

LA-SUB--96-102

**SOLVENT EXTRACTION OF THORIUM(IV), URANIUM(VI), AND
EUROPIUM(III) WITH LIPOPHILIC ALKYL-
SUBSTITUTED PYRIDINIUM SALTS**

Final Report for Subcontract 9-XZ2-1123E-1

June 1, 1992 - December 1, 1995

Submitted by

Dr. Dale D. Ensor
Tennessee Technological University
Chemistry Department
Cookeville, TN 38505

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SOLVENT EXTRACTION OF THORIUM(IV), URANIUM(VI), AND EUROPIUM(III) WITH LIPOPHILIC ALKYL-SUBSTITUTED PYRIDINIUM SALTS

ABSTRACT

In the treatment of high level nuclear wastes, aromatic pyridinium salts which are radiation-resistant are desired for the extraction of actinides and lanthanides. The solvent extraction of Th^{+4} , UO_2^{+2} , and Eu^{+3} by three aromatic extractants, 3,5 - didodecylpyridinium nitrate (35PY), 2,6-didodecylpyridinium nitrate (26PY), and 1-methyl-3,5-didodecyl-pyridinium iodide (1M35PY) has been studied in nitric acid media.

The general order of extractability of the three extractants in toluene was $1\text{M}35\text{PY} \gg 26\text{PY} > 35\text{PY}$. The overall extraction efficiency of the metal ions was $\text{Th}^{+4} > \text{UO}_2^{+2} > \text{Eu}^{+3}$. The extraction of HNO_3 , which was competitive with the extraction of metal ions, was quantitatively investigated by NaOH titration and UV spectrometry. The loading capacity suggested that the extracted species in the organic phase for thorium was $(\text{R}_4\text{N}^+)_2\text{Th}(\text{NO}_3^-)_6$, where R_4N^+ denotes 1M35PY. A comparison of 1M35PY to the well-characterized extractant, Aliquat-336, an aliphatic ammonium salt was made. At the same extractant concentration, 1M35PY extracted thorium more efficiently than Aliquat-336 at high acidity. Thorium could be readily stripped with dilute nitric acid from 1M35PY. After irradiation of 0.1M 1M35PY with ^{60}Co at 40R/min for 48 hours, no change in the extraction efficiency of thorium was observed.

BACKGROUND

In nuclear industry, an increasing concern of the public is to clean and better manage the current nuclear wastes. Since the 1940's, the mass production of nuclear weapons and the operation of nuclear power reactors have left a huge amount of high level radioactive wastes which are temporarily stored in underground tanks. These wastes would pose a permanent hazard to the human and biological cycle if they are not isolated from the environment. The hazardous components of the wastes are radioactive actinides, lanthanides, and transition metals which are mixed with the bulk components of nonradioactive elements. Some of the actinides have extremely long half lives, while the radioactive lanthanides are relatively short lived. Almost all the long-lived actinides are hazardous alpha particle emitters. It is highly desirable to separate the long-lived actinides from the short-lived lanthanides which are mainly beta or gamma emitters. The long-lived actinides, particularly plutonium, neptunium, americium, and curium, would be transmuted by neutrons in a nuclear reactor to less hazardous or nonradioactive isotopes, and the short-lived lanthanides can be stored in underground repository tanks and then decay to stable isotopes within decades. Separation of lanthanides from actinides is also critical to the transmutation of the actinides because the lanthanides tend to absorb neutrons efficiently and will prevent the efficient transmutation of americium and curium (1).

In the nuclear waste treatment, the radioactive solids are usually dissolved in nitric acid because nitric acid is compatible with the stainless steel equipment. This requires the development of radiation-resistant extractants which could efficiently separate actinide elements (thorium, uranium, plutonium, and other heavy actinides) at high concentration of nitric acid in highly radioactive fields. The ideal extractant to serve this purpose should:

- (1) have good kinetics to minimize the contact time.
- (2) be aromatic since aromatic compounds are more radiation-resistant than aliphatic compounds.
- (3) be non-organophorous compounds which are completely incinerable to limit the amounts of radioactive waste in solvent extraction.
- (4) be able to extract actinides from highly acidic nitrate media and be easy for metals to strip.

Anion exchange extractants appear to be the most promising in the treatment of nuclear wastes (2). Their short equilibrium time minimizes the contact time necessary for the extraction of metal complexes and prolongs the life time of the extractants versus the radiation degradation. Amine extractants are characterized by their high loading capacity. Metals can be selectively extracted by amine extractants, based on the anions used, and can be stripped with dilute acid from the organic phase.

Extraction of Actinides and Lanthanides with Aliphatic Amines

Danesi et al. (3) investigated the extraction of uranyl nitrate by different types of amines from nitric acid media and found that the composition in the organic phase for quaternary ammonium nitrate was $\text{RUO}_2(\text{NO}_3)_3$, where R is Aliquat-336; for tertiary and secondary ammonium nitrates, the composition was $\text{RUO}_2(\text{NO}_3)_3 \cdot (\text{RNO}_3)_n$, where R is trilaurylamine or Amberlite LA-1, a secondary amine with two long chains; for primary ammonium nitrate the composition was $\text{UO}_2(\text{NO}_3)_2 \cdot (\text{RNO}_3)_n$, where R is Primene JM-T, a long chain primary amine. The number n was dependent on the alkyl ammonium salt type. Because one mole of Aliquat-336 could extract one mole of uranyl, this quaternary ammonium salt was the most efficient in terms of extraction capacity.

Carswell and Lawrance (4) studied the extraction of thorium in nitric acid with both TNOA (Tri-n-octylamine) and TIOA (Tri-iso-octylamine), and found that thorium was extracted as the anion complex $\text{Th}(\text{NO}_3)_6^{2-}$. The authors assumed that (1) all anionic species can be extracted on the basis of a simple ion-exchange analogy, but the formation of the complex $\text{Th}(\text{NO}_3)_6^{2-}$ was favored rather than $\text{Th}(\text{NO}_3)_5^-$, possibly

owing to its symmetry; and (2) more than one anionic species was present, including $\text{Th}(\text{NO}_3)_5^-$, but extraction of $\text{Th}(\text{NO}_3)_6^{2-}$ was preferred.

Keder et al. (5) studied the extraction of Th^{4+} and UO_2^{2+} with 10% (volume ratio) TNOA. The distribution ratio (D) of Th^{4+} increased with HNO_3 concentration until the acid concentration reached 6.0 M ($D=0.66$), then D decreased with acid concentration due to the increased competition of acid extraction. Similarly, the highest D of UO_2^{2+} appeared at 7.0M HNO_3 ($D=1.2$). This general feature was also observed for other actinides such as Pu^{4+} . The author noted that the extracted anion species was not necessarily the same anion which predominated in the aqueous solution.

Lloyd and Mason (6) investigated the extraction of uranium and HNO_3 by triauryllamine nitrate. To determine the composition of the extracted species in the organic phase, they used successive titration of the organic phase with NaOH and assumed that the first end point corresponded to the acid at the outer sphere (which they called unbound acid); the second end point was the precipitation of uranium as $\text{NaUO}_2(\text{OH})_3$; and the third end point was the total hydrolysis of the amine. They suggested the major species in the organic phase were $(\text{R}_3\text{NHNO}_3)_2\text{UO}_2(\text{NO}_3)_2$, $[(\text{R}_3\text{NHNO}_3)_2]_2\text{UO}_2(\text{NO}_3)$, R_3NHNO_3 , and $\text{R}_3\text{NHNO}_3 \cdot \text{HNO}_3$.

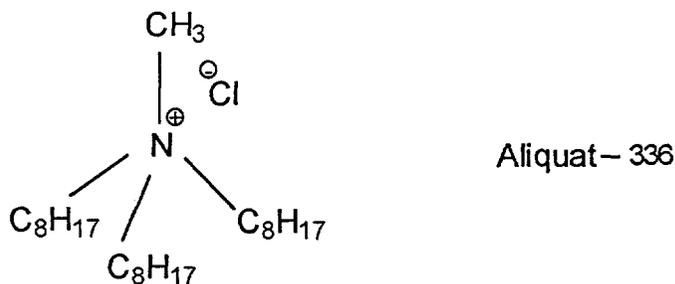
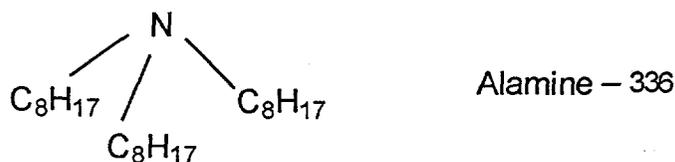


Figure 1. Structure of Alamine-336 and Aliquat-336

Horwitz and his coworkers (7) compared a tertiary amine Alamine-336 with Aliquat-336 in the extraction of Am^{3+} , Cm^{3+} , Cf^{3+} from nitrate solution. The structure of Alamine-336 and Aliquat-336 is illustrated in Figure 1. Alamine-336 is a mixture of octyl and decyl tertiary amines, with octyl group predominant. Aliquat-336 contains the same alkyl groups as Alamine-336 with addition of a methyl group to the nitrogen and is sold as the chloride. Their results showed that Aliquat-336 was superior to Alamine-336 for the transplutonium(III) ions in that the distribution ratio of Am^{3+} by Aliquat-336 was about two orders of magnitude greater than that by Alamine-336. Different solvents had remarkable effects on the distribution ratios. The empirical formula was postulated to be $(\text{R}_3\text{NH})_2\text{Am}(\text{NO}_3)_5$ for Alamine-336 and $(\text{R}_3\text{NCH}_3)\text{Am}(\text{NO}_3)_4$ for Aliquat-336. Eventually Aliquat-336 was successfully employed in the recovery of transplutonium elements produced by underground nuclear detonations. In addition, Horwitz investigated the extraction of HNO_3 with both Alamine-336 and Aliquat-336 by NaOH titration. The molar ratio of HNO_3 to the $(\text{R}_3\text{NH}^+)(\text{NO}_3^-)$ or $(\text{R}_3\text{CH}_3\text{N}^+)(\text{NO}_3^-)$ was from 0 to 1.1. The excess HNO_3 extraction was believed to result from the species $\text{H}(\text{NO}_3)_2^-$ through hydrogen bonding

with amines or ammonium salts (8,9).

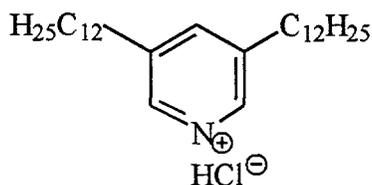
Gerontopulos and Rigalt (10) reported efficient extraction of thorium by 0.1M Aliquat-336 (in xylene) from HNO_3 solutions. The highest distribution ratio appeared at about 3M HNO_3 , and the species extracted into the organic phase was $\text{Th}(\text{NO}_3)_6^{2-}$.

Extraction of trivalent lanthanides and actinides with aliphatic amines has been studied extensively for both inter- and intra-group separations. Moore studied the separation of lanthanides in HCl , HNO_3 , and H_2SO_4 systems (14-16). The separation of the trivalent ions depended on the stability of the metal-ligand anions.

The above review of metal extractions shows that aliphatic amines or quaternary ammonium salts could efficiently extract and separate actinides and lanthanides at relatively high acidity. However, the aliphatic extractants are not radiation-resistant. Therefore aromatic amines or quaternary ammonium salts would be ideal extractants for nuclear waste treatment.

Objectives of this Study

The extractants employed in this study are aromatic substituted pyridinium salts whose structures are listed in Figure 2. Structurally, 1M35PY is analogous to Aliquat-336. 35PY and 26PY are analogous to Alamine-336 except that 35PY and 26PY are already protonated by HCl .



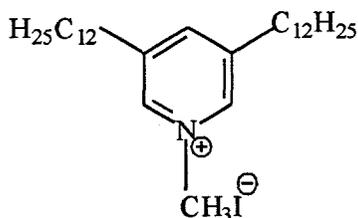
3,5-didodecylpyridinium
hydrochloride

(Abbrev. 35PY)



2,6-didodecylpyridinium
hydrochloride

(Abbrev. 26PY)



1-methyl-3,5-didodecylpyridinium iodide

(Abbrev. 1M35PY)

Figure 2. Structure and abbreviations of the extractants.

As mentioned above, Aliquat-336 is a much better extractant than Alamine-336 in the extraction of Am(III). It is interesting to investigate whether 1M35PY is likewise a stronger extractant than 35PY or 26PY. Despite the similarity, the aromatic pyridinium salts should be more stable than their aliphatic analogues. Even if the pyridinium salts are radiolyzed, the most probable damage is to cut short the aliphatic long chains and the degradation products would have little effect on the extraction.

In this study, Th(IV), U(VI), and Eu(III) were selected as appropriate representatives of actinides and lanthanides because:

- (1) Both thorium and uranium are hazardous alpha emitters.
- (2) Uranium is a valuable nuclear fuel.
- (3) Th^{4+} is a model element for Pu^{4+} because of their chemical similarity, but the natural Th^{4+} is less hazardous than Pu^{4+} and is more convenient to study.
- (4) Eu^{3+} is chemically similar to the heavier actinides whose stable valence in the aqueous solution is +3. In addition, Eu^{3+} is an abundant fission product in the nuclear waste.

The relative strength of complexes of the actinide cations in solution is $\text{An(IV)} \gg \text{An(VI)} \geq \text{An(III)} \gg \text{An(V)}$ (17). Therefore, it is expected that the extractability of thorium, uranium, and europium by the quaternary ammoniums would be $\text{Th}^{4+} \gg \text{UO}_2^{2+} \gg \text{Eu}^{3+}$.

The objectives of this study were:

- (1) to examine the solubility of the three pyridinium compounds in toluene;
- (2) to compare the three compounds for the extraction of Th^{4+} , UO_2^{2+} , and Eu^{3+} ;
- (3) to study the extraction mechanism;
- (4) to explore the possible relationship between the properties and the structure and thus provide information for further synthesis of new extractants.

EXPERIMENTAL

Materials

The extractants were provided by Los Alamos National Lab and used without further purification. These compounds were 3,5-didodecylpyridinium hydrochloride (35PY), MW 452.2, a white solid; 2,6-didodecylpyridinium hydrochloride(26PY), MW 452.2, a white solid; and 1-methyl-3,5-didodecylpyridinium iodide(1M35PY), MW 557.7, a yellow solid. Their molecular structures are illustrated in Figure 2. $^{152-154}\text{Eu}$ was provided by Oak Ridge National Lab. The sample was stored as the stock solution in a lead-shielded vial whose gamma activity was checked. Before use, an aliquot of the stock solution was transferred into a vial and evaporated to dryness by an IR lamp and then dissolved with dilute nitric acid to yield 15,000 cpm per 5 microliters. All other chemicals used were reagent grade. The purified water with resistance of greater than 14 megohms was produced by passing distilled water through the Barnstead deionized column Cat. No D0809.

Determination of Solubility

The following methods were employed to determine the solubility of the extractants in toluene.

Method I. A saturated solution of the sample was prepared in toluene, in which the solution and undissolved solid sample coexisted. After filtration, 1.0 ml of the solution was transferred onto the inner face of a dry crucible cover whose weight was known. When the toluene was evaporated, the solid was recrystallized using acetone. The mass of the dry solid was used to calculate the molar concentration of the sample in toluene.

Method II. Toluene was continuously added to the known mass of the sample until the sample was completely dissolved. The total mass of the saturated solution (sample and toluene) was weighed and the density (d) of the

solution was measured. If the mass of the sample was s , and the total mass of the solution was $s + t$, then the total volume was $(s + t)/d$ and the molar concentration was $\frac{s/M}{(s+t)/d}$, where M is the molecular weight.

Method II took less time than Method I. But 35PY, even at the concentration of 0.007M, always had a little insoluble substance (impurity) in toluene. In this case, only Method I yielded good data. The solubilities of the three pyridinium halides in toluene were 0.268M, 0.525M, and 1.03M for 35PY chloride, 26PY chloride, and 1M35PY iodide, respectively.

Conversion of the Pyridinium Halides to the Nitrate Form

All the extractants were converted to the nitrate form. 35PY and 26PY could be denoted as $R_4N^+Cl^-$, and 1M35PY as $R_4N^+I^-$, where R_4N^+ represents the pyridinium cations. Conversion of 0.0201M 35PY or 0.0201M 26PY from chloride to the nitrate form was completed by washing three times with 5M $NaNO_3$ + 1M HNO_3 , at phase ratio 1:1, shaken at 180 rpm for 4 hours each time. No chloride was found in the third aqueous raffinate using 0.1M $AgNO_3$. Three methods were tried to convert 1M35PY to the nitrate form. The most efficient procedure to convert 1M35PY to the nitrate form controlled the conversion kinetics. A complete conversion of 0.0216M 1M35PY with 5M $NaNO_3$ was completed by washing six times at phase ratio 1:1, shaking at 160 rpm for 3 min each time. Washing 0.100M 1M35PY with 5M $NaNO_3$ for 11 times in the same procedure completely converted 1M35PY to the nitrate form. No emulsion appeared during this process. The reason is that the emulsification by a surfactant is proportional to the shaking speed and shaking time. The anion exchange equilibrium was reached before the emulsification took place. A comparative test showed that 0.0216M 1M35PY could be converted with 5M $NaNO_3$ by either washing 6 times at 160 rpm for 3 min each time or by washing 5 times at 180 rpm for 30 min each time (significant emulsification in this case). This indicated that the anion exchange equilibrium was basically reached in 3 minutes in each washing.

Extraction procedure

Distribution ratio of metals between the organic phase and the aqueous phase is defined as

$$D = \frac{[M]_{org}}{[M]_{aq}} = \frac{([M]_{initial} - [M]_{aq}) \times \frac{V_{aq}}{V_{org}}}{[M]_{aq}} \quad (1)$$

where M is metal (thorium or uranyl).

In most cases, the volume ratio $\frac{V_{org}}{V_{aq}}$ is 1:1, and D is simplified as

$$D = \frac{[M]_{initial} - [M]_{aq}}{[M]_{aq}} \quad (2)$$

In this work the distribution measurements were done by a batch method. For thorium and uranium, usually 4 ml of the aqueous phase was contacted with 4 ml of the organic phase in a 10-ml vial capped with a teflon liner. The contact time was first arbitrarily set four hours but 30 minutes was found to be sufficient to reach equilibrium. For convenience, the subsequent contact time was one hour unless otherwise noted. After

equilibrium was established, the vial was centrifuged and the phases separated. An aliquot of 1 or 2 ml of the aqueous phase was taken for analysis.

If the distribution ratio was large (i.e. $D \geq 10$) or the aqueous phase contained different ratios of nitric acid and sodium nitrate, the distribution ratio could not be accurately determined from the raffinate aqueous phase. In this case, the distribution ratio was measured by back extraction of thorium from the organic phase with 0.24 M HNO_3 (emulsification occurred if the acid was too dilute). At 0.24M HNO_3 , the distribution ratio of thorium was found to be less than 0.02, and thorium was completely stripped from the organic phase with 0.24M HNO_3 at phase ratio 1:2, which could be shown by the relation between the percent extraction $E\%$ and D :

$$E\% = \frac{100D}{D + V_{aq} / V_{org}} \% \quad (3)$$

For instance, if $D \ll 0.02$ and phase ratio = 1:2, $E\% \ll 0.99\%$. This means at least 99% of thorium was stripped from the organic phase to the aqueous phase with 0.24M HNO_3 at phase ratio 1:2.

To measure the distribution ratio of Eu^{3+} , 1 ml of the aqueous phase was mixed with 1 ml of organic phase in a 13x100mm culture tube, then spiked with 5 microliter of $^{152-154}\text{Eu}^{3+}$ (15,000 cpm gamma activity). The tubes were capped and double wrapped in plastic bags before the tubes were vortexed and shaken to reach equilibrium. After centrifugation, duplicate 200 microliter aliquots of the organic phase were transferred into counting tubes. The rest of the organic phase was removed, and duplicate 200 microliter aliquots of the aqueous phase were transferred into counting tubes. The samples were counted by Packard Cobra Gamma Counting System, using a window with the energy range of 35-425 kev. The distribution ratio of $^{152-154}\text{Eu}^{3+}$ was the ratio of gamma activity of the organic phase over that of the aqueous phase since the gamma activity of $^{152-154}\text{Eu}^{3+}$ was proportional to its concentration.

Spectrometric Analysis of Th^{4+} , UO_2^{2+} with Arsenazo-III in HNO_3 Medium

Arsenazo-III forms a blue colored complex with Th^{4+} or UO_2^{2+} (14). The two complexes have maximum absorbance at 661nm and 650 nm, respectively. In the analysis, 2 ml of 5.7M HNO_3 and 2 ml of 0.05% arsenazo-III were added to the slightly acidic Th^{4+} or UO_2^{2+} solution, diluted to 25 ml, and the absorbance was measured immediately with 1 cm quartz cell at 661nm for thorium, at 650 nm for uranium.

Analysis of Th^{4+} by EDTA Titration

When $[\text{Th}^{4+}]$ was higher than 0.001M as in the loading experiments, thorium was titrated with 0.0101M EDTA using xylenol orange as indicator whose color turned from pink to bright yellow at the end point. To control the pH, 4 ml of pH2.3 buffer was added to the analyte. The buffer was prepared by adding 1M sodium acetate to 2M chloroacetic acid until pH reached 2.3 (monitored with a pH meter). The EDTA solution was prepared by weighing the calculated amount and dissolving it with deionized water, and then standardized using the standard thorium solution.

Determination of HNO_3 and NO_3^- Extracted into the Organic Phase

Usually 7ml of 0.0216M 1M35PY was equilibrated with HNO_3 solution, centrifuged; 5 ml of the top organic phase was washed with excess standard NaOH; centrifuged again, 4 ml of the raffinate NaOH solution was backed titrated with standard HNO_3 using a 10-ml buret. The concentration of the nitric acid in the organic phase was calculated from the amount of the NaOH consumed by the acid in the organic phase. This method was accurate when the concentration of HNO_3 was above 0.01M. Below this limit, the titration result was not acceptable because of the large error. Fortunately, the total concentration of HNO_3 and NO_3^- could be stripped into the aqueous phase and directly measured by UV spectroscopy.

To determine the composition of the extracted species of thorium in the loaded organic phase, it was necessary to determine the concentration of nitrate in the organic phase which was equilibrated with the aqueous phase of high concentration nitrate. Since nitrate or nitric acid has an adequate absorbance at 300nm (15,16), it is possible to directly measure the concentration of HNO_3 or NO_3^- . A calibration curve for nitrate at 300nm worked very well (see Figure 3). This calibration is good for the concentration of both HNO_3 and NO_3^- because the comparative tests showed that the acidity in the aqueous phase did not affect the absorbance of the nitrate at this condition, as is shown in Table 1.

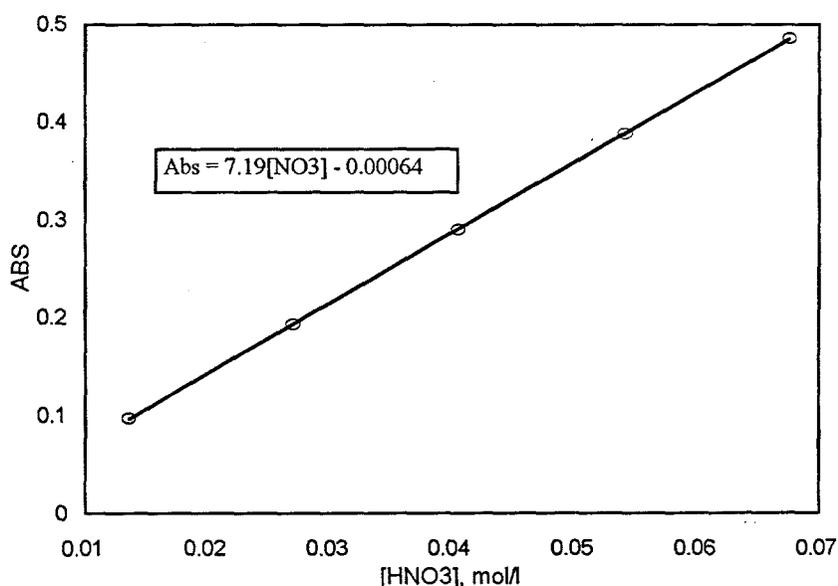


Figure 3. Calibration curve of HNO_3 vs H_2O as reference at 300nm with 1cm cell R^2 was 0.99997 for the regressed equation $\text{Abs} = 7.19[\text{NO}_3] - 0.00064$

1M35PY could be denoted as $\text{R}_4\text{N}^+\text{NO}_3^- \cdot x\text{HNO}_3$, where x depended on the aqueous phase conditions. The concentration measured by UV spectrometry was the total concentration of NO_3^- (as the anion of 1M35PY) and HNO_3 (combined with 1M35PY) while titration with NaOH could only determine the HNO_3 which was combined with 1M35PY. Therefore the UV spectrometry could determine lower concentration of HNO_3 .

Table 1. Absorbance of $\text{HNO}_3/\text{NO}_3^-$ at 300 nm at different acidity. Various volumes of 0.09481M NaOH was added to 2 ml of 0.1351M HNO_3 and diluted to 10 ml.

volume(ml) of NaOH added	pH of the solution	$[\text{NO}_3^-]$, M	Absorbance at 300nm
1	1.06	0.02702	0.1981
2	1.39	0.02702	0.1975
3	11.8	0.02702	0.1947
4	12.7	0.02702	0.1905
5	13.0	0.02702	0.1954

RESULTS AND DISCUSSION

Comparison of the Three Pyridinium Compounds for the Extraction of Thorium

In strong acidic medium the extraction by the three pyridinium nitrates was assumed to be ion pair mechanism. The metal cation forms a complex anion with ligand (nitrate), and then this complex anion replaces the simple anion of the pyridinium-anion pair.

The distribution ratio of metal ions depends on both the stability of the metal-ligand complex in the aqueous phase and the solubility of the extracted species in the organic phase. The latter is largely dependent upon the solubility of the extractant itself.

Table 2. Extraction of thorium by 35PY, 26PY, and 1M35PY versus $[\text{HNO}_3]$.

$[\text{HNO}_3]$ mol/L	Distribution ratio of thorium (D)		
	0.0201M 35PY	0.0201M 26PY	0.0216M 1M35PY
0.24	0.041	0.034	0.017
1.14	0.068	0.051	0.340
2.26	0.046	0.143	1.78
3.39	0.102	0.201	3.11
5.64	0.279	0.315	5.68

The extraction of thorium by the three pyridinium nitrates is shown in Table 2. The highest distribution

ratio by 1M35PY was about 18 times higher than that by 35PY or 26PY, therefore 1M35PY was the most efficient extractant. Most of the work thereafter was focused on the extraction behaviors of 1M35PY.

Extraction of Thorium with 1M35PY

Kinetics

The initial contact time for the extraction of thorium was 4 hours. To determine whether 4 hours was enough for the equilibrium, 5 ml of the organic phase and 15 ml of the aqueous phase were contacted for different time intervals and the $[Th]_{aq}$ was analyzed as illustrated in Figure 4.

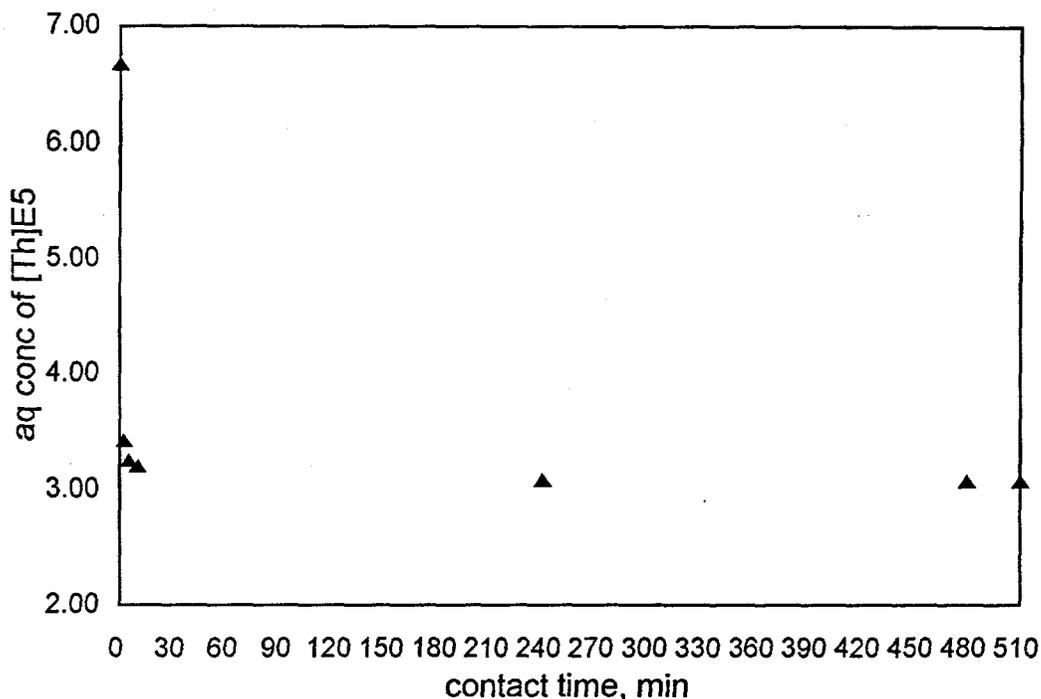


Figure 4. Kinetics of thorium extraction with 0.02M 1M35PY at 5.5M HNO_3 with a phase ratio of (org:aq) 1:3 and the initial $[Th]_{aq} = 6.7 \times 10^{-5}$ M.

The arbitrary phase ratio 1:3 was only for convenient analysis of the aqueous phase. The equilibrium was reached within about 30 minutes. If phase ratio was 1:1, the contact interface area between the two phases was increased and the equilibrium time would be shorter than that at phase ratio 1:3. Therefore the subsequent contact time was 60 minutes at 180 rpm except otherwise noted.

Extraction of Thorium versus $[HNO_3]$

The distribution ratio of thorium was measured versus $[HNO_3]$ with 0.0216M 1M35PY as shown in Table 3. The standard deviations of the repeated data were higher than those calculated from the uncertainty in the absorbance because the standard deviation here was total experimental error including that in the glassware and in extraction procedures, which could be greater than the error in any individual step. The error in the first point (at 0.24M HNO_3) was relatively large because of the extremely low distribution ratio, which was difficult to measure accurately (see the relative error vs. absorbance in Figure 2.6).

The data in Table 3 were plotted in Figure 5. The points did not form a straight line in that the last two points began to bend down. This is due to the increased competition of HNO_3 extraction against the thorium extraction at high $[\text{HNO}_3]$.

Table 3. Distribution ratios of thorium with 0.0216M 1M35PY at phase ratio 1:1.

number of repetitions	Distribution ratios of thorium at different $[\text{HNO}_3]$				
	0.24M	1.14M	2.26M	3.39M	5.6M
1	0.0097	0.31	1.63	3.28	6.26
2	0.014	0.30	1.72	3.56	6.30
3	0.017	0.29	1.62	3.45	5.40
4	0.0020	0.28	1.75	3.11	6.50
5	0.064	0.34	1.78	2.78	5.30
6		0.38	1.34	2.86	5.68
7		0.26	1.50	2.97	5.91
8		0.24	1.76	2.89	5.21
average	0.021	0.30	1.64	3.11	5.82
standard deviation	0.024	0.04	0.15	0.29	0.50

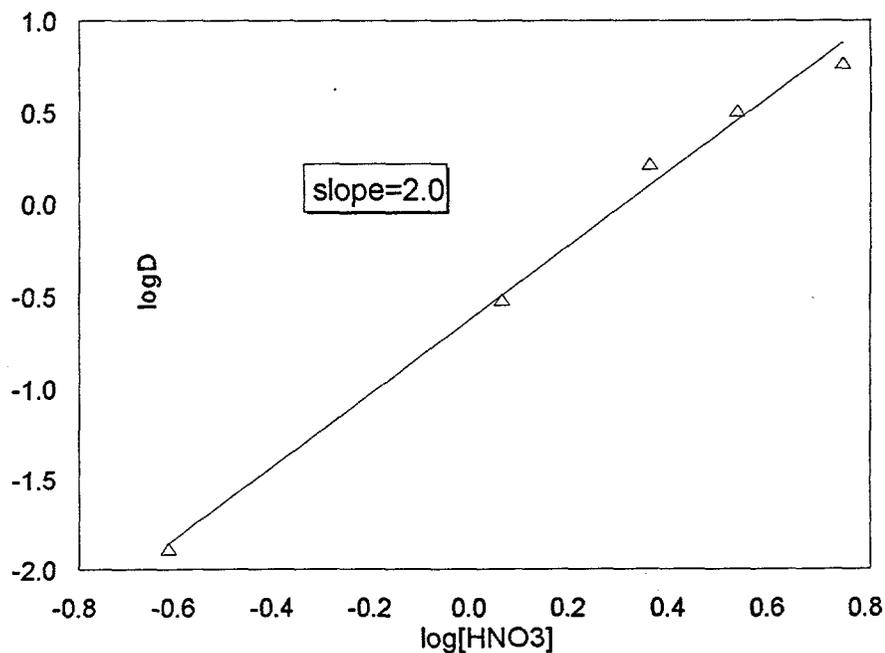


Figure 5. Distribution ratio of thorium at 0.0216M 1M35PY vs $[\text{HNO}_3]$.

Extraction of Thorium versus the Ratio of $[\text{NaNO}_3]/[\text{HNO}_3]$

To investigate the effect of nitric acid on the extraction, Th^{4+} was extracted at different $[\text{NaNO}_3]/[\text{HNO}_3]$ ratios while the total ionic strength was held at 3.39M. After extraction and centrifugation, back extraction of thorium from the loaded org phase with 0.24M HNO_3 was done to check the total mass balance (experimental recovery of thorium). The mass balance was 105-110%, as shown in Table 4. The slope of $\log D$ vs $\log[\text{HNO}_3]$ was -0.54. When the total concentration of HNO_3 and NaNO_3 was held at 4.0 M (Table 5), the slope of $\log D$ vs $\log[\text{HNO}_3]$ was -0.87. The data in both tables show that the distribution ratio increased with the ratio of $[\text{NaNO}_3]/[\text{HNO}_3]$, and the change in the slopes of $\log D$ vs $\log[\text{HNO}_3]$ shows that the effect of nitric acid on the extraction of thorium was more obvious at higher concentration. Thus high concentration of NO_3^- and low concentration of H^+ are favorable to the extraction of thorium nitrate complex.

Table 4. Extraction of Th^{4+} with 0.0216M 1M35PY vs $[\text{NaNO}_3]/[\text{HNO}_3]$.
 $[\text{NaNO}_3] + [\text{HNO}_3] = 3.39 \text{ M}$, $[\text{Th}^{4+}]_{\text{initial}} = 6.68 \times 10^{-5} \text{ M}$
 The phase ratio was 2: 5 for the forward extraction and for the back extraction the phase ratio was 1.5:3.

$[\text{HNO}_3]$ mol/l	$[\text{NaNO}_3]$ mol/l	$[\text{Th}]_{\text{E5,M}}$ in raffinate	Distribution ratio	$[\text{Th}]_{\text{E5,M}}$ stripping liquor	Recovery %
3.39	0	3.14	2.82	4.93	106
2.89	0.50	3.08	2.91	4.90	105
2.39	1.00	3.02	3.03	5.28	108
1.89	1.50	2.61	3.40	5.51	105
1.39	2.00	2.35	4.60	6.12	108
0.39	3.00	1.49	8.69	7.32	110

Table 5. Extraction of Th^{4+} with 0.0216M 1M35PY vs $[\text{NaNO}_3]/[\text{HNO}_3]$. The total concentration of HNO_3 and NaNO_3 was 4.0 M and the phase ratio was 4:4, initial $[\text{Th}^{4+}] = 6.68 \times 10^{-5} \text{ M}$.

$[\text{HNO}_3]$	$[\text{NaNO}_3]$	$[\text{Th}]_{\text{org}}$	$[\text{Th}]_{\text{aq}}$	D
4.0	0.0	5.36	1.32	4.07
3.0	1.0	5.46	1.22	4.47
2.0	2.0	5.79	0.89	6.51
1.0	3.0	6.23	0.452	13.8
0.5	3.5	6.39	0.286	22.4

Extraction of Thorium versus [1M35PY]

Thorium was extracted versus the concentration of 1M35PY while $[\text{HNO}_3]$ was fixed at 5.7M. The plot of $\log D$ vs $\log[1\text{M35PY}]$ in Figure 6 was a straight line with slope 1.92. This suggests that the extraction of thorium has a second order dependence on 1M35PY.

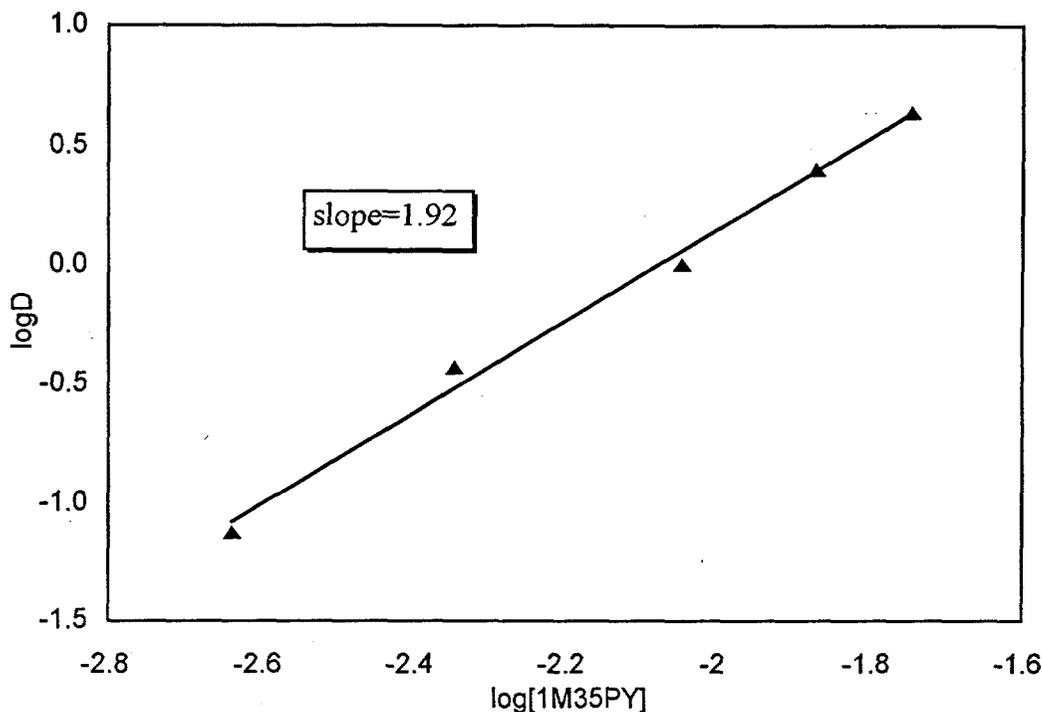


Figure 6. Distribution ratios of Th at 5.7 M HNO_3 with varying [1M35PY]

Extraction of HNO_3 by 1M35PY versus $[\text{HNO}_3]$

The extraction of HNO_3 can be expressed by Equation (4) as:



The extraction of HNO_3 was in competition with the extraction of thorium. Actually, 1M35PY first extracted HNO_3 in the pre-equilibrium before it extracted thorium. It is essential to investigate how the extraction of HNO_3 affected the extraction of thorium.

The results in Table 3.5 were obtained by titration with NaOH. The total $[\text{NO}_3^-]$ in Table 7 was measured by UV spectrometry at 300nm, which was the addition of $[\text{HNO}_3]_{\text{org}}$ and 0.0216 (the concentration of NO_3^- as the anion of 0.0216 1M35PY). So the net concentration of HNO_3 in the organic phase was the total concentration minus 0.0216M.

The results by the two methods agree quite well when the $[\text{HNO}_3]$ in the aqueous phase was above 1.14 M. Below this point, the titration result was not accepted because of poor reproducibility (because the acid concentration in the organic phase was too low). Figure 7 is a plot of the molar ratio of HNO_3 to 1M35PY in the organic phase from the data in Table 7. It is seen that 1M35PY extracted HNO_3 non-stoichiometrically, the

molar ratio being from 0 to 1.6. When the aqueous HNO_3 was above 3.39M, all the 1M35PY combined HNO_3 and there were no free forms of 1M35PY.

Table 6. Extraction of HNO_3 with 0.0216M 1M35PY*.

Initial $[\text{HNO}_3]_{\text{aq}}$, mol/l	[1M35PY] in org phase	$[\text{HNO}_3]_{\text{org}}$	$[\text{HNO}_3]_{\text{org}}$ to [1M35PY]
5.51	0.0216	0.0324	1.5
3.39	0.0216	0.0237	1.1
2.26	0.0216	0.0192	0.89
1.14	0.0216	0.0177	0.82

* The results were obtained by titration of the aqueous phase with NaOH

Table 7. Extraction of HNO_3 with 0.0216M 1M35PY*.

Initial $[\text{HNO}_3]_{\text{aq}}$, mol/l	$[\text{NO}_3^-]_{\text{total}}$ in org. phase	$[\text{NO}_3^-]_{\text{total}}$ to [1M35PY]	$[\text{HNO}_3]_{\text{org}}$ to [1M35PY]
5.71	0.0568	2.63	1.63
3.39	0.0437	2.02	1.02
2.26	0.0395	1.83	0.83
1.14	0.0313	1.45	0.45
0.50	0.0244	1.13	0.13
0.24	0.0224	1.04	0.04
0 (H_2O)	0.0214	0.99	0

* 0.0216M 1M35PY was contacted with aqueous HNO_3 and stripped by 0.24 M HClO_4 , then the aqueous phase was measured at 300nm.

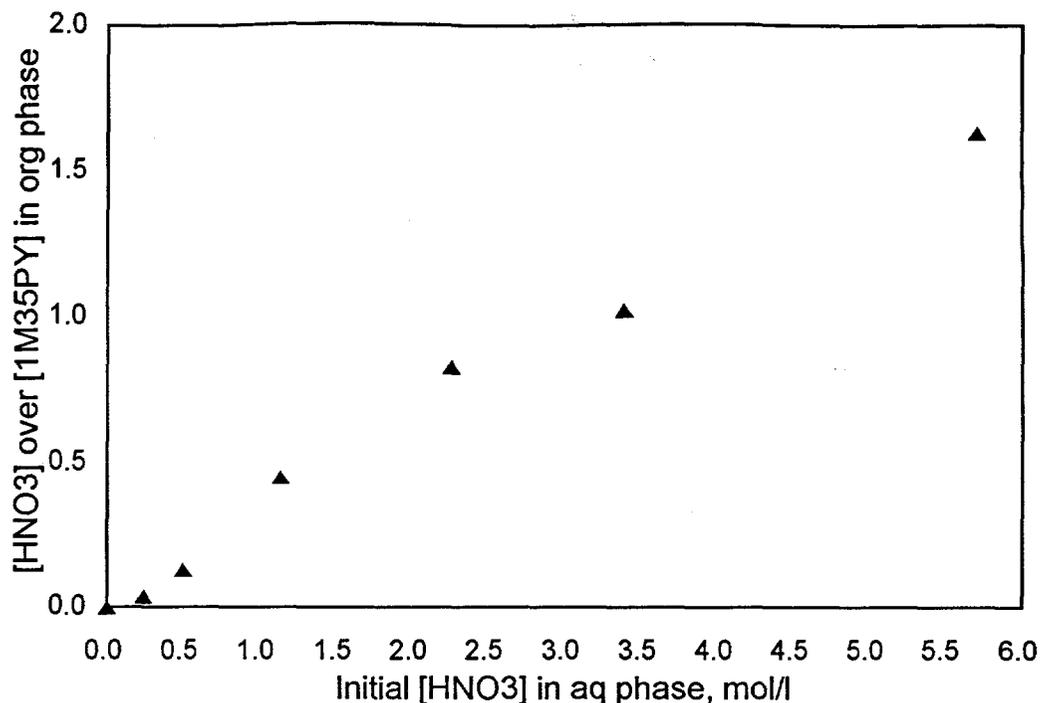


Figure 7. Extraction of HNO₃ by 0.0216M 1M35PY vs aqueous [HNO₃], measurement of HNO₃ was made using UV spectrometry at 300 nm.

Loading Capacity of Thorium by 1M35PY

The slope analysis such as $\log D$ vs $\log[1M35PY]$ gives the stoichiometry of Th⁴⁺ vs 1M35PY in the extraction reaction. The $\log D$ vs [HNO₃], however, did not show a linear relationship because of the competitive reactions between the thorium nitrate complex and nitric acid. Another useful approach to the study of the extraction mechanism is the loading capacity of thorium by the extractant. The following loading experiments have provided both the composition of the extracted species in the organic phase and the information on stoichiometry of the reactions.

In the loading experiments the [1M35PY] in the organic phase was fixed while the [Th⁴⁺] in the aqueous phase was continuously increased until the organic phase was saturated with the thorium nitrate complex. Beyond this point the ratio of [1M35PY] to [Th⁴⁺], and to [NO₃⁻] in the organic phase was constant.

Molar Ratio of Th⁴⁺ to 1M35PY

In Figure 8, among the total 12 points, the first six points were generated spectrometrically, the last six points obtained by titration with 0.0101M EDTA using xylenol orange as indicator and pH 2.3 buffer of CH₂ClCOOH and CH₃COONa. It is seen that the highest concentration of thorium (the level portion of the curve) in the organic phase was approximately 0.01M, while the concentration of 1M35PY was 0.0216M. The molar ratio of Th to 1M35PY was therefore 1:2.

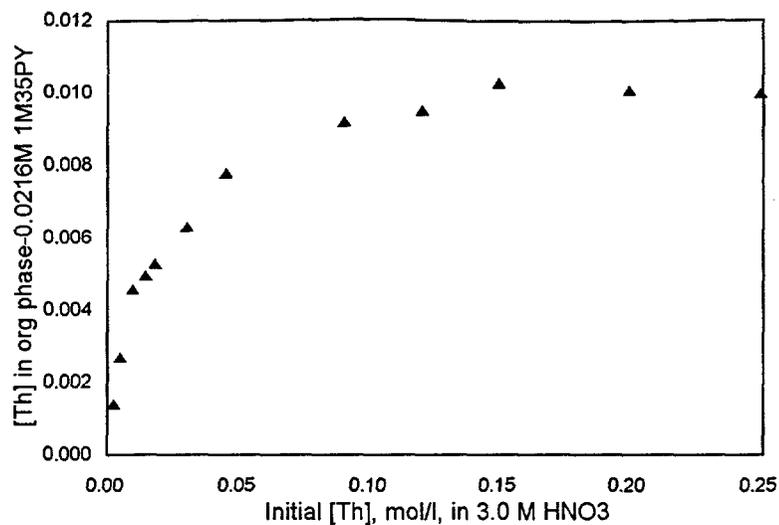


Figure 8. 0.0216M 1M35PY loaded with Th in 3.0M HNO₃ at a phase ratio of 1:1.

Molar Ratio of Nitrate to 1M35PY

To determine the molar ratio of nitrate to 1M35PY in the loaded organic phase, 3 ml of 0.0216M 1M35PY was equilibrated with 3 ml of 0.250M Th(NO₃)₄ and 3.0 M HNO₃ for 4 hours. After centrifugation, the organic phase was stripped with 0.24M HClO₄ and the stripping liquor was analyzed for NO₃⁻ at 300 nm, as illustrated in Figure 9.

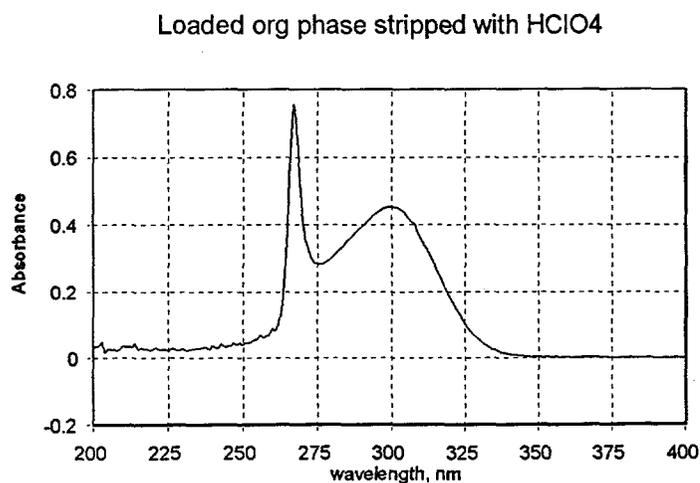


Figure 9. UV spectrum of aqueous phase that stripped Th⁴⁺ from the loaded organic phase.

The duplicate average of absorbance at 300 nm was 0.4467, which was equivalent to 0.0622 M NO_3^- (see the calibration curve in the Experimental section). Therefore the molar ratio of nitrate(0.0622M) to 1M35PY(0.0216M) in the organic phase was 2.9, or approximately 3. The sharp peak at 270 nm was due to trace amount of toluene dissolved in water. This method was verified by checking the complete stripping of the species from the organic phase and by comparing the spectra of pure standard substances (toluene in water, thorium nitrate in nitric acid), which are included in the appendix. In addition, the UV spectra of stripping liquor (HClO_4) for different organic solutions were recorded in Table 8.

Table 8. Absorbance of the stripping liquor at 300nm for different organic phase at phase ratio 1:1.

Curve	organic phase composition	aq. feed solution	Absorbance of stripping liquor	$[\text{NO}_3^-]_{\text{org}}$ or $[\text{HNO}_3]_{\text{org}}$
1	pure toluene	3.0 M HNO_3	0.0183	N/A
2	0.0216 M 1M35PY	3.0 M HNO_3	0.3172	0.0442 M
3	0.0216 M 1M35PY	3.0 M HNO_3 + 0.20M Th^{4+}	0.4416	0.0615 M

The absorbance of the first curve at 300 nm was 0.0183, close to zero. This indicated that nitric acid was not extracted into the pure toluene. The absorbance of 0.0183 was basically the background variation.

The absorbance of 0.3172 of the second curve was equivalent to 0.0442M HNO_3 and NO_3^- , which implied that the composition in the organic phase was $\text{R}_4\text{N}^+\text{NO}_3^- \cdot \text{HNO}_3$ because the total concentration of NO_3^- and HNO_3 was just the double concentration of 1M35PY.

The absorbance of 0.4416 for the third curve showed that the ratio of NO_3^- over 1M35PY was 2.9 or approximately 3. Obviously, the absorbance difference between the second curve and the third curve resulted from the extraction of thorium nitrate complex.

Composition of the Extracted Species in the Organic Phase

The result of the above loading experiments is summarized in Table 9. The overall ratio of Th^{4+} , 1M35PY, and NO_3^- was 1:2:6. Therefore the composition of the complex in the organic phase can be written as $(\text{R}_4\text{N}^+)_2\text{Th}(\text{NO}_3^-)_6$.

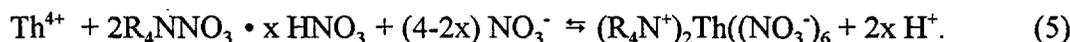
Actually, from the molar ratio of $\text{Th}^{4+} : 1\text{M35PY} = 1:2$, the composition of the complex in the organic phase could be derived by charge balance to be $(\text{R}_4\text{N}^+)_2\text{Th}(\text{NO}_3^-)_6$. Now the experiment indicated each mole of the complex had only 6 moles of NO_3^- or HNO_3 (if any). This ratio ruled out the possibility of solvated molecules such as $(\text{R}_4\text{N}^+)_2\text{Th}(\text{NO}_3^-)_6 \cdot \text{HNO}_3$.

Table 9. Molar ratio of thorium, 1M35PY, and NO_3^- in the organic phase.

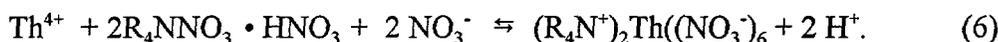
Species	Relative molar ratio	Relative molar ratio	Overall molar ratio
Thorium	1		1
1M35PY	2	1	2
NO_3^-		3	6

Stoichiometric Equation for the Extraction of Thorium

Based on the composition of the complex $(\text{R}_4\text{N}^+)_2\text{Th}(\text{NO}_3^-)_6$ and the fact that the slope of $\log D$ vs $\log[1\text{M35PY}]$ is 1.92. We can write the stoichiometric equation for the extraction of thorium.



It was assumed in Equation (5) that different amount of nitric acid was extracted by 1M35PY. The value of x , which depends on the concentration of nitric acid equilibrated with 1M35PY, can be found in Table 6 or Table 7, and the coefficient $(4-2x)$ becomes predictable at a certain concentration of HNO_3 . For example, if $[\text{HNO}_3] = 3 \text{ M}$, $x = 1$, $4 - 2x = 2$, and Equation (5) is simplified as:



Further Evidence to Support the Extraction Equation

When the concentration of nitric acid was fixed while $[\text{NO}_3^-]$ was increased in the aqueous phase, x was known and the slope of $\log D$ vs $\log[\text{NO}_3^-]$ should correspond to the value of $4-2x$. The results are shown in Figure 10, Figure 11 and Table 10.

In Figure 10, 1M35PY was pre-equilibrated with 0.50M HNO_3 and then it was contacted with thorium solution containing 0.50M HNO_3 and varied concentration of NaNO_3 . The slope of $\log D$ vs $\log[\text{NO}_3^-]$ was 3.87.

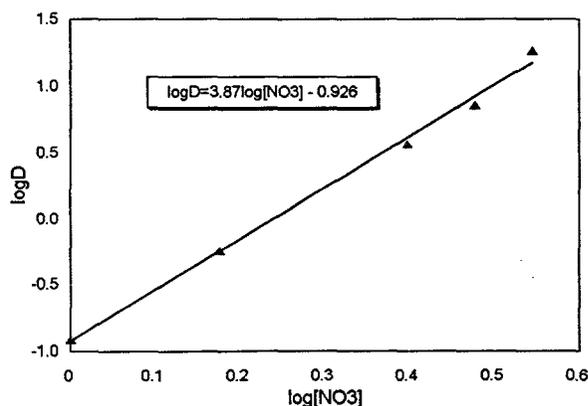


Figure 10. Extraction of thorium with 0.0216M 1M35PY at 0.50M HNO_3 while the total $[\text{NO}_3^-]$ was varied by adding NaNO_3 .

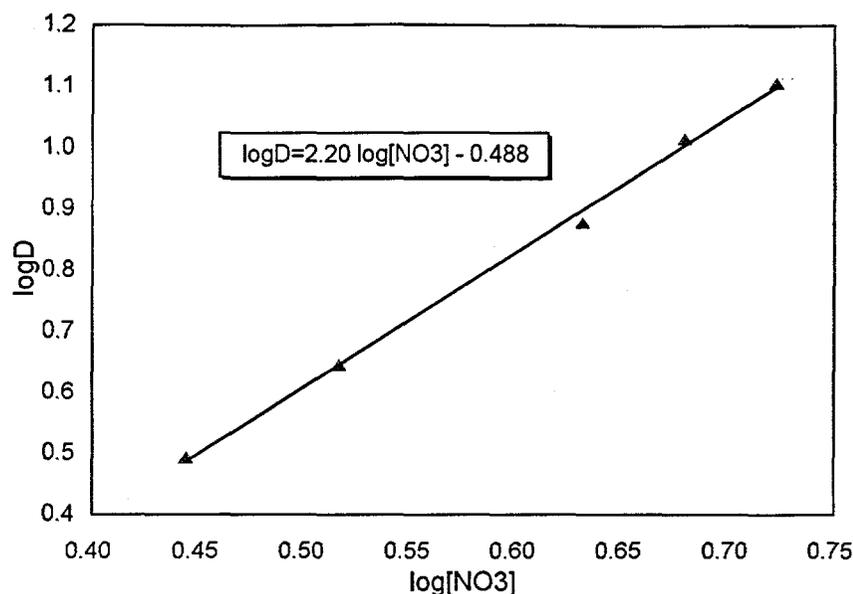


Figure 11. Extraction of thorium with 0.0216M 1M3PY at 2.26M HNO₃ while the total [NO₃⁻] was varied by adding NaNO₃.

In Figure 11, 1M3PY was pre-equilibrated with 2.28M HNO₃ and then it was contacted with thorium solution containing 2.28M HNO₃ and varied concentration of NaNO₃. The slope of logD vs log[NO₃⁻] was 2.20. These slopes are very close to the slopes predicted from Equation (3.2) and Table 6 or Table 7. For example, at 2.26M HNO₃ (the value at 2.28M HNO₃ was not available in the tables), the average value of x in Table 6 and Table 7 is 0.86, then the coefficient of 4 - 2x in Equation (3.2) is 2.28. The actual slope of logD vs log[NO₃⁻] was 2.20, very close to 2.28.

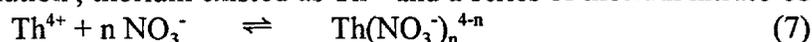
Table 10. Comparison of the actual slopes and the slopes predicted by the extraction equation.

Initial [HNO ₃] _{aq} mol/l	x obtained in acid extraction	predicted slopes (4-2x)	actual slopes of logD vs log[NO ₃ ⁻]
2.28	0.86*	2.28	2.20
0.50	0.13	3.74	3.87

* Average value at 2.26M HNO₃ in Table 6 and Table 3.6.

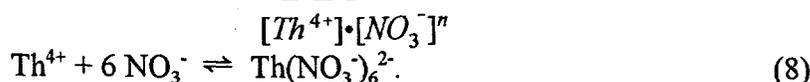
Calculation of Equilibrium Constant

In aqueous solution, thorium existed as Th⁴⁺ and a series of thorium nitrato complexes:



where $n=1\sim 6$, and stability constants $\beta_n = \frac{[Th(NO_3)_n]^{4-n}}{[Th^{4+}] \cdot [NO_3^-]^n}$

For $n=6$,



The distribution ratio (D) measured in the experiments was the ratio of thorium concentration in the organic phase over the total concentration of thorium in the aqueous phase.

$$\begin{aligned} &= \frac{[(R_4N)_2Th(NO_3)_6]}{[Th] + [Th(NO_3)] + \dots + [Th(NO_3)_6]} \quad (9) \\ &= \frac{[(R_4N)_2Th(NO_3)_6]}{[Th](1 + \beta_1[NO_3] + \dots + \beta_6[NO_3]^6)} \\ &= \frac{D_o}{(1 + \beta_1[NO_3] + \dots + \beta_6[NO_3]^6)} \\ &= \frac{D_o}{k} \end{aligned}$$

$$\text{where } D_o = \frac{[(R_4N)_2Th(NO_3)_6]}{[Th]} \quad (10)$$

$$\text{and } k = \frac{1}{(1 + \beta_1[NO_3] + \dots + \beta_6[NO_3]^6)} \quad (11)$$

The equilibrium constant K_{ex} is expressed as

$$\begin{aligned} K_{ex} &= \frac{[(R_4N)_2Th(NO_3)_6][H]^{2x}}{[Th][R_4NNO_3 \cdot xHNO_3]^2[NO_3]^{4-2x}} \\ &= \frac{D_o[H]^{2x}}{[Th][R_4NNO_3 \cdot xHNO_3]^2[NO_3]^{4-2x}} \\ &= \frac{kD[H]^{2x}}{[Th][R_4NNO_3 \cdot xHNO_3]^2[NO_3]^{4-2x}} \quad (12) \end{aligned}$$

As is shown in Equations (11) and (12), if β_n is known for $n=1\sim 6$, the equilibrium constant K_{ex} can be calculated. Unfortunately, even for $n=1\sim 4$, the stability "constant" β_n was not constant at different conditions or from different literature sources (17-19). However, if $[NO_3^-]$ was fixed, k would be assumed to be a constant, then a conditional equilibrium constant K could be defined as $K = \frac{K_{ex}}{k}$. K corresponds to that condition, and can be calculated. For example, at 5.71M HNO_3 and 0.0216M 1M35PY, $D=4.39$, $x=1.63$ (from Table 3.6), $2x=3.26$, $4-2x=0.74$, the conditional constant K is calculated as follows:

$$K = \frac{D[H]^{2x}}{[R_4NNO_3 \cdot xHNO_3]^2 [NO_3]^{4-2x}}$$

$$= \frac{4.39 \times 5.71^{3.26}}{0.0216^2 \times 5.71^{0.74}}$$

$$= 7.6 \times 10^5 .$$

Comparison of 1M35PY with Aliquat-336 for the Extraction of Thorium

A comparison of 1M35PY with Aliquat-336 was made for the extraction of thorium versus $[HNO_3]$, as shown in Figure 12. The highest D (distribution ratio) of thorium by 1M35PY was a little higher than that by Aliquat-336. For Aliquat-336, the highest D appeared at 2.26 M HNO_3 , beyond which D dropped down because of the competition of nitric acid extraction. This is in agreement with the result in reference (13), where the highest D of thorium by Aliquat-336 in xylene appeared at about 3M HNO_3 . For 1M35PY, D continuously increased with up to 5.5M HNO_3 . Somewhere beyond 5.5M HNO_3 , D would be expected to drop as in Aliquat-336. When the $[HNO_3]$ was 0.24M, Aliquat-336 still extracted significant amount of thorium but 0.24M HNO_3 could strip thorium from 0.0216M 1M35PY as shown in Table 4. So the overall distribution ratio curve of 1M35PY vs. $[HNO_3]$ was similar to that of Aliquat-336 but the former was shifted to higher $[HNO_3]$ by 1 or 2 molar. This shows that the competitive extraction of HNO_3 against the thorium nitrate complex was stronger in Aliquat-336 than in 1M35PY.

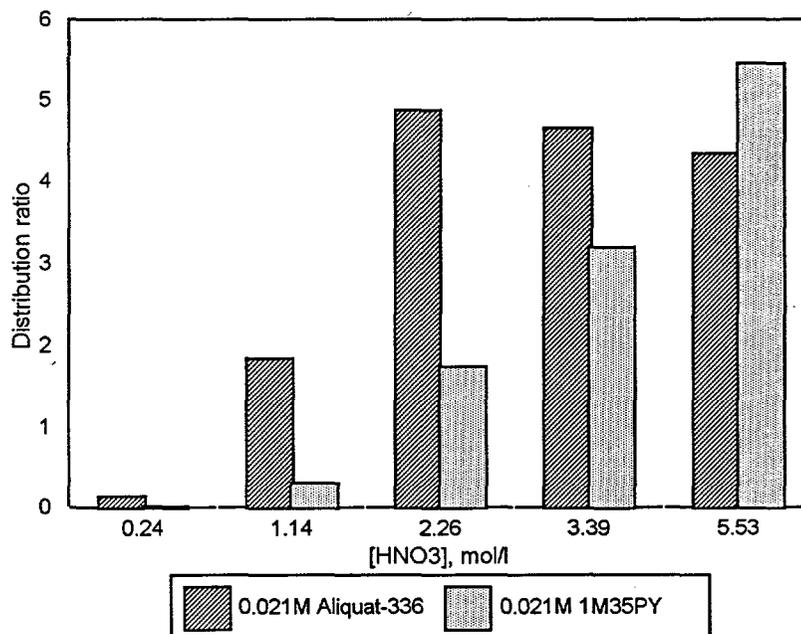


Figure 12. Comparison of Aliquat-336 with 1M35PY for the extraction of thorium at phase ratio 1:1, both extractants were converted to the nitrate form before extraction.

Extraction of Uranium by the Pyridinium Compounds

In aqueous HNO_3 solution, uranyl nitrate dissociates extensively. The stability constant K_1 of $\text{UO}_2(\text{NO}_3)^+$ is ca. 0.2, and K_2 of $\text{UO}_2(\text{NO}_3)_2$ is negligible (20). Thus the extraction of UO_2^{2+} in nitric acid is expected to be poor. The experimental data are shown in Figure 13 and Table 11.

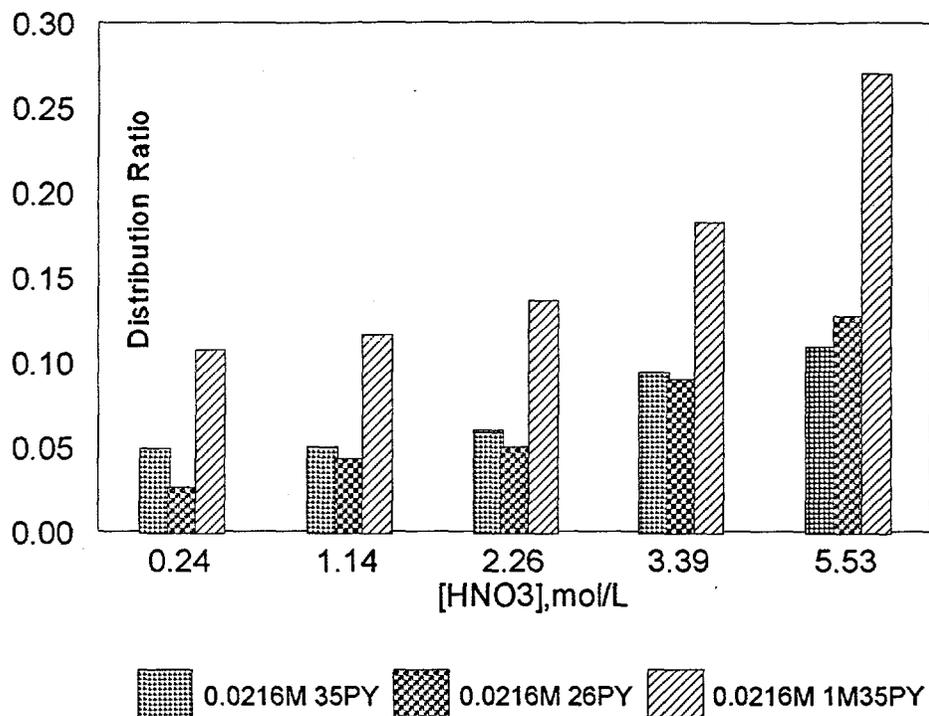


Figure 13. Extraction of UO_2^{2+} by the three pyridiniums vs $[\text{HNO}_3]$

Table 11. Extraction of UO_2^{2+} with 0.0216M Pyridinium nitrates versus $[\text{HNO}_3]$.

$[\text{HNO}_3]$ mol/L	Distribution Ratio		
	35PY	26PY	1M35PY
0.24	0.049	0.026	0.107
1.14	0.050	0.043	0.116
2.26	0.060	0.050	0.136
3.39	0.094	0.090	0.182
5.53	0.109	0.127	0.270

Extraction of Uranium Versus the Ratio of $[\text{NaNO}_3]/[\text{HNO}_3]$

To increase the extraction yield of uranyl, the concentration of HNO_3 was fixed at 0.01M (too dilute acid may cause hydrolysis of uranyl) and NaNO_3 was varied from 0.5M to 4 M. The duplicate results are shown in Table 12 and Figure 14 .

Table 12. Extraction of uranyl nitrate with 0.0216M 1M35PY by fixing $[\text{HNO}_3]$ at 0.01M and increasing $[\text{NaNO}_3]$.

$[\text{NaNO}_3]$, mol/l	Distribution 1	Distribution 2	Average Distribution
0.5	0.03	0.022	0.026
1.0	0.067	0.100	0.084
2.0	0.256	0.293	0.279
3.0	0.836	0.931	0.884
4.0	2.65	2.52	2.58

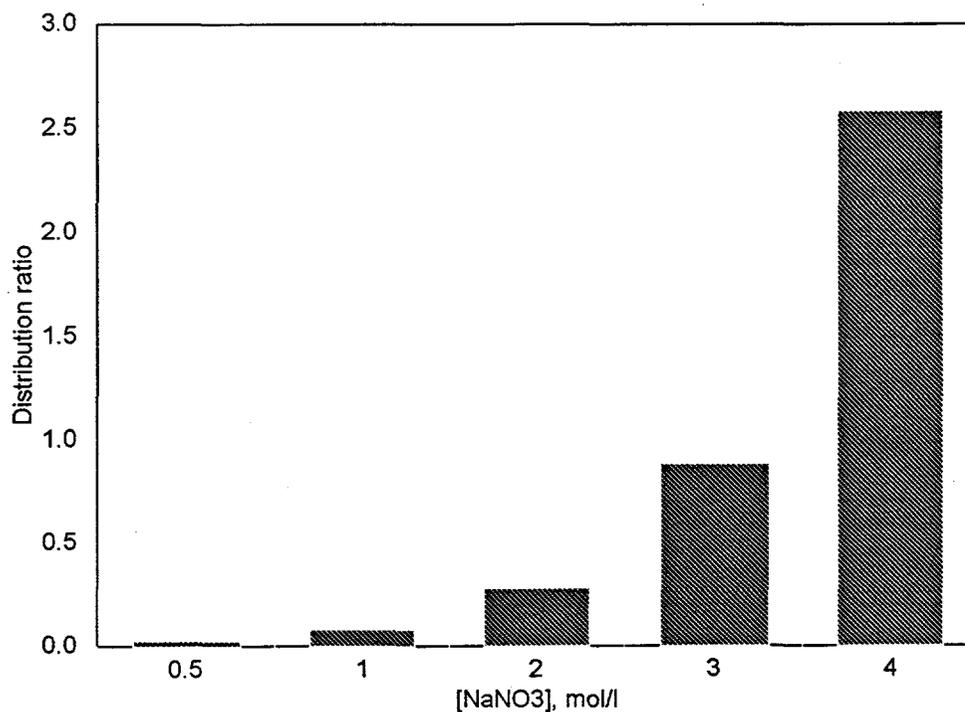


Figure 14. Extraction of uranyl with 0.0216M 1M35PY by fixing $[\text{HNO}_3]$ at 0.01M and increasing the concentration of NaNO_3 , phase ratio 1:1.

Extraction of Eu^{3+} with 0.0216M 1M35PY

Like uranyl nitrate complexes, the stability constants β_n of $\text{Eu}(\text{NO}_3)_n^{3-n}$ are small (21). The distribution ratio of Eu^{3+} from 0.24M to 5.6M HNO_3 was less than 0.0066. At 5.6M HNO_3 , the distribution ratio was 0.0028. Even when the $[\text{HNO}_3]$ was fixed at 0.01M and the $[\text{NaNO}_3]$ was increased to 4.9M, the distribution ratio of europium by 1M35PY was still less than 0.03, as shown in Figure 15. This would make it possible to remove thorium and uranyl (both are alpha particle emitters) from $\text{HNO}_3/\text{NaNO}_3$ solution while europium and other similar ions (most are gamma emitters) remain in the solution.

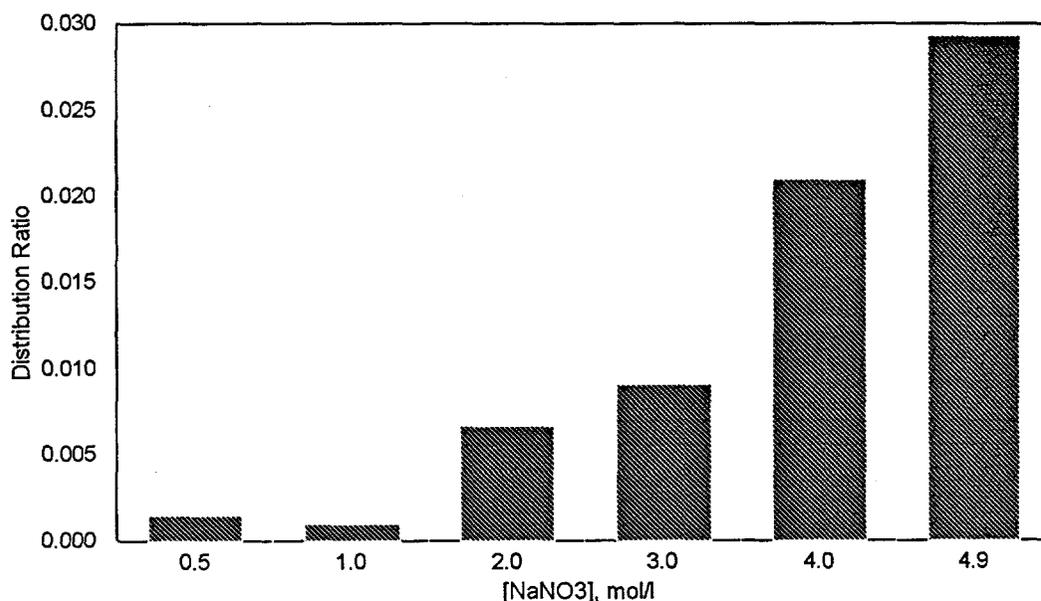


Figure 15. Extraction of $^{152-154}\text{Eu}^{3+}$ with 0.0216M 1M35PY at fixed a $[\text{HNO}_3]$ of 0.01M and varied $[\text{NaNO}_3]$.

Separation of Th^{4+} , UO_2^{2+} , and Eu^{3+} with 1M35PY

The distribution ratios of Th^{4+} , UO_2^{2+} , and Eu^{3+} by 0.0216M 1M35PY are summarized in Table 13 and Table 14. The separation factors (defined as the ratio of distribution ratios of two metals at the same conditions) have been calculated.

Table 13. Separation of Th^{4+} , UO_2^{2+} , and Eu^{3+} by 0.0216M 1M35PY at $5.6 \pm 0.1\text{M HNO}_3$. Separation factor $\alpha_{\text{Th/U}} = 21$, $\alpha_{\text{U/Eu}} > 41$

Metal ions	Distribution ratio	percent extraction
Th^{4+}	5.8	85%
UO_2^{2+}	0.27	21%
Eu^{3+}	0.0028	0.27%

Table 14 Extraction of Th^{4+} , UO_2^{2+} , and Eu^{3+} by 0.0216M 1M35PY at 0.01M HNO_3 and 4.0M NaNO_3 . Separation factor $\alpha_{\text{Th/U}} = 21$, $\alpha_{\text{U/Eu}} > 41$

Metal ions	Distribution ratio	percent extraction
Th^{4+}	$\gg 22^*$	$\gg 96\%$
UO_2^{2+}	2.58	72%
Eu^{3+}	0.021	2.1%

* D at 0.01M HNO_3 and 4.0M NaNO_3 was estimated.

The results indicate that the thorium can be separated from uranium and europium at 5.6M HNO_3 . When $[\text{HNO}_3]$ was decreased and $[\text{NaNO}_3]$ was increased, thorium and uranium can be co-extracted while europium is still not extracted.

Radiation Evaluation of 1M35PY

Since 1M35PY is expected to extract radioactive nuclides in highly radioactive environment, its resistance to radiation damage is an important index of its properties. The following samples of 0.10 M 1M35PY were converted to the nitrate form and were irradiated for different time periods, then the extraction efficiency for thorium was compared before and after the radiation, as shown in Table 15. It is seen that after the irradiation at 40 roentgens/min for up to 48 hours there were not any observable changes in the extraction capability of 0.1M 1M35PY.

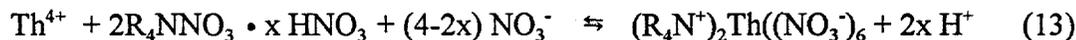
Table 15. Radiation tests of 0.10 M 1M35PY for the extraction of thorium. The initial aqueous phase was 1.672×10^{-4} M Th + 2.28M HNO₃ + 2.50M NaNO₃. Extraction was done at phase ratio 1:1, shaken at 180 rpm for 1 hour.

vial number	composition in the vial	radiation dose	[Th] _{org} × 10 ⁵ mol/l	extraction efficiency %
original	0.10M 1M35PY + 2.28M HNO ₃	zero	16.49	98.6
A	0.10M 1M35PY + 2.28M HNO ₃	40 R/min 8 hours	16.51	98.7
B	0.10M 1M35PY + 2.28M HNO ₃	40 R/min 24 hours	16.43	98.3
C	0.10M 1M35PY + 2.28M HNO ₃	40 R/min 48 hours	16.54	98.9
D	only 0.10M 1M35PY	40 R/min 8 hours	16.81	100
E	only 0.10M 1M35PY	40 R/min 24 hours	16.67	99.7
F	only 0.10M 1M35PY	40 R/min 48 hours	16.81	100

CONCLUSIONS

The thorium extraction efficiency by the three pyridinium nitrates was in the order of 1M35PY \gg 26PY $>$ 35PY. The extraction efficiency of Th^{4+} , UO_2^{2+} , and Eu^{3+} by 1M35PY was in the order of $\text{Th}^{4+} \gg \text{UO}_2^{2+} \gg \text{Eu}^{3+}$.

The loading capacity experiments have shown that the composition in the organic phase is $(\text{R}_4\text{N}^+)_2\text{Th}(\text{NO}_3)_6$, where R_4N^+ denotes the 1M35PY cation. The overall stoichiometric equation for Th^{4+} extraction can be expressed by the equation:



where x is dependent on the concentration of nitric acid in the pre-equilibrium. The extraction of HNO_3 is in competition with the extraction of metal ions. Low concentration of HNO_3 and high concentration of NaNO_3 favor the extraction of thorium and uranium. At 5.6M HNO_3 , the separation factor of thorium to uranium was 21, and the separation factor of uranium to europium was 96. When the acidity was decreased, thorium and uranium were co-extracted and europium still remained in the aqueous phase. It is expected that in the sulphate media the extraction of thorium and uranium would be more efficient than in the nitrate media.

A comparison of 1M35PY with Aliquat-336 showed that 1M35PY had a higher tendency toward the extraction of thorium and a lower tendency toward the extraction of HNO_3 . Thorium can be completely stripped from 1M35PY with dilute HNO_3 .

0.10M 1M35PY was irradiated for up to 48 hours at 40R/min without any observed decrease in the extraction efficiency, which indicated that 1M35PY is radiation-resistant. Thus 1M35PY would be a promising extractant in the nuclear waste treatment.

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