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[illegible]BJECT: Comparisons of Organic Extractants for Irradiated Uranium: Tributylphosphate vs Di-sec-butyl Phenylphosphonate, Di-n-butyl Phenylphosphonate, Tri-caprylphosphate and Tri-sec-butylphosphate

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ABSTRACT

Batch extraction scouting tests were performed to establish comparisons of distribution coefficients for uranium, thorium, fission product, and/or plutonium in systems involving several classes of organic phosphorus compounds (diluted in Amsco 125-82 and/or xylene) and aqueous nitrate or nitric acid solutions. Results have substantiated previous conclusions which suggested (1) that the branched secondary alkylphosphates and alkylphenylphosphonates would generally afford uranium separation factors (from thorium and fission products) superior to those obtainable by tributylphosphate (TBP, a normal alkylphosphate); and (2) that the phenylphosphonates would afford reasonably higher extractability of uranium. Preliminary data from irradiation tests (at ORNL and Stanford Research Institute) with di-sec-butyl phenylphosphonate also support a previous conclusion (3) that the phenyl group affords greater radiation stability of the organo-phosphorus compounds. Since the compound di-sec-butyl phenylphosphonate (DSBPP) effectively combines the above advantages (1), (2), and (3), it has received especial attention as a potential practical competitor for TBP as a recovery process extractant.

Results of preliminary counter-current extraction tests with di-n-butyl phenylphosphonate and di-sec-butyl phenylphosphonate (in simulated uranium extraction processes) are also reported. Since only low-radioactivity aqueous feeds were employed, definitive values of decontamination efficiency were not obtained; however, the distribution data from first cycle comparison tests of DSBPP versus TBP suggests that minor modifications of existing process conditions will permit uranium and plutonium decontamination factors which are somewhat higher than those now available in the first cycles of the Purex, TBP-25, and/or Interim-23 processes.

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INTRODUCTION

Previous evidence obtained by C. Blake, J. Schmitt, C. Coleman, et al., revealed certain interesting effects of organic compound structures on uranium extraction behavior in systems involving organo-phosphorus reagents and aqueous nitrate solutions, i.e., that (a) the phosphonates provided greater uranium extractability than the phosphates, and (b) branched secondary alkyl groupings influenced lower thorium extraction and/or greater uranium/thorium separation factors.

A primary objective of the scouting tests with similar reagents reported in this memo was to ascertain whether certain fission products, e.g., rare earths, ruthenium, and zirconium-niobium, might follow the extraction behavior indicated previously for thorium. If this were generally the case, it would then be assumed that the secondary alkyl phosphates or secondary alkyl phenylphosphonates might be valuable competitors with TBP as process solvents for the extraction and decontamination of uranium and plutonium.

In a more general and practical sense, the primary objective of the overall testing program was to establish broad comparisons of the several classes of organo-phosphorus compounds which might permit a knowledgeable selection of one or two "superior" compounds (which would then be studied extensively in more precise tests, and eventually in actual process demonstrations).

Though it is certainly believed that capability for reasonably higher uranium extractability and separation factors (U DC/FP DC) would be vital advantages in a substitute reagent for TBP, it is thought that the major criterion for judgment will be greater radiation and chemical stability, i.e., implying advantages for potential use with short-cooled irradiated fuels (to minimize inventory charges on fissionable materials) and future highly-irradiated power reactor fuels (5-20,000 Mwd/t). For this reason, considerable attention has been given to the promising radiation-stable extractant, di-n-butyl phenylphosphonate (DBPP), a commerically available compound reported to be about three (3) times as stable as TBP. (DBPP's higher stability has been attributed to the more effective energy absorption by its phenyl radical.) In addition, strong consideration has been given to the experimental (ORNL) compound di-sec-butyl phenylphosphonate (DSBPP), which appears to effectively combine in a single structure the above anticipated advantages of (1) the branched secondary alkyl groups, (2) and phosphonate type of P-to-C bond, and (3) the phenyl group.

Other compounds of specific interest during the study were examples of the branched alkylphosphates, i.e., tri-sec-butyl phosphates (TSBP) and tri-caprylphosphate (TCP). Some incidental attention has also been given to fission product extraction by di-2 ethylhexyl phosphoric acid (D2EHPA), tri-n-octyl phosphine oxide (TOPO), and tri-2 ethyl butyl phosphate (T2EBP).

It is emphasized that the information and conclusions from these preliminary studies are tentative and incomplete; however, the data may serve as a good starting basis for evaluating "new reagent" potentials (e.g., in the future of solvent extraction processes for power reactor fuels).

GENERAL CONCLUSION AND RECOMMENDATIONS

Di-n-butyl phenylphosphonate (a commerically available reagent) deserves more thorough consideration for future substitution in the first cycle of irradiated uranium recovery processes, such as the Purex, TBP-25, and Interim-23 processes. Its most important known advantage over tributylphosphate is its higher (x3) radiation stability. Probable disadvantage include (1) a slightly poorer potential for Zr-Nb decontamination and (2) the necessity for aromatic content (e.g., 20% xylene) in the reagent diluent, i.e., to insure solubility of the 2 DBPP$\cdot UO_2(NO_3)_2$ complex.

Di-sec-butyl phenylphosphonate (an experimental compound prepared at ORNL) also deserves such consideration, possibly with priority over the DBPP. Its most important known advantages over TBP include its potential for higher uranium decontamination from thorium and fission products (Zr-Nb and Ru) as well as for higher extractability of uranium and Pu IV. (See Figs. 1, 2, 3, and 4 which show relative distribution coefficients and uranium separation factors as function of aqueous HNO_3 concentration, and Table 1 which records comparative results in counter-current extraction tests of a simulated first cycle of the Purex process. Preliminary data from Stanford Research Institute(1), and a single 400 watt-hr/liter radiation test at ORNL, have also indicated that DSBPP is more radiation-stable (x1.5) than DBPP, or about 4 times as stable as TBP. A known possible disadvantage is the necessity for high aromatic content (e.g., 50% xylene) in the reagent diluent, i.e., to solubilize the 2 DSBPP$\cdot UO_2(NO_3)_2$ complex.

Highly purified tri-caprylphosphate, as an example of the secondary alkylphosphates, is also a potentially interesting reagent. Its important advantage over TBP is the potential for higher fission product (rare earths, Ru, and Zr-Nb) decontamination. No aromatic content in the diluent is necessary for solubility of the 2TCP$\cdot UO_2(NO_3)_2$ complex. The primary

(1) SRI Progress Report (Subcontract 1081) for April, 1959.

disadvantage discovered in tests to-date is the difficulty of preparation and purification. Efficient hydrolytic removal of unstable polyphosphates and/or their acidic decomposition products has, so far, presented a difficult problem. (The mono- and di-acid decomposition products strongly extract Zr-Nb fission products, and would adversely affect uranium decontamination.) In addition, experiments to-date indicate that the TCP compound cannot be vacuum distilled without its attendant thermal decomposition, implying that commercial preparations of the reagent with high purity may be inordinately difficult and/or expensive.

More definitive conclusions and recommendations do not seem warranted until more specific irradiation and simulated process tests (at full-level activity) have been completed. In the cases of DBPP and DSBPP, a search for practical and safe diluents is also considered as a vital development effort yet uncompleted.

The following discussions of experimental data include a few additional specific conclusions of interest in general evaluations of several classes of organo-phosphorus compounds as potential radiochemical process extractants.

Fig. 1. D.C.'s (O/A): 1.01 M TBP(A) vs. 1.11 M DSBPP(X)

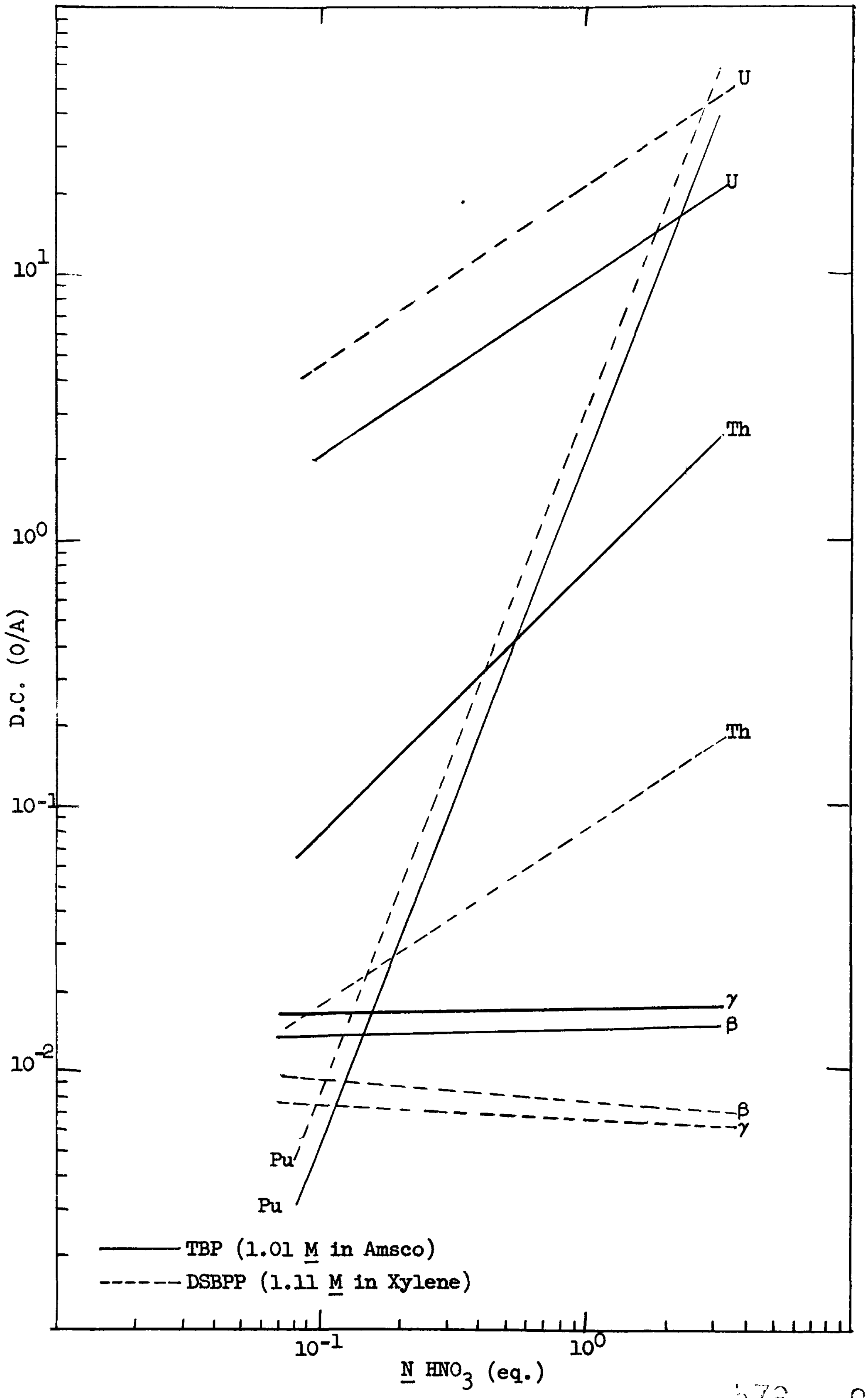

Fig. 2. D.C.'s (O/A): 1.01 $\underline{M}$ TBP(A) vs. 1.11 $\underline{M}$ DSBPP(X)

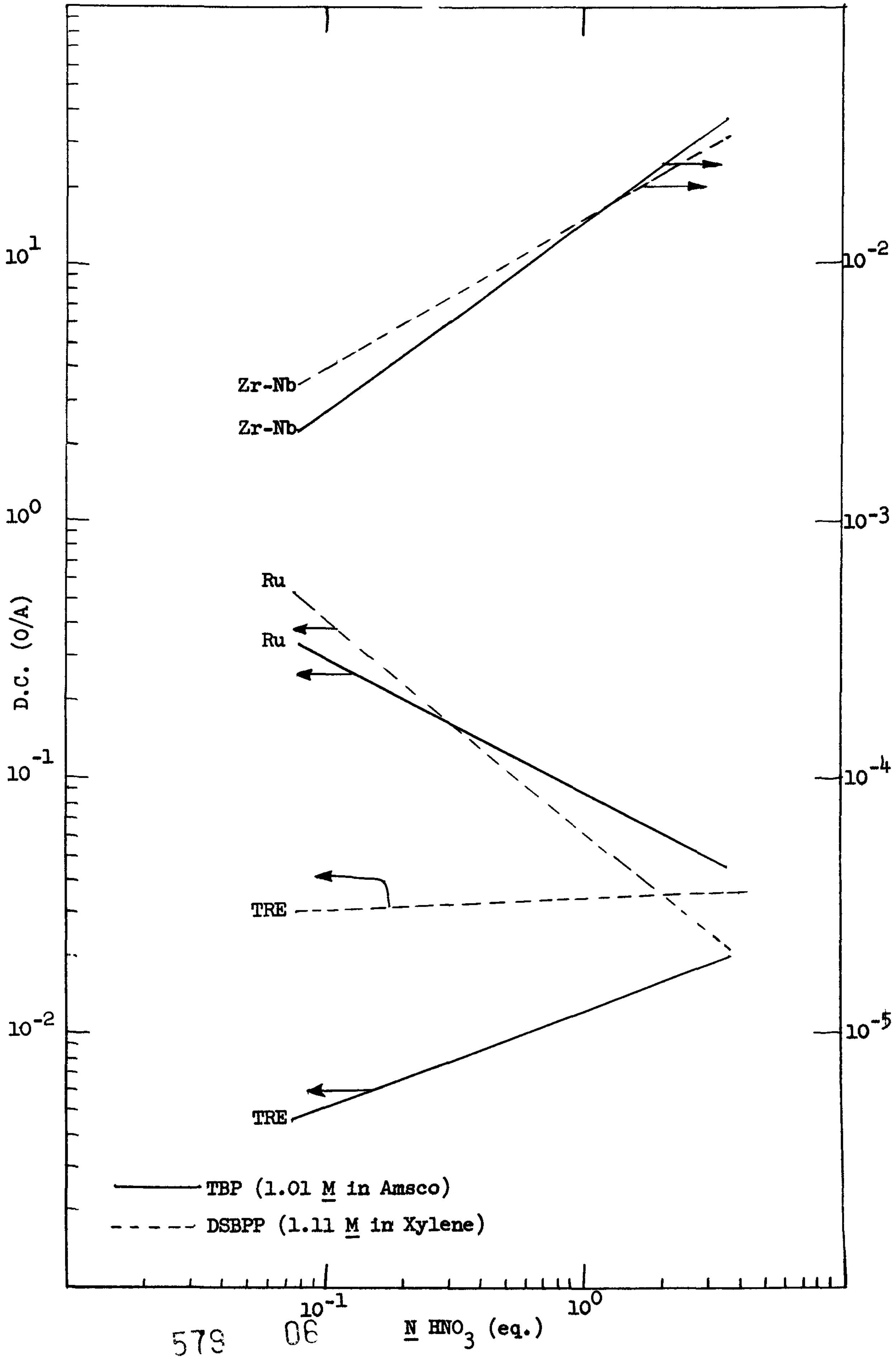

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Fig. 3. S.F.'s (U/X): 1.01 M TBP(A) vs. 1.11 M DSBPP(X)

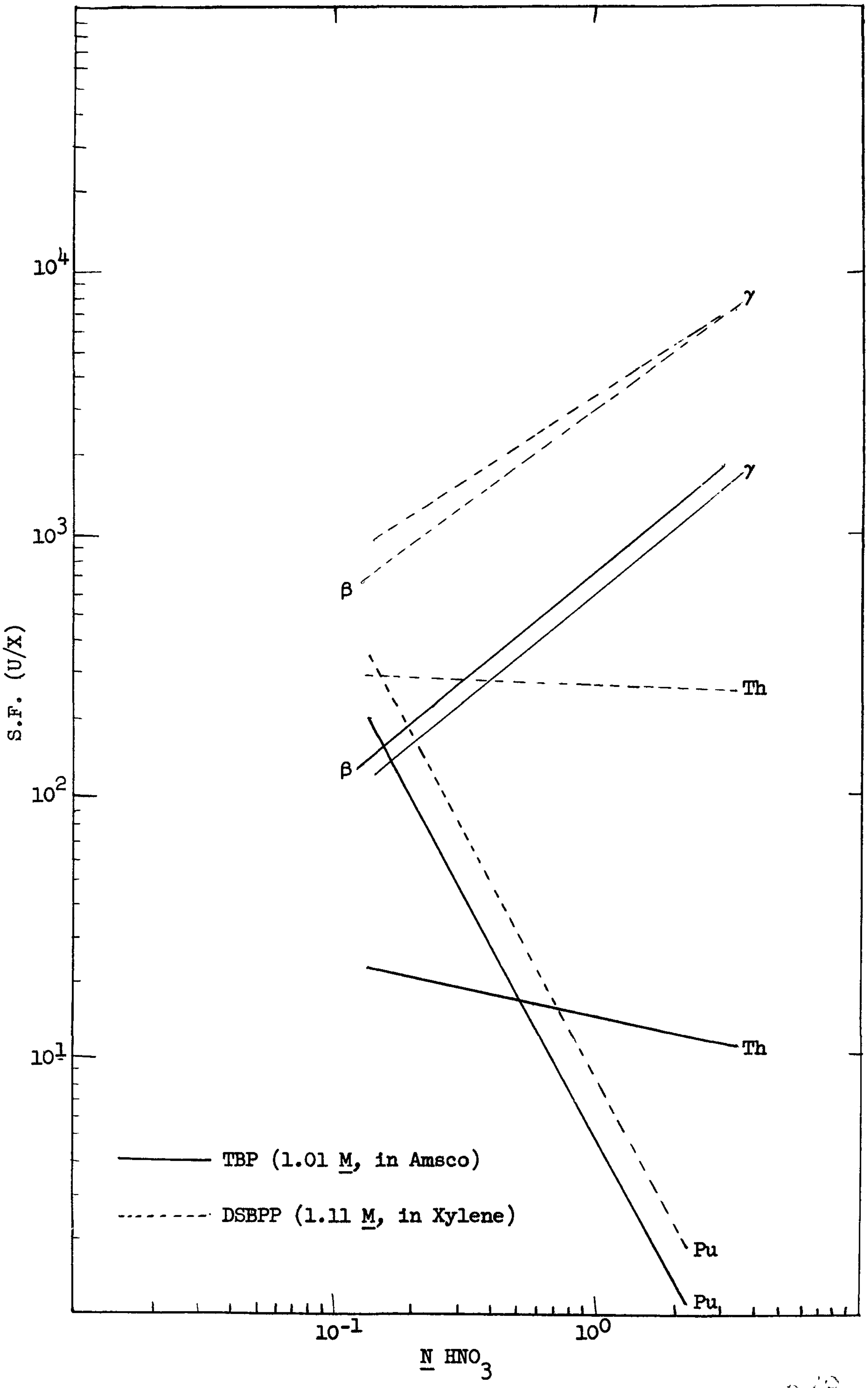

Fig. 4. S.F.'s (U/X): 1.01 M TBP(A) vs. 1.11 M DSBPP(X)

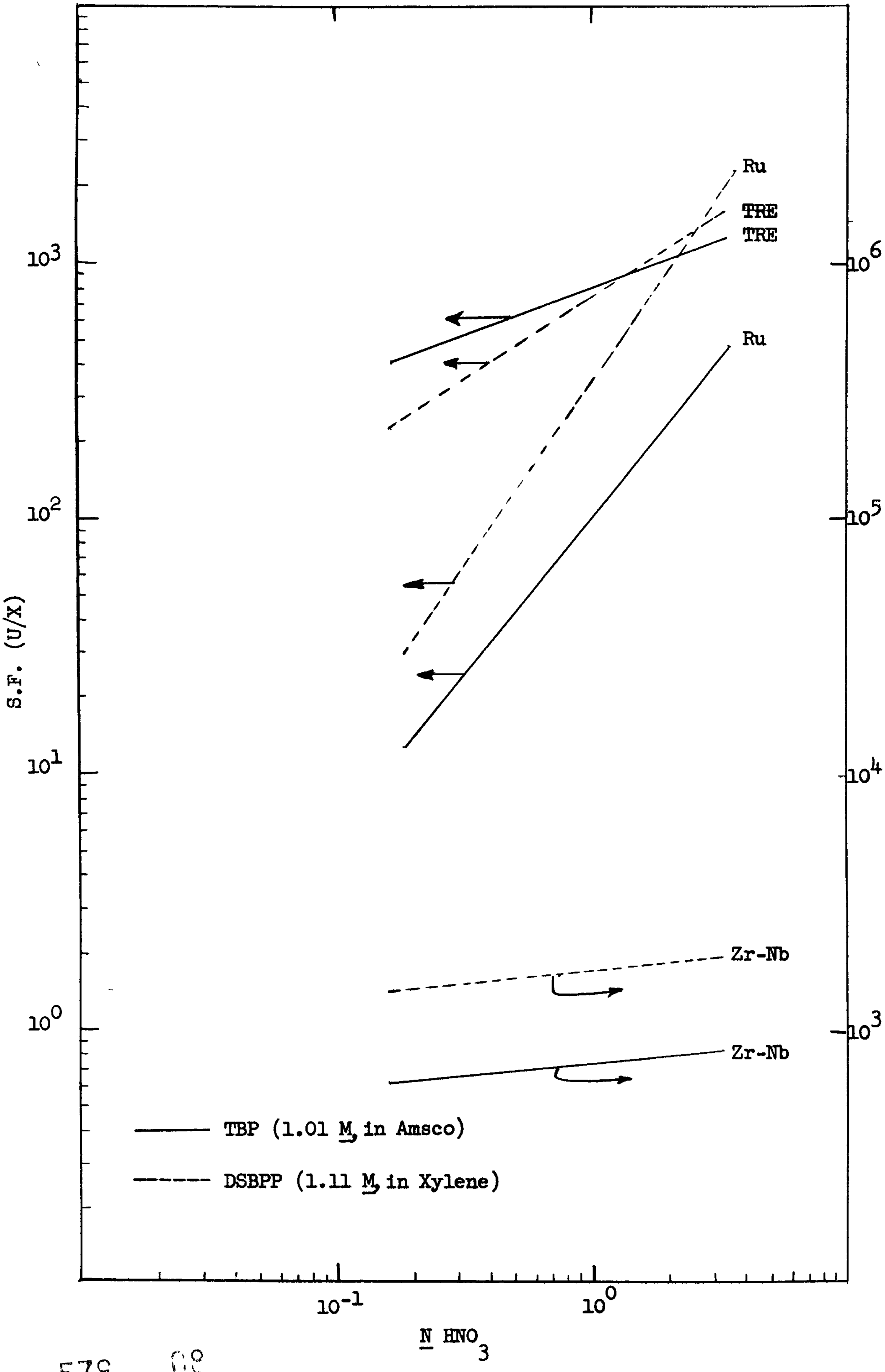

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Table 1. Comparison of U, H^+, and F.P. Extraction in 1.0 M DSBPP vs 1.0 M TBP: Counter-current Tests

(DSBPP in Xylene; TBP in Amsco 125-82)

Stage	Uranium		HNO_3		Gross β		Gross γ	
	1 M DSBPP	1 M TBP	1 M DSBPP	1 M TBP	1 M DSBPP	1 M TBP	1 M DSBPP	1 M TBP
6S-O	97.4	83.6	0.14	0.10	0.0073	0.019	0.0293	0.0393
-A	21.0	30.1	1.89	1.87	0.0169	0.0142	0.0285	0.0238
(EF^o_a)	(28.4)	(17.6)	(0.47)	(0.34)	(2.73)	(8.5)	(6.5)	(10.45)
4S-O	-	-	-	-	0.0084	0.0285	0.0337	0.0512
-A	-	-	-	-	0.159	0.0942	0.218	0.136
(EF^o_a)	(-)	(-)	(-)	(-)	(0.334)	(1.92)	(0.98)	(2.38)
2S-O	-	-	-	-	0.0345	0.0357	0.0341	0.0608
-A	-	-	-	-	2.45	0.684	3.86	1.95
(EF^o_a)	(-)	(-)	(-)	(-)	(0.089)	(0.33)	(0.056)	(0.197)
1E-O	99.0	100.0	0.14	0.08	0.047	0.0833	0.0884	0.122
-A	32.6	82.1	2.47	2.18	88.8	136.0	135.0	132.0
(EF^o_a)	(8.25)	(3.31)	(0.15)	(0.10)	(0.0014)	(0.0017)	(0.0018)	(0.0025)
3E-O	0.185	0.79	0.4	0.36	0.92	2.75	1.13	4.16
-A	0.006*	0.05*	1.6	1.84	85.2	80.6	114.0	134.0
(EF^o_a)	(84.0)	(43.0)	(0.68)	(0.53)	(0.029)	(0.093)	(0.027)	(0.084)
5E-O	-	0.007	-	0.14	0.387	1.44	0.476	2.06
-A	-	0.002	-	0.85	98.0	79.6	126.0	125.0
(EF^o_a)	(-)	(9.5)	(-)	(0.45)	(0.011)	(0.049)	(0.01)	(0.045)

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* U losses at third stage are 0.0024% and 0.02% for DSBPP and TBP, respectively.

NOTE: U in g/l, HNO_3 in N, activities in c/m/ml x 10^{-5}; $EF^o_a = DC^o_a \times FR^o_a$.
Aqueous Feed: 434 g U/l, 1.11 N HNO_3, 1.35 x 10^7 gross β c/m/ml, 1.83 x 10^7 gross γ c/m/ml, . x 10 TRE β c/m/ml, . x 10 Ru γ c/m/ml, . x 10 Zr-Nb c/m/ml.
Aqueous Scrub: 2.0 N HNO_3; Flow Ratio: F/S/O = 1/0.75/4.75; 2.5 Vol. changes.

Table 2. Data from Irradiation of DSBPP, DBPP, and TBP

	DSBPP*	DBPP*	TBP**
G (gas)	0.33	0.49	1.87
G (DBP)	0.54	0.78	2.07
G (MBP)	-	-	0.20
G (H_3PO_4)	-	-	0.03
G (H_2)	0.13	-	>1.00
G (C_1 - C_4) Hydrocarbon	0.07	-	-
Dose (whr/l)	200	400	-

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* From SRI Progress Report (CTD Subcontract 1081) for April, 1959.

**Personal communication, W. Davis.

I. Batch Extraction Tests with Fission Product Solutions: Comparison of TBP versus Branched Alkylphosphates, an Alkyl Phenylphosphonate, a Phosphine Oxide, and an Alkyl Phosphoric Acid

Preliminary scouting tests employed a common aqueous feed solution containing aluminum nitrate, nitric acid, uranium, and thorium spiked with Thorex AF solution (HNO_3-F dissolved irradiated thorium) containing protactinium and fission products. Such a solution was arbitrarily chosen to broadly typify aqueous salting systems encountered in several processes such as Purex, Interim-23 and TBP-25. The organic extractants were 0.3 M solutions (in Amsco 125-82 or xylene) of (1) tributylphosphate (TBP); (2) tricaprylphosphate (TCP); (3) tri-sec-butylphosphate (TSBP); (4) tri-(2-ethyl butyl)phosphate (T2EBP); (5) di-butyl phenylphosphonate (DBPP); and (6) di(2-ethyl hexyl)phosphoric acid (D2EHPA); and a 0.1 M solution (in Amsco 125-82) of (7) trioctylphosphine oxide (TOPO), as shown in Tables 3, 4, 5, and 6. Only small experimental quantities of the TCP, TSBP, and T2EBP were available for study, so it was desirable to gain the broadest possible spectrum of extraction information from the single comparison test.

The phosphates and the phosphonate were scrubbed with 0.1 M Na_2CO_3 and 0.01 N HNO_3 approximately three days before the tests. Following the initial extraction (distribution coefficient data shown in Tables 3 and 4) a portion of the organic phases was scrubbed (data shown in Table 5) with an acidic aluminum nitrate solution having an ionic concentration approximately equal to that of the original feed. Finally, a portion of the scrubbed organic phases was stripped (data shown in Table 6) with either a 0.01 N HNO_3 solution or a 0.2 M Na_2CO_3 solution.

Though only broadly approximating conditions which might characterize uranium recovery processes, the three tests were designed to scan the probable behavior of various products in simulated extraction, scrubbing, and stripping steps in such processes.

The data in Tables 3 and 4 indicate that the phosphate and phosphonate reagents were approximately 50% saturated (considering complexes of $2\ R_3P{\cdot}UO_2(NO_3)_2$, $4\ R_3P{\cdot}Th(NO_3)_4$, and $R_3P{\cdot}HNO_3$).

Comparing the first five reagents it will be generally noted that the uranium extraction coefficient or distribution coefficient (DC^o_a) is lowest (x1.13 to 3.4) in the TBP case, whereas the thorium DC is highest (x1.03 to 6.3), so that the separation factor (S.F. = U D.C./Th D.C.) is lowest (x2.3 to 22.8) in the TBP case. For the case of the branched compounds TCP, TSBP, and T2EBP, this information corroborates previous work by Blake, Schmitt, et al., which revealed this interesting organophosphorus structural effect on uranium and thorium extraction behavior. The observed SF data (especially in the DBPP case) is now believed to be at least partially due to the use of an aromatic, e.g., xylene (instead of the primarily paraffinic Amsco 125-82), as the reagent diluent.

The data obtained in these experiments also appear to extend similar knowledge to the cases of U/Ru and U/TRE separation factors; i.e., the U/Ru factor for TBP is lowest (x1.15 to x9.9), and the U/TRE factor for TBP is lowest (x4.6 to 26.3). The three highest variances, i.e., 22.8, 9.9, and 26.3, were associated with the TCP. Therefore, particular attention was drawn to the possibly superior qualities of tricaprylphosphate as an organic extractant for uranium recovery and decontamination processes.

However, despite the above favorable implications regarding the U/Th, U/Ru, and U/TRE separation factors, the case of Zr-Nb extraction actually appeared slightly unfavorable. Under equivalent conditions of aqueous acidity and salting strength, as noted in Tables 3 and 4, the Zr-Nb DC in the TBP case was lowest (x1.5 to 15.0), so that generally the U/Zr-Nb separation factors were approximately equal. (The extremely low value for the T2EBP was probably due to the presence of acidic decomposition products, suggesting the possibility of a significant quantity of unstable polyphosphate impurities in the given reagent. Such data also raised the question of organic impurity-effects, to some lesser degree, in each of the other reagents as well. Because of such questions it was deemed of considerable importance in "new reagent" evaluations to begin development of Zr-Nb tracer tests for reagent purity, i.e., as an adjunct to laboratory preparation procedures.)

Comparisons of protactinium extraction (important in processes such as Interim-23 or Thorex), like Zr-Nb extraction, appeared somewhat erratic. The lowest D.C.'s and/or highest U/Pa separation factors were encountered with the TSBP and DBPP reagents.

The D2EHPA, which extracts by virtue of the ion exchange mechanism, was observed (see Table 4) to be a very effective extractant for thorium, protactinium, and Zr-Nb. Such a reagent (typical of these impurities which can affect poor separation or decontamination by the trialkylphosphates) would appear to have significant value in certain scavenging operations but would have little value in separation or decontamination processes.

The TOPO (at one-third the concentration of the other tested reagents) was a quite strong extractant for uranium, protactinium, thorium, and Zr-Nb, in that order. In a general way, like D2EHPA, it did not appear specifically feasible for separation process use.

The scrubbing and stripping data in Tables 5 and 6 reflect a typical analytical difficulty often encountered in trace-level tests, i.e., the RCA results were of limited accuracy owing to the low counting rates, e.g., no Zr-Nb activity was found in the TBP samples. However, based on gross γ and β analyses, certain general conclusions may be drawn from the results; e.g., (1) in systems involving equivalent aqueous acidity and salting strength, considerably less fission product activity appeared to be retained in the uranium product streams in the TBP case, and (2) the DBPP reagent most closely approximated the TBP in overall decontamination efficiency, i.e., despite the generally better U/fission product separation factors (in the extraction step) observed previously for the TCP and TSBP reagents. Though the suspected impurity difficulties (affecting Zr-Nb and Pa extraction primarily) definitely mask the effect, it is somewhat evident that specific advantages inherent in certain higher separation factors of the branched alkyl phosphates can be realized only by adjusting process conditions to provide equal extraction factors for the uranium (or plutonium) product, e.g., by lowering the aqueous salting strength in the given TCP or TSBP cases. In general, however, practical use of such adjustments are limited and must take into account a variety of possibly deleterious effects on the multiplicity of chemical (or physical) species involved in the separation problem.

Perhaps the greatest value of the information in Table 5 and 6 is to generally point out the necessity for high purity and stability of the "new reagents," and to specifically re-emphasize the usually over-riding effects of a certain few fission products (Zr-Nb and Ru, and/or fractions thereof) on the overall decontamination efficiencies of processes.

Table 3. D.C.'s (O/A) and S.F.'s (U/X) in Extractions with TBP, TCP, TSBP, and T(2EB)P

	(0.3 M TBP in Amsco)				(0.3 M TCP in Amsco)			
	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)
U	8.08	1.61	5.02	-	9.08	0.54	17.0	-
Th	2.25	12.0	0.19	27	0.38	13.70	0.03	615
HNO_3	0.04	0.44	0.09	-	0.04	0.42	0.1	-
Gross γ	0.15	48.50	0.003	1610	0.47	48.80	0.01	1760
Gross β	0.24	77.30	0.003	1600	0.32	79.30	0.004	4270
Pa γ	0.07	0.85	0.079	64	0.22	0.90	0.24	70
Ru γ	0.001	0.55	0.002	2220	0.0004	0.58	0.0008	22000
Zr-Nb γ	0.07	40.00	0.002	2840	0.26	38.60	0.007	2530
TRE β	0.11	62.70	0.002	2760	0.015	62.80	0.0002	72600

	(0.3 M TSBP in Amsco)				(0.3 M T(2EB)P in Amsco)			
U	8.75	0.76	11.5	-	8.28	1.46	5.7	-
Th	0.47	13.5	0.035	330	0.85	12.6	0.068	84
HNO_3	0.04	0.43	0.093	-	0.04	0.45	0.09	-
Gross γ	0.19	50.5	0.004	3130	1.15	48.3	0.024	238
Gross β	0.11	80.5	0.001	8800	0.48	76.4	0.006	905
Pa γ	0.03	1.0	0.027	426	0.11	0.9	0.122	47
Ru γ	0.0004	0.57	0.0007	16400	0.002	0.7	0.002	2560
Zr-Nb γ	0.18	42.0	0.004	2670	1.2	40.3	0.030	190
TRE β	0.02	63.1	0.0003	37600	0.035	62.0	0.0006	10000

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* U and Th concentration in g/l, HNO_3 in N, and activities in c/m/ml x 10^{-5}.

NOTE: Aqueous feed solution composition: 0.5 M $Al(NO_3)_3$; 0.49 N HNO_3, 10 g. U/l, 14 g. Th/l; 7 x 10^6 Gross β c/m/ml; 5 x 10^6 Gross γ c/m/ml. Contact ratio O/A = 1.0.

Table 4. D.C.'s (O/A) and S.F.'s (U/X) in Extractions with DBPP, D2EHPA and TOPO

	(0.3 M DBPP in Xylene)				(0.3 M D2EHPA in Amsco)			
	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)
U	9.43	0.83	11.4	-	8.77	0.67	13.1	-
Th	2.25	12.2	0.184	62	12.3	0.01	1370	0.01
HNO_3	0.05	0.48	0.1	-	0.05(1)	0.7(2)	-	-
Gross γ	0.14	50.0	0.003	4200	31.9	17.5	1.82	7
Gross β	0.15	76.7	0.002	5820	5.45	73.1	0.075	175
Pa γ	0.023	0.92	0.025	456	0.99	0.22	4.5	3
Ru γ	0.0002	1.42	0.001	10200	0.007	0.46	0.015	864
Zr-Nb γ	0.129	41.3	0.003	3640	29.4	6.0	4.9	3
TRE β	0.055	61.0	0.001	12700	0.33	62.8	0.005	2460

	(0.1 M TOPO in Amsco)			
U	7.72	2.48	3.11	-
Th	1.84	12.1	0.15	21
HNO_3	-	0.48	-	-
Gross γ	4.79	42.3	0.113	28
Gross β	1.29	78.6	0.016	190
Pa γ	0.69	0.47	1.47	2
Ru γ	0.0009	0.56	0.0015	2050
Zr-Nb γ	4.63	35.0	0.132	24
TRE β	0.021	13.3	0.0016	1970

(1) Indicates ca. 84% utilization of organic acid.

(2) Ca. 30% of acidity due to displacement from organic reagent.

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* U and Th concentration in g/l, HNO_3 in N, and activities in c/m/ml x 10^{-5}.

NOTE: Aqueous feed solution composition: 0.5 M $Al(NO_3)_3$; 0.49 N HNO_3, 10 g. U/l, 14 g. Th/l; 7 x 10^6 Gross β c/m/ml; 5 x 10^6 Gross γ c/m/ml. Contact ratio O/A =1.0.

Table 5. D.C.'s (O/A) and S.F.'s (U/X) in Scrubbing Tests with TBP, TCP, TSBP, T(2EB)P, DBPP, D2EHPA, and TOPO

(0.3 M TBP in Amsco)

	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)
Gross γ	0.0025	0.034	0.074	68
Gross β	0.0022	0.026	0.085	59
Zr-Nb γ	0	0.0009	-	-

(0.3 M TCP in Amsco)

	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)
Gross γ	0.058	0.102	0.57	30
Gross β	0.024	0.053	0.46	37
Zr-Nb γ	0.027	0.023	1.2	14

(0.3 M TSBP in Amsco)

	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)
Gross γ	0.122	0.041	2.98	4
Gross β	0.012	0.016	0.75	15
Zr-Nb γ	0.095	0.015	6.25	2

(0.3 M T(2EB)P in Amsco)

	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)
Gross γ	1.07	0.048	22.1	0.26
Gross β	0.30	0.033	9.0	0.63
Zr-Nb γ	0.85	0.0033	257.0	0.02

(0.3 M DBPP in Xylene)

	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)
Gross γ	0.006	0.033	0.19	61
Gross β	0.005	0.023	0.23	51
Zr-Nb γ	0.001	0.005	0.26	45

(0.3 M D2EHPA in Amsco)

	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)
Gross γ	32.6	0.008	4070	.003
Gross β	5.4	0.141	38	0.34
Zr-Nb γ	31.6	0.002	12100	.001

(0.1 M TOPO in Amsco)

	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)
Gross γ	4.18	0.26	16	0.19
Gross β	1.85	0.026	72	0.04
Zr-Nb γ	2.62	0.232	11	0.28

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* Concentration in c/m/ml x 10^{-5}.

NOTE: Organic feed to these tests were extracts from experiments recorded in Tables 3 and 4 . Data here was obtained after two 1/1 contacts with a scrub solution of 0.5 M $Al(NO_3)_3$, 0.5 N HNO_3.

Table 6. D.C.'s (O/A) in Stripping Tests with TBP, TCP, TSBP, T(2EB)P, DBPP, D2EHPA, and TOPO

	(0.3 M TBP in Amsco)			(0.3 M TCP in Amsco)		
	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)
Gross γ	0.0008	0.0013	0.59	0.0146	0.0174	0.84
Gross β	0	0.0026	-	0.0021	0.0169	0.12
Pa γ	0.0001	0.0007	0.22	0.0001	0.0076	0.013
Zr-Nb γ	0	0.0007	-	0.0154	0.0091	1.71
	(0.3 M TSBP in Amsco)			(0.3 M T(2EB)P in Amsco)		
Gross γ	0.071	0.0935	7.6	1.00	0.021	47.4
Gross β	0.013	0.0392	3.3	0.24	0.022	10.7
Pa γ	0.010	0.0001	9.9	0.005	0.012	0.39
Zr-Nb γ	0.081	0.0877	9.2	1.10	0.003	412
	(0.3 M DBPP in Xylene)			(0.3 M D2EHPA in Amsco)		
Gross γ	0.0051	0.0015	3.5	32.7	0.154	212
Gross β	0.0033	0.0021	1.6	5.5	0.018	300
Pa γ	0.0009	0.0004	2.2	0.83	0	-
Zr-Nb γ	0.0022	0	-	33.7	0.154	219
	(0.1 M TOPO in Amsco)					
Gross γ	1.49	1.27	1.2			
Gross β	0.86	0.19	4.5			
Pa γ	0.43	0.13	3.3			
Zr-Nb γ	1.06	1.25	0.85			

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* Concentration in c/m/ml x 10^{-5}.

NOTE: Organic feed for these tests were extracts from experiments recorded in Table 5 . Strip solution was 0.01 N HNO_3 in the case of TBP, TCP, TSBPP, T(2EB)P, and DBPP. Strip solution was 0.2 M Na_2CO_3 in the case of D2EHPA and TOPO.

Ia. Batch Extraction Tests: Additional Comparisons of TBP versus DBPP, TSBP, and TCP

Since the scrubbing and stripping data from previous tests revealed high Zr-Nb DC's for the TSBP and TCP, it was considered that acidic decomposition products (possibly formed by a relatively rapid decomposition of unstable polyphosphate impurities) were contributing factors. Therefore, tests similar to those recorded in Tables 3, 4, 5, and 6 were performed with organic reagents which were freshly treated by the lime-slurry procedure, hopefully to remove and/or minimize effects of the acidic products.

The data in Table 7 indicates some improvement in the Zr-Nb DC's on scrubbing in the cases of TSBP, TCP, and DBPP; however, considerable activity still remained in the scrubbed TSBP and TCP extracts. This may possibly be an indication that the polyphosphate impurities themselves contribute to the Zr-Nb extraction. If such polymeric impurities possessed acidic groups, difficult to remove by washing with caustic solutions or $Ca(OH)_2$-slurries, it is possible to conceive the involvement of ion exchange mechanisms, e.g., similar to those known for the mono- and dialkyl phosphoric acids.

This type of information seemed to substantiate the need for a concerted study of (a) impurity tests, (b) specific reagent purification and recovery methods, and (c) Zr-Nb extraction mechanisms, e.g., possibly in addition to the known exchange reactions with mono-and di-acids. Hopefully, information obtained in such previous studies of TBP will facilitate the problem. Since the impurity problem with reagents such as TSBP and TCP may also reflect some instability of the reagents themselves, it is recognized that tests of normal hydrolysis and radiolysis rates will be required in a complete evaluation.

J. Schmitt is presently engaged in related Zr and Nb tracer studies with TBP to establish definitive bases for "new reagent" comparisons, as well as to define optimum chemical procedures for reagent purification.

Ib. Batch Extraction Tests: Pa and Zr-Nb Extraction by D2EHPA

Previous studies have shown that di-2 ethylhexyl phosphoric acid (D2EHPA), like MBP and DBP, is a strong extractant for Zr-Nb (particularly Zr, as well as Th and Pa) from nitrate or nitric acid systems. Conditions for its possible use as a Zr-Nb scavenger (from Purex-type systems) was investigated briefly. The data in Table 8 records results with 0.01 M and 0.06 M reagent concentrations, which suggests that in a three stage cycle the former is nearly as effective (74%) as the latter (79%) for Zr-Nb removal. It would have the advantage of lower uranium extraction in a possible separation process application.

Table 7. D.C.'s (O/A) in Extractions with DBPP, TSBP, TCP, and TBP
(Pretreated by $Ca(OH)_2$ slurry method.)

	0.328 M DBPP in Xylene			0.423 M TSBP in Amsco**			0.307 M TCP in Amsco			0.408 M TBP in Amsco		
	Org.	Aq.	DC_a^o	Org.	Aq.	DC_a^o	Org.	Aq.	DC_a^o	Org.	Aq.	DC_a^o
Extraction												
Gross γ	0.161	67.8	0.0024	0.299	67.7	0.0044	0.264	67.7	0.0039	0.189	67.8	0.0028
Gross β	0.222	114.0	0.0020	0.184	114.0	0.0016	0.230	114.0	0.0020	0.524	114.0	0.0046
Pa γ	0.0119	8.06*	0.0015	0.0371	8.03	0.0046	0.140	7.93	0.0176	0.0559	8.02	0.0070
Ru γ	0.008	1.63*	0.0049	0.0025	1.63	0.0015	0.005	1.63	0.0031	0.0058	1.63	0.0036
Zr-Nb γ	0.161	47.6*	0.0034	0.284	47.5	0.0060	0.142	47.7	0.0030	0.1170	47.7	0.0025
Scrubbing												
Pa γ	~0.0007	~0.008	~0.09	0.0036	0.0165	0.22	< 0.0049	0.041	< 0.12	< 0.001	0.011	< 0.09
Ru γ	~0.0015	~0.014	~0.11	< 0.0010	~0.0008	< 1.27	< 0.0025	~0.0015	< 1.5	< 0.001	0.0012	< 0.83
Zr-Nb γ	< 0.0017	0.044	< 0.04	0.176	0.0436	4.04	0.0103	0.0421	0.25	< 0.001	0.0085	< 0.13
Stripping												
Pa γ	0.0002	0.00055	0.3	0.0013	0.0023	0.56	< 0.001	0.0039	< 0.26	< 0.0003	0.0007	-
Ru γ	< 0.0005	~0.001	< 0.5	< 0.0007	< 0.00025	~2.8	< 0.002	< 0.00025	8.0	< 0.0005	< 0.0005	-
Zr-Nb γ	< 0.0005	0.0012	< 0.4	0.163	0.00126	12.9	0.0088	0.0016	5.6	< 0.0005	0.0006	-

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* By difference.
**10% xylene by volume.

Aqueous Feed: 11 g Th/l, 8.8 g U/l, 0.5 M $Al(NO_3)_3$, 0.5 N HNO_3, containing F.P.'s and Pa.
Aqueous Scrub: 0.5 M $Al(NO_3)_3$, 0.5 N HNO_3.
Aqueous Strip: 0.01 N HNO_3
Flow Ratios: 1/1

Table 8. Pa and Zr-Nb Extraction by 0.01 M and 0.06 M D2EHPA

	0.01 M D2EHPA-Amsco			0.06 M D2EHPA-Amsco		
	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)
(1st Stage)						
Gross γ	16.5	51.5	0.32	34.5	33.5	1.03
Gross β	4.49	110.0	0.041	10.9	113.0	0.10
(2nd Stage)						
Gross γ	9.53	42.0	0.23	5.63	27.9	0.20
Gross β	2.34	110.0	0.021	1.74	112.0	0.016
(3rd Stage)						
Gross γ	5.9	31.9	0.19	0.87	27.7	0.03
Gross β	1.12	109.0	0.01	0.23	111.0	0.002
Th	-	8.19	(23.46)[1]	-	0.005	(99.95)[1]
U	-	8.72	(1.13)[1]	-	0.64	(92.74)[1]
Pa γ	-	1.57	(80.62)[1]	-	0.79	(90.25)[1]
Ru γ	-	1.35	(17.18)[1]	-	1.34	(17.79)[1]
Zr-Nb γ	-	12.4	(74.06)[1]	-	10.20	(78.66)[1]

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* Activities in c/m/ml x 10^{-5}, U and Th in g/l.

NOTE: Aqueous feed composition was: 8.82 g U/l; 10.7 g Th/l; 0.5 M $Al(NO_3)_3$; 0.5 M HNO_3; 6.8 x 10^6 gross γ c/m/ml; 1.14 x 10^6 gross β c/m/ml; 8.1 x 10^5 Pa γ c/m/ml; 1.63 x 10^5 Ru γ c/m/ml; 4.78 x 10^6 Zr-Nb γ c/m/ml. One aqueous sample was contacted by three (3) successive passes of organic extractant; O/A ratio = 1.0.

(1) Total % extracted, calc. by diff. of 3EA sample and orig. aq. feed.

Ic. Batch Extraction Tests: Comparisons of DC's and SF's in TBP versus DSBPP, DBPP, and TCP Extractants as a Function of Aqueous HNO_3 Concentration

Previous batch tests, which compared fission product extractions in TBP with certain of the "new reagents," were performed with a single aqueous system (0.5 M $Al(NO_3)_3$, 0.5 N HNO_3). Since projected process applications would require knowledge of relative behavior over a considerable range of aqueous acidity and salting strength, extraction and scrubbing tests at three aqueous conditions (about 2.4 N, 0.65 N, and 0.18 N HNO_3) were performed to scan the effects on distribution coefficients and/or separation factors.

The TBP and DBPP employed in the tests were commerically available reagents, whereas the DSBPP was prepared by L. Feathers of ORNL, and the TCP was specially prepared on contract by a private laboratory. The latter reagent, as received, contained very extensive impurities (estimated at greater than 30% polyphosphate) and required extensive purification (by acid hydrolysis and caustic washing) at ORNL before use. (Evidence in the following data indicated that the purification was still incomplete, or that the reagent is inherently quite unstable.) Since it has been found that an unsaturated or aromatic diluent (e.g., xylene) appears necessary to completely solubilize the 2 $DBPP \cdot UO_2(NO_3)_2$ and 2 $DSBPP \cdot UO_2(NO_3)_2$ complexes, the approximately 1.1 M DBPP and DSBPP were prepared in pure xylene. Since diluent effects on extraction behavior represented a variable, two TBP extractants were prepared with (1) Amsco 125-82 and (2) xylene as diluents.

The three aqueous feed solutions contained the same concentrations of uranium (ca 11 g/l), thorium (ca 5 g/l), and fission products (ca 10^7 β or γ c/m/ml); however, the HNO_3 concentrations were varied, i.e., (1) 2.97 N, (2) 0.79 N, and (3) 0.2 N. The three aqueous scrub solutions were prepared with HNO_3 at approximately (1) 2.8 N, (2) 0.8 N; and (3) 0.2 N concentrations.

The amount of uranium and thorium in the system was adjusted so that the reagents would not exceed 10% saturation with either product. However, in the 3.0 N HNO_3 case it may be estimated that the reagents approached 70% total saturation with HNO_3, uranium, and thorium.

In a general way, the data in Tables 9, 10, and 11 corroborate previous indications that, on extraction, higher separation factors (than TBP) characterize the branched alkyl phosphates and alkyl phenylphosphonates. Generally better separation factors were also observed in the TBP-xylene case than in the TBP-Amsco case, which suggests that the xylene diluent in the phenylphosphonate cases contributes somewhat to the higher SF's.

The plutonium IV extraction data in Table 12 were obtained in separate tests by D. E. Horner. In general, the DSBPP, DBPP, and TCP were observed to afford higher Pu IV extraction than TBP.

Table 9. D.C.'s (O/A) and S.F.'s (U/X) in Extractions with TBP and DSBPP:

(as a Function of Aqueous HNO_3 Concentration)

	1.01 M TBP in Amsco				1.11 M DSBPP in Xylene			
	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)
(2.4 N HNO_3)								
U	10.7	0.512	21.0	-	12.6	0.333	37.8	-
Th	3.06	1.75	1.75	12	0.73	4.45	0.163	232
Gross β	1.33	104.0	0.013	1640	0.62	103.0	0.006	6300
Gross γ	3.45	195.0	0.018	1185	1.31	199.0	0.007	5730
TRE β	1.28	69.8	0.018	1150	3.4	75.0	0.045	832
RU γ	0.27	6.1	0.043	485	0.17	6.4	0.027	1420
Zr-Nb γ	1.21	35.0	0.035	607	1.15	36.0	0.032	1180
(0.65 N HNO_3)								
U	9.48	1.52	6.24	-	12.6	0.765	16.5	-
Th	1.56	3.39	0.46	14	0.27	4.74	0.057	290
Gross β	1.6	95.3	0.017	371	0.775	97.7	0.008	2080
Gross γ	3.01	179.0	0.017	371	1.13	180.0	0.006	2630
TRE β	0.82	76.0	0.011	578	1.62	76.0	0.021	775
Ru γ	0.89	4.8	0.185	34	-	5.6	-	-
Zr-Nb γ	0.22	34.0	0.006	1000	0.18	31.0	0.006	2800
(0.18 N HNO_3)								
U	8.56	2.95	2.90	-	11.6	1.55	7.5	-
Th	0.58	4.39	0.132	22	0.14	4.90	0.029	262
Gross β	1.58	98.7	0.016	182	0.84	97.6	0.009	868
Gross γ	2.77	178.0	0.016	186	1.34	187.0	0.007	1050
TRE β	0.44	67.0	0.007	442	2.55	51.0	0.05	150
Ru γ	0.75	4.6	0.163	18	1.3	5.2	0.25	30
Zr-Nb γ	0.25	38.0	0.007	445	0.31	38.0	0.008	920

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* U and Th conc. in mg/ml; F.P. activities in c/m/ml x 10^{-5}.

Feed Compositions (approx.): 11.3 g. U/l; 5.03 g. Th/l; 1.03 x 10^7 β c/m/ml; 1.84 x 10^7 γ c/m/ml; 4.2 x 10^6 Zr-Nb c/m/ml; 6.3 x 10^5 Ru c/m/ml; 8.3 x 10^6 TRE c/m/ml; HNO_3 as indic.

Org./Aq. ratio = 1.0.

Table 10. D.C.'s (O/A) and S.F.'s (U/X) in Extractions with DBPP and TCP:
(as Functions of Aqueous HNO_3 Concentrations)

	1.1 M DBPP in Xylene				1.07 M TCP in Amsco			
	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)
(2.4 N HNO_3)								
U	12.9	0.245	52.7	-	11.3	0.685	16.5	-
Th	5.15	1.17	4.4	12	0.49	2.05	0.238	69
Gross β	2.28	100.0	0.023	2310	3.02	100.0	0.030	547
Gross γ	4.07	196.0	0.021	2530	27.70	159.0	0.174	95
TRE β	5.08	78.1	0.065	810	0.40	79.1	0.005	3260
Ru γ	0.21	6.2	0.034	1550	0.05	5.6	0.009	1885
Zr-Nb γ	2.0	38.0	0.053	1000	17.50	10.3	1.7	10
(0.65 N HNO_3)								
U	12.0	0.62	19.4	-	9.58	1.28	7.47	-
Th	2.67	2.86	0.934	21	0.73	4.14	0.175	43
Gross β	1.55	98.3	0.016	1228	1.78	95.8	0.019	401
Gross γ	2.60	178.0	0.015	1328	9.62	171.0	0.056	133
TRE β	3.60	70.0	0.052	377	0.38	75.0	0.005	1480
Ru γ	0.35	5.8	0.060	322	0.27	5.4	0.05	149
Zr-Nb γ	0.34	25.0	0.014	1430	5.24	28.0	0.187	40
(0.18 N HNO_3)								
U	14.7	1.32	11.1	-	8.16	3.47	2.35	-
Th	0.1	4.08	0.025	445	0.13	4.72	0.276	9
Gross β	2.29	101.0	0.023	482	1.27	96.5	0.013	178
Gross γ	3.41	187.0	0.018	610	4.27	176.0	0.024	97
TRE β	2.02	71.0	0.028	390	0.75	68.0	0.011	214
Ru γ	1.60	5.0	0.320	35	0.38	5.1	0.075	32
Zr-Nb γ	2.82	39.0	0.007	1530	2.33	30.0	0.078	30

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* U and Th conc. in mg/ml; F.P. activities in c/m/ml x 10^{-5}.

Feed Compositions (approx.): 11.3 g. U/1; 5.03 g. Th/1; 1.03 x 10^7 β c/m/ml; 1.84 x 10^7 γ c/m/ml; 4.2 x 10^6 Zr-Nb c/m/ml; 6.3 x 10^5 Ru c/m/ml; 8.3 x 10^6 TRE c/m/ml; HNO_3 as indic.

Org./Aq. ratio = 1.0.

Table 11. D.C.'s (O/A) and S.F.'s (U/X) in Extractions with TBP and DSBPP: (as a Function of Aqueous HNO_3 Concentration)

	1.11 M TBP in Xylene				1.11 M DSBPP in Xylene			
	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)
(2.4 N HNO_3)								
U	12.6	0.40	31.5	-	12.6	0.33	38	-
Th	3.24	2.26	1.43	22	0.73	4.45	0.163	232
Gross β	0.73	106.0	0.007	4560	0.62	103.0	0.006	6300
Gross γ	1.92	199.0	0.010	3260	1.31	199.0	0.007	5730
TRE β	1.68	77.3	0.022	1450	3.40	75.0	0.045	832
Ru γ	-	6.6	-	-	0.17	6.4	0.027	1420
Zr-Nb γ	1.07	35.0	0.031	1030	1.15	36.0	0.032	1180
(0.65 N HNO_3)								
U	12.2	1.22	10.0	-	12.6	0.77	16.5	-
Th	1.43	3.94	0.363	28	0.27	4.74	0.057	290
Gross β	1.11	95.6	0.012	860	0.78	97.7	0.008	2080
Gross γ	1.40	181.0	0.008	1290	1.13	180.0	0.006	2630
TRE β	2.83	75.6	0.037	267	1.62	76.0	0.021	775
Ru γ	0.99	5.0	0.198	51	-	5.6	-	-
Zr-Nb γ	0.31	34.0	0.009	1100	0.18	31.0	0.006	2800
(0.18 N HNO_3)								
U	10.4	2.48	4.2	-	11.6	1.55	7.5	-
Th	0.46	4.62	0.1	42	0.14	4.90	0.029	262
Gross β	1.14	102.0	0.011	375	0.84	97.6	0.009	868
Gross γ	1.49	190.0	0.008	535	1.34	187.0	0.007	1050
TRE β	-	72.0	-	-	2.55	51.0	0.050	150
Ru γ	1.3	4.7	0.276	15	1.30	5.2	0.250	30
Zr-Nb γ	0.47	39.0	0.012	348	0.31	38.0	0.008	920

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* U and Th conc. in mg/ml; F.P. activities in c/m/ml x 10^{-5}.

Feed Compositions (approx.): 11.3 g. U/l; 5.03 g. Th/l; 1.03 x 10^7 β c/m/ml; 1.84 x 10^7 γ c/m/ml; 4.2 x 10^6 Zr-Nb c/m/ml; 6.3 x 10^5 Ru c/m/ml; 8.3 x 10^6 TRE c/m/ml; HNO_3 as indic.

Org./Aq. ratio = 1.0.

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Table 12. Pu(IV) Extraction from HNO_3 with Neutral Phosphates and Phosphonates (by D. E. Horner)

Aqueous Phase		Distribution Coefficients (DC_a^o)			
N HNO_3 (Feed)	N HNO_3 (Est. Eq.)	1.01 M TBP (-Amsco)	1.11 M DSBPP (-Xylene)	1.1 M DBPP (-Xylene)	1.07 M TCP (-Amsco)
0.2	0.17	0.016	0.045	0.093	0.15
0.6	0.5	0.20	0.32	0.57	0.96
1.5	1.2	4.9	6.8	12.0	-*
3.0	2.4	15.0	19.0	34.0	-*

---

* Non-homogeneity of aqueous phase prevented accurate analysis.

(Phase ratio (O/A) = 1.0; Feeds were ca. 5.5×10^{-5} M Pu)

Id. Batch Extraction Tests: Distribution Coefficients in 1 M TBP-Amsco, DSBPP-xylene, DBPP-xylene, TCP-Amsco, and TBP-xylene; Plots of Data

Figures 5, 6, 7, 8, and 9 are rough log-log plots of the distribution coefficients (DC^o_a) versus N HNO_3 data (for each extractant) recorded in Tables 9, 10, 11, and 12.

The similar slopes of the uranium lines indicate that essentially identical mechanisms control the extraction of UO_2^{+2} in the TBP, DSBPP, DBPP and TCP systems. Similar slopes also appear to characterize the plutonium (Pu IV) lines. (However, analytical difficulties in the case of the TCP system leaves it somewhat in question.)

Slopes of the thorium lines in 1.01 M TBP-Amsco and 1.11 M TBP-xylene appear to be similar; however, the latter was characterized by lower Th DC's (O/A), possibly reflecting a subtle effect of the xylene diluent. Rather major differences in the slope of thorium lines (DBPP is higher, DSBPP is lower, and TCP is essentially of zero slope) would seem to raise interesting theoretical questions (for future investigation and corroboration regarding organic structural effects on thorium extraction.

Gross β and γ slopes were approximately zero in all cases except TCP (where acidic decomposition products were felt to play a specifically major role in Zr-Nb extraction), which would generally be expected in a mixed fission product system (i.e., where most of the products have low extractability, and where the probability exists for cancellation of opposing effects of acidity on the more extractable fission product components).

Except in the abnormal TCP case, the TRE and Zr-Nb slopes seem to be of fairly consistent value. The Ru slopes appeared to be less sensitive to the TCP impurities than was the case for Th, TRE, or Zr. However, in general, this type of plot only roughly approximates the true behavior of ruthenium (and its various chemical and physical species), e.g., previous work has suggested that the ruthenium FP approaches a maximum in extraction at an queous equilibrium concentration of about 0.3 N HNO_3.

Fig. 5. D.C.'s (O/A) in 1.01 M TBP-(Amsco): Extraction

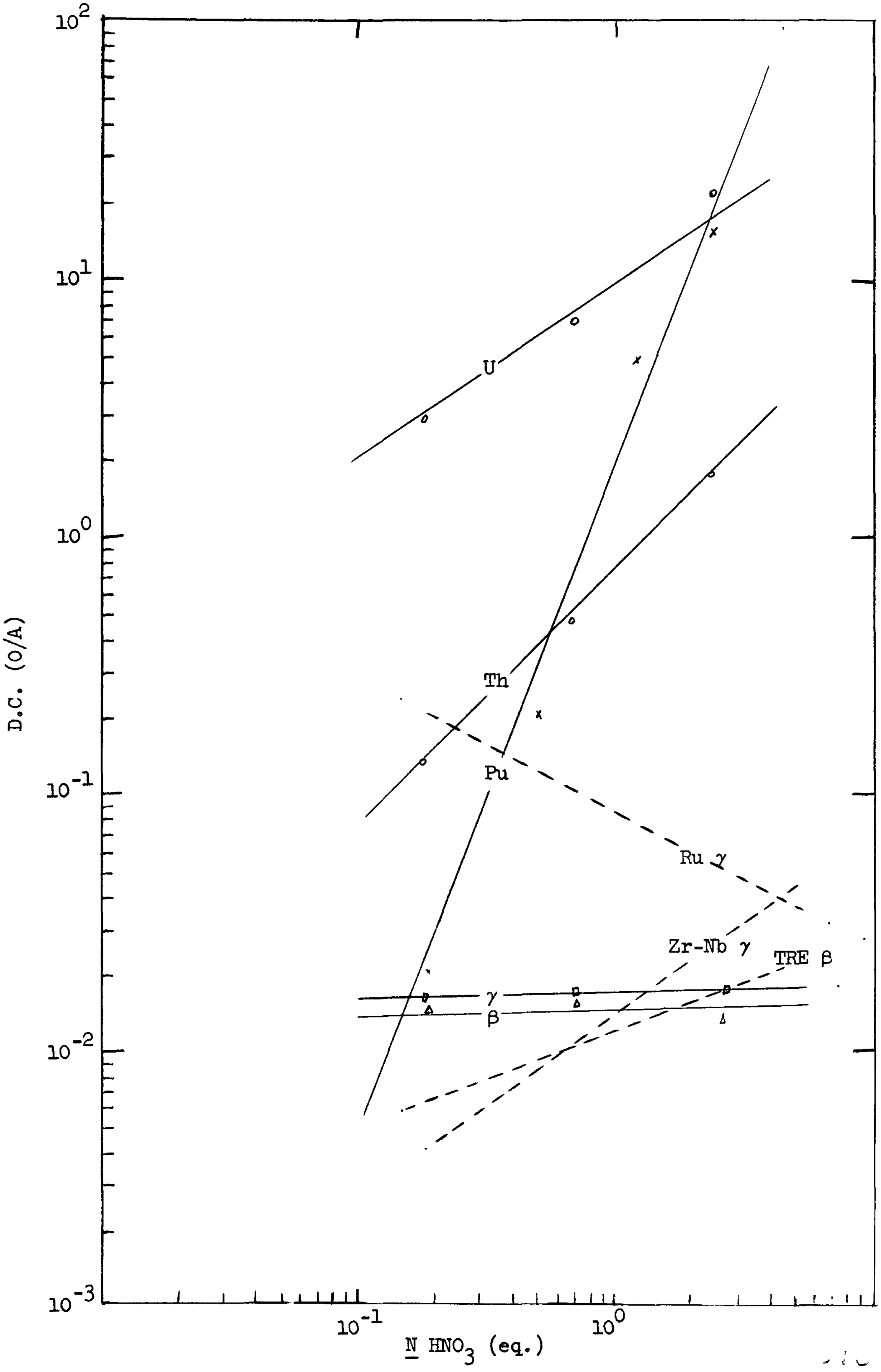

Fig. 6. D.C.'s (O/A) in 1.11 $\underline{M}$ DSBPP-(Xylene): Extraction

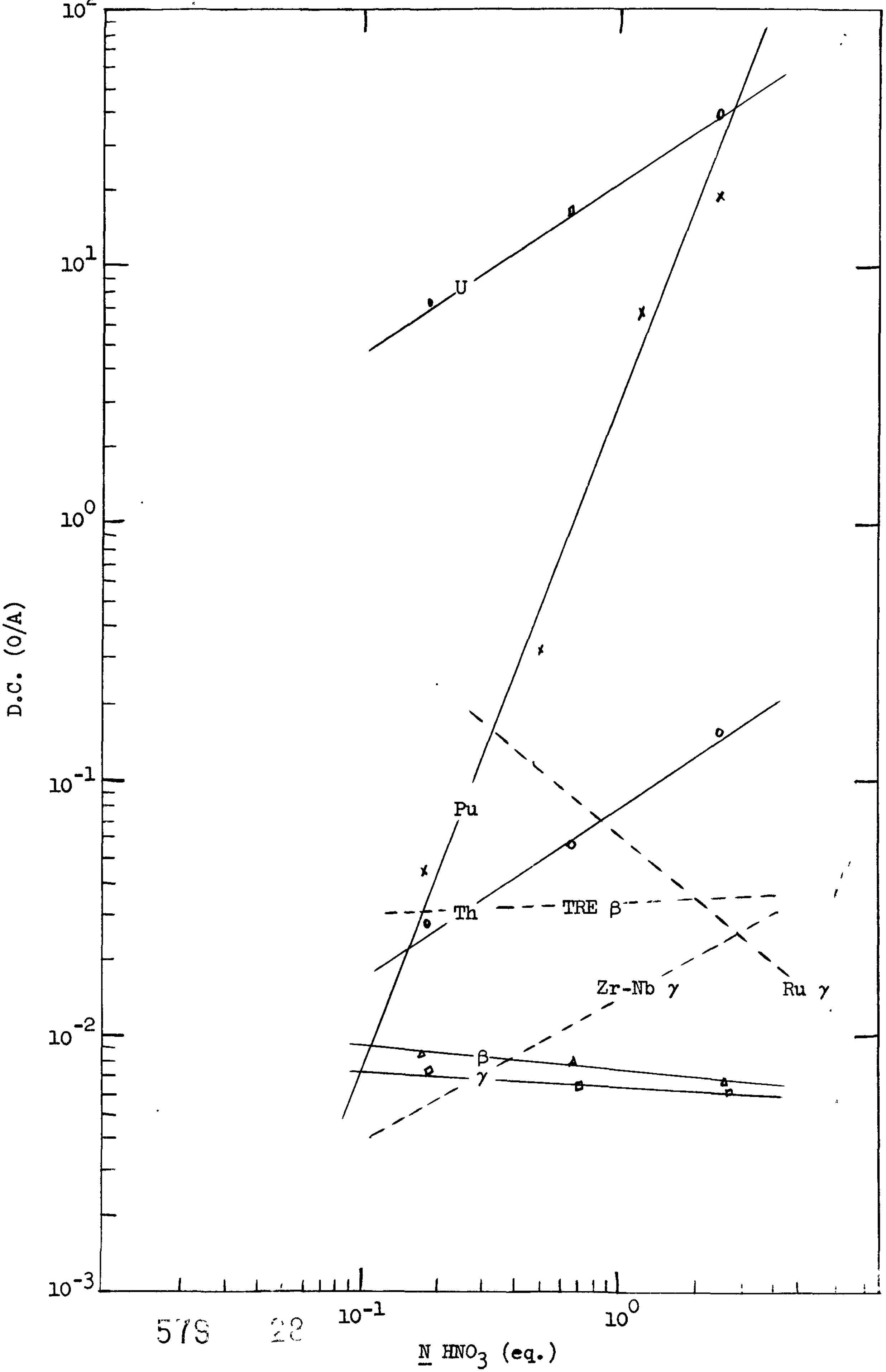

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Fig. 7. D.C.'s (O/A) in 1.1 M DBPP-(Xylene): Extraction

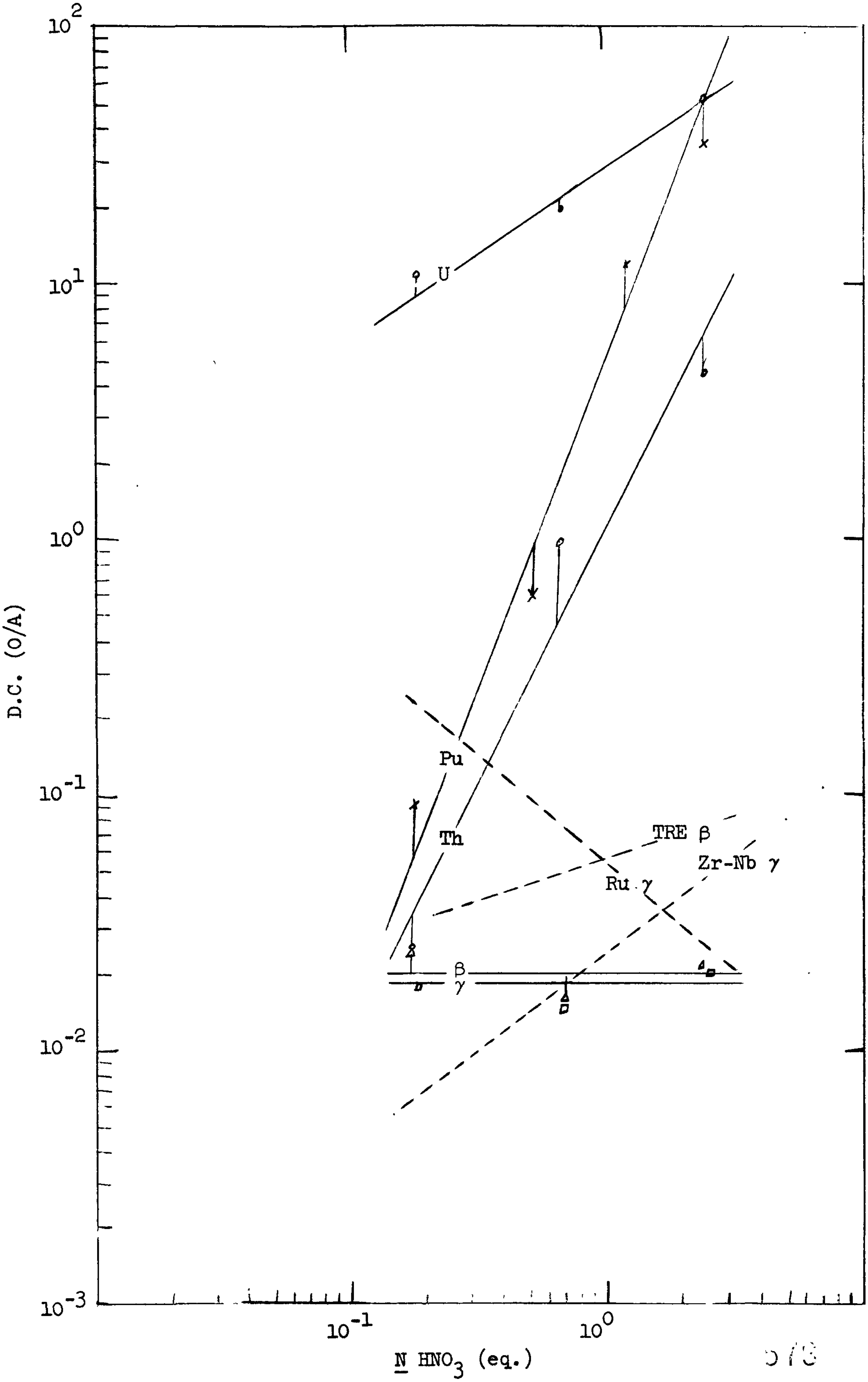


Fig. 8. D.C.'s (O/A) in 1.07 M TCP-(Amsco): Extraction

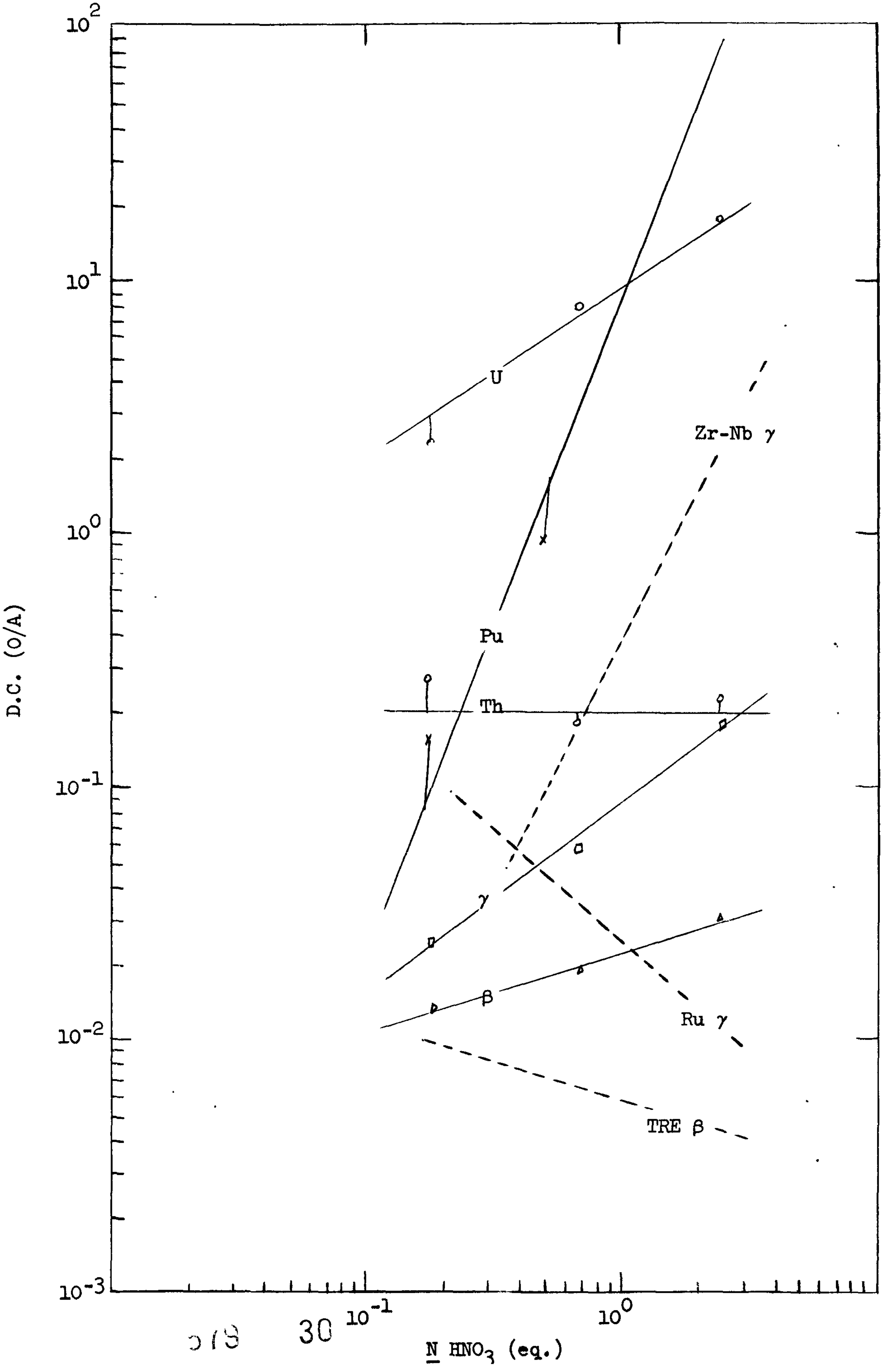
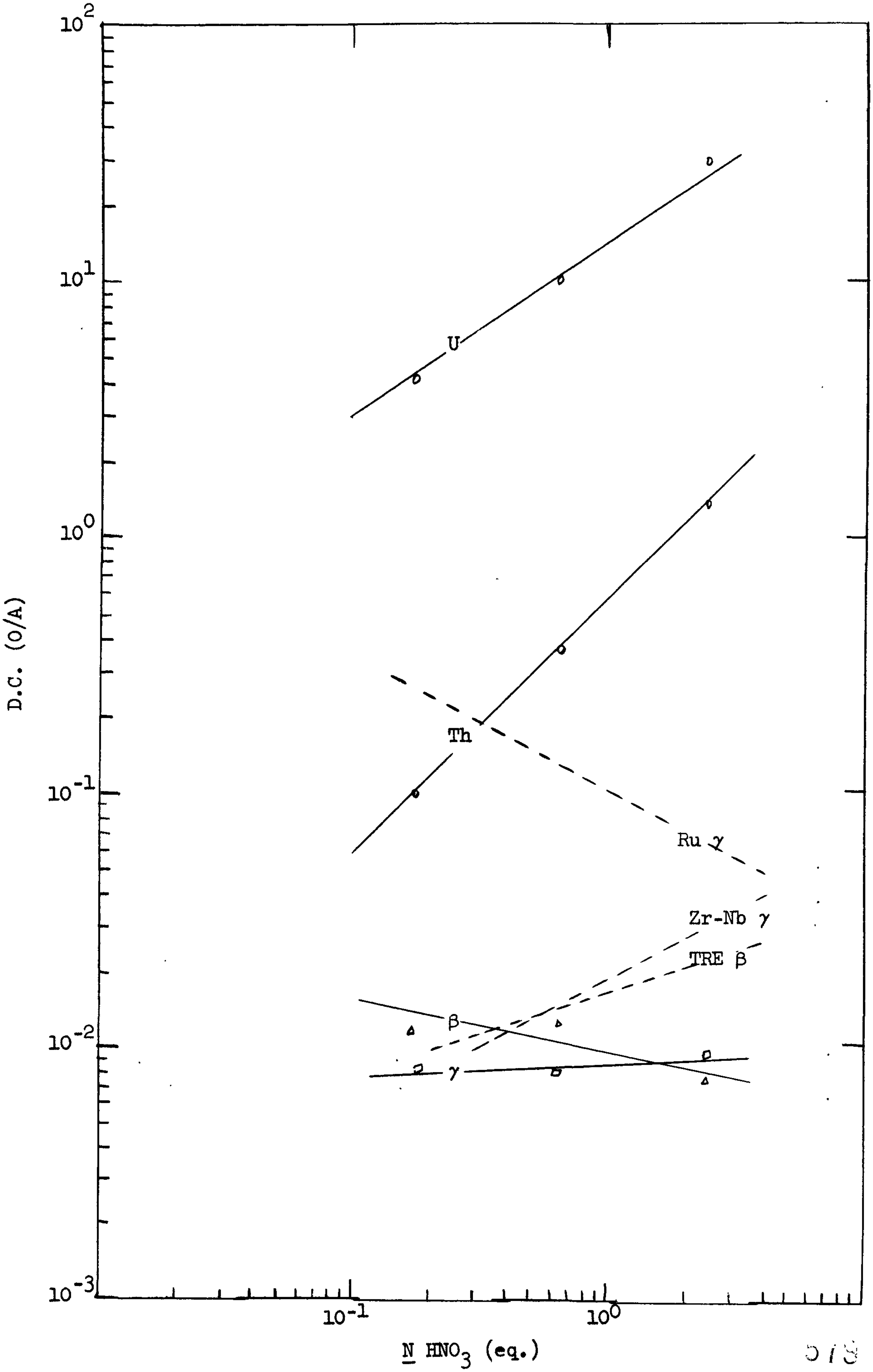


Fig. 9. D.C.'s (O/A) in 1.11 M TBP-(Xylene): Extraction



Ie. Batch Extraction Tests: Uranium/X Separation Factors in 1 M TBP-Amsco, DSBPP-xylene, DBPP-xylene, TCP-Amsco, and TBP-xylene; Plots of Data

Figures 10, 11, 12, 13, and 14 are rough log-log plots of the uranium separation factors (SF^{U}_{X}) versus N HNO_3 data (for each extractant) recorded in Tables 9, 10, 11, and 12.

As suggested by the nature of U and Pu IV data illustrated in the previous plots of distribution coefficient, the slopes of the U/Pu IV SF lines appear to be approximately equal (over the range of acidities studied) for all of the reagents.

Slopes of the thorium lines in the 1.01 M TBP-Amsco and 1.11 M TBP-xylene appear to be equal; however, the values of the U/Th SF's are higher in the latter case by a factor of about two. Major differences are observed in comparisons of the three "new reagents," i.e., the DSBPP line is approximately zero, the DBPP line has a quite steep negative slope, while the TCP line (possibly affected by acidic impurities) has a relatively steep positive slope.

The slope of the U/Ru SF line appears generally equal in the case of all five extractants: however, subtle differences are observable in the U/TRE and U/Zr-Nb lines. The U/gross β and U/gross γ lines again appear quite consistent, except in the TCP case where acidic decomposition products were felt to have major effects on Zr-Nb extractability.

Fig. 10. S.F.'s (U/X) in 1.01 M TBP-(Amsco): Extraction

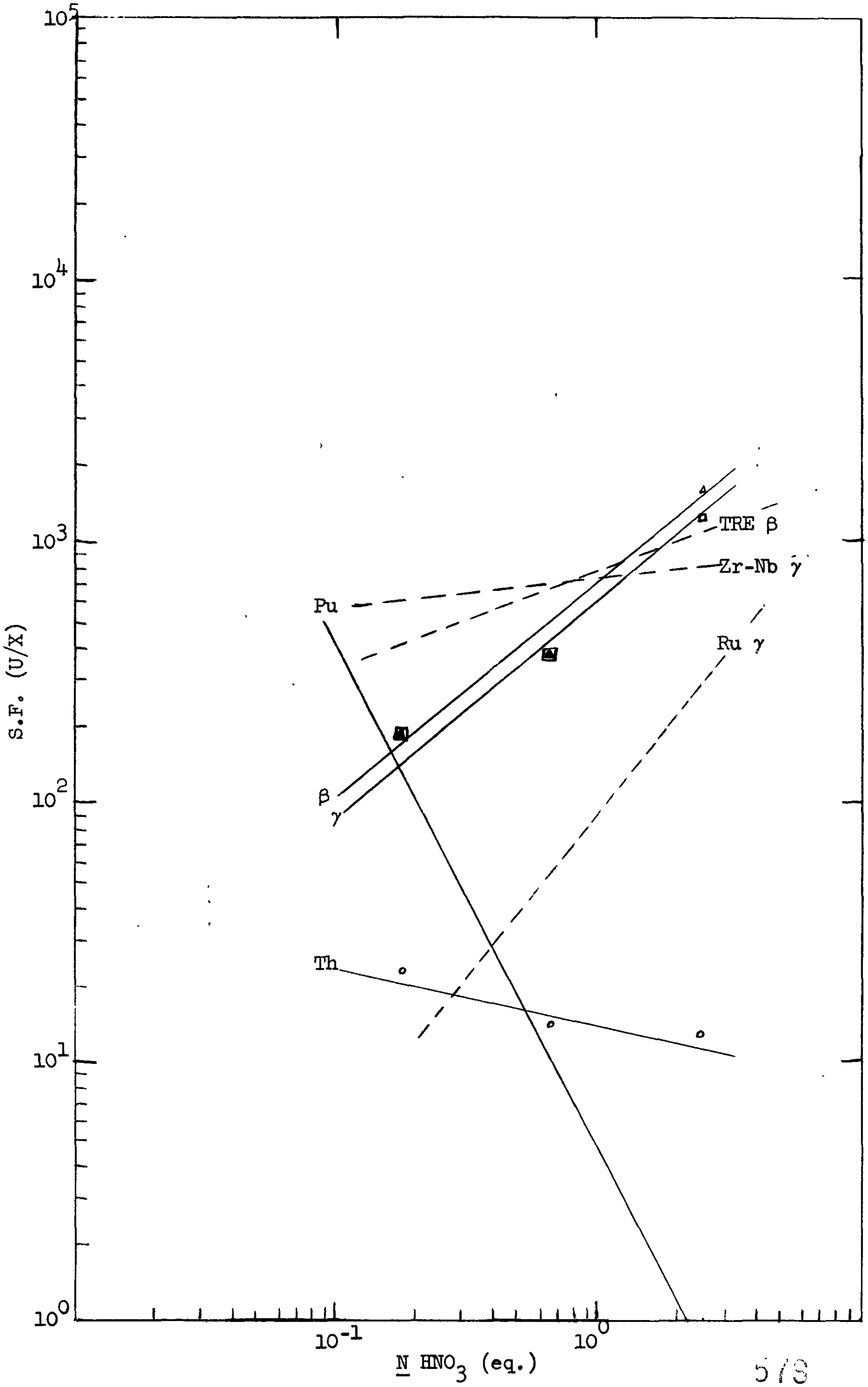


Fig. 11. S.F.'s (U/X) in 1.11 M DSBPP-(Xylene): Extraction

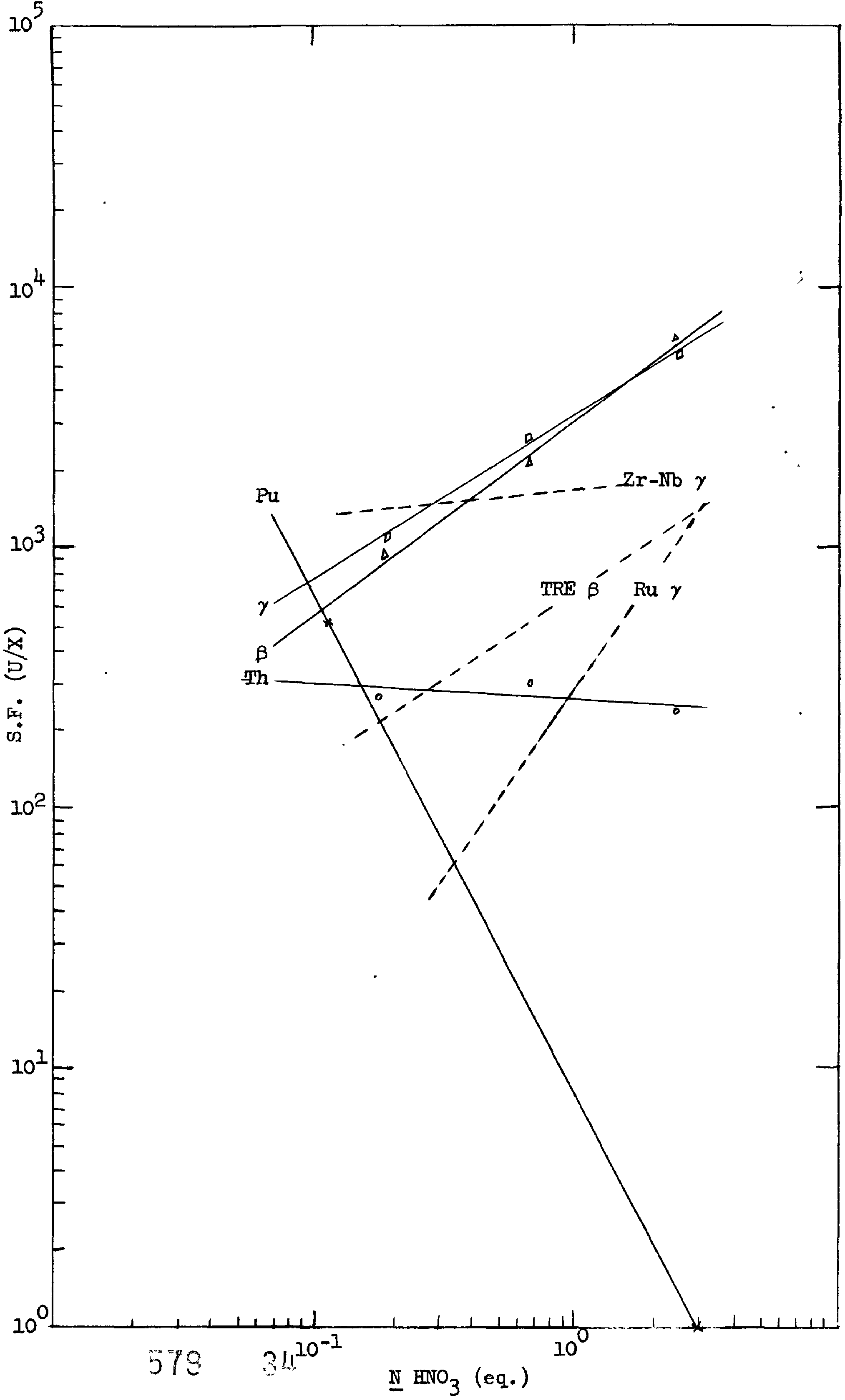


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Fig. 12. S.F.'s (U/X) in 1.1 M DBPP-(Xylene): Extraction

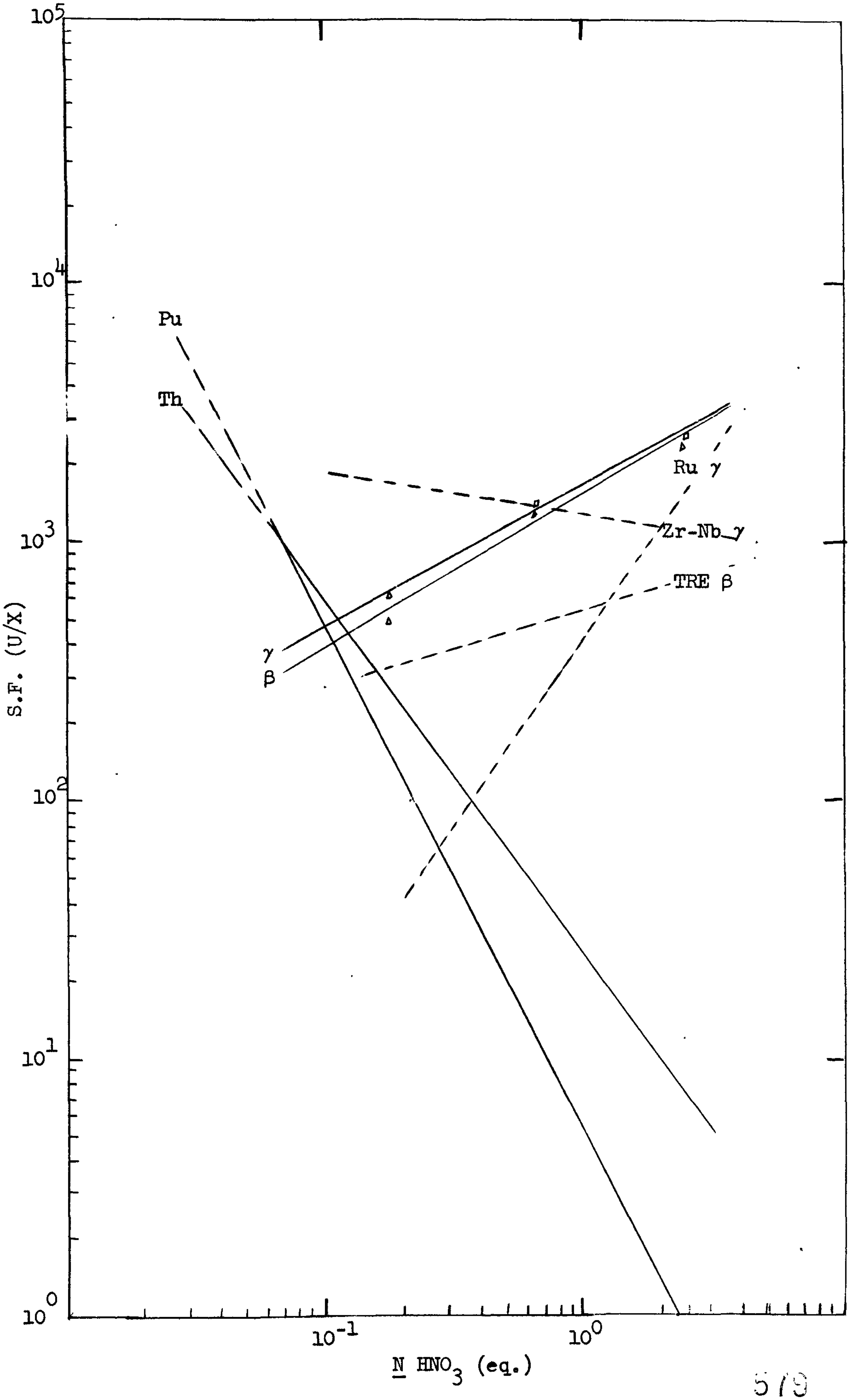


Fig. 13. S.F.'s (U/X) in 1.07 M TCP-(Amsco): Extraction (Impure)

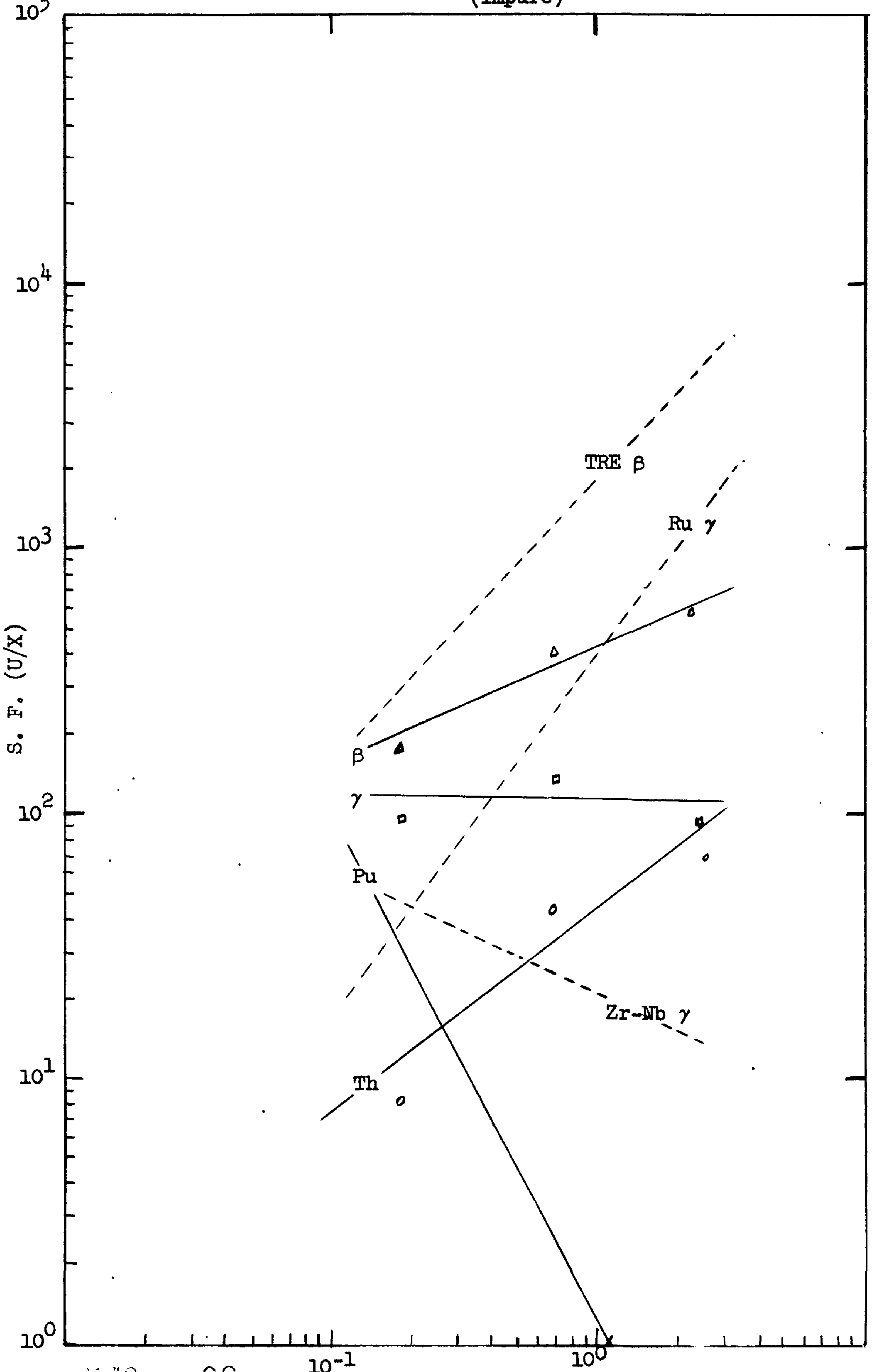
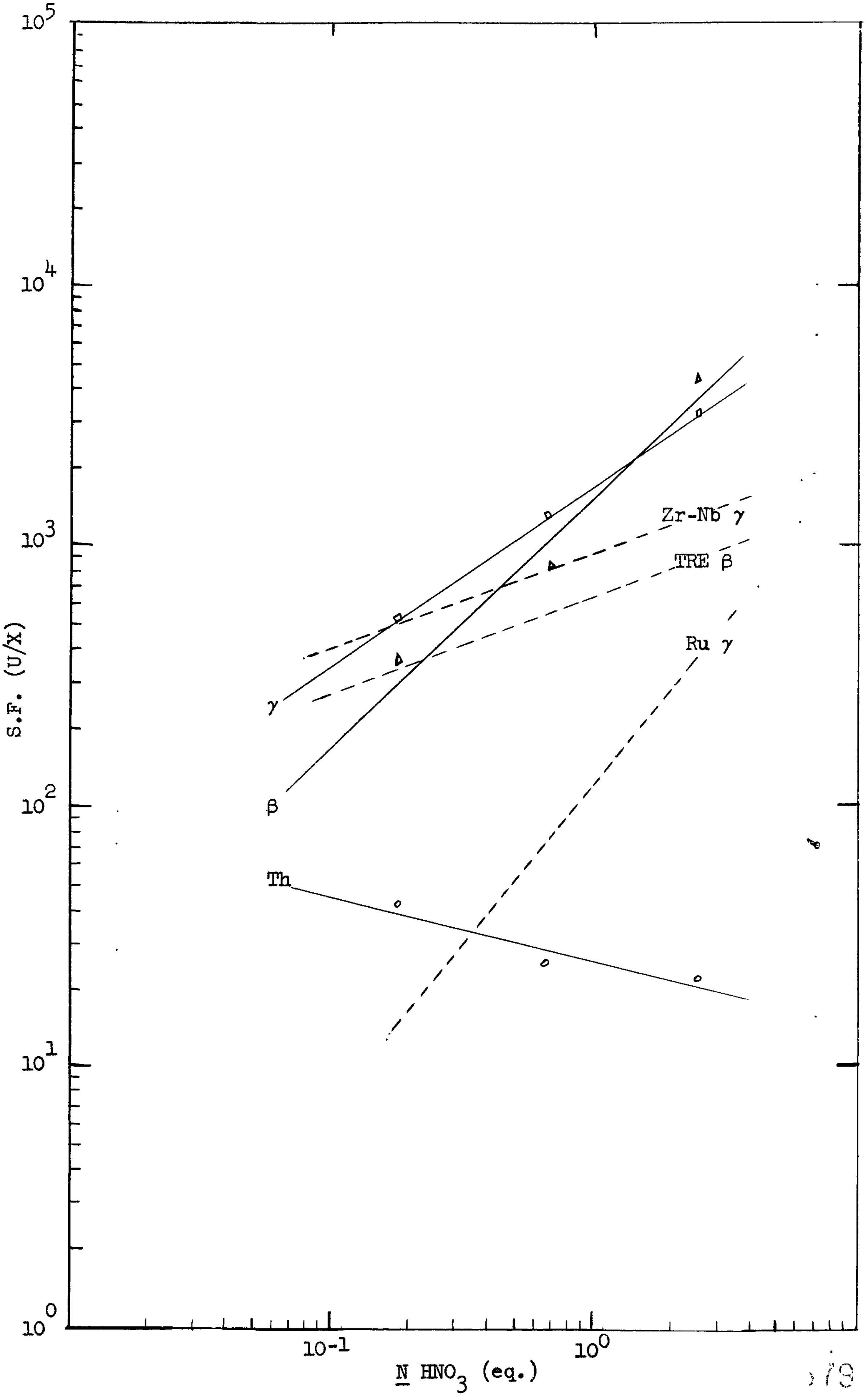


Fig. 14. S.F.'s (U/X) in 1.11 M TBP-(Xylene): Extraction



If. Batch Extraction Tests: Summary of DC versus N HNO_3 Data from Extractions with 1 M TBP-Amsco, DSBPP-xylene, TCP-Amsco and TBP-xylene

Figures 15, 16, 17, 18, and 19 summarize the comparisons of specific U, Th, Pu IV, and fission product distribution coefficient (DC_a^o) observed with the five extractants as a function of aqueous nitric acid concentration (data in Tables 9, 10, 11, and 12).

Figure 15 emphasizes the generally equivalent slopes of the U DC lines and the higher values for the alkyl phenylphosphonates. It also points out the peculiar observations previously mentioned in regard to thorium extraction by the branched alkylphosphate (TCP), the branched alkyl phenylphosphonate (DSBPP) and the normal alkyl phenylphosphonate (DBPP).

Figure 16 stresses the apparent equivalence of Pu IV DC slopes and the significantly higher Pu IV extractability by the TCP and the phosphonates. The general flatness of the gross β (dotted) and γ (solid) lines, i.e., excepting the anomalous TCP case, has been discussed previously. An important observation is that values for the DSBPP case are significantly lower than those for the TBP, while those for the normal alkyl-phosphonate (DBPP) are measurably higher.

Figure 17 shows the higher TRE extractability of the phosphonates and the significantly lower extractability of the sec-alkyl phosphate (TCP), particularly in the high-acid case.

Figure 18 shows the relatively consistent slopes of the Ru DC lines, but suggests somewhat greater acid dependency for the "new reagents" than normally observed in the TBP case.

Figure 19 emphasize the relatively consistent slopes of the Zr-Nb DC lines (excepting again the anomalous TCP case), and suggests significantly higher values for the DBPP case.

Fig. 15. U and Th D.C.'s (O/A): Extraction

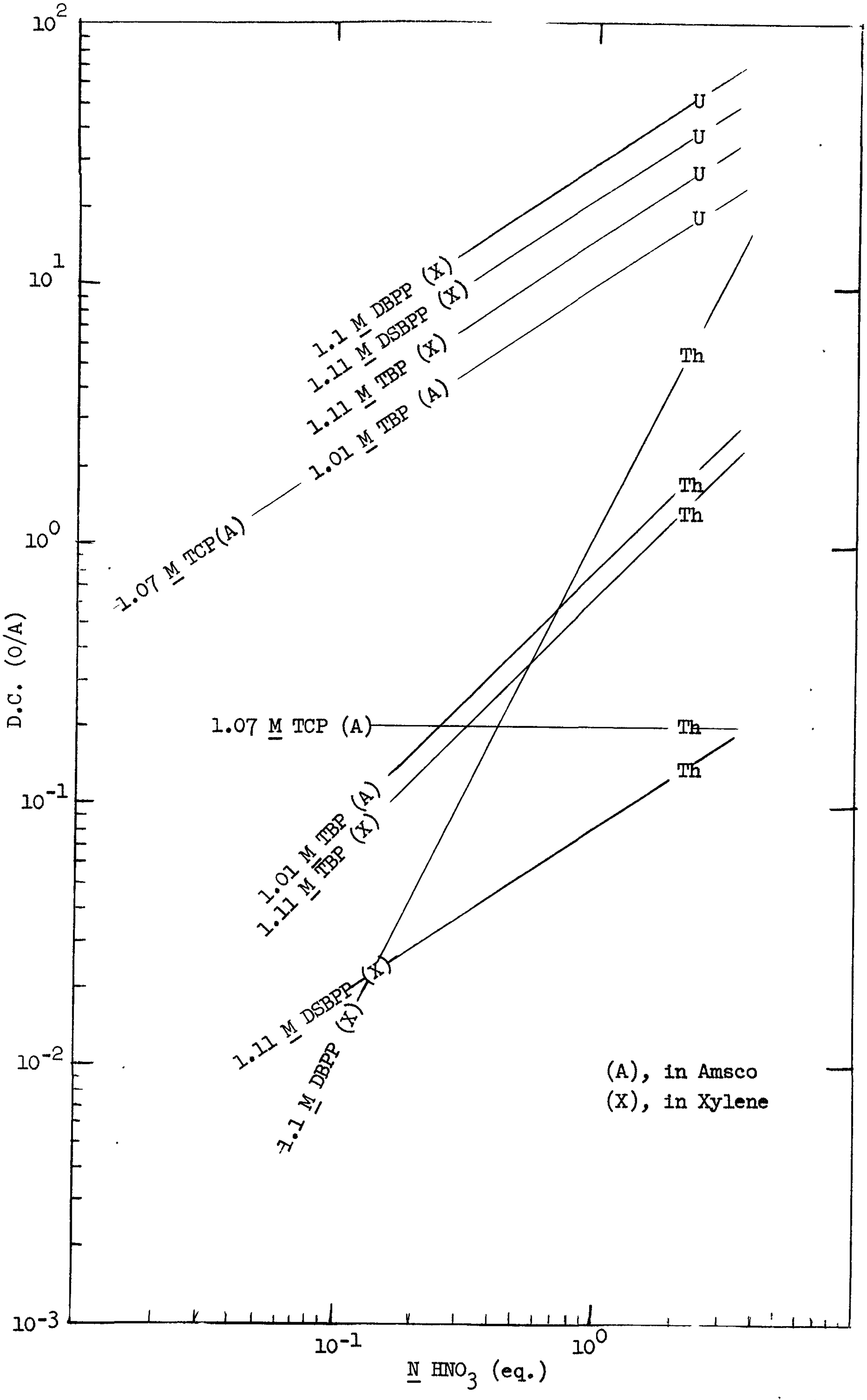


Fig. 16. Pu, Gross β, and Gross γ D.C.'s (O/A): Extraction

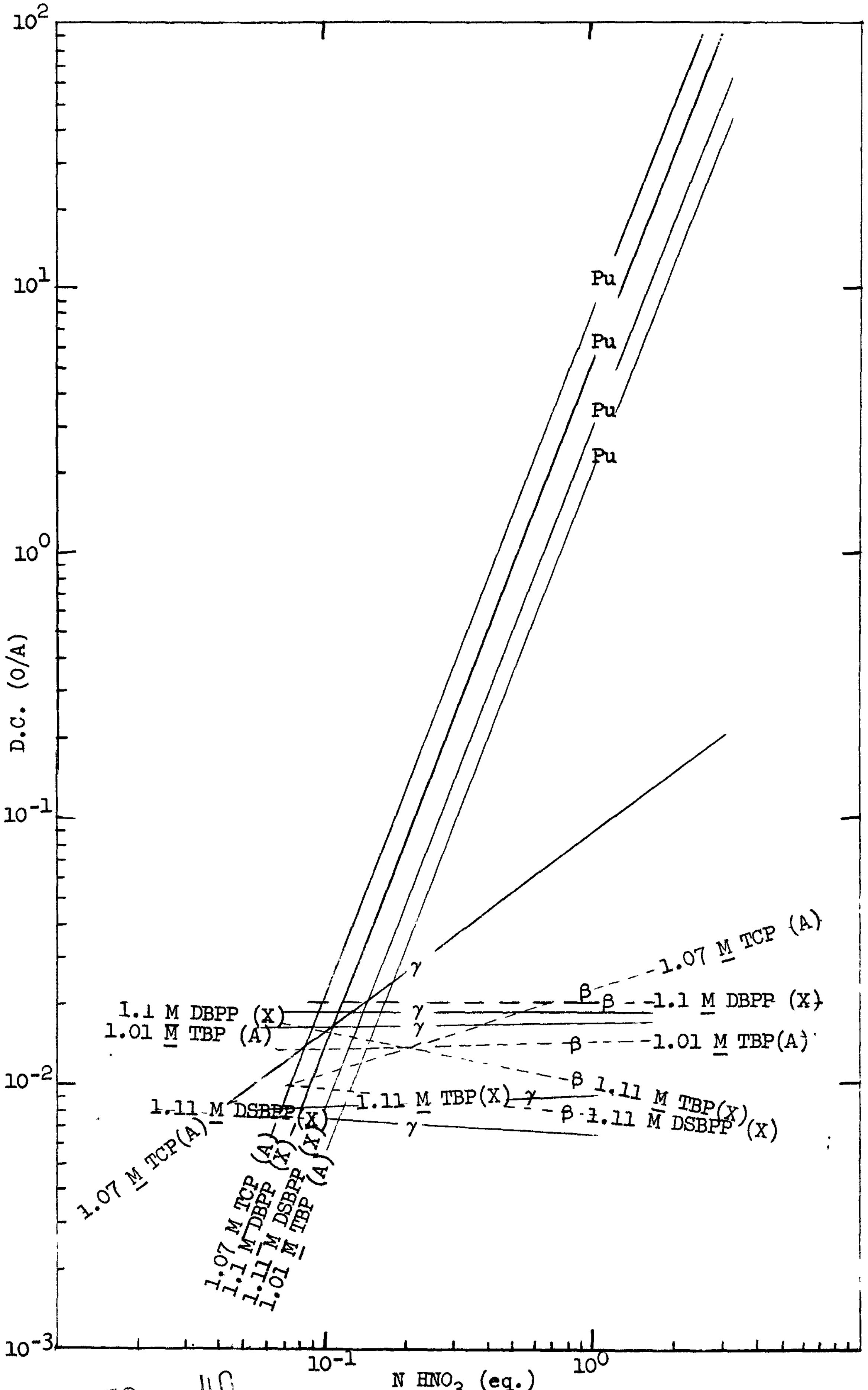


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Fig. 17. TRE D.C.'s (O/A): Extraction

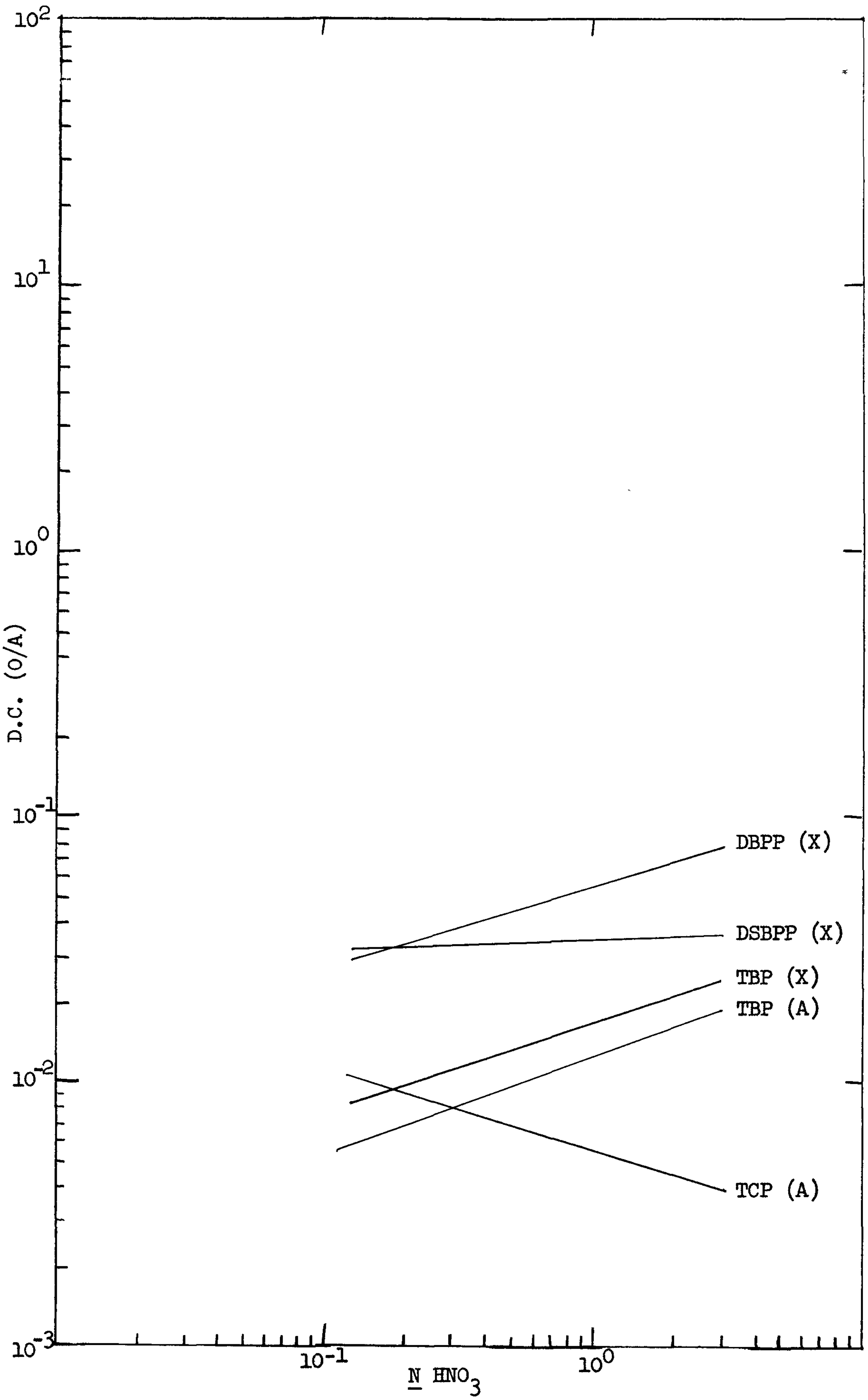

Fig. 18. Ru D.C.'s (O/A): Extraction

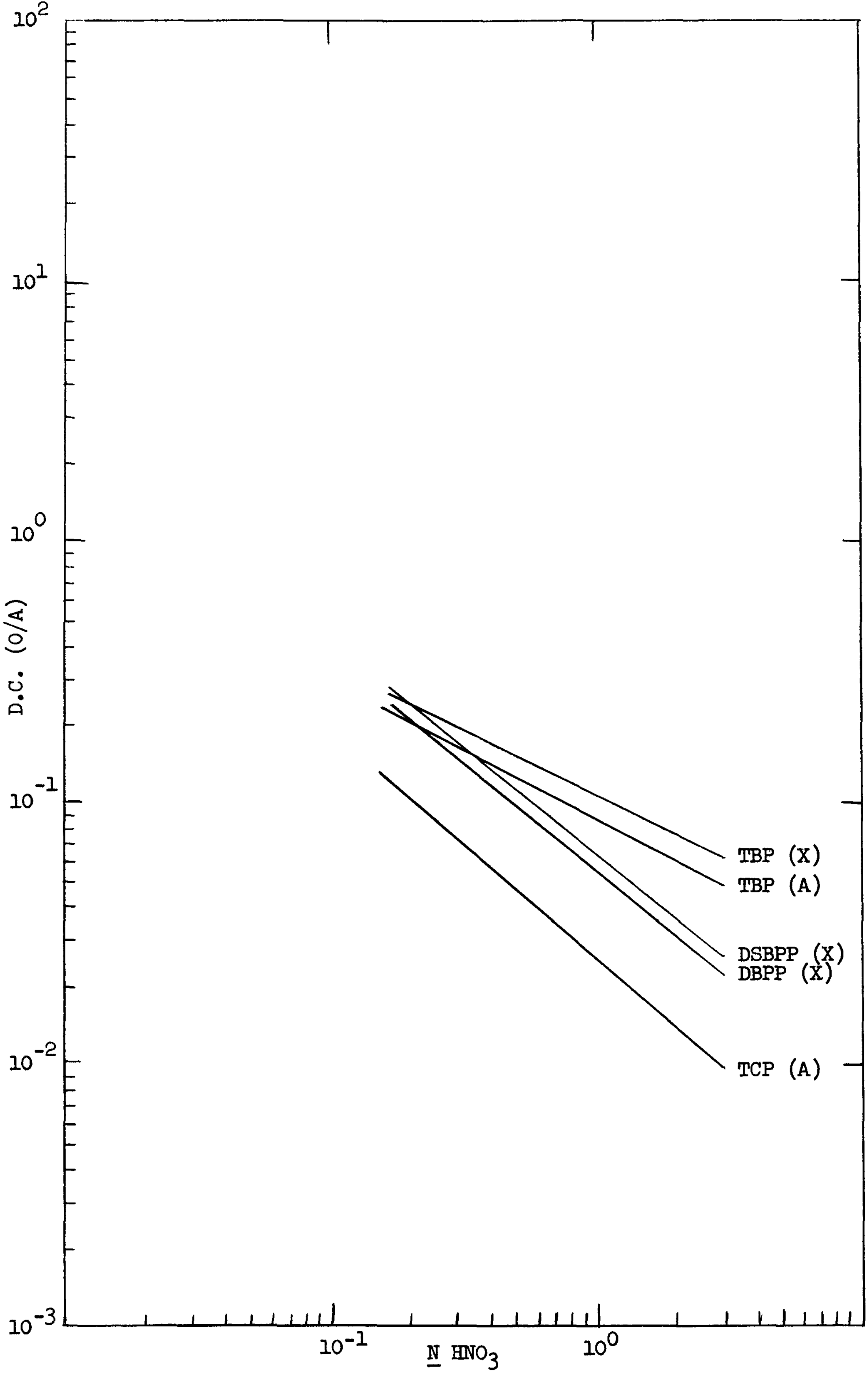

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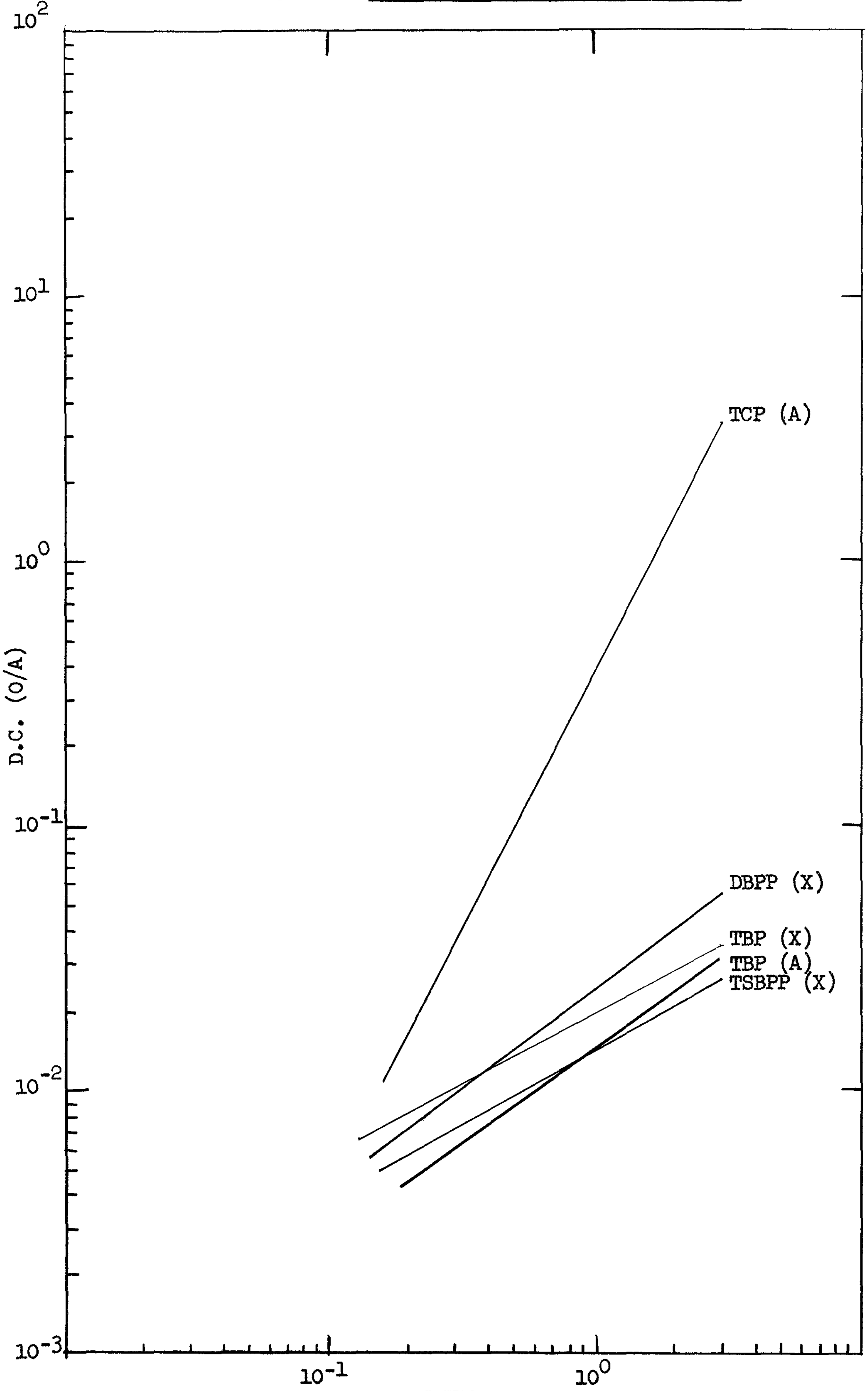
Fig. 19. Zr-Nb D.C.'s (O/A): Extraction



Ig. Batch Extraction Tests: Summary of SF versus N HNO_3 Data from Extractions with 1 M TBP-Amsco, DSBPP-xylene, DBPP-xylene, TCP-Amsco, and TBP-xylene

Figures 20, 21, 22, 23, and 24 summarize the comparisons of specific uranium separation factors (U D.C./X D.C.) from Th, Pu IV, and fission products observed with the five extractants as a function of aqueous HNO_3 concentration (data in Tables 9, 10, 11, and 12).

It seems significant that the SF's with the di-sec-butyl phenylphosphonate (DSBPP-xylene) were generally higher than those for TBP-Amsco by sizeable factors. This was true in all cases measured at the higher aqueous acidities. Such evidence is quite encouraging in light of the particular fact that radiolysis tests have shown DSBPP to be about four (4) times as stable as TBP.

Figure 20 shows the relatively consistent slope of the U/gross γ SF's (excepting the anomalous TCP case) and the relatively higher values of the 1.11 M TBP-xylene case over that of the 1.01 M TBP-Amsco case. (Since such SF's are known to generally increase with decreasing organic reagent concentration, it may be assumed that these differences in value are conservative, i.e., when considering identical TBP concentrations instead of the 10% variation in the given cases.) Figure 20 also again emphasized the generally peculiar aspects of thorium extraction in the branched alkyl phosphates and phenylphosphonates. Such considerations will become important in possible process uses, e.g., Interim-23 or Thorex applications.

Figure 21 shows the relative consistency of the slopes of U/Pu IV SF lines as well as the U/gross β SF lines. Again, the TBP-xylene case shows a significant advantage over the TBP-Amsco case.

Figure 22 corroborates the significantly better U/TRE SF's attainable by the alkylphosphates, and emphasizes that small differences characterize the U/TRE relationships between the phenylphosphonates and TBP.

Figure 23 points up the consistent slopes of U/Ru SF's and the generally superior values for the branched alkylphosphates and phenylphosphonates.

Figure 24 emphasizes the general superiority of DSBPP in the critical U/Zr-Nb SF's as well as the anomalous effect of TCP's acidic impurities on Zr-Nb extraction.

Fig. 20. Th and Gross γ S.F.'s (U/X): Extraction

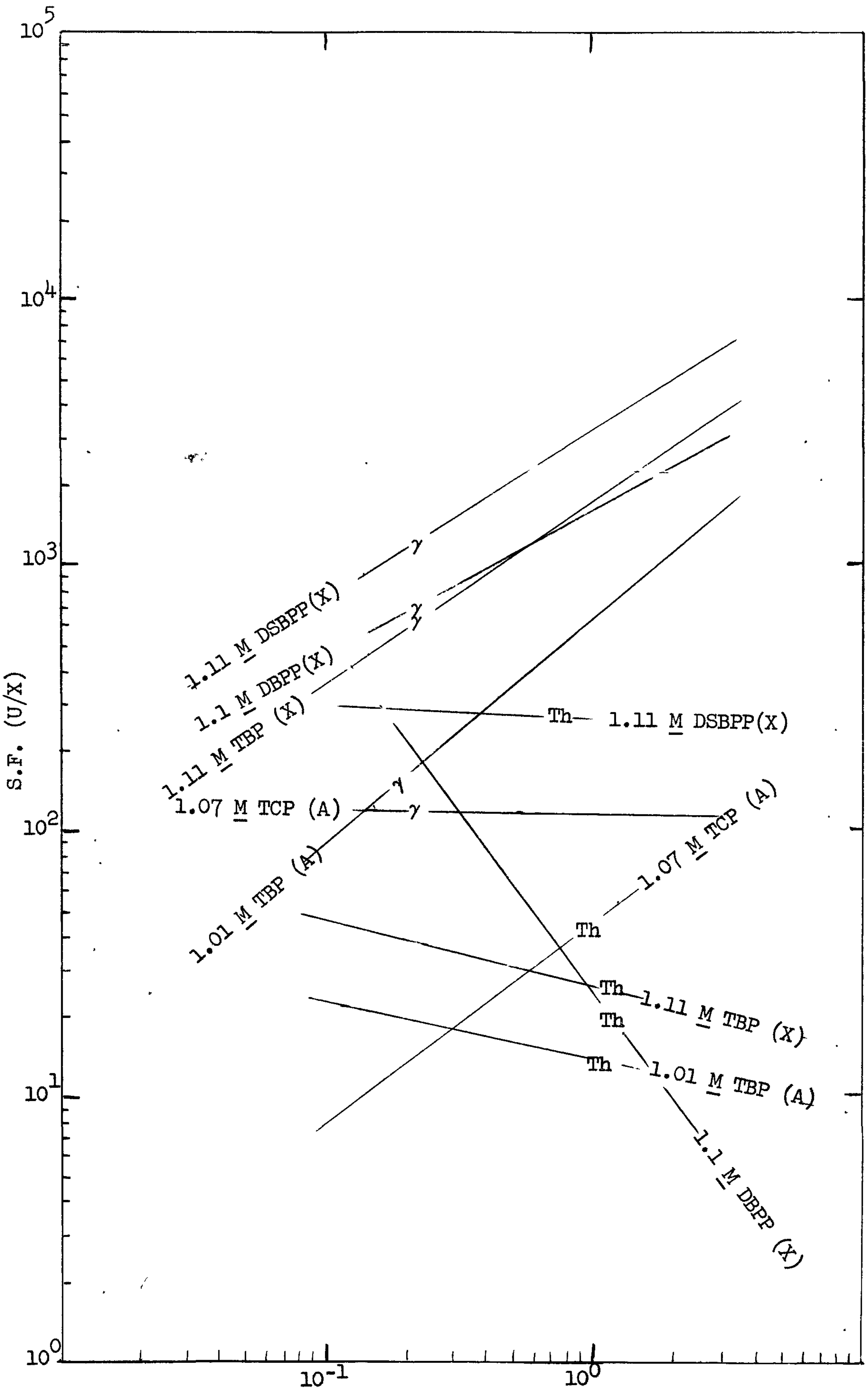


Fig. 21. Pu and Gross β S.F.'s (U/X): Extraction

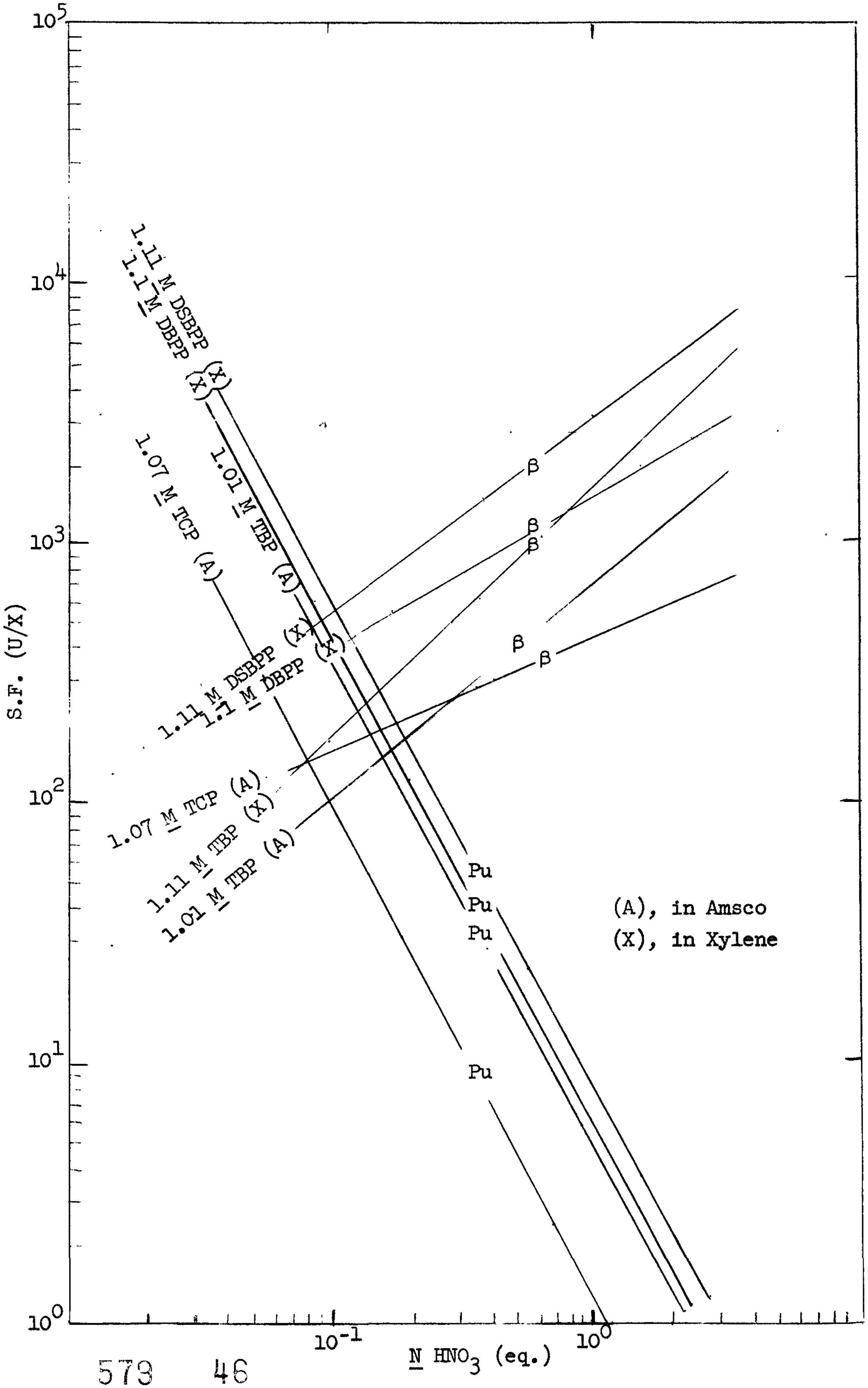


Fig. 22. S.F.'s (U/TRE): Extraction

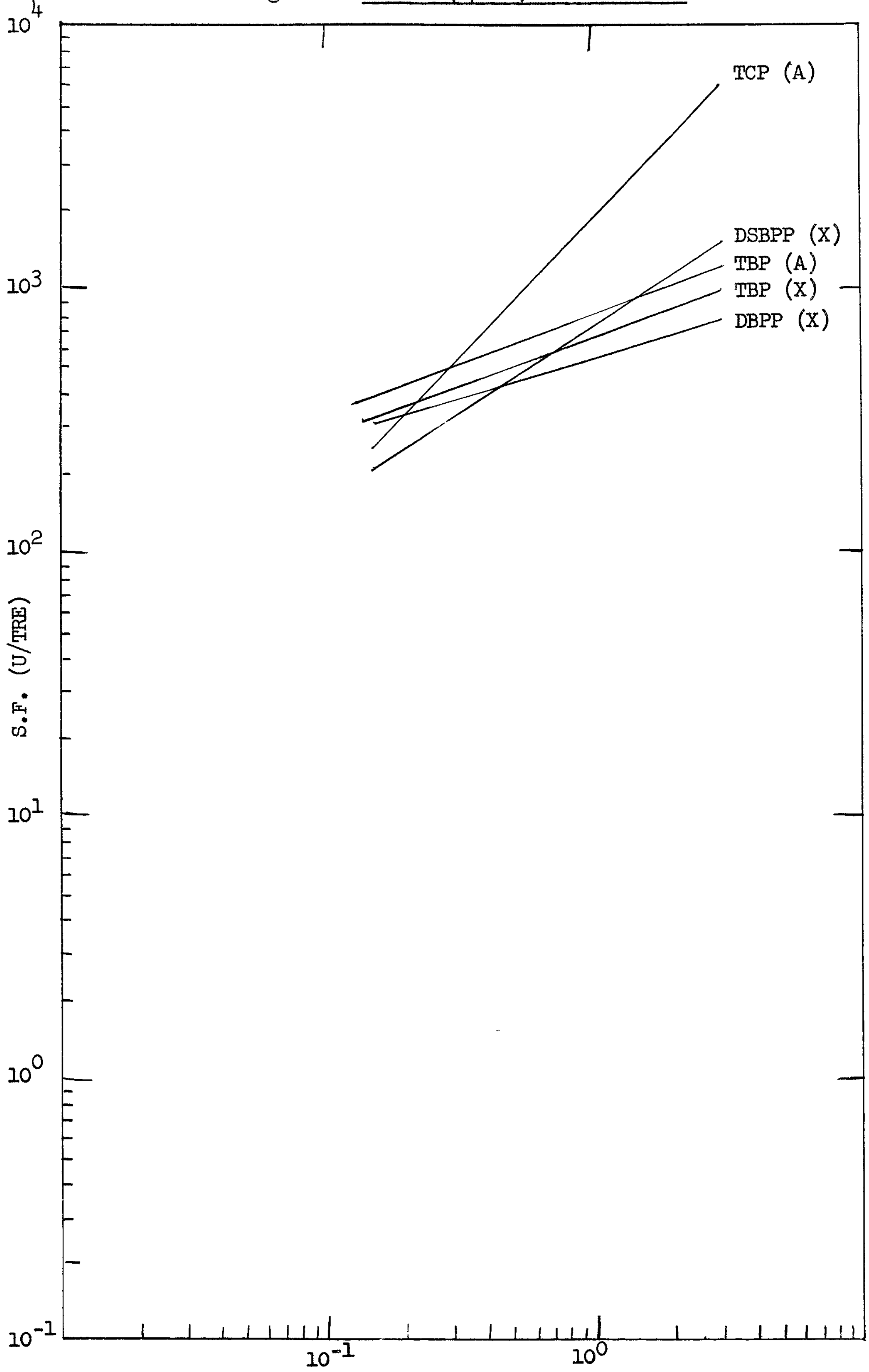


Fig. 23. S.F.'s (U/Ru): Extraction

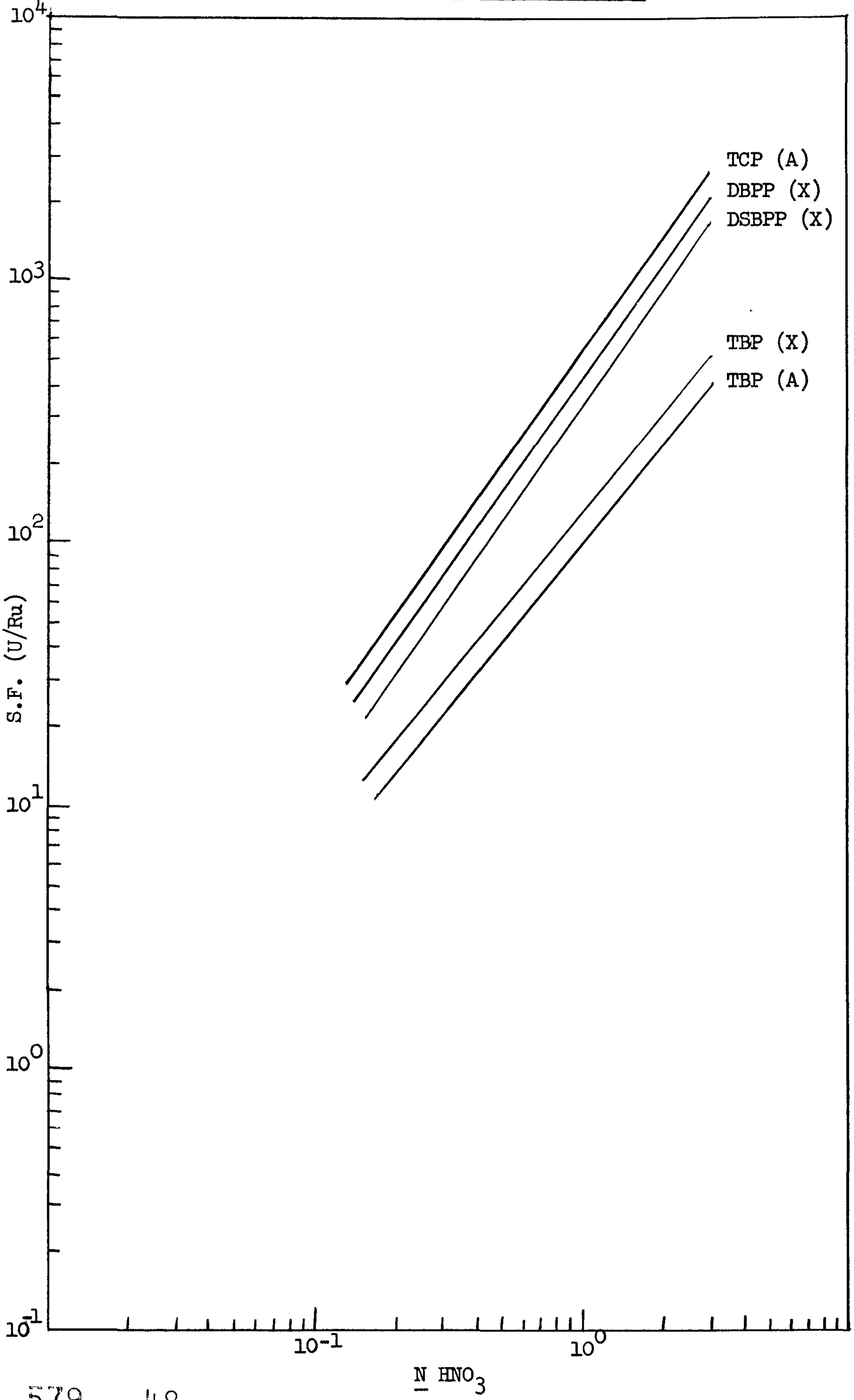
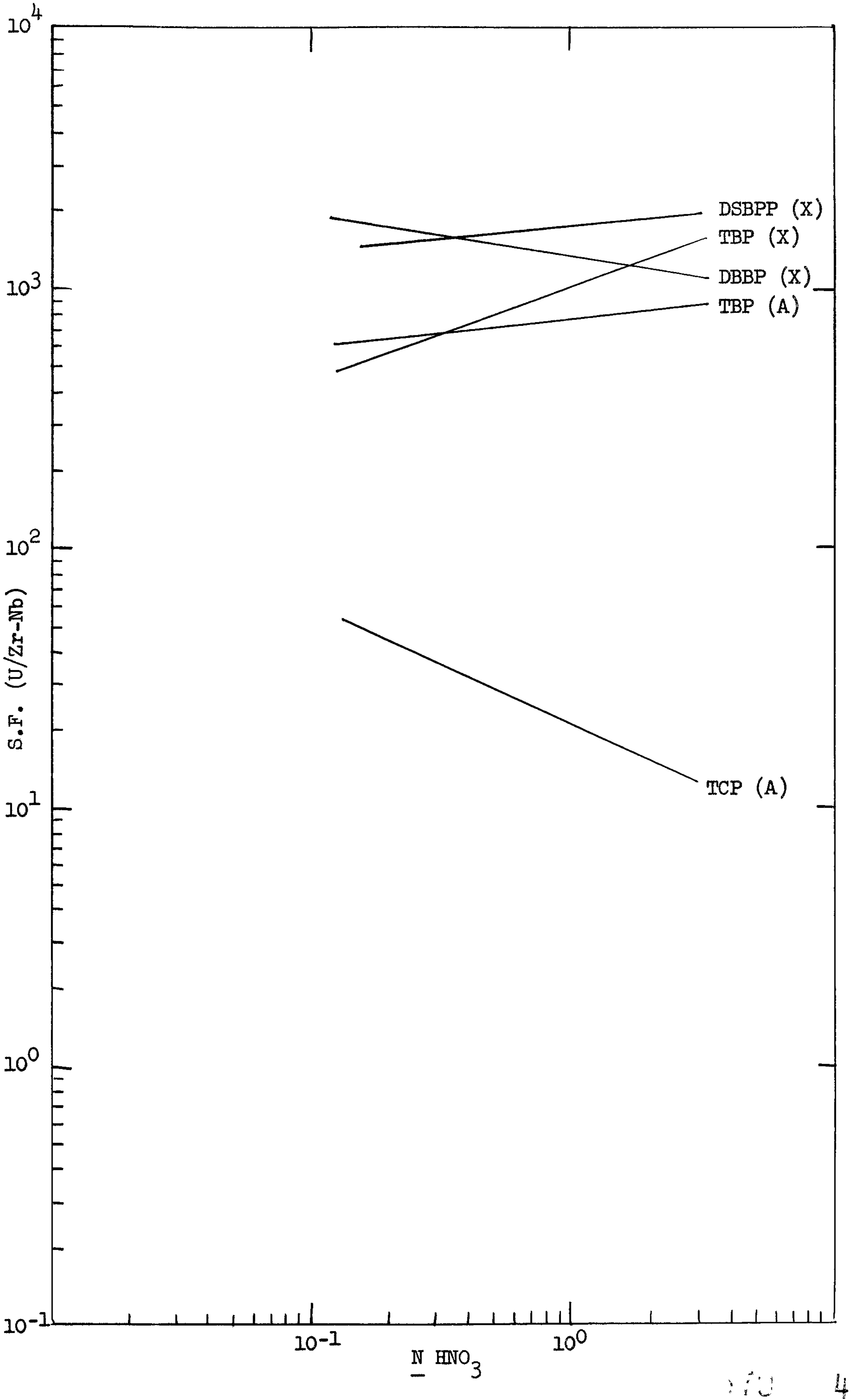


Fig. 24. S.F.'s (U/Zr-Nb): Extraction



Ih. Batch Extraction Tests: Fission Product Distribution on HNO_3 Scrubbing of 1 M TBP-Amsco, DSBPP-xylene, DBPP-xylene, TCP-Amsco, TBP-xylene

The three sets of organic extracts from the previously discussed batch extraction tests (data in Table 9, 10, and 11) were scrubbed with equal volumes of HNO_3 solutions having the same concentrations (2.8 N, 0.8 N, and 0.2 N HNO_3) employed in the original aqueous feeds. Fission product data from these scrubbing tests are recorded in Tables 13, 14, and 15. (The calculated U/X separation factors in these tables were based on the assumption that uranium DC's were equal to those obtained in the initial extraction tests, i.e., as recorded in Tables 9, 10, and 11.

Data in Table 13 points out that somewhat lower activity remained in the DSBPP-xylene extract than in the TBP-Amsco extract, and that U/gross β and U/gross γ SF's were slightly higher. Perhaps of greater general significance, however, is that the scrubbing DC's (O/A) in the DSBPP case increased more markedly on decreasing the aqueous HNO_3 concentration from 2.8 N to 0.8 N, pointing out the general advantage of more acidic scrub solutions on decontamination efficiency. In the two low-acid cases, it is also apparent (as anticipated from previous Purex studies) that ruthenium, instead of Zr-Nb, becomes the main limitation on U-decontamination.

Data in Table 14 affords similar comparative evidence of DSBPP-xylene with TBP-xylene, and reflects the generally advantageous decontamination effects of xylene, (instead of Amsco 125-82) as a TBP diluent.

Data in Table 15 illustrates the very marked effect of TCP impurities (polyphosphate and/or acidic decomposition products) on both ruthenium and Zr-Nb scrubbing DC's (and/or U-decontamination from the Ru and Zr-Nb fission products). Such impurities appeared to have little or no effect on the rare-earth distribution coefficients. The DBPP data show that FP distribution is somewhat comparable to the DSBPP and TBP cases; however, the Zr-Nb DC (i.e. DC^{o}_{a} is 0.6) in the 2.8 N test is observed to be higher by a factor of about four, signifying that considerably poorer Zr-Nb DF's would be attainable with DBPP.

Figure 25 is a rough log-log plot of the data in Tables 13, 14, and 15 illustrating graphically (1) the anomalous nature of the impure TCP, (2) the higher gross γ DC (at 2.8 N HNO_3) of DBPP, and (3) the sharp decrease of both β and γ DC's (in DSBPP and TBP) between 0.8 N and 2.8 N HNO_3.

Figure 26 plots hypothetical β and γ "DF's" (ratio of initial counts in the aqueous feed, AF, to those in the scrubbed extract, 1-SO) obtained in the five individual tests. Like Fig. 25 it shows graphically the deleterious effects of TCP impurities, as well as the apparent, "DF" superiority of the DSBPP reagent in the 2.8 N HNO_3 case.

Table 13. D.C.'s (O/A) and S.F.'s (U/X) in Scrubbing Tests: TBP(A) and DSBPP(X)
(As a Function of Aqueous HNO$_3$ Concentration)

	1.01 M TBP in Amsco				1.11 M DSBPP in Xylene			
	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)
(2.8 N HNO$_3$)								
Gross β	0.14	1.18	0.12	179	0.05	0.39	0.12	323
Gross γ	0.35	2.79	0.13	165	0.14	0.96	0.14	270
TRE β	0.02	0.93	0.02	1065	0.01	0.20	0.05	714
Ru γ	0.06	0.12	0.50	42	-	0.02	-	-
Zr-Nb γ	0.16	1.1	0.15	145	0.09	0.59	0.15	248
(0.8 N HNO$_3$)								
Gross β	0.71	1.17	0.61	10	0.37	0.34	1.08	15
Gross γ	1.09	1.58	0.69	9	0.61	0.67	0.92	18
TRE β	0.12	0.73	0.16	39	0.01	0.12	0.47	354
Ru γ	0.49	0.31	1.58	4	0.59	0.15	3.94	4
Zr-Nb γ	0.07	0.15	0.48	13	0.11	0.16	0.69	24
(0.2 N HNO$_3$)								
Gross β	0.84	1.01	0.83	4	0.63	0.36	1.75	4
Gross γ	1.32	1.39	0.95	3	1.02	0.58	1.76	4
TRE β	-	0.38	-	-	-	0.06	-	-
Ru γ	0.59	0.46	1.28	2	0.64	0.23	2.78	3
Zr-Nb γ	0.07	0.12	0.63	5	0.11	0.07	1.6	5

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* Concentration in c/m/ml x 10^{-5}.

NOTE: The organic feeds in these tests were extracts from the experiments recorded in Table 9 . The aqueous HNO$_3$ scrubb solutions had approximate concentrations as indicated.

Table 14. D.C.'s (O/A) and S.F.'s (U/X) in Scrubbing Tests: TBP(X) and DSBPP(X)

(As a Function of Aqueous HNO_3 Concentration)

	1.11 M TBP in Xylene				1.11 M DSBPP in Xylene			
	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)
(2.8 N HNO_3)								
Gross β	0.08	0.62	0.12	258	0.05	0.39	0.12	323
Gross γ	0.24	1.72	0.14	224	0.14	0.96	0.14	270
TRE β	0.01	0.39	0.03	1070	0.01	0.20	0.05	714
Ru γ	0.05	0.05	1.00	32	-	0.02	-	-
Zr-Nb γ	0.20	0.98	0.20	154	0.09	0.59	0.15	248
(0.8 N HNO_3)								
Gross β	0.42	0.53	0.80	13	0.37	0.34	1.08	15
Gross γ	0.63	0.77	0.81	12	0.61	0.67	0.92	18
TRE β	0.004	0.24	0.01	685	0.01	0.12	0.47	354
Ru γ	0.56	0.20	2.8	4	0.59	0.15	3.94	4
Zr-Nb γ	0.05	0.10	0.5	20	0.11	0.16	0.69	24
(0.2 N HNO_3)								
Gross β	0.46	0.49	0.92	5	0.63	0.36	1.75	4
Gross γ	0.68	0.71	0.96	4	1.02	0.58	1.76	4
TRE β	0.01	0.09	0.08	50	-	0.06	-	-
Ru γ	0.65	0.27	2.4	2	0.64	0.23	2.78	3
Zr-Nb γ	0.05	0.08	0.64	7	0.11	0.07	1.6	5

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* Concentration in c/m/ml x 10^{-5}.

NOTE: The organic feeds in these tests were extracts from the experiments recorded in Table 11. The aqueous HNO_3 scrub solutions had approximate concentrations as indicated.

Table 15. D.C.'s (O/A) and S.F.'s (U/X) in Scrubbing Tests: TCP(A) and DBPP(X)

(As a Function of Aqueous HNO_3 Concentration)

	1.07 M TCP in Amsco				1.1 M DBPP in Xylene			
	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)	Org. (Conc.)*	Aq. (Conc.)*	D.C. (O/A)	S.F. (U/X)
(2.8 N HNO_3)								
Gross β	2.61	0.74	3.56	5.	0.19	1.36	0.14	385
Gross γ	28.2	0.80	35.0	0.5	0.58	2.16	0.27	195
TRE β	0.005	0.64	0.01	2120	0.08	1.4	0.06	880
Ru γ	0.003	0.01	2.26	7	-	0.04	-	-
ZrNb γ	18.4	0.03	596	0.03	0.46	0.76	0.60	87
(0.8 N HNO_3)								
Gross β	1.35	0.24	5.6	1.3	0.49	1.27	0.38	51
Gross γ	8.95	0.28	32.6	0.2	0.76	1.36	0.56	35
TRE β	0.002	0.16	0.01	666	0.51	0.85	0.60	32
Ru γ	0.25	0.03	8.34	0.9	-	0.18	-	-
ZrNb γ	6.6	0.02	348	0.02	0.06	0.12	0.54	36
(0.2 N HNO_3)								
Gross β	0.73	0.11	6.45	0.4	0.69	0.64	1.08	10
Gross γ	3.65	0.15	25.0	0.1	1.16	0.91	1.28	9
TRE β	-	0.07	-	-	0.01	0.34	0.03	376
Ru γ	0.36	0.03	14.4	0.2	0.32	0.22	1.45	8
ZrNb γ	1.70	0.01	154	0.02	0.13	0.07	1.94	6

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*Concentration in c/m/ml x 10^{-5}.

NOTE: The organic feeds in these tests were extracts from the experiments recorded in Table 10. The aqueous HNO_3 scrub solutions had approximate concentrations as indicated.

Fig. 25. Gross β and γ D.C.'s (O/A): Scrubbing

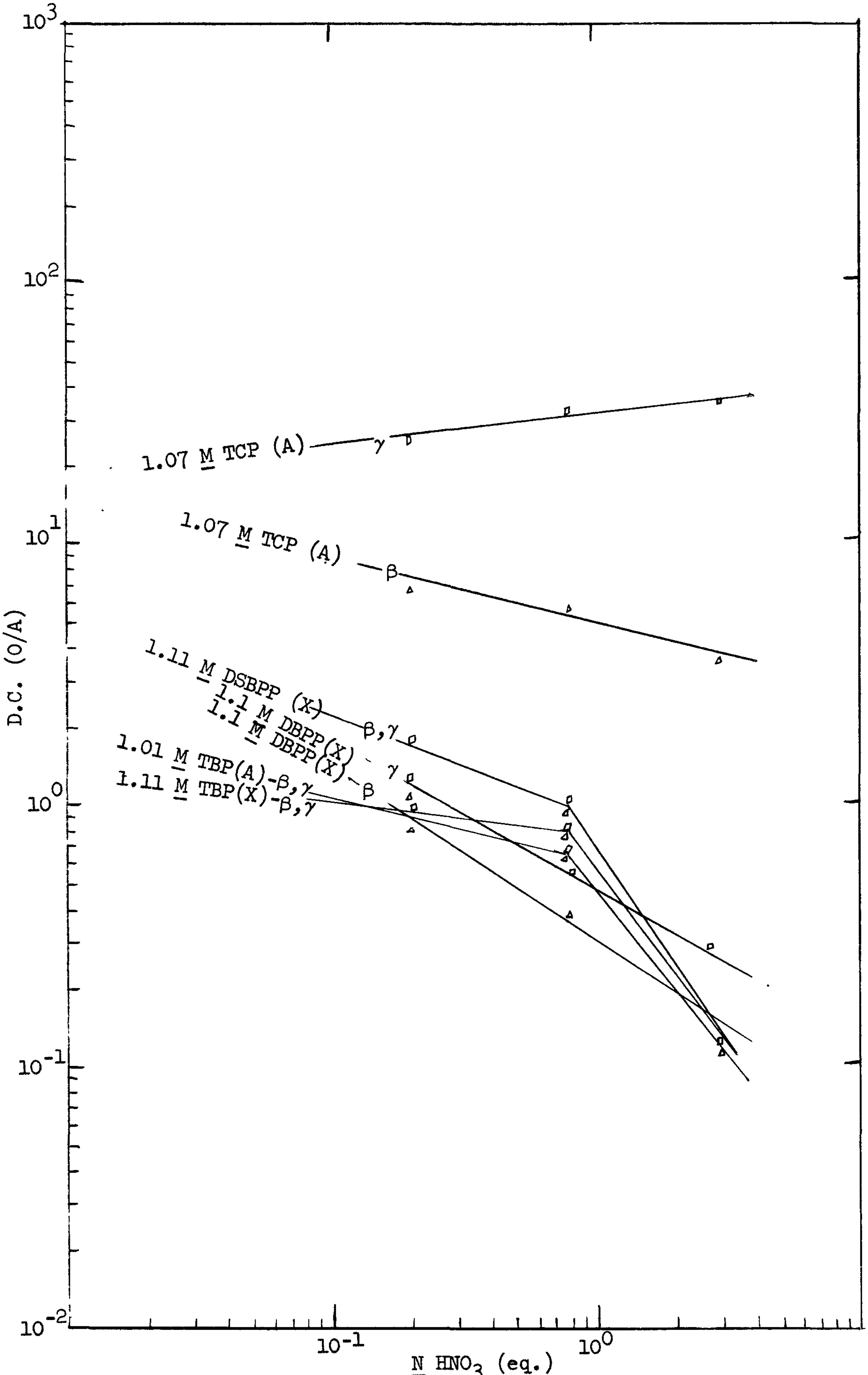
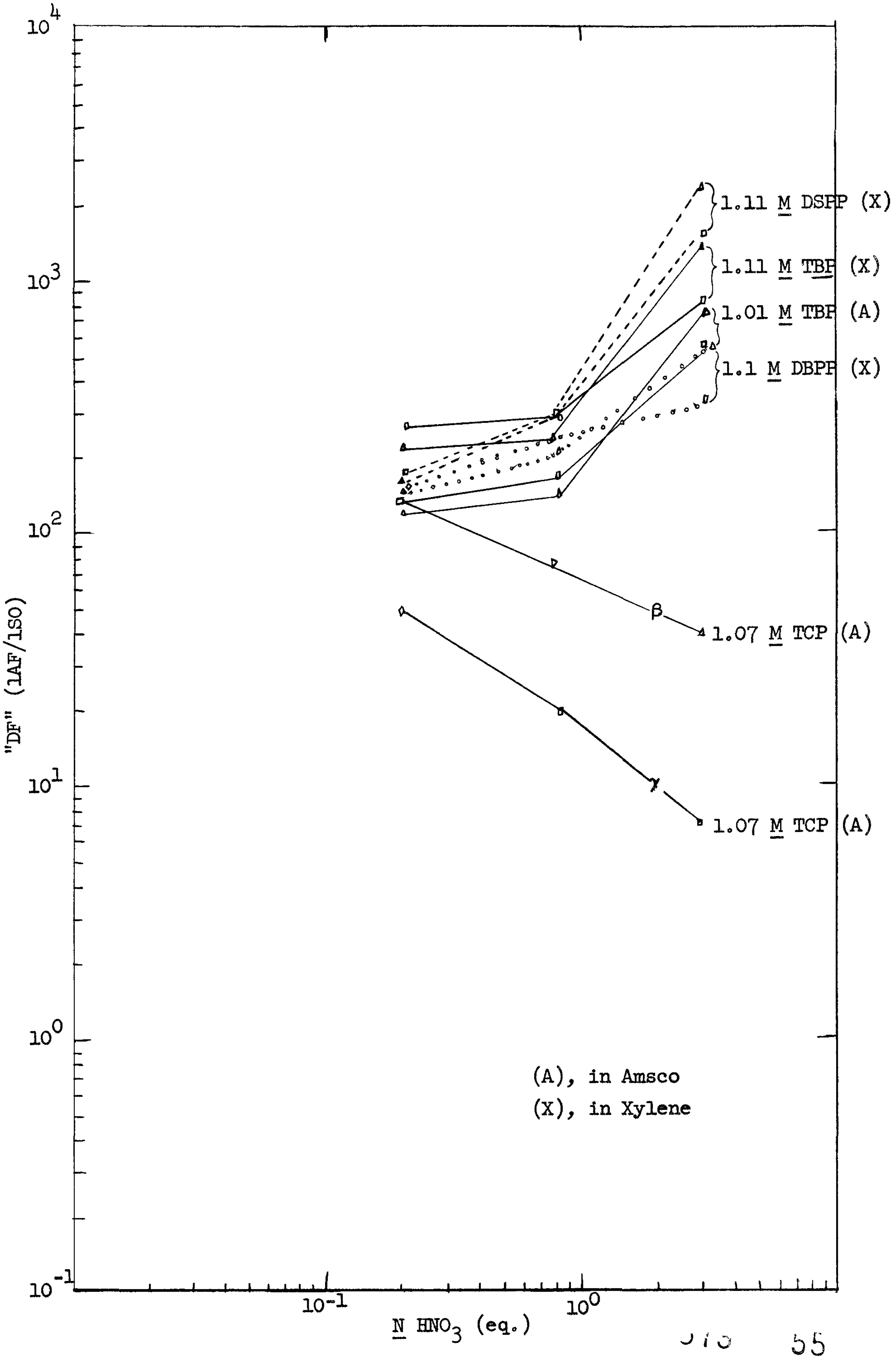


Fig. 26. Gross β and γ "DF's" (1AF/1SO): Extraction and Scrubbing



II. Batch Extraction Tests: U/X Separation Factors as a Function of Organic Reagent (alkylphosphate and alkylphosphonate) Concentration

Previous studies of the TBP-25 and Interim-23 processes, which employed 1.5 to 6.0% TBP reagent concentrations, revealed that high U/X SF's and/or U-decontamination factors were possible, i.e., when compared to the Purex or Thorex systems employing 30 to 45% TBP. Since comparisons in the batch tests, i.e., as discussed in preceding sections, were made with extractants of slightly varying (inadvertently) reagent concentrations, e.g., 1.01 M TBP vs 1.1 M DBPP and 1.11 M DSBPP, it was desirable to estimate whether or not the resulting comparative SF's were conservative and/or significant values.

Previous data obtained by R. H. Rainey and R. C. Lovelace (ORNL CF-58-6-101), as shown in Table 16, afforded an available basis for general comparisons of reagent dilution effects in cases of TBP (an alkylphosphate), di-butyl butyl phosphonate (DBBP) and diamyl amylphosphonate (DAAP), i.e., where DBBP and DAAP were structural examples of the phosphonates. Although this data was not obtained for this specific purpose, it has been used to calculate U/Th, U/Ru, U/TRE, and U/Zr-Nb separation factors as shown in Table 17. Though several of the values appeared anomalous and/or erratic, the data was employed to construct rough log-log plots of SF's versus M reagent as shown in Figs. 27, 28, 29, and 30.

These figures illustrate unquestionably the general increase of SF's with decreasing reagent concentration in the TBP case, as well as in the DBBP and DAAP cases, i.e., with the possible exception of U/Zr-Nb shown in Fig. 30.

Under conditions of the experiment it was noted that the 3% TBP and 30% TBP were saturated (considering 2 TBP·U, 4 TBP·Th, and TBP·HNO_3) to about 45% and 36%, respectively; so, it may be surmized that relative reagent saturation did not play a major role in the large observed variations of SF vs reagent concentration, although it must be granted to have caused an indeterminate SF increase on approach to the lowest concentrations.

In the cases of U/Th, U/Ru, and U/TRE SF's, as shown in Figs. 27, 28, and 29, the steeper slopes of the DBBP and DAAP lines (as opposed to the TBP case) indicate a comparatively larger effect of SF increase with reagent dilution. In general, such an indication would suggest that suitable phosphonates could offer decontamination advantage over the phosphates in process systems such as TBP-25 and Interim-23. However, the quite erratic U/Zr-Nb data, plotted in Fig. 30, appeared to suggest an anomalous behavior of Zr-Nb in the phosphonate cases, i.e., behavior which might adversely affect decontamination in dilute reagent systems. (It may be believed that acidic impurities in the given DBBP and DAAP contributed significantly to the Zr-Nb behavior and/or the considerably erratic data obtained for both Zr-Nb and Ru.) In any event, it may appear worthwhile to more thoroughly investigate such suggested anomalies in "new reagent" evaluations.

On the basis of the general inferences of the data in Table 16, it may be rather safely assumed that the previous SF comparisons of 1.01 M TBP versus 1.1 M DBPP and 1.11 M DSBPP were actually conservative, i.e., the SF's (O/A) for TBP would decrease somewhat on increasing the concentration from 1.01 M to 1.11 M, thus to actually increase the observed ratios of the phenylphosphonate SF's to the TBP SF's.

Table 16. Distribution Coefficients of Fission Products, Thorium, Uranium, and Nitric Acid in Tributyl Phosphate, Dibutyl Butylphosphonate, and Diamyl Amylphosphonate As A Function of Reagent Concentration*

		Vol. % Extractant in Amsco							
		2	3	5	10	15	20	25	30
				DC O/A					
Th	TBP	0.005	0.014	0.046	0.34	0.84	---	2.3	3.3
	DBBP	0.02	0.07	0.35	4.2	---	67	120	350
	DAAP	0.02	0.05	0.30	2.3	22.0	75	160	415
U	TBP	0.50	1.0	2.2	7.6	14	20	27	35
	DBBP	2.0	5.0	13	55	230	330	330	700
	DAAP	1.3	4.4	9.8	37	220	350	430	870
H	TBP	0.001	0.002	0.003	0.009	0.15	0.21	0.28	0.38
	DBBP	0.010	0.021	0.021	0.091	0.23	0.33	0.45	0.78
	DAAP	0.010	0.021	0.021	0.021	0.091	0.20	0.30	0.50
				DC A/O					
Ru γ	TBP	1400	1400	383	60	28	15	7.3	5.1
	DBBP	140	840	650	45	6.5	2.5	1.8	1.1
	DAAP	1340	2130	140	50	15	4.2	2.5	2.5
Zr-Nb γ	TBP	1×10^6	1×10^4	6800	1430	483	262	152	100
	DBBP	3740	3260	11	11	9.3	---	---	---
	DAAP	63	56	32	13	17	---	---	---
TRE β	TRP	2.4×10^4	1.1×10^6	3.4×10^3	446	140	62	37	27
	DBBP	2.0×10^4	7.5×10^3	1.4×10^3	100	10	---	---	---
	DAAP	2.2×10^4	1.9×10^4	2.7×10^3	250	26	---	---	---

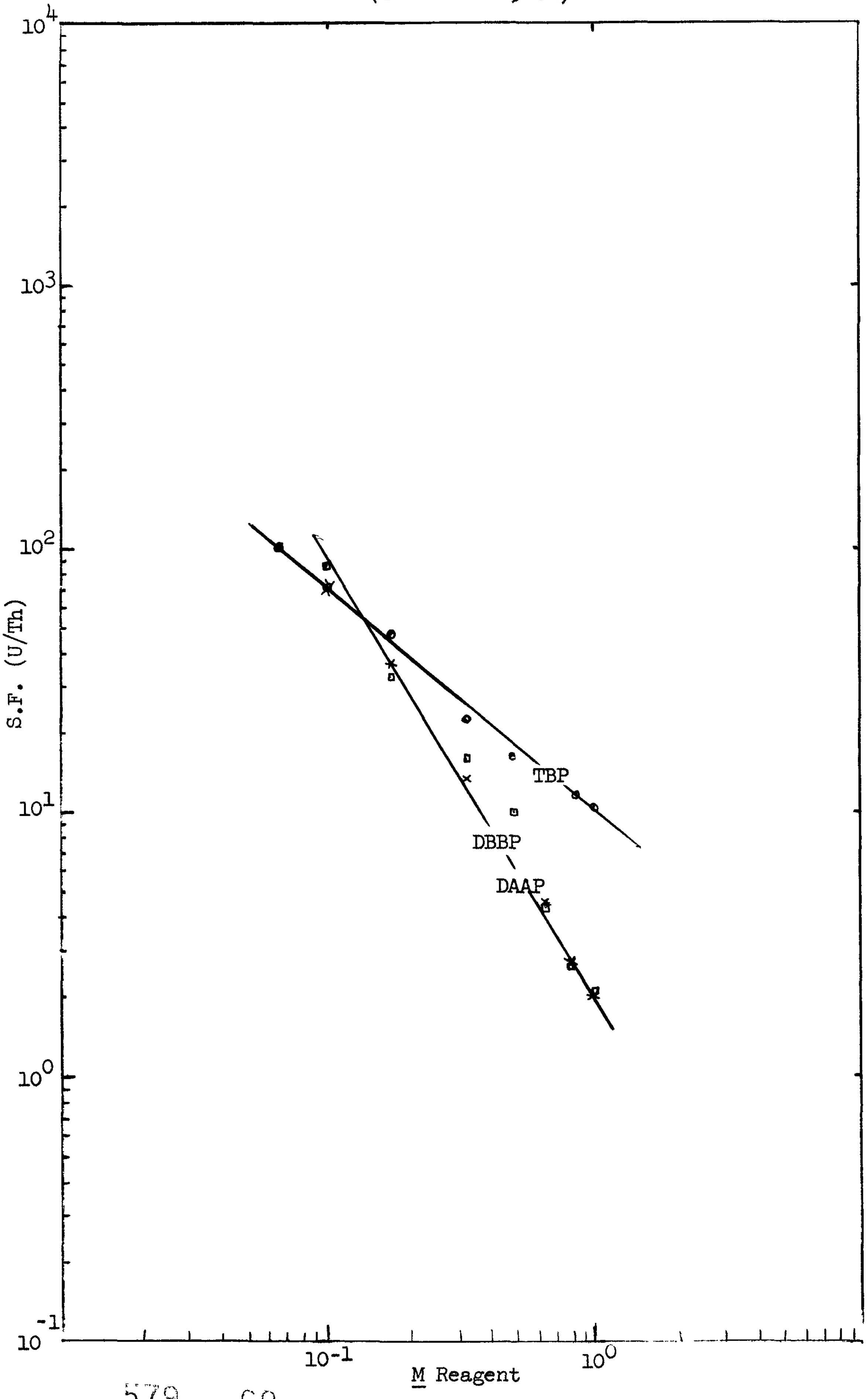
The aqueous phase initially contained 0.5 M $Al(NO_3)_3$, 0.5 M HNO_3, 10 g Th/liter, 10 g U/liter, and fission product spike.

* ORNL CF 58-6-101, R. H. Rainey and R. C. Lovelace.

Table 17. S.F.'s (U/X) as Functions of Reagent Concentration (in TBP, DBBP, and DAAP)

			Separation Factors ($S.F.{}^{U}_{X}$)			
Vol. % (in Amsco)	Reagent	$\underline{M}$ Reagent (Approx)	U/Th	U/Ru	U/Zr-Nb	U/TRE
2	TBP	0.067	100	-	50,000	12,000
	DBBP	-	100	-	-	40,000
	DAAP	-	65	-	82	-
3	TBP	0.1	72	1,400	-	-
	DBBP	-	72	4,200	-	37,400
	DAAP	-	88	9,400	246	83,500
5	TBP	0.167	48	844	15,000	7,480
	DBBP	-	37	8,450	143	18,200
	DAAP	-	33	1,370	314	26,400
10	TBP	0.333	22	455	10,900	3,390
	DBBP	-	13	2,470	605	5,500
	DAAP	-	16	1,840	481	9,250
15	TBP	0.5	17	392	6,760	1,960
	DBBP	-	-	1,500	2,140	2,300
	DAAP	-	10	3,300	3,740	5,710
20	TBP	0.67	-	300	5,240	1,240
	DBBP	-	5	826	-	-
	DAAP	-	5	1,470	-	-
25	TBP	0.83	12	197	4,070	1,000
	DBBP	-	3	595	-	-
	DAAP	-	3	1,075	-	-
30	TBP	1.0	11	179	3,500	946
	DBBP	-	2	770	-	-
	DAAP	-	2	2,180	-	-

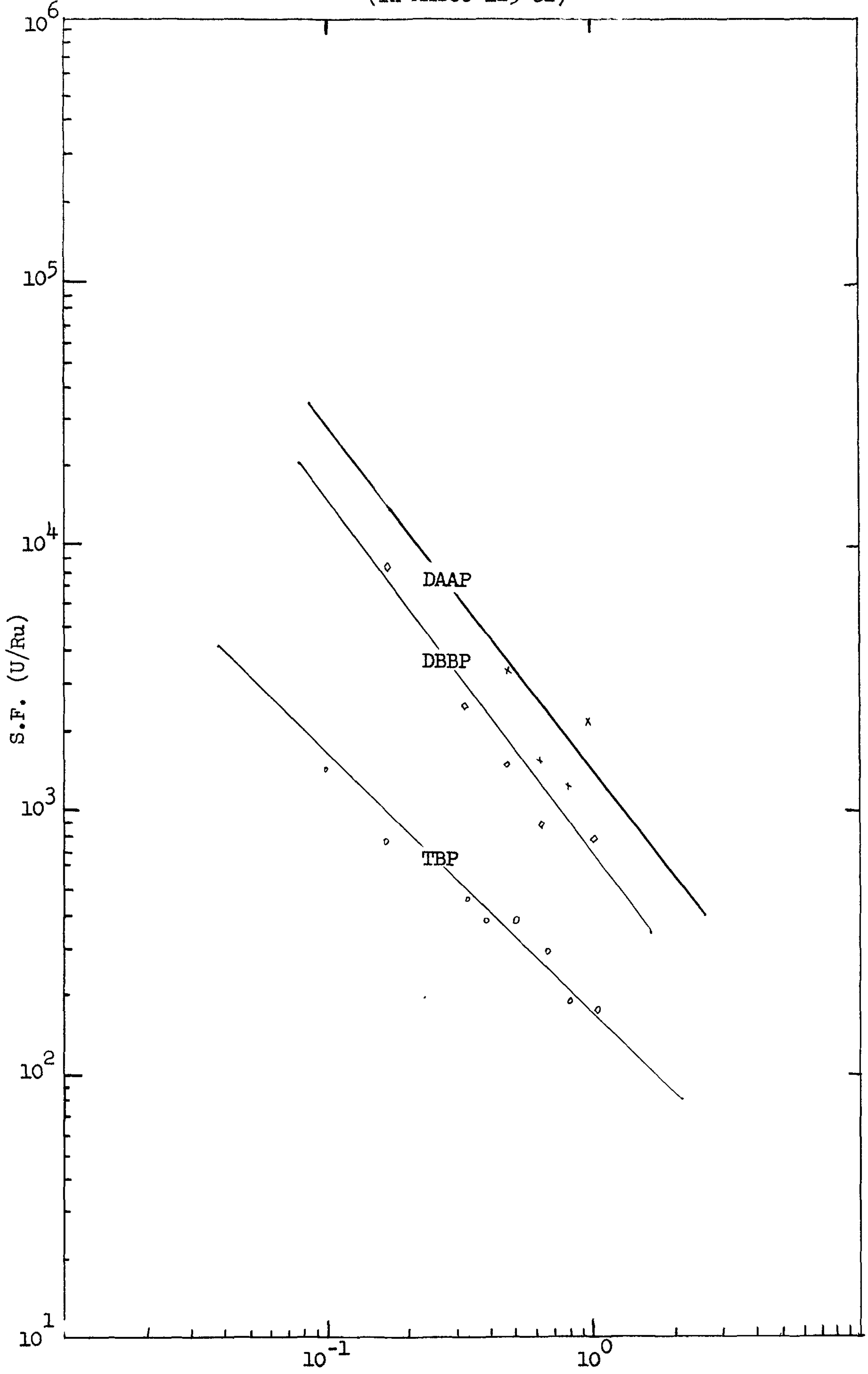
Fig. 27. S.F.'s (U/Th) vs Organic Reagent Concentration
(in Amsco 125-82)



579 60

Fig. 28. S.F.'s (U/Ru) vs Organic Reagent Concentration

(in Amsco 125-82)



579 61

Fig. 29. S.F.'s (U/TRE) vs Organic Reagent Concentration (in Amsco 125-82)

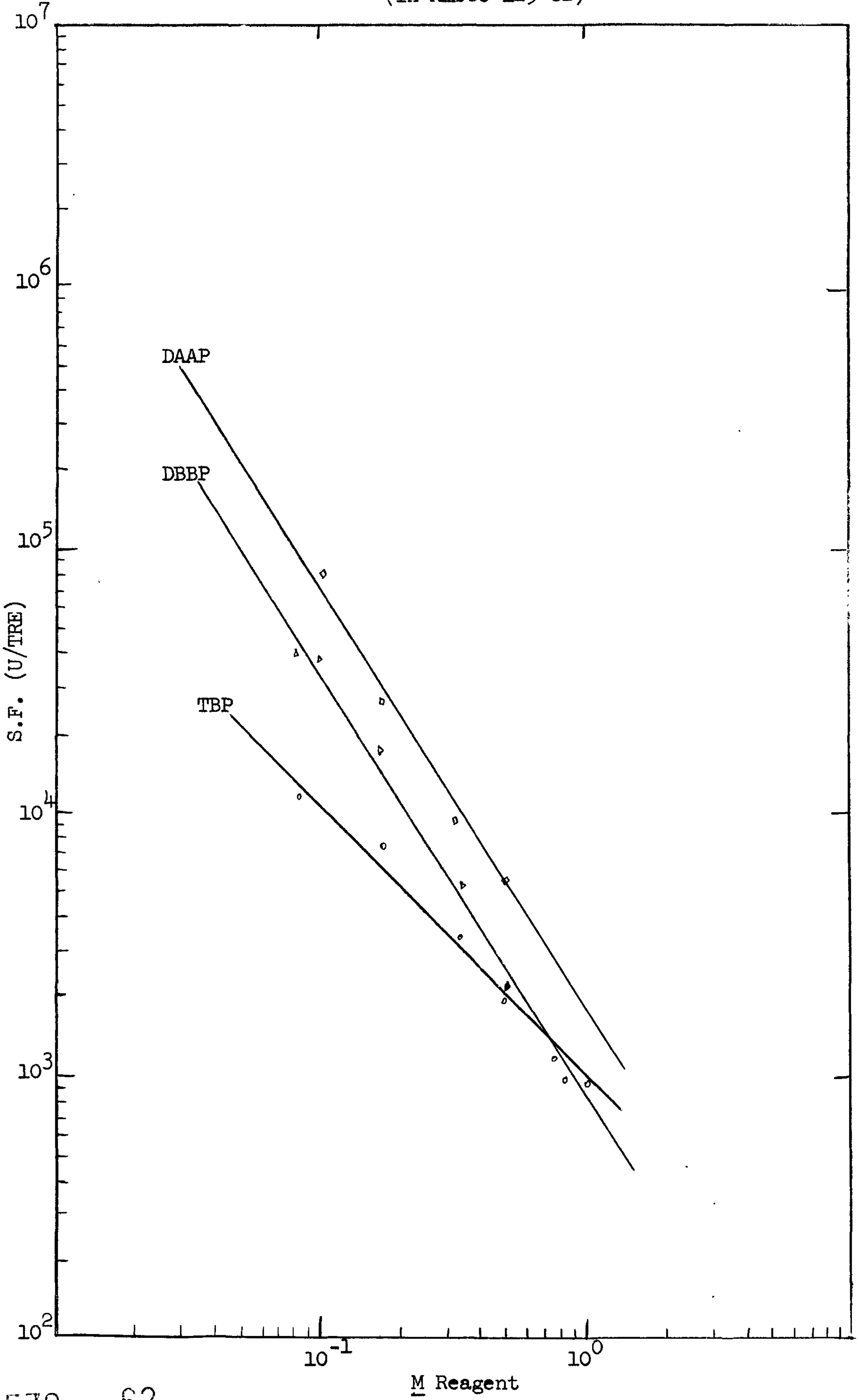
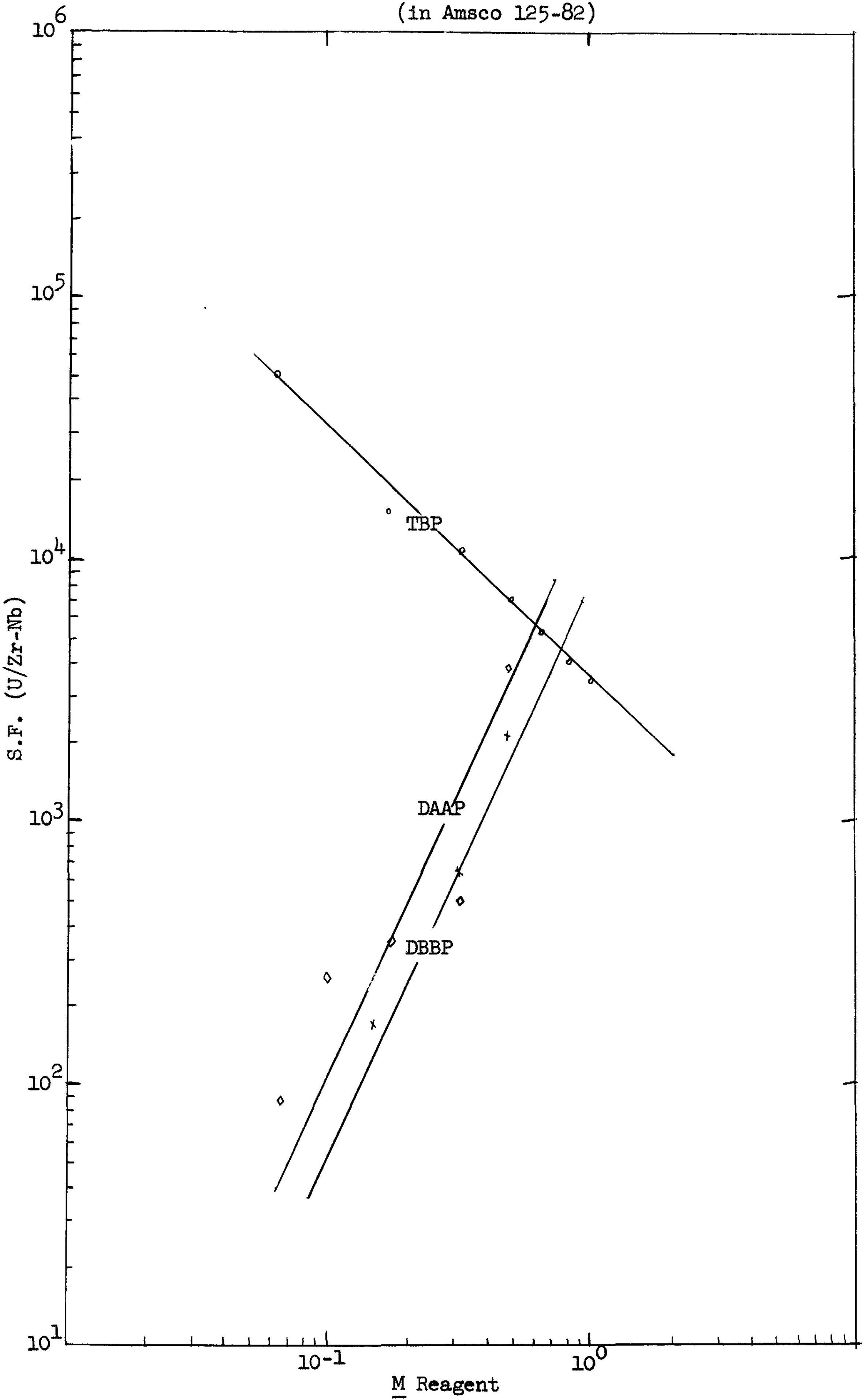


Fig. 30. S.F.'s (U/Zr-Nb) vs Organic Reagent Concentration (in Amsco 125-82)



II. Counter-current Extraction Tests: DC's and EF's of Uranium and HNO_3 in 1.0 M DBPP: Simulated Purex Conditions

Di-n-butyl phenylphosphonate (DBPP) was chosen for the initial counter-current comparison tests because (a) it is a commercially available reagent and sufficient quantities (as opposed to the small experimental batches of the secondary alkylphosphates and DSBPP) were on hand, and (b) its reported high stability to radiolysis (about three times that of TBP) makes it an interesting candidate for a future process extractant for highly irradiated uranium from power reactors, i.e., where radiation damage to the organic reagent may become a prime limitation of the solvent extraction method.

The first tests were performed with unirradiated uranium under simulated co-decontamination-cycle conditions of the Purex process (as per flowsheet listed by E. R. Irish and W. H. Reas in TID-7534, Book 1) to establish a system-profile of uranium and nitric acid distribution.

Table 18 records data from one test with aqueous conditions clearly approximating those of the flowsheet; however, the extractant was inadvertently adjusted to 0.9 M DBPP, so the aqueous feed: organic extractant flow ratio was adjusted from the usual 1/4.75 to 1/5.25 to maintain a reagent U-saturation value of about 76%. Under these conditions the data indicated a total saturation (U + HNO_3) of about 87%, with a slight reflux accounting for about 92% saturation at the feed-point. A very high U-extraction factor ($>10^3$) just below the feed-point accounted for losses of $<10^{-3}$% at the third extraction stage.

Table 19 records data from a similar run in which the HNO_3 concentration of the scrub solution was reduced to 0.01 N to ascertain the effects of a practical minimum of HNO_3-salting on U-recovery. The data indicated a reagent saturation value of about 91% at the feed-point and a U-loss of about 0.02% at the fifth extraction stage (where an extraction factor of only about 1.44 suggested that the system was near-minimum for U-recovery). Interest in such data was based on the possible desirability (owing to the high U-extractability of DBPP) of minimizing HNO_3 concentrations in the aqueous feeds to "high-level waste" evaporators; however, it was recognized that such a system would in practice probably (a) sacrifice Pu IV extractability as well as (b) efficient decontamination from the Ru and Zr-Nb fission products, and (2) would have value only if the cycle were designed specifically for U-recovery and partial decontamination.

Table 20 records data from one counter-current stripping test (with unirradiated uranium) designed for estimation of flow-ratio requirements in the 1.0 M DBPP system. Although the U-concentration in the organic field was somewhat below process conditions, the data suggests that an organic feed:aqueous strip ratio of about 0.5 (compared to 0.73 in the TBP system) will suffice in process operations. A loss of $<10^{-3}$% U was experienced in five stages.

Table 18. U Extraction in 0.9 M DBPP: Countercurrent Test
(Extractant contained 20% xylene; Amsco 125-82 diluent.)

Stage	U (conc.)*	HNO_3 (conc.)*	$D.C._U$ (O/A)	$D.C._H$ (O/A)	EF_U (DC x FR)	EF_H (DC x FR)
6S-O	84.0**	0.083**	3.13	0.041	21.9	0.29
-A	26.8	2.01				
4S-O	88.7	0.071	2.25	0.036	15.8	0.25
-A	39.5	1.96				
2S-O	88.7	0.068	2.08	0.032	14.5	0.22
-A	42.6	2.13				
1E-O	89.6	0.078	1.93	0.030	5.8	0.09
-A	46.5	2.59				
3E-O	0.182	0.430	420	0.195	1260	0.59
-A	0.00043***	2.20				
5E-O	0.0007	0.188	-	0.184	-	0.55
-A	< 0.00005	1.02				

---

* U concentration in g/l; HNO_3 in N.
** DBPP-saturation (U + HNO_3) = 87%.
***Loss at 3rd stage = 0.00069%.

Aqueous Feed: 439 g U/l, 0.94 N HNO_3.
Aqueous Scrub: 2.0 N HNO_3.
Flow Ratio: F/S/O = 1/0.75/5.25 = 4/3/21.
Stages: 5 extraction; 6 scrub Vol. changes = 2.5.

Table 19. U Extraction in 1.0 M DBPP: Counter-current Test

(Extractant contained 20% xylene; Amsco 125-82 diluent.)

Stage	U (conc.)*	HNO_3 (conc.)*	$D.C._U$ (O/A)	$D.C._H$ (O/A)	EF_U (DC x FR)	EF_H (DC x FR)
6S-O	83.0**	0.006**	1.02	0.46	6.46	2.81
-A	81.7	0.013				
4S-O	98.3	0.007	0.76	0.22	4.81	1.39
-A	129.6	0.032				
2S-O	100.9	0.015	0.65	0.20	4.11	1.26
-A	154.9	0.074				
1E-O	105.1	0.015	0.67	0.027	1.82	0.07
-A	156.2	0.56				
3E-O	3.9	0.081	6.4	0.14	17.4	0.38
-A	0.61	0.58				
5E-O	0.24	0.032	0.53	0.09	1.44	0.24
-A	0.045***	0.34				

---

* U concentration in g/l; HNO_3 in N.
** DBPP saturation (U + HNO_3) = 70%.
***Loss at 5th stage = 0.018%.

Aqueous Feed: 439 g U/l, 0.54 N HNO_3.
Aqueous Scrub: 0.01 N HNO_3.
Flow Ratio: F/S/O = 1/0.75/4.75.
Stages: 5 extraction; 6 scrub Vol. changes = 2.5

Table 20. U Stripping from 1.0 M DBPP: Counter-current Test
(Extractant contained 20% xylene; Amsco 125-82 diluent.)

Stage	U (conc.)*	HNO_3 (conc.)*	$D.C._U$ (O/A)	$D.C._H$ (O/A)	EF_U (DC x FR)	EF_H (DC x FR)
5 St-O	0.0006**	-	0.033	-	0.017	-
-A	0.018	0.005				
3 St-O	1.47	0.004	0.23	0.57	0.115	0.29
-A	6.4	0.007				
1 St-O	35.3	0.003	1.12	0.43	0.56	0.22
-A	31.2	0.007				

---

* U concentration in g/l; HNO_3 in N.
**U loss at 5th stage = 0.0009%.

Organic Feed:	1 M DBPP; 64.6 g U/l; 0.006 N HNO_3.
Aqueous Strip:	0.007 N HNO_3.
Flow Ratio:	F/St= 1/2
Stages:	5 strip Vol. changes = 2.5.

IIa. Counter-current Extraction Tests: Distribution of Pu and FP's in 1.0 M DBPP; Simulated Purex Conditions

Following the brief scouting tests with unirradiated uranium, dissolver solutions (obtained from the pilot plant section) were employed as fission-product spikes in low-level counter-current tests, primarily to determine FP distribution in the DBPP-Purex system. (Incidental studies of plutonium extraction were possible; however there were some indications from results that Pu-polymerization, i.e., in the low-acid tracer solution, might have contributed to poor extraction.)

Data in Table 21 was obtained from a test of Purex conditions, employing a quite low FP activity level in the aqueous feed. Gross β and γ DF's, through the four scrub stages, were measured at only 119 and 765, respectively; while Pu-recovery, despite sodium nitrite treatment of the feed (for oxidation to Pu IV), was only about 25%. On the basis of well-controlled batch tests (see Table 12), which indicated a very high extractability of Pu IV in 1.0 M DBPP under conditions of the given test, it was assumed that the given oxidation treatment was incomplete, and/or effective on only a limited fraction of the Pu in the aqueous feed, e.g., possibly due to a state of polymerization. Incomplete analytical results (owing partially to insufficient volumes and the low counting rates) did not permit reliable interpretation of specific FP behavior; however the relatively low gross γ EF (0.166) at the fourth scrubbing stage signifies that additional stages would have improved the γ DF (and/or Zr-Nb DF) somewhat.

Table 22 records data from tests of a "head-end treatment" of a Purex aqueous feed which was designed (on the basis of data in Table 8) to check the possibility that D2EHPA extraction could be employed to preferentially remove hypothetical DBPP-extractable fractions of the Zr-Nb fission product, i.e., prior to the co-decontamination cycle. (The final step, HS3, was intended to remove possibly deleterious soluble quantities of the organic acid from the feed by Amsco 125-82 washing.)

Table 23 records results of the subsequent counter-current test, which employed conditions similar to those in Table 19, i.e., with minimum aqueous HNO_3-salting. Gross β and γ DF's of 1500 and 970 indicated the possibility of some slight overall improvement in decontamination. The specific data revealed an overall Zr-Nb DF of about 1850 and a Ru DF of 630 at the fourth scrubbing stage, with little or no improvement through the sixth stage. (These data, obtained with low-activity feeds, are not believed to permit reliably definitive DF's, so the D2EHPA treatment may deserve future tests in a more well-defined study.)

The data for a comparable counter-current test (employing an untreated feed) is recorded in Table 24. Zr-Nb and Ru DF's of 5750 and 336 in this case would seem to suggest that the previously discussed head-end treatment actually adversely affected Zr-Nb DF's, while contributing to enhanced Ru DF's; however it is not believed that such a conclusion is justifiable at this time.

It was observed that essentially no decontamination was effected past the second scrubbing stage. The rather poor γ material balance (e.g., gross γ vs Ru γ plus Zr-Nb γ) would appear to raise the possible question of some unknown fission product in the organic product stream, i.e., 6S-O. Under conditions of this test (i.e., low aqueous acidity, ca 0.25 N HNO_3), it was expected that Ru decontamination would be adversely affected.

Table 25 records gross β and γ distribution in a stripping test. Essentially no DF's (e.g., ca 1.2) were observed. About one-sixth of the γ activity appeared to be quite effectively retained in the organic waste stream, i.e., 5 St-O.

Table 21. Pu and F.P. Extraction in 1 M DBPP: Counter-current Test
(Extractant was 20% xylene; Amsco 125-82 diluent.)

Stage	Pu α	Gross β	Gross γ	Ru γ	Zr-Nb γ
4S-O*	0.028*	0.025	0.0024	-	0
-A	0.083	0.161	0.0917	0.0096	0.0563
(EF$_a^o$)	(2.14)	(0.98)	(0.166)	(-)	(-)
2S-O	0.0344	0.0316	0.0074	-	0.0035
-A	-	2.7	1.41	0.15	0.861
(EF$_a^o$)	(-)	(0.074)	(0.033)	(-)	(0.026)
1E-O	0.038	0.0427	0.0183	<0.0045	0.0122
-A	0.14	15.0	8.58	0.68	5.19
(EF$_a^o$)	(0.74)	(0.0077)	(0.0058)	(-)	(0.0064)
3E-O	0.0075	0.328	0.0945	0.0463	0.0505
-A**	0.065	13.0	8.84	0.58	5.28
(EF$_a^o$)	(0.314)	(0.069)	(0.029)	(0.22)	(0.026)

---

* Pu recovery = 24.6%; DBPP saturation (U + HNO_3) was 90.4%.
**U loss was 0.004%.
NOTE: Pu and F.P. activities in c/m/ml x 10^{-5}; $EF_a^o = DC_a^o \times FR_a^o$.
Aqueous Feed = 437 g U/l, 1.15 N HNO_3, 0.05 N $NaNO_2$, 5.4 x 10^4 Pu α c/m/ml, 1.41 x 10^6 gross β c/m/ml, 8.73 x 10^5 gross γ c/m/ml, 7.17 x 10^4 Ru γ c/m/ml, 4.95 x 10^5 Zr-Nb γ c/m/ml.
Aqueous Scrub = 1.93 N HNO_3; Flow Ratio: F/S/O = 1/0.75/4.75; Vol. changes = 5.

Table 23. D2EHPA Head-end Extraction of Zr-Nb: Batch Tests
(0.001 M D2EHPA in Amsco 125-82; "Purex"-type Aqueous Feed.)

Stage	U	Pu α	Gross β	Gross γ	TRE β	Ru γ	Zr-Nb γ
HS3-O	-	0.001	0.0045	0.0036	0.0002	0.00022	0.0057
-A	403.1	0.731	73.1	117.0	52.2	5.37	33.0
(EF^o_a)	-	(0.0014)	(0.000006)	(0.00003)	(0.000004)	(0.00004)	(0.0002)
HE2-O	0.14	0.0028	0.0088	2.97	0.001	0.0017	2.7
-A	406.0	0.715	74.4	114.0	50.0	5.22	35.4
(EF^o_a)	(0.0003)	(0.04)	(0.001)	(0.026)	(<0.00002)	(<0.0003)	(0.08)
HE1-O	0.126	0.0044	1.45	19.1	0.0044	-	16.7
-A	383.5	0.755	76.4	120.0	51.4	5.03	35.4
(EF^o_a)	(0.0003)	(0.058)	(0.019)	(0.16)	(0.0009)	-	(0.48)

NOTE: U concentration in g/l; activities in c/m/ml x 10^{-5}; $EF^o_a = DC^o_a \times FR^o_a$.

Aqueous Feed: 390 g U/l, 0.63 N HNO_3, 8.2 x 10^4 Pu α c/m/ml, 8.1 x 10^6 gross β c/m/ml, 1.47 x 10^7 gross γ c/m/ml, 5.4 x 10^6 TRE β c/m/ml, 5.6 x 10^5 Ru γ c/m/ml, 4.4 x 10^6 Zr-Nb γ c/m/ml; extracted with two successive passes (HE1 and 2) of 0.001 M D2EHPA in 1:1 ratio; then scrubbed with one pass (HS-3) of Amsco 125-82; 25 to 43% of Zr-Nb and 1 to 12% Pu extracted; HS3-A used subsequently in counter-current tests with 1.0 M DBPP.

Table 23. Pu and F.P. Extraction in 1.0 M DBPP: Counter-current Test (Following D2EHPA Head-end Extraction of Zr-Nb.)

Stage	Pu α	Gross β	Gross γ	TRE β	Ru γ	Zr-Nb γ
6S-O	0.00149*	0.01	0.0255	0.0002	0.0018	0.005
-A	0.007	0.023	0.0541	-	-	0.009
(EF^o_a)	(0.133)	(2.78)	(2.97)	-	-	(3.54)
4S-O	0.0064	0.012	0.044	0.0003	0.0018	0.0054
-A	0.299	-	0.39	-	-	0.0565
(EF^o_a)	(0.133)	-	(0.7)	-	-	(0.6)
2S-O	0.05	0.011	0.046	0.0006	0.003	0.0111
-A	0.72	1.06	1.66	0.585	-	0.31
(EF^o_a)	(0.443)	(0.063)	(0.18)	(0.006)	-	(0.23)
1E-O	0.077	0.0164	0.063	0.0041	0.0073	0.0135
-A	0.614	72.2	109.0	46.6	5.55	20.9
(EF^o_a)	(0.326)	(0.0005)	(0.0016)	(0.0002)	(0.0035)	(0.0019)
3E-O	0.056	1.73	3.07	0.781	0.912	0.023
-A	0.569	67.6	107.0	46.6	5.76	21.1
(EF^o_a)	(0.272)	(0.082)	(0.082)	(0.046)	(0.435)	(0.003)
5E-O	0.006	0.46	0.681	0.41	0.103	0.025
-A**	0.395	66.1	95.9	48.8	3.77	21.1
(EF^o_a)	(0.041)	(0.019)	(0.019)	(0.023)	(0.074)	(0.003)

---

*Pu recovery = 1.0%

**U loss = 0.004%

NOTE: Activities in c/m/ml x 10^{-5}; EF^o_a = D.C.^o_a x F.R.

Aqueous Feed: 403 g U/1, 0.63 N HNO_3, 7.3 x 10^4 Pu α c/m/ml, 7.3 x 10^6 gross β c/m/ml, 1.17 x 10^7 gross γ c/m/ml, 5.22 x 10^6 TRE β c/m/ml, 5.37 x 10^5 Ru γ c/m/ml, 2.2 x 10^6 Zr-Nb γ c/m/ml; Aqueous Scrub: 0.01 N HNO_3; Org: 1 M DBPP, 20% xylene, in Amsco 125-82 diluent; Flow Ratio: F/S/O = 1/0.75/4.75; 3 Vol. changes.

Table 24. Pu and F.P. Extraction in 1 M DBPP: Countercurrent Test
(Extractant contained 20% xylene; Amsco 125-82 diluent.)

Stage	Pu α*	Gross β	Gross γ	TRE β	Ru γ	Zr-Nb γ
6S-0	0.006	0.0098	0.0354	< 0.0008	0.00294	0.0015
-A	0.0285	0.0147	0.0493	-	-	0.006
(EF_a^o)	(1.26)	(4.2)	(4.55)	-	-	(1.58)
4S-0	0.001	0.0091	0.040	< 0.0005	0.003	0.001
-A	0.0573	0.0380	0.115	-	0.0371	0.0044
(EF_a^o)	(0.11)	(1.52)	(2.22)	-	(0.51)	(1.46)
2S-0	0.001	0.0135	0.0484	< 0.0004	0.0035	0.0016
-A	0.205	0.353	0.859	-	0.20	0.11
(EF_a^o)	(0.032)	(0.24)	(0.35)	-	(0.114)	(0.13)
1E-0	0.0404	0.0278	0.0982	0.0028	0.002	0.014
-A	0.554	49.2	94.5	33.7	3.9	20.0
(EF_a^o)	(0.19)	(0.0016)	(0.003)	(0.0002)	(0.0014)	(0.0019)
3E-0	0.0637	1.46	3.24	0.25	1.22	0.024
-A	0.656	52.8	101.0	35.0	4.1	24.5
(EF_a^o)	(0.27)	(0.076)	(0.087)	(0.019)	(0.815)	(0.003)
5E-0	0.0209	0.508	0.947	0.30	0.208	0.052
-A	0.430	50.9	104.0	42.1	2.7	27.0
(EF_a^o)	(0.136)	(0.027)	(0.024)	(0.02)	(0.191)	(0.005)

---

*$NaNO_2$ was not added to adjust the Pu valence to +4.
NOTE: Pu and F.P. activities in c/m/ml x 10^{-5}; EF_a^o = D.C.$_a^o$ x F.R.$_a^o$;
Aqueous Feed = 1.8 M U, 0.5 N HNO_3, 5.3 x 10^4 Pu α c/m/ml, 6.75 x 10^6 gross β c/m/ml, 1.36 x 10^7 gross γ c/m/ml, 4.5 x 10^6 TRE β c/m/ml, 4.7 x 10^5 Ru γ c/m/ml, 4.1 x 10^6 Zr-Nb γ c/m/ml;
Aqueous Scrub = 0.01 N HNO_3; Flow Ratio: F/S/O = 1/0.75/4.75; Vol. changes = 2.5.

Table 25. U and F.P. Stripping from 1 M DBPP: Counter-current Test

(Extractant contained 20% xylene; Amsco 125-82 diluent.)

Stage	U	HNO_3	Gross β	Gross γ
5 St-O	0.0086	0.003	0.0016	0.0073
-A	0.243	$<$ 0.01	-	0.0009
(EF^o_a)	(0.018)	-	-	(4.1)
3 St-O	8.27	$<$ 0.01	0.0047	0.0129
-A	13.2	$<$ 0.01	-	0.0052
(EF^o_a)	(0.313)	-	-	(1.24)
1 St-O	48.2	0.01	0.0067	0.0242
-A	37.5	$<$ 0.01	0.0071	0.0187
(EF^o_a)	(0.64)	-	(0.47)	(0.65)

NOTE: U in g/1, HNO_3 in N, activities in c/m/ml x 10^{-5}; $EF^o_a = DC^o_a \times FR^o_a$.
Organic Feed = 1 M DBPP, 74.4 g U/1, 1.78 x 10^3 β c/m/ml, 4.4 x 10^3 γ c/m/ml.
Aqueous Strip = 0.01 N HNO_3; Flow Ratio: F/St= 1/2; Vol. changes = 2.5
(Organic feed was composited from extraction test recorded in Table 24.)

IIb. Counter-current Extraction Tests: U, HNO_3, FP Distribution in 0.2 M DBPP (Simulated 25-Process)

Table 26 records data from a test with 0.2 M DBPP, 10% xylene (in Amsco 125-82 diluent) as the uranium extractant in a simulated "TBP-25" process. It was observed that the uranium was rather efficiently extracted (less than 0.1% loss at the third extraction stage). A rather poor Zr-Nb DF of only 700 effectively limited the gross γ DF to about 1210; however, it is believed that $SO_4^=$ or $PO_4^=$ ion, added to the aqueous scrub solution, would effectively complex the extracted Zr-Nb to permit significantly improved overall DF's. Again it was noted that little decontamination occurred after the second scrubbing stage.

In general, it is believed that a dilute DBPP system may constitute a reasonably good substitute for either of the presently utilized TBP-25 or Interim-23 processes, i.e., where dilute TBP is employed. Initial tests of a simulated Interim-23 process have shown imperfect separation of U from Th and unexplainable U-losses; however, it is believed that minor modifications of aqueous salting strengths and flow ratios will provide a workable system for U-233 recovery from irradiated thorium (Pa-233 and FP's).

Table 26. U and F.P. Extraction in 0.2 M DBPP: Counter-current Test

(Extractant was 10% xylene; Amsco 125-82 diluent.)

Stage	U	HNO_3	Gross β	Gross γ	Ru γ	Zr-Nb γ
6S-O*	8.27	0.12	0.0103	0.122	-	0.091
-A	2.83	3.03	0.0059	0.0448	0.0005	0.026
(EF^o_a)	(5.85)	(0.08)	(3.5)	(5.45)	(-)	(7.0)
4S-O	7.27	0.10	0.0093	0.115	-	0.063
-A	5.31	3.05	0.0165	0.175	0.0013	0.08
(EF^o_a)	(2.74)	(0.06)	(1.13)	(1.31)	(-)	(1.57)
2S-O	6.9	0.08	0.0101	0.102	-	0.059
-A	8.41	3.11	0.115	0.614	-	0.35
(EF^o_a)	(1.64)	(0.05)	(0.18)	(0.33)	(-)	(0.34)
1E-O	6.21	0.06	0.138	0.799	-	0.63
-A	2.47	1.01	48.2	88.0	3.1	28.0
(EF^o_a)	(0.84)	(0.02)	(0.00095)	(0.003)	(-)	(0.0075)
3E-O	0.65	0.02	2.71	11.8	0.011	5.8
-A	0.0042**	0.93	46.9	85.6	3.1	22.6
(EF^o_a)	(51.6)	(0.007)	(0.019)	(0.046)	(0.0012)	(0.086)
5E-O	0.0025	0.02	1.56	6.05	0.0093	3.6
-A	0.0001	0.91	49.3	85.1	3.1	18.0
(EF^o_a)	(-)	(0.007)	(0.011)	(0.024)	(0.001)	(0.067)

---

* DBPP saturation ($U + HNO_3$) = 93.7%.

**U loss at third stage = 0.095%.

NOTE: U in g/l, HNO_3 in N activities in c/m/ml x 10^{-5}; $EF^o_a = DC^o_a \times FR^o_a$.

Aqueous Feed: 1.83 M $Al(NO_3)_3$, 5.05 g U/l, 0.62 N HNO_3, 5.46 x 10^6 gross β c/m/ml, 9.04 x 10^6 gross γ c/m/ml, 3.7 x 10^5 Ru γ c/m/ml, 3.9 x 10^6 Zr-Nb γ c/m/ml, 3.7 x 10^6 TREβ c/m/ml; Aqueous Scrub: 3.0 N HNO_3; Flow Ratio: F/S/O = 5/1/2; 3 Vol. changes.

IIc. Counter-current Extraction Tests: Direct Comparisons of 1 M DSBPP, 1 M TBP, and 1 M DBPP; (Simulated Purex Process)

Tables 27 and 28 record data from a series of counter-current extraction tests designed to afford direct "Purex" comparisons (co-decontamination cycle) of the two alkyl phenylphosphonates, DSBPP and DBPP, with TBP (in both Amsco 125-82 and xylene diluents). Since the aromatic diluent (xylene) had been observed in batch tests to influence separation factors in the TBP system, it was desirable to demonstrate the extent of such effects in hypothetical counter-current process tests.

Each of the four organic extractants were employed under identical flow systems and with identical aqueous feeds and scrubbing solutions, to permit the nearest possible duplication of conditions, i.e., with the exception of the variable, the extractant. The data appears to confirm expectations suggested by previous batch tests.

Data in Table 27 generally illustrates the higher U-extractability in the order of (1) DBPP, (2) DSBPP, (3) TBP-xylene, and (4) TBP-Amsco 125-82, and suggests that three extraction stages in the DBPP and DSBPP systems are essentially equivalent (regarding U-losses) to four extraction stages in the TBP-Amsco system.

Data in Table 28 illustrates the measurable superiority (x3 and x1.5) of DSBPP over TBP-Amsco 125-82 in β and γ decontamination efficiency, and the slight inferiority (x1.5) of DBPP.

However, as predicted in batch studies, the TBP-xylene very closely approximates the DSBPP in decontamination efficiency, as well as in uranium extractability. Approximately three-to-four stages in scrubbing were reasonably effective for decontamination in all cases.

Table 27. Comparison of U and H^+ Extraction in 1.0 M DSBPP, TBP, and DBPP: Counter-current Tests

	Uranium				HNO_3			
Stage	1 M DSBPP (in Xylene)	1 M TBP (in Xylene)	1 M TBP (in Amsco)	1 M DBPP (20% Xylene)*	1 M DSBPP (in Xylene)	1 M TBP (in Xylene)	1 M TBP (in Amsco)	1 M DBPP (20% Xylene)*
6S-O	97.4	92.6	83.6	90.0	0.14	0.12	0.10	0.10
-A	21.0	20.6	30.1	18.4	1.89	1.85	1.87	1.94
(EF^o_a)	(28.4)	(28.4)	(17.6)	(31.0)	(0.47)	(0.41)	(0.34)	(0.33)
1E-O	99.0	97.4	100.0	92.2	0.14	0.10	0.08	0.12
-A	32.6	30.5	82.1	19.9	2.47	2.23	2.18	2.46
(EF^o_a)	(8.25)	(8.68)	(3.31)	(12.55)	(0.15)	(0.12)	(0.10)	(0.13)
3E-O	0.185	0.156	0.79	0.117	0.4	0.35	0.36	0.37
-A	0.006	0.008	0.05	0.005	1.6	1.58	1.84	1.73
(EF^o_a)	(84.0)	(53.0)	(43.0)	(63.6)	(0.68)	(0.60)	(0.53)	(0.58)
5E-O	-	0.0013	0.007	-	-	0.13	0.14	-
-A	-	0.0011	0.002	-	-	0.75	0.85	-
(EF^o_a)	(-)	(3.2)	(9.5)	(-)	(-)	(0.47)	(0.45)	(-)

---

* In Amsco 125-82 diluent.

NOTE: U in g/l; HNO_3 in N; $EF^o_a = DC^o_a \times FR^o_a$.
Aqueous Feed: 434 g U/l, 1.11 N HNO_3, 1.35×10^7 gross β c/m/ml, 1.83×10^7 gross γ c/m/ml, . x 10 TRE β c/m/ml, . x 10 Ru γ c/m/ml, . x 10 Zr-Nb c/m/ml.
Aqueous Scrub: 2.0 N HNO_3; Flow Ratio: F/S/O = 1/0.75/4.75; 2.5 Vol. changes.

Table 28. Comparison of Gross β and γ Extraction in 1.0 M DSBPP, TBP, and DBPP: Counter-current Tests

Stage	Gross β				Gross γ			
	1 M DSBPP (in Xylene)	1 M TBP (in Xylene)	1 M TBP (in Amsco)	1 M DBPP (20% Xylene)*	1 M DSBPP (in Xylene)	1 M TBP (in Xylene)	1 M TBP (in Amsco)	1 M DBPP (20% Xylene)*
6S-O	0.0073	0.0055	0.0190	0.0340	0.0293	0.0279	0.0393	0.0632
-A	0.0169	0.0115	0.0142	0.0826	0.0285	0.0185	0.0238	0.1120
(EF_a^o)	(2.73)	(3.03)	(8.5)	(2.6)	(6.5)	(9.55)	(10.45)	(3.58)
4S-O	0.0084	-	0.0285	0.0498	0.0337	-	0.0512	0.0848
-A	0.159	-	0.0942	0.385	0.218	-	0.136	0.483
(EF_a^o)	(0.334)	(-)	(1.92)	(0.82)	(0.98)	(-)	(2.38)	(1.11)
2S-O	0.0345	0.0277	0.0357	0.122	0.0341	0.0671	0.0608	0.179
-A	2.45	1.04	0.684	3.26	3.86	1.50	1.95	4.65
(EF_a^o)	(0.089)	(0.17)	(0.33)	(0.237)	(0.056)	(0.283)	(0.197)	(0.244)
1E-O	0.047	0.053	0.0833	0.322	0.0884	0.128	0.122	0.414
-A	88.8	80.4	136.0	99.0	135.0	118.0	132.0	144.0
(EF_a^o)	(0.0014)	(0.0018)	(0.0017)	(0.0089)	(0.0018)	(0.0029)	(0.0025)	(0.0078)
3E-O	0.92	1.34	2.75	3.99	1.13	1.71	4.16	6.68
-A	85.2	88.1	80.6	93.5	114.0	127.0	134.0	147.0
(EF_a^o)	(0.029)	(0.041)	(0.093)	(0.116)	(0.027)	(0.037)	(0.084)	(0.123)
5E-O	0.387	0.573	1.44	1.87	0.476	0.732	2.06	4.79
-A	98.0	77.5	79.6	84.5	126.0	123.0	125.0	126.0
(EF_a^o)	(0.011)	(0.02)	(0.049)	(0.06)	(0.01)	(0.016)	(0.045)	(0.103)

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* In Amsco 125-82 diluent.

NOTE: Gross β and γ in c/m/ml x 10^{-5}; $EF_a^o = DC_a^o \times FR_a^o$

Aqueous Feed: 434 g U/l, 1.11 N HNO_3, 1.35 x 10^7 gross β c/m/ml, 1.83 x 10^7 gross γ c/m/ml, . x 10 TRE β c/m/ml, . x 10 Ru γ c/m/ml, . x 10 Zr-Nb c/m/ml.

Aqueous Scrub: 2.0 N HNO_3; Flow Ratio: F/S/O = 1/0.75; 2.5 Vol. changes.

III. Summary: Evaluations of the Alkyl Phenylphosphonates as Solvent Extractants in Processes for Recovery and Decontamination of Irradiated Uranium and Thorium

Studies of the organo-phosphorus compounds (A) di-sec-butyl phenylphosphonate, DSBPP (prepared in experimental quantities at Oak Ridge National Laboratory), and (B) di-n-butyl phenylphosphonate, DBPP (a commercially available product), have indicated: that (I) DSBPP is a worthy competitor of tri-n-butyl phosphate, TBP, as an extraction process reagent for the recovery and decontamination of irradiated (a) natural or slightly-enriched uranium (e.g. the Purex process, for extraction of U-238 and plutonium-239), (b) highly-enriched uranium (e.g. the TBP-25 process, for extraction of U-235), and (c) uranium-233 (e.g. the Interim-23 process, for extraction of U-233 from thorium); and, that (II) DBPP may be a worthy competitor of TBP for the recovery and decontamination of (d) irradiated thorium (e.g. the Thorex process, for the extraction of U-233 and Th-232); and/or that (III) some mixture of DSBPP and DBPP may compose a worthy competitor of TBP for general use in all four recovery processes, i.e. a, b, c, and d, above.

The greatest comparative worth of the two alkyl phenyl phosphonates, i.e. in comparisons with TBP, is conceived to lie in their higher order (x 2.65 to x 5.67) of stability to decomposition or damage by radiation, e.g. as illustrated in the following experimental data:

Radiation Damage: G Values

	DSBPP	DBPP	TBP
G (gas)	0.33	0.49	1.87
G (H_2)	0.13	-	>1.00
G (mono-acid)	0.54	0.78	2.07

G = number of molecules converted per 100 ev of energy

This greater stability may represent a significant advantage (a) in the future processing of highly irradiated power reactor fuels, and (b) in instances where the processing of fuels after short cooling periods is desirable, e.g. for reduction of inventory charges on expensive fissionable materials.

A second significant advantage of DSBPP and/or DBPP, i.e. in comparisons with TBP, lies in their higher extractability of uranium and plutonium, thereby affording the potential for lower product losses and/or fewer stages in countercurrent extraction, e.g.

Uranium Distribution Coefficient (DC_a^o)

Aqueous Phase*	1.11 M DSBPP (in xylene)	1.11 M DBPP (in xylene)	1.01 M TBP (in Amsco 125-82)
3.0 N HNO_3	37.8	52.7	31.0
0.8 N HNO_3	16.5	19.4	6.24
0.2 N HNO_3	7.5	11.1	2.9

*11.3 g U/l, 5.03 g Th/l; o/a ratio = 1.0.

In the specific case of uranium extraction, the above data suggests that very significantly lower aqueous HNO_3 or nitrate salting concentrations could be employed in process operations, i.e. to reduce chemical costs and/or to alleviate problems in evaporation of the high-level radioactive waste solutions. (It has been observed that the extracted complexes of DSBPP and DBPP, as expected, are identical in form to those of TBP, i.e. $2\ R_3P \cdot UO_2(NO_3)_2$, $R_3P \cdot HNO_3$, etc.)

Plutonium(IV) Distribution Coefficient (DC_a^o)

Aqueous Phase*	1.11 M DSBPP (in xylene)	1.11 M DBPP (in xylene)	1.01 M TBP (in Amsco 125-82)
3.0 N HNO_3	19.0	34.0	15.0
1.5 N HNO_3	6.8	12.0	4.9
0.6 N HNO_3	0.32	0.57	0.20
0.2 N HNO_3	0.045	0.093	0.016

*0.000055 M Pu(IV); o/a ratio = 1.0.

The plutonium(IV) distribution indicates that initial co-decontamination cycles (i.e. for both uranium and plutonium) would also be operable at somewhat lower aqueous acid or salting concentrations, and/or that lower product losses could be achieved under equivalent aqueous conditions.

Thorium Distribution Coefficient (DC_a^o)

Aqueous Phase*	1.11 M DSBPP (in xylene)	1.11 M DBPP (in xylene)	1.01 M TBP (in Amsco 125-82)
3.0 N HNO_3	0.163	4.4	1.75
0.8 N HNO_3	0.057	0.934	0.46
0.2 N HNO_3	0.029	0.025	0.132

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*11.3 g U/l, 5.03 g Th/l; o/a ratio = 1.0.

The lower thorium distribution in DSBPP (and/or the higher U DC/Th DC ratio) suggests that more efficient separation of U-233 from thorium (e.g. in the Interim-23 process) would be possible. The higher thorium distribution in DBPP would readily permit its use (or the use of DBPP-DSBPP mixtures) for recovery of thorium and U-233 in processes such as the Thorex process.

A third major advantage is particularly associated with the DSBPP, i.e. the potential for higher (or at least equivalent) uranium and plutonium decontamination from fission products. The lower gross β and γ distribution coefficients (and particularly the more favorable separation factors, i.e. the U DC/gross F.P. DC ratios) as tabulated below, though partially attributable to the use of the aromatic xylene (instead of the essentially aliphatic Amsco 125-82) as the reagent diluent, are known to result primarily from the secondary branching of DSBPP's butyl radical. (The data for DBPP indicates that a small disadvantage exists in its potential for F.P. decontamination; however, it is conceivable that a mixture of DBPP and DSBPP would provide a reagent comparable or equivalent with TBP in this regard.)

Gross γ Distribution Coefficient (DC_a^o)

Aqueous Phase*	1.11 M DSBPP (in xylene)	1.11 M DBPP (in xylene)	1.01 M TBP (in Amsco 125-82)
3.0 N HNO_3	0.007	0.021	0.018
0.8 N HNO_3	0.006	0.015	0.017
0.2 N HNO_3	0.007	0.018	0.016

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*11.3 g U/l, 5.03 g Th/l; o/a ratio = 1.0.

The above advantage of DSBPP in γ D.C.'s is known to reflect primarily a lower extractability of the Zr-Nb fission product. On the basis of its evidently higher U DC/gross γ DC ratio, an even larger potential advantage (than indicated in the DC data) is possible in countercurrent systems adjusted to provide equivalent uranium or plutonium extraction factors (DC times volume flow ratios).

Gross β Distribution Coefficient (DC^o_a)

Aqueous Phase*	1.11 M DSBPP (in xylene)	1.11 M DBPP (in xylene)	1.01 M TBP (in Amsco 125-82)
3.0 N HNO_3	0.006	0.023	0.013
0.8 N HNO_3	0.008	0.016	0.017
0.2 N HNO_3	0.009	0.023	0.016

*11.3 g U/l, 5.03 g Th/l; o/a ratio = 1.0.

The above advantage of DSBPP in β D.C.'s reflects primarily a lower extractability of the Ru and Zr-Nb fission products. (A slightly higher extractability of the "total rare earth" fission products was observed in the given experiments.)

The latter two above-mentioned advantages of higher uranium and plutonium extractability (in DSBPP and DBPP) and lower fission product extractability (in DSBPP, or perhaps DSBPP-DBPP mixtures) has been demonstrated in batch countercurrent tests employing the three organic extractants with identical aqueous conditions and volumetric flow ratios (simulating the system of a Purex co-decontamination cycle).

The table below illustrates the considerably higher extraction factors (EF^o_a = DC^o_a x the o/a flow ratio) of uranium in the DBPP and DSBPP, as observed in the last scrubbing stage (e.g. 6-Sc), the aqueous feed point or first extraction stage (I-Ex), and the third extraction stage (3-Ex).

Uranium Extraction Factors (EF^o_a)

Countercurrent Stage	1 M DSBPP (in xylene)	1 M DBPP* (20% xylene)*	1 M TBP (in Amsco 125-82)
6-Sc	28.4	31.0	17.6
1-Ex	8.25	12.55	3.31
3-Ex	84.0	63.6	43.0

*Amsco 125-82 diluent.

It was noted that adjustments (in the DSBPP and DBPP case) to lower aqueous HNO_3 or salting strengths could have been employed to reduce the uranium DC^o_a (and/or the EF^o_a) without sustaining product losses any greater than experienced in the given TBP system.

The lower extractability of β-emitting fission products in DSBPP, and the somewhat higher extractability in DBPP is illustrated in the data below:

Gross β Extraction Factors (EF^o_a)

Counter-current Stage	1 M DSBPP (in xylene)	1 M DBPP* (20% xylene)*	1 M TBP (in Amsco 125-82)
6-Sc	2.73	2.6	8.5
4-Sc	0.334	0.82	1.92
2-Sc	0.089	0.237	0.33
1-Ex	0.0014	0.0089	0.0017
3-Ex	0.029	0.116	0.093
5-Ex	0.011	0.06	0.049

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*Amsco 125-82 diluent.

Similar circumstances for the γ-emitting fission products is illustrated in the data below. It is pertinent to note in both the gross β and γ cases that extraction factors greater than unity (signifying little or no potential for decontamination) are attained at the fourth scrubbing stage in the given TBP system.

Gross γ Extraction Factors (EF^o_a)

Counter-current Stage	1 M DSBPP (in xylene)	1 M DBPP* (20% xylene)*	1 M TBP (in Amsco 125-82)
6-Sc	6.5	3.58	10.45
4-Sc	0.98	1.11	2.38
2-Sc	0.056	0.244	0.197
1-Ex	0.0018	0.0078	0.0025
3-Ex	0.027	0.123	0.084
5-Ex	0.01	0.103	0.045

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*Amsco 125-82 diluent.

The comparative gross β and γ decontamination factors are tabulated below. As predicted from previous batch extraction data, the higher decontamination potential of DSBPP and the lower potential of DBPP is indicated.

Gross β Decontamination Factors (DF)

Counter-current Stage	1 M DSBPP (in xylene)	1 M DBPP* (20% xylene)*	1 M TBP (in Amsco 125-82)
6-Sc	3900	840	1500
4-Sc	3380	570	1000
2-Sc	825	233	800
1-Ex	606	88	346

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*Amsco 125-82 diluent.

In the data below, it is pertinent to note in all cases that relatively small D.F.'s are achieved in the scrubbing portion of the given co-decontamination cycle, i.e. about 6 in the DBPP case versus about 3 in the DSBPP and TBP cases. (A subsequent extraction cycle, adjusted chemically to provide specific separations from Ru and Zr-Nb, would probably be expected to lessen the differences in overall decontamination achieved by the three reagents.)

Gross γ Decontamination Factor (DF)

Counter-current Stage	1 M DSBPP (in xylene)	1 M DBPP (in xylene)	1 M TBP (in Amsco 125-82)
6-Sc	1320	610	1010
4-Sc	1145	456	755
2-Sc	1130	216	636
1-Ex	458	94	316

Lowered aqueous salting strengths in the DSBPP and DBPP cases, as previously discussed, could be employed to improve their comparison with the "standard" TBP case.

Data regarding specific fission product distribution in the three extractants are presented below:

TRE β Distribution Coefficient (DC_a^o)

Aqueous Phase*	1.11 M DSBPP (in xylene)	1.11 M DBPP (in xylene)	1.01 M TBP (in Amsco 125-82)
3.0 N HNO_3	0.045	0.065	0.018
0.8 N HNO_3	0.021	0.052	0.011
0.2 N HNO_3	0.05	0.028	0.007

*11.3 g U/l, 5.03 g Th/l; o/a ratio = 1.0.

In general, the indicated higher rare earth distribution in DSBPP and DBPP would not be deleterious because the relatively low extractability characterizes the scrubbing portion as well as the extraction portion of countercurrent systems, i.e. as opposed to Ru and Zr-Nb distribution, which is characteristically high and erratic, owing to a variety of unfavorable physical and chemical properties of those fission products.

Zr-Nb γ Distribution Coefficient (DC_a^o)

Aqueous Phase*	1.11 M DSBPP (in xylene)	1.11 M DBPP (in xylene)	1.01 M TBP (in Amsco 125-82)
3.0 N HNO_3	0.032	0.053	0.035
0.8 N HNO_3	0.006	0.014	0.006
0.2 N HNO_3	0.008	0.007	0.007

*11.3 g U/l, 5.03 g Th/l; o/a ratio = 1.0.

In aqueous systems of higher acidity (e.g. 3.0 N) Zr-Nb limits decontamination in each system; while at lower acidity, as reflected below, Ru limits decontamination.

The ratios of U DC/Zr-Nb DC and U DC/Ru DC are highest in the DSBPP and DBPP cases, as suggested in previous discussions of gross β and γ distribution, emphasizing the "potential", if not the practicality, for higher decontamination of uranium from these fission products.

Ru γ Distribution Coefficient (DC_a^o)

Aqueous Phase*	1.11 M DSBPP (in xylene)	1.11 M DBPP (in xylene)	1.01 M TBP (in Amsco 125-82)
3.0 N HNO_3	0.027	0.034	0.043
0.8 N HNO_3	0.08	0.06	0.185
0.2 N HNO_3	0.25	0.32	0.163

*11.3 g U/l, 5.03 g Th/l; o/a ratio = 1.0.

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