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TRIBUTYL PHOSPHATE SOLVENT EXTRACTION OF URANIUM FROM METAL WASTE-LABORATORY INVESTIGATION

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Tributyl Phosphate Solvent Extraction of Uranium From Metal Waste - Laboratory Investigation

D. E. Ferguson, T. C. Runion

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1.0 Abstract

This report presents the progress in development of a solvent extraction process for the recovery of uranium from radioactive wastes. This process employs tributyl phosphate, diluted with an inert liquid, as the extracting solvent, and nitric acid as the salting agent.

2.0 Introduction

The increasing accumulation of uranium in the stored radioactive waste solutions at various AEC installations and the relatively limited supply of this metal demand that an efficient and economical process be devised for the recovery of this material.

Solvent extraction, where applicable, is a desirable method for uranium recovery, because of high yields and low operating and maintenance costs, and because it easily leads itself to remote control operation. The extensive research and development applied to other uranium recovery processes by solvent extraction (23, 25, and Redox) provide an excellent background in technology and experienced personnel.

The use of tributyl phosphate as a solvent for uranium, thorium, cerium and other rare earths has been investigated in separations processes for these metals at Iowa State College[1] and at Battelle Memorial Institute[2,3]. The specificity of the strong complex between uranium and tributyl phosphate, and the marked stability of the solvent to nitric acid, made this a promising solvent for the extraction, separation and decontamination of uranium metal from waste solutions[4].

There are both chemical and physical reasons (discussed in section 4) for requiring a diluent for the tributyl phosphate. Hexane was arbitrarily chosen for use as diluent in these studies, although other inert compounds are now being examined.

Although a feasible process for uranium recovery from metal waste has been demonstrated, a number of points remain to be established before the optimum procedure can be outlined. Among these are the investigation of other

solvents to secure a more satisfactory diluent for tributyl phosphate, the determination of the most economical and feasible method of feed preparation, and the investigation of the nature, and means of reducing, the uranium losses observed in the runs involving Hanford sludge. Additional effort must also be devoted to methods for solvent pretreatment and solvent clean-up.

The design and construction of 1-1/2 inch-semi-works columns for a 50 gallon scale demonstration of the process using Hanford waste solutions will be completed by September 1949.

3.0 Summary

A simple and feasible solvent extraction process has been developed through the laboratory stage at ORNL for the recovery of uranium from metal waste. The procedure involves extraction of the waste solution, made 3.0-5.0N in HNO_3, with 15% tributyl phosphate - 85% hexane, and subsequent stripping of the uranium from the solvent with water.

Uranium from ORNL waste sludge, Hanford supernatant waste solution, and Hanford waste sludge has been recovered in one counter-current batch solvent extraction cycle with resulting decontamination of the uranium to 3-7% of the natural uranium beta activity and to 20-40% of the natural uranium gamma activity. In the initial experiments, the uranium losses were 0.1% for ORNL sludge and Hanford supernatant, and 0.7% for Hanford sludge. The process was operated successfully over a wide range of HNO_3 concentrations (3.0 to 5.0M), and over a range of uranium concentrations from 70 g/l (or less) to 140 g/l. No difficulties were caused by the concentrations of $(SO_4)^{=}$ and $PO_4^{\equiv}$ that were encountered. Analyses have shown no traces of phosphates or sulfates in the uranium product solutions.

The mechanical operability of this continuous extraction process has been demonstrated satisfactorily with ORNL waste sludge in a 1 inch column. The uranium losses and fission product decontamination factors obtained were comparable with those obtained in the laboratory batch work.

A fundamental requirement for maximum decontamination of the uranium from fission products is that the process be operated under conditions such that the solvent phase approaches uranium saturation since the extraction of fission products is then at a minimum.

4.0 Experimental and Results

The wide variation in composition of any sample of waste sludge (see Table 4.0-1) indicated the necessity of making controlled studies of process variables on synthetic waste solutions. These data were then confirmed in counter-current batch equipment using actual waste solutions from ORNL and Hanford Works. Lastly, the feasibility and mechanical operability of the process was established in continuous, one inch laboratory column operation. (A schematic flowsheet is presented in the Appendix, page 49).

4.1 Mechanism of Uranium and Fission Product Extraction by Tributyl Phosphate

Within experimental error, the maximum solubility of uranium in tributyl phosphate was 0.5 moles of uranium per mole of tributyl phosphate (410 mg U/ml. Bu_3PO_4). This was determined by equilibrating saturated $UO_2(NO_3)_2$ solutions with various concentrations of tributyl phosphate in hexane at 20°C for 22 hours and analyzing both phases for uranium (see Table 4.1-1, and Fig. 1).

The high extractive power of tributyl phosphate for uranyl ion indicated the formation of a compound between the uranium and tributyl phosphate. The ratio of uranium and nitric acid to Bu_3PO_4 in the saturated mixture was found to be about 0.5 moles of uranium and about 1.0 mole of nitric acid per mole of Bu_3PO_4, indicating a complex of the general formula $UO_2(NO_3)_2 \cdot 2\ Bu_3PO_4 \cdot 2\ HNO_3$.

Although tributyl phosphate is a highly specific solvent for uranium, fission products began to extract as the concentration of uranium in the solvent was decreased from the point of saturation. In the absence of uranium, the distribution ratio of Pu^{IV} was greater than 1 (see section 4.3-1), and it was affected by the same variables that influence uranium extraction. The extraction

Table 4.1-1

Uranium Solubility in Tributyl Phosphate-Hexane Mixtures

Aqueous Phase: Saturated (558 mg/ml) $UO_2(NO_3)_2$, 0.16N HNO_3(pH 0.3)

Organic Phase: One equal vol. pass tributyl phosphate hexane mixture

Equilibrium Time: 22 hours at 20°C ± 0.2°

Run No.	Concentration of Tributyl Phosphate %	M/L	U Distribution Organic Mg/ml	M/l	Aqueous Mg/ml	Moles Bu_3PO_4 Mole U
1	1	0.036	4.12	0.0172	480	2.1
2	5	0.180	20.75	0.0871	520	2.08
3	10	0.360	41.0	0.1722	498	2.11
4	15	0.540	63.5	0.267	460	2.02
5	20	0.720	84.0	0.352	440	2.05
6	30	1.080	116.0	0.487	410.4	2.22
7	50	1.80	195.0	0.819	326.0	2.2
8	100	3.60	360.0	1.512	191.0	2.48

of Ce^{IV}[1] was also governed by these same variables. Consequently, the mechanism, whereby fission products are extracted is probably similar to that for uranium.

With equal volumes of organic and aqueous phases, the amount of uranium obtained in a 3N HNO_3 solution of ORNL waste sludge (100-150 mg/ml) was just sufficient to maintain a 15-20% solution of tributyl phosphate (0.54-0.72M) in hexane near saturation (80-90%). At this concentration the maximum decontamination from fission products was obtained.

In addition to this consideration for using this concentration of Bu_3PO_4, rather stable emulsions were encountered in experiments employing solvent concentrations greater than 30%. Also, acceptable uranium distribution coefficients in stripping with water were obtained only below 20% tributyl phosphate. Hence, the need for a diluent is obvious. Hexane (density 0.66) was arbitrarily chosen as a diluent for Bu_3PO_4 (density 0.97), although a number of other inert compounds of low density would also be satisfactory and are being investigated.

4.2 Chemical Studies on Synthetic Waste Solutions

The effects of Bu_3PO_4, salt, HNO_3 and uranium concentrations, and of temperature and equilibration time, on uranium, plutonium, and fission product extraction were studied individually in laboratory batch equipment. The degree of uranium complexing to be expected at the concentrations of sulfate and phosphate ions encountered in waste solutions was also investigated.

At uranium concentrations sufficiently low to prevent saturation of the solvent (less than 0.5M) a linear relationship existed between the amount of uranium extracted and the concentration of Bu_3PO_4 in the hexane (see Table 4.2-1). Consequently, studies made with a given Bu_3PO_4 concentration may be easily extrapolated to other solvent compositions.

Table 4.2-1

Effect of Butyl Phosphate Concentration on Uranium Extraction at Low Uranium Concentration

Aqueous Phase: 0.12M $UO(NO_3)_2$, 0.01M HNO_3

Organic Phase: One equal volume pass of tributyl phosphate - hexane mixture

Equilibration Time: 22 hours at 20 ± 0.2°C

Bu_3PO_4 %	Conc. M	Uranium Distribution			U Dist. Coeff. Org./Aq.	Moles U / Moles Bu_3PO_4
		Organic		Aqueous		
		mg/ml	M	mg/ml		
1	0.036	0.04	0.00017	26.5	0.0025	0.005
5	0.180	1.04	0.0044	26.5	0.039	0.02
10	0.360	2.77	0.0116	23.3	0.12	0.03
20	0.720	5.6	0.0235	22.0	0.25	0.03
30	1.080	8.28	0.0348	20.4	0.41	0.03

Although these initial experiments were carried out using hexane as a component of the solvent mixture, the adoption of another diluent would not alter the conclusions drawn.

4.21 Effect of Temperature and Equilibration Time

The extraction of uranium by tributyl phosphate was not appreciably affected by temperature changes in the range of 10-50°C. A series of reagent acidity, 0.1M $UO_2(NO_3)_2$ solutions was contacted in batch equipment with 20% Bu_3PO_4-80% hexane mixtures at various temperatures. The two phases were analyzed for uranium after a 5 minute equilibration period. At 10°C the uranium distribution coefficient (org./aq.) was 0.37; at 30°, 0.24, and at 50°, 0.16 (see Table 4.2-2, Fig. II).

Table 4.2-2

Effect of Temperature on Uranium Extraction with Tributyl Phosphate

Aqueous Phase: 0.1M $UO_2(NO_3)_2$, 0.05N HNO_3.
Organic Phase: One equal vol. pass of 20% tributyl phosphate-80% hexane
Equil. Time: 5 min. batch extraction.

Temp. oC	U Concentration (mg/ml)		U Dist. Coeff. (org./aq.)
	Org.	Aqueous	
10	7.10	19.15	0.37
20	6.40	22.0	0.29
30	4.90	20.48	0.235
50	3.62	23.00	0.157

Although the decrease in distribution coefficients was only a factor of two in this temperature range, this fact may be used to advantage in stripping the uranium from the organic solvent. Higher temperatures were not investigated because of the high volatility of the hexane component.

The equilibrium between uranium and tributyl phosphate was established extremely rapidly. No variation in distribution coefficients were observed when equilibration periods were extended from 10 seconds to greater than 20 hours.

4.22 The Effect of Nitric Acid on Uranium Extraction

With the organic phase at or near saturation in uranium, little effect on uranium extraction was observed upon varying the nitric acid concentration of the aqueous phase from 1.0-7.0 molar. However, at low uranium concentrations, and in the absence of other salts and complexing anions, changing the nitric acid concentration from 0.02 to 5.2 molar increased uranium distribution coefficients (org./aq.) from 0.22 to 12.8. Nitric acid concentrations higher than 5.2 resulted in a decrease in extraction coefficients (see Table 4.2-3, Fig. III).

The concentrations of nitric acid permissible in the process have an upper and lower limit. The lower limit is approximately 1.0 M since this is the lowest acidity at which solution of the waste sludge can be obtained. The maximum permissible acidity corresponds to 5.0-7.0 M since concentrations appreciably greater than this began to salt out the components of the aqueous feed. Because of the ability of nitric acid to decrease uranium complexing by sulfates and phosphates it is desirable to maintain the acid concentration as high as possible in order to minimize uranium losses from this effect and obtain maximum distribution coefficients. Analyses showed that the sulfate and phosphate content of ORNL waste sludge is from 0.05 to 0.1 molar, while total Hanford waste may contain twice this quantity of these anions.

Table 4.2-3

Effect of HNO_3 Concentration

on

Uranium Extraction

Aqueous Phase: 28 mg/ml U (0.12 M) varying acidities, indicated amounts of Na_2SO_4 and Na_3PO_4

Organic Phase: 15% Tributyl Phosphate in Hexane

One Equal volume extraction

Time of Equilibration: 2 hours at 20°C ± 0.2°

HNO_3 in Feed M	U Dist. Coeff. (O/A)			0.1M PO_4, 0.2M SO_4
	Control*	0.2M $SO_4^{=}$	0.1M $PO_4^{\equiv}$	
0.02	0.22	0.039	-**	-**
0.1	0.39	0.097	-**	-**
0.5	1.11	0.49	-**	-**
1.0	2.40	1.37	1.12	0.66
2.1	5.77	3.49	2.46	2.01
3.1	8.83	6.50	3.96	3.48
5.2	12.8	9.17	6.26	4.97
8.0	7.90	5.91	4.63	4.25

* No $SO_4^{=}$ or $PO_4^{\equiv}$ present

** Complete solution was not obtained at these acidities.

Hanford Studies

In the absence of complexing anions the uranium distribution coefficients (org./aq.) varied from 0.4 at 0.1N HNO_3 to a maximum of 12.8 at 5.2N, to 7.9 at 8.0N. In the presence of $PO_4^{\equiv}$ and $SO_4^{=}$ the distribution coefficients also reached a maximum at 5.0N nitric acid but were lower by factors of 2 to 3, the phosphate showing greater inhibiting of uranium extraction than the sulfate (see Table 4.2-3, Fig. III). However, five successive batch extractions on all those feeds at least 5.0N in HNO_3 were sufficient to remove 99.9% of the uranium.

This data was obtained from four series of batch extractions made with 15% Bu_3PO_4-85% hexane. The aqueous feeds contained 0.1M uranium, and varied in acid concentration from 0 to 8 molar. One series of feeds contained 0.1M Na_3PO_4, the second contained 0.1M Na_2SO_4, the third contained 0.1M $PO_4^{\equiv}$ and 0.2M $SO_4^{=}$, and the fourth feed contained neither anion.

The distribution of nitric acid between the solvent and aqueous phases was determined at several different acid and tributyl phosphate concentrations. The saturation solubility of nitric acid in the organic layer was ca. 1.0 mole of nitric acid per mole of tributyl phosphate (see Table 4.2-4.5, Fig. V). In the presence of appreciable quantities of uranium the amount of nitric acid transfer was not readily determined because of analytical difficulties.

4.23 Effect of Salt Concentration on Uranium Extraction

Uranium distribution coefficients were markedly improved by increases in the concentration of uranium or sodium nitrate in the aqueous phase when the uranium concentration was low. Upon equilibrating a series of aqueous feeds, 0.1M in $UO_2(NO_3)_2 \cdot 6H_2O$ containing varying concentrations of

sodium nitrate, with 20% Bu_3PO_4-80% hexane at 20°C. the resulting uranium distribution coefficient increased from 0.24 when no sodium nitrate was present to greater than 200 when the salt concentration was 5.0N (see Table 4.2-6 Fig. VI). In the absence of other salts, increasing the uranium concentration (reagent acidity) from 0.04 to 0.35M increased the distribution coefficients by a factor of six (see Table 4.2-7). Since the solvent was nearly saturated at this concentration, further increases in uranium concentration caused an apparent drop in distribution coefficients.

Table 4.2-6

Effect of $NaNO_3$ Concentration on U Extraction with Hexane-Tributyl Phosphate

Aq. Phase: 0.09M $UO_2(NO_3)_3$

Org. Phase: One eq. vol. pass 20% tributyl phosphate-80% hexane

Equil. Time: 18 hours at 20°C.

$NaNO_3$ Conc. M	U Conc. (mg/ml)		U Dist. Coeff. (Org./aq.)
	Org.	Ag.	
0.0	4.05	16.75	0.24
0.1	6.45	14.30	0.45
0.25	10.05	11.10	0.91
0.50	12.88	7.69	1.67
1.0	17.25	4.12	4.19
2.0	20.0	1.18	16.9
3.0	20.9	0.45	46.8
5.0	20.5	0.062	>200.0

Table 4.2-7

Effect of U Conc. On U Extraction with Hexane-Tributyl Phosphate

Org. Phase: One equal vol. pass. 20% tributyl phosphate - 80% hexane

Equilibration Time: 18 hours batch extraction

Temperature: 20°C ± 0.2

Initial U Conc.		U Distribution (mg/ml)		U Dist. Coeff.
Mg/ml	M	Org.	Aq.	Org. Aq.
10.6	0.045	1.02	9.62	0.11
21.0	0.088	3.80	17.20	0.23
42.4	0.181	12.90	30.0	0.43
85.0	0.356	33.50	51.3	0.65
127.0	0.50	46.60	72.4	0.64
212.0	0.93	78.0	142.5	0.56
424.0	1.87	91.6	354.0	0.26
542.0	2.28	90.0	452.0	0.20

The high dependence of uranium extraction on nitrate concentration indicated that the nitrate ion formed a component of the uranium complex in the organic phase. Results of uranium and nitrate analyses indicate that two moles of nitrate extract with each mole of uranium, excluding the nitrate from nitric acid transfer. Analyses of stripped product solutions have shown no traces of phosphates or sulfates.

4.3 Plutonium and Individual Fission Product Studies

A study of the variables affecting the solvent extraction of individual fission products and Pu by tributyl phosphate was initiated. The

Table 4.3-1

Effect of Salt ($NaNO_3$) Concentration on Bu_3PO_4 Extraction of Ce^{III}, Zr, Pu^{IV}

Aqueous Phase: 0.1M $UO_2(NO_3)_3$, 3.0M HNO_3, $NaNO_3$, tracer

Organic Phase: One equal-volume pass 15% Bu_3PO_4 in hexone

$NaNO_3$ Conc. M	Distribution Coefficients (org./aq.)		
	Ce^{III} Beta	Zr Beta	Pu^{IV} Alpha
0	0.003*	0.16	2.04
0.05	0.003	0.17	2.2
0.1	0.003	0.17	2.1
0.3	0.003	0.25	2.7
0.6	0.003	0.25	4.1
1.0	0.003	0.26	4.4
3.0	0.003	0.61	9.7
4.0	0.003	0.69	16.6

*This value is probably low.

effect of nitric acid concentration in the range of 0.1-16N and the effect of salt ($NaNO_3$) in the range of 1-5N were investigated for Ce^{III}, Zr and Pu^{IV}.

The extraction coefficient (0.001) of Ce^{III} was not appreciably changed at all concentrations of HNO_3 and salt ($NaNO_3$), while the extraction of Pu^{IV} and Zr was markedly increased by increases in salt ($NaNO_3$) and acid (HNO_3) concentrations in the presence of small amounts of uranium. In the absence of uranium and other salts the distribution coefficient for zirconium (org./aq.) (using 15% Bu_3PO_4) was 0.004 at an acid concentration of 0.2N, 0.16 at 3.7N, and 2.83 at 16N. The distribution coefficients for Pu^{IV} (org./aq.), in the presence of low uranium concentration, were 0.05 at an acid concentration of 0.2N, 5.44 at 6.1N, and 1.4 at 16N. The addition of 1.0M $NaNO_3$ increased the extraction of Pu^{IV} by a factor of 2 while 4.0M $NaNO_3$ increased the extraction coefficient by a factor of 8 (see Table 4.3-1,2). However, as the concentration of uranium approached that necessary to saturate the solvent the Pu distribution coefficients decreased sharply. For instance, a change in the degree of solvent saturation from 20% to 100% decreased the Pu distribution coefficients by factors of 5 to 10 (see Table 4.3-3). Another series of experiments was made to determine the extraction coefficients of the different valence states of plutonium. However, the results were in conclusive since the sulfates of the oxidizing and reducing agents were used and the effect of changing the valence state of Pu was obscured by the complexing action of the sulfate.

Table 4.3-2

Effect of Acid Concentration on Bu_3PO_4 Extraction of Ce^{III}, Zr, Pu^{IV}

Aq. Phase: 0.1M $UO_2(NO_3)_2$, tracer,

Org. Phase: One equal vol. pass 15% Bu_3PO_4 in hexane

HNO_3 Conc. M	Distribution Coefficients (org./aq.)		
	Ce^{III} Beta	Zr Beta	Pu^{IV} Alpha
0.2	0.001	0.004	0.05
0.3	0.001	0.004	0.05
0.5	0.001	0.005	0.09
1.1	0.001	0.007	0.23
2.7	0.001	0.16	2.04
6.1	0.001	0.267	5.44
10.2	0.001	0.716	4.38
12.4	0.001	-	-
16.0	-	2.83	1.4

Table 4.3-3

Effect of Uranium Concentration on Plutonium Distribution Coefficients

Aq. Phase 1.0N $NaNO_3$ - 3.0M HNO_3

Org. Phase - 15% Bu_3PO_4 in hexane

Pu Oxidation State	Plutonium Dist. Coeff. (org./aq.) at Varying Concentration of Uranium		
	24g U/l	70g U/l	120g U/l
Pu^{III} (note 1)	2.0	0.50	0.24
Pu^{IV} (note 2)	3.5	0.7	0.26
Pu^{IV} (note 3)	-	0.7	-
Pu^{VI} (note 4)	1.0	0.2	0.06

1. Pu^{III} Distribution - tracer reduced with $Fe(NH_4)_2(SO_4)_2$ and $2NH_2OH \cdot H_2SO_4$; solution 0.05M-$2NH_2OH \cdot H_2SO_4$
2. Pu^{IV} Distribution - Pu^{IV} Tracer as received in 1N - HNO_3; no oxidizing or reducing agents added.
3. Solution made 0.1M in $NaNO_2$.
4. Pu^{VI} Distribution - Tracer oxidized with $Ce(SO_4)_2 \cdot (NH_4)_2SO_4$; solution 0.05M-$Na_2Cr_2O_7$

4.4 Solvent Studies

In early work with tributyl phosphate a diluent was found necessary because of its high specific gravity and viscosity. Also, by using lean mixtures (20%) of solvent, saturation of uranium is more easily obtained at the uranium concentrations encountered, and the extraction of fission products is at a minimum. In addition, the uranium distribution coefficient in (aq./org.) stripping is less than 1 for Bu_3PO_4 concentrations greater than 20%. A mixture of 15% tributyl phosphate - 85% diluent was chosen as optimum for the process.

In this experimental work hexane was arbitrarily chosen as the diluent, although any solvent stable in the presence of HNO_3 and having a low viscosity and a specific gravity of 0.8 or lower should be satisfactory. The cost and pertinent physical properties of five hydrocarbons that have been tried are given below:

Solvent	Cost per gal.	Specific Grav.	Boiling Point	Flash Point °F.
N-Hexane	0.28	0.66	69	60
N-Heptane	0.28	0.68	98	60
N-Octane	10.00	0.70	126	61
Methyl Cyclohexane	1.26	0.77	101	60
"Varsol"	0.21	0.75	167-180	120

Heptane and hexane are inexpensive, but hazardous because of their low flash points. Octane is excluded by high cost. Methylcyclohexane is also relatively expensive and not significantly less volatile then heptane. Based on physical properties, "varsol" or a similar petroleum fraction is satis-

factory and will be tested as a diluent for tributyl phosphate in future work. Results of laboratory experiments under controlled conditions indicated that there was no significant difference in uranium losses or decontamination with the use of any of these five diluents.

Since some color was observed in the used solvent, a single batch of solvent was repeatedly used for extractions on solutions of ORNL sludge to determine the extent to which the solvent could be reused. With the feed solutions 3.0M in HNO_3, the solvent was reused through five complete column extraction cycles without evidence of deterioration. Uranium losses were consistantly 0.1-0.2%, and little change in separation from fission products was noted due to deterioration of the solvent. This used solvent was treated by washing with 1.0M Na_2CO_3 and compared with samples of untreated used solvent and fresh solvent in countercurrent batch extractions. On the basis of decontamination and uranium yields the results indicated that the Na_2CO_3 wash was sufficient to restore the solvent to its initial quality.

4.5 Countercurrent Batch Experiments

Uranium from ORNL waste sludge, Hanford supernatant, and Hanford metal sludge was recovered in one counter-current batch solvent extraction cycle with a decontamination of the uranium to 3-7% of the natural uranium beta activity and to 20-40% of the natural uranium gamma activity (see Table 4.5-1). The uranium losses were 0.1% for ORNL sludge and Hanford supernatant. For Hanford sludge the uranium loss was 0.7% in the initial experiments.

It had been found in countercurrent batch studies that with the solvent near saturation with uranium (0.5 moles of uranium per mole of Bu_3PO_4) the extraction of fission products and HNO_3 was low (the reliability of HNO_3

analytical methods is somewhat in doubt (Table 4.5-4). In the last stage of extraction the solvent contained 0.5N HNO_3 and 9 x 10^3 beta c/m/ml. This was reduced to 0.2N HNO_3 and 800 beta c/m/ml at the feed point. This drop in HNO_3 concentration and beta activity was attributed to the "salting out" effect as the solvent reached 70% saturation with uranium. The uranium distribution coefficients also varied from stage to stage, being approximately 2 at the feed plate while in the second stage it was 10. The lower distribution coefficient at the feed plate is likewise due to the degree (70%) of saturation of the solvent with uranium. The uranium remaining after the 5th stage (about 0.1% in the case of ORNL sludge) was not extracted with additional batch extraction stages and was constant from run to run regardless of run conditions. Thus, in the case of HW sludge 0.55 g/l of uranium (0.7% of the initial uranium concentration) was present in the aqueous in the 4th and 5th stages.

An effort was made to determine the nature of this inextractable uranium in the raffinate from this run. Since it was found that the solution of HW sludge was about 0.5N reducing, the raffinate was split into seven samples and each sample given the oxidation treatment described in Table 4.5-2. Subsequently, each aliquot was extracted twice with a double volume of 85% hexane-15% Bu_3PO_4 and again analyzed for uranium.

Table 4.5-1

Tributyl Phosphate Extraction of Uranium from Metal Waste - Counter-current Batch Runs

Feed: 3.0 to 4.5N HNO_3 solution of waste as indicated.
Solvent: 85% hexane - 15% tributyl phosphate
Scrub: 3.0N HNO_3
Strip: Water
Equipment: Countercurrent batch extractor; 5 stages of strip
Flow ratio: Solvent: Feed: Scrub: Strip=10:3:2:10

Source of Uranium Processed	Uranium Loss %	Beta Activity of Product β c/m/mg U	γ Activity of Product Mv/mg U	Beta Decontamination Factor
ORNL Sludge	0.1	2	0.001	1.5×10^4
HW Supernatant	0.1	2	0.001	3×10^4
HW Sludge	0.7	5	0.002	3×10^5
Simulated HW current waste(90 day activity)	0.4	2	0.001	2×10^4
Activity of natural U		70	0.005	-----

Table 4.5-2

Effect of Oxidation of Hanford Sludge Solution on Uranium Extraction Losses

Aqueous: Aliquots of raffinate from countercurrent batch extraction of HW waste sludge (0.55 mg U/ml) treated as indicated.
Solvent: Mixture of 85% hexane - 15% tributyl phosphate
Procedure: Two successive double volume extractions with solvent.

Sample No.	Treatment Given Raffinate Sample before Extraction	U Concentration in aqueous after extraction-mg/ml
1.	No treatment	0.55
2.	Heated for 1 hour at 100°C	0.55
3.	Added 0.2M $Na_2Cr_2O_7$-heated for 1 hour 100°C	0.34
4.	Added 0.4M $Na_2Cr_2O_7$-heated for 1 hour 100°C	0.08
5.	Added 0.5M $Al(NO_3)_3$-heated for 1 hour 100°C	0.55
6.	Added 0.5M Ce^{++++}-heated 1 hour 100°C	0.30
7.	Let stand at room temp. for 48 hours.	0.36

From the results it was concluded that the inextractable uranium was either U^{+4} or a uranium complex fairly stable under reducing conditions, and that the uranium could be extracted if the feed solution were oxidized before extraction. However, the desirability of such treatment is questionable.

The feed and product solutions of both the HW sludge and "90 day activity" runs were analyzed for specific fission products. These data

TABLE 4.5-3

Solvent Extraction Recovery of Uranium from HW Waste Sludge and Simulated Current Waste

Counter-Current Batch Extraction

Feed:
Run A
Solution of HW Waste sludge in HNO_3 - 130 mg/ml U, 4.6 N acid, $2x10^8$ β c/m/ml
Run B
Simulated current HW uranium waste: Spiked with full HW level activity from ORNL Hot Pilot (cooled approximately 90 days) 3.6 N acid - 130 mg/ml U - $4x10^6$ β c/m/ml
Scrub: 3.0 M HNO_3
Solvent: Mixture of 85% hexane - 15% tributyl phosphate
Equipment: Counter-current batch extractor: Extraction - 5 stages, scrub - 4 stages, strip - 5 stages
Flowratios: Solvent:Feed:Scrub:Strip = 10:3:2:10

Run	Extraction U Loss (%)	Decontamination Factors								β activity of product c/m/mg U
		Gross β	Gross γ	Ru	Ce	Sr	Pu	Zr	Cb	
A Hanford Sludge	0.7	$3x10^5$	$6x10^4$	$2x10^4$	$1.6x10^6$	$1.3x10^6$	2	—	—	5
B Simulated Waste	0.4	$2x10^4$	$1x10^4$	$1.5x10^4$	$5x10^4$	—	10	$3x10^3$	$3x10^4$	2

Table 4.5-4

Effect of HNO_3 Concentration on U and F. P. Extraction from Metal Waste Solution

Aqueous: Solution of ORNL Waste Sludge in HNO_3 140 mg/ml U $4x10^6$ beta c/m/ml

Solvent: Mixture of hexane and Bu_3PO_4

Five minute batch equilibration of equal volumes of solvent and feed

HNO_3 Conc. In Feed N	% Bu_3PO_4 In Solvent Mixture	Extraction Dist. Coeff. (Org./Aq.) U	Extraction Dist. Coeff. (Org./Aq.) Gross Beta	Stripping Dist. Coeff. (Org./aq.) 1st Strip	Stripping Dist. Coeff. (Org./aq.) 2nd Strip
100	10	0.5	$8x10^{-5}$	5.3	14
1.8	10	0.6	$4x10^{-5}$	5.0	17
2.6	10	0.5	$3x10^{-5}$	4.4	20
3.4	10	0.5	$4x10^{-5}$	4.8	20
4.2	10	0.5	$3x10^{-5}$	4.8	20
5.0	10	0.5	$4x10^{-5}$	-	22
5.8	10	0.5	$4x10^{-5}$	4.2	19
1.0	20	1.1	$6x10^{-4}$	1.7	3.5
1.8	20	1.4	$3x10^{-4}$	1.5	3.1
2.6	20	1.4	$1.5x10^{-4}$	1.3	3.1
3.4	20	1.5	$1.1x10^{-4}$	1.3	3.2
4.2	20	1.7	$8x10^{-5}$	1.2	2.3
5.0	20	1.6	$7x10^{-5}$	1.2	2.2
5.8	20	1.6	$7x10^{-5}$	1.1	2.1

are presented in Table 4.5-3 as individual fission product decontamination factors. It was noted that zirconium had the lowest beta decontamination factor (3×10^3) and was the major beta activity associated with the product uranium in the case of the "90 day activity" run. Ruthenium was essentially the only beta activity in the product uranium from the HW sludge (decontamination factor of 2×10^4). In each case the beta decontamination factors for other fission products were at least a factor of 10 greater than Zr, for "90 day activity", and a factor of 10 greater than Ru for two year metal waste. Thus, if this process were used to recover uranium from current HW metal waste, zirconium would be the limiting activity, and for the two year metal waste ruthenium would be the limiting activity.

4.6 Column Demonstration

The mechanical operability of this process was successfully demonstrated on a five gallon scale in a column one inch in diameter. Runs were made with both synthetic feeds and solutions of ORNL sludge.

The columns were first packed with 3/16 inch Fenske rings. This packing plugged rapidly with the undissolved solids in the feeds and was replaced with 1/4 x 1/4 inch Raschig rings. With this packing the process was found to have the same high degree of mechanical operability as for example, Redox.

The extraction column used consisted of 10 feet of extraction section and four feet of scrub section, packed with 1/4 x 1/4 inch Raschig rings. In six column runs, uranium was recovered from ORNL sludge with losses of less than 0.1% and decontaminated from beta fission products to less than 5% of the beta activity of natural uranium.

The strip column was ten feet in length and also packed with 1/4 x 1/4 inch Raschig rings. With this length of column, uranium losses were as high as 0.5%; however, it is felt that additional column height would reduce this loss to 0.1%, since successive batch strippings yielded complete recovery of the uranium from the solvent.

4.7 Uranium Distribution Coefficients in Scrubbing and Stripping

The uranium distribution coefficients in the scrubbing section varied markedly with the concentration of uranium present in the organic phase. For example, on scrubbing an organic extract, 48% saturated with uranium (30.5 g/l), with 3.0 M nitric acid the distribution coefficient was 7.24 (org./aq.). However, on scrubbing with a 3.0M HNO_3, an organic extract that was 100% (63.5 g/l) saturated, the distribution coefficient was only 1.15 (see Table 4.7-1, Fig. IX).

As the solvent approached saturation in uranium, the uranium distribution coefficients became more independent of the HNO_3 concentration of the aqueous scrub.

As was expected, the uranium distribution coefficients increased with successive batch scrubbing steps since the uranium concentration of the organic phase was decreased (see Table 4.7-2 Fig. X and XI). Uranium distribution coefficients in scrubbing as a function of tributyl phosphate concentration showed essentially the same dependence that was demonstrated in extraction (see section 4.2).

Table 4.7-1

Effect of Uranium Concentration in the Solvent on Uranium

Distribution Coefficients in Scrubbing

Solvent: 15% Bu_3PO_4-85% hexane, uranium

Scrub: 1.0 M to 5.0 M HNO_3

Conditions: Equilibration for 15 minutes with 1/6 volume scrub at 20°C.

Solvent Uranium Concentration in Scrub Section		Uranium Dist. Coeff. (O/A) in Scrubbing Nitric Acid Concentration (M)				
g/l	% of Saturation	1	2	3	4	5
30.5	48.0	2.90	5.16	7.24	8.50	9.94
43.0	67.7	1.96	3.20	4.23	5.26	5.50
47.2	74.4	1.52	2.81	3.72	4.70	4.80
50.0	78.8	1.45	2.18	3.02	3.44	3.48
55.8	87.9	1.23	1.58	2.06	2.53	2.68
63.5	100.0	0.76	0.97	1.15	1.18	1.26

The back extraction of uranium fror tributyl phosphate was affected by the same variables that controlled the initial extraction and scrubbing operations, i.e. as the HNO_3 Bu_3PO_4 and uranium concentrations were decreased the uranium extraction favored the aqueous phase. Five successive batch strippings with water were sufficient to remove 99.9% of the uranium. This operation was studied batchwise with a series of organic extracts that contained uranium and had been previously scrubbed with 3.0M HNO_3. After the

removal of the nitric acid present the distribution coefficient (org./aq.) decreased from 0.9 on the first strip to about 0.03 and the fourth (see Table 4.7-3).

Table 4.7-3

Effect of Bu_3PO_4 Concentration on Uranium Distribution Coefficient in Stripping

Org. Phase: Bu_3PO_4 - hexane 2.3 mg U/ml Bu_3PO_4
Aq. Phase: Equal volume passes of H_2O

Conc. Bu_3PO_4 in Solvent, Mixture (%)	Uranium Distribution Coefficients (org./aq.)			
	1st Strip	2nd Strip	3rd Strip	4th Strip
5	0.09	----	----	----
15	0.49	0.01	<0.01	<0.01
20	1.06	0.48	0.06	0.02
25	0.97	0.18	0.17	0.03

5.0 Bibliography

1. ISC-8 "Extraction of Cerium^{IV} Nitrate by Butyl Phosphate", Warf, J. C.; op. cit.

2. BMI-JDS-179 "Progress Report for the Month of March 1949" Bearse, et al.

3. BMI-JDS-151 "Recovery of Uranium from Monazite Sands", Nov. 15, 1948 Bearse, et al.

4. ORNL-258, "Solvent Extraction Recovery of Uranium from Metal Waste", Ellison, C. V.; Ferguson, D. E.; Runion, T. C.

6.0 Appendix

Table 4.0-1

ORNL Metal Waste Analysis[a]

Tank No.	Phase Sampled	Ionic						Radiochemical					
		U	Na	NO_3	CO_3	PO_4	SO_4	Gross β	Gross γ	Ru β	Ce β	Ce β	Sr β
		mg/ml						cts/ml/min[b]					
								$x10^{-5}$	$x10^{-3}$	$x10^{-4}$	$x10^{-4}$	$x10^{-4}$	$x10^{-2}$
W-3	Supernatant	0.02	110	13.7	33.8	2.4	104	1.9	0.58	8.3	0.06	14.3	0.52
W-4		8.9	2.3	14.5	0.4	0.1	8.3	12.7	2.1	4.0	50.0	2.9	1900
W-7		0.02	54.2	15.9	29.3	6.0	132	26.0	0.58	9.6	3.2	17.2	1.7
W-10		0.02	74.1	22.4	33.0	8.7	104	29.8	0.9	8.1	4.7	26.9	4.2
W-8[c]		16.1	39.9	15.4	27.8	7.2	227	8.5	1.4	9.4	50.3	16.9	74.1
		mg/ml						cts/g./min					
								$x10^{-6}$	$x10^{-3}$	$x10^{-5}$	$x10^{-6}$	$x10^{-5}$	$x10^{-6}$
W-3	Sludge	539	143	22.8	60	12.5	8.6	19.1	14.0	7.4	11.8	3.1	1.2
W-4		326	190	42.5	51	218	146	4.5	1.3	0.9	1.3	1.2	1.3
W-7		475	170	34.9	67	90	214	3.2	1.2	7.8	0.7	1.6	0.7
W-10		485	164	43.5	49	90	105	8.2	2.4	2.0	4.2	2.5	1.5

(a) The samples were taken 11/23/48 by P. B. Orr. Ionic results reported 1/4/49 by P. F. Thomason, and radiochemical results were reported 1/26/49 by C. S. Burros.

(b) Counting done at 10.18% geometry with no adsorber.

(c) This tank is used as a collection tank, and no uranium is precipitated here.

[redacted]

Table 4.0-2

Radiochemical Analyses of Hanford Waste Samples

(Counts Per Minute Per Gram of Uranium)

	Supernatant	Sludge
Gross β	$0.62 \times 10^9 - 2.2 \times 10^9$	$0.59 \times 10^9 - 2.14 \times 10^9$
Gross γ	$1.53 \times 10^6 - 6.43 \times 10^6$	$3.68 \times 10^5 - 5.80 \times 10^5$
Zr β	$2.91 \times 10^5 - 5.64 \times 10^5$	$3.56 \times 10^6 - 4.76 \times 10^6$
Ru β	$0.81 \times 10^8 - 5.27 \times 10^8$	$0.52 \times 10^7 - 4.25 \times 10^7$
Cb β	$0.14 \times 10^7 - 1.34 \times 10^7$	$0.51 \times 10^6 - 1.46 \times 10^6$
TRE β	$2.32 \times 10^8 - 5.64 \times 10^8$	$0.35 \times 10^9 - 1.28 \times 10^9$
Ce β	$3.51 \times 10^8 - 5.19 \times 10^8$	$7.23 \times 10^8 - 9.11 \times 10^8$
Sr β	$0.86 \times 10^7 - 2.76 \times 10^7$	$0.58 \times 10^8 - 3.92 \times 10^8$
Cs β	$0.28 \times 10^9 - 1.28 \times 10^9$	$0.51 \times 10^7 - 8.24 \times 10^7$
Pu α	$0.16 \times 10^6 - 1.17 \times 10^6$	$0.98 \times 10^5 - 1.51 \times 10^5$

*Beta Geometry = 10.2%

Alpha Geometry = 52%

Table 4.2-4

HNO_3 Distribution in the System Bu_3PO_4 - Hexane - HNO_3 - H_2O

At Varying Tributyl Phosphate Concentration

Run No.	Conc Bu_3PO_4 (%)	Conc Bu_3PO_4 M	HNO_3 Dist. (M) Org.	HNO_3 Dist. (M) Aq.	HNO_3 Dist. Coeff. Org./Aq.	Moles HNO_3 / Mole Bu_3PO_4
1	5	0.18	0.190	9.640	0.019	1.038
2	10	0.37	0.365	9.595	0.038	0.997
3	15	0.55	0.558	9.210	0.060	1.010
4	20	0.73	0.675	8.952	0.075	0.922
5	25	0.91	0.880	8.925	0.098	0.961
6	50	1.83	1.755	8.775	0.200	0.959
7	75	2.74	2.510	8.295	0.302	0.910
8	100	3.65	3.105	7.140	0.434	0.848

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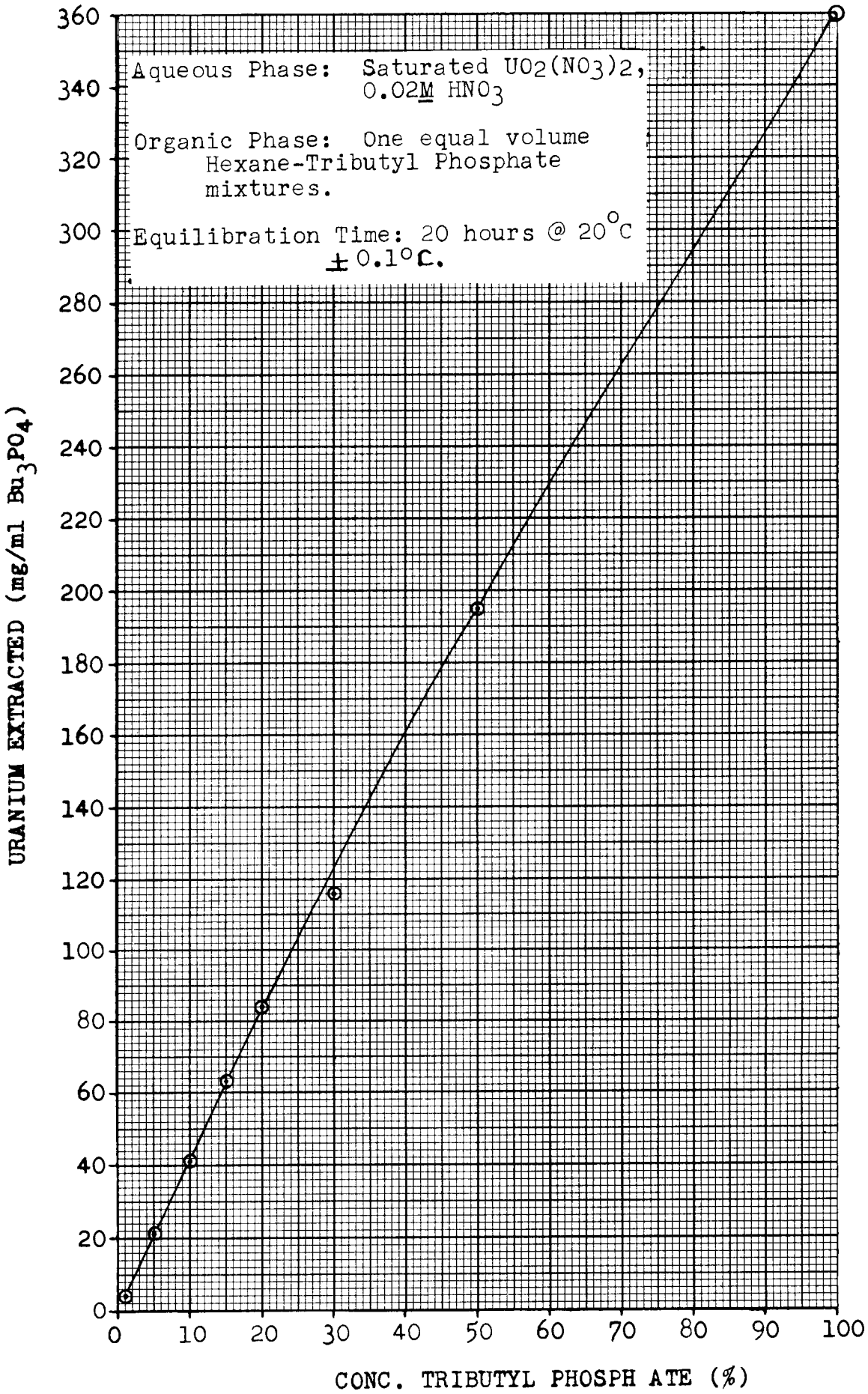
DWG. #7734

FIGURE I

URANIUM EXTRACTION BY TRIBUTYL PHOSPHATE



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DWG. #7735

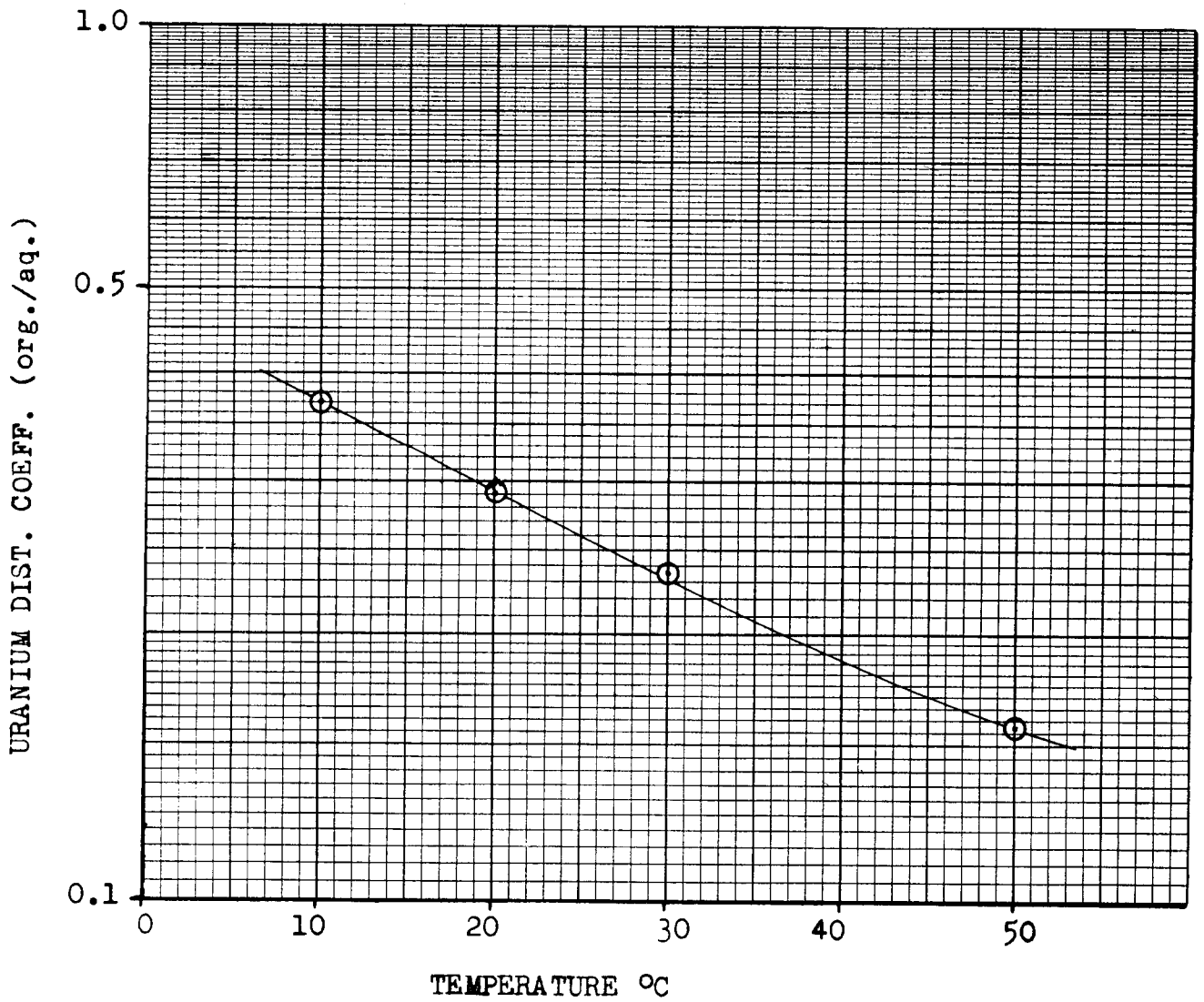
FIGURE II

EFFECT OF TEMPERATURE ON URANIUM EXTRACTION WITH HEXANE - TRIBUTYL PHOSPHATE

Aqueous Phase: 0.1M $UO_2(NO_3)_2$ reagent acidity

Organic Phase: One equal volume pass with 20% Bu_3PO_4 - 80% Hexane

Equilibration Time: 5 minutes



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DWG. #7736

FIGURE III

EFFECT OF HNO_3 CONCENTRATION ON URANIUM EXTRACTION

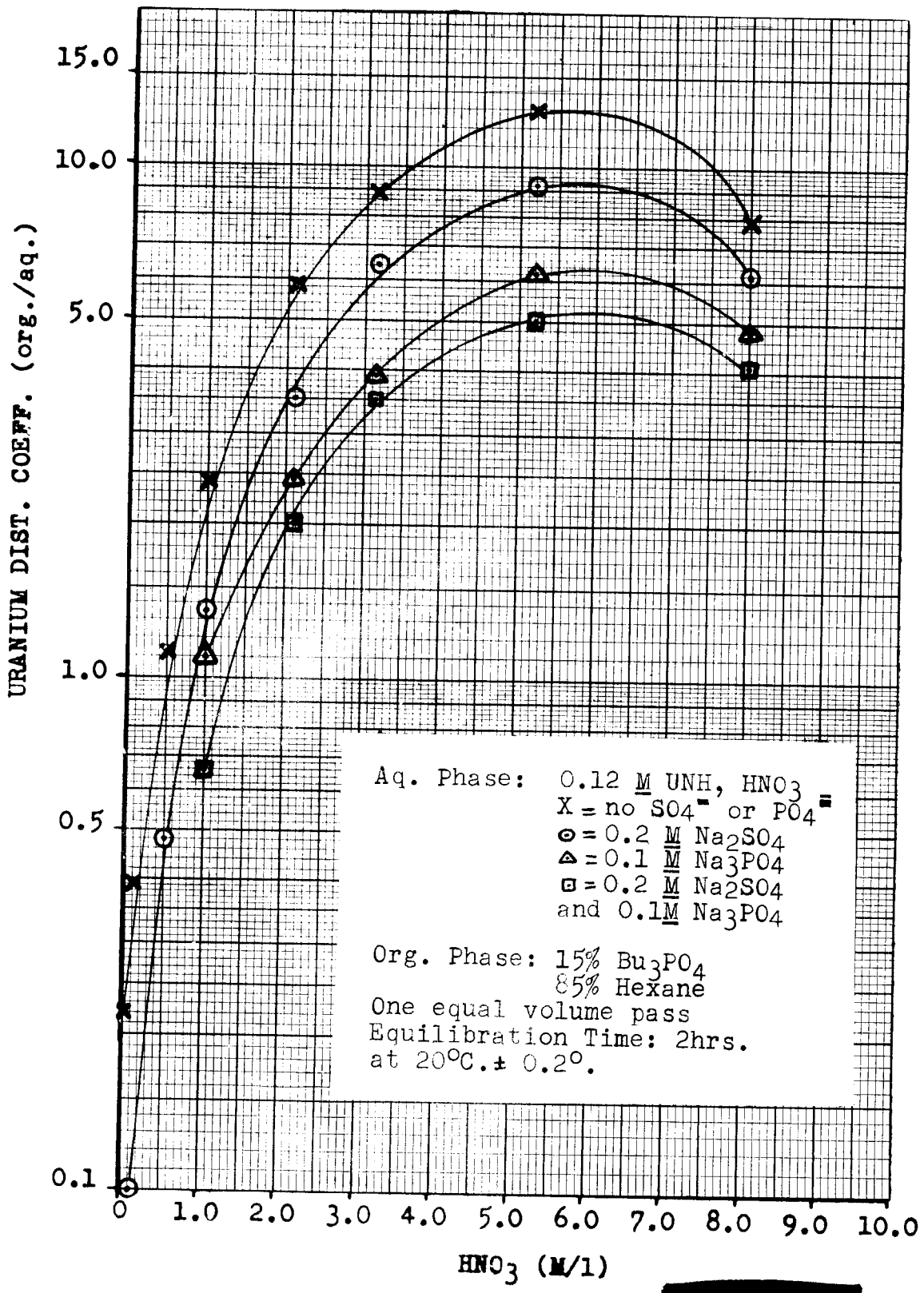

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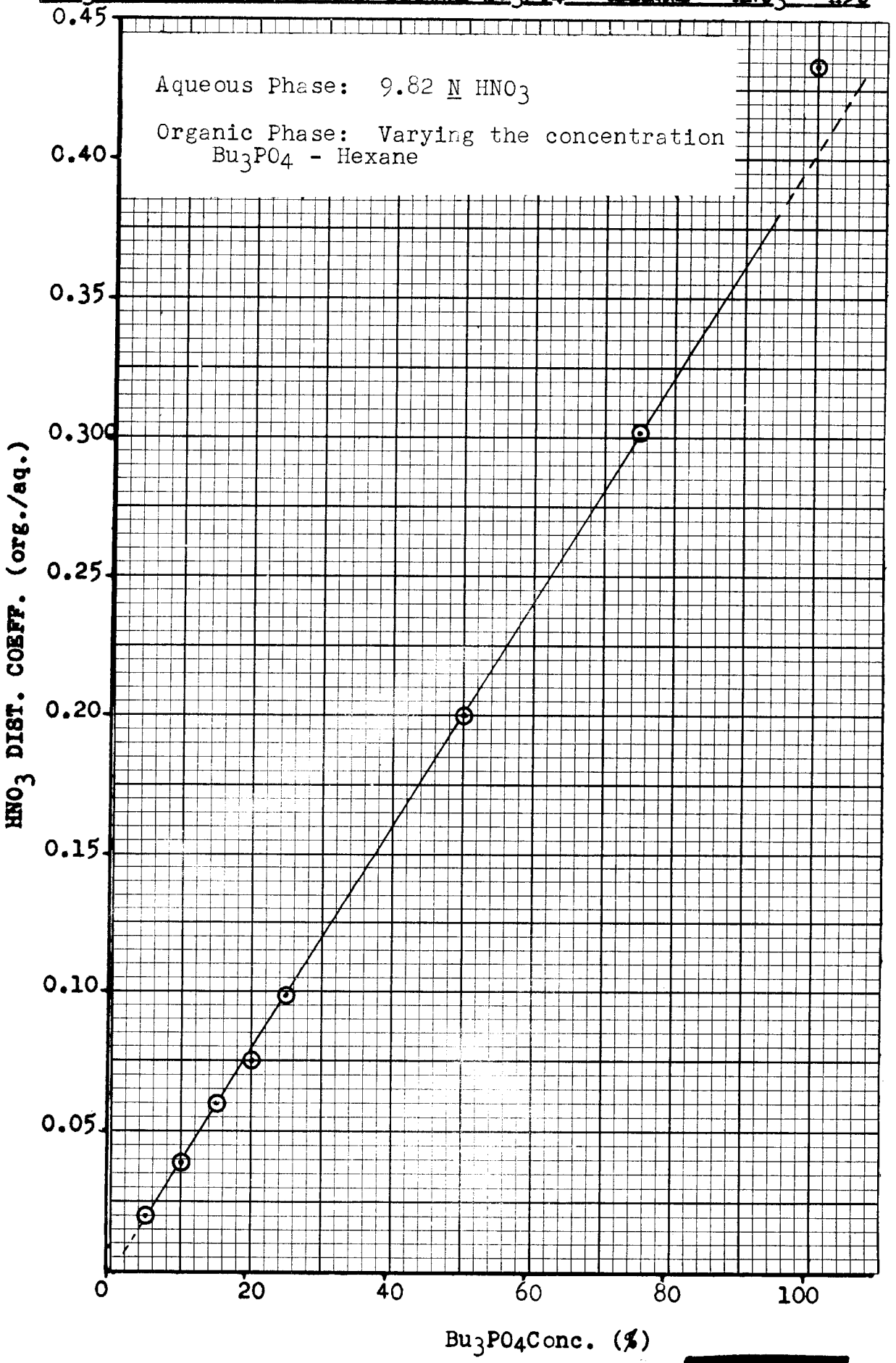
FIGURE IV DWG. #7737

HNO_3 DISTRIBUTION IN THE SYSTEM Bu_3PO_4 - HEXANE - HNO_3 - H_2O



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DWG. #7738

FIGURE V

HNO_3 DISTRIBUTION IN THE SYSTEM
HEXANE - $BuPO_4$ - HNO_3 - H_2O

Organic Solvent:
15% Bu_3PO_4 - 85% Hexane Mixture
Aqueous Phase: Varying Conc. of HNO_3
Equilibration Time: 10 minutes
Temperature: 20°C. ± 0.2°.

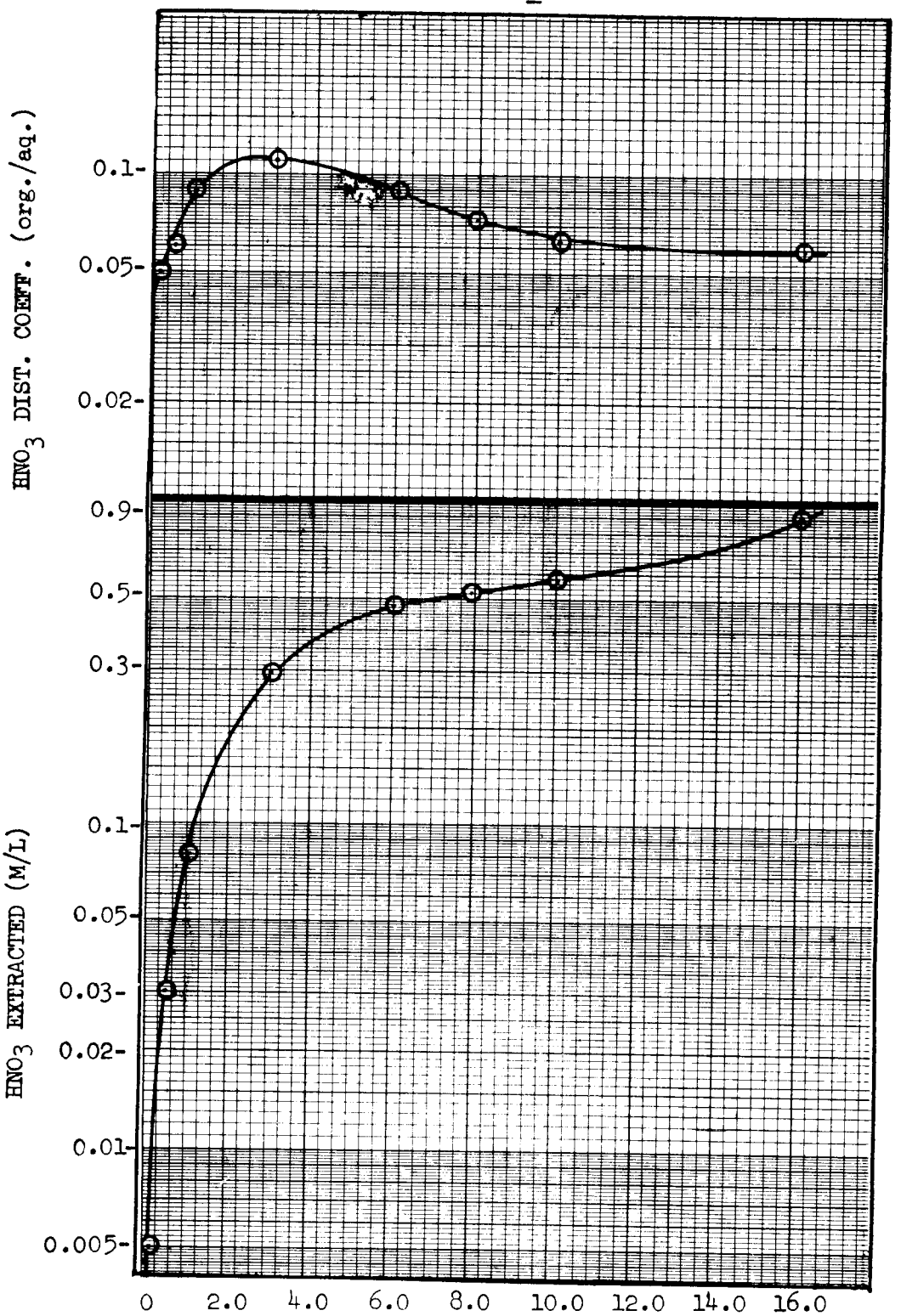

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FIGURE VI

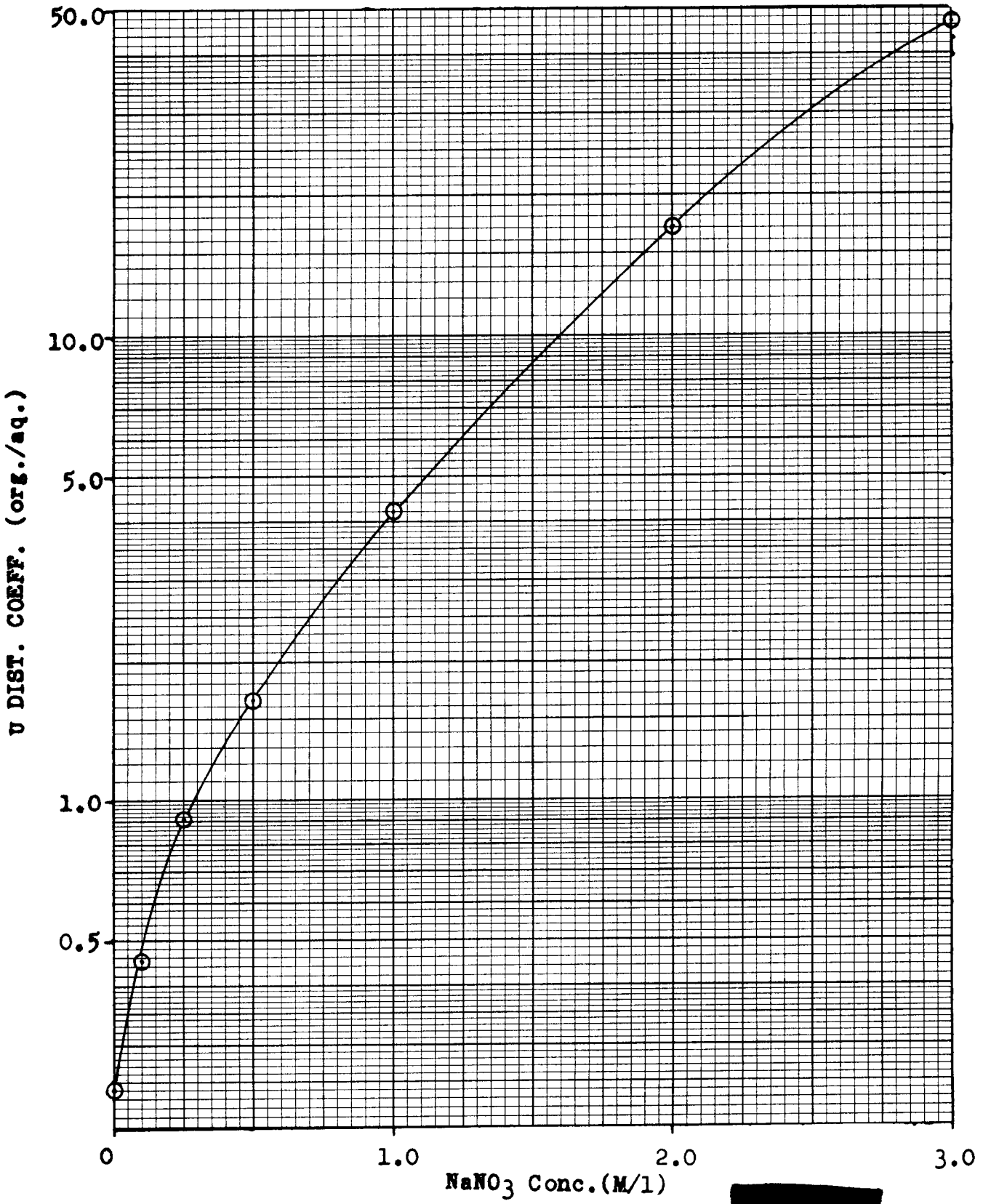
DWG. #7739

EFFECT OF $NaNO_3$ CONCENTRATION ON URANIUM EXTRACTION WITH HEXANE-TRIBUTYL PHOSPHATE

Aqueous Phase: 0.09M $UO_2(NO_3)_2 \cdot 6H_2O$, $NaNO_3$ reagent acidity

Organic Phase: One equal volume pass with 20% tributyl phosphate - 80% hexane

Equilibration Time: 18 hours at 20° C.



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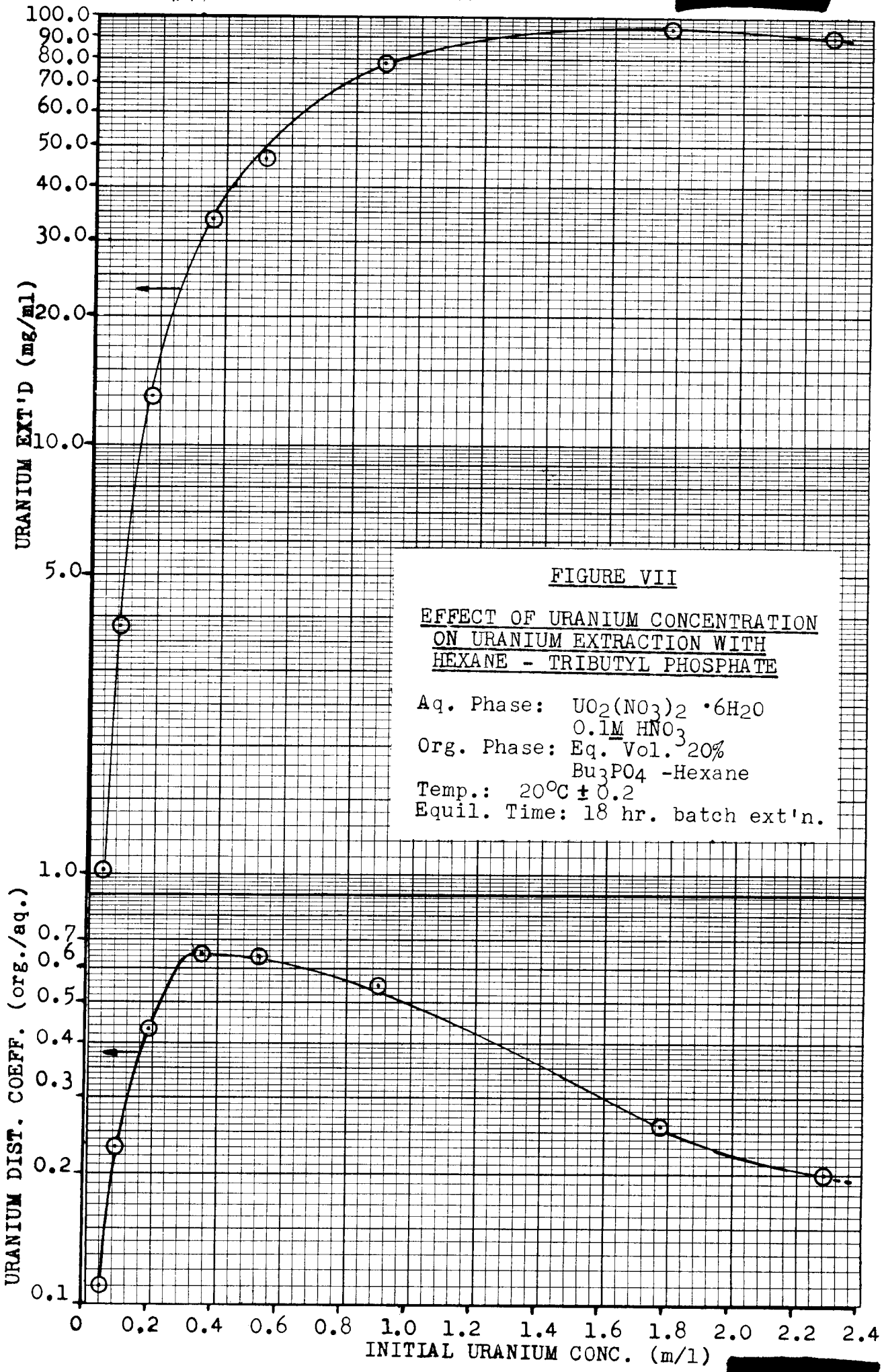


FIGURE VII

EFFECT OF URANIUM CONCENTRATION ON URANIUM EXTRACTION WITH HEXANE - TRIBUTYL PHOSPHATE

Aq. Phase: $UO_2(NO_3)_2 \cdot 6H_2O$
0.1M HNO_3
Org. Phase: Eq. Vol. 20% Bu_3PO_4 -Hexane
Temp.: 20°C ± 0.2
Equil. Time: 18 hr. batch ext'n.

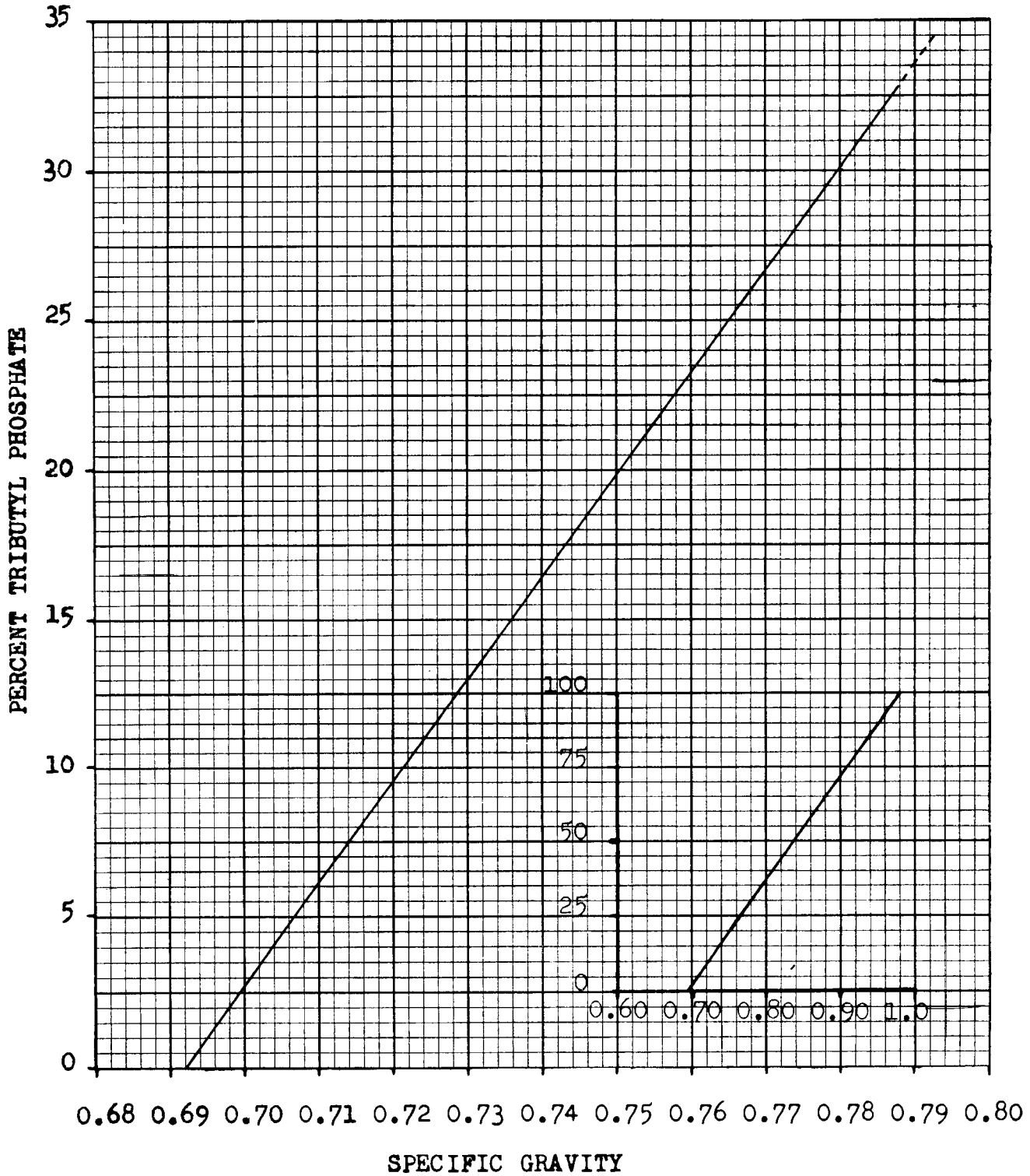
[redacted]

DWG. #7741

FIGURE VIII

SPECIFIC GRAVITY OF HEXANE-TRIBUTYL PHOSPHATE MIXTURES

Water Saturated Tributyl Phosphate
Technical Grade Hexane
Specific Gravity taken with Westphal
Balance at 20°C 0.5°



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DWG. #7742

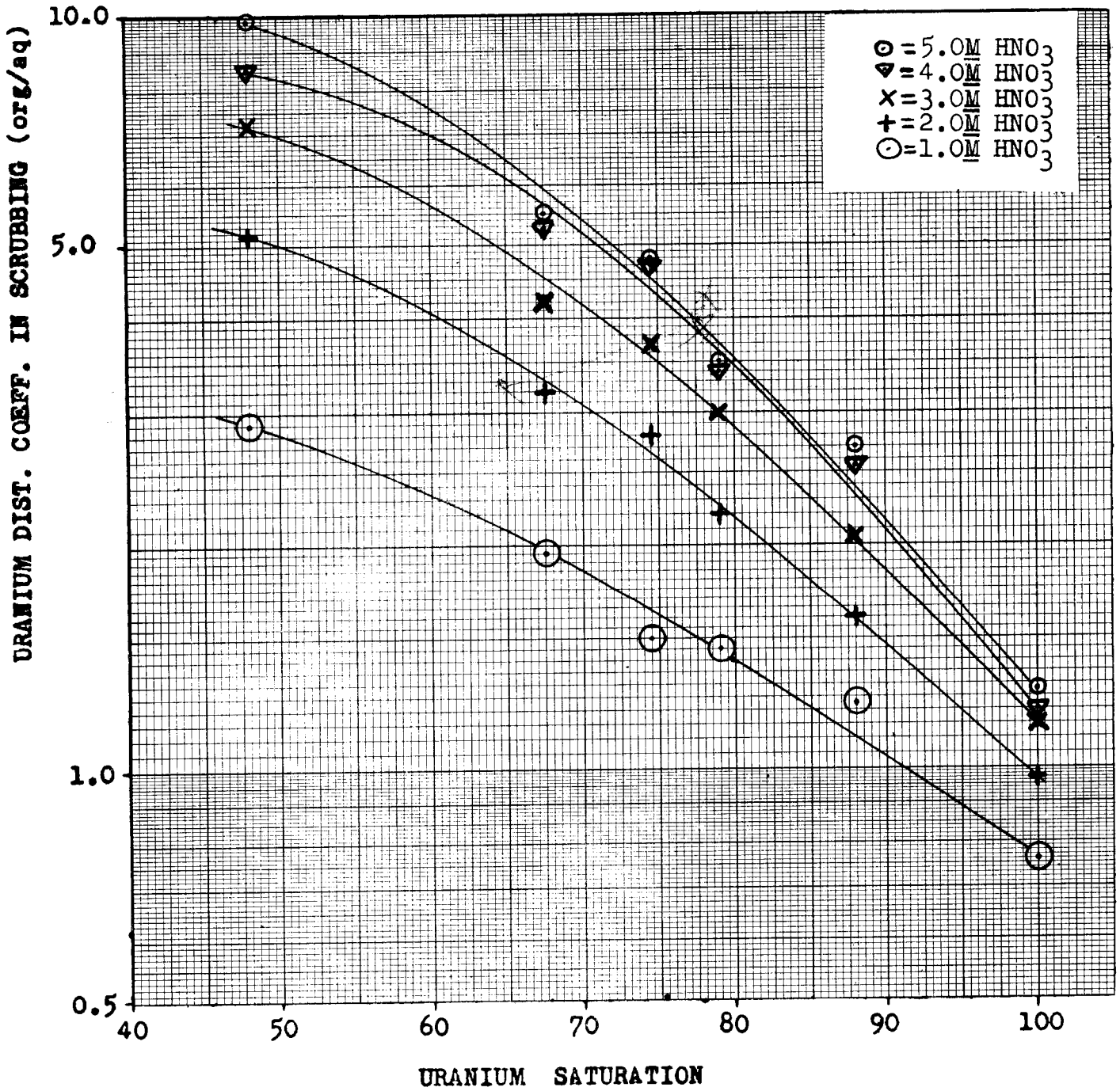
FIGURE IX

EFFECT OF SOLVENT URANIUM SATURATION ON URANIUM DISTRIBUTION COEFFICIENTS IN SCRUBBING

Solvent: 15% Bu_3PO_4 - 85% hexane containing $UO_2(NO_3)_2$

Scrub: 1.0 M to 5.0 M HNO_3

Conditions: Equilibration for 15 minutes with 1/6 volume scrub at 20°C in water bath.



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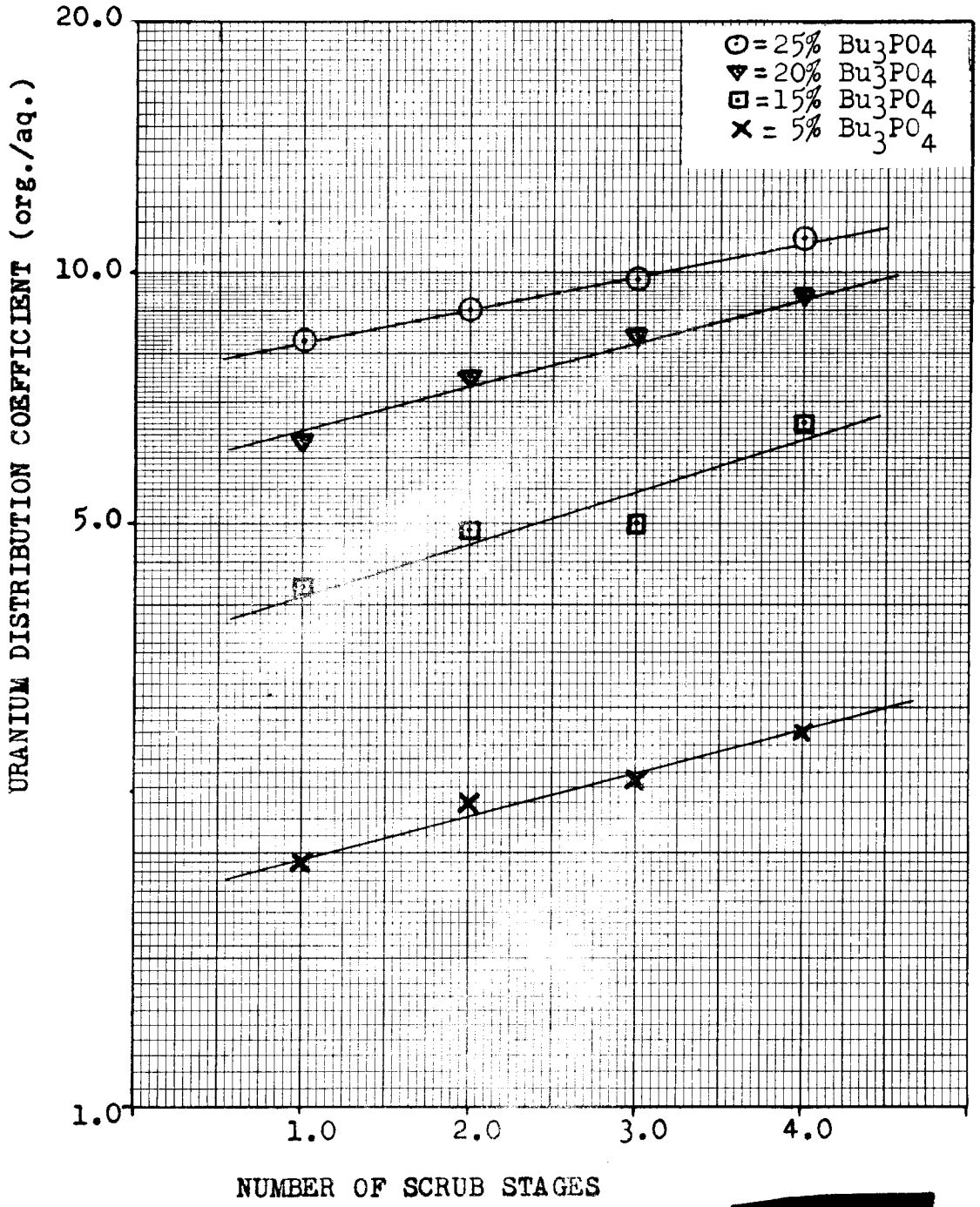
DWG. #7743

FIGURE X

URANIUM DISTRIBUTION COEFFICIENTS IN SCRUBBING - EFFECT OF Bu_3PO_4 CONCENTRATION

Organic Phase: Bu_3PO_4 - Hexane - 2.3 mgU/ml Bu_3PO_4

Aqueous Phase: Equal volume 2.0M HNO_3



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DWG. #7744

FIGURE XI

URANIUM DISTRIBUTION COEFFICIENTS IN SCRUBBING - EFFECT OF Bu_3PO_4 CONCENTRATION

Aqueous Phase: Equal volume 5.0M HNO_3

Organic Phase: Bu_3PO_4 - Hexane - 2.3 mg U/ml Bu_3PO_4

⊙ - 25% Bu_3PO_4
▼ - 20% Bu_3PO_4
⊡ - 15% Bu_3PO_4
× - .5% Bu_3PO_4

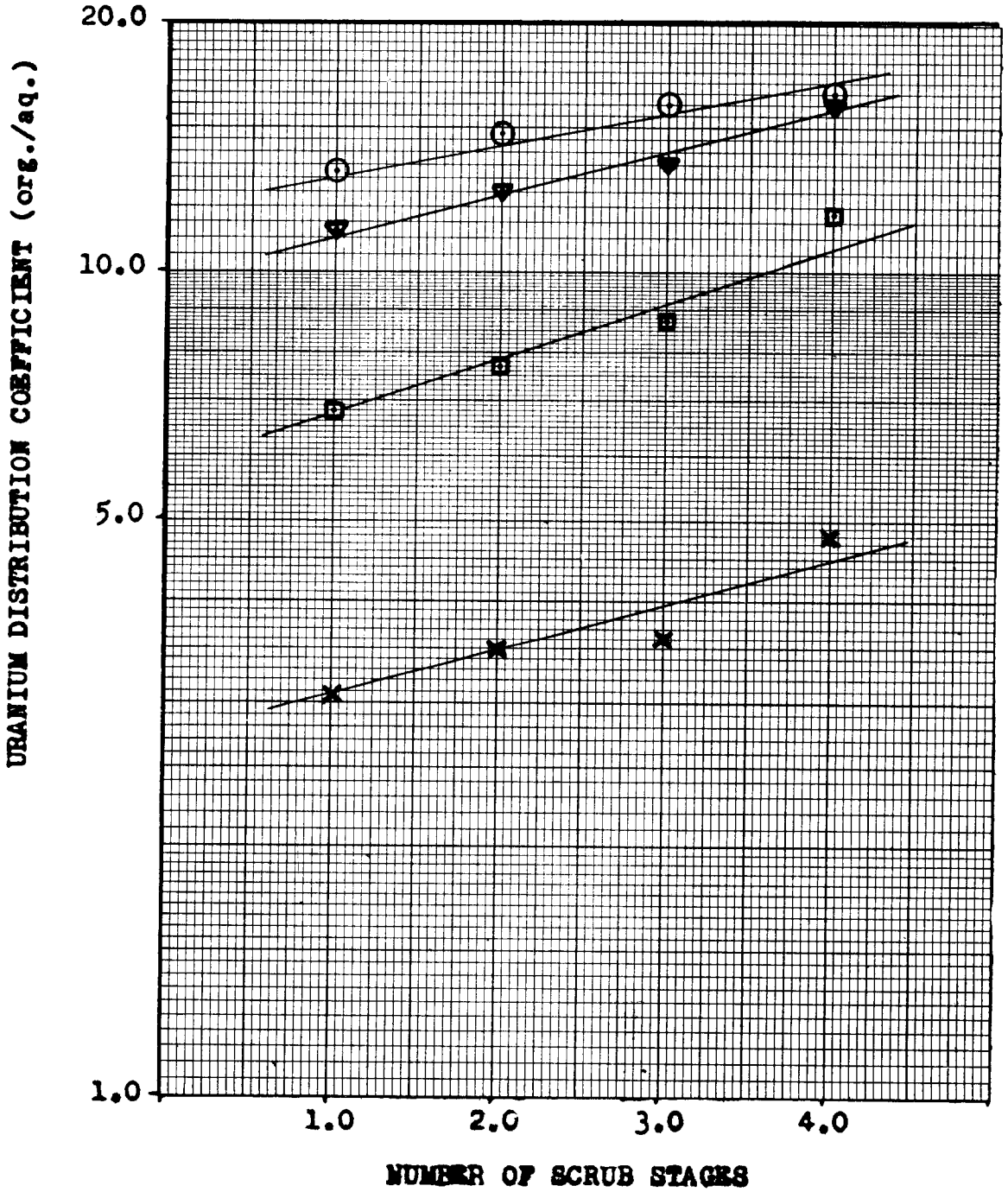

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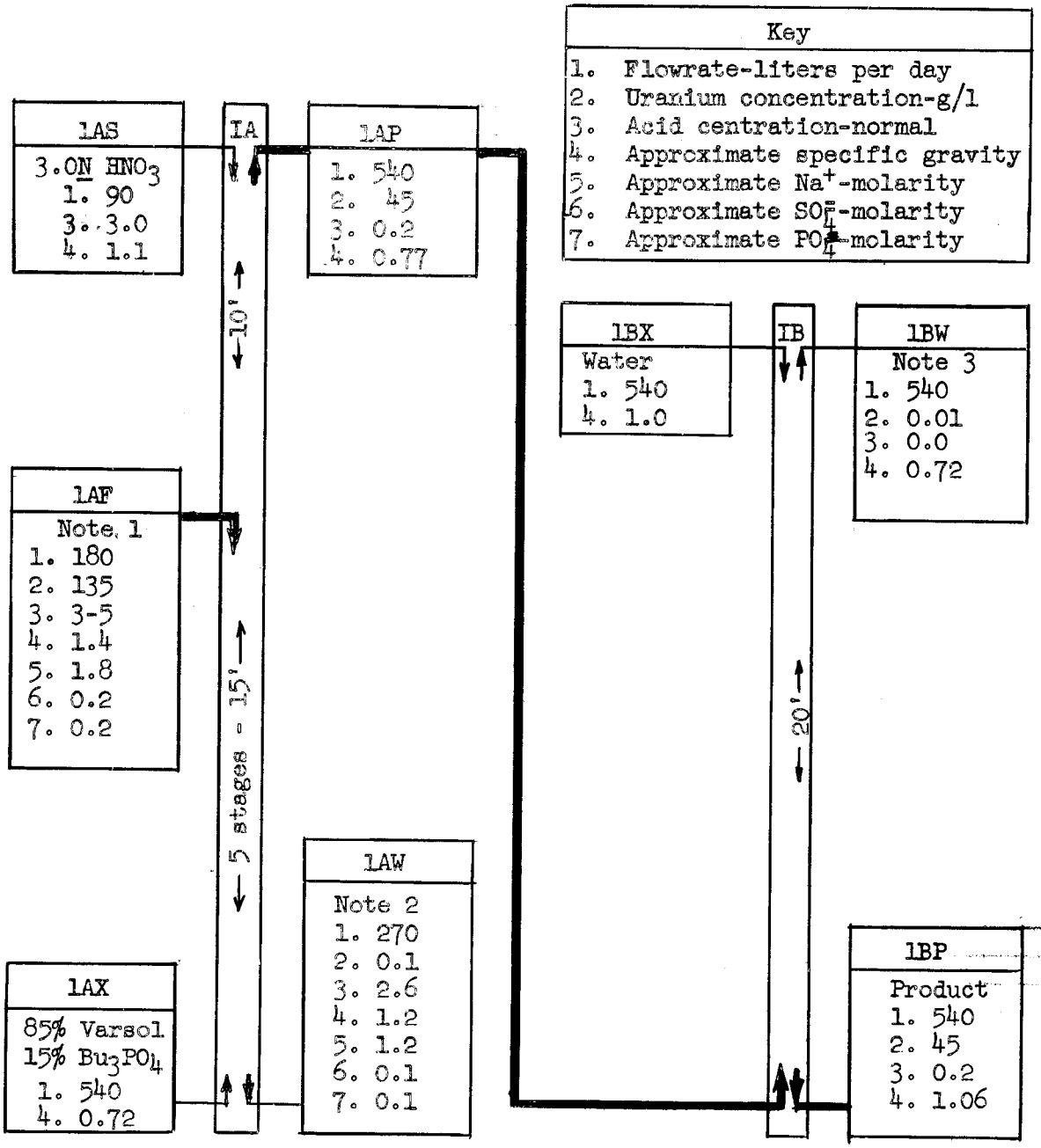
Figure XII

Waste Metal Recovery By Solvent Extraction



Basis: 24 kg of Uranium process per day - Column size IA=1-1/2 inches ID-IB=2-1/2 inches ID.

Note 1. The Optimum feed preparation method has not been determined. This flowsheet presupposes the preparation of the feed in such a manner as to reach a uranium concentration of 135 g/l with 3-5N excess acid.

Note 2. The IAW can be evaporated to 135 liters without crystallization. The IAW volume can be reduced to 35 liters with one $NaNO_3$ crystallization.

Note 3. The IBW will be washed twice with 1M Na_2CO_3-once with 0.1M HNO_3 and reused as IAX.

[redacted]

The laboratory data included in this report is recorded in secret Notebook CL-1684, 78, 1939, 2072, and 118.

We extend our appreciation to L. T. Corbin and P. F. Thomason for their assistance in supplying the necessary analytical data for this report.

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