ORNL 961
Chemistry-Transuranic
Elements

A SOLVENT EXTRACTION METHOD FOR NEPTUNIUM (237) ANALYSIS

Fletcher L. Moore

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION
UCC
POST OFFICE BOX P
OAK RIDGE, TENNESSEE

ORNL-961

This document consists of 15 pages.
This is copy 8 of 114, Series A.

Contract W-7405, eng-26

ANALYTICAL CHEMISTRY DIVISION

M. T. Kelley, Director

C. D. Susano, Associate Director

A SOLVENT EXTRACTION METHOD FOR NEPTUNIUM (237) ANALYSIS

Fletcher L. Moore

DATE ISSUED:

JUL 10 1951

OAK RIDGE NATIONAL LABORATORY
operated by
CARBIDE AND CARBON CHEMICALS COMPANY
A Division of Union Carbide and Carbon Corporation
Post Office Box P
Oak Ridge, Tennessee

ORNL 961
Chemistry-Transuranic
Elements

INTERNAL DISTRIBUTION

1. G. T. Felbeck (C&CCC)
2-3. Chemistry Library
4. Physics Library
5. Biology Library
6. Health Physics Library
7. Metallurgy Library
8-9. Training School Library
10-13. Central Files
14. C.E. Center
15. G. E. Larson
16. W. B. Humes (K-25)
17. W. D. Lavers (Y-12)
18. A. M. Weinberg
19. E. H. Taylor
20. S. D. Shipley
21. M. T. Kelley
22. F. C. VonderLage
23. R. C. Briant
24. J. A. Swartout
25. S. C. Lind
26. T. L. Stebbly
27. A. H. Snell
28. A. Hollaender
29. G. H. Clewett
30. K. Z. Morgan
31. J. S. Felton
32. A. S. Householder
33. S. Harrill
34. C. E. Winters
35. D. W. Cardwell
36. W. H. Pennington
37. R. B. Hall
38. F. L. Moore

EXTERNAL DISTRIBUTION

39. Aircraft Nuclear Propulsion Project, Oak Ridge
40-47. Argonne National Laboratory
48-49. Atomic Energy Commission, Washington
50-53. Brookhaven National Laboratory
54-55. Carbide and Carbon Chemicals Company (K-25)
56. Carbide and Carbon Chemicals Company (Y-12)
57. Chicago Patent Group
58-62. duPont Company
63-66. General Electric Company, Richland
67. Hanford Operations Office
68-69. Idaho Operations Office
70. Iowa State College
71. Kellex Corporation
72-75. Knolls Atomic Power Laboratory
76-78. Los Alamos
79-81. Mound Laboratory
82. Naval Research Laboratory
83-84. New York Operations Office
85. North American Aviation, Inc.
86. Patent Branch, Washington
87. Savannah River Operations Office
88. UCLA Medical Research Laboratory (Warren)
89. U. S. Naval Radiological Defense Laboratory
90-93. University of California Radiation Laboratory
94-95. University of Rochester
96-97. Westinghouse Electric Corporation
98-99. Wright-Patterson Air Force Base
100-114. Technical Information Service, Oak Ridge

A Solvent Extraction Method for Neptunium (237) Analysis

Abstract

A rapid and quantitative radiochemical method for the analysis of neptunium (237) is described. The method is based on the extraction of neptunium (IV) with thenoyltrifluoracetone in xylene. Neptunium (237) is separated free from other alpha emitters and from non-radioactive interferences, and the method may be readily adapted to remote control.

Introduction

The operation of nuclear reactors of higher neutron flux has brought increased interest in the determination of the long-lived neptunium (237) alpha emitter ($t_{\frac{1}{2}} = 2.2 \times 10^6$ yr.). A method[1] has been developed previously for the analysis of the neptunium (239) beta emitter; however, since this method allowed approximately 16% of the plutonium to carry through, it could not be used for the analysis of neptunium (237).

It was necessary to develop a method which would achieve a clean separation from uranium, plutonium, americium, and curium. A method not involving a carrier (such as LaF_3) was desired. Experience accumulated in the development of a solvent extraction method of analysis for plutonium[3] using the chelating agent, thenoltrifluoracetone (TTA), suggested that an effective radiochemical procedure for the analysis of neptunium (237) could be devised through the use of this reagent. Magnusson, Hindman and LaChapelle[2] extracted neptunium (237) with TTA away from plutonium and uranium under suitable reducing conditions.

Principle of the TTA Solvent Extraction Method for Np^{237}

Certain substituted fluorinated beta-diketones are known to react with metallic ions to form non-ionized chelate compounds which are soluble in non-polar solvents immiscible with water. Many of these ions can be separated from each other because of the high acid dependence of the extraction of these chelate compounds into non-polar solvents. Thanas and Crandall[4] found that very few aqueous ions extract

appreciably from 0.5 M nitric acid. These were zirconium (IV), plutonium (IV), neptunium (IV), cerium (IV), uranium (IV), iron (III), and tin (IV).

In the determination of neptunium (237) the major separations would be necessarily from plutonium and uranium which are usually present in the solutions to be analyzed. Previous workers[2] have shown that under suitable reducing conditions a solution may contain neptunium (IV), plutonium (III), and uranium (VI) and the neptunium (IV) may be extracted with TTA.

The present investigation determined the variables concerning the quantitative recovery of neptunium (237) and the decontamination from the usual interferences of other radioactive elements. The development of the radiochemical method for neptunium (237) is presented.

Experimental

The Reduction of Plutonium

It was realized that the most difficult separation would be that of plutonium. Several reducing agents were tested for effectiveness in reducing plutonium to the non-extractable Pu(III) valence state. The procedure was to reduce Pu(IV) tracer for five minutes and then extract the aqueous phase for ten minutes with an equal volume of 0.5 M TTA in xylene.

Table I

The Reduction of Pu(IV) Tracer by Various Reagents

	Final Aqueous Concentration	Reduction Conditions	% Plutonium Extraction
1.	1 M HNO_3, 0.25 M NH_2OH. HCl	5 min. at room temp.	13.1, 13.3
2.	1 M HNO_3, 0.25 M KI	5 min. at room temp.	1.6, 2.4
3.	1 M HNO_3, 0.25 M KI	12 min. at room temp.	2.0, 2.1
4.	1 M HNO_3, 0.15 M HCl, 0.024M $FeCl_2$	5 min. at room temp.	2.4, 2.5
5.	1 M HNO_3, 0.25 M $SnCl_2$, 0.8 M HCl	5 min. at room temp.	0.3, 0.3
6.	1 M HNO_3, 0.25 M NH_2OH. HCl 0.025 M $FeCl_2$, 0.15 M HCl	5 min. at room temp.	1.2, 1.2

When the hydroxylamine hydrochloride concentration was raised to 4.5 M and #1 extraction repeated, 3.1% of the plutonium was extracted. Heating the solution at boiling during the reduction period raised the extraction to 5.1%. Stannous chloride, while an effective reductant for plutonium, invariably produced emulsions due to hydrolysis. Any Sn(IV) present would also extract. When ferrous chloride was used, some Fe(III) was observed to extract. It was decided to develop the method using potassium iodide as the reductant for plutonium. Previous workers(2) produced a Pu(III), Np(IV) solution by heating the solution at boiling with 0.1 M potassium iodide and 5 M hydrochloric acid. Experiments were performed in this laboratory to determine the optimum concentration of potassium iodide necessary to hold plutonium as Pu(III) at an acid concentration suitable for the extraction of the Np(IV) -TTA chelate. The use of an aqueous phase concentration of 1 M hydrochloric acid and 2 M potassium iodide was found to effect an excellent separation from Plutonium (see Table II).

Conditions — Tracer Pu(IV) HCl and KI concentrations were varied in the aqueous phase as indicated below. One half volume of 0.5 M TTA in xylene - 10 min. extraction at room temperature. The organic phase was washed 3 min. with an equal volume of 1 M HCl and then centrifuged 3 min. before counting.

Table II

The Reduction of Pu(IV) Tracer with KI in HCl

Final Aqueous Concentration		% Plutonium Extracted
HCl (M)	KI (M)	
0.5	0.15	6.40
0.5	0.30	4.20
0.5	0.60	3.20
1.0	0.15	3.10
1.0	0.30	2.20
1.0	0.60	0.70
1.0	1.00	0.55
1.0	1.50	0.15
1.0	2.00	0.20
1.0	2.50	0.01

The Extraction of Neptunium (237) (IV) as a Function of Time

The extraction of Np(IV) as a function of time was studied in a series of experiments. Table (III) indicates that a ten minute extraction period effects essentially quantitative recovery of the Np(IV).

Conditions: Tracer Np(IV) in aqueous phase of 1 M HCl and 2 M KI. One half volume of 0.5 M TTA in xylene various extraction periods at room temperature. The organic phase was washed 3 minutes with an equal volume of 1 M HCl and then centrifuged 3 minutes before counting.

Table III

The Extraction of Neptunium (IV) as a Function of Time

Time (min.)	% Neptunium Extracted
2	86.5, 85.6
5	97.5, 97.9
8	98.1, 98.2
10	98.9, 99.2

[redacted]

The Effect of Hydrochloric Acid Concentration on the Extraction of Neptunium (IV)

The effect of hydrochloric acid concentration on the extraction of Np(IV) was studied. Table (IV) indicates that the extraction of the Np(IV) -TTA chelate is excellent from 1 M hydrochloric acid but decreases with higher acid concentrations.

Conditions: Tracer Np(IV) in 2 M KI - The HCl concentration was varied as indicated. 10 min. extraction period at room temperature with one-half volume of 0.5 M TTA in xylene. The organic phase was washed 3 minutes with an equal volume of 1 M HCl and then centrifuged 3 minutes before counting.

Table IV

The Effect of Hydrochloric Acid Concentration on the Extraction of Neptunium(IV)

HCl (M)	% Np(IV) Extracted
0.5	98.7
1.0	99.1
2.0	97.5
3.0	71.8

The Separation of Uranium and Americium

The behavior of $U^{233}O_2^{++}$ and Am^{241} tracer solutions was tested under the optimum conditions extablished above for the quantitative extraction of neptunium (IV). An effective separation from these two elements in addition to plutonium is necessary since they are often present in solutions analyzed for Np^{237}. Table (V) indicates excellent decontamination from UO_2^{++} and americium.

Table V

The Extraction of UO_2^{++} and Americium in the Method

% UO_2^{++} Extracted	% Americium Extracted
0.01, 0.01, 0.01, 0.01, 0.04, 0.04, 0.03, 0.01, 0.02, 0.05, 0.03, 0.11, 0.02	0.07, 0.09, 0.09 0.10, 0.05, 0.07

[redacted]

[redacted]

The Effect of Nitric Acid on the Extraction of Neptunium (IV)

Neptunium (IV) is known to be unstable in nitric acid[2] and previously it has been customary to destroy the nitric acid when preparing Np(IV) solutions. During the course of this work it was observed that Np(IV) could be extracted quantitatively from a solution of the concentration, 0.25 M aluminum nitrate - 1 M hydrochloric acid - 2 M potassium iodide. This suggested that Np(IV) might be stabilized on some sort of nitrate-chloride system and led to an investigation of the effect of nitric acid on the extraction. The procedure used was to add varying amounts of nitric acid to Np(IV) in hydrochloric acid. The acidity was adjusted to give a final total acidity of 1 M. The solution was adjusted to a concentration of 2 M potassium iodide and extracted for ten minutes with one-half volume of 0.5 M TTA in xylene. The organic phase was washed three minutes with an equal volume of 1 M hydrochloric acid and centrifuged three minutes before counting.

Table VI

The Effect of Nitric Acid on the Extraction of Np(IV)

	Final Aqueous Concentration	% Np(IV) Extracted	% Np(IV) Loss in Wash
1.	1 M HCl, 2 M KI, No HNO_3	99.1	0.1
2.	0.9 M HCl, 2 M KI, 0.1 M HNO_3	98.7	0.1
3.	0.75 M HCl, 2 M KI, 0.25 M HNO_3	99.0	0.1
4.	0.5 M HCl, 2 M KI, 0.5 M HNO_3	99.0	0.1
5.	0.5 M HCl, No KI, 0.5 M HNO_3	97.9	--
6.	Repeat #5	97.6	

The results in Table VI indicate that once Np(IV) is formed the use of Cl may be used to stabilize this valence state in nitric acid and thus avoid the rather cumbersome procedure of destroying the nitric acid as generally employed. This is fortuitous in that most process solutions are in a nitric acid medium. The last two extractions (#5, #6) probably indicate a slight formation of non-

[redacted]

extractable Np(V) in the absence of the potassium iodide. Negligible loss of neptunium is observed in the wash step.

The Recovery of Neptunium When Introduced Into the Method as Neptunium(V) or Neptunium(VI

The work presented above has involved only neptunium (IV) tracer. Since solutions submitted for analysis may contain Np(V) or Np(VI), it was necessary to establish suitable conditions for the quantitative reduction of these species to the extractable Np(IV) valence state.

Neptunium (V) is very stable (unlike plutonium (V)). It was observed that in solutions containing Np(V) tracer, approximately 50% was reduced with 2 M potassium iodide at room temperature in five minutes. When the reduction was performed at boiling for five minutes, ~ 99% of the Np(V) was reduced to the Np(IV) extractable valence state.

To test the efficiency of the KI as a reductant for Np(V) or neptunium(VI), two Np(VI) tracer solutions were prepared, one in 2 M nitric acid and the other in 2 M hydrochloric acid. Each solution contained 0.1 M potassium dichromate as a holding oxidant. The potassium dichromate was reduced with an excess of hydroxylamine hydrochloride and the solution was adjusted to a final concentration of 2 M potassium iodide and 1 M acid (0.5 M nitric acid, 0.5 M hydrochloric acid). A five minute reduction at boiling on a hot plate was performed. After cooling, the solution was extracted in the usual manner. Control extractions indicated the non-extractability of Np(VI). The results shown in Table VII indicate that the neptunium may be recovered quantitatively when introduced into the method as Np(VI) in nitric acid or hydrochloric acid.

Table VII

The Recovery of Neptunium Originally Present as Np(VI)

	% Neptunium Extracted	
	Original Np(VI) tracer in 2 M HNO_3, 0.1 M $K_2Cr_2O_7$	Original Np(VI) tracer in 2 M HCl, 0.1 M $K_2Cr_2O_7$
Tracer - no reduction	0.1	0
Tracer carried through the reduction step	99.5	99.7

It was found that a small amount of free iodine was liberated during the reduction period. Experiments indicated that the neptunium was maintained in the reduced extractable Np(IV) state, however, due to the high ratio of potassium iodide to iodine. Two or three drops of stannous chloride, 1 M, were found to reduce the iodine. It was decided to incorporate this step into the method. The addition of the stannous chloride also aided in the reduction of the neptunium. In a series of ten extractions it was found that quantitative recovery of neptunium (introduced as Np(VI) was effected using a five minute reduction period in a boiling water bath with 2 M potassium iodide and 2 - 3 drops of 1 M stannous chloride. When the stannous chloride was omitted, it was found necessary to perform the potassium iodide reduction for twenty minutes in a boiling water bath.

Reagents

Hydrochloric acid, 6 M - Dilute 100 milliliters of C.P. concentrated hydrochloric acid to 200 milliliters with distilled water.

Hydrochloric acid, 1 M - Dilute 50 milliliters of 6 M hydrochloric acid to 300 milliliters with distilled water.

Hydroxylamine hydrochloride, 1 M - Dissolve 69.5 grams of C.P. hydroxylamine hydrochloride and dilute to one liter with distilled water.

Stannous chloride, 1 M - Dissolve 22.57 grams of C.P. stannous chloride in 50 milliliters of 6 M hydrochloric acid and dilute to 100 milliliters with distilled water.

Potassium Iodide, 5 M - Dissolve 83 grams of c.p. potassium iodide and dilute to 100 milliliters with distilled water.

Thenoyltrifluoracetone, 0.5 M - Dissolve 111 grams of TTA and dilute to one liter with c.p. xylene. (The TTA (99%) was obtained from the University of California Radiation Laboratory).

The Analytical Procedure

1. Take an appropriate aliquot of the sample solution in a 5 ml pyrex test tube. Add enough 6 M HCl (Note 1) to make a total acidity of approximately 4 M in a 2 ml volume.

2. Add 0.4 ml of $NH_2OH.HCl$, 1 M. Warm in a boiling water bath approximately one minute. Add 2 - 3 drops of 1 M Sn Cl_2 (Note 2) from a dropping bottle and 1.6 ml of KI, 5 M. Allow to sit in the boiling water bath for ten minutes.

3. After cooling the solution to room temperature, transfer it to a separatory funnel or other extraction vessel with several drops of 1 M HCl.

4. Extract for ten minutes with 2 ml of 0.5 M TTA-xylene. Drain off the aqueous phase carefully and discard. Wash the organic phase three minutes with 2 ml of 1 M HCl. Discard the aqueous wash and transfer the organic phase into a 3 ml centrifuge cone. Centrifuge for three minutes. Take an aliquot of the organic phase, mount on a stainless steel plate (or a platinum plate) dry under an infra-red heat lamp, heat to a dull red heat over a Fisher burner, and count the Np^{237} on a Simpson proportional alpha counter.

Notes

1. The aqueous phase when extracted should be about 1 M acid. This may be 1 M HCl or, if HNO_3 is present in the original sample, the aqueous should be adjusted so that the final acid concentration is 0.5 M HCl - 0.5 M HNO_3. It is desirable to keep the HNO_3 concentration 0.5 M or less and adjust to 1 M acid with HCl.

2. If the solution to be analyzed contains mercury, simply omit the $SnCl_2$ and perform the KI reduction twenty minutes in the boiling water bath.

Separation From Other Radioactive Elements

Using the procedure described above, tracers of plutonium, americium, and uranium were carried through the analysis. The results in Table VIII indicate that excellent decontamination is achieved from these alpha-emitters under the conditions for the quantitative recovery of Np^{237}.

Table VIII

The Decontamination of Np^{237} from Neighboring Alpha-emitters

	% Extracted		
Np^{237}	Pu	Am	UO_2
99.7	0.02 (a)	0.02	0.01
98.6	0.01 (a)	0.02	0.07
99.0	0.03 (b)		0.15
99.6	0.01 (b)		0.02
99.1			0.02
99.7			

(a) Pu(IV) tracer originally

(b) Pu(VI) tracer originally

No curium tracer was available but its behavior in the TTA scheme is known to be essentially identical with that of americium[5].

Under the conditions employed for the extraction of Np^{237} (1 M acid), it is known from previous work[3] that excellent separation from aluminum nitrate and fission products, except zirconium, is achieved. Zirconium extracts under the conditions used in this method but does not interfere since alpha-counting is done for Np^{237}. If one desires to separate the zirconium, this may be done by first oxidizing the neptunium to Np(VI), extracting the zirconium, and finally performing

the Np^{237} procedure on the residual aqueous phase.

When certain plant solutions containing a small amount of mercuric nitrate (0.002 - 0.004 M) were analyzed for Np^{237}, some reduction of uranyl ion was observed. Experiments performed previously (Table VIII) had indicated negligible reduction of UO_2^{++} with potassium iodide and stannous chloride under the procedure recommended. A series of extractions was performed using uranyl nitrate tracer to show that the presence of the Hg^{++} ion caused an interference in the standard method of analysis for Np^{237}.

Table (IX)

Interference of Hg^{++} in the Standard Np^{237} Method

Conditions	% U(IV) Extracted
1. Standard method with the omission of the $SnCl_2$	0
2. Standard method with the omission of the $SnCl_2$	0
3. Standard method with the omission of the $SnCl_2$ but the addition of 1 mg. of $HgNO_3$	0
4. Standard method including $SnCl_2$ and 1 mg. of $HgNO_3$	6.4
5. Standard method including $SnCl_2$ and 2 mg. of $HgNO_3$	12.8

The reduction of some of the uranium may be explained by the reactions:

$$HgCl_2 + SnCl_2 \rightarrow Hg + SnCl_4$$

$$Hg + 4\ HI \rightarrow H_2(HgI_4) + H_2\uparrow$$

While mercuric nitrate is not usually present in plant solutions, it has been used at times to catalyze the dissolution of certain slugs. When it is suspected to be present in solutions containing uranium, it is recommended that one simply omit the stannous chloride and perform the potassium iodide reduction for twenty minutes in the boiling water bath.

Summary

The thenoyltrifluoracetone solvent extraction method for neptunium (237) described is rapid and achieves excellent separation of neptunium from uranium, plutonium, americium, curium and fission products. Suitable conditions for performing the extraction of the neptunium directly from nitric acid are presented. The elimination from interference by mercury is described, and the quantitative recovery of neptunium present in the various valence states is demonstrated.

Bibliography

1. Hudgens, J. E., Jr., MonN-13 (September, 1945).

2. Magnusson, L. B., Hindman, J. C., and LaChapelle, T. J., ANL-4066 (October, 1947).

3. Moore, F. L., and Hudgens, J. E., Jr., ORNL-153 (September, 1948).

4. Thomas, J. R., and Crandall, H. W., CN-3733 (December, 1946).

5. Thompson, S. G., Morgan, L. O., James, R. A., and Perlman, I., CC-3874 (May, 1948).