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SUBJECT: LIQUID-LIQUID EXTRACTION OF URANIUM AND PLUTONIUM FROM
HYDROCHLORIC ACID SOLUTION WITH TRI(ISO-OCTYL)AMINE
Separation of Uranium and Plutonium from Thorium and Fission Products
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LIQUID-LIQUID EXTRACTION OF URANIUM AND PLUTONIUM FROM
HYDROCHLORIC ACID SOLUTION WITH TRI(ISO-OCTYL)AMINE

Separation of Uranium and Plutonium from Thorium
and Fission Products

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A new and rapid method for the liquid-liquid extraction of uranium and plutonium from hydrochloric acid solution is based on the use of tri(iso-octyl)amine dissolved in xylene or methylisobutylketone. Uranium and/or plutonium are separated from thorium, alkalis, alkaline earths, rare earths, zirconium, niobium, ruthenium and other elements which do not form anionic species under the conditions described. The technique may be used for either tracer or macro quantities of ^{material}uranium. Several practical applications of the method for the separations chemist are proposed.

The need for a rapid and clean separation of uranium and thorium led to the development of the new liquid-liquid extraction technique described in this paper. Several papers have described the extraction of uranium and thorium from nitrate solutions. Generally, the separation of uranium from thorium in these systems is not too effective or is critically dependent on the nitrate salting strength and free acid concentration of the aqueous solution (6). Both thorium and uranium extract with mesityl oxide (11)

* Operated for the A.E.C. by Union Carbide Nuclear Company.

and the use of 2-thenoyltrifluoroacetone is impractical for this separation because the pH dependence for the extraction of uranyl and thorium is very similar (7). One of the more recent uranium extractants, tri-n-butyl phosphate, extracts varying amounts of thorium, depending on the aqueous nitrate salting strength. In fact, this reagent is often used to extract uranium and thorium from fission products (4,8). Uranium can be separated from thorium by extraction into diethyl ether (3). However, it was desirable to find a safer solvent. The separation of uranium and thorium in dilute sulfate solution by the use of long-chain tertiary or secondary amines has been reported (2). However, experience by the writer would indicate that poor selectivity from zirconium and niobium would be effected in the sulfate systems described.

Inasmuch as thorium does not form anionic complexes with the chloride ion, it was reasoned that the extraction of anionic uranyl complexes from hydrochloric acid solution would result in a clean separation of these two elements. The observation that uranium may be extracted efficiently from hydrochloric acid solution with long-chain amines has been noted previously (1,12). With the advent of new-type fuel elements, there has developed an increased interest in the hydrochloric acid system. Therefore, it was decided to investigate this system, primarily for the purpose of finding an effective method for the separation of uranium and thorium but also to study the behavior of the major fission products and several related elements.

The long-chain amine, tri(iso-octyl)amine, was selected for this study since it is cheap, readily available and possesses the desirable properties of low aqueous solubility and high organic solubility. According

to the vendor,* because of the isomeric nature of tri(iso-octyl)amine the exact structure of the molecule cannot be defined. The major constituents are thought to be dimethylhexyls and trimethylpentyls with branching of the alkyl groups starting at least two carbon atoms distance from the nitrogen.

Extraction and Decontamination of Uranium-233 Tracer from Hydrochloric Acid Solution with 5% Tri(iso-octyl)amine-Xylene

The extraction of uranium-233 tracer with 5% tri(iso-octyl)amine-xylene as a function of hydrochloric acid concentration is shown in Figure 1. The procedure used was to extract aqueous solutions of varying hydrochloric acid concentration containing 4×10^4 a c/m/ml of uranium-233 tracer with equal volumes of 5% (w/v) tri(iso-octyl)amine-xylene for two minutes at room temperature (24°C). A high-speed motor stirrer (Palo Laboratory Supplies, New York, N. Y.) with a glass paddle was found to give excellent mixing of the phases. Each phase was analyzed for uranium-233 tracer. Figure 1 indicates that uranium-233 tracer readily extracts with 5% tri(iso-octyl)amine even from dilute hydrochloric acid solution.

The extraction of uranium-233 tracer as a function of time was next investigated. Using the procedure given above and varying the time of extraction of uranium-233 tracer from 7 M hydrochloric acid, it was found that equilibrium was attained rapidly (Table I) in a manner typical of acid-type extractions. An extraction time of two minutes was chosen for all subsequent work.

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Fig.1. EXTRACTION OF URANIUM-233 TRACER WITH 5% TRI(ISO-OCTYL) AMINE - XYLENE FROM HYDROCHLORIC ACID SOLUTION.

Table I

Effect of Time on the Extraction of Uranium-233 Tracer
with 5% Tri(iso-octyl)amine-Xylene

<u>Time, min.</u>	<u>Uranium-233 Extracted, %</u>
0.5	99.2
1	99.1
2	99.2

Several experiments were performed to determine the uranium loss due to scrubbing. Equal volumes of 5% tri(iso-octyl) amine-xylene containing 8×10^5 a c/m/ml of uranium-233 were scrubbed for two minutes and, after centrifugation, each phase was analyzed for uranium-233 tracer. Using 4.6 M and 6 M hydrochloric acid scrubs the losses were found to be 0.2% and 0.1%, respectively.

It was found possible to strip the uranium-233 tracer essentially quantitatively from the organic phase by mixing thoroughly for two minutes with an equal volume of either 0.1 M hydrochloric acid, 0.1 M nitric acid or distilled water (Table II). Ammonium hydroxide can also be used to strip and precipitate the uranium.

The extraction of thorium-230 tracer with tri(iso-octyl)amine-xylene was found to be negligible from hydrochloric acid solution (Table III). Further experiments with 1.9 mg/ml of thorium carrier verified the inextractability of thorium. The presence of uranium did not appear to affect the behavior of thorium.

The extraction behavior of the major fission products was investigated in a series of experiments. The procedure used was to extract tracer solutions of various hydrochloric acid concentrations for two minutes with equal volumes of 5% tri(iso-octyl)amine-xylene. After centrifugation, each phase was analyzed. The results (Table IV) may be regarded as conservative since the organic phases were not scrubbed. The extraction of the fission product elements from hydrochloric acid solution is approximately that which would be predicted from known anionic chlorocomplexing studies (9). It can be seen that strontium and trivalent

Table II

Stripping of Uranium-233 Tracer from

5% Tri(iso-octyl)amine-xylene

<u>Stripping Agent</u>	<u>Uranium-233 Tracer Stripped, %</u>
0.1 M HCl	98.9
0.1 M HNO ₃	99.2
Distilled H ₂ O	99.8

Table III

Extraction of Thorium-230 (Ionium) Tracer from Hydrochloric Acid
Solution with 5% Tri(iso-octyl)amine-xylene

<u>HCl, M</u>	<u>Thorium-230 Extracted, %</u>
2.2	0.003
4.5	0.005
6.7	0.010
8.9	0.016
11.1	0.020

Table IV

Extraction of Fission Products from Hydrochloric Acid

Solution with 5% Tri(iso-octyl)amine-Xylene

<u>Element</u>	<u>HCl, M</u>	<u>Tracer Extracted, %</u>	<u>Element</u>	<u>HCl, M</u>	<u>Tracer Extracted, %</u>
Nb-95	2.2	0.3	Sr-85	2.1	0
	4.4	3.1		4.2	0
	4.6	6.2		6.4	0
	4.8	9.5		8.5	0
	5.0	17.4		10.6	0
	6.5	90.2	Ru-106	0.1	82.3
	6.8	96.8		0.2	77.7
	9.0	99.2		1.1	75.0
Zr-95	2.1	0.02		2.1	74.3
	4.2	0.4		4.2	72.5
	6.3	0.7		6.4	69.8
	8.4	89.6		8.5	58.6
	10.5	99.0		10.6	29.4
Eu-152-154	2.2	<0.01			
	4.3	<0.01			
	6.5	<0.02			
	8.7	<0.03			
	10.9	0.05			

rare earths do not extract appreciably from any hydrochloric acid concentration. The extraction of zirconium is negligible from low to intermediate hydrochloric acid concentrations. The extraction of niobium can be rendered slight by using lower concentrations of hydrochloric acid, at which the recovery of uranium is still very efficient (Figure 1). Obviously, greater decontamination can be effected by stripping into 0.1 M hydrochloric acid and reextracting the uranium. Ruthenium exhibited the highest extractability of any fission product tested. However, less than one percent of the original ruthenium-106 tracer accompanied the uranium through the extraction and stripping (0.1 M hydrochloric acid) steps described above. The fact that the extractable ruthenium, perhaps ruthenium (IV), does not strip with 0.1 M hydrochloric acid solution would appear to offer a satisfactory separation of these two elements. However, it is dangerous to predict the behavior of ruthenium tracer and one must test the extraction behavior of any particular solution. The extraction behavior of radiocesium was not studied because it does not form anionic species in hydrochloric acid solution. The extraction behavior of protactinium(V) is quite similar to that of uranium(VI), and the neptunium chemistry is essentially the same as that of plutonium of the same valence state (11). Americium(III) and curium(III) do not extract in this system. Those elements which form anionic complexes at the particular hydrochloric acid concentration used for the extraction of uranium would, of course, extract also. In fact, this offers a rapid method of removing elements such as iron(III), cobalt(II), zinc(II), zirconium(IV), hafnium(IV), vanadium(V), niobium(V), protactinium(V), chromium(VI), molybdenum(VI), uranium(VI,IV), plutonium(VI,IV) and neptunium(VI,V,IV) from thorium in

hydrochloric acid solution. The extraction of iron, vanadium and chromium may be minimized by reduction to the lower oxidation states, if desired.

The data given in this paper refer strictly to the hydrochloric acid system. The presence of other anions may change the extraction characteristics of the various elements.

Extraction of Plutonium-239 Tracer from Hydrochloric Acid

Solution with 5% Tri(iso-octyl)amine-Xylene

From chemical considerations it would be predicted that plutonium(III) would exhibit an extraction behavior similar to that of europium(III) in the system hydrochloric acid -- tri(iso-octyl)amine-xylene. Also, plutonium(IV) would behave approximately like niobium(V) and plutonium(VI) would be very similar to uranium(VI). To maintain plutonium in the hexavalent state, it is necessary to use a holding oxidant. It was found possible to employ potassium dichromate in dilute hydrochloric acid as an oxidant. Since potassium dichromate is appreciably reduced at hydrochloric acid concentrations greater than approximately 5 M, the oxidation and extraction of plutonium was performed in slightly weaker hydrochloric acid solution. Plutonium-239 tracer in 4.8 M hydrochloric acid solution was oxidized by heating in a bath of boiling water for five minutes with various concentrations of potassium dichromate. After cooling to room temperature, the solutions were extracted for two minutes with equal volumes of 5% tri(iso-octyl)amine-xylene. After centrifugation, the phases were analyzed for plutonium-239. Table V indicates that plutonium-239 tracer extracts very efficiently under the conditions described. The separation of plutonium and uranium from most of the fission products would be effective at the acidity used. The decrease in plutonium

Table V

Extraction of Plutonium-239 Tracer from Hydrochloric Acid

Solution with 5% Tri(iso-octyl)amine-xylene

<u>Exp.</u>	<u>HCl, M</u>	<u>K₂Cr₂O₇, M</u>	<u>Pu-239 Tracer Extracted, %</u>	<u>Remarks</u>
1.	4.8	0	60.8	---
2.	4.8	0.09	1.2	organic phase cloudy. slight ppt. in aqueous phase.
3.	4.8	0.05	83.2	some reduction of K ₂ Cr ₂ O ₇ .
4.	4.8	0.02	98.9	clear phases - very slight amount of K ₂ Cr ₂ O ₇ reduction.
5.	4.8	0.01	99.8	clear phases. no K ₂ Cr ₂ O ₇ reduction.
6.	6.4	0.01	99.8	

extraction at higher concentrations of potassium dichromate may be related to dichromate complexing of the plutonium-239 tracer. Dichromic acid was observed to extract with the plutonium(VI) tracer. It was found that the plutonium tracer readily stripped into 0.1 M hydrochloric acid solution similar to the behavior of uranium. Since the dichromic acid did not appear to strip, this offers an effective separation from plutonium and uranium. Obviously, one may effect a separation of uranium from plutonium in this system by maintaining the latter in the trivalent state.

The behavior of ruthenium tracer under the conditions given above for the oxidation and extraction of plutonium tracer should be noted here. Experiments using ruthenium-106 tracer under the conditions described in Table V (experiment 5) indicated that approximately 11% of the original ruthenium-106 tracer followed through the uranium extraction and stripping steps (0.1 M hydrochloric acid). Therefore, the separation of ruthenium from plutonium may be more difficult than from uranium. No study to increase the ruthenium decontamination was performed at this time since it was beyond the scope of this work.

Extraction of Macro Uranium from Hydrochloric Acid Solution
with Tri(iso-octyl)amine

Experiments were performed to determine the behavior of macro quantities of uranium in the hydrochloric acid -- tri(iso-octyl)amine-xylene system. The same extraction procedure used for the uranium-233 tracer study was employed, except milligram quantities of uranium were used with the uranium-233 tracer. All phases were analyzed for uranium-233 by alpha counting and ionic analyses for uranium. Table VI indicates that excellent extraction of macro uranium is possible, even from rather dilute hydrochloric acid solution.

As the uranium concentration was increased the formation of a yellow uranium-containing oil was observed to collect at the bottom of the xylene phase. At higher uranium concentrations a gel formed at the interface. This phenomenon could be prevented by (1) increasing the hydrochloric acid concentration of the original aqueous phase (Table VI), (2) the addition of acetone in the original aqueous phase (Table VI), (3) the use of solvents more polar than xylene (Table VII), (4) increasing the concentration of tri(iso-octyl)amine in xylene. (For instance, when experiment 13, Table VI was repeated using 20% tri(iso-octyl)amine-xylene, no gel formation occurred and 99.1% of the uranium extracted). Since the phases are clearly defined at uranium concentrations as high as approximately 10 mg/ml, it is quite simple to separate them.

While xylene was favored as the solvent for tri(iso-octyl)amine because of its relatively greater resistance to chemical attack and radiation, several other solvents were tested briefly (Table VII). Methylisobutylketone was found to exhibit the best mechanical behavior of the solvents tested and gave almost as efficient extraction of uranium as xylene. At higher aqueous concentrations of uranium, methylisobutylketone may be used to dilute the xylene as solvent for tri(iso-octyl)amine and eliminate gel formation (Tables VII, VIII). Similarly, methylisobutylketone may be used to dilute solvents like amsco, kerosene or carbon tetrachloride to effect good mechanical behavior of the phases. At higher concentrations of uranium, 20% tri(iso-octyl)amine in methylisobutylketone was found to be a very effective extractant (Table VIII). Thus, in the range of approximately 15 mg/ml of uranium in 9 M hydrochloric acid solution, excellent extraction and phase behavior was observed using 20% tri(iso-octyl)amine-xylene.

Table VI

Extraction of Macro Uranium from Hydrochloric Acid Solution
with 5% Tri(iso-octyl)amine-xylene

Exp.	HCl, M	Uranium Concentration mg/ml	Uranium Extracted, %	Remarks
1.	4	1	97.9	Excellent phase behavior.
2.	6	1	99.1	" " "
3.	6	2	99.0	" " "
4.	6	3.9	99.0	Yellow oil containing the uranium observed at bottom of organic phase.
5.	6	7.8	98.2	" " "
6.	6	11.7	87.6	" " "
7.	7.6	11.7	94.4	Phase behavior much better than in Exp. 6.
8.	4.8*	10.6	93.6	Excellent phase behavior.
9.	9	2.1	99.0	" " "
10.	9	4.2	98.8	Yellow oil containing the uranium at bottom of organic phase.
11.	10	4.2	98.1	Excellent phase behavior.
12.	9	8.4	97.9	Clear phases - yellow oil at interface.
13.	9	16.8	82.7	Gel at interface.

* 30 volume percent acetone present in the original aqueous phase.

Table VII

Extraction of Uranium from Hydrochloric Acid Solution with
5% Tri(iso-octyl)amine in Various Solvents

Solvent	Uranium Extracted, %	Remarks
1. Diisobutylcarbinol	59.0	Clear phases, organic viscous.
2. Diisopropylketone	94.7	Slight amount yellow oil at interface.
3. Methylisobutylketone	93.5	Excellent phase behavior.
4. Carbon Tetrachloride	94.7	Yellow gel at interface.
5. Amsco 125-82	99.0	Yellow gel at interface.
6. Xylene	97.9	" " " "
7. Xylene- methylisobutylketone (1:1)	97.0	v. slight amount of solid at interface.
8. Xylene- methylisobutylketone (4:1)	97.4	small amount of solid at interface.

Each aqueous phase contained 8.4 mg/ml of uranium in 9 M hydrochloric
acid before extraction.

Table VIII

Extraction of Macro Uranium from 9 M Hydrochloric Acid Solution
with 20% Tri(iso-octyl)amine in Various Solvents

Uranium Concentration mg/ml	Solvent	Uranium Extracted, %	Remarks
15.1	Xylene	99.2	Excellent phase behavior.
30.2	Xylene	99.0	Heavy liquid at interface.
"	Methylisobutylketone	98.5	Excellent phase behavior.
"	Xylene-methylisobutylketone (1:1)	99.0	Slight amount solid at interface.
45.3	Xylene	97.4	Gel at interface.
"	Methylisobutylketone	97.5	Excellent phase behavior.
"	Xylene-methylisobutylketone (1:1)	98.1	Small amount solid at interface.
60.4	Xylene	95.6	Heavy gel at interface.
"	Methylisobutylketone	94.4	Excellent phase behavior.
"	Xylene-methylisobutylketone (1:1)	95.9	Slight amount solid at interface.

At higher concentrations of uranium excellent extraction occurred but a gel formed at the interface. The use of 20% tri(iso-octyl)amine-methylisobutylketone was found quite satisfactory using original aqueous phase concentrations of 9 M hydrochloric acid containing 60.4 mg/ml of uranium. The capacity of the 20% tri(iso-octyl)amine - methylisobutylketone was not determined, but analyses indicated that greater than 57 mg/ml could be loaded into the organic phase without gel formation or other mechanical difficulty.

Since the long-chain tertiary amines are excellent acid extractants, several experiments were performed in which tri(iso-octyl)amine-xylene, previously saturated with hydrochloric acid, was used. No difference in the extraction of tracer or macro uranium was observed. This fact may be useful to the separations chemist interested in recycling the hydrochloric acid - loaded solvent.

General Applications to Metal Separations

The method discussed in this paper offers some practical applications for the separations chemist. Several of these are cited below.

1. Rapid separations for the analytical chemist: The rapid separation of uranium and/or plutonium in hydrochloric acid solution from thorium (UX_1), alkalis, alkaline earths, rare earths, zirconium, niobium, ruthenium enables the analytical chemist to eliminate these interferences in specific determinations and purifications of uranium or plutonium.

2. Potential uses in hydrometallurgical processes:

a) Recovery of uranium from hydrochloric acid solutions in various ion exchange and liquid-liquid extraction processes currently in use (5) for ore processing.

Thus, the necessity of converting from chloride to nitrate solution could be avoided, and impurities such as zirconium, titanium, and thorium which tend to load the phosphate type extractants could be eliminated.

b) Recently-developed hydrochloric acid dissolution techniques for new-type nuclear fuel elements produce solutions from which uranium and plutonium may be extracted as chlorides at room temperature from the fission products and, particularly, from macro quantities of zirconium.

c) It appears that it is possible to effect a much greater extraction of uranium and plutonium from dilute hydrochloric acid solution in the amine system than is possible in the tri-n-butyl phosphate system (10). This fact enables the separations chemist to accomplish greater decontamination of uranium and plutonium from zirconium and niobium without resorting to the use of chloride salts, a technique which aggravates the present waste disposal problem.

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