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Section B

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The Solvent Extraction of Pu(IV) by
Trifluoroacetylacetone

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J. C. Reid

January 15, 1945

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Abstracts

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I. The Solvent Extraction of Pu(IV) by Trifluoroacetylacetone (TFA).

Certain variables of the extraction step of the proposed solvent extraction process using TFA have been investigated. The extraction of Pu(IV) by TFA in benzene was found to vary with the time of shaking of the benzene and aqueous layers. Initially the extraction coefficient into benzene rose to a maximum within one or two minutes after which it rapidly fell off to 1/10 to 1/5 of its peak value. It was established that the drop from this peak value was due to some change in the TFA and not of the Pu(IV). After 15-20 minutes of shaking, the extraction coefficient is relatively constant except that a very slow reduction of Pu(IV) to Pu(III) was observed. Reproducible values of the extraction coefficient were determined under a variety of conditions as a guide to the selection of favorable extraction conditions.

II. The Behavior of TFA in Water Solutions.

The hydrolysis of TFA in alkaline solution is described. In acid solution the TFA appears to set up a reversible equilibrium with some other substance which has not been identified.

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I. The Solvent Extraction of Pu(IV) by

Trifluoro-acetylacetone (T.F.A.)

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H. W. Crandall and J. R. Thomas

In CN-2486 Calvin proposed a liquid-liquid extraction method for use as an extraction decontamination process for plutonium. The extraction procedure consists of selectively extracting Pu(IV) as a non-ionized chelate compound of TFA which is soluble in organic solvents immiscible with water. In CN-2486 preliminary results were presented with respect to the extracting power of TFA in benzene for Pu(IV) and the dependence of the extraction coefficient E upon the acidity of the water layer and the TFA concentration in the benzene layer. Further, extraction coefficients were determined in $\text{UNH-Na}_2\text{SO}_4$ solutions.

Since these preliminary experiments were reported it has been observed that the extraction coefficient is markedly dependent upon the time of contact, i.e. time of vigorous shaking of the aqueous and organic solvent layers. In Figure 1, a plot of E against time of shaking is shown. The shaking was 300 vibrations per minute with 1/2 inch amplitude on a mechanical shaker.

The curves shown in Figure 1 may be separated into three components. The initial rapid rise to the peak may be interpreted as the formation of the Pu(IV) chelate compound and its diffusion into the benzene. The rapid drop from the peak may be interpreted as the setting up of some moderately rapid equilibrium which is complete at the break of the curve. The slight slope of the curves at longer times is due to some slower process different from those determining the shape of the curves at short times of shaking.

To ascertain whether the change responsible for the rapid drop from the peak is due to the TFA or to some change in the nature of the plutonium itself, the following experiment was performed. A phase consisting of TFA in benzene was shaken with an aqueous phase 0.5 M in HNO_3 for approximately three hours before any plutonium was added. At the end of the shaking period Pu(IV) tracer was added and the extraction coefficient determined after shaking for one minute. This result is to be compared with the value of the extraction coefficient obtained in a separate experiment with 30 seconds shaking of a 0.5 M nitric acid solution containing Pu(IV) in the presence of a fresh TFA benzene layer. The results are shown in Table 1. All experiments performed were done with volumes of 10 cc benzene layer and 20 cc aqueous layer.

$E = \frac{(\text{Pu(IV)})_B}{(\text{Pu}_W)}$ the ratio of the concentrations of plutonium in

the benzene layer divided by the concentration of plutonium in the aqueous layer.

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Figure 1. Variation of E with Time of Shaking

Conditions: 20 ml of 0.5 N HNO_3
10 ml benzene

○ 0.7 ml TFA
◇ 0.4 ml TFA

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Table 1

The Effect of Shaking on the Extracting
Power of TFA for Pu(IV)

Conditions: 10 ml benzene layer
20 ml aqueous layer, 0.5 M HNO₃

Experiment	ml TFA	Time of Shaking in absence of Pu	Time of shaking in presence of Pu	E
I	0.2	0	30 sec.	8.0
II	0.2	3 hrs.	1 min.	0.1
II Cont'd	0.2 Add'l	No Additional	1 min. after fresh TFA was added	2.3
			3 min. after fresh TFA was added	1.1

To the same benzene layer that extracted Pu(IV) relatively poorly (the second experiment of Table 1), a fresh portion of TFA was added and the layers were shaken for one minute and the extraction coefficient measured. The layers were shaken for two minutes more and the extraction coefficient was again determined.

As may be seen from the results shown in Table 1, the extracting efficiency of the TFA was greatly reduced by the preliminary treatment of shaking, but the plutonium was in an extractable condition since the addition of fresh TFA caused the extraction coefficient to increase by a large factor. The fact that the extraction coefficient falls off with two minutes of further shaking of the layers after the addition of the fresh TFA indicates that it is again falling off from its peak value.

It was suggested that impurities in the commercial benzene used were causing the change in the extracting power of the TFA. Highly purified, thiophene free benzene was substituted for the commercial benzene in an experiment duplicating one of those shown in Figure 1. No change in the shape of the curve was noted. To test the effect of the nitric acid on the extracting power of TFA, a duplicate experiment was performed substituting hydrochloric acid for nitric acid. No significant difference in the behavior of the extraction coefficient with time of shaking was observed.

In order to determine in which phase the change in the character of the TFA was occurring experiments IV and V were performed. In experiment IV TFA was allowed to stand in 0.5 M nitric acid overnight after which benzene and Pu(IV) tracer were

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added and the extraction coefficient of the Pu(IV) was determined. In experiment V TFA was allowed to stand overnight in benzene after which 0.5 M nitric and Pu(IV) tracer were added and the extraction coefficient of the Pu(IV) was determined. The results appear in Table 2.

Table 2

The Effect of Standing in Nitric
Acid and Benzene on the Extracting Power of TFA

Conditions: 10 ml benzene
20 ml 0.5 M HNO₃

Experiment	ml TFA	Time TFA in Solution	Time of Shaking after Addition of Pu(IV)	E
IV	0.20	12 hours (acid)	30 sec.	0.05
V	0.20	12 hours (benzene)	30 sec.	8.0

The results indicate that TFA undergoes some change upon standing in the acid solution which results in a large drop in the extracting power of the TFA. The standing in benzene had no effect upon the extracting power of the TFA. This change is believed to be the factor causing the rapid drop of the extraction coefficient from its peak value with increasing shaking time as illustrated by the second region of the curves shown in Figure 1.

The third region of the same curves is apparently a slow reduction of plutonium to the +3 oxidation state. This was first suspected from the following experiments. Plutonium, initially in the +4 oxidation state, was allowed to remain in the TFA-benzene-acid system for a shaking period of 10-12 hours. At the end of that time the Pu distribution was determined. Immediately thereafter a fresh increment of TFA was added to the benzene and the new plutonium distribution was determined. After this a new increment of Pu(IV) activity was added and the resulting distribution was determined. The results are listed in Table 3.

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Table 3

Evidence of Reduction of Pu(IV) by
TFA

Conditions: 10 ml benzene
20 ml 0.5 M HNO₃

Experimental Conditions	ml TFA	Time of Shaking	E
---	0.2	10-12 hours	0.1
Fresh TFA added	0.4	1 min.	2.5
Fresh Pu(IV) added	0.4	2 min.	6.7

From the results it appears that the Pu(IV) was changed after the 10-12 hour shaking so that it was not as extractable as the fresh Pu(IV) that was added. Reduction of plutonium to the +3 oxidation state is the simplest explanation of these results.

A further experiment performed by W. H. Reas conclusively showed that TFA, its decomposition products, or equilibrium products can reduce Pu(IV) to Pu(III). Reas measured the lines in the absorption spectrum of Pu(IV) in a 0.5 M nitric acid solution with one milliliter of TFA in 10 ml of solution. The spectrum was different from the spectrum of Pu(IV) in 0.5 M nitric acid alone. The difference was believed to be due to the formation of some complex ion of Pu(IV) with TFA or one of its decomposition or equilibrium products. After standing for five days the spectrum appeared about the same. However, after two weeks the spectrum corresponded to that of Pu(III) in nitric acid. While this evidence proves that reduction occurs, none of the experiments performed to date give any quantitative measure of the rate of reduction except to show that it is slow relative to the other processes involved in the systems that have been investigated. The rate of reduction of plutonium as measured by the slopes in the third region of the curves in Figure 1 appears to vary roughly with the amount of plutonium in the water layer and one measurement in 0.5 M nitric acid where the extraction coefficient was 5 showed 12.8 percent reduction in one hour of shaking. The rate of reduction of Pu(IV) is undergoing further study at the present time.

After it became apparent that the T F A was involved in a reversible equilibrium (from the work of Reid reported in Section II of this report) the variation of the extraction coefficient with HNO₃, TFA, UNH, and Na₂SO₄ concentrations was studied. The samples were all shaken for 1-1/2 hours which allowed ample time for the TFA

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equilibrium to be established. To eliminate any possible effect of reduction, the Pu(IV) activity was always added after the 1-1/2 hours of shaking and the measurement was made immediately following its addition. The results are shown in Table 4. Each single result represents the average of at least two duplicate determinations. The duplicate results reproduced each other within ten percent.

Table 4

Variation of E with Extraction Variables

Conditions: 10 ml benzene
20 ml aqueous layer

ml TFA	HNO ₃ moles/l	Na ₂ SO ₄ moles/l	UO ₂ (NO ₃) ₂ moles/l	NaNO ₃ moles/l	E
0.70	0.50				22-20
0.50	0.50				11.5
0.40	0.50				5.6
0.30	0.50				2.9
0.20	0.50				0.3
0.30	0.25				21-23
0.20	0.25				8.5
0.10	0.25				0.92
0.30	0.75				0.51
0.30	1.00				0.15
0.30	0.638	0.5			0.018
0.30	0.334	0.1			0.075
0.30	0.268	0.02			0.18
0.30	0.50		0.8		0.46
0.30	0.50		0.5		0.84
0.30	0.50		0.1		2.2
0.3	0.50	0.1	0.8		0.27
0.3	0.50	0.5	0.8		0.081
0.3	0.50			1.6	0.98

When Na₂SO₄ was added the free H⁺ concentration was adjusted to be 0.25 M in each case and the calculated free sulfate ion concentration was as follows:

0.50 M Na₂SO₄ 0.114 M SO₄⁼
0.10 M Na₂SO₄ 0.017 M SO₄⁼
0.02 M Na₂SO₄ 0.003 M SO₄⁼.

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The first three sections of Table 4 show the variation of E with nitric acid and TFA concentrations. In a previous report CN-2486 it was reported that E followed a fourth power dependence law $E = K \frac{(TFA)^4}{(H^+)^4}$. The points upon which this law was based could

not be duplicated since they were in a region where the shaking time was very critical. Inasmuch as the true H^+ and TFA concentrations in the heterogeneous extraction system cannot be evaluated without further data, the true dependence upon HNO_3 and TFA concentrations cannot be stated. Empirically E varies directly as the stoichiometric TFA concentration to the second or third power and inversely as the third or fourth power of the stoichiometric H^+ concentration.

In the fourth section of Table 4 it is shown that the sulfate complex with Pu(IV) is much stronger than the Pu(IV) chelate complex for the extraction coefficients with Na_2SO_4 present are much lower than in the identical experiment performed in the absence of Na_2SO_4 . In the last two sections, the variation in E with UNH and UNH- Na_2SO_4 mixtures is shown. The dropping off of E with UNH was thought to be due to the effect of nitrate ion complexing of Pu(IV). To substantiate this 1.6 M $NaNO_3$ was substituted for 0.8 M UNH in one experiment. As may be seen E also dropped in the presence of $NaNO_3$ but not as far as when the comparable amount of UNH was used. The entire effect of UNH upon the extraction coefficient may still be due to nitrate ion as the discrepancy between the UNH and the $NaNO_3$ result may be due to a difference in the ionic strength of the two solutions. The ionic strength cannot be exactly determined in the case of UNH because of the possibility of weak salt formation in the solution. In the presence of UO_2^{2+} , the marked effect of Na_2SO_4 upon the extraction coefficient is greatly diminished. It is believed that the relatively small lowering of the extraction coefficient by Na_2SO_4 when UO_2^{2+} is present in excess is due to the formation of a uranyl sulfate complex ion which lowers the free sulfate ion concentration and correspondingly the extent of the Pu(IV) sulfate complexing.

From the results in Table 4 conditions can be selected to obtain a range of desired extraction coefficients neglecting the as yet undetermined effect of reduction of Pu(IV) by TFA. Shaking times of 15-20 minutes are required to achieve equilibrium extraction. Results reported in CN-2486 that conflict with values in Table 4 are due to uncontrolled shaking times. In most of those experiments, the shaking times were of the order of 30 seconds so the extraction coefficients are much higher than the equilibrium values. The high values can be achieved, however, under equilibrium conditions by a relatively small increase in the TFA concentration.

In the immediate future experiments are planned to study the reduction of Pu(IV) by TFA and to further study the decontamination properties of the process.

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II. The Behavior of TFA in Water Solutions

James C. Reid

TFA is not stable in alkali, being hydrolyzed to acetone and trifluoroacetic acid. The reaction is moderately rapid; the ketone is 80% hydrolyzed after fourteen hours standing in tenth normal alkali at room temperature.

TFA is stable in solutions of nitric, hydrochloric or sulfuric acid as concentrated as 0.5 normal. Higher concentrations have not been quantitatively investigated, although it is known that the ketone can be steam distilled from 10% sulfuric acid with at least 75% recovery.

Although TFA is recoverable quantitatively from acid solutions, it appears to enter into an equilibrium with some substance, as yet unidentified, which is ineffective in the extraction of Pu. This process is being investigated.

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