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CHEMICAL TECHNOLOGY DIVISION
CHEMICAL DEVELOPMENT SECTION C
PROGRESS REPORT FOR
OCTOBER-DECEMBER 1961

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CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section C
Progress Report for
October-December 1961

K. B. Brown

Date Issued

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

ABSTRACT

Recovery of Thorium (and Uranium) from Granitic Rock

Recovery of thorium by acid leaching ten additional granite samples (36-82 ppm thorium) from the Conway formation in New Hampshire ranged from about 50 to 85%, and averaged about 70%. Study of the effect of grind size on the recovery of thorium from Conway and Pikes Peak granites showed no significant differences in the range minus 20 to minus 200 mesh. The thorium concentration in a sized Conway granite sample was found to be much greater in the fine than in the coarse fractions, whereas Pikes Peak granite showed only slight thorium enrichment in the finer fractions. Uranium recoveries in acid leaching of four different granite samples were not improved by adding an oxidant.

Collection and Analysis of Granite Samples

Rice University (under ORNL subcontract) has made a field survey of the Conway granite formations in New Hampshire. Over 500 field spectroradiometric determinations were made on an extensive portion of the 400 square miles of outcrop area with a portable, single-channel, transistorized, gamma-ray pulse height analyzer. Preliminary analysis of the data indicates that the accessible surface of the Conway granite averages at least 40 ppm thorium.

Collection and Analysis of Lateritic Soils

The thorium concentration ranged 5-16 ppm in twenty-two samples of sub-lateritic soil from Mississippi, Alabama, Georgia, and Virginia.

Final Cycle Plutonium Recovery by Amine Extraction

In continued batch countercurrent testing with simulated Purex IBP solution of the proposed chemical flowsheet for final cycle plutonium recovery by amine extraction, the extraction profile with the amine (TLA) concentration decreased from 0.3 to 0.15 M again confirmed the predicted extraction isotherm. The product solution contained 23 g Pu/liter (nominal x20 concentration factor), and the stripped organic and the raffinate contained, resp., 0.001 and <0.002 g/liter.

Extraction and Separation of Zirconium and Hafnium

Results are summarized for tests on the extraction and separation of zirconium and hafnium with amines and organophosphorus esters and acids. All three extractant classes showed some promise but the studies were not sufficiently extensive to define complete processes.

Separation of Rare Earths and Transplutoniums

Extraction of all lanthanides from concentrated LiCl and mixed LiCl-AlCl₃ solutions by various tertiary amines was greater than that of yttrium. Order of extractability and differences from yttrium varied with composition of both organic and aqueous solutions. Scandium varied widely in extractability with solution composition, being similar to europium under some conditions and to americium under others. Amine extractions of rare earths from thiocyanate solutions were very small.

Extraction of Nitric Acid and Iron Sulfate from Purex 1WW Solution

Approximately 90% of the nitrate and iron and a major portion of the sulfate were extracted from synthetic Purex 1WW solution with a primary amine. This treatment produces a solution of low salt content which is highly amenable to solvent extraction recovery of strontium and possibly cesium.

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1.0 PROCESS CHEMISTRY OF URANIUM AND THORIUM

1.1 Recovery of Thorium (and Uranium) from Granitic Rock

(D. J. Crouse, F. J. Hurst)

As described previously,^{1,2} granitic rock is being studied as an important, long-range thorium reserve for the nuclear power industry. Recent effort has emphasized the Conway granite of New Hampshire since this source represents a very large reserve which is relatively rich in thorium and which is amenable to processing. Approximately 400 sq mi of New Hampshire has outcroppings of Conway granite. This material is a coarse-grained alkali granite consisting of approximately equal amounts of quartz, potassium feldspar and plagioclase. Minor portions (5-10% of mapped outcrop area) consist of finer grained material probably in the form of tabular zones or dikes, which generally is somewhat less rich in thorium and uranium than the main body.

1.1.1 Leaching of Conway and White Mountain Granite Samples.

The two samples of Conway granite (GA-3 and GF) studied previously were both from the Redstone Quarry at Conway, N. H. They contained ~70 ppm thorium and gave good recoveries (~80%) in acid leaching. A number of new Conway samples, obtained from widely scattered locations, have been generally lower in thorium content but have also shown favorable response to acid leaching (Table 1). The thorium concentration in the ten new samples ranged from 36 to 82 ppm, averaging 56 ppm while the uranium concentration ranged from 6 to 19 ppm, averaging 11 ppm. Leaching for 6 hrs at R.T. with 2 N H₂SO₄ (130 lbs H₂SO₄/ton of granite) dissolved 49-85% of the thorium and 26-73% of the uranium; average recoveries of thorium and uranium were 69% and 53% respectively. The average acid consumption in leaching was 80 lbs H₂SO₄ per ton of granite.

Nine samples of rock from the White Mountain Magma Series, which were taken in the vicinity of the Conway granite formations and which represent less important textural and mineralogical variants (monzonite, granodiorite, syenite, etc.) were also studied briefly. These samples contained 15 to 73 ppm (averaging 33 ppm) thorium and 2-9 ppm uranium. Recoveries in leaching (Table 2) varied over a relatively wide range, being 50-80% for five of the samples but only 25-40% for the other four.

It should be noted (Tables 1 and 2) that the total thorium accounted for in the above tests by wet chemical analysis was often in poor agreement with the amount indicated to be present from analysis of the head sample by the gamma spectrometric method. Many of the material balance figures calculated on this basis were considerably outside the extremities of the expected 100±15% range. Wet chemical analyses of the head samples have also shown consistently lower thorium than the Rice gamma spectrometric measurements. In contrast, gamma spectrometric determinations at Rice and ORNL have shown excellent agreement. Attempts are being made to resolve the differences between the two methods of analysis.

Table 1. Leaching of Conway Granite

Conditions: Pulverized ore; 6 hr leach @ R.T. with 2 N H₂SO₄, 60% pulp density
(130 lb of H₂SO₄ per ton of ore)

Sample No.	Sample Location	Head Analysis, ^a ppm		Recovery, ^b %		Thorium Material Balance, ^c %	Acid Consumption ^d
		Th	U	Th	U		
MCK-118-C-25	Mt. Ascutney, Vt.	36	6.4	80	49	92	55
MCK-12-C-2	Birch Hill Quarry, North Conway quadrangle	46	10	85	61	87	77
MCK-17C-C-6	North Conway quad.	47	13	49	26	77	89
MCK-19-C-8	Crawford Notch quad.	48	12	53	39	80	107
MCK-103-C-20	Mt. Chocorua quad.	51	7.8	81	69	98	86
MCK-56-C-19	Plymouth quad. (fine-grained)	54	12	80	73	78	90
MCK-11-C-1	Cathedral Ledges, North Conway quad.	56	6.9	59	51	82	72
MCK-55-C-18	Plymouth quad. (coarse-grained)	64	12	80	60	66	72
MCK-27-C-13	Franconia quad.	76	14	51	50	70	79
MCK-13-C-3	Redstone Quarry, North Conway quad.	82	19	76	48	85	88
GA-3	Redstone Quarry, North Conway quad.	72	14	82	67	87	51
GF	Redstone Quarry, North Conway quad.	71	16	82	69	96	65

^aBy gamma spectrometric method at Rice University.

^bBased on total found by wet chemical analysis in the leach solution and residue.

^cBased on total found by wet chemical analysis compared to the head analysis by the gamma spectrometric method.

^dlbs H₂SO₄ per ton of granite.

Table 2. Leaching of Miscellaneous Rocks from the White Mountain Magma Series

Conditions: pulverized ore; 6 hr leach @ R.T. with 2 N H₂SO₄, 60% pulp density (130 lbs H₂SO₄ per ton of ore)

Sample No.	Description	Head Analysis, ^a ppm		Recovery, ^b %		Thorium Material Balance, ^c %	Acid Consumption ^d
		Th	U	Th	U		
MCK-117-C-24	Hornblende biotite monzonite; Mt. Ascutney, Vt.	15	1.8	37	34	90	82
MCK-106-C-21	Syenite (?); Percy quadrangle	16	2.6	63	30	69	51
MCK-18-C-7	Aplitic granite; North Conway quad.	17	5.9	36	23	106	217
MCK-3-B-3	Breccia granodiorite; Winnepesaukee quad.	28	4.9	31	11	79	86
MCK-14A-C-4	Green granite; Redstone Quarry, North Conway quad.	34	9.1	53	43	88	85
MCK-20-C-9	Quartz syenite-granite; Crawford Notch quad.	35	9.3	70	42	86	103
MCK-21-C-10	Syenite; Crawford Notch quad.	23	3.6	27	29	83	126
MCK-14B-C-5	Mt. Oeola (?) green granite; North Conway quad.	41	7.9	61	52	81	91
MCK-17F-C-6	Aplitic rock in Conway granite; North Conway quad.	73	24	78	74	81	77

^aBy gamma spectrometric method at Rice University.

^bBased on total found by wet chemical analysis.

^cBased on total found by wet chemical analysis compared to the head analysis by gamma spectrometric method.

^dlbs H₂SO₄ per ton of granite.

1.1.2 Effect of Ore Particle Size on Leachability of Conway and Pikes Peak Granites. Most earlier¹ granite leaching tests were made on -48 mesh material since petrographic examination of the samples had indicated that good liberation of the minerals was obtained by grinding to this mesh size. Subsequently, it was shown with seven different samples that grinding to -200 mesh did not improve recoveries. Recent tests with Pikes Peak and Conway granite samples have shown that grinds much coarser than -48 mesh apparently can be tolerated without loss of leaching efficiency.

The Conway and Pikes Peak samples were stage-ground to -20, -28, -35, -48, and -200 mesh and leached at 50 and 60% pulp density with 2 N H₂SO₄ at R.T. The test results (Table 3) show no consistent significant variation in thorium and uranium recoveries with change in grind size in this range. Acid consumption in leaching the -200 mesh samples was, however, appreciably higher than with the coarser materials. Reducing the pulp density from 60 to 50% (50% increase in amount of acid added) increased recoveries from both the Conway and Pikes Peak granite by a few percent.

1.1.3 Distribution of Thorium in Sized Granite Fractions. Separation of a Conway granite sample into sized fractions by dry screening showed the -325 mesh fraction to be 3.5 times more concentrated in thorium than the coarsest fraction (Table 4). About 38% of the total thorium was found in the -325 mesh fraction which comprised 17% of the ore by weight.

In contrast, sized fractions of Pikes Peak granite were relatively uniform in thorium concentration. The thorium concentration in the -325 mesh fraction was only 1.5 times that in the coarsest fraction.

1.1.4 Effect of Added Sodium Chlorate on Uranium Recoveries. In tests with four different granite samples, addition of sodium chlorate to the leach slurry had little effect on uranium recoveries (Table 5). The small variations shown can probably be attributed to analytical uncertainties since material balances for the tests were rather poor (81-122%). With the Dillon Tunnel and Conway samples, the final EMF of the liquors was approximately the same with or without addition of the oxidizing agent. Addition of 4 lbs sodium chlorate per ton of ore appreciably increased the EMF in tests with the Boulder and Cathedral Peak samples.

1.2 Collection and Analysis of Granite Samples (work performed at Rice University on Subcontract 1491 - J. A. S. Adams and J. J. W. Rogers, Codirectors)

During the last two summers Rice University, under subcontract to ORNL, has been conducting field surveys of granites and other types of thorium bearing rocks. Samples of a wide variety of granites and associated rocks throughout the United

Table 3. Effect of Granite Particle Size on Leachability

Conditions: 30 g sample of granite leached at ~25°C with 20 or 30 ml of 2 N H₂SO₄ (equivalent to 130 and 195 lbs H₂SO₄ per ton respectively at 60 and 50% pulp densities); filtered, washed

Grind Mesh Size	Leach Pulp Density, %	Leach Time, hr	Final pH	Recovery, ^a %		Acid Consumption ^b
				Th	U	
<u>Conway (GF-1, 76 ppm Th, 16 ppm U)</u>						
-20	60	24	0.6	89	72	78
-28			0.5	90	77	73
-35			0.5	91	79	78
-48			0.5	90	78	79
-200			0.6	87	74	89
-20	50	6	0.3	88	73	66
-28			0.3	89	74	68
-35			0.3	90	72	63
-48			0.3	89	78	74
-200			0.3	89	72	86
-20	50	24	0.4	92	77	82
-28			0.4	93	79	82
-35			0.4	95	79	85
-48			0.4	94	80	82
-200			0.4	90	78	105
<u>Pikes Peak (GG-1, 24 ppm Th, 4 ppm U)</u>						
-20	60	24	0.6	69	46	96
-28			0.6	76	37	93
-35			0.7	74	48	98
-48			0.7	76	46	102
-200			0.8	74	49	109
-20	50	6	0.3	68	36	73
-28			0.3	77	33	74
-35			0.4	80	39	83
-48			0.4	72	32	90
-200			0.5	75	44	105
-20	50	24	0.6	81	53	103
-28			0.6	82	49	107
-35			0.6	81	53	111
-48			0.6	81	49	116
-200			0.6	78	50	126

^aBased on total found by wet chemical analysis of leach solution and residue. Thorium material balances ranged 86-104% based on the gamma spectrometric head analysis.

^blbs of H₂SO₄ per ton of granite.

Table 4. Distribution of Thorium in Sized Granite Samples
(Head ores stage-ground to -48 mesh)

Mesh Size (Tyler)	% of Total Weight	Thorium Analysis, ^a ppm	Thorium, % of Total ^b
<u>Conway Granite (GF-1, 76 ppm Th)</u>			
-48+65	28.5	48	17.4
-65+100	20.9	55	14.6
-100+150	15.5	57	11.2
-150+200	9.4	76	9.1
-200+325	8.5	85	9.2
-325	17.2	176	38.5
	<u>100.0</u>		<u>100.0</u>
<u>Pikes Peak Granite (GG-1, 24 ppm Th)</u>			
-48+65	27.8	20	25.3
-65+100	25.4	19	22.0
-100+150	11.3	22	11.3
-150+200	11.3	22	11.3
-200+325	7.8	26	9.2
-325	16.4	28	20.9
	<u>100.0</u>		<u>100.0</u>

^aBy gamma spectrometric method at ORNL.

^bBased on total thorium found. This was 91-104% of head analysis.

States were obtained in 1960. During 1961, attention was focused on the Conway granites of New Hampshire which are especially promising from the standpoint of thorium grade and tonnage.

1.2.1 Thorium and Uranium Contents of Many Different Granites.

Analyses by the gamma spectrometric method were completed on many more of the rock samples collected in the summer of 1960 (Table 6). Samples from New Hampshire, particularly those classified as Conway granite, continued to show the highest average thorium content although local "hot spots" were also found in Southwestern Maine, Vermont, Massachusetts, and Rhode Island. Three samples of Conway granite from the adjacent Winnepesaukee and Wolfeboro quadrangles in New Hampshire were somewhat lower in thorium content than Conway samples from areas slightly north of this region.

1.2.2 Field Survey of the Conway Granite.

In the summer of 1961, the Conway granite formations in New Hampshire were surveyed with a portable single-channel, gamma-ray pulse height analyzer, developed for direct determination of thorium in the field. Over 500 field spectroradiometric determinations of thorium were made on the Conway granite and related rocks of the White Mountain Magma Series. The sampling spectrum covered an extensive portion of the accessible 400 square miles of Conway granite outcrop area.

Table 5. Effect of Sodium Chlorate on Uranium Recoveries

Conditions: 30 g samples of -48 mesh granite were leached with 20 ml 2 N H₂SO₄ for 6 hr at 25-27°C. In some tests, solid NaClO₃ was added at the beginning of the leach.

Granite Sample	NaClO ₃ , lb/ton of Granite	Final EMF ^a	Total Fe Extracted, ppm	Fe(III), % of Total Fe	Uranium Recovery, %
Boulder (GB-3, 6 ppm U)	0	+0.336	4000	9	28
	1	0.335	3960	8	18
	4	0.371	3660	31	25
Dillon Tunnel (GE, 8 ppm U)	0	0.317	6530	14	42
	1	0.311	6610	13	37
	4	0.318	6230	15	38
Cathedral Peak (GH, 10 ppm U)	0	0.313	5460	6	36
	1	0.314	5450	6	29
	4	0.340	5070	19	41
Conway (GF, 16 ppm U)	0	0.312	9260	5	73
	1	0.308	9290	5	71
	4	0.314	8980	5	77

^aPt vs saturated calomel electrodes.

A preliminary calibration curve for the field instrument is given in Figure 1 and a plot of frequency versus counts per minute (and ppm thorium) is given in Figure 2. From these raw data, it is clear that the accessible surface of the Conway granite averages at least 40 ppm thorium. In addition to the field thorium measurements, samples were taken at most of the stations. A total of twenty feet of core was obtained at several stations through the courtesy of the New Hampshire Department of Highways and Public Works. Six large samples in the range 40-70 pounds were sent to ORNL for leaching studies.

Laboratory and statistical analysis of the data and samples at Rice is now underway to determine the following:

- 1) What effect weathering has on the thorium concentration as shown by the cores and the freshness of rock at each station.
- 2) Whether thorium concentration is a function of any geologic parameter, e.g., position in the intrusion, elevation, faults, or other structure.
- 3) A final calibration curve for the field instrument.

The instrument used for the field measurements was developed at Rice and consists of a regular Harshaw 3"x3" NaI crystal mounted by Harshaw with a multiplier phototube. Power to this detector is supplied by mercury batteries. The signal from the

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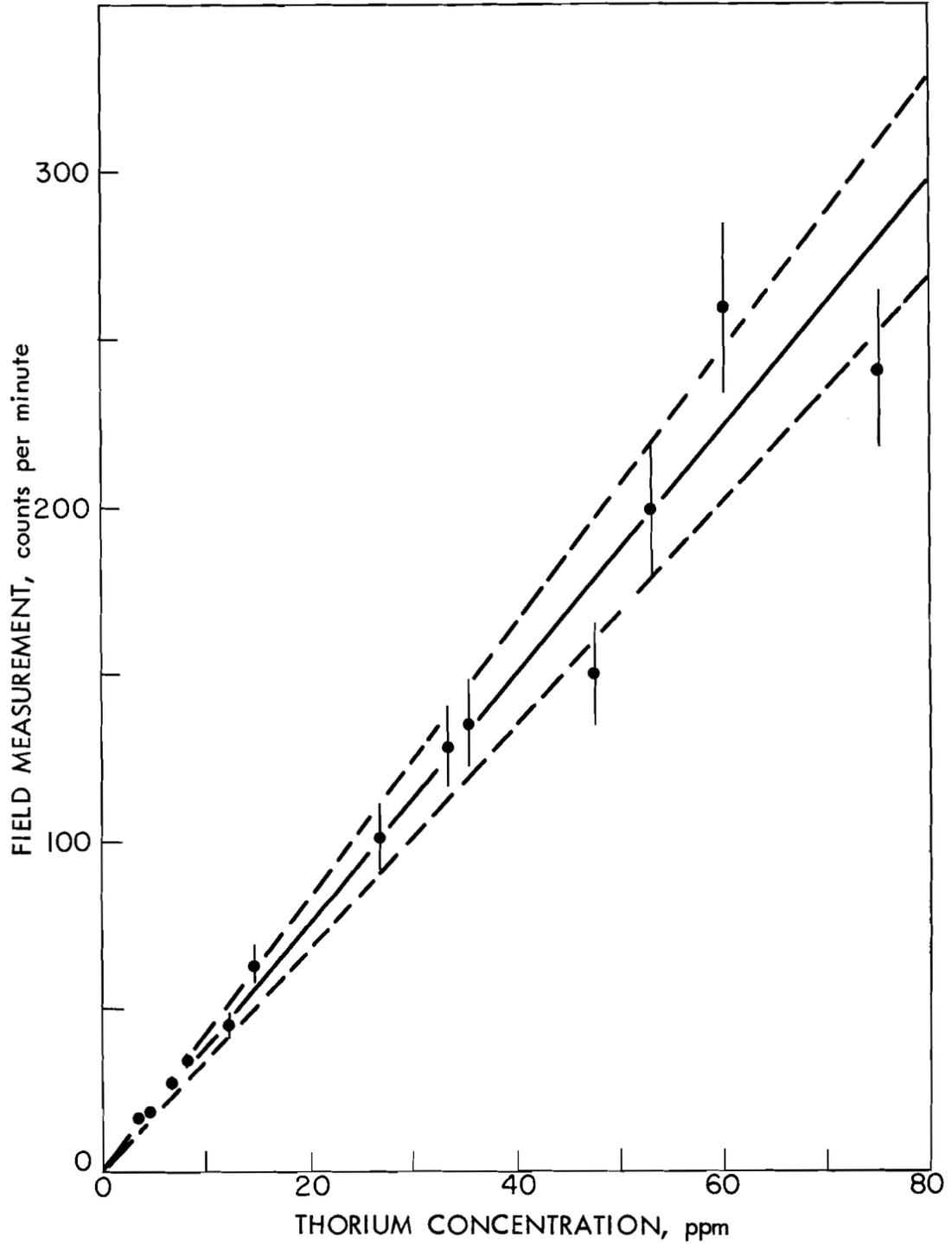


Fig. 1. Preliminary calibration of field instrument.

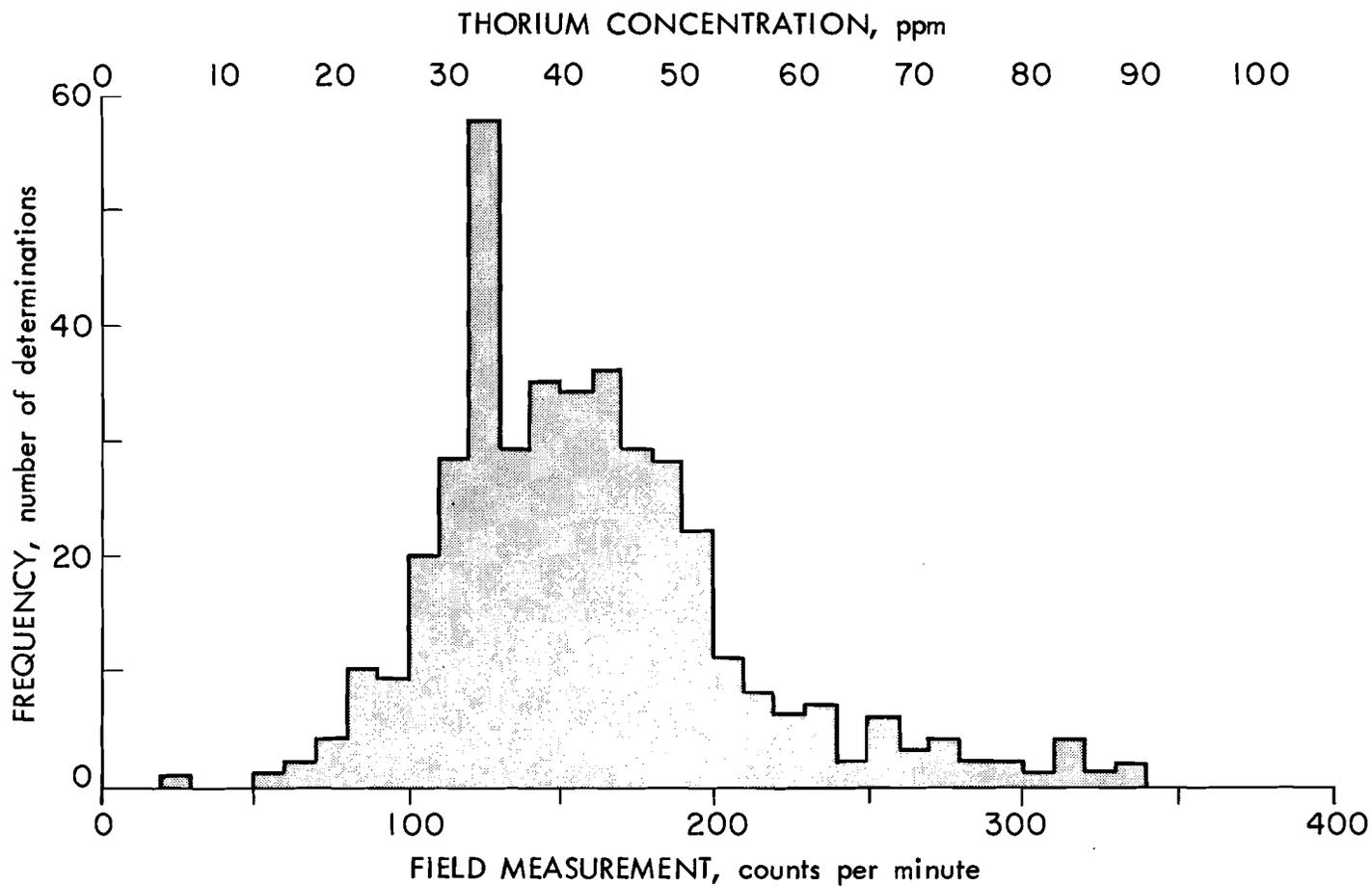


Fig. 2. Frequency plot of 430 Thorium determinations on Conway granite.

detector is taken in sequence to an amplifier, a discriminator, anti-coincidence circuit, a binary scaler with three levels, and finally to a register. Everything but the register is transistorized to reduce weight and power requirements. The entire instrument (except for the shield), encased for field use, weighs less than 40 pounds. With a 65 pound shield for the NaI crystal, geometry effects can be reduced to less than 10% in most cases at the 2.62 mev level. At the thorium concentrations found in most cases in the Conway formations, field spectroradiometric determinations could be made in 10-15 minutes at the 95% confidence level.

1.3 Thorium Content of Some Lateritic Soils (Rice University)

Some (22) field measurements and samples were taken of lateritic soils in Mississippi, Alabama, Georgia, and Virginia. These soils proved to be low in thorium (5-16 ppm) and nothing more is planned in connection with these particular samples, although other lateritic soils will be investigated.

Table 6. Thorium and Uranium Content of Granite Samples
(Analyses by gamma spectrometry at Rice University)

Sample No.	Analysis, ppm		Comments
	Th	U	
<u>White Mountain Magma Series</u>			
MCK-34-C-17	11	2.1	Landaff granite; Moosilauke quadrangle
MCK-22-C-11	32	13	Mt. Oeola granite; Crawford Notch quad.
MCK-18-C-7	17	5.9	Fine-grained aplitic granite; North Conway quad.
MCK-4B-B-4	6.1	1.3	Syenite; Winnepesaukee quad.
MCK-2-B-2	29	5.6	Conway granite; Winnepesaukee quad.
MCK-1-B-1	32	5.0	Breccia granodiorite; Winnepesaukee quad.
MCK-5-D-1	26	4.4	Conway granite; Wolfeboro quad.
MCK-8-D-4	13	3.9	Granodiorite; Wolfeboro quad.
MCK-6-D-2	24	4.7	Conway granite; Wolfeboro quad.
MCK-117-V-C-24	15	1.8	Hornblende biotite monzonite; Mt. Ascutney, Vt.
MCK-116-V-C-23	13	2.1	Hornblende biotite syenite; Mt. Ascutney, Vt.
MCK-17F-C-6	73 ^a	24	Fine-grained aplitic rock (not a dike) within Conway granite; North Conway quad.

Table 6 (Cont'd)

Sample No.	Analysis, ppm		Comments
	Th	U	
MCK-17C-C-6	47 ^a	13	Typical coarse-grained Conway Granite at same locality
MCK-13-C-3	82 ^a	19 ^a	Typical Conway granite; Redstone Quarry, North Conway quad.
MCK-19-C-8	48 ^a	12	Typical Conway granite; Crawford notch quad.
MCK-55-C-18	64 ^a	12	Conway granite; rock is fine-grained; grades into coarse-grained C-19; Plymouth quad.
MCK-56-C-19	54 ^a	12 ^a	Coarse-grained Conway granite; same locality as C-18
MCK-103-C-20	51 ^a	7.8 ^a	Typical Conway granite; Mt. Chocorua quad.
<u>Southwestern Maine</u>			
MCK-60-Me-3	13	4.5	Granite; Mt. Waldo batholith
MCK-61-Me-4	33	10	Granite from quarry; Jonesboro, Maine
MCK-62-Me-5	22	6.5	Somes Sound pink granite; Halls quarry
MCK-63-Me-6	30	6.8	Granite; Mt. Waldo batholith, Frankport quarry
MCK-64-Me-7	32	9.0	Deer Isle grey granite; the Granite Corp. quarry
MCK-65-Me-8	32	9.0	Deer Isle pink granite; the Granite Corp. quarry
MCK-66-Me-9	22	6.6	Somes Sound pink granite
MCK-67-Me-10	27	5.5	Somes Sound pink granite
MCK-71-Me-14	13	3.0	Grey granite; Hocking granite quarry
MCK-73-Me-16	19	8.2	Grey granite; Beisaw quarry
MCK-74-Me-17	19	9.5	Grey granite; Maine and New Hampshire granite quarry
MCK-75-Me-18-A	11	3.0	Medium-grained granite; Dodlin Hill quarry
MCK-75-Me-18-B	27	4.4	Fine-grained granite; Dodlin Hill quarry
MCK-78-Me-21	66	3.6	Grey granite; Downal quarry

Table 6 (Cont'd)

Sample No.	Analysis, ppm		Comments
	Th	U	
MCK-80-Me-23	78	12	Pink and green granite; upper portion of Swenson quarry
MCK-81-Me-24	41	6.4	Pink granite; lower portion of Swenson quarry
MCK-59-Me-2	23 ^a	5.6	Granite; Mt. Waldo batholith; Bucksport quarry
MCK-68-Me-11	21 ^a	6.0	Somes Sound pink granite; Desert Mountain
MCK-69-Me-12	20 ^a	5.1	Somes Sound grey granite; Desert Mountain
MCK-70-Me-13	16 ^a	6.7	Grey granite; Lincolnville quarry
MCK-77-Me-20	35 ^a	4.4	Metamorphic rock (?); Freeport quarry
MCK-79-Me-22	19 ^a	3.4	Grey granite; North Kennebunkport quarry
MCK-76-Me-19	21	3.8	Quartz monzonite; Hallowell quarry
<u>New Hampshire Magma Series</u>			
MCK-24-NH-1	97	16	Bickford white granite; Crawford Notch quad.
MCK-25-NH-(L)-2	16	5.4	Littleton quartzite, 1' from dikelet of Bickford granite
MCK-26-NH-3	24	8.0	Intrusive breccia; Franconia quad.
MCK-29-NH-5	18	5.3	Kinsman quartz monzonite; Franconia Notch quad.
MCK-30-NH-6	3.9	1.2	Dark fine-grained dike cutting NH-5; Franconia quad.
MCK-31-NH-7	15	6.2	Kinsman quartz monzonite; Franconia quad.
MCK-32-NH-8	13	2.3	Sugar Hill quartz monzonite; Moosilauke quad.
MCK-33-NH-9	109	8.2	Kinsman quartz monzonite; Franconia quad.
MCK-40-NH-11	14	1.9	Moody Ledge granite; Moosilauke quad.
MCK-41-NH-12	6.0	1.3	Moody Ledge granite (?); Moosilauke quad.

Table 6 (Cont'd)

Sample No.	Analysis, ppm		Comments
	Th	U	
MCK-42-NH-13	29	9.0	French Pond granite (grey); Moosilauke quad.
MCK-43-NH-14	48	9.1	French Pond granite (pink); Moosilauke quad.
MCK-99-NH-18	22	14	Concord granite; Concord quad.
MCK-102-NH-19	23	8.8	Tamworth granite; Mt. Chocorua quad.
MCK-122-NH-21	15	5.9	Concord granite; Monadnock quad.
MCK-38-NH-10	13 ^a	3.3	Bethlehem gneiss; Moosilauke quad.
MCK-44-NH-15	35 ^a	6.7	French Pond granite (pink); Moosilauke quad.
MCK-57-NH-15	11 ^a	7.7	Concord granite; Plymouth quad.
MCK-108-V-1	6.2 ^a	4.0	Barre granite; Barre, Vt.
MCK-109-V-2	7.7	2.8	Quartz monzonite; Groton State Forest, Vt.
MCK-110-V-3	10 ^a	5.8	Granodiorite; St. Johnsbury quad.
MCK-121-NH-20	13 ^a	2.1	Kinsman quartz monzonite; Lovewell Mt. quad.
MCK-114-NH	28 ^a	5.1	Lebanon granite; Hanover quad.
MCK-115-NH	23 ^a	4.2	Lebanon granite; Hanover quad.
<u>Oliverian Magma Series</u>			
MCK-45-OL-1	22	3.3	Owls Head granite; Rumney quad.
MCK-48-OL-4	51 ^a	14	Discontinuous aplite dike cutting OL-5; Rumney quad.
MCK-49-OL-5	24 ^a	4.1	Owls Head granite; Rumney quad.
MCK-50-OL-6	39 ^a	14	Aplite dike cutting OL-7; Rumney quad.
MCK-51-OL-7	18 ^a	3.7	Owls Head granite; Rumney quad.
MCK-52-OL-8	25 ^a	5.3 ^a	Owls Head granite from top of Blueberry Mountain; Rumney quad.
MCK-119-OL-13	6.3 ^a	2.8	Quartz monzonite; Bellows Falls quad.

Table 6 (Cont'd)

Sample No.	Analysis, ppm		Comments
	Th	U	
<u>Massachusetts</u>			
MCK-82-Mass-1	13	3.3	Granodiorite; Swingles quarry, Quincy
MCK-84-Mass-3	31	1.4	Granite; Milford quarry
MCK-87-Mass-4	8.6	1.3	Pink granite; Milford quarry
MCK-92-Mass-5	10	2.7	Dedham granodiorite; Brockton quad.
MCK-93-Mass-6	38	8.9	Riebeckite granite; Brockton quad.
MCK-94-Mass-7	16	5.3	Dedham granodiorite; old quarry; Brockton quad.
MCK-95-Mass-8	27	5.0	Granite; Fletcher quarry; N. Chelmsford, Mass.
MCK-96-Mass-9	12	5.0	Granite; Billerica, Mass.
MCK-83-Mass-2	15 ^a	4.8	Granite; Plymouth quarry, Weymouth, Mass.
<u>Rhode Island</u>			
MCK-85-RI-1	28	14	Naragansett Pier granite
MCK-88-RI-3	20	1.8	Esmond granite; Georgiaville quad.
MCK-91-RI-6F	60	3.1	Westerly granite from quarry; fine-grained, pink
MCK-91-RI-6M	68	3.3	Westerly granite from quarry; medium-grained, pink
MCK-89C-RI-4	16 ^a	3.9	Scituate granite; North Scituate quad.
<u>Oklahoma</u>			
MCK-124	16	3.8	"Pellow Pink" granite; Granite, Okla.
MCK-125	14	2.8	"Indian Rose" granite; Granite, Okla.
MCK-128	18	6.0	"Century Mottled Pink" granite; Century, Okla.
MCK-129	10	1.7	"Century Tweed" granite; Mill Creek, Okla.
MCK-123	17 ^a	4.4 ^a	"Mohogany Red" granite; Granite, Okla.

Table 6 (Cont'd)

Sample No.	Analysis, ppm		Comments
	Th	U	
MCK-126	15 ^a	3.8	"Century Maroon" granite; Granite, Okla.
MCK-127	10 ^a	2.3	"Century Rose" granite; Century, Okla.
<u>Pend-Oreille Area, Idaho</u>			
AD-SP-1p	16	4.4	Bayview granodiorite
AD-SP-2p	9.9	2.5	Porphyritic Bayview granodiorite
AD-SP-3	9.6	7.1	Bayview granodiorite
<u>Montana (Boulder batholith)</u>			
AD-BB-2	19	4.3	Butte quartz monzonite
AD-BB-3	7.5	1.6	Raders Creek granite
AD-BB-5	23	5.2	Clancey granodiorite
<u>Missouri</u>			
MCK-101	38	19	Missouri Red granite; Haywards quarry; Graniteville, Mo.
<u>Miscellaneous</u>			
MCK-112-V-5	0.76	0.10	Bethel White quartz monzonite; Bethel, Vt.
MCK-113-V-H-1	12	3.3	Fairlee quartz monzonite; Fairlee, Vt.; Highlandcroft Magma Series

^aDifferent from value previously² reported. In most cases the new value is based on redeterminations and is considered more accurate, largely because of better counting statistics. Some of the corrections resulted from recalculation of previous radiometric data.

2.0 SOLVENT EXTRACTION TECHNOLOGY

2.1 Final Cycle Plutonium Recovery by Amine Extraction (C. F. Coleman, F. A. Kappelmann, J. P. Eubanks)

The amine extraction of plutonium nitrate is being examined to develop one or more flowsheets suitable for final cycle plutonium recovery and purification, after typical Purex extraction and partition from uranium. To compete successfully with TBP extraction-ion exchange cycles already designed, an amine extraction flowsheet must provide high decontamination and should provide reasonably high concentration in a single cycle, besides fulfilling its apparent promise of simplicity and much lower nitric acid consumption.

In continued batch countercurrent testing* of the proposed chemical flowsheet (Fig. 3) with simulated lBP solution,³ the extraction profile obtained with 0.155 M trilaurylamine (TLA) in diethylbenzene again confirmed the predicted extraction isotherms.² At flow rate A/O = 4/1 in four extraction stages the raffinate contained <0.002 g Pu/liter, <0.2% of the head. There was very little refluxing in the scrub section with 0.5 M HNO₃ at A/O = 2/5. The product, stripped with 3 M acetic acid at A/O ≈ 1/5, contained 23.6 g Pu/liter, and the stripped extractant contained ~0.001 g Pu/liter.

The simulated lBP feed solutions (Table 7) and extractant solutions (Table 8) were prepared as previously described,³ and the same contactors were used. The flowsheet conditions used for the last 35 cycles are shown in Fig. 3, with the terminal profiles. Flowsheet conditions for three preceding runs are summarized in Table 8. The profiles were not sampled in these; run samples are listed in Table 9.

2.1.1 Profiles. All solutions were analyzed after cycle 42 of Run 2C, giving the $\Sigma\alpha$ profiles shown in Table 10 and Fig. 3. As in the profile analysis of Run 1, only the odd-numbered stages contained solutions at this point. This included raffinate (Stage 1) and product (Stage 11), but not stripped extractant (Stage 16); the stripped extractant analysis from cycle 41 was used. Concentrations for other even-numbered stages in the extraction and stripping sections were calculated by material balance, and are marked by parentheses in both table and graph. The concentration changes through the scrub section were so slight that the resulting small differences were too erratic for satisfactory material balance calculation of the missing concentrations.

The profile data are replotted as extraction, scrub, and stripping isotherms in Fig. 4. As before, the extraction equilibrium curve was drawn according to the empirical relations

*These tests were carried out in the Chemical Isolation Laboratory with the cooperation of R. E. Leuze and co-workers.

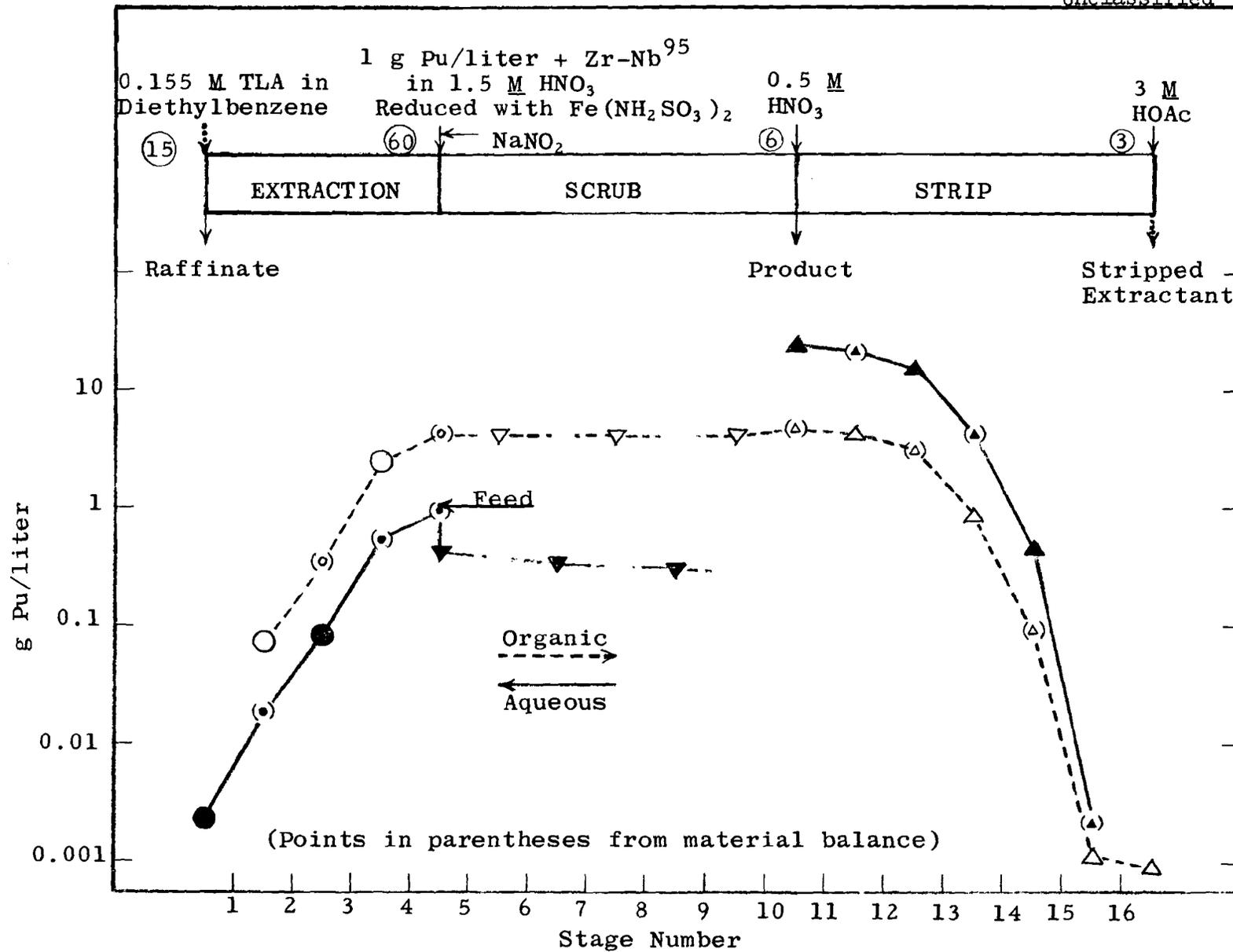


Fig. 3. Flowsheet and Profile, Plutonium Purification Cycle, Batch Countercurrent Run No. 2C.

Table 7. Feed Solution Analyses

Simulated LBP

Batch No.	Used In		H+ <u>M</u>	Pu α		Am α	Gross γ
	Run	Cycles		Total	(IV)		
5	2	1-12	1.5	6.92×10^7	6.92×10^7	5.56×10^4	7.41×10^5
6	2A	13-24 } 1-4 }	1.5	6.89×10^7	6.9×10^7	4.03×10^4	6.92×10^5
7		5-19	1.57	6.76×10^7	6.86×10^7	4.56×10^4	6.89×10^5
8	(2C	20-24 } 7-10) }	1.57	6.71×10^7	6.9×10^7	4.78×10^4	7.67×10^5
9		2B	1-14	1.50	6.84×10^7	6.96×10^7	4.5×10^4
10		15-32	not analyzed				a
11	2C	1-6	1.5	7.2×10^7	7.11×10^7	-	2.42×10^{3a}
12		11-28	1.6	7.43×10^7	7.23×10^7	4.4×10^4	-
13		29-42	1.5	7.14×10^7	7.0×10^7	6.0×10^4	7.0×10^5

^aNo Zr-Nb tracer present.

Preparation: Plutonium nitrate solution reduced with ferrous sulfamate (quantity equivalent to 0.3 M Fe(NH₂SO₃)₂ in final volume), reoxidized with nitrite (NaNO₂: Fe = 7:1 mole ratio), and spiked (except Batches 9, 10, 11) with Zr⁹⁵-Nb⁹⁵ tracer at $\sim 7 \times 10^5$ γ counts/min ml in the final solution volume.

Table 8. Flowsheet Conditions

(cf. Fig. 3)

Extract/Feed/Scrub/Strip = 15/60/6/3 ml per cycle
TLA: Alamine 304 (Batch 86J) in diethylbenzene

Run No.	Cycle Nos.	TLA, <u>M</u>	HNO ₃	HOAc	Zr-Nb Tracer
			Scrub, <u>M</u>	Strip, <u>M</u>	
2	1-24	0.1	0.25	3	7×10^5
2A	1-24	0.1	0.5	3	7×10^5
2B	1-32	0.1	0.5	3	none
2C	1-6	0.155	0.5	3	none
	7-42	0.155	0.5	3	7×10^5

Table 9. Plutonium Distribution in Run Samples

(cf. Fig. 3)

Run No.	Cycle No. ^a	$\Sigma \alpha$ /min ml			% of $\Sigma \alpha$ in Feed ^b			g Pu/liter in Product ^e
		Raffinate ^c	Product	Org. ^d	Raffinate ^c	Product	Org. ^d	
2	2	6.94x10 ⁶			10			
	8	1.16x10 ⁷	4.92x10 ⁸		17	34		7.0
	12	1.8x10 ⁷	6.21x10 ⁸		26	44		8.8
	14-15	2.13x10 ⁷	6.19x10 ⁸	4.35x10 ⁴	31	45	0.015	8.8
	20-21	3.12x10 ⁷	7.05x10 ⁸	3.53x10 ⁴	45	51	0.012	10.0
	22-23	3.02x10 ⁷	7.78x10 ⁸	1.38x10 ⁴	44	56	0.005	11.1
2A	10-11	1.61x10 ⁷	1.08x10 ⁹	1.57x10 ⁴	23	79	0.006	15.4
	20-21	1.39x10 ⁷	1.3x10 ⁹	7.6x10 ³	20	94	0.003	18.5
	22-23	1.39x10 ⁷	1.18x10 ⁹	1.03x10 ⁴	20	86	0.004	16.8
2B ^f								
2C	20-21	1.18x10 ⁶	1.7x10 ⁹	4.43x10 ³	1.6	114	0.0015	24.2
	28-29	2.94x10 ⁵	1.62x10 ⁹	1.06x10 ⁴	0.4	113	0.004	23.1
	34-35	2.32x10 ⁵	1.61x10 ⁹	2.75x10 ⁴	0.3	113	0.009	23.0
	40-41	2.05x10 ⁵	1.62x10 ⁹	6.75x10 ⁴	0.3	113	0.024	23.1
	42	1.64x10 ⁵	1.66x10 ⁹		0.2	116		23.7

^aRaffinate and product discharged only after even-numbered cycles, stripped extractant only after odd-numbered.

^b0.97 to 1.03 g Pu/liter in feed batches.

^cNot corrected for Am α , reported at (4-6)x10⁴ counts/min ml in feed and in the same range in raffinates.

^d"Org." = stripped extractant.

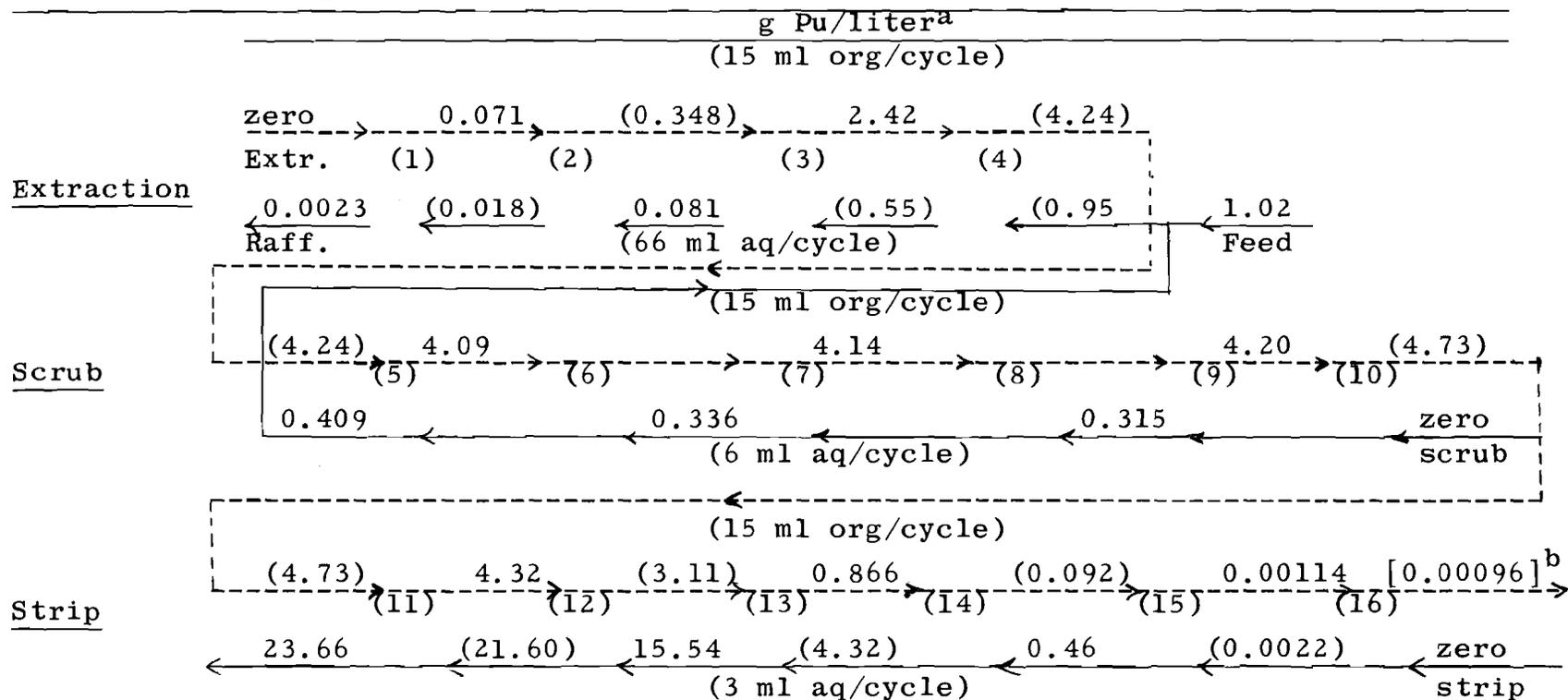
^eg Pu/liter from $\Sigma \alpha$, assuming all non-Pu α negligible in the product.

^fNo α measurements in Run 2B, which was used to determine minimum γ levels.

Table 10. Profile of Plutonium Purification Cycle,

Batch Countercurrent Run No. 2C

Simulated IBP feed (Table 7); 0.155 N TLA in diethylbenzene;
0.5 M HNO₃ scrub; 3 M HOAc strip; single-diamond contact pattern



^aCalculated from $\Sigma \alpha$. Numbers in parentheses obtained by material balance.

^b[0.00096] in stripped organic of preceding cycle.

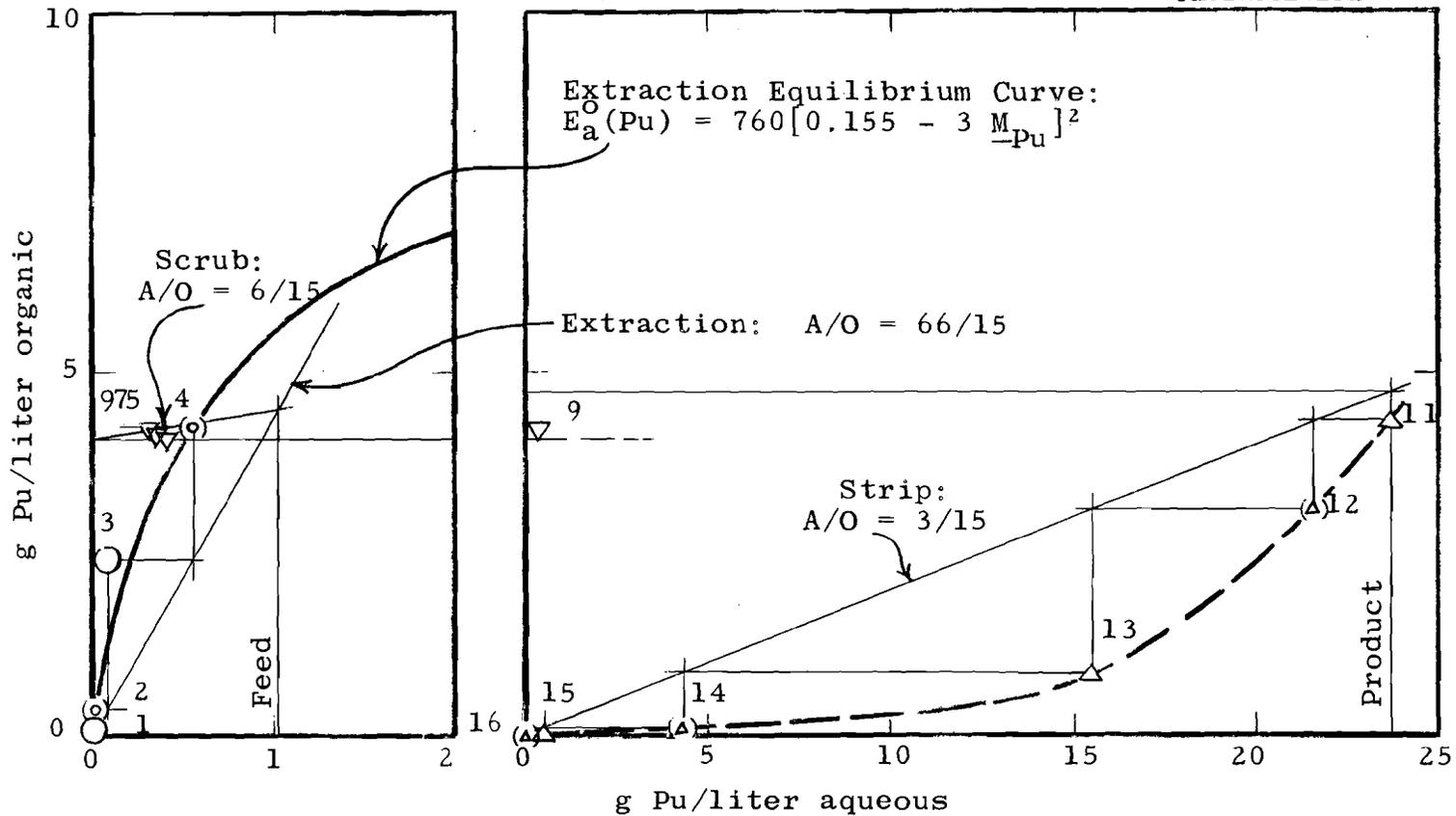


Fig. 4. McCabe-Thiele Diagram, Plutonium Purification Cycle, Batch Countercurrent Run No. 2C.

previously established for extraction from $\sim 1.5 \text{ M HNO}_3$, with TLA in diethylbenzene:² $E(\text{Pu}) \approx E_1 [\underline{M}_{\text{amine}} - 3 \underline{M}_{\text{Pu}}]^2$ and $\log E_1 \approx 3.5 - 2.5\sqrt{\underline{M}_{\text{SO}_4}}$, and here again the equilibrium stage points fall close to the predicted curve.

The scrub-section compositions are grouped closely together (Fig. 4). Their position above the extraction equilibrium curve, i.e., with higher O/A distribution coefficients than in extraction, is surprising if it represents actual steady-state equilibrium. Lower distribution coefficients are expected because of the lower nitrate concentration than in the extraction section, only partially compensated by the absence of sulfate. These results might indicate significantly slow rate of equilibration in the scrub section.*

The stripping proceeded smoothly and essentially completely at phase ratio A/O = 3/15. The equilibrium points (Fig. 4) fell along a smooth curve, similar (allowing for the different phase ratio) to that obtained from the previous profile.³ The product concentrations throughout the run (Table 9) were consistently higher than the feed times the nominal flow ratio. This is probably due to a consistent loss of a small but significant fraction of the aqueous volume in passing through the stripping stages. If entirely to account for the excess concentration, the product volume would be 2.6 instead of 3 ml. The product volumes were not measured in the glove-box operation, and this much difference would not have been readily observed.

2.1.2 Run Samples. In the run reported previously with 0.2 M TLA,³ the loss of plutonium (actually, $\Sigma\alpha$) in the raffinate was <0.1% at phase ratio A/O = 66/15, and rose to 7% when the phase ratio was changed to 66/5. In Run 2 (Tables 8 and 9) the phase ratio was returned to A/O = 66/15 and the TLA concentration was decreased to 0.1 M. This did not change the amine:plutonium ratio, but was expected to decrease the extraction coefficient by a factor of 9 and the extraction fraction by a factor of 3 because of the dilution. The raffinate plutonium loss rose to 45%. When the scrub was changed from 0.25 M to 0.5 M HNO₃, the raffinate plutonium loss dropped slightly, to 20%. (Since the scrub composition could have little effect on the composition of the ten-fold greater volume of feed, this indicates that there was appreciable refluxing of plutonium in scrubbing with 0.25 M HNO₃). When the TLA concentration was increased to 0.155 M (Run 2C), the raffinate loss dropped to 0.2% of the $\Sigma\alpha$ (including americium), and hence presumably considerably less than 0.2% of the plutonium.

*The contact conditions were 5 min stirring with hollow inter-phase stirrer in unbaffled cylindrical separatory funnel, 14 ml org. + 6 ml aq., followed by usually 3-5 min settling.

2.1.3 Gamma Activity. As previously reported, Zr-Nb⁹⁵ gamma activity, from a level of $\sim 10^6$ γ counts/min ml in the feed, could not be distinguished from background gamma either by gross γ (through lead) or γ scan. Run 2 was performed before the γ scans were available from Run 1 to show that no Zr-Nb values could be obtained from the gross measurements, and the different run conditions used were selected in part to provide a direct test of that point. Even when the Zr-Nb tracer was omitted from the feed, the product gross γ remained at $\sim 2 \times 10^4$ counts/min ml, about the same as when the tracer was present. Thus, most of the gamma activity found in the product must be due to plutonium itself, or to a contaminant from the plutonium stock that is extracted and stripped with it.

Preliminary examination of the γ scans suggests that most of the activity is actually due to plutonium, even though its principal gammas at < 0.1 mev were eliminated by lead filter. Significant peaks were found at ~ 0.4 and ~ 0.2 mev (besides larger peaks at ~ 0.1 mev and lower energies), with only slight indications at ~ 0.76 mev for Zr-Nb. The ~ 0.4 mev peak matches the 0.384 mev gamma of Pu²³⁹, and the peak near 0.2 mev might be related to its 0.124 mev gamma. As much of the total gamma as is due to plutonium should correlate well with the product alpha, and this may prove to leave a small difference accurately enough defined to have some use as a measure of the Zr-Nb content.

2.2 Extraction and Separation of Zirconium and Hafnium

(D. J. Crouse, J. G. Moore, F. J. Hurst)

Preliminary studies of the separation of zirconium and hafnium with amines and organophosphorus esters and acids were made in 1957 and early 1958. Each of the extractant classes showed some promise but, owing to other commitments, the studies were terminated prior to development and demonstration of complete processes.

The early data obtained in this investigation were reported in ORNL-2346.⁴ The balance of the data were not reported since progress reports were not issued in 1958 and the studies were not sufficiently complete to merit a topical report. Recently several inquiries have been received concerning availability of information on Zr-Hf separation at ORNL. Summarization of the data, even at this late date, is apparently warranted and this is done below.

2.2.1 Extraction with Amines

From Sulfate Solutions. Effective extraction of zirconium and hafnium from sulfate solutions was obtained with primary, secondary, and tertiary amines. Zirconium was extracted preferentially, the measured separation factor (Zr/Hf) being on the order of 5-10. All of the data in the sulfate system have been reported previously.⁴

From Hydrochloric Acid.* Zirconium and hafnium were extracted from hydrochloric acid solutions at relatively high acid concentrations (8-10 M), with the zirconium being preferentially extracted.

The rate of extraction from 8 M HCl was studied with tri(iso-octyl)amine in benzene (Table 11). The data were somewhat erratic but indicated that equilibrium was essentially reached within 5 min. The measured separation factors (Zr/Hf) were in the range 17 to 35. In the tests at an organic/aqueous phase ratio of 8/1, a third liquid phase formed owing to the limited miscibility of the amine--zirconium--chloride salt in the diluent. Addition of 5-8 vol % tridecanol to the diluent prevented third phase formation in tests with tri(iso-octyl)amine but also appreciably decreased the extraction efficiency and lowered the separation factors (Table 12). This was true with both benzene and Esso Heavy Aromatic (HAN) diluents. Extraction coefficients with the latter diluent were higher than with benzene but separation factors were approximately the same, i.e., 10-20.

Table 11. Rate of Zirconium--Hafnium Extraction with Tri(iso-octyl)amine

Organic: 0.1 M tri(iso-octyl)amine in benzene
 Aqueous: 8 M HCl containing 1.4 g/liter of (Zr Hf) oxide (~1.5% Hf)

Contact Time, Min	Phase Ratio, a/o	Total Oxide in Organic, ^a g/liter	Extraction Coefficient ^a E_{α}^O		Separation Factor (Zr/Hf)
			Zr	Hf	
2	1	1.0	3.0	0.11	27
	8 ^b	2.1	2.0	0.16	13
5	1	1.1	3.8	0.11	35
	8 ^b	2.3	2.2	0.12	18
15	1	1.1	3.8	0.18	21
	8 ^b	2.3	2.1	0.12	17
30	1	1.0	3.4	0.17	20
	8 ^b	2.2	2.0	0.12	17

^aCalculated on basis of analyses of head and final aqueous.

^bThird liquid phase formed owing to limited miscibility of the amine salt in the diluent.

*Extraction of zirconium and hafnium from hydrochloric acid with amines has also been studied by Moore^{5,6} of the ORNL Analytical Chemistry Division and by Cerrai and Testa.^{7,8}

Table 12. Effect of Diluent Choice on Amine Extraction of Zirconium-Hafnium

Organic: 0.1 M tri(iso-octyl)amine in indicated diluent
 Aqueous: 8 M HCl containing 1.4 g/liter of (ZrHf) oxide
 (~1.5% Hf)
 Contact time: 30 min

Diluent	Phase Ratio, a/o	Total Oxide in Organic, ^a g/liter	Extraction Coefficient ^a (E_a^O)		Separation Factor (Zr/Hf)
			Zr	Hf	
Benzene	1	1.0	3.4	0.17	20
	8 ^b	2.2	2.0	0.12	17
92% benzene--8% tridecanol	1	0.51	0.6	0.05	12
	8	0.91	0.7	0.08	9
HAN ^c	1 ^b	1.2	10	1.0	10
	8 ^b	3.5	4	0.21	19
95% HAN--5% tridecanol	8	1.2	0.9	0.08	11
92% kerosene--8% tridecanol	1	0.63	0.9	0.07	13
	8 ^b	-	-	-	-

^aCalculated on basis of analyses of head and final aqueous.

^bThird liquid phase formed.

^cHAN = Heavy Aromatic Naphtha (Esso).

In studies (Table 13) of the effect of hydrochloric acid concentration, zirconium extraction with tri(iso-octyl)amine was extremely weak from 6-7 M HCl but became appreciable ($E_a^O = 0.7$) from 8 M HCl. The coefficients were 11 and 6 from 10 M and 12 M HCl respectively. The hafnium extraction coefficient increased over the total range (6-12 M) of acid concentration. The net effect was that the separation factor (Zr/Hf) was at a maximum near 8 M HCl and decreased with increase in acid concentration above this level.

In tests (Table 14) with other amines, extraction of zirconium by di(tridecyl)amine (secondary amine with branching distant from the nitrogen) was significant ($E_a^O = 0.6$) from 8 M HCl and strong ($E_a^O = 24$) from 10 M HCl. The separation factor (Zr/Hf) which was ~15 from 8 M HCl decreased to 3.5 from 10 M HCl. A primary amine and S-24 amine (secondary with branching close to the nitrogen) showed negligible zirconium extraction from 8 M HCl and relatively weak extraction ($E_a^O = 0.3-0.9$) from 10 M HCl.

Since high hydrochloric acid concentrations are needed for effective extraction of zirconium and hafnium with amines, stripping is easily accomplished with water or dilute hydrochloric acid. Measured coefficients for stripping zirconium from tri(iso-octyl)-amine were >100 for both water and 1 M HCl.

Table 13. Effect of HCl Concentration on Zirconium-Hafnium Extraction

Organic: 0.1 M tri(iso-octyl)amine in 95% benzene--5% tridecanol
 Aqueous: HCl solutions containing 1.4 g/liter of (ZrHf) oxide (~1.5% Hf)
 Contact time: 30 min

HCl Conc., M	Phase Ratio, a/o	Total Oxide in Organic, ^a g/liter	Extraction Coefficient ^a (E_a^O)		Separation Factor (Zr/Hf)
			Zr	Hf	
6	1	0.04	b	b	-
	8	0.13	b	b	-
7	1	0.08	0.06	0.007	9
	8	0.15	0.11	0.026	4
8	8	0.91	0.74	0.08	9
10	1	1.2	11	1.8	6
	8	3.7	4.3	0.8	5
12	1	1.1	6.1	2.5	2.5
	8	2.9	3.0	1.5	2

^aCalculated on basis of analyses of head and final aqueous.

^bAmount of transfer too low to get useful analyses.

Table 14. Effect of Amine Choice on Extraction of Zirconium-Hafnium

Organic: 0.1 M amine in benzene
 Aqueous: 8 M or 10 M HCl containing 1.4 g/liter of (ZrHf) oxide (~1.5% Hf)
 Contact time: 30 min

Amine	Phase Ratio, a/o	Total Oxide in Organic, ^a g/liter	Extraction Coefficient ^a (E_a^O)		Separation Factor (Zr/Hf)
			Zr	Hf	
<u>Extractions from 8 M HCl</u>					
Di(tridecyl)	1	0.50	0.58	0.04	14
	8	0.80	0.63	0.04	16
S-24	1	0.04	0.03	0.005	6
	8	b	-	-	-
1(3-ethylpentyl- 4-ethyloctyl)	1	b	-	-	-
	8	b	-	-	-
<u>Extractions from 10 M HCl</u>					
Di(tridecyl)	1	1.3	24	6.8	3.5
S-24	1	0.64	0.91	0.13	7
1(3-ethylpentyl- 4-ethyloctyl)	1	0.34	0.35	0.07	5

^aCalculated on the basis of analyses of the head and final aqueous.

^bAmount extracted too low to measure.

2.2.2 Extraction with Organophosphorus Esters. The tributyl phosphate (TBP) extraction process⁹ is presently used commercially for separating and recovering zirconium and hafnium from nitric acid. A phosphonate and a phosphine oxide* were briefly studied to determine if they would give separation factors higher than those obtained with TBP. These compounds, because of their higher extraction power compared to TBP, allow operation with lower nitrate salting in the aqueous phase.

Extractions from Nitric Acid. Extraction tests were made with 0.1 M solutions of diamyl amyolphosphonate (DAAP) and tri(n-octyl)phosphine oxide (TOPO) in kerosene and benzene diluents from solutions containing 1-7 M HNO₃ and 2-30 grams per liter of (Zr/Hf) oxide. The extraction data were highly erratic and thus are not presented in detail. Large differences in results were obtained depending on the method of preparation of the aqueous head solution. For example, in tests with TOPO, the zirconium extraction coefficient was 1-2 orders of magnitude higher when extractions were from solution prepared by dissolving zirconium nitrate in nitric acid than when the solution was prepared by precipitating zirconium with ammonia from zirconyl chloride solution and redissolving the precipitate in hot nitric acid. The separation factors (Zr/Hf), in these tests varied from 2 to 30 for TOPO and from 10 to 45 for DAAP, depending on test conditions. Since separation factors reported⁹ for TBP vary in this approximate range also, it does not appear that the use of this particular phosphonate or phosphine oxide has any appreciable advantage over use of TBP. A more definitive comparison of these reagents would be necessary to substantiate this conclusion.

Extractions from Hydrochloric Acid. Strong extraction of zirconium was obtained from 3-5 M HCl with 0.1 M TOPO in kerosene but the separation factor (Zr/Hf) was only ~2.5 (Table 15). Extraction of zirconium with 0.1 M DAAP from 5 M HCl was weak ($E_a^O = 0.35$) but the measured separation factor was higher (~12). To determine the effect of extractant concentration on zirconium extraction, some additional tests were made with a 1.0 M solution of DAAP and zirconyl chloride--hydrochloric acid solutions which contained no hafnium. A coefficient of 2.7 was obtained from 5 M HCl:

HCl Conc'n. M	Zr, g/liter		Zirconium Extraction Coefficient (E_a^O)
	Organic	Aqueous	
2	<0.1	8.9	<0.01
3	0.15	8.8	0.02
4	1.3	8.3	0.16
5	10.5	3.9	2.7

*The extraction of zirconium from acid solutions with TOPO has previously been studied by White and Ross.¹⁰

Table 15. Extraction from HCl Solutions with DAAP and TOPO

Organic: 0.1 M extractant in kerosene
 Aqueous: HCl solutions containing 1.2 g/liter (Zr/Hf) oxide
 Phase ratio, a/o: 1/1
 Contact time: 30 min

Extractant	HCl Conc'n. M	Total Oxide in Organic, g/liter	Extraction Coefficient (E_a)		Separation Factor (Zr/Hf)
			Zr	Hf	
TOPO	1	0.11	0.13	0.05	2.6
	3	1.1	34	14	2.4
	5	1.2	a	a	-
DAAP	1	<0.01	-	-	-
	3	<0.01	-	-	-
	5	0.35	0.35	0.03	12

^aToo little left in aqueous for analysis.

The aqueous/organic phase ratio in the above tests was 2/1 and the contact time was 5 min. The above tests suggest that DAAP is worthy of further examination as an extractant for processing chloride solutions of zirconium and hafnium.

2.2.3 Extractions with Di(2-ethylhexyl)phosphoric Acid (D2EHPA)

From Sulfate Solutions. Initial tests (reported in ORNL-2346) in which the elements were extracted from separate solutions with 0.1 M D2EHPA, showed stronger extraction of hafnium than zirconium, the indicated separation factors (Hf/Zr) in kerosene and benzene diluents ranging from 10 to >40. These high separation factors were not confirmed in later tests in which the elements were extracted together from the same solution with D2EHPA in kerosene. The separation factors (Hf/Zr) in the latter tests were in the range 1.5-4.

From Chloride and Chloride--Sulfate Solutions. Zirconium was preferentially extracted from hydrochloric acid (1-5 M) with D2EHPA but the measured separation factors (Zr/Hf) were low (1.5-2.5). Addition of sulfate to the system reversed the extraction order, presumably because zirconium is more strongly complexed by sulfate than is hafnium. For example, addition of 1, 3, and 5 moles of sodium sulfate per mole of zirconium to a 1 M HCl solution containing ~0.2 M zirconium increased the separation factor (Hf/Zr) from 0.6 to 1.5, 3.4, and 5.0 respectively. Interpretation of the extraction data was extremely difficult because of the relatively slow extraction in this system and the slow rate of exchange between hafnium and zirconium. Contact times in the order of 30 min or longer were required to reach equilibrium.

3.0 SEPARATION OF RARE EARTHS AND TRANSPLUTONIUMS

3.1 Extraction of Rare Earths from Chloride Solutions by Tertiary Amines (A. Faure, B. Weaver, J. R. Collins)

Previous studies¹¹ have shown that tertiary amines extract the transplutonium elements from concentrated chloride solutions far more readily than they do the lanthanide group of elements. A process based on these studies will probably be used for separation of the two groups of elements in the production of "large" quantities of the transplutoniums. The original investigation gave most attention to americium and europium as examples of the groups. The individual lanthanides were studied only sufficiently to find that differences within this group were very small compared to the difference between the two groups.

This report covers further progress in a study of the behavior of several lanthanides in extraction by amines. The study has also been extended to include the other IIIA elements, yttrium and scandium, the latter only very briefly. Experiments were performed to determine the extractability of each of the elements from 11 N LiCl, 0.01 N HCl and from 8 N LiCl, 2 N AlCl₃ by a few different tertiary amines in a few different diluents. Comparisons were made of the extractabilities of each of the lanthanides with yttrium under given conditions. The effects of reagent concentration and salt concentration were determined for some of the extractants.

3.1.1 Experimental. Appropriate aliquots of tracer Ce¹⁴⁴, Eu¹⁵², Tb¹⁶⁰, Ho¹⁶⁶, Tm¹⁷⁰, Lu¹⁷⁷, Y⁹¹, and Sc⁴⁶ were evaporated to near dryness in small beakers and taken up by 10 ml volumes of the salt solution used. The spiked solution was contacted with an equal volume of the diluted amine chloride by vigorous shaking by hand or by 10 minutes of machine shaking or turning. Phases were separated after settling, and the gamma activity in a 2 ml aliquot of each phase was measured in a well-type scintillation counter. Distribution coefficients = (activity in organic)/(activity in aqueous). Some results were checked by backwashing with a similar aqueous. For the first experiments the only tracers available were Ce¹⁴⁴, Eu¹⁵², Tb¹⁶⁰, Ho¹⁶⁶, and Y⁹¹. Gamma activity in the Y⁹¹ was low because only 0.2% of the disintegrations produce gammas. The supply of Tb¹⁶⁰ was small, and the 23 hr Ho¹⁶⁶ soon decayed. Later new supplies of Ho¹⁶⁶, Tm¹⁷⁰, and Lu¹⁷⁷ were obtained and used, while Tb¹⁶⁰ was omitted. The Sc⁴⁶ was obtained still later and used by itself for a series of experiments. The extremely high dependence of extraction on salt concentration was cause for some discrepancies between series of experiments that were performed at different times.

Extractants used were trialkylamine (mixed octyl and decyl, Alamine 336), triisooctyl amine (TIOA), and n-butyl didodecylamine (XE-204). Diluents were diethylbenzene (DEB), diisopropylbenzene (DIPB), and Amsco 125-82 modified with tridecyl alcohol

(TDA). The amines were converted to chlorides by contacting their solutions with 2 N HCl and washed 3 times with 2 N LiCl to remove excess acid.

3.1.2 Relative Extraction of Various Elements. Distribution coefficients for extraction of various lanthanides from 11 N LiCl, 0.01 N HCl by various amine-diluent combinations have been compared with those of yttrium under the same conditions. The data are plotted in Fig. 5, where the extractability of yttrium is assigned an arbitrary value of 1 in each case. The remarkable fact is that in all cases studied yttrium was considerably less extractable than any of the lanthanides. The order of extraction of the lanthanides varied with the composition of both extractant and salt solution, but europium was at the peak in all of these cases.

Extraction of lanthanides from 8 N LiCl, 2 N AlCl₃ by most but not all extractants studied increased with atomic number (Fig. 6). Differences within the group and from yttrium were smaller than in extractions from 11 N LiCl, 0.01 N HCl.

3.1.3 Reagent Concentration Dependence. Previous work had shown that extraction of americium and europium was approximately proportional to the square of the reagent concentration under most conditions; values varying from 1.4 to 2.2 were obtained for the power dependence. Accurate determination of dependence of extraction on reagent concentration is difficult when low reagent concentrations are used, because of the very low distribution coefficients of this whole group of elements. Recently however extractions of this series of elements from 11 N LiCl, 0.01 N HCl by XE-204 have been compared at concentrations of 0.1 M, 0.5 M, and 1.0 M reagent. The data are in Table 16. The overall power dependence was ~2.0 for yttrium and the heavier lanthanides but apparently somewhat higher for the lighter lanthanides. Thus the separations between the lighter elements and yttrium apparently increase at higher reagent concentrations. From the very limited evidence in Figure 7 it is suggested that the power dependence might be slightly higher between 0.5 M and 1.0 M than between 0.1 M and 0.5 M reagent.

Table 16. Extraction Dependence on Reagent Concentration
XE-204 in DIPB; 11 N LiCl, 0.01 N HCl

	E_a^O			Power	$\frac{E_a^O(M)}{E_a^O(Y)}$	$\frac{E_a^O(M)}{E_a^O(Y)}$
	0.1 <u>M</u>	0.5 <u>M</u>	1.0 <u>M</u>	Dependence	0.1 <u>M</u>	1.0 <u>M</u>
Ce	0.0051	0.141	0.79	2.16	5.1	7.3
Eu	0.0053	0.183	0.99	2.20	5.3	8.9
Ho	0.0033	0.078	0.38	2.02	3.3	3.6
Tm	0.0031	0.067	0.34	2.00	3.1	3.3
Lu	0.0031	0.061	0.30	1.95	3.1	3.0
Y	0.00098	0.0228	0.114	1.98	-	-

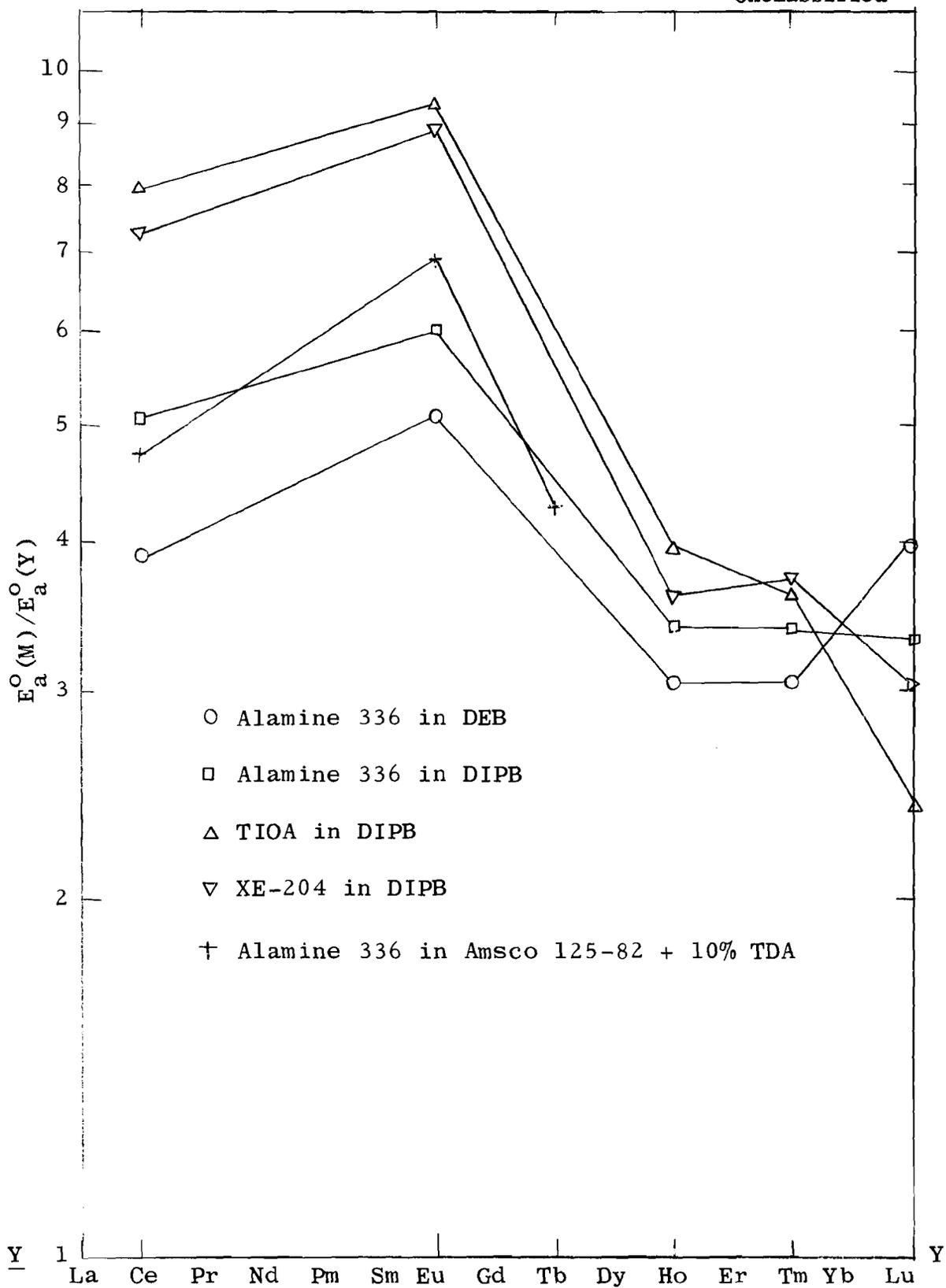


Fig. 5. Relative Extraction of Lanthanides and Yttrium from 11 N LiCl, 0.01 N HCl.

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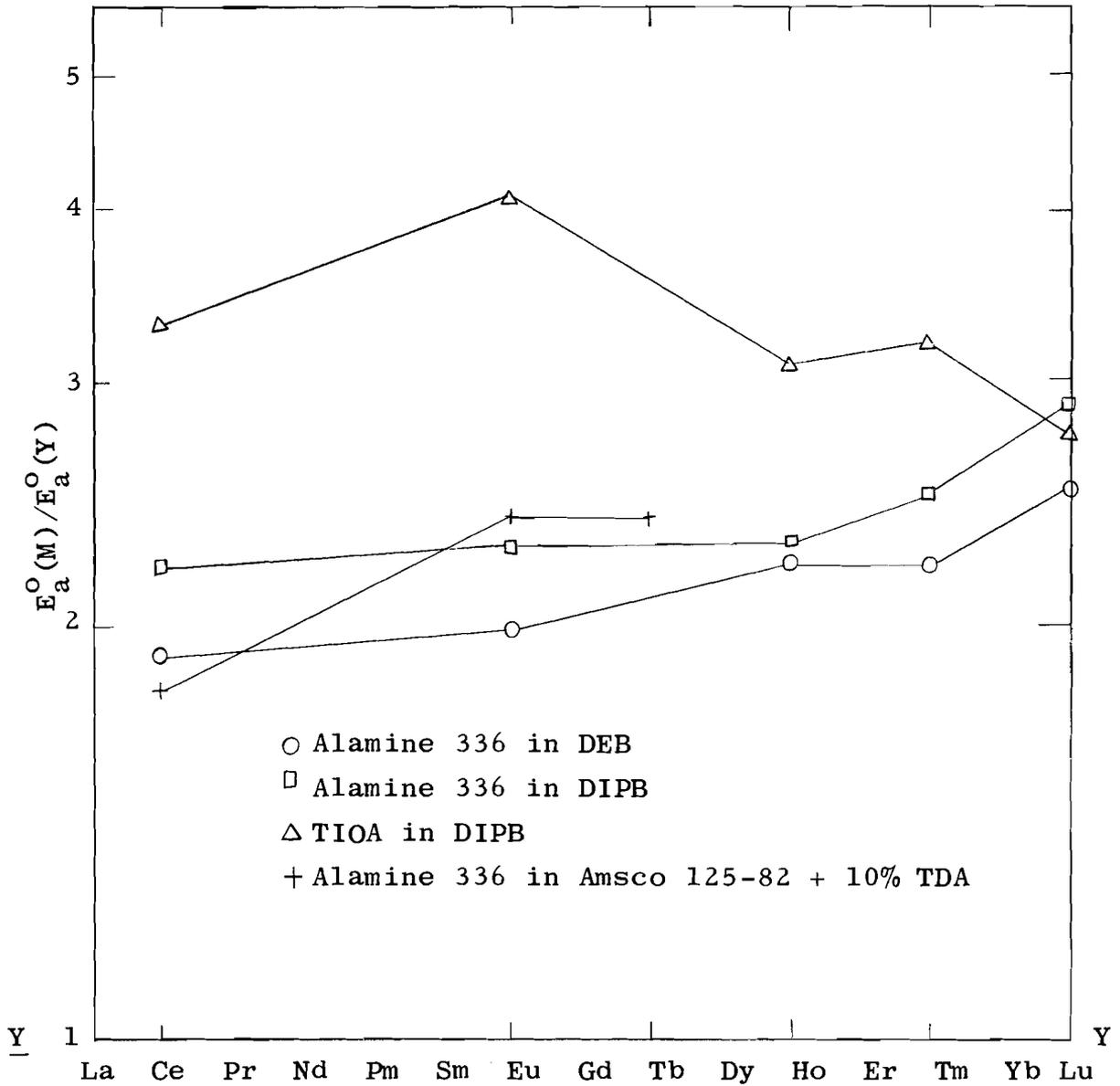


Fig. 6. Relative Extraction of Lanthanides and Yttrium from 8 N LiCl, 2 N AlCl₃.

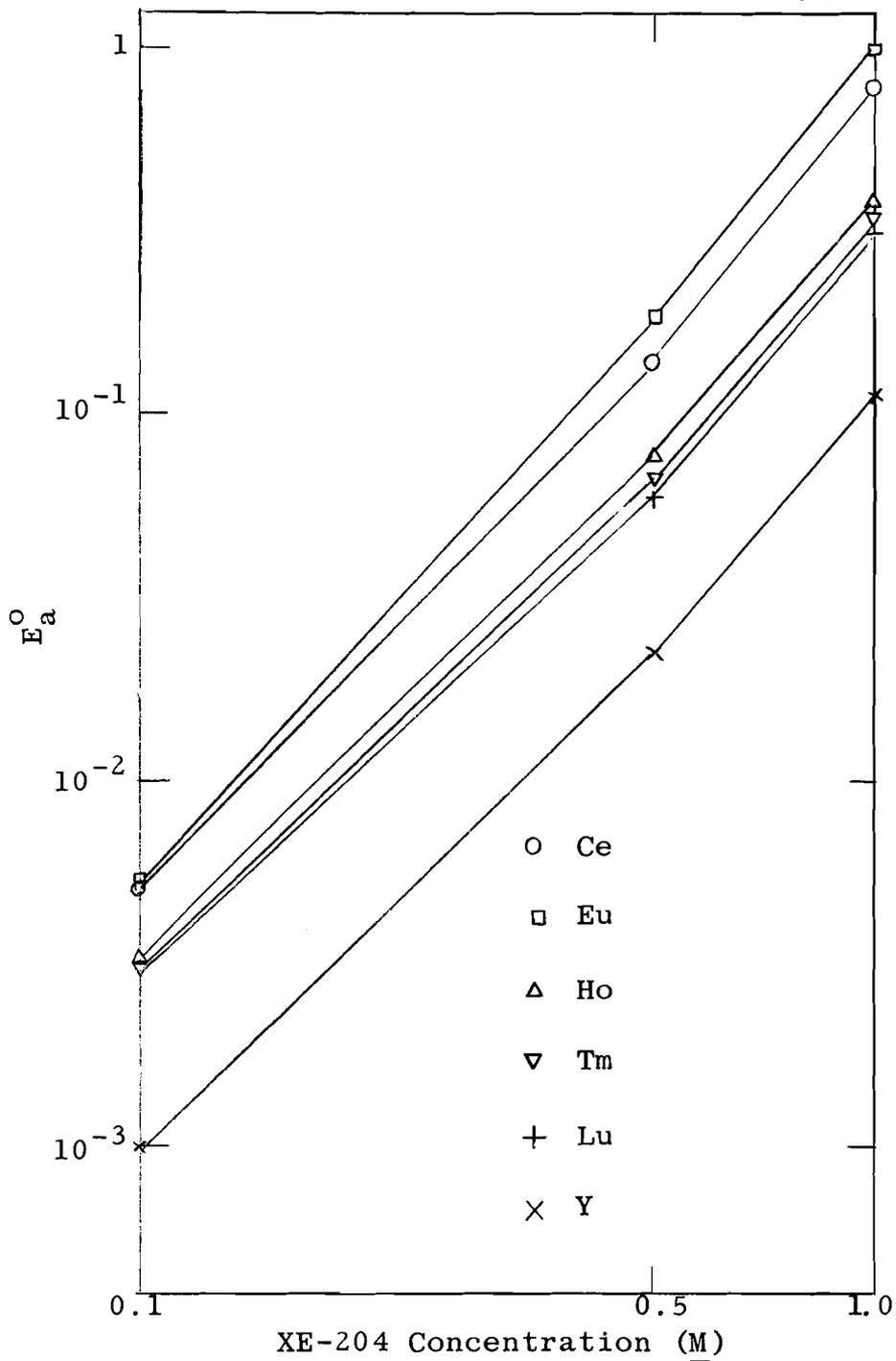


Fig. 7. Extraction Dependence on Reagent Concentration.
XE-204 in DIPB
11 N LiCl, 0.01 N HCl
(Abscissa Multiplied x2)

3.1.4 Effects of Modifiers. Solutions of the foregoing amines in aliphatic diluents divide into two organic phases on conversion to chlorides unless they are modified by a small amount of some other solvent, such as a heavy alcohol. In the determination of reagent concentration dependence of americium and europium extraction, the question arose as to whether a series of samples of diluted reagent should contain modifier and amine in constant ratio or modifier and diluent in constant ratio. In the former case the modifier would be considered part of the reagent, in the latter case part of the diluent. This question was resolved in favor of the former by three experiments with europium extraction. For these experiments a 1.0 M TIOA base solution was prepared, containing 10% w/v TDA as modifier. The diluent used was DIPB, and the final solution contained 32% w/v DIPB. In the first experiment dilutions were made to 0.5 M, 0.2 M and 0.1 M amine with more DIPB, (modifier/amine constant). In the second experiment the diluent was 10% w/v TDA in DIPB (modifier concentration constant). In the third experiment the diluent was a mixture of 10 parts TDA and 32 parts DIPB (modifier/diluent constant).

In only the first case was there a rectilinear relationship, with extraction proportional to the 1.9 power of reagent concentration (Fig. 8). When the modifier concentration was constant, the curve was much steeper in the upper range of amine concentration. When the modifier to diluent ratio remained constant, it had a still greater effect at high amine concentration but appeared to increase extraction at very low amine concentration. A test of the extractability of europium by pure TDA from 11 N LiCl, 0.01 N HCl gave a coefficient of 0.0017. This is slightly higher than that for 0.1 M TIOA in DIPB with 10% TDA.

The conclusion is that in this system, the modifier must be considered as part of the reagent and the ratio of modifier to amine must be kept constant in reagent concentration experiments. However, in practice with aliphatic diluents, a third phase may be produced at high dilution. This has been observed in at least one case. In such cases the original modifier concentration must be high enough to permit dilution without incompatibility. A subject of interest for further study with various extraction systems based on aliphatic diluents is the relation of reagent concentration to minimum concentrations of modifiers required for phase stability.

3.1.5 Salt Concentration Dependence. Previous work showed that extraction of americium by the amines tested was proportional to about the 18th power of the salt concentration between 7 N and 11 N chloride as pure LiCl or mixed LiCl-AlCl₃. Extractions of europium and yttrium by TIOA in DIPB and of europium, yttrium, and scandium by Alamine 336 in DIPB from concentrated LiCl have been studied recently. With 0.8 M TIOA in DIPB, extraction of europium was proportional to about the 24th power of the salt concentration between 9.5 and 12 N LiCl (Fig. 9). Extraction of yttrium was

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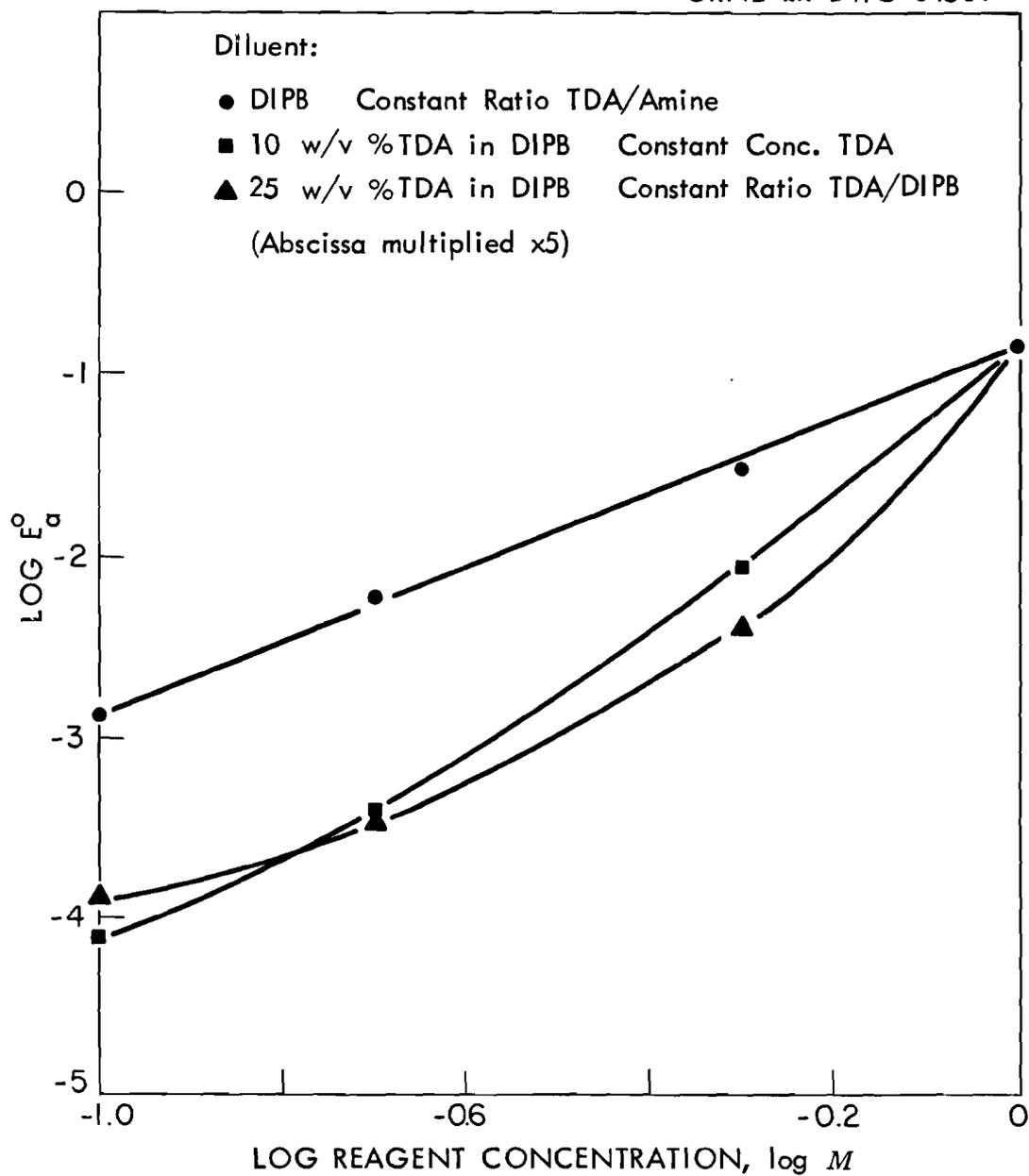


Fig. 8. Reagent-modifier-diluent relationship base extractant:
1 M TIOA + 10 w/v % TDA in DIPB.

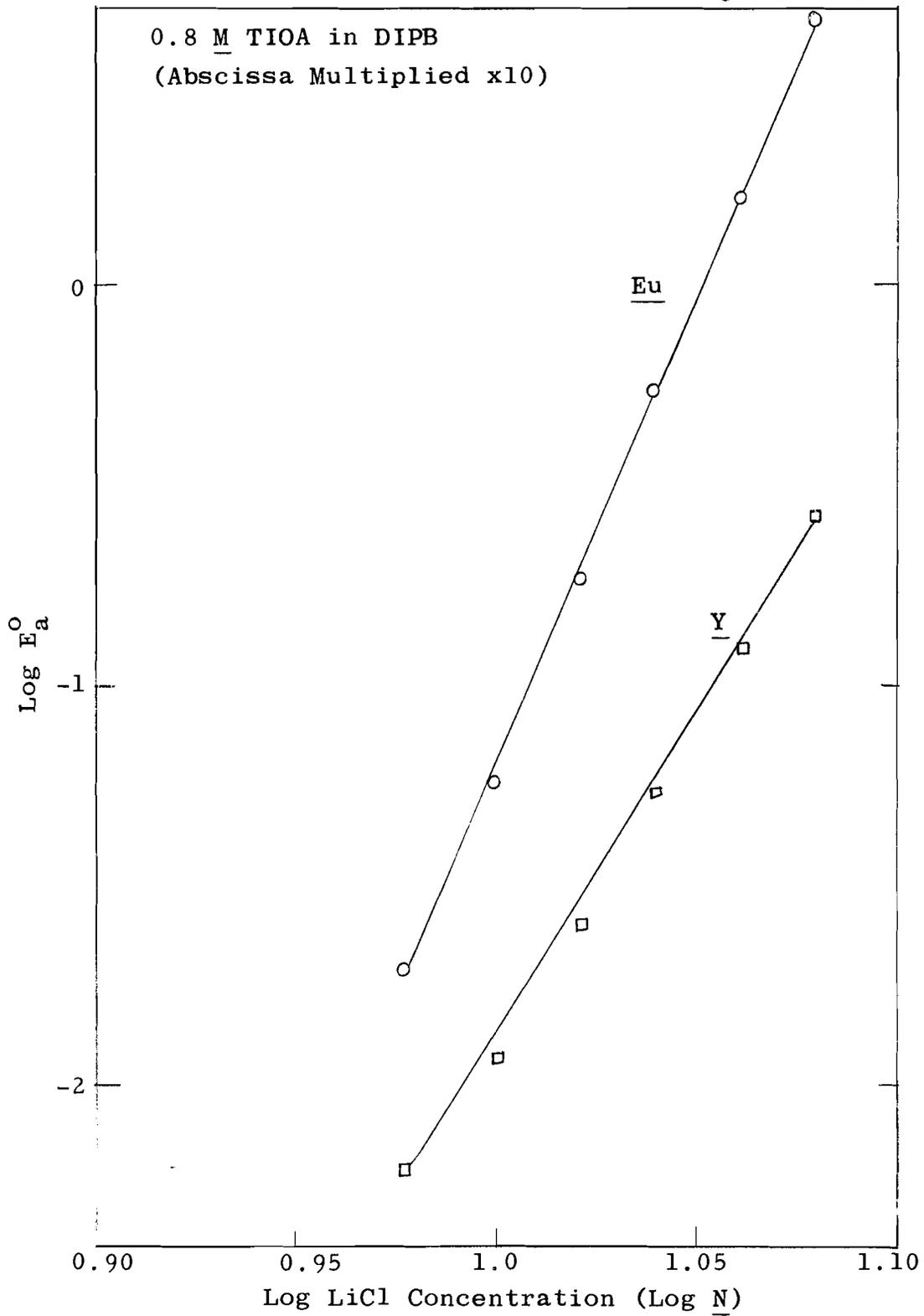


Fig. 9. Extraction Dependence on LiCl Concentration.

proportional to the 16th power of the chloride concentration. An 0.8 M solution of Alamine 336 in DIPB showed a non-rectilinear effect with an overall power dependence of 22.6 for europium and 12.2 for yttrium (Fig. 10). Extraction of scandium by the same reagent was more complex with a mean power dependence of ~19 over the range of 8 N to 12 N LiCl. The indicated possible separation between europium and yttrium increased with chloride concentration, while that between scandium and europium decreased and reversed at very high chloride concentrations. At lower concentrations scandium behavior was parallel to that of yttrium, Scandium behavior at high chloride concentrations appears to be contrary to the usual behavior of this element, which ordinarily has chemical properties different in magnitude from those of any of the lanthanide series.

3.1.6 Other Scandium Extractions. Scandium was extracted from 11 N LiCl and from 8 N LiCl, 2 N AlCl₃ by TIOA, XE-204 and Alamine 336 in DIPB. It was predicted that extraction of scandium would be lower than that of yttrium, in continuation of the series: transplutoniums >> lanthanides > yttrium. On the contrary, scandium extractions in the few systems studied were comparable to or greater than those of europium (Table 17). Even more noteworthy were the very high extractions from 8 N LiCl, 2 N AlCl₃, which were comparable to or greater than those of americium. The influence of aluminum on this extraction was tested by extraction with 0.8 M Alamine 336 in DIPB from 8 N AlCl₃. The distribution coefficient was 0.23, which is ~20 times that from 8 N LiCl.

Table 17. Extraction of Scandium

Reagent	DIPB Diluent	
	11 N LiCl, 0.01 N HCl	8 N LiCl, 2 N AlCl ₃
0.8 M TIOA	1.97	5.2
0.8 M Alamine 336	0.41	2.6
1.0 M XE-204	0.53	9.4

3.1.7 Discussion of Yttrium Extraction Data. The relative inextractability of yttrium with respect to the whole series of lanthanides is unique in the authors' knowledge. In all other known extraction systems, yttrium behaves as though it were an element between holmium and thulium. Solubilities of yttrium salts fall within the same or a narrower range of elements. The relationship of yttrium to the lanthanides in basic precipitations varies with salt concentration, but yttrium never precipitates ahead of nor behind the whole lanthanide series. The elution positions of yttrium in a variety of ion exchange systems are all between gadolinium and erbium.

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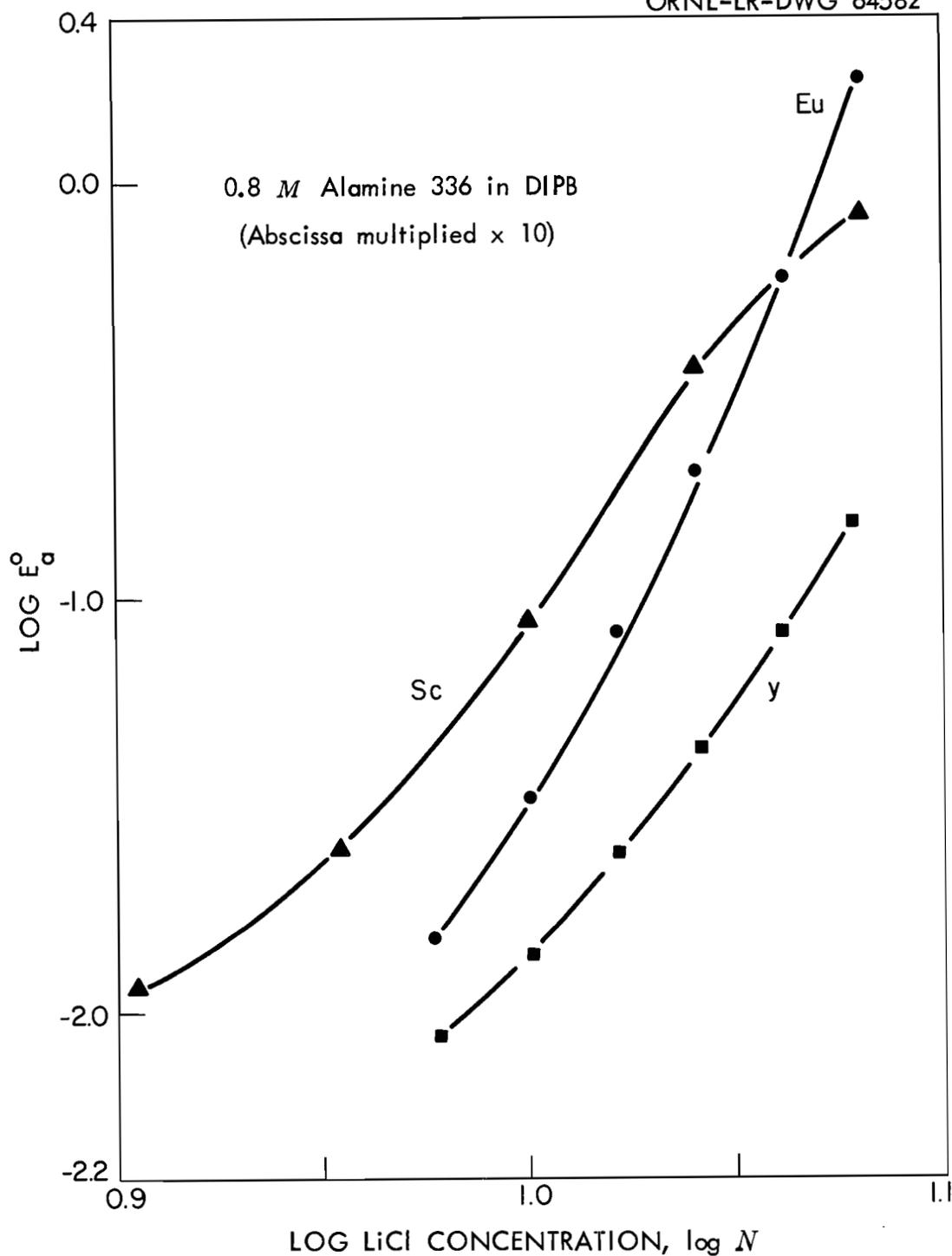


Fig. 10. Extraction dependence on LiCl concentration.

The unique behavior of yttrium in amine chloride extractions, with a minimum separation factor of ~ 2.5 from the least extractable lanthanide, suggests applications of this separation system. There may be other amine-diluent compositions still more favorable to separation. An obvious disadvantage is low capacity, resulting from loading restrictions with dilute amines and low solubility of rare earth chlorides in concentrated LiCl. Moreover the very low distribution coefficients of even the lanthanides would require unfavorably high organic/aqueous phase ratios. Probably the most likely application would be in special radiochemical separations. The results in this present study do demonstrate that in the planned application of amine chloride extraction to transplutonium purification fission-product yttrium will be removed even more thoroughly than the lanthanides.

The wide variety of results obtained from extraction under the various conditions studied indicate that reliable predictions cannot be made regarding the behavior of lanthanides or yttrium in any other set of conditions. This fact is illustrated by the differences in order and magnitude of extractabilities by such slightly different amines as TIOA and Alamine 336 in the same diluent. In the previous work on separation between the transplutonium and lanthanide groups, a nearly constant separation factor of 100-130 was obtained between americium and europium under a great variety of conditions. The presently observed wide diversity of results with the other lanthanides indicates that if one of them had been used as the representative of the group, the separation factors obtained would not have been nearly so constant. A correlary conclusion can be made that the comparison of transplutonium elements, which has been limited to extraction by Alamine 336 in diethylbenzene, should be extended to extraction by other amine-diluent compositions. There might be different orders and magnitudes of extraction more favorable to separations within this group.

The short survey of scandium extraction indicates an even wider diversity of behavior than that shown by the lanthanides and yttrium. There is no obvious correlation of this chemistry with position in the periodic system.

3.2 Extraction of Rare Earths from Thiocyanate Solutions by Amines (A. Faure and B. Weaver)

A brief survey was made of extraction of americium, europium, and yttrium by tertiary amines and a secondary amine from thiocyanate solutions, in which rare earths are highly complexed. Extractions were all very small (Table 18).

Table 18. Extractions by Amines from Thiocyanate Solutions

Organic	Aqueous	E_a^0		
		Y	Eu	Am
0.8 M Alamine 336 chloride in DIPB	6 M NH_4SCN	0.007	0.016	
0.8 M Alamine 336 sulfate in DIPB	6 M NH_4SCN	0.004	0.005	0.006
0.8 M Alamine 336 sulfate in DIPB	8 M NH_4SCN	0.005	0.002	
0.8 M Alamine 336 sulfate in DIPB	3 M NH_4SCN , 0.01 N HCl	0.0005	0.0015	
0.8 M Alamine 336 sulfate in DIPB	4 M NH_4SCN , 0.01 N HCl	0.002	0.0007	
10% TIOA thiocyanate in xylene	5 M NH_4SCN , 0.01 N HCl	0.0001	0.0001	
0.8 M LA-1 thiocyanate in xylene	5 M NH_4SCN , 0.01 N HCl	0.0004	0.0006	

4.0 FISSION PRODUCT RECOVERY

4.1 Extraction of Nitric Acid and Iron Sulfate from Purex 1WW Solution (D. J. Crouse)

The extraction of nitric acid and iron sulfate from Purex 1WW solution with amines is being studied as a means of producing a feed solution highly amenable to strontium and cesium recovery by solvent extraction. In preliminary tests with a primary amine (Primene JM), approximately 90% of the nitrate and iron and a major portion of the sulfate were removed from synthetic Purex 1WW solution in a single contact.

In the process¹² developed for recovery of strontium from Purex waste by extraction with di(2-ethylhexyl)phosphoric acid, the aqueous feed solution is adjusted with caustic to pH 4-5 prior to extraction. To avoid precipitation of iron at this pH, sodium tartrate (or citrate, acetate, etc.) is added, approximately 2 moles of tartrate per mole of iron being required to give a stable feed. Since the Purex 1WW solution usually contains ~4 M HNO_3 and 0.5 M Fe, the sodium added in the feed adjustment step is about 10 times that present (~0.6 M) in the original 1WW solution. The added sodium competes for the extractant, appreciably decreasing both the strontium extraction coefficient and the strontium/sodium separation. The reagents being studied¹³ as cesium extractants require similar adjustment of the feed prior to the extraction step. In this case, limiting the sodium

competition is of even greater potential advantage than in the case of strontium, since cesium extraction coefficients are relatively low.

Extraction of nitric acid and iron sulfate was studied by contacting ~0.2 M Primene JM in Amsco 123-15 diluent with synthetic Purex 1WW solution at various organic/aqueous phase ratios ranging from 10 to 26. To avoid excessive pH rise at phase ratios higher than 20, where the amine added would be greater than the equivalent amount of free acid in the 1WW solution, a portion of the amine was used in the form of the sulfate salt. As shown in Figure 11, at the lower organic/aqueous phase ratios, only nitric acid and a small amount of sulfuric acid were extracted. For example, at a phase ratio of 15/1, extractions of nitrate, sulfate, and iron were 75, 9, and <1% respectively. At the highest phase ratio tested (26/1), 95% of the nitrate, 88% of the iron, and 58% of the sulfate were extracted. More complete extraction could, of course, be obtained at higher phase ratios. Phase separation was rapid in all tests.

Since Primene JM has a high (~25%) initial solubility loss (owing to the presence of low molecular weight amines) to aqueous liquors, the amine was scrubbed with dilute sulfuric acid, reconverted to the free base form, and diluted to the desired concentration prior to use. The synthetic Purex 1WW solution used in the above tests contained in moles/liter, 4.0 H⁺, 0.5 Fe(III), 0.6 Na, 0.1 Al, 0.01 Cr, 0.01 Ni, 0.01 U, 4.45 NO₃, and 1.0 SO₄.

Thus far no tests have been made on stripping the nitrate, sulfate and iron from the amine. A basic strip (NaOH, Na₂CO₃) would be required to convert the amine to the free amine form for recycle. From the chemical standpoint there is no question that contact with excess base would effectively regenerate the amine. However, it still must be demonstrated that this step can be accomplished without the formation of troublesome emulsions due to precipitation of iron (and probably other metals) in the stripping system.

In addition to reducing the salt content of the Purex 1WW solution before strontium and cesium extraction, amine extraction should also remove several fission product and transuranium elements. For example, under proper conditions, effective removal of rare earths, zirconium (and possibly niobium), plutonium, technetium, and possibly other radionuclides would be expected, whereas strontium and cesium should remain in the aqueous phase. Conditions could probably be controlled so that the rare earths could be left with the strontium-cesium stream when desired.

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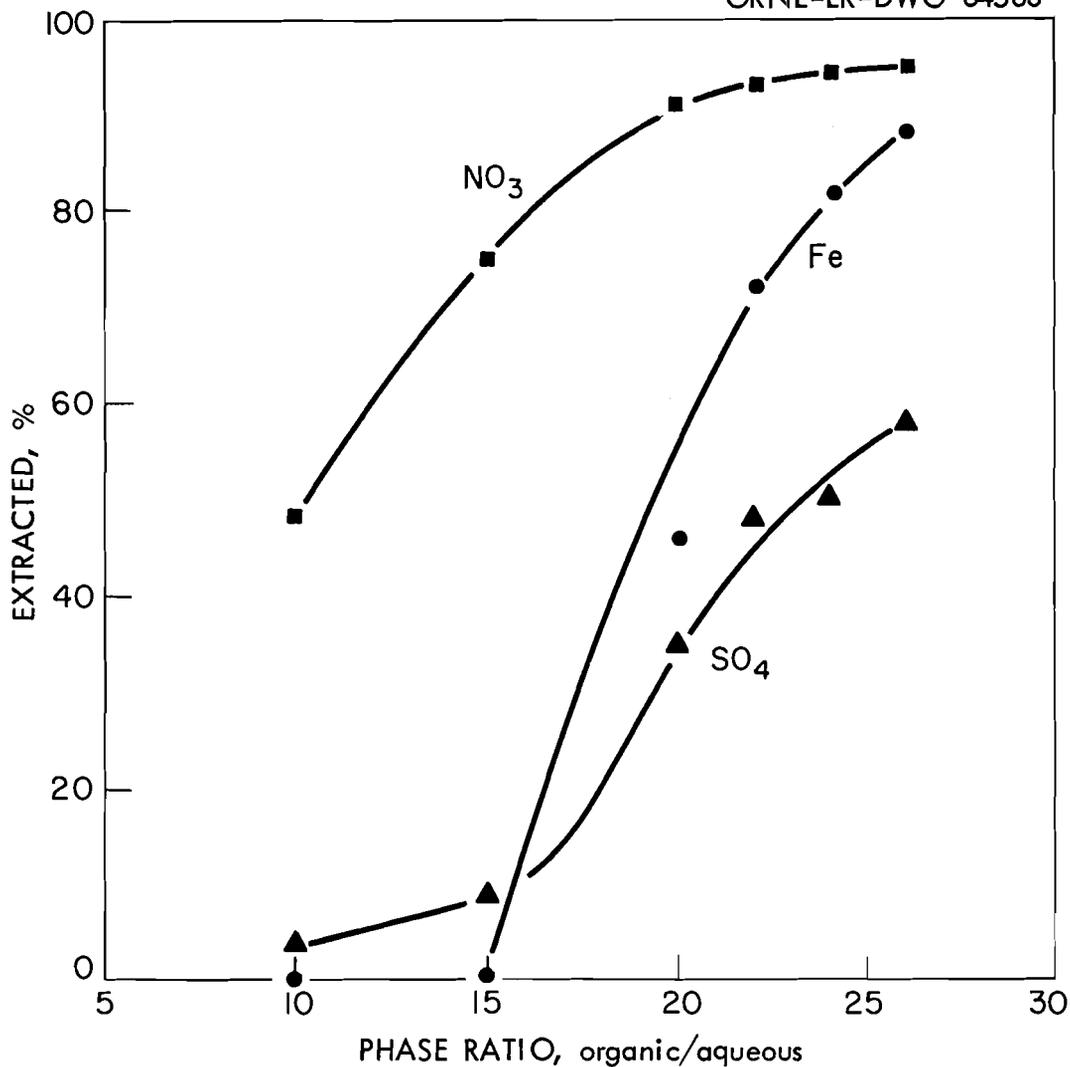


Fig. 11. Extraction of nitric acid and ferric sulfate from synthetic Purex 1WW solution. Organic: $\sim 0.2 M$ Primene JM in Amsco 123-15 (at phase ratios of 22, 24, and 26 respectively, 9, 17, and 25% of the total amine was converted to the sulfate salt form prior to testing). Contact time: 5 min.

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