

SECRET

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

ORNL153 7a

CHEMISTRY-SEPARATION
PROCESSES FOR PLUTONIUM

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES



3 4456 0360313 4

LABORATORY RECORDS
1954

Inv
55

Inv
55

Inv
55

CHEMISTRY DIVISION

A SOLVENT EXTRACTION METHOD FOR PLUTONIUM ANALYSIS

F. L. MOORE
J. E. HUDGENS, JR.

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

LIBRARY LOAN COPY

DO NOT TRANSFER TO ANOTHER PERSON

If you wish someone else to see this document,
send in name with document and the library will
transfer a loan.

CAUTION

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE
NATIONAL DEFENSE OF THE UNITED STATES OF AMERICA
IN SUCH A MANNER THAT THE DISCLOSURE OF ITS CONTENTS
IN ANY MANNER TO AN UNAUTHORIZED PERSON OR
PERSONS IS PROHIBITED BY FEDERAL STATUTES,
REGULATIONS AND EXECUTIVE ORDINANCES, AND PENALTIES
UNDER APPLICABLE FEDERAL LAWS.

RESTRICTED DATA

THIS DOCUMENT CONTAINS RESTRICTED DATA
DEFINED IN EXECUTIVE ORDER 11652

OAK RIDGE NATIONAL LABORATORY

OPERATED BY
CARBIDE AND CARBON CHEMICALS CORPORATION
FOR THE
ATOMIC ENERGY COMMISSION

POST OFFICE BOX P
OAK RIDGE, TENNESSEE

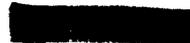
SECRET

thorium and zirconium from plutonium. (The use of thenoyltrifluoroacetone is effective in this separation.) Fryxell and Kleinschmidt⁽²⁾ extracted plutonium (III) and plutonium (IV) into chloroform as a cupferron complex. They found the average recovery to be 86% and on the basis of this value suggested that a 15% correction for recovery be applied to the results obtained with this solvent extraction method. Greenlee and Winner⁽³⁾ devised a method for the analysis of plutonium (IV) and plutonium (III - IV) mixtures based on a solvent extraction with acetyltrifluoroacetone in benzene; however, relatively concentrated solutions were used and both the aqueous and organic phases were analyzed by using a lanthanum fluoride method similar to that given by Koshland⁽⁵⁾. The chelate process for the extraction and decontamination of plutonium was investigated by Thomas and Crandall⁽⁸⁾ who found that thenoyltrifluoroacetone was the most economical ketone for complexing plutonium (IV). These investigations were on a semi-works scale and the separations process as given was time-consuming and was not readily adaptable to use as an analytical method.

Favorable results obtained by other investigators⁽⁸⁾ in the use of thenoyltrifluoroacetone (hereafter designated as TTA) as a complexing agent for plutonium (IV) indicated that an effective radiochemical procedure for the analysis of total plutonium could be devised through the use of this reagent.

Principle of the TTA Solvent Extraction Method for Plutonium

Many substituted fluorinated 1-3 diketones⁽⁸⁾ are known to react with metallic ions to form unionized chelate compounds which are soluble in



non-polar solvents immiscible with water. These ions can be separated one from the other by taking advantage of the high acid dependence of the extraction of these chelate compounds into non-polar solvents. Thomas and Crandall⁽⁸⁾ found that very few aqueous ions extract appreciably from 0.5 M nitric acid. These authors report that plutonium (IV), zirconium (IV), neptunium (IV), cerium (IV), uranium (IV), iron (III), and tin (IV) can be readily extracted while those ions showing very little tendency to extract from 0.5 M nitric acid with TTA are the ions of plutonium (III), plutonium (VI), plutonium (V), uranyl, tin (II), nickel (II), cobalt (II), chromium (III), thorium (IV), iron (II), aluminum (III), bismuth (III), neptunium (V), columbium (V), the alkali elements, the alkaline earth elements, and the rare earth elements with the exception of cerium (IV).

Previous investigators (loc. cit.) have shown that the valence state of plutonium, the hydrogen ion concentration, the extraction rate, and the concentration of other sample constituents affect markedly the distribution coefficient which is obtained in a solvent extraction with a benzene solution of TTA. Since the method must be capable of separating plutonium from a large number of different sample compositions we have studied these variables and have arrived at conditions for the extraction which will insure quantitative extraction of the plutonium. Suitable reagents for re-extracting the plutonium from the organic solution in a form which can be counted without self absorption have also been studied. The effectiveness of the decontamination from other radioactive elements was determined and methods of pre-treatment of general process solutions to make possible the quantitative extraction of

the plutonium were studied.

Effect of the Nitric Acid Concentration of the Extraction of Plutonium (IV)

Since many solutions submitted for plutonium analysis contain nitric acid, a study of the effect of the nitric acid concentration in the aqueous solution on the extraction of plutonium (IV) with 0.5 molar solutions of TTA in benzene was made.

In these experiments a stock plutonium (IV) tracer solution was evaporated to dryness and taken up with 16 M nitric acid. Experiments in this laboratory have shown that no oxidation or disproportionation of plutonium (IV) occurs when heated in concentrated nitric acid solution. Proper dilutions were made from this solution. The procedure used was to mix in a separatory funnel equal volumes of the aqueous nitric acid phase and 0.5 M TTA in benzene. A two minute extraction period was used, no attempt being made to achieve equilibrium. The aqueous phase was counted for the plutonium (IV) which was not extracted. The plutonium extracted most readily from a nitric acid concentration of 1 molar. At higher concentrations presumably complexing of the plutonium (IV) by the nitrate ion becomes appreciable while at lower concentrations of nitric acid the hydrolysis of plutonium (IV) limits the quantity of plutonium which can be extracted.

[REDACTED]

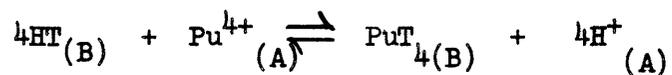
Table I

Effect of Nitric Acid Concentration on the Extraction of Pu (IV)
with Thenoyltrifluoroacetone

<u>M</u> HNO ₃	Percent Pu (IV) Remaining in the Aqueous Phase
16	100
14	100
12	100
10	100
8	100
6	100
4	64.8
2	20.8
1	17.7
0.5	23.6
0.1	44.9

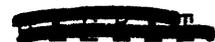
Extraction Rate Studies of Plutonium (IV)

The rate of extraction of plutonium (IV) from aqueous solutions 0.5 M in nitric acid or 0.5 M in hydrochloric acid by 0.5 M TTA in benzene was determined by Thomas and Crandall⁽⁸⁾. As shown in Table I, the plutonium most readily extracted from a nitric acid concentration of 1 M. The extraction rate has therefore been determined at this concentration. The reaction for the chelation of plutonium (IV) with TTA may be written:



for which the equilibrium constant may be expressed:

$$K = \frac{(\text{PuT}_4)_B (\text{H}^+)_A^4}{(\text{Pu}^{4+})_A (\text{HTT})_B^4}$$



where "HT" represents TTA, the parentheses refer to activities and the subscripts "B" and "A" refer to benzene and aqueous phases respectively. The value of the equilibrium constant for the chelating system in 1 M nitric acid was found to be $\sim 1 \times 10^3$. This value is not the true thermodynamic value since the effect of ionic strength was not considered. However, it may be regarded as the apparent equilibrium constant for the conditions set forth in the TTA solvent extraction procedure given below.

A study of the extraction rate was made by preparing an aqueous solution of 1 M nitric acid containing a known tracer concentration of plutonium (IV) and extracting aliquots of this solution for different lengths of time with an equal volume of TTA in benzene. The effect of the concentration of TTA in the benzene solution on the extraction rate and on the distribution coefficient was determined from the data shown in Table II. A 0.5 M benzene solution of TTA was chosen for further investigation since the plutonium was extracted as efficiently by this concentration as with the higher concentrations.

Table II

Rate of Extraction of Pu (IV) from 1 M Nitric Acid

Solutions by Different Concentrations of TTA in Benzene

Time Allowed for Fractional Approach to Equilibrium	Percent Pu Remaining in the Aqueous Phase					
	0.5M TTA	1M TTA	2M TTA	3M* TTA	4M* TTA	5M TTA
30 sec.	2.76	2.74	2.17	1.44	1.46	4.36
1 min.	2.72	2.20	1.09	1.39	0.26	3.14
1-1/2 min.	2.76	1.25	1.20	0.75	0.70	0.49
2 min.	1.96	1.55	1.94	1.13	1.21	0.28
5 min.	1.62	0.23	0.54	0.39	0.39	0.48
8 min.	0.86	0.43	0.34	0.23	0.28	0.70
12 min.	0.32	0.26	0.22	0.21	0.24	0.35
16 min.	0.29	0.28	0.20	0.22	0.15	0.28

*A tendency toward emulsion formation was observed at these concentrations and as a result the time the phases were allowed to remain in intimate contact was difficult to control.

~~SECRET~~

Extraction of Plutonium (IV) from TTA-Benzene Solutions

The removal of plutonium from a TTA-benzene solution may be accomplished (1) by evaporating the solution to dryness and destroying the residual organic matter (2) by equilibrating the solution with an aqueous solution capable of reducing the plutonium to the more aqueous soluble plutonium (III) valence state or (3) by equilibrating the solution with aqueous solutions containing reagents having a stronger affinity for the plutonium ion than does the TTA. Since the evaporation and destruction of the organic material is a time-consuming procedure, the principal effort was expended in exploring the latter two possibilities. Thomas and Crandall⁽⁸⁾ re-extracted plutonium from benzene solutions of acetyltrifluoroacetone (TFA) by reducing the plutonium (IV)-TFA chelate in benzene to plutonium (III) in the aqueous phase with stannous chloride and by reducing the plutonium (IV)-TTA chelate in benzene to plutonium (III) in the aqueous phase with ferrous chloride. The writers have performed experiments which indicate that stannous chloride and ferrous chloride reduce the plutonium (IV) too slowly to be practical for use in an analytical method.

Studies of the extraction of plutonium from TTA-benzene solutions into oxalic acid solutions demonstrated that quantitative extraction can be achieved; however, the concentration of this reagent as well as the concentrations of stannous chloride and ferrous chloride which can be used is limited by the quantity of solid material which can be mounted with the plutonium for alpha counting. Strong nitric acid solutions (8 M and stronger) readily extract the plutonium from TTA-benzene solutions; however, the use of strong nitric acid with organic solvents is hazardous. Since hydrofluoric acid forms a strong

~~SECRET~~

complex with plutonium and can be completely volatilized, several experiments were performed in which aqueous solutions containing different concentrations of hydrofluoric acid were shaken in a separatory funnel with TTA-benzene solutions containing plutonium (IV). The plutonium was extracted nearly quantitatively into solutions containing greater than 0.3 M concentrations of hydrofluoric acid (See Table III). Hydrofluoric acid (0.5 M) was chosen as the most effective reagent for the removal of plutonium from TTA-benzene solution. While the fluoride ion is not present in the usual samples submitted for analysis at this installation, it should be noted here that the fluoride ion must be destroyed or complexed before attempting to extract plutonium from aqueous nitric acid solutions.

Table III

Extraction of Tracer Plutonium (IV) from TTA-Benzene Solutions by Aqueous Hydrofluoric Acid Solutions.

(Volume of organic phase = volume of aqueous phase)

Hydrofluoric Acid Concentration (moles per liter)	Time Allowed for Fractional Approach to Equilibrium	Percent* Plutonium Extracted
0.1	5 min.	90.9
0.3	5 min.	97.6
0.5	5 min.	97.6
0.6	5 min.	97.6
0.7	5 min.	97.3
0.9	5 min.	97.6

*The plutonium concentration in both the organic phase and in the aqueous phase was determined and these values represent averages of the results obtained.

The Preparation of Pure Plutonium (IV) Solutions

Since the usual samples which are submitted for analysis may contain

[REDACTED]

plutonium in one or more of its several valence states, in order to prepare a pure plutonium (IV) solution, it is necessary first to achieve reproducibly the quantitative reduction of the plutonium to the plutonium (III) valence state and then to add a reagent known to oxidize plutonium just to the (IV) valence state.

Five reagents were tested for the reduction of plutonium (IV) or (VI) to the (III) valence state. The method used was to add a known quantity of each reagent to an aqueous solution of plutonium (IV) tracer. The nitric acid concentration of this solution was then adjusted to 1 M and the mixture stirred vigorously for five minutes. The solution was then shaken in a separatory funnel for two minutes with an equal volume of a 0.5 M solution of TTA in benzene. (Thomas and Crandall⁽⁸⁾ and Greenlee and Winner⁽³⁾ demonstrated that plutonium (III) does not chelate at this acid concentration with TTA or TFA.) Quantitative reduction was effected by hydroxylamine hydrochloride and ferrous chloride (Table IV). Since any ferric ion produced by the oxidation would be extracted under these conditions, hydroxylamine hydrochloride was selected for further work.

Table IV

Comparison of Several Reducing Reagents for the Reduction of Plutonium (IV) to Plutonium (III).

Reagent Used	Concentration	Percent Pu (IV) Reduced After Five Minutes.
H ₂ O ₂	6%	27.1
NH ₂ OH . HCl	0.2 <u>M</u>	100
(NH ₂) ₂ H ₂ SO ₄	0.02 <u>M</u>	33.6
FeCl ₂	0.02 M	100
H ₂ SO ₃	1.2%	25.1

Oxidation of Plutonium (III) to Plutonium (IV)

Thomas and Crandall⁽⁸⁾ used nitrous acid to oxidize plutonium (III) to plutonium (IV). Experiments indicated that the oxidation of plutonium (III) by sodium nitrite is almost instantaneous. The method used was to prepare a solution of plutonium (III) by the reduction of plutonium (IV) with a solution 0.2 M in hydroxylamine hydrochloride and 1 M in nitric acid (See Table IV). This solution was then made ~0.17 M in sodium nitrite. Two one-half volume extractions of ten minutes each using 0.5 M TTA in benzene resulted in a recovery of 99.8% of the total plutonium introduced before the reduction and oxidation steps. Therefore, sodium nitrite was chosen as the reagent best suited for the oxidation of plutonium (III) to plutonium (IV).

Separation of Plutonium from Other Radioactive Elements

Experiments have been performed in which plutonium tracer was added to pure solutions of other radioactive elements. The plutonium was quantitatively recovered from 0.15 M nitric acid solutions containing uranium (150 mg/ml) and tracer concentrations of cesium, columbium, ruthenium, cerium, rare earths and negligible concentrations of these elements were both extracted into a 0.5 M TTA-benzene solutions and re-extracted into 0.5 M hydrofluoric acid solutions. As might be expected from the work of Thomas and Crandall⁽⁸⁾ and from chemical considerations, zirconium activity is almost quantitatively extracted into a 0.5 M TTA-benzene solution from nitric acid concentrations of 0.5 M - 1.5 M and re-extracted into the aqueous hydrofluoric acid solutions. If it is desirable to recover the plutonium free of zirconium activity in a particular case, this may be done by reducing the plutonium to the non-extractable plutonium (III) valence state and then extracting the zirconium out of

██████████

[REDACTED]

the aqueous phase with 0.5 M TTA solution in benzene. The plutonium can then be oxidized to the extractable (IV) valence state and extracted in the usual manner. Usually this separation is unnecessary unless the level of zirconium activity is high enough to be hazardous from a health standpoint and to interfere in the determination of the alpha activity of the sample.

The presence of americium which is an alpha emitter must be considered in any plutonium separation. Usually americium is eliminated with the rare earth group in process purification procedure and the traces found in product plutonium solutions are due to the decay of Pu²⁴¹. As nuclear reactors of higher neutron flux are placed in operation, greater concentrations of americium will be found associated with these product solutions. Werner and Perlman⁽⁹⁾ separated americium from lanthanum and neodymium by extracting the americium from a solution the pH of which had been previously adjusted to 3.27 into a 0.2 M TTA solution in benzene. (Lanthanum and neodymium extract at a pH of ~5.) One would not expect appreciable concentrations of americium to extract from an aqueous solution 1 M in nitric acid (pH = ~0.1). However, in order to roughly evaluate the separation which can be achieved an aqueous solution 1 M in nitric acid and containing americium tracer was thoroughly mixed for ten minutes with two one-half volume portions of a 0.5 M TTA solution in benzene. The organic phases were combined and mixed for five minutes with three one-half volume portions of a 0.5 M hydrofluoric acid solution. Less than 2% of the americium activity added to test the procedure was found in the hydrofluoric acid solution.

General Application of the TTA-Benzene Solvent Extraction Method

Early attempts to apply the TTA-benzene solvent extraction method for

[REDACTED]

plutonium to solutions from the uranium decontamination process as used by the pilot plant at this installation were unsuccessful. A typical process solution may contain uranium (150 mg/ml), nitric acid (0.1 M - 0.4 M) and plutonium (9×10^6 to 10^8 counts per minute per milliliter). Recoveries varied from 70-85% consistently when the extraction method which recovered pure tracer plutonium quantitatively was used. The presence of a polymeric form of plutonium (IV) in process solutions was suspected. Several investigators (4, 1, 6, 7) have studied a highly polymerized form of plutonium (IV). This form can be quantitatively carried on lanthanum fluoride⁽⁷⁾ but exhibits abnormal chemical behavior in other reactions. Quantitative carrying of plutonium from these solutions on lanthanum fluoride but poor extraction with the TTA method were demonstrated in this laboratory and taken as further indication of the presence of the abnormal form of plutonium (IV). Kraus⁽⁶⁾ suggested that monomeric solutions of plutonium may be prepared by heating the polymer with solutions containing a concentration of 6 M or greater nitric acid. The writers were able to convert the polymerized form of plutonium to the extractable normal form by heating the solution containing the polymer for several minutes with concentrated nitric acid. For example, a process solution which contained 30% of the plutonium in the non-extractable form was heated several minutes in concentrated nitric acid, after which it was possible to extract the plutonium quantitatively. Treatment of the polymerized plutonium solution with hot 2 M nitric acid and with cold concentrated nitric acid was unsuccessful in destroying the polymer. Since many of the process solutions may be diluted to secure a satisfactory counting rate, the dilution is made in a manner (see detailed procedure) to insure destruction of any plutonium polymer present. Experiments from many extractions performed on process solutions containing aluminum nitrate up to 2 M indicated that negligible amounts of aluminum extracted as shown by visual observation and no self absorption of plutonium.

██████████

██████████

Reagents

Hydrofluoric acid, 0.5 M, was prepared by diluting 3.7 milliliters of reagent grade (48%) hydrofluoric acid to 200 milliliters with distilled water. This reagent was stored in a hard rubber bottle.

Hydroxylamine hydrochloride, 1 M, was prepared by dissolving 69.5 grams of C. P. hydroxylamine hydrochloride and diluting to one liter with distilled water.

Nitric acid, 2 M, was prepared by diluting 25 milliliters of C. P. concentrated nitric acid to 200 milliliters with distilled water.

Sodium nitrite, 1 M, was prepared by dissolving 69 grams of C. P. sodium nitrite and diluting to one liter with distilled water.

Thenoyltrifluoroacetone, 0.5 M, was prepared by dissolving 111 grams of TTA and diluting to one liter with C. P. benzene. The TTA (99+%) was obtained from the University of California Radiation Laboratory.

The Analytical Procedure

The choice of the sample size is governed by the magnitude of the concentration of plutonium activity and of the beta and gamma ray emitters in the original solution. The presence of high levels of beta and gamma ray emitters must be considered because of the health hazard involved and also the fact that a beta ray counting rate of over 10^9 counts per minute will interfere with the alpha counting on the Simpson proportional alpha counter. A suitable aliquot of the sample is pipetted into a 100 ml. volumetric flask containing 13 milliliters of concentrated nitric acid. The solution is carefully heated to a low boil over a hot plate and the temperature is held just under boiling for five minutes. The solution is then made to volume with distilled water. The nitric

██████████

acid concentration of this solution should be approximately 2 molar.

One milliliter of the treated solution is added to a 10 ml. beaker containing 3 milliliters of 2 M nitric acid solution and 1 milliliter of 1 M hydroxylamine hydrochloride solution. The solution is then thoroughly mixed and warmed at $\sim 80^{\circ}$ C. for five minutes. The volume of the solution is adjusted to approximately 4 milliliters by the addition of several drops of 1 M nitric acid. The solution is transferred to a 30 ml. separatory funnel with 2 milliliters of sodium nitrite (1 M), mixed thoroughly and allowed to stand until bubbles of gas are no longer evolved. Three milliliters of 0.5 M TTA-benzene solution are then added and the two phases thoroughly mixed for ten minutes with a mechanical stirrer or by shaking the funnel manually. After clean phase separation is achieved the aqueous phase is drained to another separatory funnel, a fresh 3 milliliter volume of 0.5 M TTA-benzene solution is added, and the ten minute mixing period repeated. The phases are allowed to separate cleanly and the aqueous phase is drained off and discarded. The two organic phases are combined in one funnel.

Three milliliters of a 0.5 M hydrofluoric acid solution are added and this solution thoroughly mixed with the organic solution for ten minutes. The aqueous phase is then drained into a clean glass-stoppered graduated cylinder. Two additional five minute extractions are performed using 3 milliliter portions of 0.5 M hydrofluoric acid. The aqueous phases are combined in the graduated cylinder and mixed thoroughly. A suitable aliquot is pipetted onto a platinum plate and this aliquot evaporated to dryness under an infra-red heat lamp. In the evaporation of large sample aliquots, a circle of a suitable lacquer is usually painted around the edge of the platinum plate to prevent the sample from running over the edge. The platinum plate containing the evaporated sample aliquot is heated to a dull red heat over a "Fisher" burner to destroy residual

[REDACTED]

organic material and counted in one of the several types of alpha counting devices. In this laboratory, the Simpson proportional alpha counter is used almost exclusively.

Summary

The thenoyltrifluoroacetone solvent extraction method described in this paper is applicable to a large number of different types of samples, it has few interferences and is readily adaptable to remote control techniques. The method achieves a clean separation of plutonium from cesium, columbium, ruthenium, cerium, rare earths, uranium, and aluminum.

[REDACTED]

170 [REDACTED]

Bibliography

- (1) Carniglia, S. C., CN-2330 (November, 1944).
- (2) Fryxell, R., and Kleinschmidt, R., MDDC-461 (October, 1946).
- (3) Greenlee, R. W., and Winner, B. M., CN-3676 (November, 1946).
- (4) King, E. L., MDDC-393 (October, 1946).
- (5) Koshland, D. E., CN-2041 (January, 1945).
- (6) Kraus, K. A., CN-3399 (June, 1945).
- (7) Kraus, K. A., and Howland, J. J., CN-1764 (July, 1944).
- (8) Thomas, J. R., and Crandall, H. W., CN-3733 (December, 1946).
- (9) Werner, L. B., and Perlman, I., BC-1 (April, 1946).
- (10) Wolter, F. J., ISC-14, (May, 1946).
- (11) Wolter, F. J., and Brown, H. D., CN-2719 (June, 1945).

[REDACTED]