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FOR PLUTONIUM AND URANIUM
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DISTRIBUTION OF URANYL NITRATE BETWEEN
Al(NO₃)₃ AND TRIBUTYL PHOSPHATE

by

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ABSTRACT

The distribution of uranyl nitrate was measured from aluminum nitrate and nitric acid solutions into diluted tri-n-butyl phosphate. This information is useful for designing solvent extraction processes for recovery of uranium from aluminum nitrate or nitric acid solutions.

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DISTRIBUTION OF URANYL NITRATE BETWEEN
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INTRODUCTION

Uranium is recovered from irradiated uranium-aluminum fuel by chemical processing. The most popular type of chemical process for radioactive materials is solvent extraction, which depends for its effectiveness on the extraction of uranium from an aqueous phase into an organic phase under conditions that minimize the extraction of fission products. For processing fuel elements of uranium alloyed with aluminum, a possible process might involve dissolution of the uranium-aluminum alloy in nitric acid, and extraction of the uranium into an organic phase, leaving the aluminum and most of the fission products in the aqueous phase. The solvent extraction process should be designed to have the minimum extraction capacity to recover uranium since any extra extracting capacity tends to increase extraction of fission products with the uranium.

The extractant chosen for investigation was a solution of 6% tri-n-butyl phosphate (TBP) in n-dodecane. The choice of this TBP concentration was influenced by the ratio of organic phase to aqueous phase flow rates attainable in solvent extraction equipment (about one organic volume to ten aqueous volumes), and by the mole ratio of uranium to aluminum expected for the feed solutions, about 0.01. Equilibrium measurements of the distribution of uranyl nitrate between the organic phase and the aluminum nitrate aqueous phase were undertaken to discover the minimum conditions for recovery of uranium.

SUMMARY

The distribution of uranyl nitrate as a function of uranium concentration was measured at 40°C between (1) 6% TBP and acid-deficient aluminum nitrate solutions; (2) 6% TBP and dilute (0.01M and 0.05M) nitric acid; and (3) 18% TBP and 3M nitric acid. The distribution of U-233 tracer was measured as a function of acidity between nitric acid and 12 and 18% TBP. The data are presented in Figures 1 to 4.

DISCUSSION

EXPERIMENTAL

Aqueous phases were prepared by mixing stock solution of aluminum nitrate and analyzing the resulting solutions for aluminum and acid deficiency* or acidity, then adding differing amounts of uranyl nitrate solution to portions of each aluminum solution. These solutions were prepared from C.P. reagents; acid-deficient solutions

* Acid-deficient solutions of aluminum nitrate are solutions which contain less than the stoichiometric amount of nitrate ion.

of aluminum nitrate were prepared by dissolving aluminum powder in aluminum nitrate solutions. In the preparation of aqueous phases for nitric acid systems, uranium stock solution was added to nitric acid.

Purified tri-n-butyl phosphate and n-dodecane were mixed to prepare the organic extractant. The tri-n-butyl phosphate (TBP) was washed successively with 0.1M $K_2Cr_2O_7$ - 0.1M H_2SO_4 , water, 1M NaOH, and water. The washed TBP was dried by evaporation at reduced pressure and passed through an alumina bed to remove residual water. The product was dry 100% TBP. The organic extractant was prepared by diluting a weighed amount of 100% TBP with n-dodecane (95% pure, obtained from the Humphrey-Wilkinson Co., North Haven, Conn.).

The organic and aqueous phases were equilibrated by mixing in a thermostatted water bath. After equilibration, the mixed phases were centrifuged and separated. Duplicate analyses were performed on each phase; in all cases, both phases were analyzed for uranyl ion. The pH of the aqueous aluminum phases was determined after equilibration; analyses for aluminum and acid deficiency were performed before equilibration. In the nitric acid systems, both the aqueous and the organic phases were analyzed for acid after equilibration.

Uranium concentrations were determined by measuring the absorbance of the uranyl thiocyanate complex on a Beckman DU spectrophotometer. Aqueous phases were measured directly; the uranium was removed from the organic phase by stripping with 0.1M Na_2CO_3 , and the acidified carbonate solutions were analyzed. It was experimentally verified that aluminum ion did not interfere with this analysis.

In the absence of aluminum, nitric acid concentrations were determined by titration with standard sodium hydroxide. The uranium was complexed with KF solution to prevent it from interfering with the analyses. Both the organic and aqueous phases were analyzed directly. When aluminum was present, the acidity or acid deficiency was determined by addition of a known amount of standardized HCl, precipitation of the aluminum as K_3AlF_6 by addition of KF, and back-titration of the excess added acid with standardized sodium hydroxide. Most of the aluminum solutions were acid deficient, so that, because of the presence of $Al(OH)^{++}$ and $Al(OH)_2^+$ ions, less sodium hydroxide was required to neutralize the solution than would be necessary to neutralize the added standard acid alone. Where the acidity of the solution was low, its pH was also measured.

Aluminum concentration was measured by adding an excess of standard dihydrogen disodium ethylenediaminetetraacetate ("Versene") and back-titrating the excess "Versene" at pH 4 to 4.5 with a standard zinc sulfate solution⁽¹⁾.

The accuracy of the analyses varied with the concentration of the measured ion. The estimated errors in the analyses are:

<u>Ion Measured</u>	<u>Estimated Errors</u>	
	<u>Range of Measurement, M</u>	<u>Estimated Error, %</u>
Aluminum	0.2 to 2.0	3
Uranyl	0.15 to 1.5×10^{-4}	3
	$< 1.5 \times 10^{-4}$	5
<u>Acidity</u>		
No aluminum present	0.05 to 5 HNO ₃	1 to 2
Aluminum present	0 HNO ₃	20
Aluminum present	0.2 to 1 acid deficient	5

RESULTS

The distribution of uranium as a function of uranium concentration was measured at four aluminum concentrations, and at two or three different "acid-deficient concentrations" for each aluminum concentration. The eleven curves drawn from these measurements are shown in Figure 1; the data are presented in Table I. All measurements were made at 40°C and the organic phase was 6 volume per cent TBP. The acid deficiency (or acidity) for each curve in Figure 1 is the average for the set of measurements included in the curve. It was planned that the acid deficiency would be constant for each curve, but since the uranium stock solution contained nitric acid, the addition of the uranium stock solution to the aluminum nitrate solution changed the acid deficiency. The exact value for the acid deficiency (or acidity) was obtained by measuring the pH of the final solution and correcting the initial acid deficiency using KAPL data⁽²⁾ for the dependence of pH on the acid deficiency (acidity) at various aluminum nitrate concentrations.

The distribution of uranium between 6% TBP and two concentrations of dilute acid, 0.01 and 0.05M HNO₃, was measured at 27°C (Figure 2, Table II). Distribution coefficients at low concentrations were determined by measuring the distribution coefficient of U-233. The extraction of uranium by 18% TBP from an aqueous phase which was approximately 3M HNO₃ was measured at 40°C (Figure 3, Table III). The extraction of nitric acid and U-233 tracer by 18 and 12% TBP were also measured at 40°C (Figure 4).

The data are of value in the design of solvent extraction processes for the extraction of uranium with 6% TBP from an aluminum-salted aqueous phase, and for the extraction of uranium from a nitric acid-salted system by 18% TBP. These data permit a prediction of the starting point for process development, but additional data are required for complete design of a solvent extraction process.

For a process in the aluminum nitrate - 6% TBP system, the additional data necessary to specify the extraction process completely are the distribution of uranyl nitrate and nitric acid between 6% TBP

and mixed aluminum nitrate - nitric acid solutions that contain varying concentrations of uranium, nitric acid, and aluminum nitrate. For a process in the nitric acid - 18% TBP system, the additional data required include the distribution of uranium and nitric acid between 18% TBP and solutions of varying uranium and acid concentrations.

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TABLE I
DISTRIBUTION OF URANIUM BETWEEN
ALUMINUM NITRATE AND 6% TBP AT 40°C

<u>Al(NO₃)₃,</u> <u>M</u>	<u>Acid</u> <u>Deficiency,</u> <u>M</u>	<u>pH</u>	<u>UO₂(NO₃)₂, M</u>		<u>E o/a</u>
			<u>Organic</u>	<u>Aqueous</u>	
0.490	0.019	1.87	--	--	--
(.493)*	(.009)	1.74	0.0242	0.0269	0.900
(.493)	(.001 HNO ₃)	1.60	.0413	.0609	.678
.496	(.01 HNO ₃)	1.45	.0516	.0943	.547
(.493)	(.02 HNO ₃)	1.32	.0603	.138	.437
.491	.237	3.18	--	--	--
(.504)	(.23)	3.05	.0130	.0371	.350
(.504)	(.22)	3.01	.0253	.0749	.338
.506	(.21)	2.94	.0351	.110	.319
(.501)	(.20)	2.89	.0450	.153	.294
.517	.548	3.35	--	--	--
(.516)	(.54)	3.30	.00646	.0453	.143
(.516)	(.53)	3.22	.0148	.0899	.165
.515	(.52)	3.14	.0222	.123	.180
(.516)	(.51)	3.08	.0325	.170	.191
.730	.010	1.40	.0000	--	--
(.733)	(.00)	1.34	.0360	.0148	2.43
(.733)	(.01 HNO ₃)	1.20	.0576	.0450	1.28
.735	(.02 HNO ₃)	1.10	.0683	.0757	.902
(.733)	(.03 HNO ₃)	.99	.0755	.122	.619

* All numbers in parentheses were calculated by correcting a previous measurement.

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TABLE I (Continued)

<u>Al(NO₃)₃, M</u>	<u>Acid Deficiency, M</u>	<u>pH</u>	<u>UO₂(NO₃)₂, M</u>		<u>E o/a</u>
			<u>Organic</u>	<u>Aqueous</u>	
0.755	0.295	2.80	--	--	--
(.755)	(.285)	2.73	0.0265	0.0235	1.13
(.755)	(.275)	2.70	.0446	.0572	0.780
.755	(.265)	2.67	.0548	.0885	.619
(.755)	(.255)	2.61	.0647	.134	.483
.742	.514	3.08	--	--	--
(.742)	(.504)	3.04	.0171	.0353	.484
(.742)	(.494)	2.98	.0306	.0725	.422
.743	(.484)	2.95	.0398	.108	.369
(.742)	(.474)	2.91	.0505	.152	.332
1.05	.013	1.03	--	--	--
(1.08)	(.011)	1.10	.0125	.000488	25.6
1.08	(.009)	1.08	.0210	.00102	20.6
1.08	(.007)	1.05	.0272	.00159	17.1
(1.04)	(.003)	0.95	.0464	.00482	9.63
(1.04)	(.007 HNO ₃)	.82	.0735	.0273	2.69
1.03	(.017 HNO ₃)	.78	.0836	.0594	1.41
(1.04)	(.027 HNO ₃)	.70	.0900	.108	.833

TABLE I (Continued)

<u>Al(NO₃)₃, M</u>	<u>Acid Deficiency, M</u>	<u>pH</u>	<u>UO₂(NO₃)₂, M</u>		<u>E o/a</u>
			<u>Organic</u>	<u>Aqueous</u>	
1.01	0.295	2.50	--	--	--
(.992)	(.294)	2.49	0.00427	0.000597	8.42
.987	(.293)	2.49	.0104	.00147	7.07
.996	(.291)	2.49	.0183	.00306	5.98
(1.01)	(.285)	2.48	.0387	.0115	3.37
(1.01)	(.275)	2.42	.0602	.0371	1.62
1.01	(.265)	2.39	.0724	.0712	1.02
(1.01)	(.255)	2.32	.0815	.117	.697
1.05	.772	2.90	--	--	--
(1.06)	(.76)	2.80	.0294	.0220	1.34
(1.06)	(.75)	2.77	.0468	.0552	.848
1.06	(.74)	2.72	.0581	.0855	.680
(1.06)	(.73)	2.68	.0677	.133	.509
1.18	.002 HNO ₃	0.74	--	--	--
(1.22)	(.01 HNO ₃)	.83	.0348	.00105	33.1
(1.22)	(.013 HNO ₃)	.80	.0503	.00264	19.1
1.22	(.016 HNO ₃)	.78	.0651	.00644	10.1
(1.22)	(.022 HNO ₃)	.79	.0858	.0328	2.62
1.22	.279	2.20	--	--	--
(1.23)	(.275)	2.18	.0177	.000742	23.9
1.24	(.273)	2.18	.0277	.00158	17.5
(1.23)	(.268)	2.15	.0517	.00602	8.59
1.23	(.255)	2.15	.0802	.0403	1.99

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TABLE II

DISTRIBUTION OF URANIUM BETWEEN
NITRIC ACID AND 6% TBP AT 40°C

<u>UO₂(NO₃)₂, M</u>			
<u>Organic</u>	<u>Aqueous</u>	<u>E o/a</u>	<u>pH</u>
0.0000208	0.00975	2.13×10^{-3}	1.97
.000559	.0477	1.17×10^{-2}	1.83
.00312	.0959	3.25×10^{-2}	1.71
.00819	.148	6.53×10^{-2}	1.61
.0204	.229	8.91×10^{-2}	1.42
Tracer 379 d/m-ml	4.84×10^6 d/m-ml	7.83×10^{-5}	1.72
Tracer 292 d/m-ml	4.90×10^6 d/m-ml	5.96×10^{-5}	1.72
.0000795	.00963	8.26×10^{-3}	1.28
.000937	.0489	1.92×10^{-2}	1.23
.00364	.0947	3.84×10^{-2}	1.19
.00931	.145	6.42×10^{-2}	1.15
.0227	.225	1.01×10^{-1}	1.07
Tracer 2.25×10^4 d/m-ml	4.80×10^6 d/m-ml	4.69×10^{-3}	1.23

TABLE III

DISTRIBUTION OF URANIUM BETWEEN
NITRIC ACID AND 18% TBP AT 40°C

<u>UO₂(NO₃)₂, M</u>		<u>HNO₃, M</u>		<u>E o/a</u>	
<u>Organic</u>	<u>Aqueous</u>	<u>Organic</u>	<u>Aqueous</u>	<u>HNO₃</u>	<u>UO₂⁺⁺</u>
0.292	0.813	0.061	3.18	0.019	0.36
0.263	0.282	0.089	3.11	0.029	0.93
0.233	0.132	0.127	3.24	0.039	1.77
0.207	0.0754	0.154	3.14	0.049	2.75
0.184	0.0534	0.177	3.14	0.056	3.45
0.159	0.0356	0.205	3.11	0.066	4.47
0.112	0.0165	0.267	3.11	0.086	6.79
0.051	0.00506	0.337	3.10	0.11	10.0
0.018	0.00156	0.378	3.04	0.124	11.5
0.0106	0.00085	0.381	3.05	0.125	12.4

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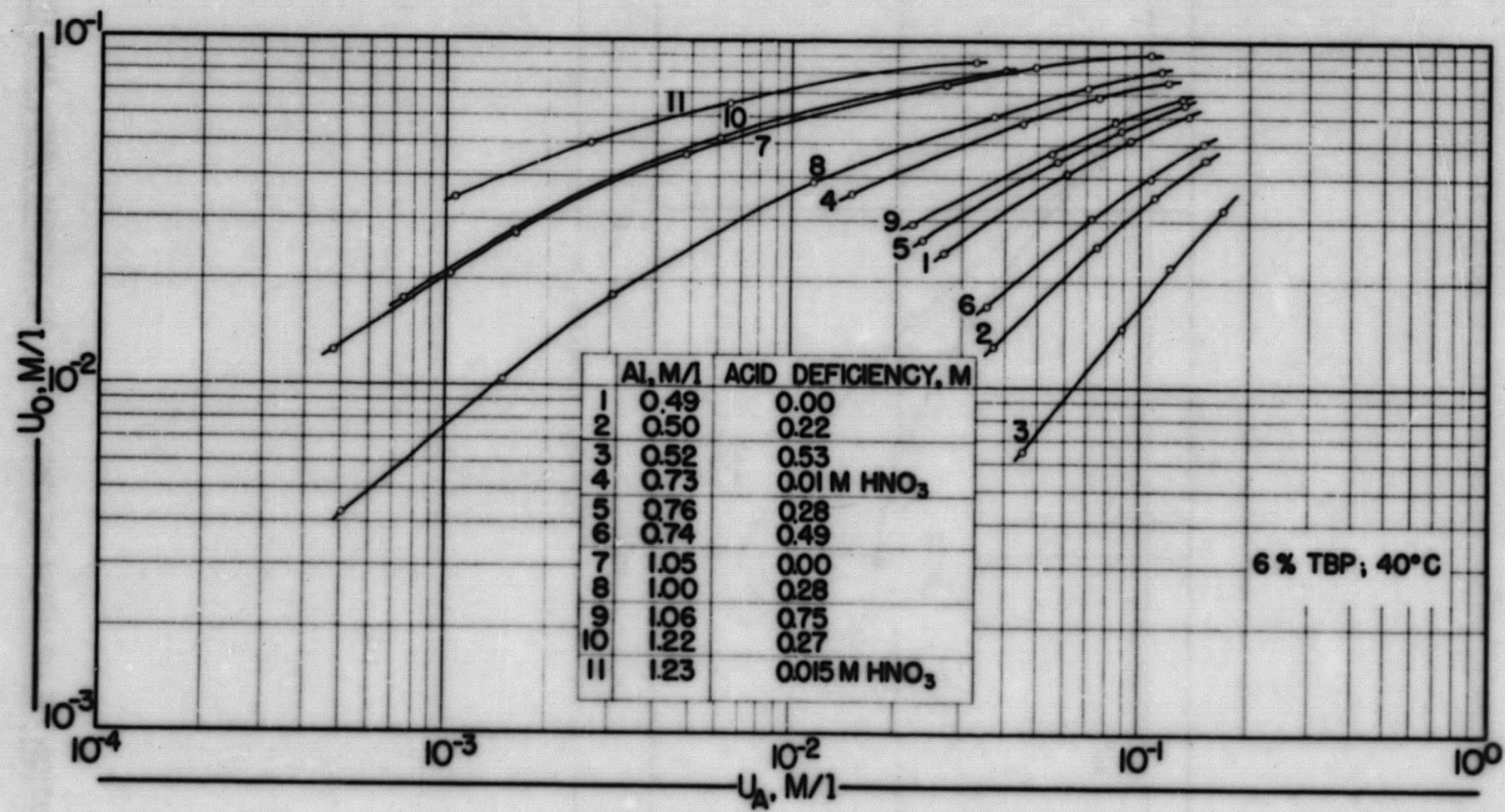
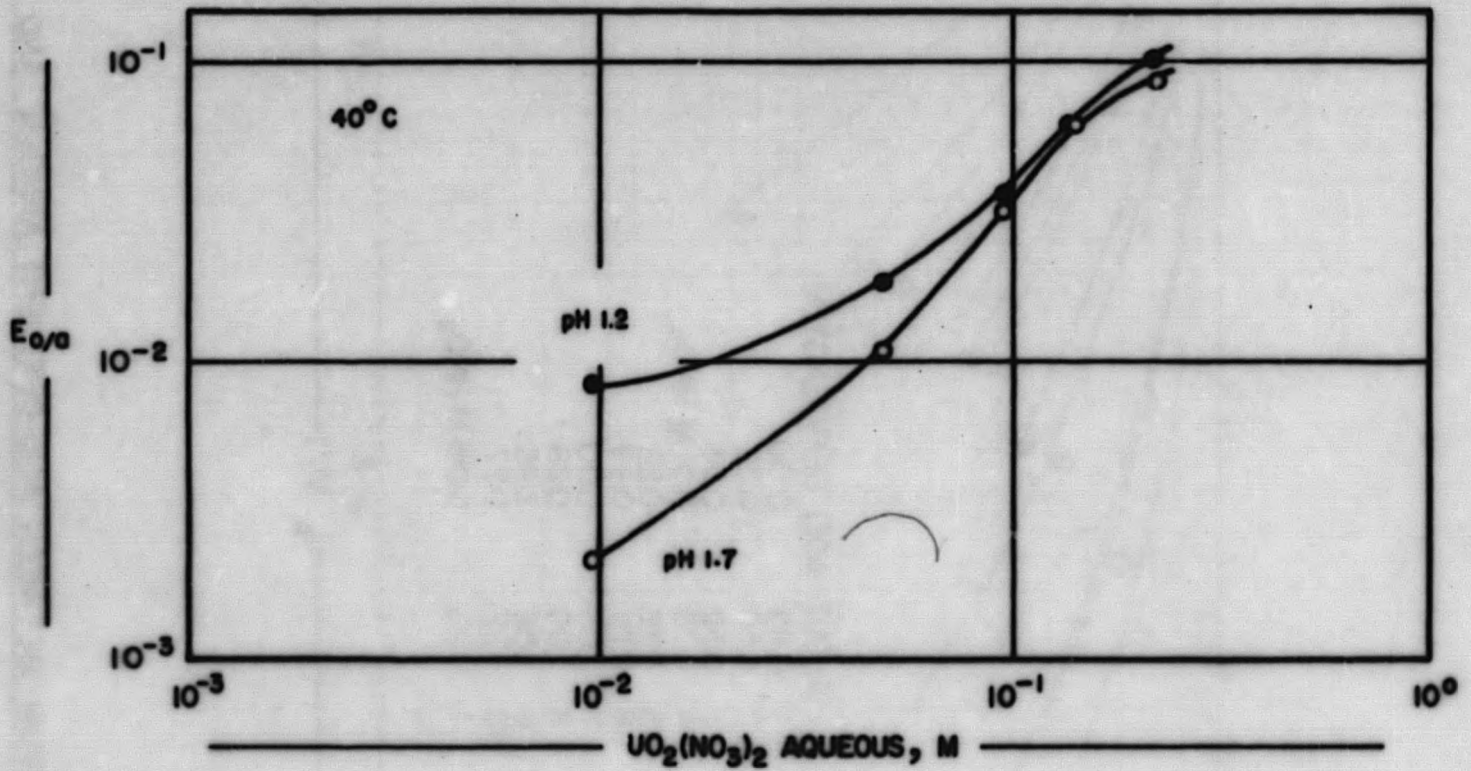


FIGURE 1

DISTRIBUTION OF URANIUM BETWEEN ACID-DEFICIENT $Al(NO_3)_3$ AND 6% TBP

FIGURE 2

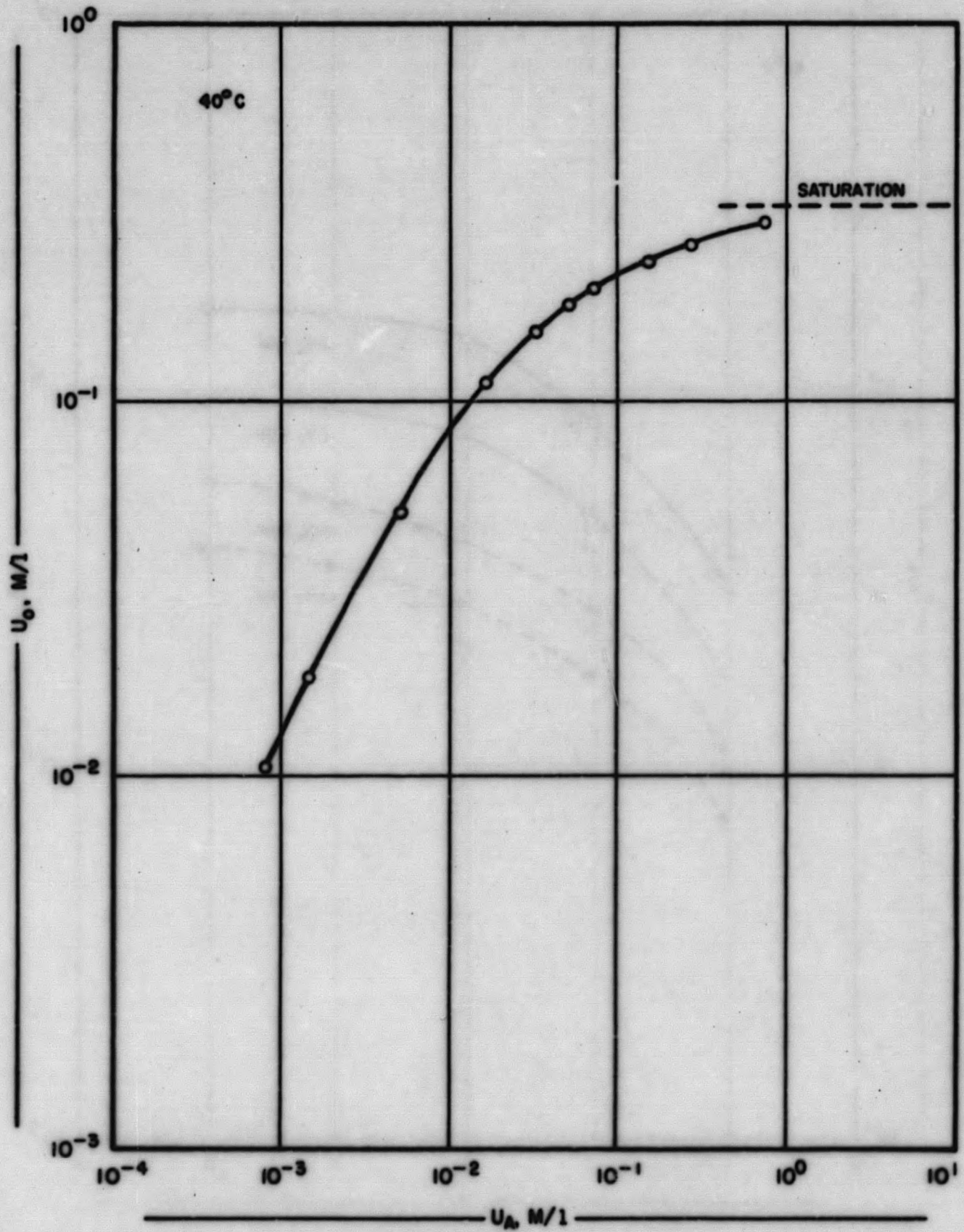


DISTRIBUTION OF URANIUM BETWEEN 0.01 TO 0.05M HNO_3 AND 6% TBP

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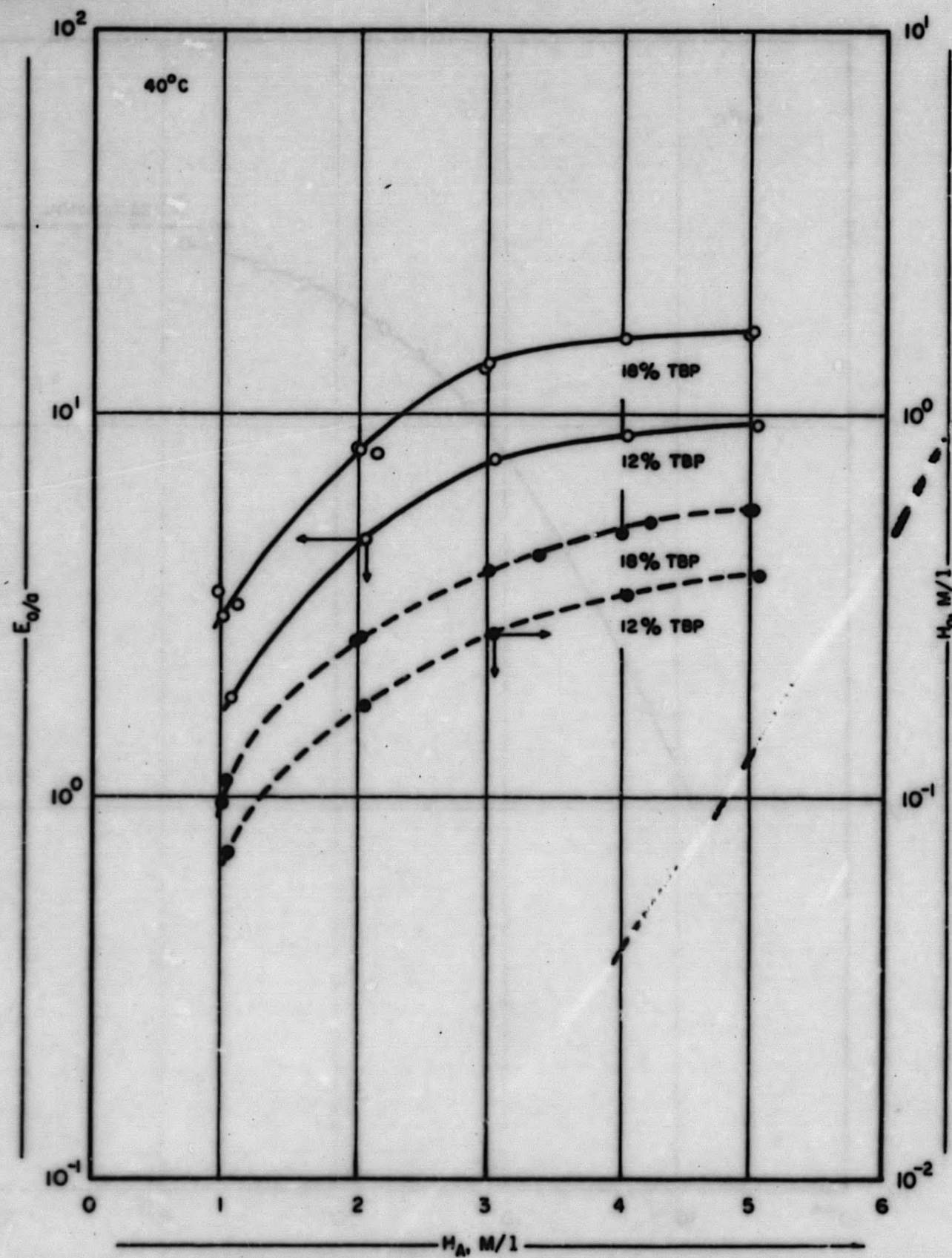
FIGURE 3



DISTRIBUTION OF URANIUM BETWEEN 3M HNO₃ AND 18% TBP

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FIGURE 4



**DISTRIBUTION OF TRACER U-233
BETWEEN NITRIC ACID AND 18% AND 12% TBP**

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