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EXTRACTION OF NIOBIUM-95 FROM NITRIC ACID SOLUTIONS WITH TRI-*n*-BUTYL PHOSPHATE

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OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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ABSTRACT

The distribution coefficient (DC o/a) of Nb-95 between aqueous nitric acid and 30% Tri-n-butyl phosphate (TBP) in n-dodecane increased from ~0.004 in 0.1 N acid deficient solution to 0.05 in 4 M HNO_3 for the extractable portion of the niobium. Greater than 70% of the niobium was unextractable. The presence of 3% chemically degraded TBP, 7% chemically degraded Amsco, or both decreased the amount of unextractable niobium to <20% and degraded TBP increased the distribution of the extractable portion. The aqueous solubility of the niobium extractant in the degraded reagents varied inversely with the acidity of the aqueous phase. The maximum DC o/a from acid deficient solutions containing solvent degradation products was ~0.008. The organic to aqueous DC o/a were higher than the aqueous to organic values for all solutions examined. Niobium retention was maximum by solvents containing both degraded TBP and Amsco, increasing from 6% to ~50% as the aqueous acidity decreased from 5 to 0.1 M HNO_3. Niobium-95 was removed from nitric acid solutions containing 20 g/liter Zr and Zr-95 by adsorption on unfired Vycor glass.

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1.0 INTRODUCTION

The distribution of Nb-95 between aqueous solutions containing up to 4 M nitric acid and organic solutions of 30% tributyl phosphate (TBP) in n-dodecane was determined with and without chemically degraded TBP and/or degraded Amsco present. In addition, a glass chromatographic technique was developed for removing Nb-95 from nitric acid solutions containing macro zirconium and tracer amounts of Zr-Nb-95. A few zirconium distribution coefficients are also given.

The solvent extraction behavior of niobium and zirconium is of considerable importance since these elements are the major contaminants in product streams in the processing of irradiated uranium by TBP extraction from nitric acid solutions. Many studies have been made on the extraction of zirconium from nitric acid by TBP (1-7) but few on the behavior of niobium. Hardy and Scargill (8, 9) presented a detailed report on the extraction of niobium from >2 M HNO_3, and Scadden and Ballou (10) reported on the separation of zirconium and niobium from nitric acid solutions containing oxalic acid by using mixed butylphosphoric acids. This report presents the results of experiments made to extend the distribution coefficients (DC o/a) of niobium to solutions containing <2 M HNO_3 and the effects of the chemical degradation products of both TBP and Amsco 125-82.

Appreciation is expressed to the Analytical Chemistry Division, particularly the groups headed by G. R. Wilson and E. I. Wyatt, for analytical support and to John Surak for the development of a chemical analytical method for zirconium.

2.0 REAGENTS AND EXPERIMENTAL TECHNIQUES

2.1 Purified Tributyl Phosphate (TBP)

Technical grade TBP from Commercial Solvents Corp. was purified by boiling with dilute sodium hydroxide (12). One volume of TBP was added to 5 vol of 0.1 N NaOH and the mixture distilled at atmospheric pressure until 2 vol of distillate had collected. The mixture remaining in the pot was cooled to room temperature, and the TBP was separated from the aqueous and washed three times with equal volumes of water. The desired

solution was then prepared by dilution with Eastman Kodak practical grade n-dodecane. The n-dodecane was used as the reference diluent since it may be obtained in reproducible quality whereas Amsco 125-82 cannot.

2.2 Degraded TBP and Amsco

Two degraded solutions were prepared, TBP and 30% TBP in Amsco. In both cases the organic solutions were mixed with an equal volume of 6 M HNO_3 and boiled. After 6 hr refluxing, the organic phase was removed and washed three times with equal volumes of water. Prior to washing, the 100% TBP contained ~3 M HNO_3 and the 30% TBP in Amsco, ~1 M HNO_3. These organics were diluted to the desired concentration with 30% freshly purified TBP in n-dodecane.

2.3 Niobium Tracer Solutions

Niobium-95 tracer solutions were prepared by a procedure based on that of Hardy and Scargill (13). Several milliliters of concentrated nitric acid and 30% H_2O_2 were added to an oxalic acid solution containing 1-5 mc of Zr-95 and its associated Nb-95 daughter activity. This was evaporated almost to dryness to destroy the oxalate and then made up to about 20 ml with 2 M HNO_3. The Zr-95 activity was removed by contacting this solution several times (in a plastic container) with equal volumes of 0.5 M 2-thenoyl-trifluoroacetone (TTA) in benzene or xylene; the raffinate was washed with benzene to remove the TTA, and then air was bubbled through the aqueous phase to remove any residual benzene. This solution was immediately made up to 100 ml with 4 to 10 M HNO_3 as desired and heated 1 hr at 100°C in a closed plastic bottle to stabilize the niobium (9). This stock solution, whose activity was >99% Nb-95, was diluted to the desired acidity prior to use.

2.4 Experimental Techniques

The Martin technique (11) was used to determine the distribution coefficients (DC o/a = concentration in the organic phase/concentration in the aqueous phase) for the extractable species of niobium as well as the percentage of the niobium in the solutions that is difficult to extract into and strip from the organic phase. The organic solutions were

first equilibrated three times with an aqueous solution containing the same concentration of nitric acid as the niobium solution to be examined. The niobium solutions and the pretreated organic solution were then equilibrated in plastic containers with various solvent/aqueous volume ratios. After contact the phases were separated and centrifuged 15 min, and the niobium content was determined by measuring the gross γ activity in each phase. A linear coordinate plot was made with the activity in the organic phase as the ordinate and that in the aqueous as the abscissa (e.g., Fig. 1). For solutions containing two species of niobium, one soluble only in the aqueous phase and the other soluble in and existing in the same form in both phases, a straight line is obtained which may be extrapolated to the abscissa. The intercept is a function of the amount of unextractable species, and the slope of the line, the distribution coefficient of the extractable species. Data obtained by contacting organic solutions containing Nb-95 with nitric acid solutions containing no niobium were treated similarly. For organic solutions containing an extracted niobium species that is reversible as well as one that is not, the straight line intercepts the ordinate, the intercept is a function of the fraction of niobium retained by the organic and the slope, the distribution coefficients. The method of least squares was used to determine the best straight-line fit for the data. In cases where visual inspection of the data indicated a straight line with a curved section in the region obtained with the lower organic/aqueous volume ratios, only the data for the straight-line portion were used.

Examples of data obtained by this method are presented in Fig. 1. In the first experiment (Fig. 1a) the organic/aqueous volume ratios varied from 2 to 15 and the contact time was 15 min. The equation for the best straight-line fit of the data (derived by the least squares method) was $y = 0.026x - 9.62 \times 10^3$, indicating a slope (DC o/a) of 0.026 and an intercept at $x = 3.70 \times 10^5$. Since the initial solution contained 4.26×10^5 c/m·ml Nb-95, 87% of the niobium was unextractable. Similarly, the organic to aqueous value (Fig. 1b) was determined by using aqueous/organic volume ratios of 0.5 to 10 and an equilibration time of 15 min. The expression derived from these data was $y = 0.015x + 57$, indicating

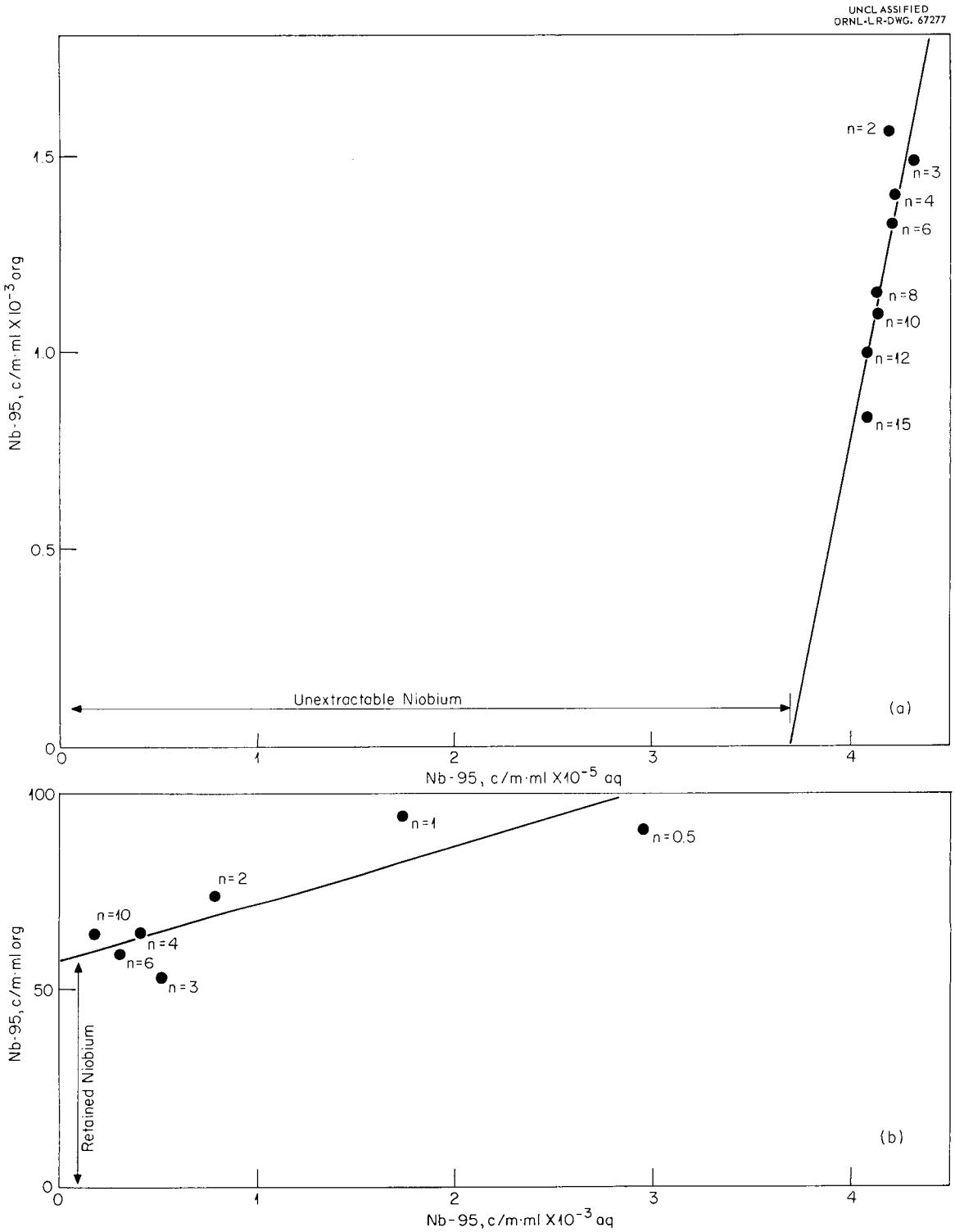

Fig. 1. Distribution of niobium between 1 M HNO_3 and 30% TBP-n-dodecane. (a) Aqueous organic measurement, n = org/aq vol ratio; (b) organic to aqueous measurement, n = aq/org vol ratio.

a DC o/a of 0.015 for the transfer of niobium from the organic to the aqueous phase with an intercept at y = 57. Since the initial Nb-95 in the organic was 1.49×10^3 c/m·ml, 3.8% of the extracted niobium was retained by the organic.

The distribution coefficients for several systems were approximated by the multiple contact method with only three or four contacts. Aqueous solutions containing Nb-95 were contacted with equal volumes of organics that had been preequilibrated three times with equivalent acid solution containing no activity. Both phases were sampled and counted. The organic phase was then equilibrated with consecutive equal volumes of an aqueous solution of the same acidity as the feed, and the raffinate with equal volumes of organic that had been preequilibrated with acid.

3.0 EXTRACTION OF Nb-95

3.1 30% TBP-n-Dodecane

Most of the niobium in nitric acid solutions less concentrated than 4 M was unextractable by freshly purified 30% TBP-n-dodecane. The aqueous/organic DC o/a of the extractable portion was low, ranging from ~0.004 in a 0.07 N acid deficient 0.13 M $Al(NO_3)_3$ solution to a maximum of ~0.05 in 4.3 M HNO_3. The percentage of the niobium in an unextractable form decreased from >90% to ~70% as the acidity increased (Table 1).

The DC o/a obtained by contacting an organic solution containing Nb-95 with nitric acid solutions decreased from ~0.1 at 4 M HNO_3 to 0.015 at 1 M HNO_3 and then increased to 0.038 at 0.5 M HNO_3. In experiments with <0.5 M HNO_3, the maximum niobium activity in the organic phase was < 100 c/m·ml. These data were so scattered and the material balances so poor that distribution coefficients were not calculated. The amount of niobium retained by the organics ranged from 3 to 8% in the 0.5 M to 4 M HNO_3 tests, with the minimum at 2 M HNO_3 and the maximum at 0.5 M.

Fifteen-minute equilibrations were used in these experiments since the results of batch contacts with 30% TBP n-dodecane with and without degraded TBP-Amsco present indicated no appreciable change in distribution coefficient with further contact time. In the preliminary tests the

Table 1. Extraction of Niobium from Nitric Acid with 30% TBP-n-dodecane

HNO_3 Conc., M	Aqueous to Organic		Organic to Aqueous	
	DC o/a	% Unext.	DC o/a	% Retained
4	0.049	67	0.11	4.5
2	0.023	71	0.021	2.6
1	0.026	87	0.015	3.8
0.5	0.024	91	0.038	7.6
0.1	0.014	95	b	b
0.1 a.d. (a)	0.0067	95	b	b

a 0.1 N a.d.-0.13 M $Al(NO_3)_3$

b Value could not be calculated because of the scatter of the data and poor material balances. The maximum Nb-95 concentration in the organic was < 100 c/m·ml.

organic solutions were contacted with equal volumes of 4 M HNO_3 containing 2.3×10^5 c/m·ml Nb-95 for 5 to 360 min and Nb-95 activity was determined after various time intervals. The 100 ± 20% activity balance probably accounts for the random variation in the distribution coefficients (Table 2).

Table 2. Effect of Contact Time on Nb-95 Extraction from 4 M HNO_3
Reagents degraded by boiling 30% TBP-Amsco solution 6 hr with 6 M HNO_3

Contact Time, min	D.C. o/a			
	70% Dodecane-30% TBP		63% Dodecane-27% TBP-3% Degraded TBP-7% Degraded Amsco	
	Aq to Org	Org to Aq	Aq to Org	Org to Aq
5	0.050	0.31	0.39	0.92
15	0.054	0.26	0.30	0.78
30	0.053	0.22	0.44	0.64
60	0.061	0.22	0.48	0.58
120	0.061	0.27	0.50	0.76
180	0.062	0.25	0.50	0.82
240	0.053	0.24	0.30	0.78
300	0.061	0.23	0.27	0.64
360	0.059	0.25	0.26	0.61

3.2 27% TBP-3% Degraded TBP in n-Dodecane

The presence of 3% degraded TBP in 27% TBP-n-dodecane increased the DC o/a of the extractable niobium from $\leq$ 4 M HNO_3 by a factor of 10 or greater and decreased the unextractable niobium from >60% to <20% (Table 3). The aqueous-to-organic DC o/a ranged from 0.2 to 0.7 for nitric acid concentrations of 0.1 to 4 M. Organic-to-aqueous values for the same acid concentrations ranged from 0.3 to 1.6, with -1 to 15% of the activity retained by the organic. In both sets of experiments the value was minimum with 2.0 M HNO_3. Little niobium was extracted from a 0.1 N acid deficient 0.13 M $Al(NO_3)_3$ solution (60 to 170 c/m·ml from a feed containing 2 x 10^5 c/m·ml). The data were scattered, and material balances were so poor that the distribution coefficient was not calculated. The small amount of activity transferred indicates either a very low coefficient ($\leq 10^{-4}$) or a large percentage of unextractable niobium. The percentage of unextractable niobium in the other tests ranged from -7 to 18%, these small negative values probably reflecting the lack of precision in the experiments.

Table 3. Extraction of Niobium-95 by 27% Purified TBP-70% n-dodecane-3% Degraded TBP

Feed at room temperature except when specified otherwise

HNO_3 Conc., M	Contact Time, Min	Feed Age, hr	Aq to Org		Org to Aq	
			DC o/a	% Unext.	DC o/a	% Unext.
4	15	<0.2	0.53	6	0.82	-1
	15	24	0.56	11	0.85	-1
2	5	<0.2	0.26	-3	0.33	0
	15	<0.2	0.22	-4	0.26	2
	15	72.5	0.25	-4	0.30	1
	30	<0.2	0.23	-4	0.28	1
1	5	<0.2	0.35	2	0.34	2
	15	24	0.42	4	0.52	0
	15	1 (100°C)	0.25	-7	0.33	13
0.5	5	<0.2	0.48	-2	0.46	3
	15	<0.2	0.48	-2	0.45	1
	15	24	0.66	12	0.76	2
0.1	15	<0.2	0.53	4	1.55	-1
	15	24	0.48	18	1.60	-1
	60	<0.2	0.22	4	0.32	15

The small variations with different feed agings and contact times, except with 0.1 M HNO_3, probably indicate a lack of precision in the results. The data for a single acidity show good agreement; for example, the aqueous-to-organic DC o/a with 0.5 M HNO_3 varies from 0.43 to 0.66. In a graph of the combined data most of the points are on a single straight line, indicating a distribution coefficient of 0.48 with none of the niobium in an unextractable form (Fig. 2). There is no explanation for the large discrepancies with 0.1 M HNO_3.

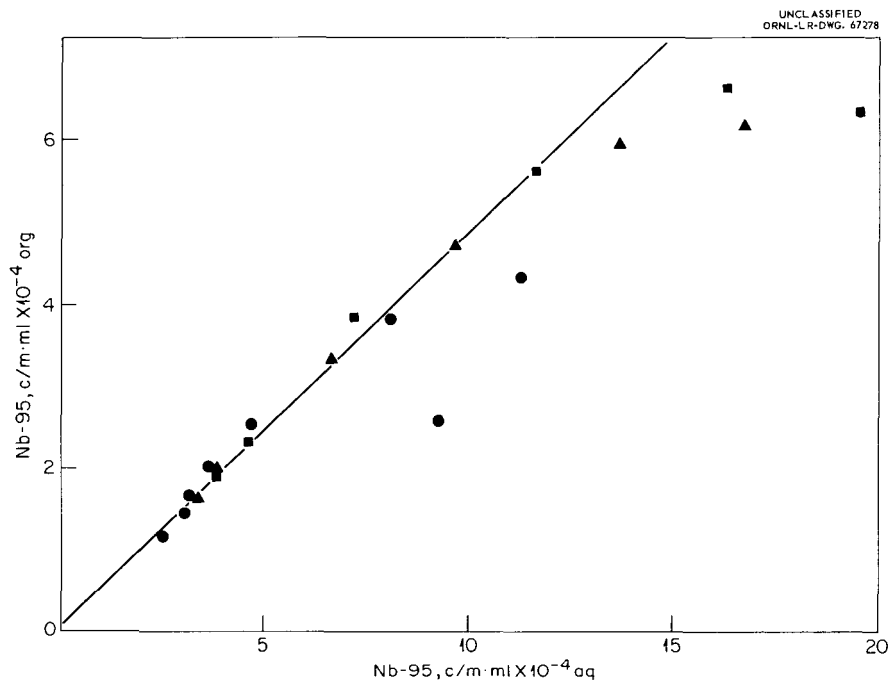

Fig. 2. Extraction of Nb-95 from 0.5 M HNO_3 with degraded TBP.

Some of the data from aqueous to organic equilibrations made with $\leq$ 2 M HNO_3 deviated from a straight-line function, producing a downward curvature in the region of the lower organic/aqueous volume ratios, e.g. those with 0.5 M HNO_3 (Fig. 2). A probable explanation for this curvature is the presence of an extractant in the solvent which forms a stronger complex with niobium than does TBP and is more soluble in the aqueous phase than is TBP. With decreasing organic/aqueous volume ratios, the amount of the extractant in the system decreases, decreasing the niobium distribution coefficient. The effect would be most obvious in the region

in which the organic phase is contacted with the greatest volume of aqueous. These observations are in agreement with extraction behavior that would be expected from solutions containing di-n-butyl phosphate (14).

The solubility of the extractant in the aqueous phase was demonstrated by washing solvent containing degraded TBP several times with equal volumes of 0.5 M HNO_3 prior to equilibration with 0.5 M HNO_3 containing 2×10^5 c/m.ml Nb-95. The DC o/a decreased with increased washings. When a single aqueous feed solution was equilibrated consecutively with two organic solutions that had been washed the same number of times, the DC o/a was higher for the second contact; this indicates a larger amount of extractant in the system, i.e., the feed solution had not removed as much extractant from the second organic phase (Table 4).

Table 4. Effect of Multiple Washings on Extraction of Niobium with Degraded TBP

Experiment Number	Number of Washes	DC o/a
(1)	3	0.17
(2)	4	0.14
(3)	5	0.12
(4)	7	0.085
(5)	a	0.107

[a] The aqueous from experiment 4 was equilibrated again with organic that had been prewashed seven times.

3.3 30% TBP-n-Dodecane Containing Degraded TBP-Amsco

The amount of niobium retained by the organic was greater for solutions of 30% TBP-n-dodecane containing degraded TBP-Amsco than with the solutions containing degraded TBP alone. The solvent was composed of 63% n-dodecane, 27% freshly purified TBP, 3% degraded TBP, and 7% degraded Amsco with the TBP-Amsco degraded together as a 30% solution. Although niobium distribution coefficients were less than those with organic containing 3% degraded TBP, this was probably due to the difference in degradation conditions (Sect. 2.2).

The aqueous to organic DC o/a decreased from ~0.4 at 4 M HNO_3 to 0.02 at 0.5 M HNO_3. Although the DC o/a could not be calculated for 0.1 M HNO_3 because of excessive curvature (see below) and for 0.1 N acid deficiency because of scatter, the maximum org/aq concentration ratios observed were 0.02 and 0.008, respectively. In the determination of the percentage of extractable niobium, extrapolation of the straight-line portion of the data from the tests with $\leq$ 2 M HNO_3 gave positive y intercepts with values equivalent to 0.8 to 2.5% of the original feed concentration. These results indicate the presence of small quantities of extractant, which result in a niobium DC o/a greater than that indicated by the straight-line portion of the data (Table 5).

The organic-to-aqueous DC o/a ranged from 0.04 to 0.6 for acidities ranging from 0.1 N acid deficiency to 4 M HNO_3. With the exception of the acid-deficient test, the amount of extracted niobium retained by the organic increased as the acidity decreased, with a maximum of ~50% at 0.1 M HNO_3. Thus, from an aqueous feed containing ~1.6×10^5 c/m·ml Nb-95, the organic would retain about 500 c/m·ml. In the acid-deficient test only 6% of the activity was retained, 200 c/m·ml from a feed containing 4×10^5 c/m·ml (Table 5).

The loss of the niobium extractant to the aqueous phase when degraded TBP was present (Sect. 3.2) was also observed in these experiments, but the loss increased markedly as the aqueous acidity decreased. The DC o/a could not be calculated from the graph of the data for 0.1 M HNO_3 (Fig. 3) as had been done for the previous experiments. The loss of the extractant at low acidities was confirmed by washing freshly degraded 30% TBP-Amsco with 0.1 M HNO_3. After precautions to minimize organic entrainment had been taken, this aqueous solution was mixed with freshly purified 30% TBP-dodecane, and enough concentrated nitric acid was added to raise the aqueous acidity to 4 M HNO_3. With the resulting organic solution the DC o/a was 0.55 for both aqueous-to-organic and organic-to-aqueous experiments, with ~6% of the niobium unextractable and retained by the organic (Fig. 4). The aqueous-to-organic DC o/a was 10 times that with purified TBP and ~1.5 times that with degraded TBP and Amsco. Thus the extractant that had transferred to the 0.1 M HNO_3 transferred to the 30% TBP-n-dodecane at the higher acidity.

Table 5. Extraction of Niobium-95 with Solvent Containing Degraded TBP and Amsco[a]

Room temperature except as specified

HNO_3 Conc. M	Contact Time, min	Feed Age, hr	Aqueous to Organic DC o/a	Aqueous to Organic % Unext.	Aqueous to Organic % Complex[b]	Organic to Aqueous DC o/a	Organic to Aqueous % Retained
4.0	15	<0.2	0.38	6	-	0.61	6
4.0	15	24	0.37	7	-	0.59	6
4.0	15	1 (100°C)	0.34	2	-	0.63	9
4.0[c]	15	1 (100°C)	0.40	4	-	0.66	10
2.1	15	<0.2	0.12	-4	-	0.21	12
2.1	15	24	0.13	3	-	0.23	9
2.0	15	1 (100°C)	0.08	<0	2.5	0.24	20
2.2	60	1 (100°C)	0.10	<0	1.9	0.26	9
1.1	15	<0.2	0.05	<0	1.3	0.20	9
1.1	15	24	0.06	<0	1.4	0.12	12
1.2	15	1 (100°C)	0.05	<0	1.7	0.22	9
1.2	60	1 (100°C)	0.07	<0	0.8	0.12	10
0.5	15	<0.2	0.02	<0	1.8	0.24	53
0.5	15	24	0.03	<0	1.5	0.28	14
0.5	15	1 (100°C)	0.02	<0	2.0	0.09	14
0.1	15	<0.2	d	-	-	0.16	47
0.1	15	24	d	-	-	0.10	51
0.1	15	<0.2	d	-	-	0.09	51
0.1	15	1 (100°C)	d	-	-	0.07	30
0.1	60	1 (100°C)	d	-	-	0.02	33
0.1 Na.d.	15	1 (100°C)	e	-	-	0.04	6

[a] 63% n-dodecane, 27% purified TBP, 3% degraded TBP, 7% degraded Amsco. Amsco and TBP degraded by boiling 30% TBP in Amsco 6 hr with 6 M HNO_3.

[b] (y intercept value/original feed concentration) x 100. This value is given when the data show a negative % unextractable >10%, and has been named "% strongly complexed" for convenience.

[c] Different Nb-95 stock solution used to prepare the feed.

[d] DC o/a could not be calculated as the others; maximum org conc/aq conc = 0.02.

[e] Much scatter; DC o/a either $\leq$ 0.008 or a major percentage unextractable.

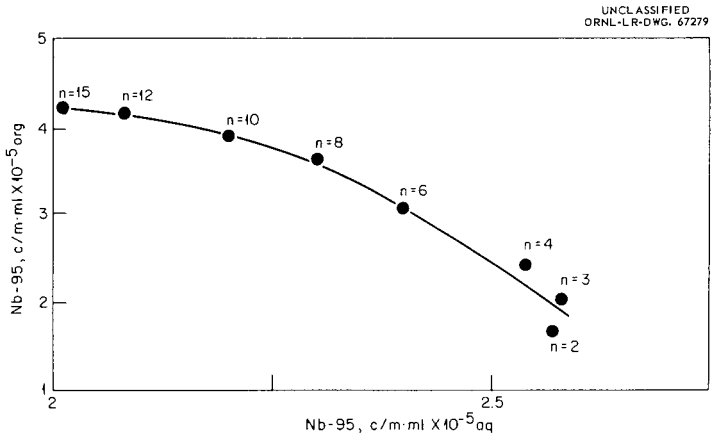

Fig. 3. Aqueous to organic distribution of niobium-95 from 0.1 M HNO_3 into 30% TBP-n-dodecane containing TBP-Amsco degradation products.

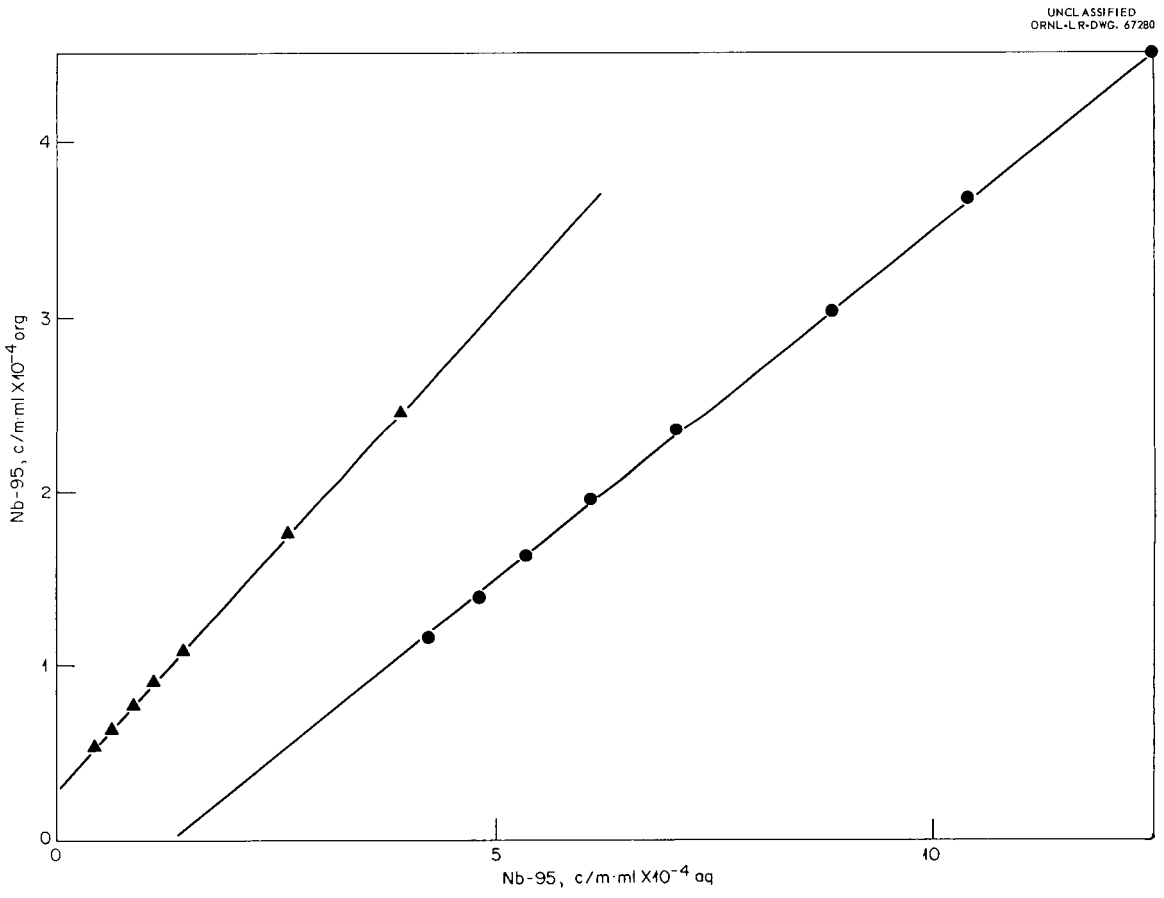

Fig. 4. Extraction of niobium-95 from 4 M HNO_3 with 30% TBP-n-dodecane containing TBP-Amsco degradation products.

Qualitatively, the addition of degraded Amsco alone to 30% TBP-n-dodecane increased the percentage of extractable niobium but had little or no effect on the DC o/a. The presence of 7% degraded Amsco decreased the unextractable niobium from 80-90% to ~60% in 2 M HNO_3 and from 60-70% to ~40% in 4 M HNO_3. The DC o/a changed from ~0.1 to ~0.06 and ~0.1 to ~0.2, respectively. These values were obtained in a series of multiple-contact experiments made to determine the effect of adding various combinations of degraded TBP and Amsco to 30% TBP-n-dodecane (Table 6). The maximum aqueous to organic DC o/a for both 2 and 4 M HNO_3 was obtained with the organic solutions containing degraded TBP and Amsco that had been degraded separately. The coefficients were ~0.4 and ~0.8, respectively, with 10% of the niobium unextractable in both cases. The slightly lower value observed with TBP and Amsco degraded together was probably due to the difference in degradation conditions as mentioned above (Sect. 2.2).

In contrast to the aqueous-to-organic experiment, the maximum DC o/a in organic-to-aqueous tests were obtained with TBP and Amsco degraded together, but the solutions containing TBP degraded singly retained much more activity. The coefficients for the TBP-Amsco degraded together were 0.5 and 0.9 for 2 and 4 M HNO_3, respectively, and were as much as twice the values obtained in the corresponding aqueous-to-organic experiments. The coefficients that could be measured were the same for the other degraded solutions in both sets of equilibrations. Some of the activity material balances were so poor that the coefficients were not calculated.

4.0 REMOVAL OF Nb-95 FROM ZIRCONIUM SOLUTIONS

Niobium-95 may be removed from nitric acid solutions containing zirconium by adsorption on unfired Vycor glass powder (15). Preliminary solvent extraction experiments with zirconium had shown that the sensitivity of the chemical analytical methods were not sufficient to follow the course of the zirconium in dilute nitric acid systems. The removal of Nb-95 by Vycor glass allowed the use of direct γ counting as a means of analysis for zirconium. The niobium daughter was removed from stock solutions containing ~10 M HNO_3, 20 g/liter Zr, 10^6 c/m·ml Zr-Nb-95, and

Table 6. Extraction of Nb-95 from 2 and 4 M HNO_3 by TBP Reagents Degraded by Refluxing 6 hr with 6 M HNO_3

	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5[a]	Exp. 6[b]
Dodecane, %	70	70	63	63	63	63
TBP, %	30	30	27	30	27	27
Degraded TBP, %	--	--	3	--	3	3
Amsco, %	--	--	7	--	--	--
Degraded Amsco, %	--	--	--	7	7	7
	2 M HNO_3, 1.4 x 10^5 c/m.ml Nb-95					
Aq to Org						
DC o/a	~ 0.08	~ 0.1	~ 0.2	~ 0.06	~ 0.4	~ 0.3
% unextractable	~80	~90	~20	~60	~10	~30
Org to Aq						
DC o/a	c	c	~ 0.2	c	~ 0.4	~ 0.5
% retained	c	c	~60	c	~50	~ 2
	4 M HNO_3, 1.8 x 10^5 c/m.ml Nb-95					
Aq to Org						
DC o/a	~ 0.1	~ 0.1	~ 0.7	~ 0.2	~ 0.8	~ 0.4
% unextractable	~60	~70	~10	~40	~10	~20
Org to Aq						
DC o/a	c	c	~ 0.7	c	~ 0.8	~ 0.9
% retained	c	c	~40	c	~40	~10

[a] TBP and Amsco degraded separately.
[b] TBP and Amsco degraded as a 30% TBP in Amsco solution.
[c] Could not calculate because of poor material balance of activity.

50 g/liter 100 mesh unfired Vycor glass by passing the solution twice through two columns, 13 mm high by 10 mm dia, containing 1 g of -100 mesh unfired Vycor. The activity in the resulting solution ranged from 90 to 99% Zr-95. This solution could then be diluted to the desired acid and zirconium concentrations.

The coefficients obtained by chemical analysis and by γ counting showed good agreement. By chemical analysis, the DC o/a for zirconium between 30% TBP-n-dodecane and a solution containing ~4 M HNO_3, ~1 g/liter Zr, and 10^4-10^5 c/m.ml γ, ranged from 0.25 to 0.44 for the aqueous-to-organic and 0.33 to 0.44 for the organic-to-aqueous tests. A γ count of the phases indicated coefficients of 0.25 to 0.5 and 0.34 to 0.4, respectively (Table 7). Hickok and Cannon give a value of 0.25 with 4 M HNO_3, 0.0115 M Zr, and 1 M TBP-n-dodecane (6). The coefficients were

obtained by the multiple-contact method. In preliminary experiments with chemical analyses, the DC o/a for zirconium between nitric acid containing ~1 g/liter Zr and 30% TBP-n-dodecane ranged from <0.002 with 1 M HNO_3 to ~1 with 6 M HNO_3. In the comparison tests ~4 M HNO_3 was used since the quantity of zirconium used was convenient for chemical analysis.

Table 7. Extraction of Zirconium from Nitric Acid with 30% TBP-n-Dodecane

Multiple contact method, 5-min contacts

HNO_3, M	Zr, g/liter	γ Activity, c/m·ml	Zr-Nb, %	DC o/a Aq-to-Org Chem. Analysis	DC o/a Aq-to-Org γ Count	DC o/a Org-to-Aq Chem. Analysis	DC o/a Org-to-Aq γ Count
4.9	1.38	6.6×10^5	96	0.39	0.50	0.33	0.40
4.3	1.08	6.2×10^5	90	0.30	0.31	0.44	0.35
4.1	1.15	6.2×10^4	99	0.25 - 0.44[a]	0.25	0.33	0.34

[a] Analytical difficulties.

Investigation of the solvent extraction of zirconium from nitric acid by TBP and its chemical degradation products was discontinued. There are several publications on TBP extraction (2-6), and recently an excellent study was published on the extraction of zirconium by di-n-butyl phosphoric acid (7).

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