MARTIN MARIETTA ENERGY SYSYEMS LIBRARIES
3 4456 0322246 6

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

ORNL-3273
UC-4 – Chemistry
TID-4500 (17th ed., Rev.)

SEPARATION OF TRANSPLUTONIUM ELEMENTS BY PHOSPHONATE EXTRACTION

R. D. Baybarz

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

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

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ORNL-3273

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section A

SEPARATION OF TRANSPLUTONIUM ELEMENTS BY PHOSPHONATE EXTRACTION

R. D. Baybarz

DATE ISSUED

JUL 20 1962

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

MARTIN MARIETTA ENERGY SYSYEMS LIBRARIES

3 4456 0322246 6

ABSTRACT

A process developed and tested on a laboratory scale for separating transcurium elements from americium and curium consists in preferential solvent extraction of the transcurium elements with 2-ethylhexylphenylphosphonic acid from dilute HCl solutions. Single-stage separation factors of 100 were found between californium and curium. Extraction positions of americium, curium, berkelium, californium, einsteinium, and fermium were determined. Extraction varied with the inverse third power of the acid composition in the range 1-4 N and directly with the third power of the extractant concentration.

CONTENTS

	Page
1.0 Introduction	1
2.0 Proposed Flowsheet	1
3.0 Laboratory Experiments	2
3.1 Extractability of Transplutonium Elements	2
3.2 Relative Extractability of Lanthanides	4
3.3 Extractability of Contaminant Ions	4
3.4 Effect of Acid Concentration	4
3.5 Effect of Acid Composition	6
3.6 Effect of Reagent Concentration	6
3.7 Effect of Diluent	8
3.8 Kinetics of Extraction, Scrubbing, and Stripping	8
3.9 Effect of Degradation Products and Radiation	8
4.0 Experimental Procedure	10
5.0 References	10

1.0 INTRODUCTION

This report covers a study of the extraction of the transplutonium elements by 2-ethylhexylphenylphosphonic acid [2-EH(ØP)A] from mineral acid solutions, and its application for separating the transcurium elements from americium and curium. The 2-ethylhexylphenylphosphonic acid extraction system is proposed as the second phase of a multiphase separation process to produce and isolate macro quantities of the transcurium elements. The initial step is separation of the actinide elements from fission products by tertiary amine extraction (1,2).

Methods of separating the transplutonium elements have mainly depended on chromatographic elutions from ion exchange columns, i.e., by α-hydroxyisobutyrate lactate, and glycolate (3) from Dowex 50 resin and by LiCl from Dowex 1 resin (4). The transplutonium elements, with their very high specific activities, are less efficiently separated by the resin process because of radiation damage to the resin and decomposition of the solution. Liquid-liquid extraction is not affected by the gas production from radiolysis of water, it may be made continuous, and concentrations in all parts of the system may be controlled to decrease radiation damage to the extractant.

Solvent extraction methods have been proposed by Peppard et al. (5-7) for separating Bk^{4+} from Cm^{3+} or Cf^{3+} by di-2-ethylhexylphosphoric acid vs HNO_3, and Cf^{3+} from Cm^{3+} by the use of di-2-ethylhexylphosphoric acid and 2-ethylhexylphenylphosphonic acid vs HCl.

The author gratefully acknowledges the helpful assistance of S. Fried (Lawrence Radiation Laboratory, Berkeley) in procurement of the transcurium isotopes, and of R. E. Leuze for helpful and critical suggestions.

2.0 PROPOSED FLOWSHEET

A proposed flowsheet for separation of berkelium, californium, and einsteinium from americium and curium (Fig. 1) based on distribution coefficient data determined in laboratory tests indicated that such a separation is feasible. In this flowsheet the feed is 1 M HCl, scrub 1.5 M HCl, and extractant 1.0 M 2-EH(ØP)A in diethylbenzene (DEB), at flow ratios of 1/1/2. With 8 extraction and 5 scrub stages, the californium recovery is calculated to be >99.99%, berkelium recovery 99.9%, and the decontamination factor from curium $>10^4$.

The above flowsheet has not been tested because of very limited supply of berkelium, but in tests with americium and californium, between which the separation factor is 130, only a few stages were necessary to give separations greater than were measurable with the limited amount of californium available. In a batch countercurrent experiment with 3 scrub and 4 extraction stages, 99.9% of the californium

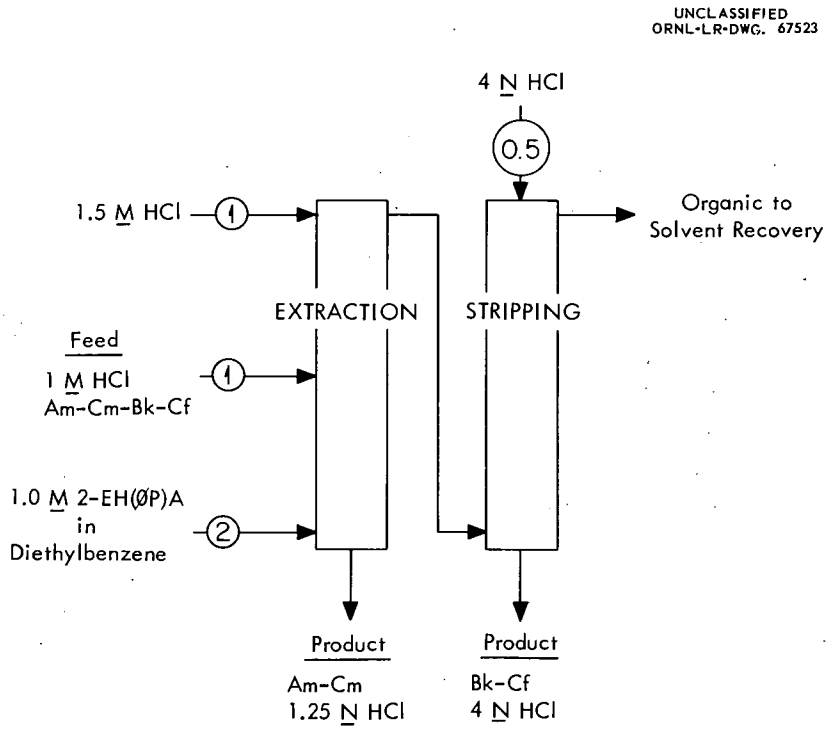

Fig. 1. Transplutonium element separation flowsheet.

was extracted with a decontamination factor from americium of 10^3. The conditions were: feed, 1.4 N HCl; scrub, 1.8 N HCl; extractant, 1.0 M 2-EH(ØP)A in diethylbenzene; flow ratio, 1/1/2. In the 40 cycles through which the experiment was run, the inefficiency of transferring small (10 ml) volumes in separatory funnels and the uncertainty of counting low-activity samples decreased the separation factor below the calculated value.

3.0 LABORATORY EXPERIMENTS

3.1 Extractability of Transplutonium Elements

In the 2-EH(ØP)A vs HCl system, the extractability of the transplutonium elements increased with increasing Z (Fig. 2), but not uniformly. The extractability of californium was a factor of 100 greater than that of curium, and californium recovery and purity would be high with only a few stages. With 10 stages, a separation factor of 10^{10} is theoretically possible in a continuous countercurrent system.

Because of the separation factors between various transplutonium pairs,

Pair	Separation Factor	Pair	Separation Factor
Cm-Am	1.3	Es-Cf	1.2
Bk-Cm	30	Fm-Es	2.5
Cf-Bk	3.3		

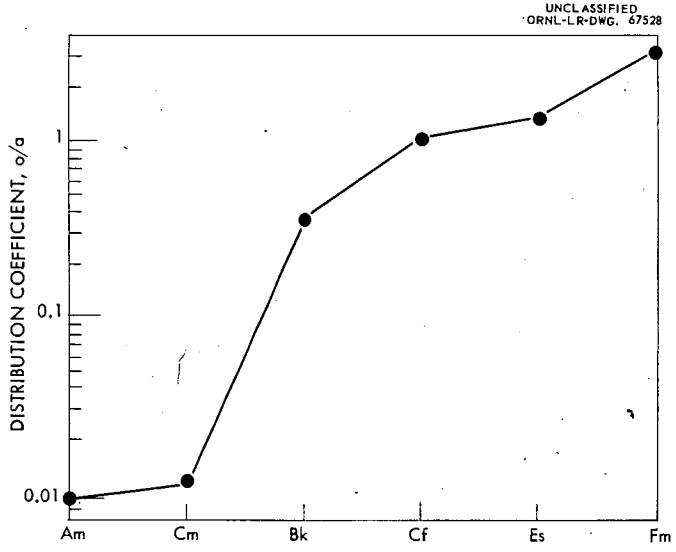

Fig. 2. Relative extractability of transplutonium elements by 1 M 2-EH(ØP)A in DEB from 2 M HCl.

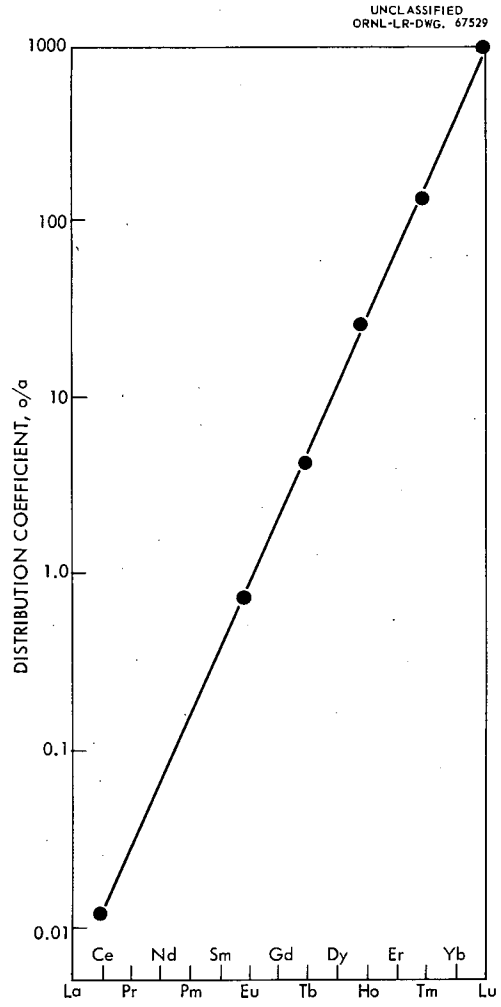

Fig. 3. Relative extractability of lanthanides by 1 M 2-EH(ØP)A in DEB from 2 M HCl.

berkelium could also be separated from the transcurium and transberkelium elements and fermium from californium and einsteinium, but americium would not be separated from curium or californium from einsteinium.

3.2 Relative Extractability of Lanthanides

The extractability of the lanthanides increased regularly with increasing Z (Fig. 3). The separation factor between adjacent lanthanides was ~2.5 and was consistent for the entire series.

3.3 Extractability of Contaminant Ions

A brief investigation of the extractability of possible contaminant ions (Fig. 4) showed that Zr^{4+}, Ti^{3+}, Fe^{3+}, Sn^{2+}, MoO_4^{2-}, UO_2^{2+}, and Pu^{4+} will be extracted with the Cf^{3+}. Of these extracted ions, Zr^{4+}, MoO_4^{2-}, UO_2^{2+}, and Pu^{4+} can be made to remain in the solvent when the Cf^{3+} is stripped with 4 N HCl. Elements which will not be extracted but remain with the americium and curium are Sr^{2+}, Ru^{3+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Cd^{2+}, Ni^{2+}, Cr^{3+}, Co^{3+}, and Mn^{2+}.

3.4 Effect of Acid Concentration

The extraction of californium was inversely proportional to the third power of the hydrogen ion concentration at low acidities (Fig. 5). The extractability of both lanthanides and actinides reached a minimum and then became more extractable at higher acidities (Fig. 6). The separation factors remained constant to 5.5 M HCl, where the americium distribution coefficient was minimum. At high acidities the distribution coefficients started to converge, resulting in lower separation factors.

The distribution coefficient minimum shifts to higher acid concentrations with decreasing ionic radius. The minima for the lanthanides and transplutonium elements increase with Z. The 2-EH(ØP)A is dimeric (9) and the extracted element participates in an eight-membered ring through hydrogen bonding. The stability of the chelate complex would be expected to increase with decreasing ionic radius (8):

Element	Ionic Radius, A	HCl Conc at Extraction Minimum, N	Element	Ionic Radius, A	HCl Conc at Extraction Minimum, N
Ce^{3+}	1.034	5.2	Tm^{3+}	0.869	8.5
Eu^{3+}	0.950	6.5	Am^{3+}	0.99	5.5
Tb^{3+}	0.923	7.5	Cf^{3+}		7.0

The 2-EH(ØP)A does not extract acid into the organic phase since the HCl distribution coefficient is <0.005 in acid range 1 to 8 N. The extracted species is

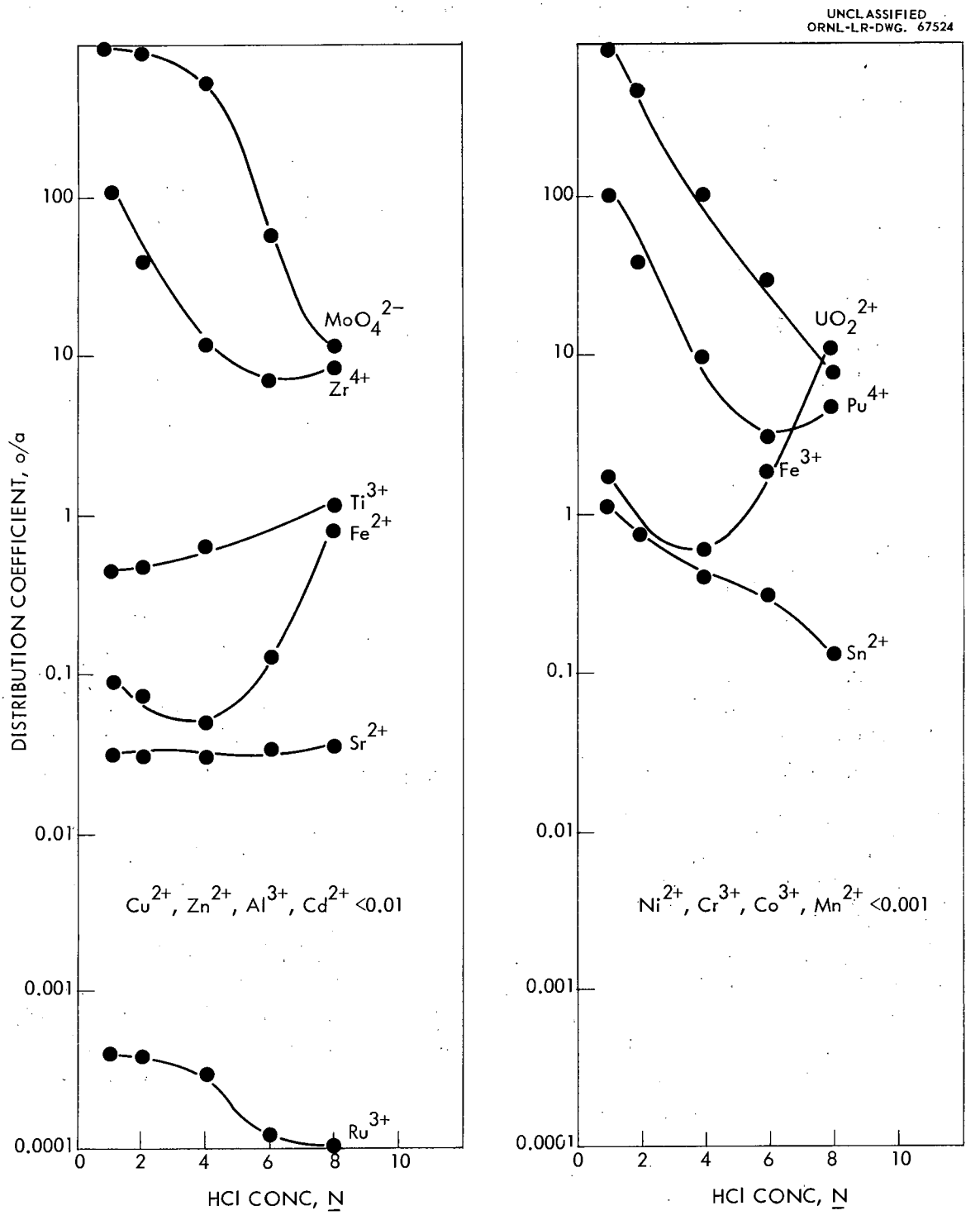

Fig. 4. Extractability of various contaminant ions by 1 M 2-EH(ØP)A in DEB.

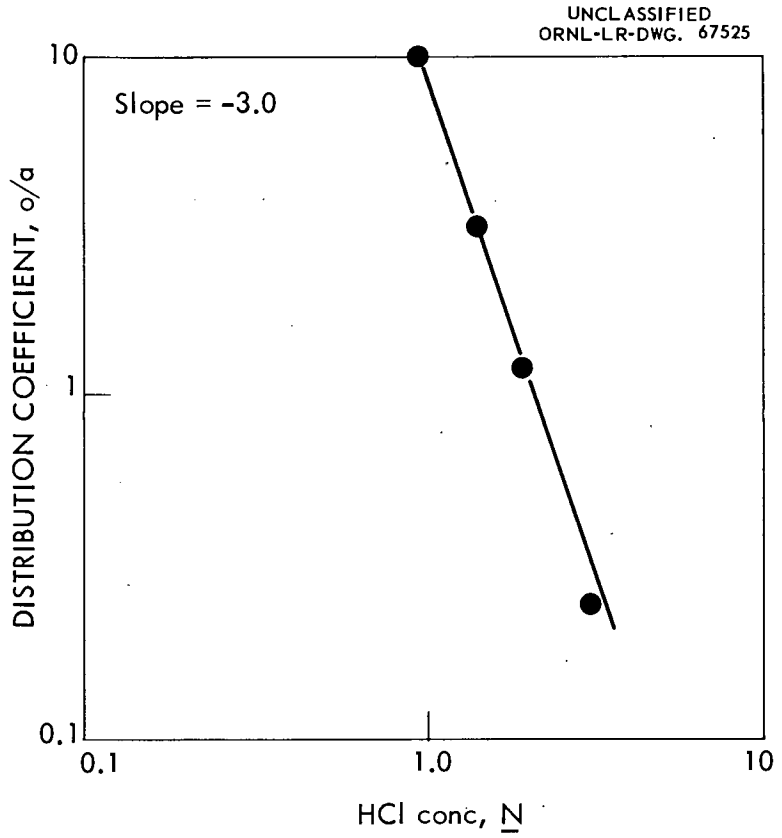

Fig. 5. Dependence of californium extraction by 1 M 2-EH(ØP)A in DEB on hydrogen ion concentration.

the cation with no associated anions, postulated to be a complex consisting of the metal ion associated with three dimers of the phosphonate, $M[[2\text{-EH(ØP)A}]_2]_3$, probably with solvate water.

3.5 Effect of Acid Composition

The extraction of the transplutonium elements from acid solutions into 2-EH(ØP)A varies with the anion in the order $ClO_4^- > Cl^- > NO_3^-$. The distribution coefficients for californium in the systems 1 M 2-EH(ØP)A-DEB vs 2 N $HClO_4$, HCl, and HNO_3 were 9.5, 1.1, and 0.9, respectively. The decrease in californium extractability implies complexing in the aqueous phase, nitrate complexing being more noticeable than chloride.

3.6 Effect of Reagent Concentration

In the HCl range 1-4 N the distribution coefficients were proportional to the cube of the 2-EH(ØP)A molarity in the organic phase (Fig. 7) in the extraction of californium from 1.3 N HCl into varying concentrations of 2-EH(ØP)A in DEB.

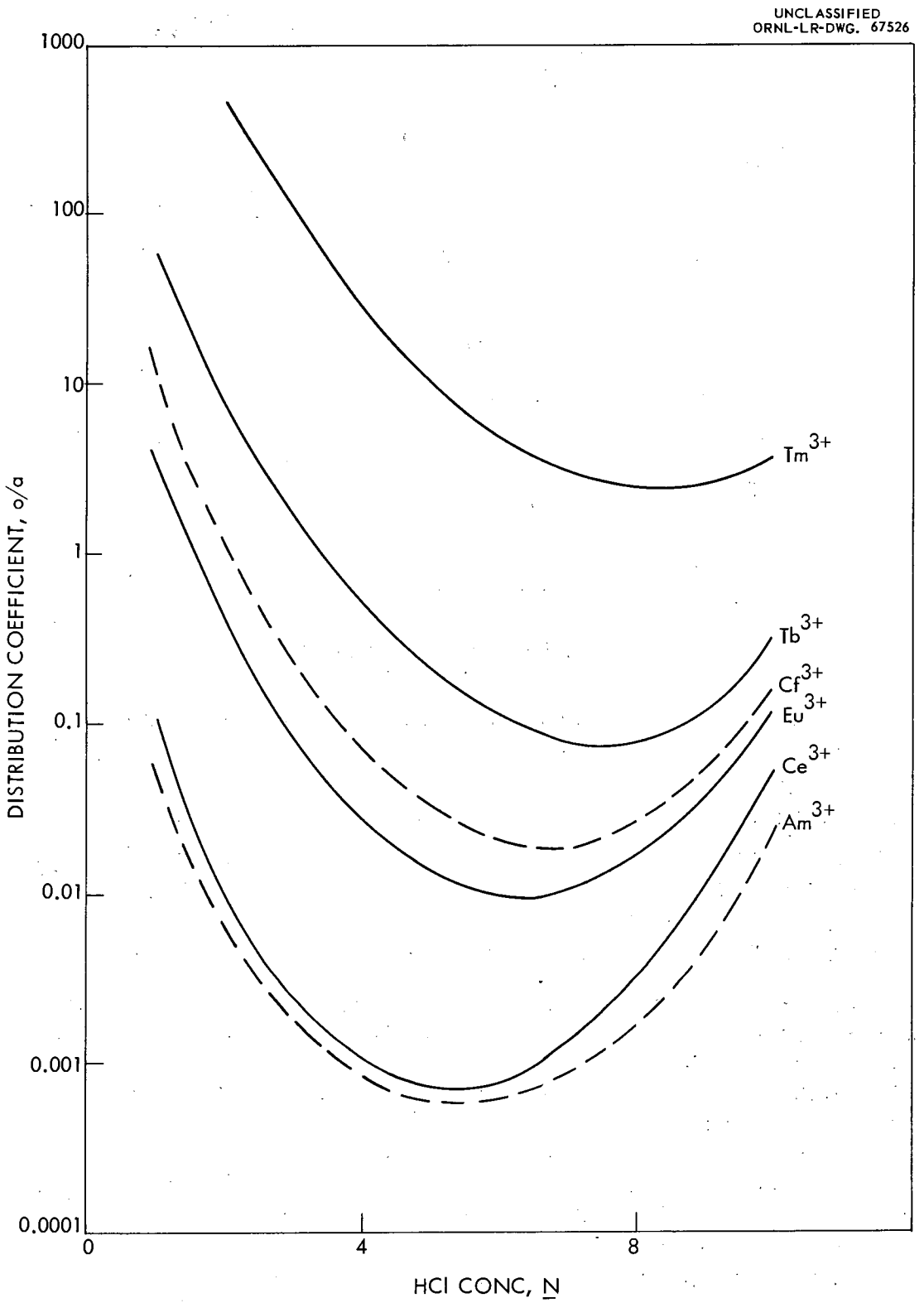

Fig. 6. Effect of acid concentration on extractability of lanthanides and actinides by 1 M 2-EH(ØP)A in DEB.

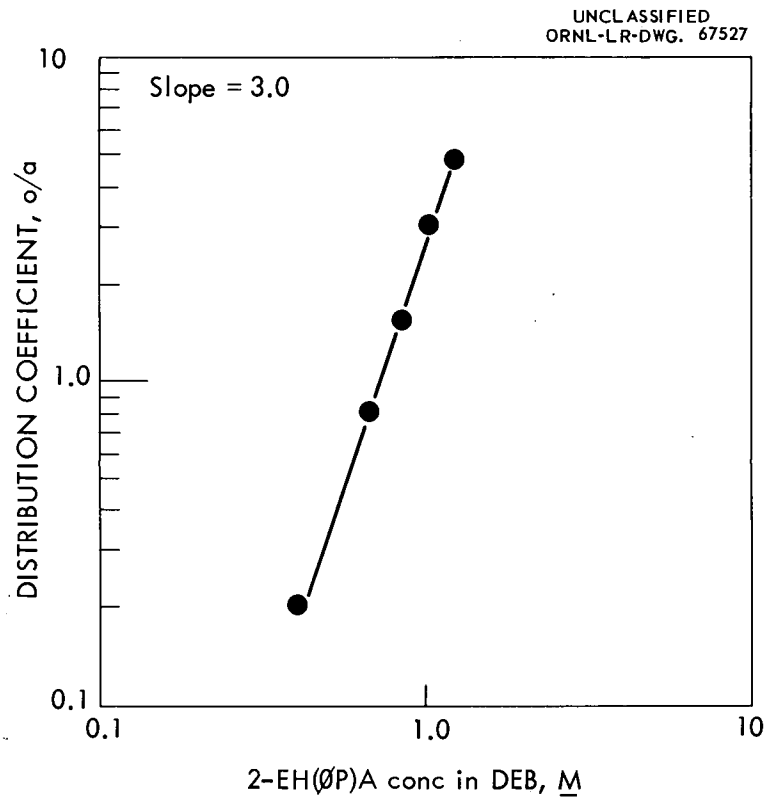

Fig. 7. Effect of extractant concentration on extraction of californium from 1.3 N HCl.

3.7 Effect of Diluent

The extraction of europium was affected by the nature of the solvent diluent, i.e., cyclohexane, heptane, carbon tetrachloride, or benzene. Europium extraction from 2 N HCl into constant 1 M 2-EH(ØP)A was greatly increased when some of the aliphatic diluents were used instead of the benzene type (Table 1). The increase in europium extractability is in the same sequence as water solubility in the pure diluent. The effect of the diluent on europium extraction is probably connected with the permanent or induced diluent dipole (10) through the diluent water content.

3.8 Kinetics of Extraction, Scrubbing, and Stripping

A brief investigation of the rate of mass transfer showed that the extraction, scrubbing, and stripping reactions took place almost instantaneously. No change in extraction coefficients was noted after 5 sec equilibration. The extracted material was as easily stripped after one week in the organic phase as initially, indicating no polymerization upon standing.

3.9 Effect of Degradation Products and Radiation

The degradation products from 2-ethylhexylphenylphosphonic acid are

Table 1. Effect of Diluent on Extraction of Europium from 2 N HCl by 1.0 M 2-EH(ØP)A

Diluent	Eu D.C.	H_2O Solubility, g/liter of solvent
n-Heptane	4.78	0.014
Amsco 125-82	3.48	
n-Dodecane	3.35	
Decalin	2.08	
Cyclohexane	2.01	0.04
Triethylbenzene	0.89	
Diethylbenzene	0.61	
Carbon tetrachloride	0.52	0.15
Solvesso-100	0.42	
Xylene	0.40	0.38
Toluene	0.37	0.50
Benzene	0.31	0.60

2-ethylhexanol and phenylphosphonic acid. The phenylphosphonic acid is water soluble and caused no difficulty in extraction, but the addition of 15 vol % 2-ethylhexanol in 1 M 2-EH(ØP)A-DEB decreased the distribution coefficients of californium and americium a factor of 10:

2-EHOH, %	Cf D.C.	Am D.C.
Control	0.94	0.009
2	0.44	0.005
5	0.32	0.003
10	0.16	0.002
15	0.09	0.001

However, the separation factor between californium and americium remained constant at ~100.

Preliminary data on the radiation stability of 2-EH(ØP)A in DEB indicate that irradiation at levels likely to be encountered in processing will have no significant effect on the separation power or on the chemistry of the extraction. A 1.0 M 2-EH(ØP)A solution in DEB was equilibrated with 1.5 M HCl-20 g/liter Am-241 for a total of 20 whr/liter exposure to a radiation. No change in americium extraction or in physical characteristics was noted. Exposure of the organic solution equilibrated with 1.5 M HCl to Co-60 irradiation to 100 whr/liter resulted in an amber coloration in the organic phase, but there was no change in the californium-americium separation or extraction. From data on the effect

of 2-ethylhexanol on extraction, any appreciable degradation from irradiation would have become evident in decreased extraction coefficients for californium and americium.

4.0 EXPERIMENTAL PROCEDURE

Due to the limited quantity of Cf-252 available, the experiments were designed to obtain maximum information with minimum volumes of solution. The solvent extraction experiments involving californium were made with 1-ml volumes of organic and aqueous phases at an activity level of $\sim 10^4$ d/m/ml. The phases were shaken by hand and centrifuged for phase separation, and samples were put on platinum plates for counting. Californium-252 was determined by spontaneous fission counting with no interference from other types of radiation. Berkelium was determined by gas proportional counting of the 90-kev β radiation with no other types of radiation present. Americium, curium, einsteinium, and fermium were determined by α pulse height analysis.

The full ester di-2-ethylhexylphenylphosphonate was obtained from Victor Chemical Company and the half ester was prepared by refluxing the full ester with 50% excess 3 M NaOH for ~24 hr to split off one alcohol group. The alcohol was removed by steam distillation and the 2-ethylhexylphenylphosphonic acid was recovered by acidifying with HCl. The resulting material was centrifuged for clarification and used without further purification.

5.0 REFERENCES

1. R. D. Baybarz and Boyd Weaver, "Separation of Transplutoniums from Lanthanides by Tertiary Amine Extraction," ORNL-3185 (December 1961).

2. R. D. Baybarz and H. B. Kinser, "Separation of Transplutoniums from Lanthanides by Tertiary Amine Extraction. II. Contaminant Ions," ORNL-3244 (February 1962).

3. G. R. Choppin, B. G. Harvey, and S. G. Thompson, J. Inorg. Nucl. Chem. 2, 66 (1956).

4. E. K. Hulet, R. G. Gutmacher, and M. S. Coops, J. Inorg. Nucl. Chem. 17, 350 (1961).

5. D. F. Peppard, S. W. Moline, and G. W. Mason, J. Inorg. Nucl. Chem. 4, 344 (1957).

6. D. F. Peppard, G. W. Mason, W. T. Driscoll, and S. McCarty, J. Inorg. Nucl. Chem. 12, 141 (1959).

7. D. F. Peppard, G. W. Mason, and I. Hucker, J. Inorg. Nucl. Chem. 18, 245 (1961).

8. J. J. Katz, G. T. Seaborg, "The Chemistry of the Actinide Elements," p. 437, John Wiley and Sons, New York, 1957.

9. D. F. Peppard, J. R. Ferraro, and G. W. Mason, J. Inorg. Nucl. Chem. 12, 60 (1959).

10. T. V. Healy, J. Inorg. Nucl. Chem. 19, 328 (1961).

ORNL-3273
UC-4 – Chemistry
TID-4500 (17th ed., Rev.)

INTERNAL DISTRIBUTION

1. Biology Library
2-3. Central Research Library
4. Laboratory Shift Supervisor
5. Reactor Division Library
6. ORNL – Y-12 Technical Library Document Reference Section
7-41. Laboratory Records Department
42. Laboratory Records, ORNL R.C.
43. R. F. Apple
44. C. F. Baes
45. P. S. Baker
46. R. D. Baybarz
47. G. M. Begun
48. J. E. Bigelow
49. C. A. Blake
50. F. F. Blankenship
51. J. O. Blomeke
52. E. G. Bohlmann
53. J. C. Bresee
54. R. E. Brooksbank
55. K. B. Brown
56. W. D. Burch
57. T. A. Butler
58. A. E. Cameron
59. D. O. Campbell
60. G. H. Cartledge
61. A. Chetham-Strode
62. J. M. Chilton
63. W. E. Clark
64. J. H. Cooper
65. D. J. Crouse
66. W. C. Davis
67. J. S. Drury
68. L. M. Ferris
69. J. R. Flanary
70. J. H. Frye, Jr.
71. E. J. Frederick
72. J. M. Googin (Y-12)
73. C. E. Guthrie
74. P. A. Haas
75. J. C. Hart
76. R. F. Hibbs (Y-12)
77. D. E. Horner
78. H. P. House
79. A. R. Irvine
80. E. V. Jones
81. R. G. Jordan (Y-12)
82. F. A. Kappelman
83. G. W. Keilholtz
84. C. E. Lamb
85. P. M. Lantz
86. C. E. Larson
87. R. E. Leuze
88. W. H. Lewis
89. M. L. Lloyd
90. J. T. Long
91. L. O. Love
92. W. J. McDowell
93. W. T. McDuffee
94. H. F. McDuffie
95. H. C. Meyer
96. J. G. Moore
97. J. P. Murray (K-25)
98. E. L. Nicholson
99. F. L. Peishel
100. S. J. Rimshaw
101. J. T. Roberts
102. H. Russell
103. A. D. Ryon
104. F. M. Scheitlin
105. J. W. Schmitt
106. F. D. Seeley
107. E. M. Shank
108. M. J. Skinner
109. G. A. Strasser (Y-12)
110. E. G. Struxness
111. J. A. Swartout
112. P. F. Thomason
113. V. C. A. Vaughen
114. B. Weaver
115. A. M. Weinberg
116. M. E. Whatley
117. J. C. White
118. W. R. Whitson
119. D. L. Katz (consultant)
120. J. J. Katz (consultant)
121. T. H. Pigford (consultant)
122. H. Worthington (consultant)

EXTERNAL DISTRIBUTION

123. S. Fried, Lawrence Radiation Laboratory, Berkeley
124. Division of Research and Development, AEC, ORO
125-640. Given distribution as shown in TID-4500 (17th ed., Rev.) under Chemistry category