conditions were realized, by keeping the top thermometer equal to the head temperature and the bottom thermometer half way between the head temperature and the pot temperature.

C. Calibration of Column

The efficiency of the distillation column was determined by using a 1-methylnaphthalene--2-methylnaphthalene test mixture. This test mixture has been reported to give excellent results with a distillation column very similar to the one used in this work. While Feldman[13] used an ultraviolet absorption technique to analyze the 1-methylnaphthalene--2-methylnaphthalene system, high temperature vapor phase chromatography was used in this work.

The analysis was made by measuring the ratio of peak areas which, because of the same molecular weights of the two naphthalenes, gave both weight per cent and mole per cent. It seemed reasonable to expect such similar compounds to have very

[13] J. Feldman, et al., Industrial and Engineering Chemistry, 45, No. 1, 1953.

nearly the same response in a thermal conductivity cell; e.g., as in the case of the xylenes. A known mixture was analyzed to prove this hypothesis.

The test mixture was charged to the distillation column and the pressure was adjusted to the desired operating pressure. The heaters were then brought up to operating temperatures; the column was preflooded and then allowed to reflux until equilibrium was reached, as indicated by constant distillate composition. The distillate was analyzed by vapor phase chromatography. The through-put was determined as described above. The still pot was then removed and the small volume of distillate used to determine the through-put was added to the still pot and the still pot composition was analyzed. The Fenske equation for a total condenser at total reflux was used to calculate the number of theoretical plates and the height equivalent to a theoretical plate (HETP).

$$N + 1 = \frac{\log (x_A/x_B)\ (y_B/y_A)}{\log \alpha_{Average}}$$

where N = number of theoretical plates,

x_A = mole fraction A in liquid,

y_A = mole fraction A in vapor,

x_B = mole fraction B in liquid,

y_B = mole fraction B in vapor,

and

α = relative volatility

defined as $(y_1/y_2)\ (x_1/x_2)$ at equilibrium,

where y_1 = mole fraction of most volatile component in vapor,

x_1 = mole fraction of most volatile component in liquid,

y_2 = mole fraction of least volatile component in vapor,

and x_2 = mole fraction of least volatile component in liquid.

D. Extraction-Scrub Studies

A small portion of each cut from the eight distillations of the rapid volatilizations was taken and either fresh TBP or fresh Amsco 125-82 was added to it to make a mixture which was 30 per cent TBP and 70 per cent Amsco by volume. A stock solution of the same composition was made up for control.

Two-milliliter aliquots of each organic solution were contacted with one-milliliter portions of an aqueous stock stolution in ground glass vials by shaking for 30 seconds. Five minutes were allowed for separation of phases, and two 10- or 50-λ aliquots of each organic phase were samples for counting.

A one-milliliter portion of each organic phase was transferred and contacted with one-milliliter of 4N nitric acid as a scrub. The organic phase was again sampled and counted.

E. Extraction-Strip Studies

One-milliliter aliquots of the organic solutions (made up to 30 per cent TBP and 70 per cent Amsco from each distillation cut) were contacted with equal volumes of aqueous stock solution. Stripping was accomplished by contacting 0.5 ml of the organic phase with an equal volume of 0.01N nitric acid solution. Each organic phase was sampled twice and counted.

F. Sample Preparation and Counting Procedures

Sample preparation was performed in a manner very similar to Wischow[14] and Tuck.[15] Sample preparation is very important in alpha counting because

[14] R. P. Wischow, Rate of Solvent Extraction; Nitric Acid and Uranyl Nitrate with Tributylphosphate as the Extracting Agent. Ph.D. Thesis, Vanderbilt University (1958).

[15] D. G. Tuck, "The Preparation of Samples for Alpha Counting by the Direct Evaporation of Organic Solutions," Analytica Chimica Acta, 17, (1957).

of self absorption in the sample. Thus, it is very important to dry liquid samples such that residual film thicknesses are reproducible if different samples are to be compared. The organic sample from an equilibration was pipetted on the center of a cool, 50-mm-diameter watch glass. The watch glass was then carefully placed on a hot aluminum ring under a 250-watt heat lamp. After a predetermined time, the watch glass was removed, cooled and counted. Table IV gives data on the reproducibility of equilibration and sampling.

In order to insure stability of counting equipment, a standard sample was prepared and counted daily on both the alpha and beta-gamma detectors. Backgrounds were also run daily to detect any contamination on the counters.

TABLE IV

REPRODUCIBILITY OF SAMPLING TECHNIQUE

10λ Samples Prepared From Same Source (5-Minute Counts)			
α(C/5 Min-10λ)		βγ(C/5 Min-10λ)	
3804	3862	3592	3597
3813	3501	3641	3845
3603	3871	3470	3713
3843	3755	3726	3760
3768	3657	3568	3805
3540	3774	3665	3932
(Average = 3733 ± 213)		(Average = 3693 ± 210)	
50λ Samples Prepared From Same Source (5-Minute Counts)			
α(C/5 Min-50λ)		βγ(C/5 Min-50λ)	
16982	17558	6267	6864
17075	17799	6411	6590
17656	17116	6443	6682
17231	16820	6186	6065
17140	16938	6247	6165
(Average = 17232 ± 415)		(Average = 6392 ± 253)	

IV. DISCUSSION OF EXPERIMENTAL RESULTS

A. Calibration of Distillation Column

The distillation column was calibrated as described in Chapter III. The column was found to have 41.7 theoretical plates at total reflux and 50 mm mercury pressure, with a boil-up of 528 ml/hr. The data for this calculation may be found in Table V.

TABLE V

DISTILLATION COLUMN CALIBRATION DATA

Distillate	Boil-Up
8.9% 1-methylnaphthalene	528 ml/hr
91.81% 2-methylnaphthalene	
α = 1.11†	Packing
Pot	Podbielniak No. 2117 stainless steel
88.65% 1-methylnaphthalene	Packed Height
11.35% 2-methylnaphthalene	46 inches
Theoretical Plates at Total Reflux	HETP
41.7	1.08 inches

†Taken from Feldman, et.al., loc. cit.; it is stated to be constant over a wide range of pressure.

B. Preliminary Distillations

In order to establish operating criteria for the fractional distillation apparatus, a preliminary distillation was carried out at 15 mm mercury. The charge for this distillation was 750 ml of 30 per cent fresh TBP in Amsco 125-82. The data are given in Table VI. This distillation proceeded quite smoothly until the pot was almost dry. No discoloration was noticed in the

cuts; a little color was noticed in the pot as the pot approached dryness.

TABLE VI

PRELIMINARY DISTILLATION OF UNIRRADIATED SOLVENT

Charge . . . . . 510 gm
Reflux Ratio 4/1
Operating Pressure . . . . . 15 mm Hg
Pot Residue. . . . . 20 gm
Cold Trap Residue. . . . . 3 gm
Average Boil-Up. . . . . 214 ml/hr

Cut No.	Wt. % Charge	Wt. % Distilled	Reflux Temp. (° C)	Pot Temp. (° C)
1	5.3	5.3	-	-
2	7.0	12.3	58.3	102.6
3	7.0	19.3	61.4	110.0
4	7.0	26.3	62.5	113.0
5	7.0	33.3	67.8	111.8
6	7.2	40.5	71.8	112.0
7	7.0	47.5	75.2	118.0
8	7.2	54.7	77.4	133.2
9	7.2	61.9	81.2	135.4
10	7.2	69.1	88.8	168.0
11	2.9	72.0	94.4	176.7
12	2.0	74.0	102.0	189.5
13	6.1	80.1	164.4	186.0
14	6.7	86.8	164.5	186.0
15	5.7	92.5	164.7	199.0

Also, in order to determine thermal degradation of TBP, distilled at 50 mm mercury, a charge of 500 ml of fresh TBP was partially distilled (about 50 per cent). No noticeable color change occurred in the distillate or the pot.

C. Distillation of Irradiated TBP--Amsco 125-82 Solvent

The first attempt to distill the irradiated TBP--Amsco 125-82 solvent was unsuccessful. This distillation was run at a pressure of 50 mm mercury. The distillation was plagued by frequent shutdowns. The cold trap was stopped up frequently by light gases and the mercury pressure regulator was clogged up several times by gases which managed to get through the cold trap and become adsorbed on the mercury. The distillate had a greenish-yellow cast and early cuts contained an aqueous phase consisting of a few drops of water stained deep red. Cold trap products were distinctly bright green and extremely volatile. The material in the pot turned to a black syrupy slurry a few hours after cuts were started. This syrup became thicker as the distillation proceeded and became impossible to distill after about 90 per cent of the Amsco fraction had been distilled. No reliable data could be derived from this distillation, other than the information that the irradiated solvent would be difficult to distill.

In order to check the results of the above distillation, a duplicate distillation was run. The same results were observed. However, when the pot material became impossible to distill it was centrifuged in an attempt to remove solids. A large part of the solids was removed and a black syrupy liquid was observed to be left. This liquid was then evaporated at 0.5 mm mercury pressure and the condensate was collected and observed to be a clear yellow liquid. The residue from the evaporation was a tarry black material. The condensate from the evaporation was then charged to the fractionating column and distilled in the usual manner. The distillate was only slightly discolored and attained a steady reflux temperature of 194.3 ± 3° C until the pot was almost dry. The reflux temperature corresponds to the boiling point of TBP.

As the distillation approached dry pot a sudden decomposition took place with large quantities of gases liberated. Gases with an apparent boiling point near that of butane were collected in the cold trap.

D. Results of Washing Irradiated Solvent and Then Fractionally Distilling

In order to attempt to wash out residual natural uranium and acidic radiolysis products which might be causing decomposition during the distillation period, a charge was washed six time with a 10 per cent sodium carbonate (by weight) aqueous solution in a volume ratio of 1/1 and then once with a 1/1 ratio of water. The solvent was then dried over calcium chloride. This reduced the activity of the irradiated solvent from 5.4 ± 0.7 c/min-10λ to 0.4 ± 0.2 c/min-10λ; the background was 0.2 ± 0.1 c/min.

The solvent was allowed to reflux in order for the column to come to equilibrium. As the solvent refluxed, the pot material discolored slightly over a several hour period and then a tan precipitate suddenly formed. This precipitate appeared to be a polymeric type material, and it prevented further distillation. The material in the still pot was removed and centrifuged. The supernatant liquid was removed; further distillation was attempted but an additional amount of precipitate appeared and the pot material continued to degrade, accompanied by discolored distillate.

The precipitate was assumed to be insoluble in hydrocarbons and was washed with iso-octane. The weight of the precipitate before washing was 213 gm or 31 per cent of the charge to the still. After washing with iso-octane and drying at 100° C it weighed 40 gm. This indicated that the precipitate had formed a gel with the solvent when it was centrifuged or that it was soluble in iso-octane to some extent. The dried precipitate was ash white with a soapy

appearance. It appeared to be insoluble in iso-octane, benzene, and methanol, but it dissolved in water. When hydrochloric acid was added to the water, an oily layer appeared on the surface. This oily layer had very nearly the specific gravity of water as illustrated by its lack of bouyancy.

E. Rapid Volatilization

It was thought that if the radiolysis products causing decomposition during the distillation were high boiling materials, it might be possible to rapidly evaporate the TBP and Amsco 125-82 under a high vacuum, thus preventing thermal decomposition due to the low temperature and short residence time. It was also thought to be desirable to separate the TBP and Amsco 125-82 by this method, and then to fractionally distill them separately. The separation of these two materials by a simple evaporation was possible due to their large boiling point differences.

Four of these flash distillations were performed on the materials outlined below:

1. Unwashed irradiated solvent
2. Control (fresh 30 per cent TBP--Amsco by volume) - unwashed
3. Irradiated solvent - washed with sodium carbonate
4. Control (fresh 30 per cent TBP--Amsco by volume) - washed with sodium carbonate

The wash solution was an aqueous solution of 10 per cent sodium carbonate by weight. The wash volume ratio of solvent to sodium carbonate was 2/1. Six one-liter washes were carried out. The washes were included because some benefit from sodium carbonate washes was evidenced in the previously discussed distillation.

The material balances for these rapid volatilizations may be found in Table VII. In all cases, evaporation of the Amsco fraction took place between 35° and 110° C, with 90 per cent distilling between 40° and 60° C. The TBP fraction distilled between 110° and 120° C. The pot residue had an apparent distillation temperature of 170° C.

TABLE VII

MATERIAL BALANCES FOR RAPID VOLATILIZATIONS

	Charge (Gm)	Fraction of Charge			
		Amsco	TBP	Residue	Cold Trap
Irradiated, washed	1543	0.61	0.36	0.011	0.023
Control, washed	1636	0.64	0.34	0.0092	0.0098
Irradiated, unwashed	1601	0.61	0.34	0.022	0.015
Control, unwashed	1647	0.65	0.34	0.0086	0.0055

F. Fractional Distillations of Rapid Volatilizations

The fractional distillations of the rapid volatilizations are summarized in Tables VIII A to XI B. The distillation curves are shown in Figures 4 to 11. In all cases the fractional distillations proceeded quite smoothly. All of the Amsco fractions from the rapid volatilizations were water white. When distilled, they all produced water white distillates except for two cuts. Cut No. 21 of the irradiated, unwashed Amsco and cut No. 22 of the irradiated, washed Amsco had a slight green color. It was possible to distill all but a small pot residue. The residue was slightly discolored in all cases.

The TBP fractions from the rapid volatilizations of the unirradiated solvents were water white and remained that way until distilled. At that time the pot material yellowed slightly, but the distillate was water white. The

TABLE VIII A
DISTILLATION OF AMSCO FRACTION FROM RAPID VOLATILIZATION
AND EXTRACTION-SCRUB RESULTS
Unwashed Irradiated Solvent

Charge . . . . . 970 gm
Reflux Ratio 10/1
Operating Pressure . . 50 mm Hg
Pot Residue . . . . . 21 gm
Cold Trap Residue . . . 3 gm
Average Boil-Up . . . . 560 ml/hr

Dist. Cut No.	Wt. (%) Charge	Wt. (%) Distilled	Temperature (° C) Reflux	Temperature (° C) Pot	Extraction (C/Min-10λ) α	Extraction (C/Min-10λ) βγ	Scrub (C/Min-10λ) α	Scrub (C/Min-10λ) βγ
			67.8					
1	3.69	3.69	83.3	107	614	413	635	238
2	3.77	7.46	85.2	108	691	463	665	242
3	3.77	11.23	86.8	108	637	463	559	179
4	8.20	19.43	88.8	114	623	437	572	207
5	4.54	23.97	90.1	116	710	473	542	204
6	4.33	28.30	92.7	118	659	405	603	220
7	3.74	32.04	94.8	119	673	487	625	228
8	3.76	35.80	96.0	120	708	458	567	241
9	4.05	39.85	97.8	120	697	487	595	224
10	4.61	44.46	99.4	121	660	442	579	203
11	4.49	48.95	101.1	122	692	439	630	212
12	4.13	53.08	102.0	122	613	409	629	217
13	5.09	58.17	103.4	122	609	400	610	231
14	3.83	62.00	104.6	124	605	423	577	247
15	3.30	65.30	106.3	125	623	479	566	217
16	4.71	70.01	108.2	125	615	451	560	216
17	6.20	76.21	111.8	128	615	479	580	239
18	4.14	80.35	116.4	134	653	452	612	226
19	3.98	84.33	120.8	135	612	446	556	239
20	3.96	88.29	123.0	143	629	459	598	250
21†	3.86	92.15	124.7	188	719	437	592	328
22	2.78	94.93	132.3	190	602	418	549	316

†Cut No. 21 had a green cast.

TABLE VIII B
DISTILLATION OF TBP FRACTION FROM RAPID VOLATILIZATION
AND EXTRACTION-SCRUB RESULTS
Unwashed Irradiated Solvent

Charge . . . . . 548 gm
Relux Ratio. 5/1
Operating Pressure . . 20 mm Hg

Pot Residue . . . . . 85.2 gm
Cold Trap Residue . . . 8 gm
Average Boil-Up . . . . 287 ml/hr

Dist. Cut No.	Wt. (%) Charge	Wt. (%) Distilled	Temperature (° C) Reflux	Temperature (° C) Pot	Extraction (C/Min-10λ) α	Extraction (C/Min-10λ) βγ	Scrub (C/Min-10λ) α	Scrub (C/Min-10λ) βγ
			60.0					
1	6.43	6.43	171.2	195	615	255	613	234
2	4.23	10.65	171.5	196	657	509	680	310
3	9.55	20.20	172.2	196	628	497	612	288
4	8.70	28.90	172.7	195	647	486	554	257
5	10.01	38.91	172.3	195	635	491	658	283
6	8.50	47.41	172.2	195	600	509	601	280
7	9.14	56.55	173.0	195	589	449	630	259
8	8.29	64.84	173.4	196	713	481	607	227
9	8.55	73.39	173.0	196	666	492	607	245
10	3.92	77.31	Decomposition noticed		617	454	601	234

TABLE IX A
DISTILLATION OF AMSCO FRACTION FROM RAPID VOLATILIZATION
AND EXTRACTION-SCRUB RESULTS
Unwashed Unirradiated Solvent

Charge . . . . . 1030 gm
Reflux Ratio 10/1
Operating Pressure . . 50 mm Hg
Pot Residue . . . . . 54 gm
Cold Trap Residue . . . 5 gm
Average Boil-Up . . . .580 ml/hr

Dist. Cut No.	Wt. (%)		Temperature (° C)		Extraction (C/Min-10λ)		Scrub (C/Min-10λ)	
	Charge	Distilled	Reflux	Pot	α	βγ	α	βγ
			50.0					
1	3.59	3.59	84.7	---	607	478	578	218
2	4.96	8.55	85.5	107	626	521	590	196
3	4.09	12.64	88.4	112	519	479	548	241
4	4.20	16.84	88.2	115	543	451	503	182
5	3.92	20.76	88.6	115	509	453	496	233
6	3.88	24.64	89.5	122	588	490	614	266
7	3.78	28.42	91.3	123	625	521	661	251
8	4.00	32.42	94.6	125	590	480	653	255
9	3.65	36.07	96.2	125	621	480	607	234
10	3.65	39.72	96.9	121	632	493	583	202
11	4.49	44.21	98.2	119	651	501	583	274
12	3.65	47.86	100.3	120	607	462	677	187
13	3.79	51.65	101.5	120	619	481	577	213
14	4.03	55.68	102.8	121	621	529	706	196
15	3.64	59.32	103.4	122	597	451	565	203
16	4.36	63.68	104.8	133	617	513	577	218
17	4.90	68.58	106.5	135	624	428	626	225
18	3.68	72.26	107.9	130	670	461	550	186
19	4.01	76.27	112.7	133	644	426	577	205
20	3.69	79.96	115.3	135	610	472	607	213
21	4.93	84.89	119.2	137	625	456	607	222

TABLE IX B
DISTILLATION OF TBP FRACTION FROM RAPID VOLATILIZATION
AND EXTRACTION-SCRUB RESULTS
Unwashed Unirradiated Solvent

Charge 583
Reflux Ratio 5/1
Operating Pressure . . 20 mm Hg
Pot Residue . . . . . 30 gm
Cold Trap Residue . . 7 gm
Average Boil-Up . . .185 ml/hr

Dist. Cut No.	Wt. (%) Charge	Wt. (%) Distilled	Temperature (° C) Reflux	Temperature (° C) Pot	Extraction (C/Min-10λ) α	Extraction (C/Min-10λ) βγ	Scrub (C/Min-10λ) α	Scrub (C/Min-10λ) βγ
			85.6					
1	9.54	9.54	171.8	186	656	330	549	189
2	9.05	18.59	172.6	186	618	462	592	333
3	9.00	27.59	173.5	186	630	458	525	227
4	8.80	36.39	173.6	186	624	519	545	212
5	9.80	46.19	174.0	185	611	437	437	219
6	8.15	54.34	174.0	185	621	460	578	220
7	8.74	62.81	174.6	192	625	419	578	245
8	8.24	71.05	173.8	192	597	424	589	207
9	10.29	81.34	173.8	220	604	421	596	213
			(Decomposition)					

TABLE X A
DISTILLATION OF AMSCO FRACTION FROM RAPID VOLATILIZATION
AND EXTRACTION-SCRUB RESULTS
Washed Irradiated Solvent

Charge . . . . . 878 gm
Reflux Ratio 10/1
Operating Pressure . . 50 mm Hg
Pot Residue . . . . . 16 gm
Cold Trap Residue . . Negligible
Average Boil-Up . . .620 ml/hr

Dist. Cut No.	Wt. (%) Charge	Wt. (%) Distilled	Temperature (° C) Reflux	Temperature (° C) Pot	Extraction (C/Min-10λ) α	Extraction (C/Min-10λ) βγ	Scrub (C/Min-10λ) α	Scrub (C/Min-10λ) βγ
			68.2					
1	4.15	4.15	85.3	110	717	368	701	271
2	4.06	8.21	87.8	111	718	383	740	301
3	4.14	12.35	88.4	112	729	458	649	197
4	4.13	16.75	89.1	114	720	466	744	206
5	4.09	20.84	90.2	115	726	328	684	184
6	4.21	25.05	92.2	117	703	473	669	219
7	4.24	29.29	94.8	117	734	517	652	210
8	4.11	33.40	95.6	118	743	590	559	182
9	4.36	37.76	97.2	119	723	492	647	201
10	4.21	41.97	98.4	120	684	507	710	212
11	4.75	46.72	99.6	122	732	497	663	232
12	4.34	51.06	101.0	123	715	451	621	212
13	5.10	56.16	103.0	126	701	494	648	233
14	4.14	60.30	103.8	125	722	398	730	231
15	4.20	64.50	104.7	135	731	338	687	217
16	4.31	68.81	106.8	135	665	228	657	164
17	4.24	73.05	107.3	136	728	273	710	191
18	4.24	77.29	113.0	139	755	356	707	216
19	4.24	81.53	115.9	147	720	200	644	177
20	4.30	85.83	119.5	149	698	356	705	244
21	4.31	90.14	123.0	161	665	214	642	196
22†	4.34	94.48	124.4	199	638	319	551	228
23	3.22	97.70	130.6	180	681	465	709	279

†Cut No. 22 had a green cast.

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TABLE X B
DISTILLATION OF TBP FRACTION FROM RAPID VOLATILIZATION
AND EXTRACTION-SCRUB RESULTS
Washed Irradiated Solvent

Charge . . . . . 556 gm
Reflux Ratio 10/1
Operating Pressure . . 50 mm Hg

Pot Residue . . . . . 43.4 gm
Cold Trap Residue . . . 63.3 gm
Average Boil-Up . . . . 635 ml/hr

Dist. Cut No.	Wt. (%)		Temperature (° C)		Extraction (C/Min-10λ)		Scrub (C/Min-10λ)	
	Charge	Distilled	Reflux	Pot	α	βγ	α	βγ
			85.0					
1	3.24	3.24	150.0		174	58	58	39
2	9.44	12.68	195.0		695	344	659	325
3	8.79	21.47	194.3	215	759	480	552	282
4	8.79	30.26	194.4	216	699	505	695	260
5	11.20	41.46	194.3	220	730	485	656	231
6	14.20	55.66	193.0	221	717	581	691	289
7	16.20	71.86	194.0	Decomposed	736	482	712	238

TABLE XI A
DISTILLATION OF AMSCO FRACTION FROM RAPID VOLATILIZATION
AND EXTRACTION-SCRUB RESULTS
Washed Unirradiated Solvent

Charge . . . . . 1017 gm
Reflux Ratio 10/1
Operating Pressure . . 50 mm Hg
Pot Residue . . . . . 41 gm
Cold Trap Residue . . 112 gm
Average Boil-Up . . . 650 ml/hr

Dist. Cut No.	Wt. (%) Charge	Wt. (%) Distilled	Temperature (° C) Reflux	Temperature (° C) Pot	Extraction (C/Min-10λ) α	Extraction (C/Min-10λ) βγ	Scrub (C/Min-10λ) α	Scrub (C/Min-10λ) βγ
			75.1					
1	3.66	3.66	84.2	109	670	425	677	203
2	3.49	7.15	85.5	109	624	316	614	201
3	3.49	10.64	86.8	109	640	406	658	210
4	3.60	14.24	88.0	110	659	444	632	199
5	3.55	17.79	88.4	112	708	443	629	193
6	3.72	21.51	89.10	113	737	490	638	239
7	3.59	25.10	90.05	114	679	471	636	199
8	3.66	28.76	92.40	114	668	412	693	207
9	3.54	32.30	94.20	115	679	430	636	201
10	3.94	36.24	95.50	117	665	439	619	182
11	3.60	39.84	96.50	117	638	445	623	188
12	3.16	43.00	97.0	118	745	471	728	248
13	4.24	47.24	98.7	124	710	472	707	231
14	3.61	50.85	101.2	125	722	479	Cut Spilled	
15	3.51	54.36	102.1	126	687	426	671	199
16	3.60	57.96	103.0	126	733	462	697	227
17	3.86	61.82	104.0	126	727	487	717	224
18	3.65	65.47	104.7	134	705	450	689	238
19	5.27	70.74	106.7	137	716	488	632	227
20	5.95	76.69	111.2	138	696	482	663	233
21	8.96	85.65	117.3	-	662	469	671	233
22	3.76	89.41	123.0	148	707	428	697	234
23	3.68	93.09	124.2	191	747	467	652	208
24	1.87	94.96	124.2	191	738	459	651	209

TABLE XI B
DISTILLATION OF TBP FRACTION FROM RAPID VOLATILIZATION
AND EXTRACTION-SCRUB RESULTS
Washed Unirradiated Solvent

Charge . . . . . 554 gm
Reflux Ratio 10/1
Operating Pressure . . 50 mm
Pot Residue . . . . . 73 gm
Cold Trap Residue . . 45 gm
Average Boil-Up . . .780 ml/hr

Dist. Cut No.	Wt. (%)		Temperature (° C)		Extraction (C/Min-10λ)		Scrub (C/Min-10λ)	
	Charge	Distilled	Reflux	Pot	α	βγ	α	βγ
			80.0					
1	5.30	5.30	193.6	211	708	280	703	196
2	8.45	13.75	193.6	215	706	483	647	196
3	8.65	22.40	193.5	215	735	482	697	243
4	8.39	30.79	193.6	215	742	474	675	216
5	8.80	39.59	193.6	215	695	464	663	187
6	8.55	48.14	193.6	215	690	465	668	230
7	9.71	57.85	192.6	220	697	437	660	226
8	8.39	66.24	188	220	695	426	702	228
9	5.98	72.22	Decomposed; considerable gas		562	346	649	173

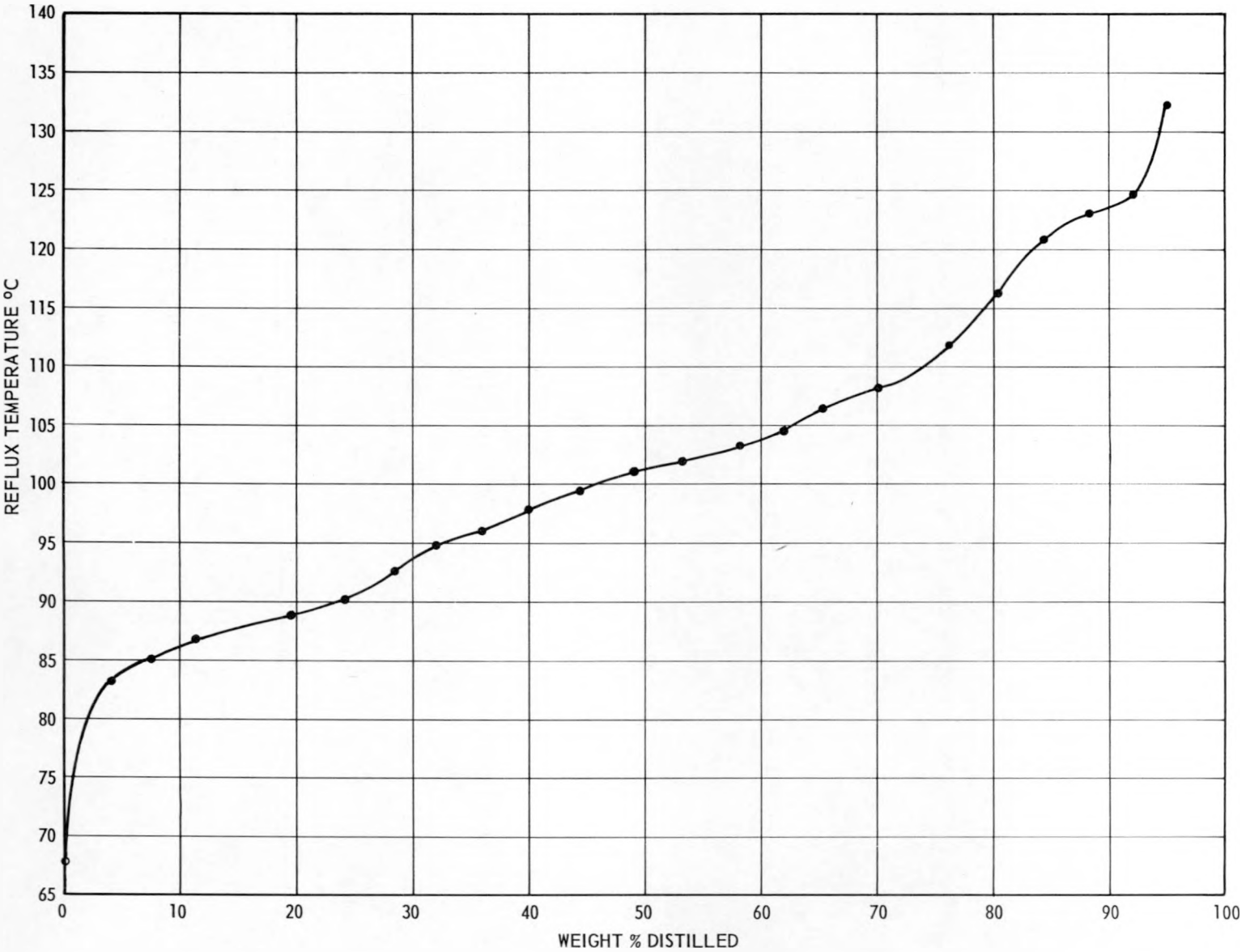

Figure 4. Distillation Curve for Amsco Fraction; Unwashed Irradiated Solvent.

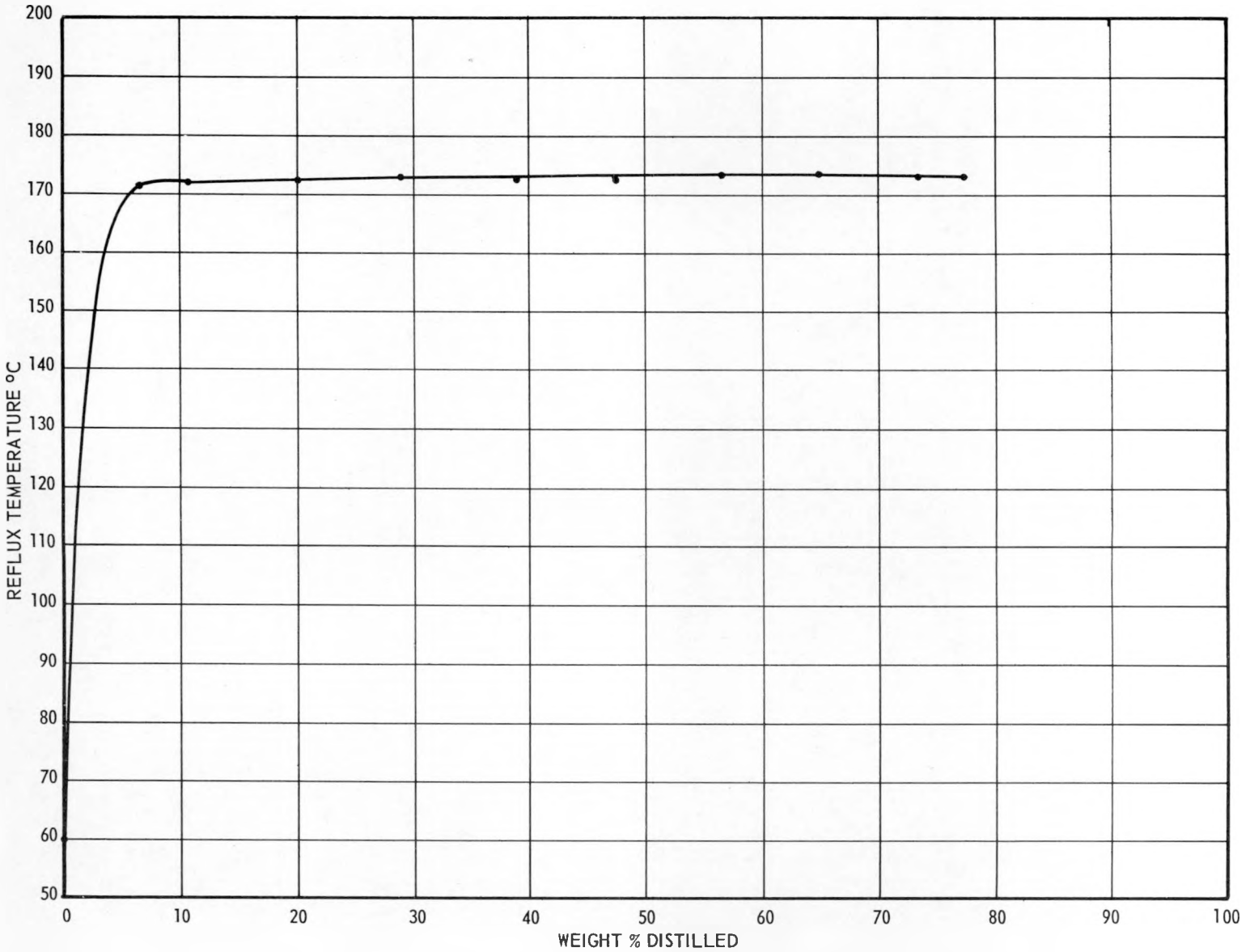

Figure 5. Distillation Curve for TBP Fraction; Unwashed Irradiated Solvent.

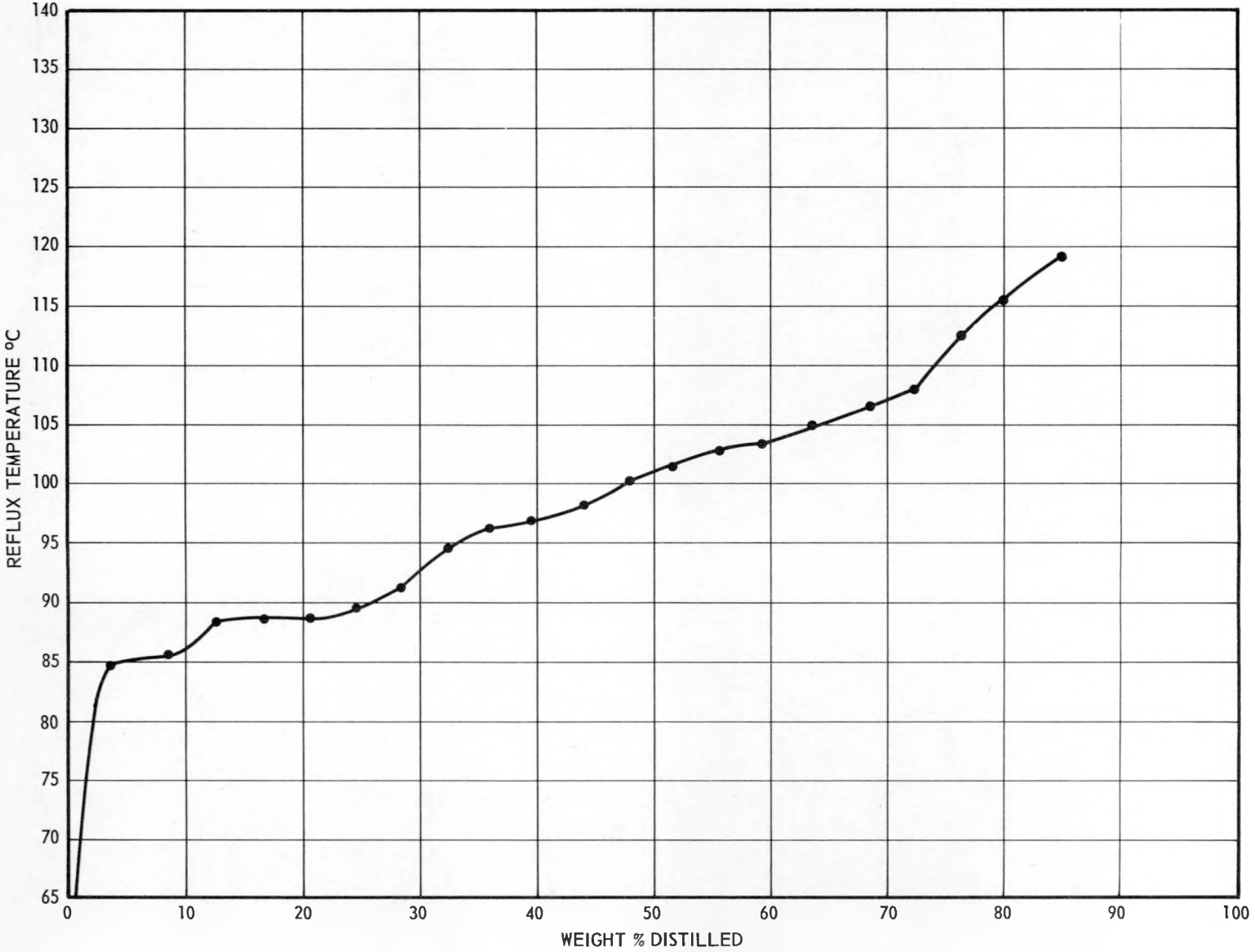

Figure 6. Distillation Curve for Amsco Fraction; Unwashed Unirradiated Solvent.

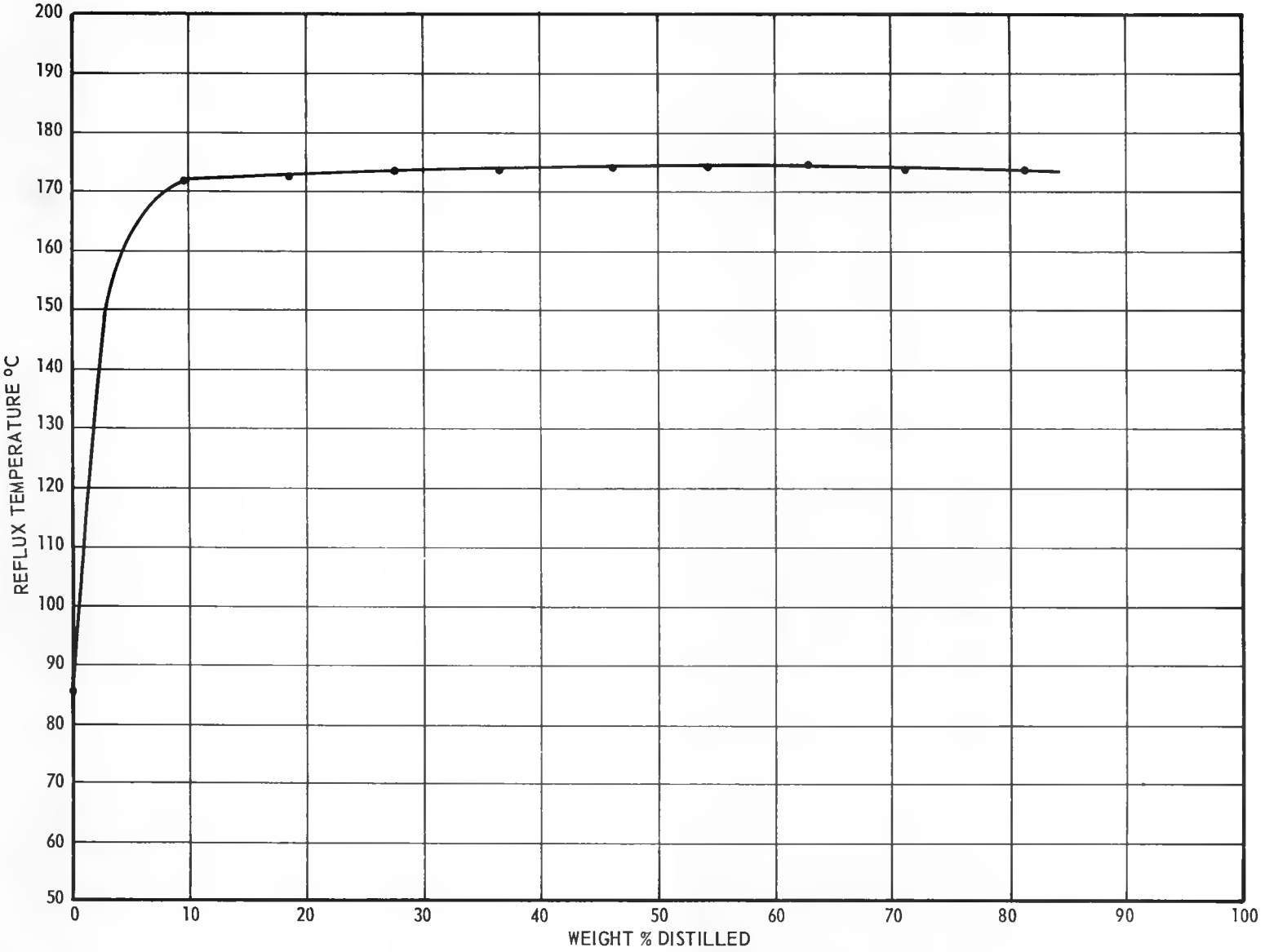

Figure 7. Distillation Curve for TBP Fraction; Unwashed Unirradiated Solvent.

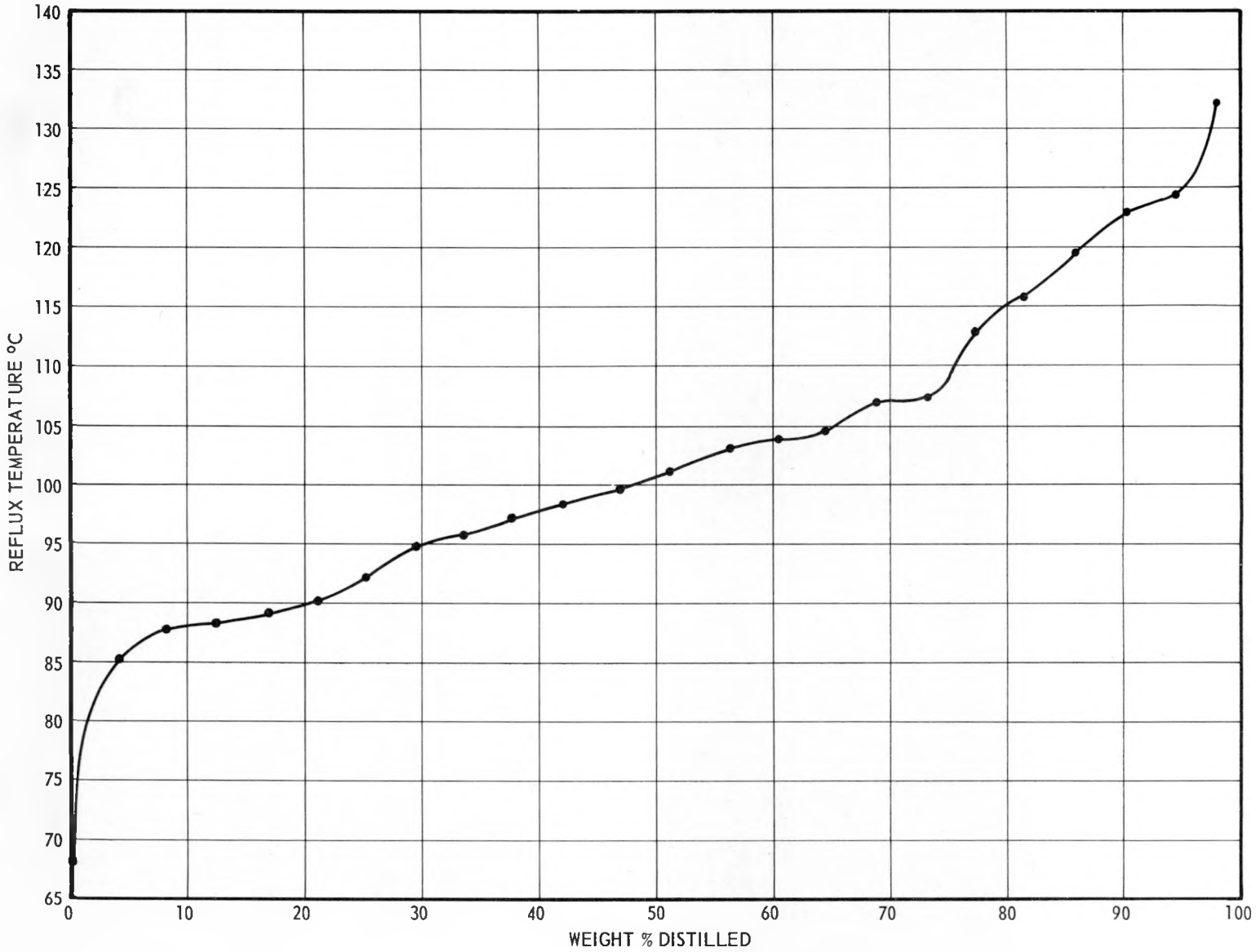

Figure 8. Distillation Curve for Amsco Fraction; Washed Irradiated Solvent.

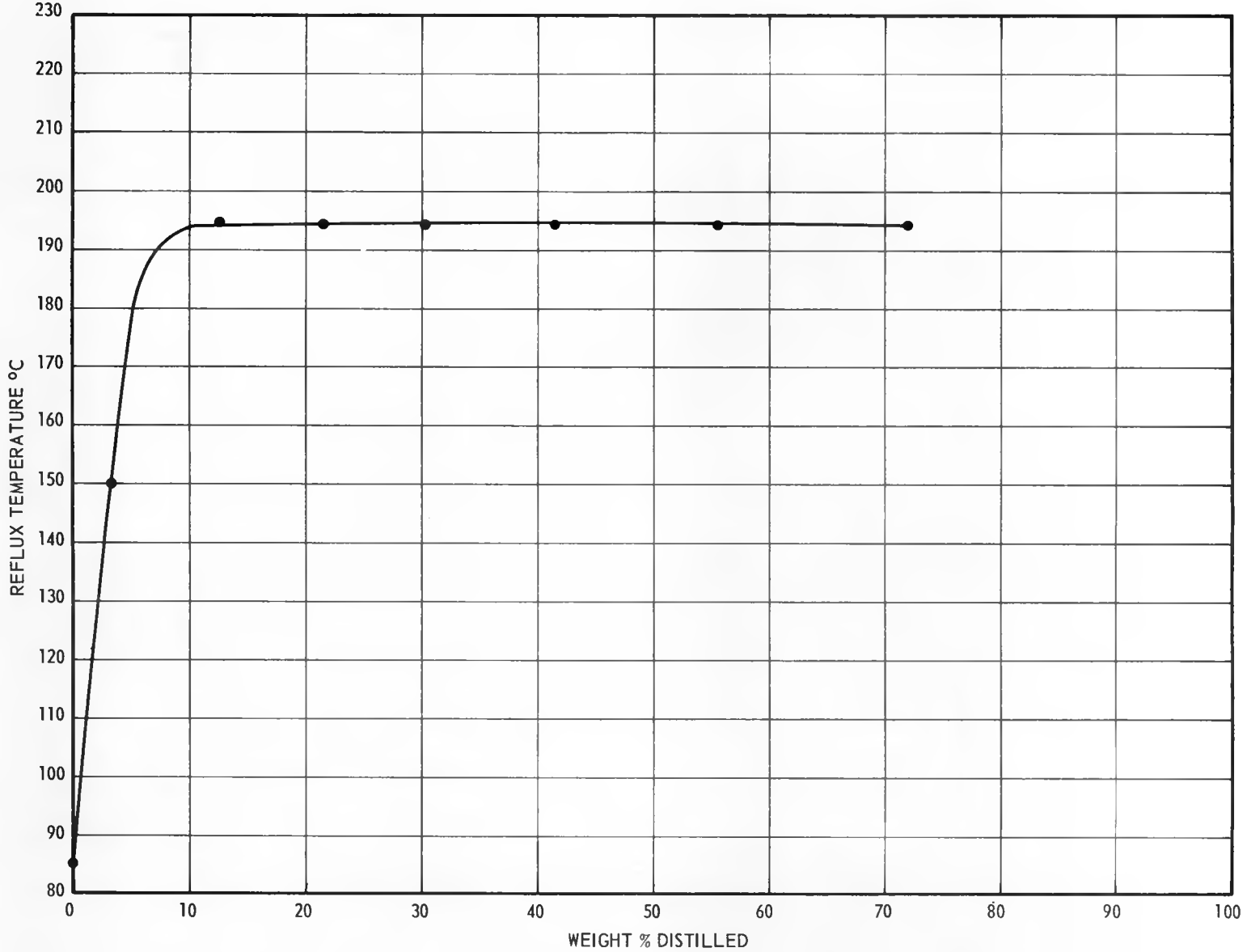

Figure 9. Distillation Curve for TBP Fraction; Washed Irradiated Solvent.

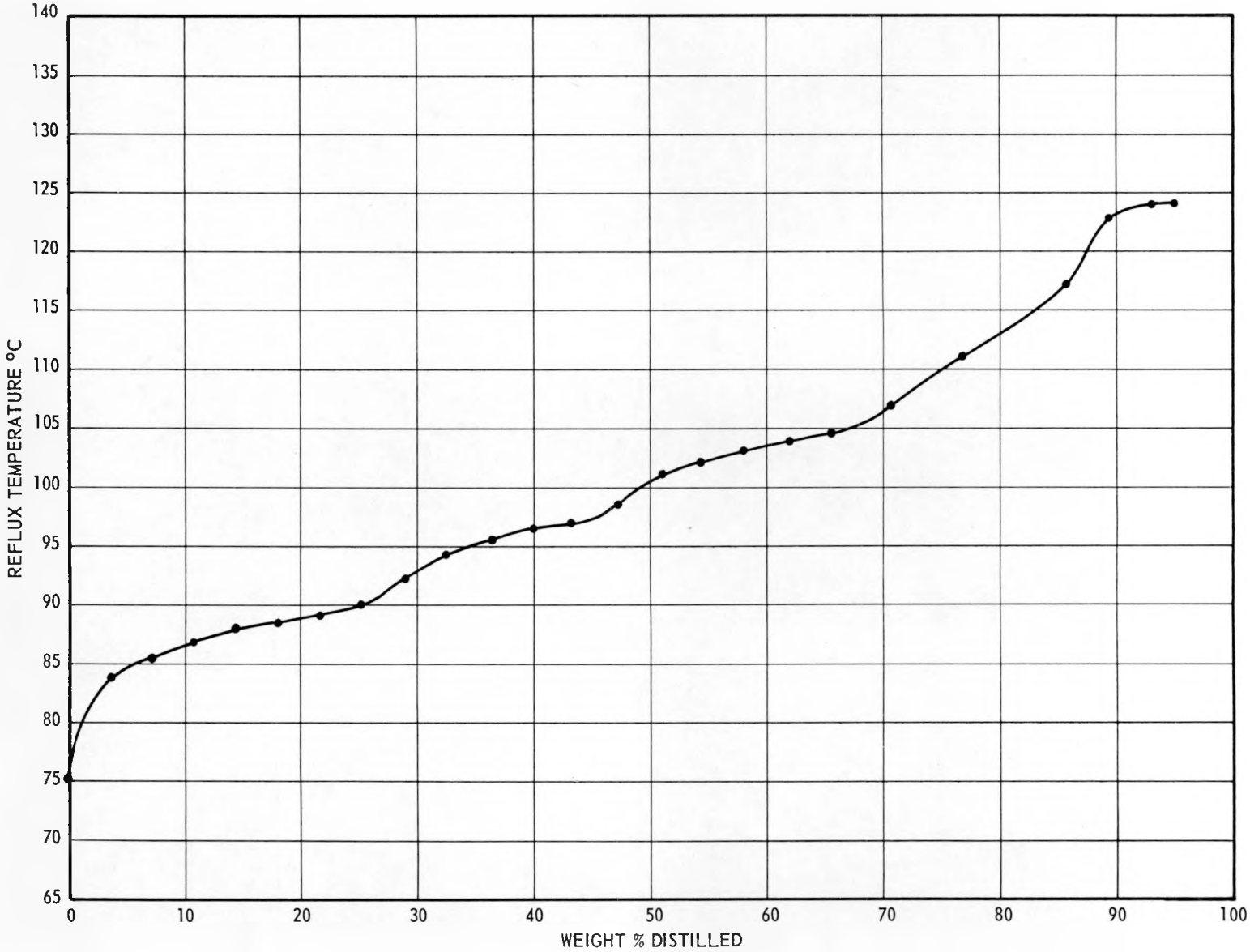

Figure 10. Distillation Curve for Amsco Fraction; Washed Unirradiated Solvent.

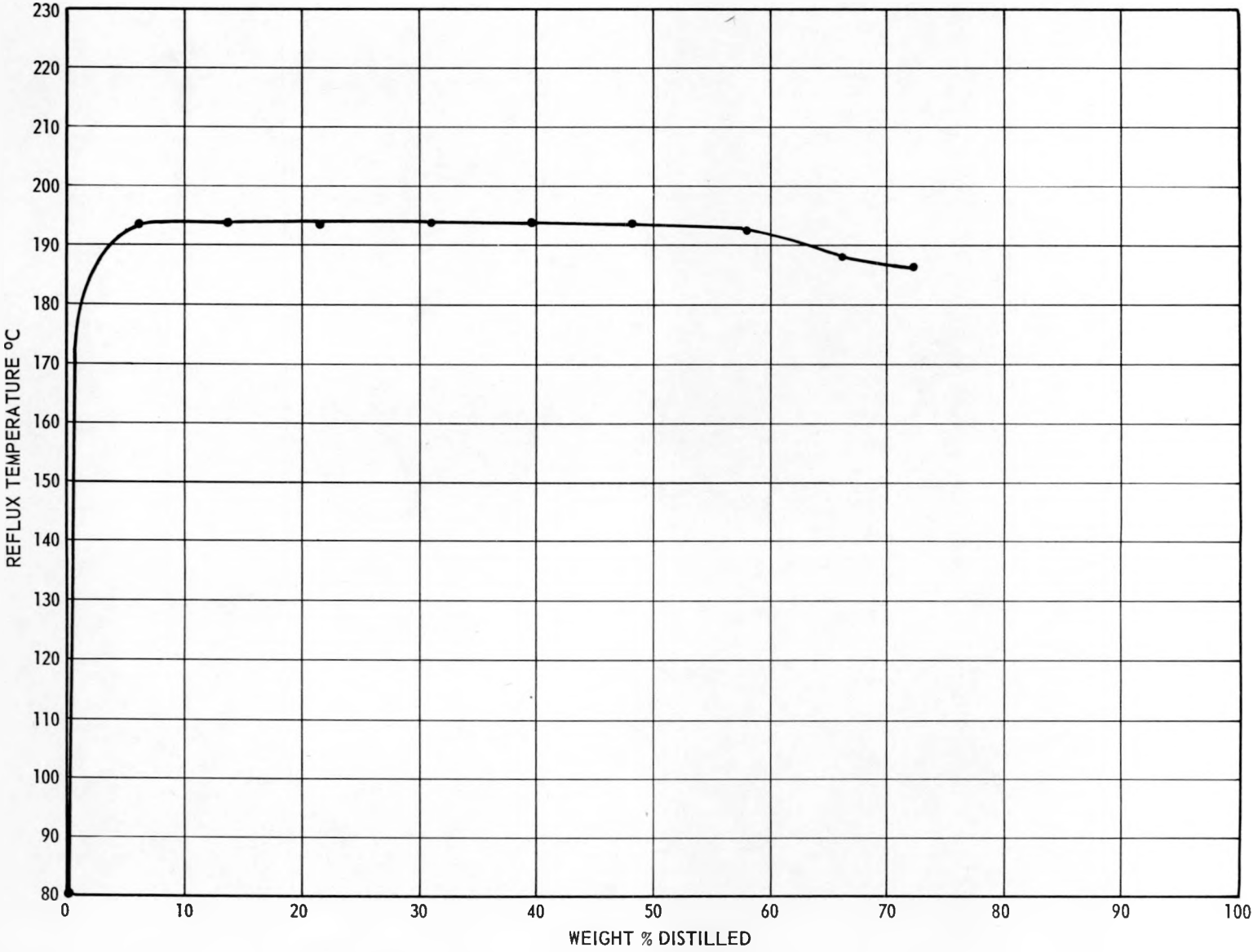

Figure 11. Distillation Curve for TBP Fraction; Washed Unirradiated Solvent.

TBP fractions from the rapid volatilizations were almost water white at first but yellowed upon standing for a day. This could have been due to entrainment during the rapid volatilization. When fractionated, the pot material turned quite black and the distillate had a tan cast to it. However, no solid material was observed in the pot.

It was observed in all the TBP fractionations that when the distillation was approximately 70 per cent complete the pot material decomposed. This could be due to the build-up in concentration in the pot of some species which could cause a rapid decomposition of the pot material. However, it is more probable that it was due to a superheating of the pot material which could not be detected by the pot thermometer because of a very low liquid level in the still pot.

When decomposition of the TBP occurred, it was quite rapid and large amounts of gas were evolved. Satisfactory material balances on the TBP distillations were impossible because the gases given off during the decomposition overloaded the cold trap and much of the gas was lost. The gas collected in the cold trap had a boiling point in the range of butane.

G. Contact Studies

The purpose of the contact studies was to test the extraction characteristics of the distillation fractions. The presence of any troublesome degradation product could then be easily discerned, especially if the product distilled within a narrow range. Conceivably, a particular cut containing a pernicious contaminant could then be studied in detail to determine identity and behavior; however, such detailed study was outside the scope of this project.

1. Extraction-Scrub Studies

Each cut of the distillations from the rapid volatilizations was made up to 30 per cent TBP--70 per cent Amsco 125-82 and contacted with an aqueous stock solution (a hypothetical Thorex feed) of the following composition:

40 mg/liter U^{233}; 40 mc/liter Ru^{106} - Rh^{106}; 4.86N HNO_3

Each organic phase was then scrubbed with 4.0N nitric acid. Duplicate samples were prepared and counted according to the procedure outlined in Chapter III, Sections D and F. The counting results of the individual equilibrations are presented in Tables VIII A to XI B, along with the distillation data.

The alpha activity in the aqueous stock solution was determined by successively extracting an aliquot of the solution until essentially all of the alpha activity had been extracted. The organic volumes were then combined and sampled. Thus, if x ml of aqueous stock solution is extracted by y ml of 30 per cent TBP--70 per cent Amsco 125-82, extracted A times, and the organic phases combined and found to count C c/min-ml, then the activity in the aqueous solution is given by AyC/x. This method of determining the alpha activity for the aqueous solution gives the same self absorption in the sample as in the case of samples prepared in the extraction, scrub, and strip studies. Thus, distribution coefficients and decontamination factors, not needed for the comparative type study performed, can be calculated from the data in this report. The uranium distribution coefficient for extraction, needed for calculation of the decontamination factor, can readily be calculated by

$$\text{Distribution Coefficient} = \frac{C_{organic}}{C_{aqueous} - C_{organic}}$$

where $C_{organic}$ is the activity of 10λ of the organic phase, and $C_{aqueous}$ is 1355 c/min - 10λ for the extraction-scrub studies.

The ruthenium-rhodium activity in the aqueous stock solution used in the extraction-scrub studies was 48,500 βγ c/min -10λ. This was determined by direct count of aliquots of the aqueous stock solution, since self absorption in the dried sample was negligible.

The average standard deviation associated with the alpha counts in Tables VIII A to XI B is 11 c/min - 10λ. The average standard deviation of the beta-gamma counts is 9 c/min - 10λ. All counts were made for a duration of at least 5 minutes.

2. Extraction-Strip Studies

In addition to the extraction-scrub studies, each cut of the distillations from the rapid volatilizations, made up to 30 per cent TBP--70 per cent Amsco 125-82, was contacted with an aqueous stock solution of the following composition:

15 mg/liter U^{233}; 15 mc/liter Ru^{106} - Rh^{106}; 4.47N HNO_3.

Each organic phase was then stripped with 0.01N nitric acid. Duplicate samples were prepared and counted. The results of these studies are presented in Tables XII to XV.

The alpha activity of the aqueous stock solution was determined to be 3757 c/min - 50λ by the procedure described in Part 1 of this section, and the beta-gamma activity to be 81,080 c/min - 50λ. The average standard deviation of the alpha counts for the extraction studies in this section is

26 c/min - 50λ, and that for the beta-gamma counts is 16 c/min - 50λ. The average standard deviation for the strip studies is 15 c/min - 50λ for the alpha counts, while that for the beta-gamma counts is 9 c/min - 50λ.

TABLE XII
EXTRACTION-STRIP RESULTS
Unwashed Irradiated Solvent

Amsco Fraction					TBP Fraction			
Extraction (C/Min-50λ)		Strip (C/Min-50λ)		Dist. Cut No.	Extraction (C/Min-50λ)		Strip (C/Min-50λ)	
α	βγ	α	βγ		α	βγ	α	βγ
3490	1433	1736	508	1	3110	855	41	131
3381	1222	1094	345	2	3218	1316	933	411
3424	1298	1281	231	3	3277	1406	1016	390
3429	1243	1154	417	4	3379	1304	1185	375
3481	1334	1225	303	5	3337	1275	1005	386
3359	1119	1204	423	6	3400	1374	1391	344
3606	1055	647	191	7	3085	879	1235	417
3422	1105	654	227	8	3111	1314	1090	357
3295	1427	860	549	9	3273	1403	1112	403
3595	1109	512	204	10	3194	1367	1081	340
3296	1009	449	157	11				
3387	1453	1261	390	12				
3426	2921	2336	894	13				
3365	2955	2705	791	14				
3248	1386	1300	405	15				
3517	1334	1554	480	16				
3147	1306	1287	433	17				
3422	1431	2093	438	18				
3435	1362	1083	427	19				
3165	2080	1441	430	20				

TABLE XIII
EXTRACTION-STRIP RESULTS
Unwashed Unirradiated Solvent

Amsco Fraction					TBP Fraction			
Extraction (C/Min-50λ)		Strip (C/Min-50λ)		Dist. Cut No.	Extraction (C/Min-50λ)		Strip (C/Min-50λ)	
α	βγ	α	βγ		α	βγ	α	βγ
3399	1131	1024	275	1	3304	824	614	203
3455	1096	1187	331	2	3254	1051	1118	308
3455	1188	1124	415	3	3423	1243	1139	305
3308	1167	1202	328	4	3403	1265	1225	339
3440	1238	1202	359	5	3426	1206	1176	330
3413	1212	1154	320	6	3488	1270	1139	334
3229	1100	1213	335	7	3341	1167	1113	299
3411	1247	1107	316	8	3404	1256	1013	319
3269	1154	1100	301	9	3443	1131	731	257
3427	1181	1041	286	10				
3486	1133	1039	279	11				
3350	1190	1153	309	12				
3522	1215	1430	334	13				
3531	1325	1223	345	14				
3467	1279	1208	331	15				
3452	1221	1208	360	16				
3437	1256	1114	348	17				
3395	1228	1197	324	18				
3310	1165	1051	269	19				
3465	1228	1180	344	20				
3376	1010	997	255	21				
3502	1385	1136	373	22				

TABLE XIV
EXTRACTION-STRIP RESULTS
Washed Irradiated Solvent

Amsco Fraction					TBP Fraction			
Extraction (C/Min-50λ)		Strip (C/Min-50λ)		Dist. Cut No.	Extraction (C/Min-50λ)		Strip (C/Min-50λ)	
α	βγ	α	βγ		α	βγ	α	βγ
3455	1056	232	332	1	225	69	93	52
3456	1326	1425	329	2	3263	1001	146	190
3332	1290	1330	330	3	3435	1358	969	373
3243	1247	1317	372	4	3446	1311	627	271
3371	1284	1278	326	5	3378	1248	1112	415
3450	1344	1243	325	6	3180	1246	1122	357
3433	1296	1300	330	7	3320	1237	671	310
3405	1229	1268	321	8				
3270	1302	1287	356	9				
3505	1271	1288	421	10				
3415	1267	1271	387	11				
3037	1244	1132	349	12				
3199	1242	1160	405	13				
3294	1366	1136	462	14				
3385	1254	1141	336	15				
3480	1262	1126	377	16				
3376	1231	1121	355	17				
3544	1428	1060	345	18				
3491	1236	1069	336	19				
3446	1329	930	293	20				
3231	1406	1023	329	21				
3144	1348	1292	476	22				
3507	1385	1123	314	23				

TABLE XV
EXTRACTION-STRIP RESULTS
Washed Unirradiated Solvent

Amsco Fraction					TBP Fraction			
Extraction (C/Min-50λ)		Strip (C/Min-50λ)		Dist. Cut No.	Extraction (C/Min-50λ)		Strip (C/Min-50λ)	
α	βγ	α	βγ		α	βγ	α	βγ
3454	1252	1115	335	1	3339	1000	89	82
3393	1424	1189	320	2	3275	1225	992	265
3408	1247	1153	300	3	3622	1266	842	227
3545	1327	1219	354	4	3206	1273	1157	348
3505	1202	1009	268	5	3308	1166	1172	329
3317	1178	850	452	6	3389	1320	1151	336
3509	1195	1012	312	7	3474	1320	1147	397
3250	1168	1000	356	8	3495	1431	1070	352
3276	1276	1089	385	9	3166	1141	798	236
3306	119	612	266	10				
3376	5070	2837	1549	11				
3388	1310	1060	334	12				
3399	1298	1183	376	13				
3453	1294	1093	335	14				
3560	1302	1152	338	15				
3336	1432	1444	451	16				
3454	1243	1114	320	17				
3441	1350	1055	335	18				
3525	1286	1166	334	19				
3414	1154	1108	336	20				
3381	1221	940	337	21				
3439	1202	870	275	22				
3148	1119	825	323	23				
3325	1282	1221	357	24				

V. SUMMARY

The feasibility of purifying irradiation-degraded Purex-type solvent by distillation was proved by these studies. It appears that direct distillation of the TBP-Amsco mixture is beset by too many difficulties to prove technically feasible; however, flash distillation of the mixture into the separate TBP and Amsco components allows the fractional distillation of each component to be performed in a trouble-free manner.

The distillation of irradiated (121-watt-hr/liter) TBP-Amsco mixture yields a considerable quantity of light gases and a greenish-yellow aqueous component. The pot material develops into a black, syrup-type slurry with considerable solid formation. The distillation rapidly becomes unwieldy.

The distillation of irradiated TBP-Amsco mixture is improved somewhat by washing the mixture with sodium carbonate. Less discoloration of the pot material occurs; however, a considerable amount of gel-type precipitate forms to preclude the attainment of reasonable yields.

Due to the large difference in boiling points of TBP and Amsco, flash distillation can be used to readily separate the mixture into the TBP and Amsco components, with high yields. Each component can then be fractionally distilled, without the attendant difficulties mentioned above. Only one cut each of the irradiated Amsco, washed and unwashed, contained any coloration. Due to the small charge of TBP used in the present studies, the yields for TBP recovery were relatively low (70 to 80 per cent). The yields can be increased by use of a larger charge.

The fractional distillation of the TBP-Amsco components, after flash distillation, does not differ substantially from the distillation of unwashed TBP-Amsco components.

Contact studies made with U^{233} and Ru^{106} -Rh^{106} show that the extraction, scrubbing, and stripping characteristics of the distilled, irradiated fractions are comparable to the distilled, unirradiated fractions.

Respectfully submitted:

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