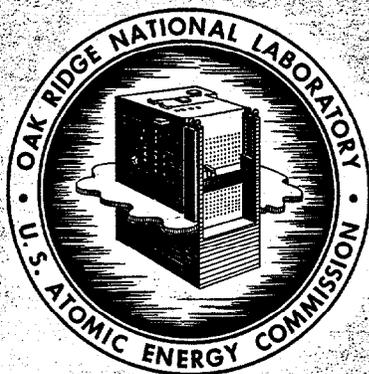


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COMPARISON OF DIALKYL PHENYLPHOSPHONATES
WITH TRI-n-BUTYL PHOSPHATE IN NITRATE
SYSTEMS: EXTRACTION PROPERTIES, STABILITY,
AND EFFECT OF DILUENT ON THE RECOVERY
OF URANIUM AND THORIUM FROM SPENT FUELS

C. A. Blake, Jr.
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J. M. Schmitt
R. G. Mansfield



OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

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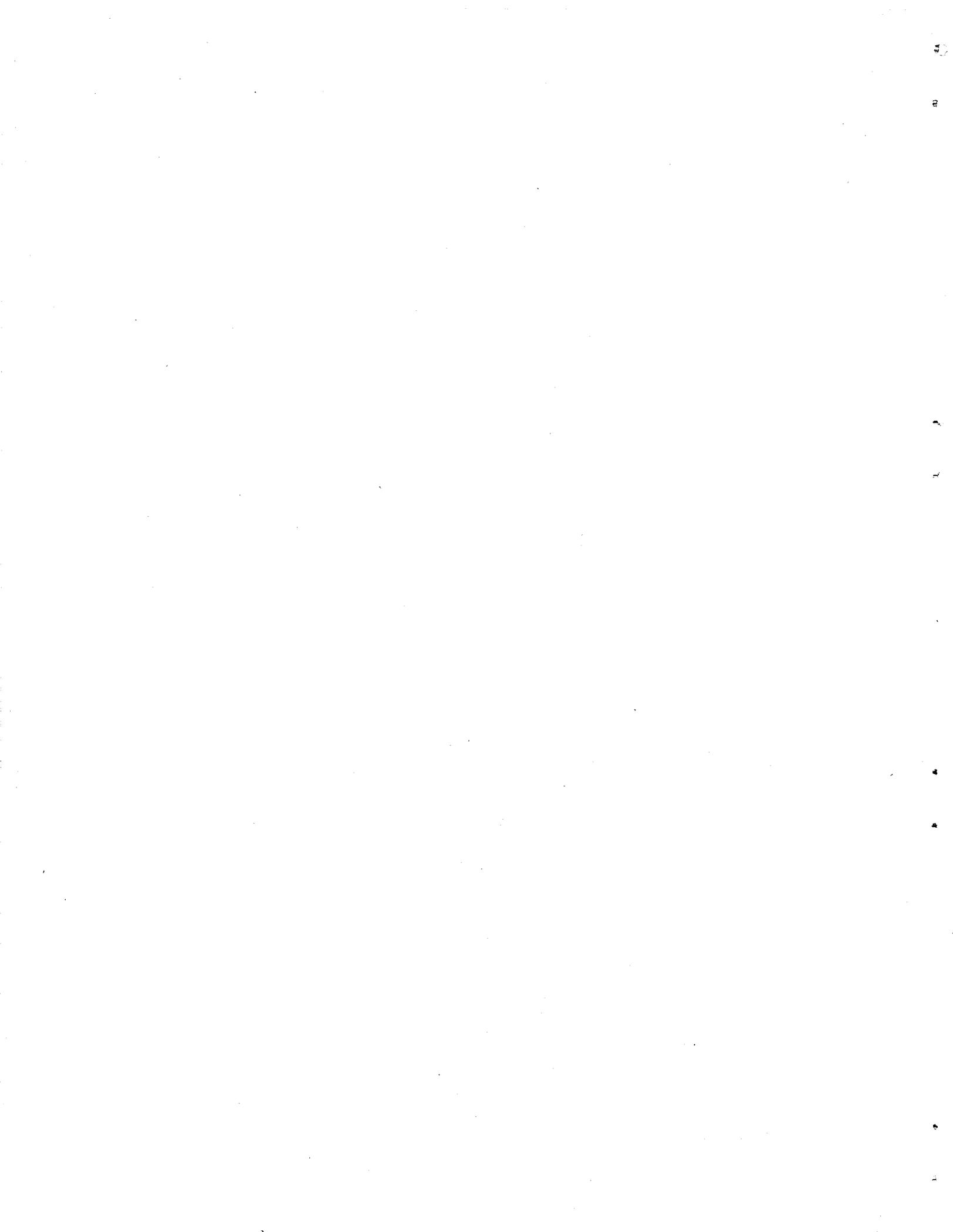
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ABSTRACT

Di-n-butyl phenylphosphonate (DBPP) and di-sec-butyl phenylphosphonate (DSBPP) were investigated as possible substitutes for tri-n-butyl phosphate (TBP), the reagent presently employed in the reprocessing of uranium and thorium nuclear reactor fuels. The phenylphosphonates form complexes with uranium and thorium that are mostly insoluble in the aliphatic solvents commonly used as diluents for TBP but that are soluble in other diluent types, for example, aromatics and CCl_4 . Therefore, the phosphonates were diluted with aromatics and the TBP was diluted with both aliphatic and aromatic diluents.

DSBPP-aromatic solutions showed advantages over TBP-aromatic solutions during batch contact with nitric acid systems in the following respects: higher uranium extractability (1.2 to 1.8 times higher); better stability to radiation and chemical degradation (1.3 times better); higher separation of uranium from thorium (U/Th, 10 times higher) and from fission products (U/gross β , about 2.4 times higher; U/gross γ , about 1.4 times higher). Plutonium extractions with DSBPP and with TBP were nearly identical.

The TBP-aromatic solvent combination also showed advantages over the TBP-aliphatic solvent combination in regard to radiation stability (2.4 times better), uranium extractability (1.5 times better), plutonium(IV) extractability (twice as good), U/gross γ separation (3.1 times higher) and U/gross β separation (2.4 times higher). The comparison of the DSBPP-aromatic solvent combination with TBP in the usual aliphatic diluent is consequently much more favorable to DSBPP than comparison with the TBP-aromatic.

DBPP-aromatic solutions extracted uranium, thorium, plutonium, and fission products better than did TBP in either diluent system. The uranium-thorium separability was between those of the two TBP systems, and the uranium-gross β - γ separability was about the same as for the TBP-aromatic but better than the TBP-aliphatic combination.

Under irradiation the DBPP-aromatic was slightly more stable than the TBP-aliphatic, but not as stable as the TBP-aromatic.

Countercurrent batch testing with simulated Purex feeds verified the single-batch contact data pertaining to uranium extractions with each reagent system and also verified the differences between TBP-aliphatic and TBP-aromatic systems.

A more complete evaluation of the cumulative effect of the several factors involved (stability, selectivity, extraction power) in comparing the reagent-diluent systems must be obtained by testing in equipment capable of treating feeds of much higher fission product activity levels (about a hundred times higher).

DSBPP can be recommended for extractions from nitrate systems where separation of uranium from thorium is required.

The higher uranium extractability shown by DSBPP and by DBPP in comparison with TBP suggests their use to permit lower aqueous nitric acid or nitrate salting concentrations in a uranium recovery operation, for example, to effect reduction in chemical costs and/or to alleviate problems in nitric acid evaporation and recovery from high-level radioactive waste solutions.

Since use of aromatic instead of aliphatic diluents with TBP improves its uranium extractability and fission product separability, such diluents can be considered where the performance of the TBP-aliphatic combination is marginal.



1. INTRODUCTION

Present reactor fuel processes for the recovery, separation, and decontamination of uranium-plutonium²³⁹ (Purex Process),¹ thorium-uranium²³³ (Thorex and Interim-23 Processes),^{2,3} and uranium²³⁵ (TBP-25 Process),⁴ are based on solvent extraction by tri-n-butyl phosphate (TBP). This reagent, normally diluted in aliphatic solvents is successfully and routinely used in the production-scale handling of uranium and thorium fuels irradiated up to 1000 Mwd/ton and with relatively long cooling times before processing. Solvent exposures to radiation are usually in the range 0.02 to 0.2 whr/liter.

It is anticipated that future power reactor fuels will be irradiated to as high as 10,000 to 20,000 Mwd/ton and that in the first cycles of the Purex or Thorex type processes, the organic reagents will be exposed to aqueous feed solutions that will be about 10 times more radioactive than present-day feeds. Laboratory tests of simulated systems employing solvent exposures in the range 0.5 to 1.0 whr of gamma radiation per liter (Co⁶⁰ provided the radiation) showed that increased radiation induced the decomposition of the extracting phase and consequently produced decontamination difficulties, particularly with respect to the ruthenium fission product. Similar studies in the range 4 to 25 whr/liter showed a marked reduction (2 to 25 times) in the decontamination from both ruthenium and zirconium-niobium fission products, significant losses of plutonium and other products, and severe emulsification with attendant difficulties after phase contacting.

Scope of the Report

In the future processing of the much-higher-activity feeds, it seems that the available solvent extraction systems may be pushed to the limit of their capabilities. For these reasons, attention is being paid to the development of alternate extractant-diluent combinations with better solvent qualities. For example, numerous studies have been and are being made of the properties of various diluents. This report, however, is concerned principally with the extractant portion of the solvent and, in particular, with the properties of certain neutral organophosphorus extractants. Emphasis was placed upon seeking increased radiation stability and separability of uranium from its fission products without an accompanying large increase in uranium extractability.

Since early tests^{5,6} indicated di-sec-butyl phenylphosphonate (DSBPP) to be a likely candidate, it was studied in some detail and its behavior compared with that of di-n-butyl phenylphosphonate (DBPP) and TBP by a series of laboratory batch and countercurrent extraction experiments at tracer levels. The batch countercurrent extraction experiments studied product recovery and the decontamination achievable under conditions currently used in the first cycle of the Purex process. The individual batch extractions, however, covered a considerable range of organic reagent concentrations and aqueous-phase nitric acid concentrations in order to define more widely the conditions for the optimal employment of DSBPP (and DBPP) in a variety of potential extraction systems, some of which depart significantly from those in present use.

Much of the data reported here have appeared in previous reports^{5-8,21-26} and a paper.⁹ Related studies have also been reported by ORNL and other laboratories. The high extraction ability of neutral organophosphorus

compounds with one or more alkyl groups bonded directly to the central phosphorus atom has long been known.¹⁰⁻¹⁴ However, attempts to utilize certain commercial types as alternatives to TBP were only partially successful^{15,16} because nearly all metal-ion extractions were increased with little or no improvement in the decontamination of uranium from other metal ions. The depression of thorium extraction by neutral extractants that have secondary alkyl branching has been noted at ORNL⁵⁻⁹ and Savannah River.¹⁷ These and other reports¹⁸ describe uranium extraction properties as well. Application of this type of reagent to uranium-thorium separation processes, for example, Interim-23 and U²³³ purification, has also been suggested^{13,15} and tested.¹⁹ Di-2-amyl 2-butylphosphonate was studied as an alternative to TBP by Siddall,²⁰ who cites its high uranium extractability and better ability to separate uranium from niobium-zirconium. The high extraction power allows uranium recovery from feeds with lower-than-usual nitrate concentrations but necessitates stripping at elevated temperatures in order to decrease the large volume of strip solution required at 30°C. Increasing the temperature to 70°C decreased the uranium extraction coefficient by a factor of about 2.8 (extraction with TBP in the same temperature range decreased by a factor of but 1.5), but the ratio of the aqueous to the organic flow was still about 2:1.

2. BATCH TESTS: COMPARISON OF DISTRIBUTION COEFFICIENTS
(URANIUM, THORIUM, PLUTONIUM, AND FISSION PRODUCTS)
AND SEPARATION FACTORS AS FUNCTIONS OF
NITRIC ACID CONCENTRATION IN AQUEOUS PHASE

2.1. Extraction Tests

In scouting tests, approximately 1 M solutions of tri-n-butyl phosphate (TBP), di-sec-butyl phenylphosphonate (DSBPP, prepared as described in Sec 5.), and di-n-butyl phenylphosphonate (DBPP, made by the Victor

Chemical Works) in either Amsco 125-82 or xylene, were washed well with 0.2 M Na_2CO_3 solutions and then batch contacted with fission product-spiked aqueous solutions containing about 11 g of uranium per liter, 5 g of thorium per liter, and varying concentrations of nitric acid. Plutonium extraction behavior of the same reagents was also tested in nitric acid solutions containing 0.1 to 0.2 g of plutonium(IV) per liter, but not other metal ions. The purpose of these tests was to determine the effect of acidity and/or salting with HNO_3 on distribution coefficients (Table 1, Fig. 1) and on the U/X (X = elements other than uranium, e.g., Th, Zr-Nb, Ru, and RE's) separation factors (Table 2, Fig. 2). A summation of the observations of significance follows.

1. Thorium extraction with DSBPP was very much lower than with TBP, and the uranium extraction was somewhat higher. As a consequence, the U/Th (uranium-from-thorium) separation factor with DSBPP was higher than with TBP. When both reagents were used in an aromatic (xylene), the ratio of factors was about 10 throughout the acidity range 0.2 to 2.4 M HNO_3 .

2. DSBPP and TBP, both in xylene, had nearly identical plutonium(IV) extractability in the acid range 0.5 to 2.0 M HNO_3 . The dependence of extraction on acidity was high, varying approximately with $(\text{HNO}_3)^{2.5}$. In the same range of acidity uranium and thorium extraction varied more nearly with (HNO_3) . Data for plutonium extraction above about 2 M HNO_3 were not obtained, but both uranium and thorium showed maximum extraction in the range 4 to 6 M HNO_3 .

3. The aromatic diluent (xylene) for TBP, rather than aliphatic Amsco 125-82, in the range 0.2 to 2.5 M HNO_3 increased its extractability for uranium (1.5 times), for plutonium (2 times) and its separative ability U/gross β - γ (2.4 to 3.1 times).

Table 1. Distribution Coefficients, D_a^0 : Batch Equilibration

Organic phase: 1 M reagent in indicated diluent

Aqueous phase: (1) 0.047 M U(11g/liter); 0.021 M Th(5g/liter);
1.03 x 10⁷ β counts min⁻¹ ml⁻¹; 1.84 x 10⁷
γ counts min⁻¹ ml⁻¹; 4.2 x 10⁶ Zr-Nb γ
counts min⁻¹ ml⁻¹; 6.3 x 10⁵ Ru γ counts
min⁻¹ ml⁻¹; 8.3 x 10⁶ TRE β counts min⁻¹
ml⁻¹; HNO₃ as indicated. (For all tests
except those with plutonium)(2) ~0.0006 M Pu(0.1-0.2g/liter); HNO₃ as
indicated. (For plutonium tests only)Equal volumes of aqueous and organic phases; 10-min contact;
motor-driven turbine mixers in open cylindrical separatory fun-
nels; room temperature

Element or Activity	Equilibrium Aqueous HNO ₃ (M)	D_a^0			
		TBP in Amsco 125-82	TBP in Xylene	DSBPP in Xylene	DBPP in Xylene
U	2.4	21.0	31.5	38.0	52.7
	0.65	6.2	10.0	16.5	19.4
	0.18	2.9	4.2	7.5	11.1
Th	2.4	1.75	1.43	0.16	4.40
	0.65	0.46	0.36	0.06	0.93
	0.18	0.13	0.10	0.03	
Gross β	2.4	0.013	0.007	0.006	0.023
	0.65	0.017	0.012	0.008	0.016
	0.18	0.016	0.011	0.009	0.023
Gross γ	2.4	0.018	0.010	0.007	0.021
	0.65	0.017	0.008	0.006	0.015
	0.18	0.016	0.008	0.007	0.018
Ru γ	2.4	0.043		0.027	0.034
	0.65	0.185	0.198		0.060
	0.18	0.163	0.276	0.250	0.320
Zr-Nb γ	2.4	0.035	0.031	0.032	0.053
	0.65	0.006	0.009	0.006	0.014
	0.18	0.007	0.012	0.008	0.007
TRE ^a β	2.4	0.018	0.022	0.045	0.065
	0.65	0.011	0.037	0.021	0.052
	0.18	0.007		0.050	0.028
Pu(IV)	2.0	9.5	17	17	27
	1.5	4.4	8.5	8.4	14
	1.0	1.5	3.0	3.0	5
	0.5	0.21	0.48	0.54	0.9

a. Total rare earths.

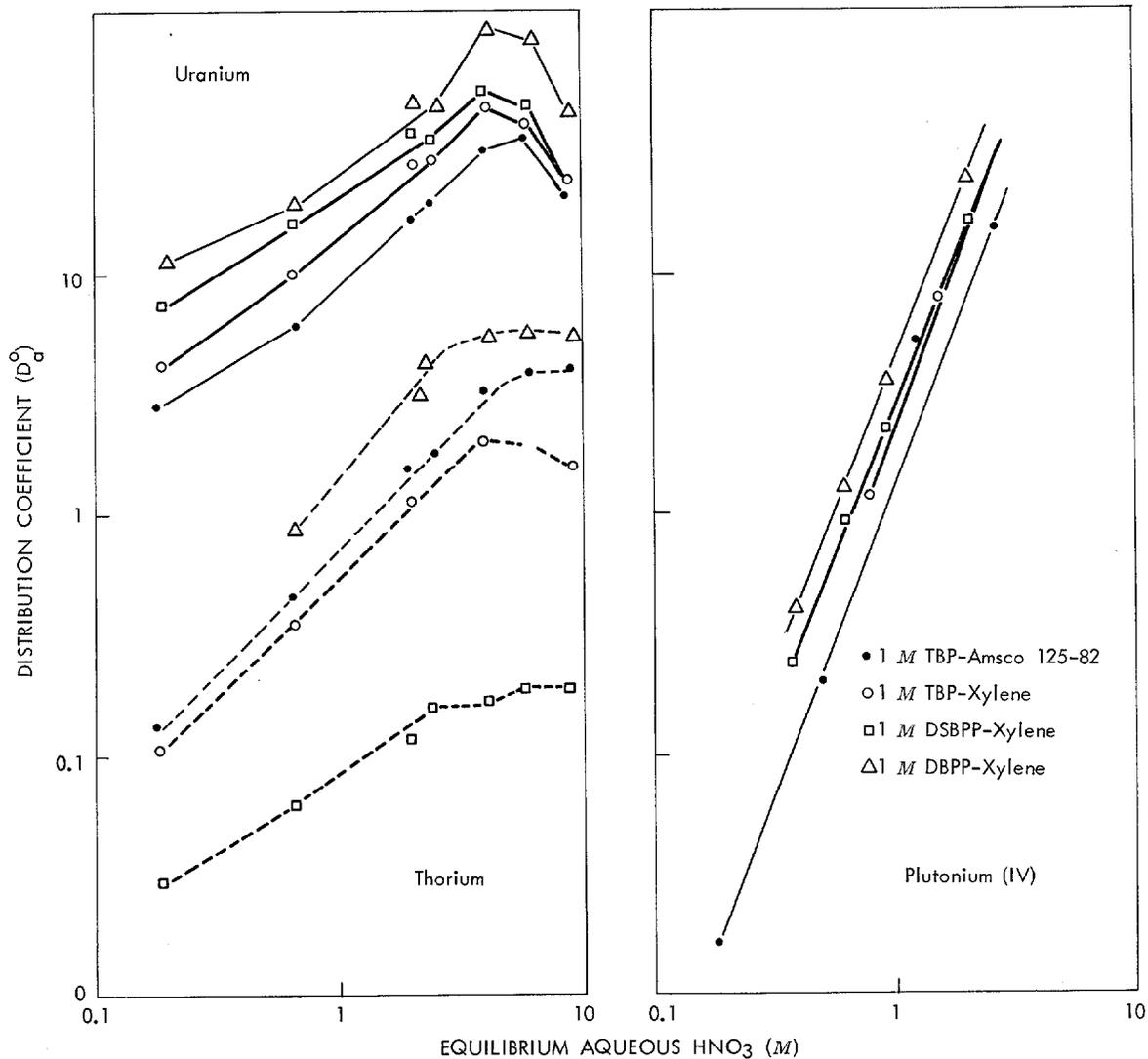
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Fig. 1. Uranium, thorium, and plutonium distribution coefficients. (Feed compositions and test conditions given in Table 1.) Additional data for uranium and thorium not appearing in Table 1, but reported previously⁶ has been included. Test conditions slightly different, but allow valid comparison.

Table 2. Separation Factors, $D_a^0(U)/D_a^0(X)$: Batch Equilibration

1 M reagent in indicated diluent

Separation factor (SF_X^U) calculated from
extraction data, Table 1

Element or Activity	Equilibrium Aqueous HNO_3 (M)	SF_X^U			
		TBP in Amsco 125-82	TBP in Xylene	DSBPP in Xylene	DBPP in Xylene
Th	2.4	12	22	232	12
	0.65	14	28	290	21
	0.18	22	42	262	
Gross β	2.4	1640	4560	6300	2310
	0.65	371	860	2080	1228
	0.18	182	375	868	482
Gross γ	2.4	1185	3260	5730	2530
	0.65	371	1290	2630	1328
	0.18	186	535	1050	610
Ru γ	2.4	485		1420	1550
	0.65	34	51		322
	0.18	18	15	30	35
Zr-Nb γ	2.4	607	1030	1180	1000
	0.65	1000	1100	2800	1430
	0.18	445	348	920	1530
TRE ^a β	2.4	1150	1450	832	810
	0.65	578	267	775	377
	0.18	442		150	390

a. Total rare earths.

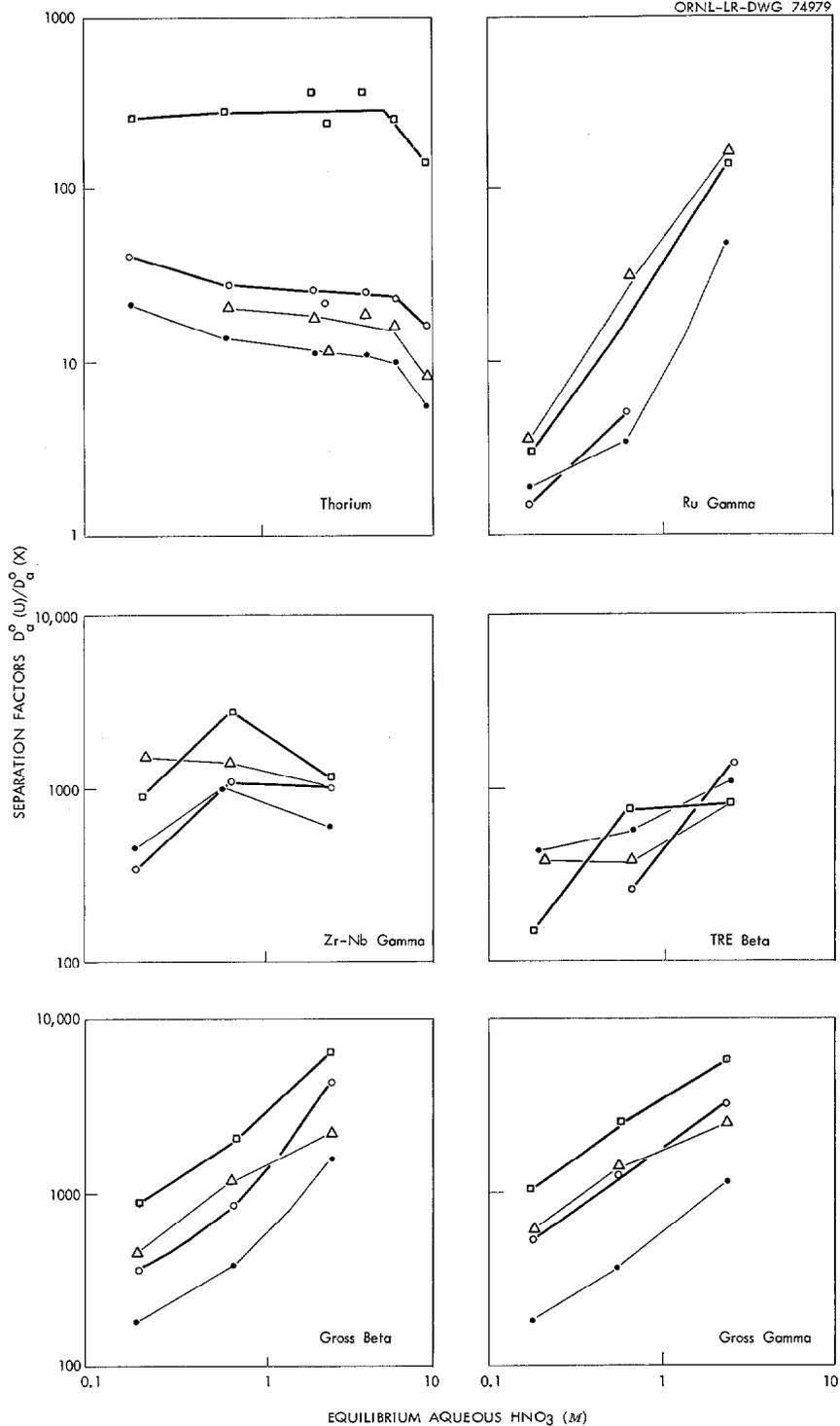
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Fig. 2. Separation factors, uranium from other metal ions

- 1 M TBP-Amsco □ 1 M DSBPP-Xylene
- 1 M TBP-Xylene △ 1 M DBPP-Xylene

(Calculated from extraction data of Table 1 and Fig. 1).

4. When both DSBPP and TBP were employed in an aromatic diluent, the former had somewhat higher uranium and somewhat lower fission product extractability. The resulting U/gross β - γ separability of the DSBPP was 2.4 to 1.4 times higher in the range 0.2 to 2.5 M HNO_3 .

5. When DSBPP-xylene systems were compared with TBP-Amsco systems (similar to solvents in process use), there was a wider gap between their separative abilities, U/gross β - γ . Again, the factors varied in the acidity range 0.2 to 2.5 M HNO_3 . For U/gross β they were 5.6 to 3.9, and for U/gross γ they were 7.1 to 4.8.

6. Gross fission product decontamination was limited at different acidity levels by different fission products. The literature describes tests in relatively simple aqueous systems to show that the extraction of zirconium increases with acidity,²⁹ while the coefficients of the extracting ruthenium species^{29,30} decrease with increasing acidity. Although the actual behavior of these elements is characteristically erratic (see Sec 2.2, scrubbing) zirconium-niobium would be expected to limit the gross fission product decontamination at high acidity (e.g., 3.0 N), and ruthenium would limit the decontamination at low acidity. The total activity level in these tests, set by safety considerations, was not high enough to permit the desired accuracy in analytical results. Some of the fission product (particularly for zirconium-niobium and the rare earths) data may, therefore, be limited by analytical error. The data of Table 1 are nevertheless in fair agreement with the above expectations. Raising the acidity from 0.2 to 2.2 N HNO_3 increased zirconium-niobium extraction by factors of 3 to 8, but decreased ruthenium extraction by factors of 4 to 10. Rare earth extraction changed less, increasing by only 1 to 2 times in this acidity range. The nonlinear variations in the U/X separabilities at

different acidities, whether they were real or the products of analytical error, compensated to produce U/gross β - γ separations that varied regularly with acidity.

7. There are higher rare earth distribution coefficients with the reagents in xylene, as compared with TBP-Amsco. The order of reagents in separation ability, U/RE, varied with acidity (molarity of the HNO_3 in the aqueous phase). Separation factors with the three reagents in xylene were everywhere poorer than that with TBP-Amsco except around 0.7 M HNO_3 with DSBPP-xylene and around 2.4 M HNO_3 with TBP-xylene. As will be shown in Sec 2.2, the rare earths are extracted reversibly, and aqueous scrubbing is effective. In actual process systems, the use of high extraction reagent saturation with uranium is known to afford a major suppression of rare earth extraction, and, in view of the low extraction coefficients for rare earths, no difficulty is expected in the separation of uranium from rare earths.

8. DBPP in xylene had generally higher extractability for each metal than did TBP in either xylene or Amsco; its U/Th separability was between those for TBP-Xylene and TBP-Amsco and its U/gross β - γ separability was about the same as that for TBP-xylene, but better than that for TBP-Amsco. The high uranium and thorium extractability might permit its use for recovery of thorium and uranium²³³ in processes such as the Thorex process.

9. The higher uranium extractability with both DSBPP and DBPP suggests their use would permit lower aqueous HNO_3 or nitrate salting concentrations in a uranium recovery operation; that is to say, the use of DSBPP and DBPP would effect a reduction in chemical costs and/or alleviate problems in HNO_3 evaporation and recovery from highly radioactive waste solutions. If

simultaneous plutonium recovery is required, the loss of plutonium extractability (Fig. 1) at lower acidity is an important factor for consideration.

10. The higher uranium extractability with DSBPP-xylene, TBP-xylene, and particularly with DBPP-xylene requires more severe stripping conditions than a TBP-Amsco combination would need in a similar system (see Sec 3.2).

The data of this section are summarized more concisely in Table 3 in terms of extraction (Table 3, Part A) and separations (Table 3, Part B) achieved in the system where the aqueous HNO_3 concentration was about 2.4 N. This is a condition that approximates that of the last extraction stage (lowest uranium loading, highest fission product extraction) of a general process operation. In addition, in support of point 9, the concentration of HNO_3 that permitted the uranium distribution coefficient with each reagent to be 20 (approximately equal to the value observed in conditions of a codecontamination cycle of the Purex process) was determined by interpolation from the plots of Fig. 1 (e.g., for the system DSBPP-xylene and $\text{HNO}_3 = 0.9$ M). Also, the U/X separation factors at each of these reagent-acidity combinations are tabulated (Table 3, Part C). The net U/FP β - γ separation factor was largest with DSBPP-xylene, lowest with DBPP-xylene, although in no case did they vary greatly from that shown by the TBP-Amsco combinations. As discussed in point 6 above, this reflects the changes in zirconium-niobium, ruthenium, and rare earths extractability with acidity. The superiority of DSBPP in the separation of uranium from thorium is clearly evident. Though the data, for the reasons mentioned earlier, are subject to analytical error, they indicate that reductions of acid or salt in aqueous feeds may be possible with changes

Table 3. Summary of Batch Extraction Data

Selected from Tables 1 and 2, or
by interpolation from Fig. 2

Product (X) ^a	Extractant Phase (1 M in reagent)			
	TBP in Amsco 125-82	TBP in Xylene	DSBPP in Xylene	DBPP in Xylene
A. Distribution Coefficients, D_a^0 , Equilibrium Aqueous $\text{HNO}_3 = 2.4 \text{ M}$				
U	21	32	38	53
Pu(IV)	15	~28	~28	~28
Th	1.8	1.4	0.2	4.4
F.P. (β, γ)	0.02	0.01	0.007	0.02
B. Separation Factors, $D_a^0(\text{U})/D_a^0(\text{X})$, Equilibrium Aqueous $\text{HNO}_3 = 2.4 \text{ M}$				
Pu(IV) ^b	1.4	1.1	1.4	1.4
Th	12	23	235	12
F.P. (β, γ)	1400	3900	5800	2400
Ru(γ)	500		1400	1550
Zr-Nb(γ)	600	1030	1180	1000
TRE(β)	1100	1450	840	810
C. Separation Factors, $D_a^0(\text{U})/D_a^0(\text{X})$, Equilibrium Aqueous HNO_3 for $D_a^0(\text{U}) = 20^c$				
Pu(IV) ^b	1.4	2.9	2.9	10
Th	12	25	280	20
F.P. (β, γ)	1400	2200	3000	1350
Ru(γ)	500		300	300
Zr-Nb(γ)	600	1000	2300	1400
TRE(β)	1100	700	800	400
	(2.4 M HNO_3) ^c	(1.4 M HNO_3)	(0.9 M HNO_3)	(0.7 M HNO_3)

a. X = elements other than uranium.

b. Calculated from separate batch extractions, Table 1.

c. These are the nitric acid concentrations required to make D_a^0 equal 20.

in diluent and/or reagent, except perhaps when limited by the required plutonium recovery, since its extraction varied strongly with acidity.

2.2. Scrubbing Tests

The previously discussed data, obtained from batch extraction tests, allowed comparisons of potential U/FP separation factors attainable with the four extraction mixtures. However, it is known from process experience that the potential may not always be realized. Specific fission products such as ruthenium and zirconium-niobium are most often characterized in aqueous feed solutions by several troublesome species that behave in different ways and are sometimes strongly affected by various organic impurities in the extractant (e.g., by degradation products from the hydrolysis and radiolysis of reagents and diluents). Therefore, a more complete picture of anticipated process behavior can be obtained in batch tests by observing the results of subsequent aqueous scrubbing of the organic extracts from the extraction cycle.

Therefore, a series of such scrubbing-cycles tests (on organic extracts from the previously described tests, and employing aqueous nitric acid solutions at the same HNO_3 concentration as those used in the initial extraction step) were performed to establish the distribution coefficients and U/X separation factors for pertinent fission product fractions. The U/X separation factors are summarized in Table 4. The numbers in parentheses are separation factors obtained as described in Sec 2.1 and quoted from Table 2.

The U/Zr-Nb and U/Ru separation factors in the scrubbing step were a tenth to a hundredth of those for the extraction step. This behavior is typical of process experience and is qualitatively in accord with the

Table 4. U/X Separation Factors in Scrubbing Tests
with 1 M Extraction Reagents

Product X	U/X Separation Factors $D_a^0(U)/D_a^0(X)$			
	TBP in Amsco	TBP in Xylene	DSBPP in Xylene	DBPP in Xylene
2.4 M HNO_3^a				
Ru(γ)	42 (485) ^b	32	(1420) ^a	(1550)
Zr-Nb(γ)	145 (607)	154 (607)	248 (1180)	87 (1000)
Gross γ	165 (1185)	224 (3260)	270 (5730)	195 (2530)
Gross β	179 (1640)	258 (4560)	323 (6300)	385 (2310)
TRE(β)	1065 (1150)	1070 (1450)	714 (832)	880 (810)
0.7 M HNO_3^a				
Ru(γ)	4 (34)	4 (51)	4	(322)
Zr-Nb(γ)	13 (1000)	20 (1100)	24 (2800)	36 (1430)
Gross γ	9 (371)	12 (1290)	18 (2630)	35 (1328)
Gross β	10 (371)	13 (860)	15 (2090)	51 (1228)
0.2 M HNO_3^a				
Ru(γ)	2 (18)	2 (15)	3 (30)	8 (35)
Zr-Nb(γ)	5 (445)	7 (348)	5 (920)	6 (1530)
Gross γ	3 (186)	4 (535)	4 (1050)	9 (610)
Gross β	4 (182)	5 (375)	4 (482)	10 (482)
TRE(β)	(442)	50	(150)	376 (390)

a. Acidity of aqueous scrub solution and of the initial aqueous feed.

b. Numbers in parenthesis are values obtained in previous extraction test (Table 2).

extraction chemistry of zirconium-niobium and ruthenium. For example, the most extractable species of ruthenium constitute only a portion of the gross ruthenium.³⁰ Thus, while the observed ruthenium D_a^0 may be low, the coefficient for the extracted species may be much higher. The latter coefficient is more nearly representative of the scrubbing coefficient, and a low scrubbing decontamination factor (DF) is observed. In addition to probable similar behavior, zirconium is much easier to extract than niobium, and its D_a^0 will be higher than that observed for the zirconium-niobium combination, and the scrub DF will be lower than that achieved during extraction. Indeed, the gross β and γ DF's reflect these trends. It should be remembered that while these coefficients have been obtained in the absence of any large effects due to the degradation products of the reagent or diluent, small amounts of solvent impurities or degradation products can cause extraction of fission products, particularly zirconium, and such activity is difficultly stripped by dilute acid.

The rare earth data indicate nearly reversible extraction in the 0.2 and 2.8 M HNO_3 stripping tests.

A plot of the scrubbing data would resemble Fig. 2 (Separation factors from extraction tests), except for the order of magnitude of most of the factors. There are small differences favoring DSBPP over TBP (both in xylene), somewhat larger differences between TBP-Amsco and TBP-xylene, and mildly erratic behavior with DBPP.

3. LABORATORY COUNTERCURRENT TESTS: COMPARISON OF URANIUM, HNO_3 , AND FISSION PRODUCT DISTRIBUTION BETWEEN THE ORGANIC AND AQUEOUS PHASES

3.1. Extraction and Scrubbing Tests

Laboratory batch countercurrent tests with the three reagents were made in order to provide further comparisons and evaluations of their

process applicability. The aqueous solutions, organic extractants, and liquid flow conditions were established to simulate those employed in the extraction step of the codecontamination cycle of the Purex process. TBP was tested in both Amsco 125-82 and xylene, DSBPP was in xylene, and DBPP was in a mixture of Amsco 125-82 and xylene. (The DBPP-uranyl nitrate complex had previously been shown to be soluble in diluents of lower aromatic content than permitted by DSBPP.) Aqueous solutions and volumetric flow ratios were identical in all cases. The test conditions and results are recorded in Tables 5 and 6.

The level of fission product activity permitted in the laboratory in which the experiments were run was too low for the fission product β and γ determinations to be of significance in any of the scrub stages above the second. For example, in the test with TBP-Amsco the gross β activity of the 6th scrub stage organic phase (about 2000 counts $\text{min}^{-1} \text{ml}^{-1}$) was shown by means of a parallel test with no fission product spike to be entirely accounted for by the activity of the natural uranium decay chain. Accordingly, no fission product data are reported for the upper scrub stages. In order for significant scrub data to be obtained the tests must be run in a facility in which the fission product activity level may be increased, preferably a hundredfold.

In comparisons with TBP-Amsco as the reference case, the data illustrate higher uranium extraction factors ($EF_a^0 = DC_a^0 \times \text{the O/A flow ratio}$) with the TBP-, DSBPP-, and the DBPP-xylene extractants. This is evident in the last scrubbing stage (6-Sc), the aqueous feed point or first extraction stage (1-Ex), and particularly in the third extraction stage (3-Ex). The differences between extraction factors in this last extraction stage reflect

Table 5. Comparison of Uranium and HNO₃ Extraction in 1.0 M DSBPP, TBP, and DBPP: Countercurrent Tests

Uranium in g/liter; HNO₃ in N; $EF_a^0 = DC_a^0 \times FR_a^0$ (EF = extraction factor; DC = distribution coefficient; FR = flow ratio).
 Aqueous Feed: 434 g U per liter, 1.11 N HNO₃, 1.35 x 10⁷ gross β counts min⁻¹ ml⁻¹, 1.83 x 10⁷ gross γ counts min⁻¹ ml⁻¹
 Aqueous Scrub: 2.0 N HNO₃; flow ratio: (feed:scrub:organic volume ratio) = 1/0.75/4.75; 2.5 volume changes

Stage	Uranium Extraction				HNO ₃ Extraction			
	1 M TBP- Amsco	1 M TBP- Xylene	1 M DSBPP- Xylene	1 M DBPP- 80 Amsco/20 Xylene	1 M TBP- Amsco	1 M TBP- Xylene	1 M DSBPP- Xylene	1 M DBPP- 80 Amsco/20 Xylene
6S-0 ^a	83.6	92.6	97.4	90.0	0.10	0.12	0.14	0.10
6S-A	30.1	20.6	21.0	18.4	1.87	1.85	1.89	1.94
(EF _a ⁰)	(17.6)	(28.4)	(28.4)	(31.0)	(0.34)	(0.41)	(0.47)	(0.33)
1E-0	100.0	97.4	99.0	92.2	0.08	0.10	0.14	0.12
1E-A	82.1	30.5	32.6	19.9	2.18	2.23	2.47	2.46
(EF _a ⁰)	(3.31)	(8.68)	(8.25)	(12.55)	(0.10)	(0.12)	(0.15)	(0.13)
3E-0	0.79	0.156	0.185	0.117	0.36	0.35	0.4	0.37
3E-A	0.05	0.008	0.006	0.005	1.84	1.58	1.6	1.73
(EF _a ⁰)	(43.0)	(53.0)	(84.0)	(63.6)	(0.53)	(0.60)	(0.68)	(0.58)

^aUranium or HNO₃ analyses in sixth scrub stage: A = aqueous phase, 0 = organic. In other entries in this column 1E = first extraction stage, etc.

Table 6. Comparison of Gross β and γ Extraction in 1.0 M DSBPP, TBP, and DBPP:
 Countercurrent Tests

Gross β and γ in counts $\text{min}^{-1} \text{ml}^{-1} \times 10^{-5}$; $EF_a^0 = DC_{a7}^0 \times FR_a^0$
 Aqueous Feed: 434 g U/liter, 1.11 N HNO_3 , 1.35×10^7 gross β
 counts $\text{min}^{-1} \text{ml}^{-1}$, 1.83×10^7 gross γ counts $\text{min}^{-1} \text{ml}^{-1}$
 Aqueous Scrub: 2.0 N HNO_3 ; flow ratio: (feed:scrub:organic
 volume ratio) = $1/\sqrt{0.75/4.75}$; 2.5 volume changes

Stage	Gross β				Gross γ			
	1 M TBP- Amsco	1 M TBP- Xylene	1 M DSBPP- Xylene	1 M DBPP- 80 Amsco/20 Xylene	1 M TBP- Amsco	1 M TBP- Xylene	1 M DSBPP- Xylene	1 M DBPP- 80 Amsco/20 Xylene
2S-0 ^a	0.0357	0.0277	0.0345	0.122	0.0608	0.0671	0.0341	0.179
2S-A	0.684	1.04	2.45	3.26	1.95	1.50	3.86	4.65
(EF_a^0)	(0.33)	(0.17)	(0.089)	(0.237)	(0.197)	(0.283)	(0.056)	(0.244)
1E-0 ^a	0.0833	0.053	0.047	0.322	0.122	0.128	0.0884	0.414
1E-A	136.0	80.4	88.8	99.0	132.0	118.0	135.0	144.0
(EF_a^0)	(0.0017)	(0.0018)	(0.0014)	(0.0089)	(0.0025)	(0.0029)	(0.0018)	(0.0078)
3E-0	2.75	1.34	0.92	3.99	4.16	1.71	1.13	6.68
3E-A	80.6	88.1	85.2	93.5	134.0	127.0	114.0	147.0
(EF_a^0)	(0.093)	(0.041)	(0.029)	(0.166)	(0.084)	(0.037)	(0.027)	(0.123)
5E-0	1.44	0.573	0.387	1.87	2.06	0.732	0.476	4.79
5E-A	79.6	77.5	98.0	84.5	125.0	123.0	126.0	126.0
(EF_a^0)	(0.049)	(0.02)	(0.011)	(0.06)	(0.045)	(0.016)	(0.01)	(0.103)

^aGross β - γ analyses in second scrub stage: A = aqueous phase, O = organic. In other entries in this column, 1E = first extraction stage, etc.

the previously observed differences in the uranium extraction coefficients for the reagents (Table 1). Adjustments could have been made to lower the aqueous HNO_3 or salting strengths with the xylene-diluted reagents without sustaining product losses greater than those experienced with TBP-Amsco. [As indicated previously in the batch equilibration data (Table 3), operable salting strengths should decrease in the order TBP, DSBPP, and DBPP.]

The lower extractability of the gross β -emitting fission products in DSBPP, the somewhat higher extractability in DBPP, and the lower EF's (extraction factors) with xylene diluent are illustrated in the extraction factors of Table 5.

Similar extraction trends appear in the data for the gross γ -emitting fission products. In both the gross β and γ cases extraction factors of unity are being approached rapidly by all reagents and especially by DBPP and TBP as early as the 2nd scrub stage. This could signify little potential for further decontamination, but again, the analytical limit imposed by the low activity level of the feed does not permit conclusive support of this observation.

Because of the low level of fission product activity in the aqueous feed and the lack of uranium analyses in the intermediate scrub stages it was impossible to calculate accurate DF's (decontamination factors) for uranium from X metal ions for any stage other than that at the feed point (1-Ex). These appear in Table 7.

As predictable from the previous batch extraction data, the decontamination decreased in the order DSBPP-xylene, TBP-xylene, TBP-Amsco, and DBPP-Amsco-xylene.

Table 7. Uranium-from-Fission Product Decontamination
Factors at the Feed Point

See Table 5 for test conditions.

$$DF = \frac{EF_U}{EF_X} \left(\frac{1 + EF_X}{1 + EF_U} \right)$$

Activity	1 M TBP in Amsco 125-82	1 M TBP in Xylene	1 M DSBPP in Xylene	1 M DBPP-80/20 Amsco 125-82/Xylene
Gross γ	300	310	495	119
Gross β	455	512	635	105

3.2. Stripping Tests

Table 8 shows data from two simple countercurrent stripping tests with DBPP; these tests were designed to give an estimate of its required organic-extract: strip-solution flow ratio.

Although the uranium concentrations in the two organic phases were somewhat below process conditions, the data suggest a useful 1 M-DBPP: strip-solution ratio of about 0.5, with 0.007 to 0.01 M HNO_3 in the aqueous phase. In comparison, the usual Purex process employs nearly equal volumes of organic and strip phases. The volume of strip solution can be reduced by stripping at elevated temperatures. The present tests do not include a demonstration of this, but it is known that uranium extraction coefficients with organic phosphorus reagents generally decrease with increasing temperature. (Siddall, for example, showed²⁰ a decrease in uranium extraction with di(2-amyl)-2-butylphosphonate by a factor of ~2.8 when the temperature was raised from 30 to 70°C.) Uranium losses of less than 0.001% and 0.02% were experienced in five stripping stages after extraction without and with

fission product spike, respectively. Essentially, no U/FP decontamination was achieved in stripping (DF's U/gross β and U/gross γ , about 1.1).

No tests were made with DSBPP because this reagent has lower uranium extractability than DBPP (Table 1) and the strip volume that it requires will be smaller and will approach that required by TBP.

Table 8. Countercurrent Stripping from 1 M DBPP

Test 1: Organic Extract: 1 M DBPP; diluent, Amsco 125-82
and xylene (80 vols to 20 vols);
64.6 g U/liter; 0.06 M HNO₃
Aqueous Extract: 0.007 M HNO₃

Test 2: Organic Extract: 1 M DBPP; diluent, Amsco 125-82
and xylene (70 vols to 30 vols);
74.4 g U/liter; 1780 β counts min⁻¹ ml⁻¹;
4440 γ counts min⁻¹ ml⁻¹
Aqueous Extract: 0.01 M HNO₃

Flow ratio: organic feed: strip solution = 1:2

Volume changes: 2.5

	Test 1		Test 2		Gross β (counts min ⁻¹ ml ⁻¹)	Gross γ (counts min ⁻¹ ml ⁻¹)
	U (g/liter)	HNO ₃ M	U (g/liter)	HNO ₃ M		
5 St-0	0.0006		0.0086	0.003	160	730
5 St-A (EF _a ⁰)	0.018 (0.017)	0.005	0.243 (0.018)	0.01		
3 St-0	1.47	0.004	8.27	<0.01	470	1290
3 St-A (EF _a ⁰)	6.4 (0.115)	0.007 (0.29)	13.2 (0.313)	<0.01		
1 St-0	35.3	0.003	48.2	0.01	670	2420
1 St-A (EF _a ⁰)	31.2 (0.56)	0.007 (0.22)	37.5 (0.64)	<0.01		

4. ALTERNATIVE DILUENTS

The combined favorable comparisons of DSBPP with TBP in regard to radiolysis stability, fission product decontamination, and uranium extractability, may be considered to be somewhat offset by the unfavorable comparison regarding insolubility of the $2\text{DSBPP}\cdot\text{UO}_2(\text{NO}_3)_2$ complex in aliphatic diluents such as Amsco 125-82. Xylene, though effective in regard to the solubility of the $2\text{DSBPP}\cdot\text{UO}_2(\text{NO}_3)_2$ complex, is not desirable for process applications because of its low flash point (63°F).

A brief investigation of alternative commercial diluents indicated that Solvesso 100, a high-aromatic hydrocarbon fraction with a flash point of 118°F , afforded complete solubility of the $2\text{DSBPP}\cdot\text{UO}_2(\text{NO}_3)_2$ complex. Among other commercial diluents tested with regard to solubility of the complex, it also appears that carbon tetrachloride, Esso heavy-aromatic naphtha, Amsco G, Solvesso 150, diethylbenzene, and diisopropylbenzene are possibly useful candidates, whereas other solvents such as Shell 140 and Amsco 110-15 incompletely dissolve the complex.

Batch equilibrations of TBP dissolved in Amsco 125-82 or Solvesso 100 with an aqueous uranium solution containing fission products showed again the separative advantages resulting from the use of an aromatic diluent (Table 9). In the Solvesso-100 diluent DSBPP again had higher U/FP separative ability than did TBP.

A brief countercurrent test with DSBPP in Solvesso 100 showed no deleterious physical or chemical effects from the use of the aromatic diluent, with the expected good decontamination of uranium from fission products.

Table 9. Uranium/Fission-Product Separation Factors

Aqueous phase: 3 N HNO₃, 10.1 g U per liter,
10 g Th per liter, fission product spike

Aqueous/organic phase ratio: 1.

Reagent	Separation Factors $D_a^0(\text{U})/D_a^0(\text{F.P.})$	
	Gross β	Gross γ
1.0 <u>M</u> TBP-Amsco 125-82	1085	1125
1.0 <u>M</u> TBP-Solvesso 100	3260	3670
1.0 <u>M</u> DSBPP-Solvesso 100	5300	4550

The highly branched alkyl chains of Solvesso 100 make it susceptible to chemical attack. A search for chemically stable simple aromatic diluents with suitable physical properties is a part of another study.³¹ Preliminary indications from that study favor the use of alkylbenzenes that have suitably high flash points, for example, n-hexylbenzene.

5. RADIATION STABILITY

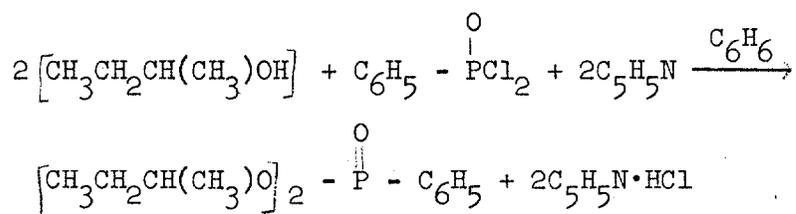
The pure phenylphosphonates possess radiation stability higher than that of TBP by virtue of their protective benzene structure. The stability (in terms of G values, the number of molecules acid formed during irradiation totaling 100 ev of absorbed energy, with respect to the formation of acidic decomposition products) has been determined²⁷ for the three reagents (no diluent or HNO₃ present). The G values for the pure TBP, DSBPP, and DBPP of 2.3, 0.54, and 0.78 indicate relative radiation stabilities of 1:4.3:2.9, respectively.

Of pertinence, however, to process use is the stability of the reagent when carried in a diluent and in contact with an aqueous radioactive acid

feed. Tests simulating this condition have been made in CO^{60} irradiations.²² The reagents were dissolved to a 1 M concentration in the indicated diluents, HNO_3 was extracted, and the reagent-diluent- HNO_3 phase was irradiated. The G values, again with respect to the formation of acidic decomposition products, for TBP-Amsco, TBP-Solvesso 100, DSBPP-Solvesso 100, and DBPP-Solvesso 100 were 0.75, 0.31, 0.24, and 0.51 with relative stabilities of 1/2.4/3.1/1.5. The stability of TBP was improved by a factor of 2.4 when the aromatic diluent, Solvesso 100, was used instead of Amsco 125-82. Aromatic diluents had been noted previously^{22,28} to afford a measure of radiation protection to TBP, but it is apparent that little or no improvement was realized by dissolving the phenylphosphonate in Solvesso 100, rather than in Amsco 125-82. Where the pure DSBPP, for example, was more stable than pure TBP by a factor of 4.3, dissolution of both in the aromatic diluent decreased this advantage to a factor of but 1.3. The corresponding factors for DBPP were 2.9 and 0.6, respectively.

6. PREPARATION OF DI-SEC-BUTYL PHENYLPHOSPHONATE

Di-sec-butyl phenylphosphonate was synthesized by the reaction of sec-butyl alcohol with benzene phosphorus oxydichloride in the presence of pyridine. Reagents were used in molar proportions as set forth by Kosolapoff (Organophosphorus Compounds, John Wiley and Sons, New York, 1950): sec-butyl alcohol, 6.75 moles; pyridine, 6.75 moles; benzene phosphorus oxydichloride, 3.38 moles; and 1200 ml of benzene reacted to yield the phenylphosphonate according to the following equation:



The sec-butyl alcohol, pyridine, and benzene were transferred to a 5-liter, three-neck round-bottom flask equipped with a reflux condenser, dropping funnel, and electric stirrer. The flask was kept cool while the reagents were mixed and throughout the synthesis by surrounding the flask with crushed ice. The benzene phosphorus oxydichloride was added dropwise to the solution over a period of 2 hr. The mixture was then hydrolyzed by boiling with 3 M HCl for 1 hr under total reflux. The organic and aqueous phases were separated, and the organic phase was repeatedly washed with quarter volumes of 2% aqueous NaOH and then equal volumes of water. The product was distilled at 127°C and 315 μ . The yield was about 87%, analyzing 61.8% C, 8.7% H, 11.2% P, as compared to the theoretical 62.2% C, 8.5% H, 11.5% P.

7. CONCLUSIONS

DSBPP can be recommended for extractions from nitrate systems where separation of uranium from thorium is required. In addition its radiation and chemical stability and ability to separate uranium from fission products are slightly higher than those of TBP under comparable conditions.

DSBPP and DBPP have higher uranium extractability than does TBP, suggesting their use would permit lower aqueous HNO₃ or nitrate salting concentrations in a uranium recovery operation, i.e., their use could effect a reduction in chemical costs and/or alleviate problems in HNO₃ evaporation and recovery from high-level radioactive waste solutions. It is necessary to use an aromatic diluent with both reagents to retain solubility of extracted metal salts in the organic extract.

Use of aromatic instead of aliphatic diluents with TBP improves its uranium extractability (1.5 times higher), plutonium extractability (2

times higher) and uranium/gross β - γ separability (2.5 to 3.1 times higher) and should be considered where the performance of the TBP-aliphatic combination is marginal.

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