Distribution Categories:
Chemistry (UC-4)
Chemical Separations Processes for
Plutonium and Uranium (UC-10)

ANL-79-85

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

MASTER

DI-*n*-AMYL-*n*-AMYLPHOSPHONATE AND TRICAPRYLMETHYLAMMONIUM
NITRATE AS POTENTIAL EXTRACTANTS FOR
REPROCESSING Th-U FUELS*

by

H. Diamond, C. S. Sabau, E. P. Horwitz,
G. F. Vandegrift, and G. W. Mason

Chemistry Division

September 1979

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

* Work performed under the auspices of the Division of Nuclear Power Development, Fuel Reprocessing Branch, and the Office of Basic Energy Sciences of the U.S. Department of Energy.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

jeq

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
I. INTRODUCTION	1
II. DI- <i>n</i> -AMYL- <i>n</i> -AMYLPHOSPHONATE (DA[AP])	2
A. The DA[AP] Extractant	2
1. Purification of DA[AP]	2
2. Selection of Concentration	3
B. Extraction into 2 ^F DA[AP]	3
1. K _d for Tracer ²³³ U, ²³⁰ Th, ²³⁹ Pu(IV) from 2 <i>M</i> HNO ₃	3
2. Loading Curves for Uranium and Thorium in DA[AP]-DD	5
C. Extraction from Formic Acid Solutions	6
1. Uranium and Thorium in 2 ^F DA[AP]-DD-HCOOH-HNO ₃	7
2. Plutonium in Formic Acid	11
3. Extraction of HNO ₃ and HCOOH into DA[AP]-DD	14
D. A Countercurrent Separation of Thorium from DA[AP]-DD	15
E. Conclusions	20
III. TRICAPRYLMETHYLAMMONIUM NITRATE (TCMA·NO ₃)	22
A. Purification of TCMA·NO ₃	22
B. Third-Phase Formation - TCMA·NO ₃	23
C. Extraction of Macro-Concentrations of Thorium and Uranium into TCMA·NO ₃ -AR100	23
D. Thorium-Uranium Separations	30
E. Countercurrent Separation TCMA·NO ₃ -AR100	32
F. Discussion - TCMA·NO ₃	33
ACKNOWLEDGMENTS	34
REFERENCES	36

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	The Separate Distributions of Various Concentrations of Uranium and Thorium between 2 <i>M</i> HNO ₃ and 2 <i>F</i> DA[AP]-DD at 50°C	6
2.	The Variation of Tracer-Level Uranium and Thorium K _d 's with Calculated Formate Ion Concentration	9
3.	Spectrum of 0.0088 <i>M</i> Pu(IV) in 3.9 <i>M</i> HCOOH	11
4.	Spectrum of Pu(III) in Formic Acid	12
5.	Separate Distributions of HNO ₃ and HCOOH between Water and 2.0 <i>F</i> DA[AP]-DD at 23°C	14
6.	Effect of Free DA[AP] Concentration upon the Distribution Coefficient of Formic Acid	15
7.	Scheme for Selective Reextraction of Thorium from a DA[AP]-DD Feed Containing Both Uranium and Thorium	16
8.	Densities at 50°C after Nine Cycles	18
9.	Concentration of Thorium at 50°C in the Organic Phase and in the Aqueous Phase after Nine Cycles	18
10.	Concentration of Uranium at 50°C in the Organic Phase and in the Aqueous Phase after Nine Cycles	19
11.	Concentration of HNO ₃ at 50°C in the Organic Phase and in the Aqueous Phase after Nine Cycles	19
12.	Separate Distributions of Various Amounts of Uranium and Thorium between 2 <i>M</i> HNO ₃ and 0.73 <i>F</i> TCMA·NO ₃ -AR100 at 50°C	27
13.	The Effect of 2 <i>M</i> HNO ₃ and 6 <i>M</i> HNO ₃ upon K _d 's for 0.73 <i>F</i> TCMA·NO ₃ -AR100 at 50°C, and Various Aqueous Concentrations of Uranium and Thorium	28
14.	Relation between Thorium and Uranium Distribution Coefficients and Free TCMA, (TCMA) _f	29
15.	Scheme for Selective Reextraction of Uranium from a TCMA·NO ₃ -AR100 Solution of Uranium and Thorium	32

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Maximum Thorium Concentrations (50°C) in DA[AP] of Various Concentrations of <i>n</i> -Dodecane	3
2.	Distribution Coefficients for Small Amounts of Th, U, and Pu(IV) between 2 <i>M</i> HNO ₃ and 2 <i>F</i> DA[AP]-DD at 50°C	5
3.	Tracer-level Distribution Coefficients for Thorium and Uranium between the Listed Aqueous Phase and 2 <i>F</i> DA[AP]-DD at 50°C	8
4.	Distribution of Uranium and Thorium Tracers between 0.84 <i>F</i> DH[HP]-DD and 0.3 <i>M</i> HCOOH Containing Various Amounts of HNO ₃ at 50°C	8
5.	Effect of Various DA[AP] Concentrations upon Uranium and Thorium <i>K_d</i> 's in 0.3 <i>M</i> HNO ₃ and 2 <i>M</i> HCOOH	8
6.	Selective Scrubbing of Thorium and Uranium with a Solution of 4 <i>M</i> HCOOH and 0.3 <i>M</i> HNO ₃ at 50°C	10
7.	Selective Scrubbing of Thorium and Uranium with a Solution of 1.00 <i>M</i> HCOOH and 0.100 <i>M</i> HNO ₃ at 50°C	10
8.	Molar Extinction Coefficients for Pu(III), Pu(IV), and Pu(VI) in 3.90 <i>M</i> Formic Acid at 25°C	13
9.	Composition of the Organic and Aqueous Phases at 50°C after the Ninth Cycle	17
10.	Comparison between Observed and Computed Concentrations of Thorium after Nine Cycles, and Computed Concentrations after 30 Cycles	21
11.	The Equilibrium Distribution of Thorium between 2 <i>M</i> HNO ₃ and 0.56 <i>F</i> TCMA·NO ₃ in Diethylbenzene at 50 and 65°C	24
12.	The Equilibrium Distribution of Thorium between 2 <i>M</i> HNO ₃ and 0.4 <i>F</i> and 0.8 <i>F</i> TCMA·NO ₃ in Diethylbenzene at 65°C	25
13.	The Equilibrium Distribution of Thorium between 2 <i>M</i> HNO ₃ and 0.6 <i>F</i> and 0.73 <i>F</i> TCMA·NO ₃ -AR100 at 65°C	26
14.	The Separate Equilibrium Distributions of Thorium and Uranium between 2 <i>M</i> HNO ₃ and 0.73 <i>F</i> TCMA·NO ₃ -AR100 at 50°C	27
15.	Equilibrium Distribution of Uranium-Thorium Mixtures between 2 <i>M</i> HNO ₃ and 0.82 <i>F</i> TCMA·NO ₃ -AR100 at 50°C	30

16.	Equilibrium Concentrations of Uranium and Thorium after Each of Five Successive Aqueous Scrubs of a Uranium-Thorium Solution in 0.82 $\bar{F}$ TCMA·NO ₃ -AR100 at 50°C	31
17.	Composition of the Organic Phase and the Aqueous Phase (65°C) after the 11th Cycle of the TCMA·NO ₃ -AR100 Countercurrent Flow Test	34

DI-*n*-AMYL-*n*-AMYLPHOSPHONATE AND TRICAPRYLMETHYLAMMONIUM
NITRATE AS POTENTIAL EXTRACTANTS FOR
REPROCESSING Th-U FUELS

by

H. Diamond, C. S. Sabau, E. P. Horwitz,
G. F. Vandegrift, and G. W. Mason

ABSTRACT

Both 2*F* di-*n*-amyl-*n*-amylphosphonate in *n*-dodecane (DA[AP]-DD) and 0.77*F* tricaprylmethylammonium nitrate in "Aromatic 100" (TCMA·NO₃-AR100) extract uranium and thorium into relatively concentrated organic solutions. Countercurrent-flow tests with each extractant have demonstrated effective uranium-thorium separations by selective stripping from the organic phase. Both extractants offer advantageous alternatives to tributylphosphate (Thorex) in reprocessing irradiated mixed ThO₂-UO₂ fuels.

Formic acid is used for removing thorium from DA[AP]-DD; dilute HNO₃ removes uranium from TCMA·NO₃-AR100. Spectra of plutonium in formic acid are shown. The use of concentrated TCMA·NO₃-AR100 at 50-65°C avoids viscosity problems and suppresses third-phase formation. Thorium extracts into concentrated TCMA·NO₃-AR100 in greater amounts than would be predicted from stoichiometric assumptions.

I. INTRODUCTION

Mixed thorium and uranium oxides are envisioned as possible alternatives for breeder reactor fuels. They not only reduce the production of plutonium, but also substantially supplement the finite supply of economically obtainable uranium. The high-energy γ -rays associated with the ²³²U decay products, which have in the past been viewed as industrial nuisances because of the extensive shielding required for handling reprocessed thorium and uranium, may now be considered a valuable deterrent to illegal diversion.

Currently, irradiated Th-U fuels are reprocessed using variants of the Thorex process.¹ This process is based on the liquid-liquid extraction of Th(IV) and U(VI) from HNO₃ using tri-*n*-butylphosphate (TBP). The Thorex process suffers from several disadvantages: a low distribution coefficient (K_d)* for thorium, a small U(VI)/Th(IV) separation factor, and the formation of a second organic phase at low thorium concentration. Although the present work was terminated earlier than had been originally planned, two extractants, di-*n*-amyl-*n*-amylphosphonate, DA[AP], and tricaprylmethylammonium nitrate, TCMA·NO₃, are shown to be attractive alternatives to TBP. Both reagents in their respective diluents can be used as concentrated solutions; both have

* K_d is the ratio of the organic-phase concentration of a species to its aqueous-phase concentration when the two phases are in equilibrium.

high distribution coefficients, K_d 's, for thorium, uranium, and plutonium from nitric acid solutions. The separation factor $U(VI)/Th(IV)$ for DA[AP] in *n*-dodecane, although small when dilute HNO_3 is used, can be made large by using formic acid. The separation factor $Th(IV)/U(VI)$ for TCMA $\cdot$ NO₃ is sufficiently large using dilute HNO_3 . A study of plutonium in formic acid was initiated.

Current objectives in reprocessing irradiated Th-U oxide fuel are to separate thorium from uranium and possibly recover the plutonium with sufficient contamination to require heavy shielding for fabrication and transportation. Protactinium, which is also produced in the Th-U fuel cycle, would decay 1000-fold during cooling and thus would not be an important source of ^{233}U or γ -radiation. A prototype dissolver solution would contain 1.5M thorium, 0.5M uranium, a small amount of plutonium, 0.5M aluminum, 0.01M zirconium, 0.0005M mercury, 0.05M fluoride (complexed), and 2M HNO_3 .

II. DI-*n*-AMYL-*n*-AMYLPHOSPHONATE (DA[AP])

The phosphoryl oxygen in phosphonate esters, $R(RO)_2PO$, such as DA[AP] is more basic than in phosphate esters, $(RO)_3PO$, such as TBP. This leads to higher K_d 's for the extraction of uranium and thorium from nitric acid solutions into DA[AP] than into TBP.² The similarities between the two classes of neutral esters are strong enough²⁻⁴ to allow many of the lessons learned in the much-studied TBP systems to be applied to DA[AP]. The high uranium K_d in DA[AP] makes possible a good uranium-thorium separation based upon back-extraction of thorium into formic acid.

A. The DA[AP] Extractant

Initial investigations included both DA[AP] and di-*n*-hexyl-*n*-hexylphosphonate (DH[HP]), but only DA[AP] work was advanced. The extractant DA[AP] has a lower formula weight (292.24) than does DH[HP] and both extractants have a specific gravity of 0.93. Preliminary experimental work indicated that the maximum heavy-element concentration in the organic phase was favored by DA[AP]. Neither of the phosphonates is in current production, but Borg-Warner supplied a gallon of DA[AP] and Specialty Organics (Irwindale, CA) offered to produce small quantities of it.

1. Purification of DA[AP]

A small portion of DA[AP] was purified by vacuum distillation at 170°C and about 0.8 torr. Larger amounts were purified by the following procedure:

- (1) The DA[AP] was diluted to 30 vol % with *n*-heptane. This was scrubbed five times with one-half volume of 0.25M Na₂CO₃.
- (2) The organic phase was scrubbed five more times with one-half volume of water. As the Na₂CO₃ was removed, phase separation became difficult and overnight settling was required.
- (3) The *n*-heptane was largely evaporated at room temperature under a nitrogen stream. The evaporation was completed by pumping for 8 h at room temperature.

2. Selection of Concentration

The optimum concentration of DA[AP] in *n*-dodecane (DD) is dictated by the extraction properties and heavy-metal capacities of the organic phases and by the requirement for uranium-thorium separation. Table 1 shows the effect of DA[AP] concentration upon the maximum thorium concentration in the organic phase in extractions of thorium from aqueous HNO₃ solutions. No third-phase formation was observed in these measurements; but upon cooling to room temperature, some cloudiness in the organic phase, such as reported by Siddall,² was seen. The pure DA[AP] (Table 1) required centrifuging for good phase separation; the diluted organic phases readily separated from the aqueous phases upon standing.

Table 1. Maximum Thorium Concentrations (50°C)
in DA[AP] of Various Concentrations
in *n*-Dodecane

Concentration of DA[AP], formula weights/L	0.95	1.5	2.0	3.18 ^a
Maximum thorium concentration in organic phase, mol/L	0.25 ^b	0.41	0.47 ₅	0.70 ^c
DA[AP]/Th _{max}	3.8	3.7	4.2	4.5

^aUndiluted DA[AP].

^bTaken at 1.2*M* HNO₃; all other data were taken at 2*M* HNO₃.

^cSingle datum.

As seen in Section III.C.2, the separation of uranium and thorium in a DA[AP]-HCOOH-HNO₃ system becomes poorer as the concentration of DA[AP] increases. At 2*F* DA[AP]-DD, the capacity for heavy metals is high and the attainable uranium-thorium separation factors are good, so this near-optimum concentration was chosen for further study.

B. Extraction into 2*F* DA[AP]

1. K_d for Tracer ²³³U, ²³⁰Th, and ²³⁹Pu(IV) from 2*M* HNO₃

The measurements of tracer K_d's required avoidance of the potential errors caused by:

- (1) Disproportionation of Pu(IV).
- (2) The possible existence of Pu(IV) polymer.

- (3) The reduction of available organic DA[AP] concentration by significant amounts of heavy elements.
- (4) The formation of *n*-amyl-*n*-amylphosphonic acid by the acid-catalyzed hydrolysis of DA[AP].

Tracer solutions of ^{233}U , ^{230}Th , and ^{239}Pu were used to measure the K_d 's between $2M$ HNO_3 and $2F$ DA[AP]-DD at 50°C ; in the case of plutonium, $2M$ HNO_3 with $0.1M$ NaNO_2 was used to preserve the Pu(IV) state. Alpha-scintillation counting was used for the measurement of ^{233}U and ^{239}Pu , and γ -counting (67.8 keV) for the measurement of ^{230}Th . The aqueous phase formed after the first equilibration with ^{233}U was discarded to remove the small amount of ^{232}U progeny present in that tracer.

The presence of unsuspected plutonium polymer or the disproportionation of a small amount of Pu(IV) can lead to erroneous K_d values for Pu(IV). A criterion of three successive equilibrations of plutonium-spiked $2F$ DA[AP]-DD with $2M$ HNO_3 plus $0.1M$ NaNO_2 , with each equilibration yielding a similar K_d , allowed confidence that neither of these effects interfered with the measurement. Earlier work (not reported) failed to meet the criterion when $2M$ HNO_3 was used without the nitrite; disproportionation of Pu(IV) to Pu(III) and Pu(VI) is a reasonable explanation for the failure.

Neutral phosphonate esters such as DA[AP] are subject to acid-catalyzed hydrolysis; the phosphonic acid hydrolytic products can then distort K_d measurements, particularly at low concentrations. A measurement of the K_d for very low concentrations of Pu(IV) in $0.1M$ HCl can indicate the presence of the *n*-amyl-*n*-amylphosphonic acid hydrolytic product. Di-*n*-amyl-*n*-amylphosphonate (DA[AP]) would be expected to have a very low K_d for Pu(IV) from $0.1M$ HCl ; in sharp distinction, the hydrolytic product would have a very high K_d for Pu(IV) from $0.1M$ HCl . The plutonium remaining in the organic phase after extensive scrubbing with $0.1M$ HCl could then be reasonably ascribed to complexing by the hydrolytic product.

Portions of the final plutonium-rich organic phases from three separate extraction experiments (duration of each was about 4 h, with more than 1 h at 50°C) were each scrubbed three times with $0.098M$ HCl , $O/A = 0.1$. The remaining plutonium concentrations were $1.5 \times 10^{-3}M$, $3.9 \times 10^{-4}M$, and $1.8 \times 10^{-5}M$. Such determinations cannot quantify the *n*-amyl-*n*-amylphosphonic acid concentration, but they indicate its presence and the order-of-magnitude concentration of heavy elements necessary to overwhelm any effect of the presence of this hydrolytic product.

In other uranium and thorium K_d determinations, reported in Table 2, the concentrations used were sufficiently high (and the experiments completed so rapidly) that little error owing to the hydrolytic product would be expected. The plutonium result in Table 2 is subject to the ambiguity that 13% of the plutonium remained in the organic phase after the $0.098M$ - HCl scrubs. No correction is applied for this effect because the K_d for Pu(IV) between $2M$ HNO_3 and the expected *n*-amyl-*n*-amylphosphonic acid concentrations is not known and may well be trivially small. Even if this were not so, the error would not be greater than 13%. The last column in Table 2 presents evaluated K_d 's, corrected for the reduction of the concentration of available DA[AP] by

Table 2. Distribution Coefficients for Small Amounts of Th, U, and Pu(IV) between 2M HNO₃ and 2F DA[AP]-DD at 50°C

Isotope(s)	Concentration Organic Phase, mol/L	Forward (F) or Backward (B) Direction ^a	Counting Method	Measured K _d	Adopted K _d
²³⁰ Th, ²³² Th	0.099	F	γ	66 ± 7	72 ± 8
²³³ U, ²³⁸ U	0.018	F	γ	283 ± 7	285 ± 15
²³³ U, ²³⁸ U	0.126	F	γ	244 ± 11	
²³³ U	0.006	B	α	252 ± 26	
²³⁹ Pu ^b	0.0005	F	α	333	
²³⁹ Pu ^b	0.0005	B ₁	α	343	
²³⁹ Pu ^b	0.0005	B ₂	α	334	335 ^c
²³⁹ Pu ^b	0.0005	B ₃	α	333	

^aForward direction is defined as the tracer moving from the aqueous to the organic phase. The subscripts of B refer to successive strips of a single organic solution.

^bThe aqueous phase is 2M HNO₃ plus 0.1M NaNO₂.

^cNo allowance is made for the 13% of Pu activity remaining in the organic phase after scrubbing with HCl; see text.

the finite amounts of uranium and thorium; the data represented in Fig. 1 were used for this correction. The high K_d's reported here are an attractive feature of DA[AP] extraction.

2. Loading Curves for Uranium and Thorium in DA[AP]-DD

The distribution of uranium and (separately) thorium between 2M HNO₃ and 2F DA[AP]-DD at 50°C was measured for different heavy-metal-ion concentrations. These simple systems allow the estimation of the effect of heavy-metal concentration upon the distribution coefficients, and thus aid estimates of the extraction of uranium and thorium (and plutonium) from the more complex dissolver solutions. The results are shown in Fig. 1. Thorium values are higher than those attainable with TBP. There is no simple integral number of DA[AP] molecules tied up by each atom of extracted uranium or thorium.

Fig. 1. The Separate Distributions of Various Concentrations of Uranium and Thorium between 2M HNO₃ and 2F DA[AP]-DD at 50°C

C. Extraction from Formic Acid Solutions

The choice of formic acid for the selective back-extraction of thorium is attractive for the following reasons:

- (1) Formic acid complexes thorium much more strongly than it complexes uranium.
- (2) It is easily removed by heating with HNO₃ or by distillation.
- (3) It is compatible with commonly used stainless-steel equipment.
- (4) It prevents the formation of plutonium polymers.

The experimental work was first directed at evaluating the effect of formic-nitric acid mixtures on the distribution coefficient, and then scaling these results to practical concentrations.

There are order-of-magnitude differences in the complexing of UO₂²⁺, Th⁴⁺, and Pu⁴⁺ by formate ion. The stability constant is defined as

$$\beta_n = [ML_n^{v-n}] / ([M^{+v}][L^-]^n)$$

where M is the actinide ion whose valence is v, L⁻ is the formate ion ligand, and n is an integer. Magon *et al.*⁵ found the log₁₀ of β₁, β₂, and β₃ for uranium to be 1.83, 3.13, and 3.52. In similar measurements, Portanova *et al.*⁶ found log₁₀ of β₁, β₂, and β₃ to be 3.09, 5.15, and 6.73 for thorium.

The much stronger complexing of Pu(IV) is apparent in the work of Nebel and Schwabe,⁷ where the Pu(IV) acetate complexes are seen to be more stable than the acetate complexes of thorium as measured by Portanova *et al.*⁶ Bilal and Herrman⁸ measured $\log_{10} \beta_5$ for Pu(IV) and formate ion to be 15.9.

The dissociation constant for formic acid was studied by Harned and Embree.⁹ Their paper reviews prior work. At 50°C, $pK_a = 3.78$; the observed pK_a increases about 0.048 per unit of ionic strength. In this paper, a value of 3.8 will be used. Magon *et al.*⁵ found HCOOH to be a stronger acid ($pK_a = 3.56$, 1M NaClO₄, 20°C).

McKay *et al.*¹⁰ showed quite low K_d 's for Pu(IV) in TBP-HCOOH-HNO₃ systems. The low uranium distributions into 20% TBP-kerosene led to a negative recommendation for uranium-plutonium separation using formic acid. The high K_d (U) and high capacity of DA[AP]-DD can be addressed to the objections raised in their study.

Germain *et al.*¹¹ used formic acid and hydroxylamine to reduce and selectively strip plutonium from TBP and amine extractants, and a patent has been issued.¹² Arsene and Germain¹³ studied the separation of Pu(IV) from uranium in TBP-HNO₃-HCOOH systems.

1. Uranium and Thorium in 2F DA[AP]-DD-HCOOH-HNO₃

As the reaction

proceeds to the right, the resulting increase of H^+ and NO_3^- ions tends to increase the $K_d(\text{Th})$. This limits the stripping of large amounts of thorium from the organic phase; thus, studies of the extraction at practical concentrations are needed.

a. Tracer Concentration K_d 's

Some distribution-coefficient measurements for tracer-level uranium and thorium are given in Table 3. The very low $K_d(\text{Th})$ shown for a system containing no HNO₃ is not unexpected; the extracted species in all other cases is probably $\text{Th}(\text{NO}_3)_4$. The dependence of distribution coefficients upon formate-ion concentration is best shown by some preliminary measurements in which the extractant was 0.84F di-*n*-hexyl-*n*-hexylphosphonate in *n*-dodecane (DH[HP]-DD). The data are shown in Table 4 and Fig. 2.

b. The Variation of the Separation Factor with DA[AP] Concentration

The separation factor, $\alpha [= K_d(\text{U})/K_d(\text{Th})]$, does not vary much with HCOO^- concentration (Table 3), but it is highly dependent upon the organic DA[AP] concentration. This is seen in Table 5, where α declines from 85 in 0.95F DA[AP]-DD to a merely adequate 15 in 2.0F DA[AP]-DD. If greater separation factors are required, they can be obtained at a small cost to the capacity of the organic phase for heavy metals (*cf.* Table 1).

Table 3. Tracer-level Distribution Coefficients for Thorium and Uranium between the Listed Aqueous Phase and 2*F* DA[AP]-DD at 50°C

Aqueous Phase		$K_d(\text{Th})$	$K_d(\text{U})$	$\alpha = \frac{K_d(\text{U})}{K_d(\text{Th})}$
HNO_3 , mol/L	HCOOH , mol/L			
0.300	2.00	0.85	13	15
0.300	4.00	0.30	5.57	19
0.019	2.00		1.64	
0	3.92	0.037 ± 0.007	0.54	15
0.100	0.500		8.5	
0.100	2.00		4	
0	0.1	0.0045 ± 0.0010		

Table 4. Distribution of Uranium and Thorium Tracers between 0.84*F* DH[HP]-DD and 0.3*M* HCOOH Containing Various Amounts of HNO_3 at 50°C

HNO_3 , mol/L	Calculated ^a HCOO^- Conc., mol/L $\cdot 10^{-4}$	$K_d(\text{Th})$	$K_d(\text{U})$
0.100	4.73	0.025	0.98
0.200	2.37	0.106	3.12
0.300	1.58	0.247	6.3
0.5	0.95	1.36	14.9

^aBased on all activity coefficients being 1, and $\text{p}K_a = 3.8$.

Table 5. Effect of Various DA[AP] Concentrations upon Uranium and Thorium K_d 's in 0.3*M* HNO_3 and 2*M* HCOOH. (Tracer concentrations of uranium and thorium; equilibration temperature, 50°C)

DA[AP] Conc., formula wt/L	$K_d(\text{U})$	$K_d(\text{Th})$	$\alpha = \frac{K_d(\text{U})}{K_d(\text{Th})}$
0.95	9.9	0.116	85
1.5	9.2	0.42	22.1
2.0	13.0	0.85	15.2

Fig. 2. The Variation of Tracer-Level Uranium and Thorium K_d 's with Calculated Formate Ion Concentration. [The extractant was DH[HP]-DD. The aqueous phase was 0.3M HCOOH with various HNO_3 concentrations (Table 4)]

c. Stripping Experiments

The complex distribution of high concentrations of uranium and thorium were first addressed by measuring successive aqueous scrubs of 2F DA[AP]-DD containing HNO_3 , uranium, and thorium.

A 2F DA[AP]-DD solution was loaded with thorium, uranium, and HNO_3 from an aqueous solution having the heavy-metal concentration that might be expected in a dissolver solution (see Tables 6 and 7). This organic phase was then scrubbed with successive portions of fresh aqueous HNO_3 -HCOOH solution. The transfers of uranium and thorium were measured by γ -ray analysis, and the nitrogen content of the aqueous phase was measured by Kjeldahl analysis. No poor phase separations or phase inversions were observed.

Table 6. Selective Scrubbing of Thorium and Uranium with a Solution of 4M HCOOH and 0.3M HNO₃ at 50°C^a

After Scrub No.	Aqueous Phase, mol/L		Organic Phase, mol/L		K _d (U)	K _d (Th)	$\alpha = \frac{K_d(U)}{K_d(Th)}$
	[Th]	[U]	[Th]	[U]			
1	0.16	0.014	0.26	0.10	7.1	1.7	4
2	0.12	0.006	0.14	0.097	16	1.2	13
3	0.083	0.006	0.061	0.090	15	0.73	20
4	0.037	0.0084	0.024	0.082	9.7	0.64	15

^aThe initial organic phase is 2.0M DA[AP]-DD, 0.12M U, and 0.42M Th. Each scrub is a fresh equal-volume solution of 4M HCOOH, 0.3M HNO₃.

Table 7. Selective Scrubbing of Thorium and Uranium with a Solution of 1.00M HCOOH and 0.100M HNO₃ at 50°C^a

Scrub No. (n)	0	1	2	3	4	5
[U] _{org} , mol/L	0.148	0.1415	0.134	0.127	0.116	0.1019
[U] _{aq} , mol/L	0.0497	0.0065	0.0073	0.0073	0.0113	0.0137
K _d (U)	2.98	21.9	18.4	17.3	10.3	7.45
[Th] _{org} , mol/L	0.410	0.265	0.148	0.0646	0.0232	0.0052
[Th] _{aq} , mol/L	0.164	0.145	0.117	0.0839	0.0413	0.0180
K _d (Th)	2.51	1.83	1.27	0.769	0.563	0.2918
[NO ₃ ⁻] _{aq}	3.53	0.90	0.58	0.42	0.31	0.22
$\alpha = K_d(U)/K_d(Th)$	1.19	12.0	14.5	22.5	18.2	25.5

^aAn organic phase is formed (scrub 0) by extracting into 2.0M DA[AP]-DD from an aqueous phase containing titrated amounts of HNO₃, thorium, and uranium. Each n-numbered scrub comes from equilibrating the (n-1)th organic phase with an equal volume of fresh 1.00M HCOOH, 0.100M HNO₃ at 50°C.

Table 6 shows the results of successive scrubs with 4M HCOOH, 0.3M HNO₃. The uranium remained in the organic phase, but the K_d(Th) never became low enough to make a separation scheme easy. Both the total thorium content and the HNO₃ combined to keep the thorium K_d too high.

Table 7 contains the results of a scrubbing experiment in which the aqueous HCOOH and HNO₃ concentrations were reduced. Substantial amounts of HNO₃ were carried from the original aqueous solution in producing the organic phase. By the fifth aqueous scrub, only 10% of the HNO₃ could be

ascribed to transfer from the organic phase. Most of the measured nitrogen in the aqueous phase came from the original $0.1M$ HNO_3 , or from the nitrates $[Th(NO_3)_4, UO_2(NO_3)_2]$ removed from the organic phase.

The information in Tables 6 and 7 led to a choice of $3.90M$ $HCOOH$ containing no HNO_3 as the aqueous input in the countercurrent extraction test (see Section II.D).

2. Plutonium in Formic Acid

The spectra of $Pu(III)$ and $Pu(IV)$ in $3.90M$ $HCOOH$ are shown in Figs. 3 and 4. A Cary 14 spectrophotometer was used with a $3.90M$ formic acid reference cell. The peak heights, measured from background to maxima,

Fig. 3. Spectrum of $0.0088M$ $Pu(IV)$ in $3.9M$ $HCOOH$. (The baseline is $3.90M$ $HCOOH$.)

Fig. 4. Spectrum of Pu(III) in Formic Acid. (The total plutonium concentration is 0.0087M in 3.90M HCOOH; the baseline is an empty cell.)

provide the molar extinction coefficients reported in Table 8. Less complete spectra of Pu(IV) in formic acid can be found in Nebel and Schwabe,⁷ Bilal and Herrmann,⁸ Arsene and Germain,¹³ and Talbert and Costanze.¹⁴ No Pu(III) formic acid spectra are in the literature, but Crisler¹⁵ lists some infrared peaks.

No disproportionation of Pu(IV) in 3.9M HCOOH was observed in 18 days; none was expected. Pu(III) in formic acid is readily prepared by hydrogen reduction (in the presence of platinum black) for 2 h at room temperature. The color change (to purple) was observed in 10 min.

There is a precipitation of plutonium under some formic-nitric acid conditions. Bilal and Herrman⁸ observed that a precipitate formed and then dissolved during the denitration of a Pu(IV) solution with formic acid. In this laboratory, a solution of Pu(IV) in nitric acid was evaporated to

Table 8. Molar Extinction Coefficients^a for Pu(III), Pu(IV), and Pu(VI) in 3.90M Formic Acid at 25°C.

Wavelength, nm	ϵ Pu(III) mol ⁻¹ cm ⁻¹ L	ϵ Pu(IV), mol ⁻¹ cm ⁻¹ L	Pu(VI)
457	<0.06	46	
510		25	
554		15	
563	39	(b)	
602	39	3.4 ^b	
665		25	
686		29	
790	13	(b)	
837		18 ^b	strong, narrow
913		23	
1010		22	
1105	36	14 ^b	
1202	27	7.4 ^b	

^aThe error in the larger coefficients is estimated to be 10%.

^bInterferences with peaks from other spectra.

apparent dryness in a tube on a hot-plate that was set at 150°C. The tube was chilled with ice-water, and cold 3.90M HCOOH was added. The plutonium apparently dissolved, but a precipitate formed slowly. After three days at room temperature, the supernatant contained 0.01M Pu(IV) by spectrophotometric analysis. A small amount of Pu(VI) was present. McKay *et al.*¹⁰ used solutions that were 28 g/L (0.117M) in plutonium, 1M HCOOH, and 0.6M HNO₃; they did not report the formation of any precipitate.

The Pu(VI) mentioned in the preceding paragraph exhibited only a small decline in the height of the 837-nm peak in the 18 days (mostly in the dark). Pu(VI) is not readily reduced by 3.90M HCOOH at room temperature.

There is apparently no danger of plutonium polymer formation in the presence of formic acid or formates. Tallent *et al.*¹⁴ have found that small amounts of formic acid redissolve plutonium gel phases.

The behavior of plutonium in DA[AP]-HCOOH-HNO₃ systems has not yet been studied. In some TBP-HCOOH-HNO₃ systems, Pu(IV) was found in the aqueous phase (McKay *et al.*,¹⁰ Bathellier *et al.*,¹² and Arsene and Germain¹³).

3. Extraction of HNO_3 and HCOOH into 2*F* DA[AP]-DD

The two acids, HNO_3 and HCOOH , were separately equilibrated with 2*F* DA[AP]-DD at room temperature; the acid concentration of each phase was determined by titration to a phenolphthalein end point. The results are shown in Fig. 5; HCOOH extracts more readily than HNO_3 . The free DA[AP], DA[AP]_f , is defined as the original concentration of DA[AP], (2*F*), minus the concentration of extracted acid. A plot of K_d (HCOOH) vs. DA[AP]_f (Fig. 6) shows a linear relationship: the K_d varies as 0.9 times the DA[AP]_f concentration. Arsene and Germain¹³ found a slope of only 0.63 for the extraction of formic acid by free TBP (as one might expect from the lower basicity of its phosphoryl group). There is no comparable simple relationship for free DA[AP] and HNO_3 extraction.

Fig. 5. Separate Distributions of HNO_3 and HCOOH between Water and 2.0*F* DA[AP]-DD at 23°C

Fig. 6. Effect of Free DA[AP] Concentration upon the Distribution Coefficient of Formic Acid. (The same data as those shown in Fig. 5 are used.)

D. A Countercurrent Separation of Thorium from DA[AP]-DD

A countercurrent test was devised to selectively remove thorium from a DA[AP]-DD organic phase. At the end of the separation, the thorium would be found in the aqueous phase; the uranium would remain in the organic phase. The scheme is represented in Fig. 7. An organic feed was prepared by equilibrating 150 mL of 2F DA[AP]-DD with 64 mL of 1.5M HNO_3 , 1M Th, 0.32M U. The results (Fig. 7) approximate the uranium, thorium, and HNO_3 concentrations that might be expected from contacting a dissolver solution. Seven jacketed glass separatory vessels (I-VII) with stainless-steel centrifugal stirrers were kept at 49 to 51°C.

At the beginning of the test, each vessel contained 20 mL of 3.90M HCOOH ; vessels I, II, and III contained 10 mL of 2F DA[AP]-DD organic scrub; vessel IV contained 10 mL of the organic feed solution and 10 mL of the organic scrub; vessels V, VI, and VII contained 20 mL of the organic scrub solution. These were stirred 3 to 5 minutes and allowed to settle so that the phases might separate. This was the end of the first cycle.

After each cycle (except the last), the contents of each separatory vessel was drained into a centrifuge cone (centrifuging was not needed, but was employed to speed separation in some cases). The organic phase was transferred to the next higher numbered vessel; the aqueous phase was transferred

Fig. 7. Scheme for Selective Reextraction of Thorium from a DA[AP]-DD Feed Containing Both Uranium and Thorium

to the next lower numbered vessel. This is called the double-diamond pattern;¹⁶ it comprises a coarser correspondence to true countercurrent flow than would be obtained by transferring only one phase per cycle, but the uranium and thorium are separated in fewer cycles. The organic effluent from each cycle was removed from vessel VII; the aqueous effluent from each cycle was removed from vessel I. Additional organic scrub was added to vessel I, and aqueous solution was added to vessel VII after each cycle.

After the ninth cycle, each phase in each vessel was analyzed for uranium,¹⁷ thorium,¹⁸ and nitrogen. Volumetric flasks were filled with each solution at 50°C and the densities were determined. Each analysis was related to sample weight, and from this, the molarities at 50°C were calculated. The results are given in Table 9, and are graphically presented in Figs. 8-11.

The uranium results exhibit the attainment of a steady state, since there is a material balance between the uranium input and effluent. The uranium is obtained with the thorium content depleted by a factor of 38. This decontamination factor would be reduced as the thorium approaches steady state, as discussed below. The thorium results show that a steady state has not been reached by the ninth cycle. However, the recovery of the thorium is good, and the decontamination from uranium is better than a factor of 800.

Table 9. Composition of the Organic and Aqueous Phases (mol/L) at 50°C after the Ninth Cycle

Vessel Number	Phase	Th, mol/L	$K_d(\text{Th})$	U, mol/L	$K_d(\text{U})$	Free ^a HNO ₃ , mol/L	$K_d(\text{HNO}_3)$	$\alpha = \frac{K_d(\text{U})}{K_d(\text{Th})}$	Density at 50°C, g/mL
I	ORG	0.00245	0.035	0.000126	—	0.203	0.51	—	0.888
	AQU	0.0697		$<4 \times 10^{-5}$		0.396			1.030
II	ORG	0.0434	0.44	0.000939	10.8	0.206	0.66	25	0.923
	AQU	0.0987		8.68×10^{-5}		0.313			1.060
III	ORG	0.0518	0.37	0.00611	12.5	0.412	0.62	34	0.933
	AQU	0.140		0.000487		0.667			1.074
IV	ORG	0.184	0.98	0.0641	15.2	0.377	0.43	16	0.972
	AQU	0.187		0.00421		0.869			1.096
V	ORG	0.0703	0.39	0.0653	12.5	0.542	0.73	32	0.953
	AQU	0.180		0.00521		0.743			1.097
VI	ORG	0.00174	0.016	0.0959	8.1	0.033	0.07		0.920
	AQU	0.103		0.0118		0.454			1.068
VII	ORG	0.00455	0.142	0.0653	26	-0.039 ^a	—	180	0.893
	AQU	0.032		0.00251		0.194			1.047

^aAll measured nitrogen is taken to be NO₃⁻. In the organic phase, "free HNO₃" is defined as: measured nitrogen assumed to be NO₃⁻ less 4 × Th concentration and 2 × U concentration. A negative number reflects upon the adequacy of this definition.

Fig. 8. Densities at 50°C after Nine Cycles

Fig. 9. Concentration of Thorium (mol/L) at 50°C in the Organic Phase and in the Aqueous Phase after Nine Cycles

Fig. 10. Concentration of Uranium (mol/L) at 50°C in the Organic Phase and in the Aqueous Phase after Nine Cycles

Fig. 11. Concentration of HNO₃ (mol/L) at 50°C in the Organic Phase and in the Aqueous Phase after Nine Cycles

In order to project the effect of more cycles, and to understand the results, a series of computer-based models were examined. Inspection of Fig. 9 shows that the aqueous thorium concentration pattern is surprisingly high on the higher numbered side (vessel V) of the input, even though the net motion of the thorium is toward vessel number I. Such a pattern could only occur if the $K_d(\text{Th})$ in vessel IV exceeded 1 during the early cycles and fell to the observed 0.93 by the ninth cycle. Trial and error produced a model in which this $K_d(\text{Th})$ for vessel IV declined regularly from 2.32 to 0.93 in nine even decrements and remained at 0.93 thereafter. This is chemically reasonable: as the thorium concentration built up in vessel IV, the $K_d(\text{Th})$ could be expected to decline. (A more sophisticated approach would show a sharp rise and then a slow decline in $K_d(\text{Th})$ for vessel IV, but this would lie well beyond the quality of the data.) The $K_d(\text{Th})$ for vessels III and V were assumed to be 0.4 of the $K_d(\text{Th})$ of vessel IV, and those for the other vessels were set at 0.1 when there was little thorium in the vessel (less than 2.2×10^{-3} mol) and at 0.4 when there was more. The K_d assignments can be supported by the measured $K_d(\text{Th})$ values in Table 9. Table 10 compares the experimental thorium results with the computer calculation after 9 and 30 cycles. The uranium modeling results were in good agreement with the experiment, except for surprisingly high uranium concentrations in both the organic and aqueous portions of vessel VI. The uranium calculations are not shown because neither the experimental nor modeling results are sensitive to K_d , when the K_d 's are either very high or very low.

The separation was successful, but it would have been greatly improved if the aqueous volume had been increased.

E. Conclusions

A system that extracts uranium, thorium, and plutonium from a nitric acid dissolver solution and then selectively removes the thorium has been defined. The system comprises (1) 2*F* di-*n*-amyl-*n*-amylphosphonate in *n*-dodecane and (2) aqueous formic acid solution. The former is used for the extraction of the three heavy elements from the dissolver solution and the latter for the separation of thorium. Very high concentrations of heavy elements (and hence a low inventory of solvents) were employed. The presence of HNO_3 [from the dissolver solution and from the stripping of $\text{Th}(\text{NO}_3)_4$] did not inhibit the uranium-thorium separation, even when concentrations were increased to practical levels. The 2*F* DA[AP]-DD-formic acid system is worthy of further study, if aqueous reprocessing of irradiated ThO_2 - UO_2 fuels is contemplated.

Spectra of plutonium in 3.9*M* formic acid have been presented.

Table 10. Comparison between Observed and Computed Concentrations of Thorium after Nine Cycles, and Computed Concentrations after 30 Cycles

Stage Number	Thorium in Aqueous Phase, mol/L			Thorium in Organic Phase, mol/L		
	Measured 9 cycles	Calculated 9 cycles	Calculated 30 cycles	Measured 9 cycles	Calculated 9 cycles	Calculated 30 cycles
I	0.070	0.09	0.17	0.0025	0.0090	0.069
II	0.099	0.12	0.21	0.043	0.049	0.083
III	0.14	0.16	0.22	0.051	0.065	0.085
IV	0.19	0.21	0.22	0.18	0.21	0.21
V	0.18	0.21	0.21	0.070	0.081	0.083
VI	0.10	0.096	0.082	0.0017	0.0097	0.008
VII	0.032	0.008	0.007	0.0046	0.0008	0.0007

III. TRICAPRYLMETHYLAMMONIUM NITRATE (TCMA·NO₃)

Another alternative to the Thorex (TBP) process is based upon the quaternary ammonium species, TCMA, derived from the readily available commercial product "Aliquat-336".* There is extensive literature, principally by Koch,¹⁹⁻²¹ showing high distribution coefficients for uranium, thorium, and Pu(IV) from HNO₃ into organic solutions of TCMA·NO₃, whereas important fission products have low distribution coefficients.¹⁹ In this report, conditions have been established for the extraction of large amounts of uranium and thorium into a concentrated TCMA solution without the usual problems of third-phase formation or high viscosity. The uranium can be selectively stripped from the organic phase into dilute HNO₃, leaving thorium in the organic phase. A successful countercurrent demonstration of a uranium-thorium separation at practical concentrations is reported.

A. Purification of TCMA·NO₃²²

The steps taken in the purification procedure were as follows:

- (1) "Aliquat-336," which comes as a viscous mixture of, principally, quaternary amines in the chloride form, was heated to about 80°C at reduced pressure to remove any isopropyl alcohol that might remain from the manufacturing process.
- (2) A 30 vol % solution of Aliquat-336 in cyclohexane was scrubbed twice with equal volumes of 5% NaHCO₃ solution, then twice more with a very dilute NaCl solution. (The small amount of NaCl inhibits emulsion formation.)
- (3) The organic layer was then extracted three times with threefold greater volumes of 1:1 acetonitrile:water. The quaternary amines extract into the acetonitrile-H₂O phase; the primary, secondary, and tertiary amines remain in the cyclohexane.
- (4) The water and acetonitrile were distilled away at 80°C, using reduced pressure.
- (5) A small weighed portion of the remaining quaternary ammonium chloride was dissolved in a solvent and scrubbed three times with twice the volume of 2M HNO₃. The chloride in the aqueous phase was then titrated with AgNO₃ to a potentiometric end point with an ion-specific silver/silver chloride electrode and a calomel reference electrode.²³
- (6) The purified TCMA·Cl was dissolved in the solvent of choice and converted to the nitrate form by three equilibrations with twice the volume of 2M HNO₃. The nitrate form of TCMA turns brown in a few days, but its extraction properties were not noticeably changed (none of the experiments reported here involved TCMA that had been in the nitrate form longer than four weeks).

There was only one effect observed that implied the presence of an impurity in TCMA cleaned as described above. Tracer-level uranium K_d's at low HNO₃ concentrations were higher than similar K_d's measured with ~0.015M uranium.

* Supplied by General Mills Chemicals, Inc., Kankakee IL.

B. Third Phase Formation - TCMA·NO₃

Two difficulties in the exploitation of TCMA·NO₃ are (1) the higher viscosity of its organic solutions, and (2) the tendency for thorium-loaded TCMA·NO₃ solutions to form heavy and light organic phases. These difficulties are avoided by working at higher than room temperatures, using high TCMA·NO₃ concentrations, and by choosing a solvent that suppresses third-phase formation.

In Table 11, changing the temperature from 50 to 65°C is shown to have no apparent effect upon the minimum concentration of thorium in the organic layer needed for the formation of a third phase in 0.56*F* TCMA·NO₃ in diethylbenzene (DEB). The $K_d(\text{Th})$ from 2*M* HNO₃ is reduced at the higher temperature, but is very large in both cases. Gerontopulos and Rigali²⁴ have also reported a small negative temperature coefficient for thorium extraction into TCMA.

The phase disengagement time, defined as the time interval between cessation of stirring and the disappearance of bubbles from the interface, is reduced at the higher temperature.

The effect of increasing the TCMA·NO₃ concentration on third-phase formation is shown in Table 12. Doubling the TCMA·NO₃ concentration in diethylbenzene increases more than fivefold the concentration of Th_{org} at which a third phase is formed. A large effect is also seen in Table 13.

Koch¹⁹ noticed an inhibition of third-phase formation when "Aromatic 100" (AR100, formerly "Solvesso 100") was used as the diluent. In comparing the onset of third-phase formation in Table 13 to that in Table 12, AR100 is shown to be a better solvent than diethylbenzene, even at a lower TCMA·NO₃ concentration. The effect is not readily predictable; AR100 is a mixture of C₈, C₉, and C₁₀ aromatics (most trimethylbenzene isomers²⁷) whose boiling point is 156-168°C. This is not greatly dissimilar to diethylbenzene (bp = 181°C).

C. Extraction of Macro-Concentrations of Thorium and Uranium into TCMA·NO₃-AR100

Unusually high concentrations of uranium and thorium can be extracted from 2*M* HNO₃ solutions into 0.7 to 0.8*F* TCMA·NO₃-AR100 at 50-65°C. This may allow savings in organic inventory and equipment capacity. Equilibrium concentration curves for thorium and uranium are given in Tables 13 and 14 and in Fig. 12. The thorium, uranium, and plutonium in a dissolver solution such as the one described in Section I.A. would be extracted into a fivefold greater volume of 0.73*F* TCMA·NO₃-AR100 without third-phase formation.

There is little advantage in increasing the HNO₃ concentration of a dissolver solution. In Fig. 13, the extractions of uranium and thorium from 6*M* and 2*M* HNO₃ into 0.73*F* TCMA·NO₃-AR100 are compared. The $K_d(\text{U})$ is increased more than the $K_d(\text{Th})$ by the increased HNO₃ concentration.

Table 11. The Equilibrium Distribution of Thorium
between 2*M* HNO₃ and 0.56*F* TCMA·NO₃ in
Diethylbenzene at 50 and 65°C

K_d	Th_{org}^a , mol/L	Th_{aq} , mol/L	Disengage- ment Time, s	Volumes of Two Organic Phases, mL Heavy-Light
50°C				
	4.64×10^{-1}	1.17×10^{-2}	114	1.30 - 0.70
	3.7×10^{-1}	1.52×10^{-2}	99	1.31 - 0.69
	2.79×10^{-1}	6.6×10^{-3}	57	1.27 - 0.65
	1.89×10^{-1}	1.49×10^{-3}	42	1.76 - 0.37
	1.42×10^{-1}	9.5×10^{-4}	34	1.87 - 0.11
169	1.13×10^{-1}	6.7×10^{-4}	54	one phase ↓
206	9.5×10^{-2}	4.60×10^{-4}	71	
245	7.6×10^{-2}	3.09×10^{-4}	67	
238	4.73×10^{-2}	1.99×10^{-4}	59	
381	7.6×10^{-3}	1.98×10^{-5}	76	
420	4.74×10^{-3}	1.18×10^{-5}	70	
376	1.90×10^{-3}	5.03×10^{-6}	67	
391	7.6×10^{-4}	1.93×10^{-6}	69	
368	4.74×10^{-4}	1.26×10^{-6}	66	
65°C				
	4.57×10^{-1}	1.86×10^{-2}	58	1.3 - 0.7
	3.68×10^{-1}	1.18×10^{-2}	94	1.3 - 0.7
	2.78×10^{-1}	7.31×10^{-3}	48	1.3 - 0.6
	1.88×10^{-1}	2.13×10^{-3}	37	1.7 - 0.25
	1.41×10^{-1}	1.18×10^{-3}	54	2.0 - 0.1
154	1.13×10^{-1}	7.4×10^{-4}	53	one phase ↓
156	9.44×10^{-2}	6.05×10^{-4}	52	
223	7.6×10^{-2}	3.40×10^{-4}	54	
259	4.73×10^{-2}	1.83×10^{-4}	51	
288	1.89×10^{-2}	6.6×10^{-5}	48	
396	4.74×10^{-3}	1.19×10^{-5}	50	
309	1.89×10^{-3}	6.1×10^{-6}	52	
383	7.6×10^{-4}	1.9×10^{-6}		
384	1.90×10^{-4}	4.93×10^{-7}		

^a Where two organic phases occur, the concentration represents the total amount (moles) of thorium in the two organic phases divided by the total volume.

Table 12. The Equilibrium Distribution of Thorium between
2M HNO₃ and 0.4*F* and 0.8*F* TCMA·NO₃ in Diethyl-
Benzene at 65°C

K_d	Th_{org}^a , mol/L	Th_{aq} , mol/L	Disengage- ment Time, s	Volumes of Two Organic Phases, mL Heavy-Light
0.4 <i>F</i> TCMA·NO ₃				
	4.6×10^{-1}	1.73×10^{-2}	47	0.90 - 1.10
	3.68×10^{-1}	1.22×10^{-2}	95	0.92 - 1.18
	2.78×10^{-1}	7.33×10^{-3}	139	0.88 - 1.10
	1.87×10^{-1}	3.55×10^{-3}	126	1.00 - 1.05
	1.41×10^{-1}	1.58×10^{-3}	72	1.10 - 0.80
	1.13×10^{-1}	8.44×10^{-4}	36	1.40 - 0.70
	9.4×10^{-2}	6.44×10^{-4}	30	1.40 - 0.58
	7.6×10^{-2}	4.34×10^{-4}	29	1.54 - 0.48
137	4.72×10^{-2}	3.43×10^{-4}	41	one phase
172	7.56×10^{-2}	4.34×10^{-4}	43	↓
194	7.56×10^{-3}	3.89×10^{-5}	41	
0.8 <i>F</i> TCMA·NO ₃				
	4.8×10^{-1}	1.94×10^{-2}	157	1.80 - 0.20
	3.67×10^{-1}	1.92×10^{-2}	167	1.88 - 0.12
90	2.82×10^{-1}	3.14×10^{-3}	123	one phase
175	1.89×10^{-1}	1.08×10^{-3}	180	↓
226	1.14×10^{-1}	5.03×10^{-4}	140	
380	4.74×10^{-2}	1.25×10^{-4}	111	
424	4.74×10^{-3}	1.11×10^{-5}	48	
477	1.90×10^{-3}	3.9×10^{-6}	83	
539	7.6×10^{-4}	1.4×10^{-6}	85	
482	1.90×10^{-4}	3.93×10^{-7}	80	

^aWhere two organic phases occur, the concentration represents the total amount (moles) of thorium in the two organic phases divided by the total volume.

Table 13. The Equilibrium Distribution of Thorium
between 2M HNO₃ and 0.6F and 0.73F
TCMA·NO₃-AR100 at 65°C

K_d	Th_{org}^a , mol/L	Th_{aq} , mol/L	Disengage- ment Time, s	Volumes of Two Organic Phases, mL Heavy-Light
0.6 <i>F</i> TCMA·NO ₃				
	7.09×10^{-1}	5.33×10^{-2}	18	1.60 - 0.40
	6.13×10^{-1}	5.49×10^{-2}	39	1.58 - 0.42
	4.44×10^{-1}	3.30×10^{-2}	29	1.65 - 0.35
	4.66×10^{-1}	3.01×10^{-2}	25	1.65 - 0.35
	3.61×10^{-1}	1.99×10^{-2}	60	1.65 - 0.30
35	2.78×10^{-1}	7.88×10^{-3}	163	one phase
276	4.7×10^{-2}	1.71×10^{-4}	84	↓
402	7.59×10^{-4}	1.80×10^{-6}	69	
0.73 <i>F</i> TCMA·NO ₃				
	7.36×10^{-1}	4.09×10^{-2}	78	1.80 - 0.20
	6.45×10^{-1}	3.54×10^{-2}	127	1.90 - 0.10
18.6	5.5×10^{-1}	2.97×10^{-2}	183	one phase
22	4.67×10^{-1}	2.12×10^{-2}	198	↓
22	3.73×10^{-1}	1.69×10^{-2}	186	
85	2.94×10^{-1}	3.4×10^{-2}	186	
172	1.98×10^{-1}	1.15×10^{-3}	193	
344	7.96×10^{-2}	2.31×10^{-4}	108	
480	1.99×10^{-2}	4.15×10^{-5}	99	
474	4.72×10^{-3}	9.95×10^{-6}	84	

^aWhere two organic phases occur, the concentration represents the total amount (moles) of thorium in the two organic phases divided by the total volume.

Table 14. The Separate Equilibrium Distributions of Thorium and Uranium between 2M HNO₃ and 0.73F TCMA·NO₃-AR100 at 50°C

Thorium			Uranium		
K _d (Th)	Th _{org} , mol/L	Th _{aq} , mol/L	K _d (U)	U _{org} , mol/L	U _{aq} , mol/L
16.6	0.62 ^a	0.038	2.12	0.76	0.357
18.3	0.54	0.030	2.90	0.65	0.225
73	0.28	0.039	3.67	0.55	0.151
245	0.095	0.00039	4.84	0.306	0.063
490	0.0190	0.000039	4.97	0.080	0.0160
508	0.00075	1.5 × 10 ⁻⁶	6.17	0.0207	0.00336
			6.2	0.0066	0.00106

^aTwo organic phases occurred: the volume of the heavier phase was ~1.9 mL, and that of the lighter phase, ~0.1 mL.

Fig. 12. Separate Distributions of Various Amounts of Uranium and Thorium between 2M HNO₃ and 0.73F TCMA·NO₃-AR100 at 50°C

Fig. 13. The Effect of 2M HNO₃ and 6M HNO₃ upon K_d 's for 0.73F TCMA·NO₃-AR100 at 50°C, and Various Aqueous Concentrations of Uranium and Thorium

The extracted species have been established as $Q_2Th(NO_3)_6$ ²⁴⁻²⁶ and $QUO_2(NO_3)_3$,^{21,26} where $Q = TCMA^+$, by spectroscopic and conductivity methods, and by the variation of K_d with TCMA concentration. We have seen no report of organic concentrations of uranium or thorium in excess of these stoichiometric limits. In this laboratory, Th:TCMA ratios of 1.2:2 (instead of 1:2) have been observed in extractions entailing only one organic phase. (We define a phase as something that separates with a perceptible meniscus; this is a more operational definition than the "appearance of cloudiness" test used elsewhere.²)

The preparation of an extra-stoichiometric organic-thorium concentration was repeated with careful attention to analytical details because its existence was unexpected. A 2M HNO₃, 0.54M thorium solution containing ²³⁰Th tracer was prepared from a stock solution that had been subjected to two independent analyses of thorium content. Equal volumes of 2M HNO₃-scrubbed 0.77F TCMA·NO₃-AR100, and the above aqueous solution were equilibrated at 65°C. The 67.8-keV ²³⁰Th peak in each phase was observed with a Ge(Li) detector. No allowance was made for any change in the volumes of the organic or aqueous phases during equilibration. The resultant thorium concentration in the 0.77F TCMA·NO₃-AR100 is 0.47M, 23% in excess of stoichiometric expectation. The standard error is estimated to be less than 5%.

A regularity in K_d 's can be observed when the $\log_{10} K_d$ for uranium or thorium is compared to the $\log_{10}$ of the free TCMA, $(TCMA)_f$, defined as the original TCMA concentration less twice the organic thorium concentration and/or less the organic uranium concentration. These are shown in Fig. 14. The variation of $K_d(Th)$ with the 1.1 power of $(TCMA)_f$ resembles the 1.3 power dependency of Np(IV)²⁸ and Pu(IV)²⁹ upon TCMA concentrations in AR100 solvent.

Fig. 14. Relation between Thorium and Uranium Distribution Coefficients and Free TCMA, $(TCMA)_f$. (The thorium data are from Table 13 (65°C) and Table 14 (50°C). The uranium data are from Table 14. The K_d 's were measured with 0.73F $TCMA \cdot NO_3$ -AR100 and 2M HNO_3 . $(TCMA)_f = 0.73 - 2 \cdot [Th]_{org} - [U]_{org}$.)

At tracer levels, the $K_d(Th)$ is two orders of magnitude greater than the $K_d(U)$. The ratio between the two K_d 's declines as the aqueous concentrations increase (Figs. 13 and 14), but even at high concentrations, the thorium extracts better than the uranium. Some measurements were made in which uranium and thorium were present in approximately the same ratio as expected in a dissolver solution. The results in Table 15 show that an excess of $TCMA \cdot NO_3$ is required to extract uranium from the dissolver solution. Since some scrubbing is required to rid the organic phase of fission products, such an excess of $TCMA \cdot NO_3$ would in fact be present, and the $K_d(U)$ is high enough to ensure uranium extraction. Information on some additional mixtures extracted with $TCMA \cdot NO_3$ solutions that have been scrubbed with dilute nitric acid is reported below.

Table 15. Equilibrium Distribution of Uranium-Thorium Mixtures between 2M HNO₃ and 0.82F TCMA·NO₃-AR100 at 50°C

Aqueous Phase		Organic Phase		K _d (U)	K _d (Th)
U, mol/L	Th, mol/L	U, mol/L	Th, mol/L		
0.100	0.099	0.029	0.342	0.29	3.45
0.108	0.060	0.032	0.42	0.30	6.94
0.128	0.037	0.042	0.325	0.33	8.78
0.071	0.060	0.049	0.264	0.69	4.38

D. Thorium-Uranium Separations

After a TCMA·NO₃-AR100 solution has extracted the uranium and thorium (and plutonium) from a dissolver solution, and after the organic phase has undergone scrubbing to remove unwanted fission products, the uranium may be selectively back-extracted into dilute HNO₃. At the very high TCMA·NO₃ concentrations chosen, the acid must be dilute to retrieve the uranium. The HNO₃ that is carried into the organic phase along with the heavy elements may be an important component of the total acid in the uranium-thorium separation run. Koch²⁰ has studied the K_d(HNO₃) as a function of TCMA·NO₃ concentration in AR100. Some higher K_d(HNO₃) values than those predicted from an extrapolation of Koch's curves were found in this work: in equilibrium with 2M HNO₃, 0.82F TCMA·NO₃-AR100 was 1.0M in HNO₃; 0.75F TCMA·NO₃-AR100 in equilibrium with 2M HNO₃ was 0.813M in HNO₃; and 0.77F TCMA·NO₃-AR100, after many equilibrations with 0.1M HNO₃, was 0.095M in HNO₃. The large HNO₃ extraction may be analogous to the extensive extraction of heavy metals by concentrated TCMA solutions (Section III.C.).

Table 16 summarizes scrubbing experiments that demonstrate selective uranium back-extraction from TCMA mixtures of uranium and thorium. A 0.82F TCMA·NO₃-AR100 solution was scrubbed with 0.0113M or 0.215M HNO₃ and then equilibrated with a 2M HNO₃ solution of uranium and thorium. The organic phase was then scrubbed five successive times with the specified dilute HNO₃. The uranium K_d's are a little higher than desired using 0.215M HNO₃; the separation factors are too low for effective uranium-thorium separation when 0.0113M HNO₃ is the scrubbing solution. The K_d(U) increases slightly as the competing thorium and acid are removed from the organic phase by successive scrubs.

In separate measurements using 0.015M uranium solutions and 0.82F TCMA·NO₃-AR100 equilibrated with the same acid as the aqueous solutions, the following uranium K_d's at 50°C were obtained: for 0.469M HNO₃, K_d(U) = 3.08; for 0.204M HNO₃, K_d(U) = 1.04; and for 0.101M HNO₃, K_d(U) = 0.51. These results, together with the results in Table 16 and the curves of Koch,¹⁹ were used to select the conditions for the countercurrent flow test (below).

Table 16. Equilibrium Concentrations of Uranium and Thorium after Each of Five Successive Aqueous Scrubs of a Uranium-Thorium Solution in 0.82*F* TCMA·NO₃-AR100 at 50°C

Scrub Number	O/A ^a	K _d (Th)	[Th] _{org} , mol/L	[Th] _{aq} , mol/L	K _d (U)	[U] _{org} , mol/L	[U] _{aq} , mol/L
I. organic phase: 0.284 <i>M</i> thorium and 0.047 <i>M</i> uranium; acid, 0.215 <i>M</i> HNO ₃ .							
1	1.08	11.3	0.267	0.0237	0.56	0.0160	0.0284
2	0.92	11.8	0.247	0.0209	1.29	0.0091	0.0074
3	0.77	12.2	0.218	0.0179	1.56	0.0058	0.0037
4	0.46	16.5	0.188	0.0114	2.29	0.0044	0.00193
5	0.31	13.6	0.121	0.0089	2.18	0.0030	0.0014
II. organic phase 0.347 <i>M</i> thorium and 0.0542 <i>M</i> uranium; acid, 0.0113 <i>M</i> HNO ₃ .							
1	1.08	10.9	0.296	0.0273	0.68	0.0214	0.0313
2	0.92	7.7	0.275	0.036	0.87	0.0093	0.0108
3	0.77	6.3	0.215	0.034	1.30	0.0055	0.0042
4	0.46	5.0	0.147	0.029	1.72	0.0036	0.00211
5	0.31	3.1	0.063	0.0205	1.42	0.0022	0.00154
III. organic phase: 0.242 <i>M</i> thorium and 0.0611 <i>M</i> uranium; acid, 0.0113 <i>M</i> HNO ₃ .							
1	1.08	19.1	0.220	0.0115	0.86	0.0254	0.0297
2	0.92	8.	0.184	0.0223	0.98	0.0108	0.0110
3	0.77	5.4	0.130	0.0242	1.23	0.0053	0.0043
4	0.46	4.5	0.0806	0.0180	1.25	0.0025	0.00198
5	0.31	1.32	0.0112	0.0085	1.35	0.00196	0.00145
IV. organic phase: tracer levels of uranium (~0.015 <i>M</i>) and thorium; acid, 0.215 <i>M</i> HNO ₃ .							
1	1.08	54.8			1.52		
2	0.92	21			1.07		
3	0.77	17			1.29		
4	0.46	16			2.47		
5	0.31	12			2.58		

^aVolumetric ratio of the organic phase to the aqueous phase.

E. Countercurrent Separation TCMA·NO₃-AR100

Seven jacketed separatory funnels were operated at 65°C as depicted in Fig. 15. After each cycle, the organic phase moved to the next higher numbered vessel, and the aqueous phase was transferred to the next lower

Fig. 15. Scheme for Selective Reextraction of Uranium from a TCMA·NO₃-AR100 Solution of Uranium and Thorium. (The organic feed was injected at vessel IV, the organic scrub at vessel I, and the aqueous phase at vessel VII. The organic phase was transferred to the right after each cycle, and the aqueous phase went to the left.)

numbered vessel (double-diamond pattern). The feed solution, 0.77F TCMA·NO₃-AR100, 0.287M thorium, and 0.0897M uranium, was introduced at the central vessel number IV. The organic scrub solution was 0.77F TCMA·NO₃-AR100 that had been scrubbed extensively with 0.1M HNO₃; it was added at the lowest numbered vessel to be used. The aqueous phase was 0.1M HNO₃; it was added to the highest numbered vessel. The lower numbered vessels I-III were the scrub section, here; the organic/aqueous volume ratio was 1:4. In the remaining vessels, this ratio was 1:2.

The feed solution was chosen to give uranium, thorium, and HNO_3 concentrations that would occur in the extractant from a typical dissolver solution. The $\text{TCMA}\cdot\text{NO}_3\text{-AR100}$ was scrubbed with $0.1M$ HNO_3 and 90 mL of it were equilibrated at 65°C with 17.5 mL of a solution containing $2M$ HNO_3 , $1.39M$ thorium, and $0.514M$ uranium.

The extraction was started in vessel IV: 7 mL of feed, 7 mL of organic scrub, and 28 mL of $0.1M$ HNO_3 were equilibrated for at least three minutes with the aid of stainless-steel centrifugal stirrers. The phases were then separated by gravity in about one minute, drained into separate containers, and transferred (organic phase to vessel V; aqueous phase to vessel III). A new cycle was started by repeating the loading of vessel IV, adding 28 mL of $0.1M$ HNO_3 to vessel V, and 7 mL of the organic scrub solution to vessel III. The second cycle then involved three vessels; the third cycle, five; and the fourth cycle, all seven vessels. After the fourth cycle, the organic phase containing the thorium was withdrawn from vessel VII and the aqueous uranium solution was withdrawn from vessel I; fresh scrub was added to vessel I, fresh feed to vessel IV, and fresh $0.1M$ HNO_3 was added to vessel VII. After the 11th cycle, the procedure was stopped, and the uranium and thorium contents of each of the remaining 14 phases were analyzed. The results are shown in Table 17 and in Figs. 16 and 17.

After 11 cycles, near steady-state conditions were reached: the effluent uranium concentration agreed with the steady-state expectation within 3%; the thorium effluent concentration was 11% below the expected steady-state amounts. The HNO_3 in the system came from the $0.1M$ HNO_3 aqueous phase, the small amount in the organic scrub, and that introduced with the organic feed. The pattern of thorium K_d 's (Table 16) implies that the acid was largely carried off by the aqueous layer.

The uranium effluent (vessel I, aqueous) was decontaminated from the thorium by a factor greater than 3400; the thorium (vessel VII, organic) was purified from the uranium 166-fold. In the course of the 71 equilibrations, no interfacial solids were observed, no third-phase formation occurred, and no difficulty in phase separation was encountered. (In a single worst case, the phases separated under gravity in 2.5 minutes.)

F. Discussion - $\text{TCMA}\cdot\text{NO}_3$

Extraction using highly concentrated $\text{TCMA}\cdot\text{NO}_3\text{-AR100}$ is a very good alternative to the Thorex process. Thorium and uranium are selectively extracted by $\text{TCMA}\cdot\text{NO}_3\text{-AR100}$ from a nitric acid dissolver solution into a concentrated organic phase; the $\text{TCMA}\cdot\text{NO}_3\text{-AR100}$ then lends itself to a simple uranium-thorium separation. The fate of Pu(IV) in this system has not been studied by us, but others^{19,20,25} have shown that Pu(IV) extracts readily into $\text{TCMA}\cdot\text{NO}_3$, that it can be reduced to Pu(III) and thus follow the uranium,¹¹ or that it can (probably) be allowed to remain with the thorium. The fission products are apparently less troublesome¹⁹ than in phosphoryl-based separations, but they have not been studied at high $\text{TCMA}\cdot\text{NO}_3\text{-AR100}$ concentrations. Conditions were found that avoided difficulties arising from solvent capacity, interface problems, or second-organic-phase formation. The separation of thorium from uranium at practical concentrations was successfully demonstrated.

Table 17. Composition of the Organic Phase and the Aqueous Phase (65°C) after the 11th Cycle of the TCMA·NO₃-AR100 Countercurrent Flow Test^a

Vessel Number	Phase	Th, mol/L	K _d (Th)	U, mol/L	K _d (U)	$\alpha = \frac{K_d(\text{Th})}{K_d(\text{U})}$
I	ORG	0.0054	>25.1	0.0127	0.55	>46
	AQU	$<2.14 \times 10^{-5}$		0.0231		
II	ORG	0.0230	8.37	0.0181	0.62	13
	AQU	0.00275		0.0292		
III	ORG	0.064	9.53	0.0196	0.68	15
	AQU	0.0067		0.0288		
IV	ORG	0.204	10.9	0.0197	0.62	18
	AQU	0.0188		0.0315		
V	ORG	0.206	6.78	0.00495	0.48	14
	AQU	0.0303		0.0101		
VI	ORG	0.198	5.93	0.00116	0.47	13
	AQU	0.0335		0.00245		
VII	ORG	0.127	4.85	0.000239	0.54	9
	AQU	0.0261		0.000440		

^aOrganic feed = 0.0897M uranium and 0.287M thorium.

ACKNOWLEDGMENTS

Analytical work was done by A. M. Essling, I. M. Fox, R. M. Crooks, and M. F. Bouchard. Helpful discussions were held with A. Siczek, W. Seefeldt, G. R. Dyrkacz, D. Cohen, J. C. Sullivan, O. K. Tallent, C. A. A. Bloomquist and M. Steindler. We thank C. A. Pittinger of Exxon for supplying the AR100.

Fig. 16.

Results of the TCMA·NO₃-AR100 Countercurrent Flow Test after 11 Cycles

Fig. 17.

Densities at 65°C of the Organic and Aqueous Phases after 11 Cycles of the TCMA·NO₃-AR100 Countercurrent Flow Test (The organic phase is denoted by the open circles; the aqueous phase by the squares.)

REFERENCES

1. Reviewed in R. L. Stevenson and P. E. Smith, *Reactor Handbook: Volume II, Fuel Reprocessing*, 2nd Ed., S. M. Stroller and R. B. Richards, Eds. pp. 216-225 (1961).
2. T. H. Siddall, *Ind. Eng. Chem.* **51**, 41 (1959).
3. T. H. Siddall, *J. Am. Chem. Soc.* **81**, 4176 (1959).
4. T. H. Siddall, AEC Conf. 1958, 15/p/521.
5. L. Magon, R. Portanova, B. Zarli, and A. Bismondo, *J. Inorg. Nucl. Chem.* **34**, 1971 (1972).
6. R. Portanova, G. Tomat, A. Cassol, and L. Magon, *J. Inorg. Nucl. Chem.* **34**, 1685 (1972).
7. E. Nebel and K. Schwabe, *Z. Phys. Chem. (Leipzig)* **224**, 29 (1963).
8. Von B. A. Bilal and F. Herrmann, *Radiochim. Acta* **22**, 125 (1975).
9. H. S. Harned and N. D. Embree, *J. Am. Chem. Soc.* **56**, 1042 (1934).
10. H. A. C. McKay, J. H. Miles, and H. S. Park, *Possible Use of Carboxylic Acid for U/Pu Separation in Nuclear-Fuel Reprocessing*, Harwell Report AERE R 8509, p. 33 (1976).
11. M. Germain, A. Bathellier, and P. Berard, *Use of Formic Acid for Stripping Plutonium*, Proc. Int. Solvent Extraction Conf. 1974, G. V. Jeffreys, Ed., Vol. 3, pp. 2075-91 (1974).
12. A. Bathellier and Michael Germain, *Method of Selective Stripping of Plutonium from Organic Solvents*, U.S. Patent 3,981,961.
13. A. Arsene and M. Germain, *Rev. Roum. Chem.* **20**, 251 (1975).
14. O. K. Tallent and D. A. Costanza, Oak Ridge National Laboratory Report ORNL-TM-2949, pp. 57-59 (1970).
15. L. R. Crisler, *Production of Plutonium Formate and Plutonium Dioxide*, U.S. Patent 3,660,047 (1972).
16. D. F. Peppard and M. A. Peppard, *Ind. Eng. Chem.* **46**, 34 (1964).
17. W. J. Maeck, G. L. Booman, M. C. Elliot, and J. E. Rein, *Anal. Chem.* **31**, 1130 (1959). ASTM Designation: E 318-69 (Reapproved 1974).
18. P. F. Thomason, M. A. Perry, and W. M. Byerly, *Anal. Chem.* **21**, 1239 (1949).
19. G. Koch, *Kerntechnik* **7**, 394 (1965).

20. G. Koch, *Reprocessing by Quaternary Ammonium Nitrates: Laboratory Studies*, in *Solvent Extraction Chemistry of Metals*, H. A. C. McKay, T. V. Healy, I. L. Jenkins, and A. Naylor, Eds., McMillan, London, pp. 247-66 (1966).
21. G. Koch, *Radiochim. Acta* 4, 128 (1965).
22. G. R. Drykacz, ANL, private communication (1978).
23. H. K. Frensdorff, *J. Am. Chem. Soc.* 93, 600 (1971).
24. P. Gerontopulos and L. Rigali, *Radiochim. Acta* 3, 122 (1964).
25. R. Shabance and H. Ruf, *Radiochim. Acta* 24, 15 (1977).
26. P. R. Danesi, F. Orlandini, and G. J. Scibona, *J. Inorg. Nucl. Chem.* 27, 449 (1965).
27. J. N. C. Van Geel, Thesis (1968), (cited in reference 28).
28. R. Swarup and S. K. Patil, *J. Inorg. Nucl. Chem.* 38, 1203 (1976).
29. Lopez-Mencharo and A. Ghem. *Eurochem. Symp. on Aqueous Reprocessing Chemistry for Irradiated Fuels*, Brussels, p. 147 (1963), (cited in reference 28).

Distribution for ANL-79-85Internal:

W. E. Massey	G. F. Vandegrift (3)
H. Diamond (3)	L. Burris
E. P. Horwitz (3)	G. M. Kesser
G. W. Mason (3)	A. Melton
C. S. Sabau (3)	M. J. Steindler (3)
P. R. Fields	D. S. Webster
J. Unik	A. B. Krisciunas
G. J. Bernstein	ANL Contract File
A. Siczek	ANL Libraries (5)
R. Leonard	TIS Files (6)

External:

DOE-TIC, for distribution per UC-4 and -10 (190)
 Manager, Chicago Operations and Regional Office, DOE
 Chief, Office of Patent Counsel, DOE-CORO
 President, Argonne Universities Association
 Chemistry Division Review Committee:

- F. A. Cotton, Texas A&M U.
- H. F. Franzen, Iowa State U.
- J. R. Huizenga, U. Rochester
- A. W. Jache, Marquette U.
- E. L. Muettert, U. California, Berkeley
- F. S. Rowland, U. California, Irvine
- A. Schriesheim, Exxon Research & Engineering, Linden
- T. T. Sugihara, Texas A&M U.
- J. H. Wang, SUNY at Buffalo

Chemical Engineering Division Review Committee:

- C. B. Alcock, U. Toronto
- R. C. Axtmann, Princeton U.
- R. E. Balzhiser, Electric Power Research Inst.
- J. T. Banchemo, U. Notre Dame
- T. Cole, Ford Motor Co.
- P. W. Gilles, U. Kansas
- R. I. Newman, Allied Chemical Corp.
- G. M. Rosenblatt, Pennsylvania State U.
- G. E. Benedict, General Atomic
- D. J. Crouse, Oak Ridge National Lab.
- W. S. Groenier, Oak Ridge National Lab.
- M. L. Hyder, Savannah River Lab.
- D. A. Orth, Savannah River Lab.
- J. D. Spencer, Savannah River Lab.
- D. W. Tedder, Georgia Inst. Technology
- M. J. Thompson, Savannah River Lab.
- B. L. Vondra, Oak Ridge National Lab.