UNCLASSIFIED

AEC RESEARCH AND DEVELOPMENT REPORT

HW-59032

MASTER

# AN ANALYTICAL METHOD FOR NEPTUNIUM-237 USING ANION EXCHANGE

**F. P. ROBERTS**

JANUARY 28, 1959

**HANFORD LABORATORIES**

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

GENERAL ELECTRIC

UNCLASSIFIED

# DISCLAIMER

UNCLASSIFIED

HW-59032

UC-4, Chemistry-General
(TID-4500, 14th Ed.)

# AN ANALYTICAL METHOD FOR NEPTUNIUM-237 USING ANION EXCHANGE

By

F. P. Roberts

Chemical Research
Chemical Research and Development Operation

January 28, 1959

HANFORD ATOMIC PRODUCTS OPERATIONS
RICHLAND, WASHINGTON

Work performed under Contract No. W-31-109-Eng-52 between
the Atomic Energy Commission and General Electric Company

Printed by/for the U. S. Atomic Energy Commission

Printed in USA. Price 50 cents. Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

UNCLASSIFIED

# AN ANALYTICAL METHOD FOR NEPTUNIUM-237 USING ANION EXCHANGE

## INTRODUCTION

The analytical method(1, 2) for neptunium used by the laboratories supporting Hanford separation processes is based on the extraction of neptunium(IV) by TTA followed by total alpha counting of neptunium-237 and gamma counting of neptunium-239 tracer, added to permit yield measurements. Alpha energy analysis is used to determine the purity of the neptunium-237. In samples containing high plutonium-to-neptunium ratios and/or high beta-gamma activity, repeated extractions are essential to insure sufficient decontamination to permit neptunium-237 determination by alpha energy analysis and neptunium-239 determination by gamma energy analysis.

Anion exchange should also be applicable to the separation of neptunium from interferences. Neptunium(IV) is strongly absorbed on anion exchange resins from nitric acid solution.(3) Ryan's work on the recovery of plutonium by anion exchange(4) shows that a high degree of separation from uranium, americium and fission products as well as most commonly found impurities is achieved. The determination of neptunium by use of anion exchange resins should be feasible if a method for separation of plutonium is found. This paper describes the development of such a method.

## SUMMARY AND CONCLUSIONS

A method has been developed for separation of neptunium from plutonium, uranium, americium, curium and fission products by anion exchange with sufficient decontamination to permit neptunium-237 estimation by alpha energy analysis and neptunium-239 estimation by gamma spectrometry. The sample is spiked with neptunium-239 tracer to permit yield corrections and loaded on a small column of Dowex 1, X-4 (100-200 mesh) from 8 M nitric acid in the presence of ferrous sulfamate and semicarbazide. After washing the resin with 30 to 40 column volumes of a 4.5 M nitric acid solution containing ferrous sulfamate and semicarbazide, the neptunium is eluted with 0.005 M ceric sulfate in dilute nitric acid and mounted for total alpha counting, alpha energy analysis, and gamma energy analysis. Neptunium recoveries of 95 per cent have been obtained while plutonium decontamination factors are $5 \times 10^4$. Decontamination factors for uranium, americium, curium and gross fission products are all greater than $10^4$. Uranium, up to 180 g/l in the column feed, does not interfere. The plutonium decontamination factor can be increased by a factor of 10 to 100 by following the nitric acid-ferrous sulfamate-semicarbazide wash by a wash with 0.1 M $NH_4I$ in 12 M HCl. This is followed by neptunium elution with 6.5 M HCl containing 0.004 M HF. The method is applicable to the high salt samples from the Redox process as well as Purex process samples.

## DISCUSSION

An ion exchange resin may be considered as an ionic salt in which one of the ions is attached to an insoluble organic material of high molecular weight. In the case of Dowex 1 resins, the attached group is a quarternary amine and the movable ion is any negatively-charged ion. In the operation of the ion exchange column the movable anion is replaced by the anion of the solution passed through the column and occurs according to the law of mass action.(5)

$$R^+A^- + B^+ = RB + A^-$$

The equilibrium distribution coefficient is widely used as a measure of the degree of absorption of an ion by the resin and is defined by

$$Kd = \frac{Mr}{Ms} \times \text{ ml solution/gram of resin}$$

for cases of very low ion concentrations. Mr and Ms are the amounts in the resin phase and solution, respectively. From the theory developed by Mayer and Tompkins(6) it can be shown that the volume of solution passed through the column to bring the concentration of the ion in the effluent to maximum is proportional to the Kd value. Thus ions with widely different Kd values may be separated easily by column operations.

There are few elements other than Neptunium(IV), Plutonium(IV) and Thorium(IV) known to form strong anionic nitrate complexes in nitric acid absorbable on anion exchangers. Table I lists some of the known distribution coefficients of ions in nitric acid which are of interest in the separation of neptunium.

## TABLE I

## DISTRIBUTION COEFFICIENTS OF SOME IONS IN $HNO_3$ ON ANION EXCHANGE RESIN*

| HNO3 Moles/Liter | 2 | 4 | 6 | 8 | 10 | 12 | |
|---|---|---|---|---|---|---|---|
| Ion | Kd | | | | | | Reference |
| Neptunium(V) | 0.3 | 4 | 10 | 10.5 | 10.5 | 10 | 7 |
| Neptunium(IV) | 300 | 600 | 1800 | 2000 | 2500 | 2400 | 3 |
| Plutonium(IV) | | 700 | 2000 | 3500 | | | 4 |
| Plutonium(III) | | | Not absorbed | | | | 7 |
| Thorium(IV) | 15 | 50 | 200 | 300 | 200 | | 8 |
| Protactinium(V) | 2 | 8 | 10 | 10 | 4 | | 7 |
| Uranium(VI) | 0.1 | 3 | 7 | 8 | | | 9 |
| Zirconium(IV) | 0.1 | 0.3 | 0.8 | 0.9 | 0.7 | | 7 |
| Ruthenium(IV) | 50 | 20 | 10 | 8 | 4 | | 7 |
| Aluminum(III) | | | Not absorbed | | | | 9 |
| Americium(III) | | | Not absorbed | | | | 9 |
| Curium(III) | | | Not absorbed | | | | 9 |
| Iron(III) | | | Not absorbed | | | | 9 |
| Rare Earth(III) | | | Not absorbed | | | | 9 |

* This data should be considered qualitative rather than quantitative because resins of different cross linkages were used by different authors.

The anion exchange behavior of metal complexes in chloride systems has been widely studied.(7, 9, 10, 11) Uranium, neptunium and plutonium in IV and VI oxidation states show quite similar absorption characteristics.(12) Many other elements are absorbed from hydrochloric acid systems. For these reasons and since the Purex and Redox processes are nitrate systems, the nitric acid system appears more attractive for the separation of tracer quantities of neptunium from uranium, plutonium and mixed fission products.

## EXPERIMENTAL

### Reagents and Materials

Analytical grade Dowex 1* resins were used throughout the entire study. These were converted to the nitrate form by washing with 7.0 M $HNO_3$. No other purification steps were used.

Ferrous sulfamate stock solutions were prepared by dissolving high purity iron powder in a slight stoichiometric excess of sulfamic acid solution. The semicarbazide was kept under refrigeration to prevent decomposition. A reducing solution was prepared containing 0.01 M ferrous sulfamate, 0.1 M semicarbazide and nitric acid. It was necessary to prepare the reducing solution each day, as this mixture deteriorates rapidly.

The neptunium-239 tracer was obtained by thermal neutron irradiation of uranium-238.

### Apparatus

Glass columns, 3 mm x 7 cm, with a 10 ml reservoir were used in all experiments. Flow rates were controlled by applying a vacuum to the bottom of the column. For highly radioactive samples the effluent from the loading and wash steps was continuously "slurped" into a waste container.

The alpha energy analyzer used was a four-place gridded chamber.(13) A scintillation counter with three-inch NaI(Tl) crystal was used as a gamma detector. A 256-channel pulse height analyzer(14) was used with the alpha and gamma detectors.

---

* Supplied by Bio-Rad Laboratories, Berkeley, California

## Absorption of Neptunium on Dowex-1 Resin

Semicarbazide has been used by other workers(7) as a reductant for neptunium. Preliminary studies with neptunium-239 and plutonium-239 tracers showed that neptunium is quantitatively absorbed from 0.1 M semicarbazide in 7.0 M $HNO_3$, but little separation from plutonium is achieved. When ferrous sulfamate was substituted for semicarbazide, there was better plutonium separation but gas formation on the resin resulted and high plutonium decontamination was not obtained. When both ferrous sulfamate and semicarbazide were present, gas formation was markedly reduced and an excellent separation from plutonium resulted.

To determine the effect of nitric acid concentration on the absorption of neptunium, neptunium-239 tracer was loaded on Dowex 1, X-4 columns from a solution of the reducing mixture with various nitric acid concentrations. The columns were washed with several column volumes of nitric acid at the same concentration as the feed. The neptunium-239 gamma activity in the effluent was compared with the neptunium-239 gamma activity added. Table II shows the results of this experiment.

TABLE II

NEPTUNIUM ABSORPTION ON DOWEX 1, X-4 FROM 0.01 M FERROUS SULFAMATE - 0.1 M SEMICARBAZIDE AND NITRIC ACID

| Nitric Acid in Feed M | $Np^{239}$ Activity in Effluent, c/m | $Np^{239}$ Activity Added, c/m | Per Cent Np Absorbed |
|---|---|---|---|
| 3.0 | 28,655 | 97,105 | 57.0 |
| 4.0 | 10,390 | 97,105 | 89.3 |
| 4.5 | 1,140 | 97,105 | 98.8 |
| 5.0 | 1,810 | 97,105 | 98.1 |
| 5.5 | 990 | 97,105 | 99.0 |
| 6.0 | 2,106 | 130,566 | 98.4 |
| 6.5 | 298 | 130,566 | 99.8 |
| 7.0 | 1,780 | 130,566 | 98.6 |

The removal of plutonium from the resin in the presence of ferrous sulfamate and semicarbazide was studied as a function of nitric acid concentration. In this experiment, $3.1 \times 10^7$ d/m of tetravalent plutonium-239 was absorbed on columns of Dowex 1, X-4 from 7.0 M nitric acid. The plutonium was then eluted with 0.01 M ferrous sulfamate, 0.1 M semicarbazide in nitric acid. A total of 36 column volumes of the reducing solution was passed through each column at a flow rate of 0.3 milliliters per minute. The remaining plutonium was eluted with 5 milliliters 0.35 M nitric acid and determined by alpha counting. The decontamination factor was calculated by:

$$DF = \frac{\text{D/M Pu Loaded on Column}}{\text{D/M Pu Eluted with 0.35 } \underline{M} \text{ } HNO_3}$$

Table III shows the results for different acid concentrations.

### TABLE III

### PLUTONIUM DECONTAMINATION OF DOWEX 1, X-4 WITH FERROUS SULFAMATE - SEMICARBAZIDE AT DIFFERENT NITRIC ACID CONCENTRATIONS

| Nitric Acid Concentration of Wash (Moles per Liter) | Pu Loaded on Column (D/M) | Pu Eluted with 0.35 M $HNO_3$ (D/M) | Decontamination Factor |
|---|---|---|---|
| 3 | $3.1 \times 10^7$ | $< 50$ | $> 10^5$ |
| 4 | $3.1 \times 10^7$ | $< 50$ | $> 10^5$ |
| 4.5 | $3.1 \times 10^7$ | 500 | $6 \times 10^4$ |
| 5.0 | $3.1 \times 10^7$ | $2.2 \times 10^4$ | 1400 |
| 6.0 | $3.1 \times 10^7$ | $6.1 \times 10^4$ | 510 |
| 7.0 | $3.1 \times 10^7$ | $5.2 \times 10^5$ | 60 |
| 8.0 | $3.1 \times 10^7$ | $2.4 \times 10^6$ | 13 |

## Elution of Neptunium from Dowex 1 Resin

Various elutriants were tested to find a condition under which neptunium could be removed from the resin in a small volume. Both dilute nitric acid and hydrochloric acid eluted neptunium rather slowly and required several milliliters of elutriant for quantitative recovery. The rate of elution was increased by oxidizing neptunium(IV) to a higher valence state. For this purpose ceric sulfate was used. Table IV gives a comparison of elution rates for different elutriants.

## TABLE IV

## COMPARISON OF RATES OF ELUTION OF NEPTUNIUM FROM DOWEX 1, X-4 BY DIFFERENT ELUTRIANTS

| Elutriant | Per Cent Neptunium Eluted in Fraction* 1 | 2 | 3 | Total Neptunium Eluted in All Three Fractions |
|---|---|---|---|---|
| HCl 0.1 M | 29.6 | 6.9 | 4.6 | 51.1% |
| $HNO_3$ 0.25 M | 50.4 | 12.6 | 8.1 | 71.1% |
| $Ce(SO_4)_4$ 0.001 M + $HNO_3$ 0.25 M | 87.5 | 9.4 | 1.0 | 97.9% |
| $Ce(SO_4)_2$ 0.010 M + $HNO_3$ 0.25 M | 90.2 | 8.8 | 0.6 | 99.6% |

* Two-column volumes in fraction

### Effect of Uranium on Neptunium Recovery

The data in Tables I and II would indicate the optimum nitric acid concentration for loading and washing the resin is 4.5 moles per liter. However, when samples containing gross quantities of uranium were analyzed using 4.5 M nitric acid to load the sample on the resin, neptunium yields were low. Dilution of the sample increased the yield markedly, as is shown in Table V.

## TABLE V

## EFFECT OF URANIUM CONCENTRATION ON NEPTUNIUM YIELD

| Uranium, Milligrams per Milliliter | Per Cent Neptunium Recovered |
|---|---|
| 244 | 76.4 |
| 122 | 94.1 |
| 24.4 | 95.8 |

Also it was found that the neptunium recovery in samples containing gross quantities of uranium was dependent on the nitric acid concentration as is shown in Table VI.

## TABLE VI

## EFFECT OF NITRIC ACID CONCENTRATION ON NEPTUNIUM RECOVERY IN SAMPLES OF HIGH URANIUM CONTENT

| $HNO_3$ (moles/liter) | Per Cent Neptunium Recovered |
|---|---|
| 3.8 | 75.7 |
| 5.8 | 84.2 |
| 7.7 | 96.0 |

Uranium concentration = 180 milligrams per milliliter in all three runs.

### Separation of Neptunium from Other Elements

From the data presented above the procedure suggested is to load the column from 8.0 M nitric acid, 0.1 M semicarbazide, 0.01 M ferrous sulfamate, followed by washing with 40 column volumes of 4.5 M $HNO_3$, 0.1 M semicarbazide and 0.01 M ferrous sulfamate. The neptunium is then eluted with 0.005 M ceric sulfate in 0.25 M nitric acid.

Typical recovery and decontamination values obtained from solutions spiked with various contaminants under these conditions are shown in Table VII.

## TABLE VII

| Element | Per Cent Found in Neptunium Fraction |
|---|---|
| Neptunium | 96 |
| Plutonium | 0.002 |
| Americium-Curium | <0.001 |
| Uranium | <0.001 |
| Ruthenium | 0.008 |
| Zirconium | 0.003 |
| Niobium | 0.003 |

## Further Plutonium Decontamination

Under the conditions described ~~in~~ the preceeding paragraphs the plutonium decontamination factor appears to be limited to about 5 x $10^4$ for practical volumes of wash solution. However, an increased decontamination factor is obtained by converting the resin to the chloride form by washing with 12 M HCl and passing 0.1 M $NH_4I$ and 12 HCl through the column. From eight to ten column-volumes of this wash solution increases the overall plutonium decontamination factor to $10^6$.

Elution of neptunium from the chloride-form resin is accomplished with 6.5 M HCl - 0.004 M HF. This elutriant removes neptunium rapidly, as is shown in Table VIII.

TABLE VIII

ELUTION OF NEPTUNIUM(IV) FROM $Cl^-$ FORM DOWEX 1 x 4 (100 - 200 mesh) BY 6.5 M HCl, 0.004 M HF

| Column Volumes of Elutriant | Per Cent Neptunium Eluted |
|---|---|
| 4 | 93.8 |
| 8 | 98.8 |
| 12 | 99.2 |
| 16 | 99.4 |

## Application of Method to Purex and Redox Samples

Samples of Purex first cycle feed and first cycle waste were carried through the procedure given in the appendix.

Examples of recovery and decontamination are shown for the ferrous sulfamate - semicarbazide wash and the combined ferrous - semicarbazide and $NH_4I$ - HCl washes. Neptunium recoveries were based on recovery of neptunium-239 spike added to original sample.

## TABLE IX

## ANALYSIS OF PUREX SAMPLES

| | First Cycle Feed | | First Cycle Waste | |
|---|---|---|---|---|
| | 1 | 2 | 1 | 2 |
| Neptunium Recovery | 94% | 94.5% | 94% | 96% |
| Plutonium Decontamination Factor | $5 \times 10^4$ | $5 \times 10^6$ | $4 \times 10^3$ | $8 \times 10^4$ |
| Beta Decontamination Factor | ----- | ----- | $1.21 \times 10^4$ | $2.3 \times 10^4$ |

1. Ferrous sulfamate - semicarbazide wash only.
2. Combined ferrous sulfamate - semicarbazide and $NH_4I$ - HCl washes.

The lower plutonium decontamination factor observed in the sample of first cycle waste may have been caused by absorption of plutonium to solids present in the sample and subsequent removal during the wash and elution steps.

Synthetic Redox samples were prepared and, with neptunium-239 tracer, recoveries were determined by using the procedure given in the appendix. It was necessary to reduce the dichromate present in these samples with excess 3.0 M ferrous sulfamate. The high salt content in this type of sample had no adverse effect on the column and gave higher recoveries than the Purex type samples. This indicates that aluminum nitrate may be beneficial. Recoveries obtained in several runs are shown in Table X.

## TABLE X

## NEPTUNIUM RECOVERIES FROM SYNTHETIC REDOX SAMPLES

| Run | First Cycle Feed | First Cycle Waste |
|---|---|---|
| 1 | 100.9% | 98.3% |
| 2 | 98.4% | 97.9% |
| 3 | 99.9% | 99.0% |
| 4 | 98.6% | ---- |

## REFERENCES

1. Moore, F. L., "Separation and Determination of Neptunium by Liquid-Liquid Extraction", Anal. Chem. 29, 941 (1957).
2. Schneider, R. A., Chemical Processing Department Analytical Technical Manual, HW-53368 (1958).
3. Sheppard, J. C. and G. V. Becker, Recovery Progress Report, HW-49825, June 4, 1857 (Secret).
4. Ryan, J. L. and E. J. Wheelwright, "Application of Anion Exchange to the Reprocessing of Plutonium", Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Paper P/1915 (1958).
5. Samuelson, Olaf, Ion Exchangers in Analytical Chemistry, New York: John Wiley and Sons, Inc., 1953.
6. Mayer, S. W. and E. R. Tomkins, J. Am. Chem. Soc. 69, 2866 (1947).
7. Wish, L. and M. Ramell, Sequential Analysis of Tracer Amounts of Neptunium, Uranium, and Plutonium in Fission Product Mixtures by Anion Exchange, USNRDL-TR-117 (1956).
8. Daran, J., J. Inorg. and Nucl. Chem. 5, 237-9 (1958).
9. Kraus, K. A. and F. Nelson, Am. Soc. Testing Materials, Spec. Tech. Publ. No. 195 (1958).
10. Kraus, K. A. and F. Nelson, "Anion Exchange Studies of the Fission Products", International Conference on the Peaceful Uses of Atomic Energy, Paper P/837 (1955).
11. Nelson, F., et al., Chemical Division Annual Progress Report, June, 1957, ORNL-2386, p. 92.
12. Nelson, F., et al., Chemical Division Annual Progress Report, June, 1958, ORNL-2584, p. 59.
13. Brauer, F. P. and R. E. Connally, Report in Preparation.
14. Schumann, R. W. and J. P. McMahon, "Argonne 256-Channel Pulse-Height Analyzer", Rev. Sci. Instr. 27, 675-687, September, 1956.

## APPENDIX

### Suggested Procedure

1. Take an appropriate aliquot of the sample in a mixing vessel. Adjust acidity to approximately 8.0 M with 16 M $HNO_3$.
2. Add an equal volume of a solution containing 8.0 M $HNO_3$, 0.02 M ferrous sulfamate and 0.2 semicarbazide. Note 1.
3. Add enough neptunium-239 tracer (ca $10^5$ d/m) to determine yield.
4. Pass prepared sample through a 3 mm x 7 cm column of Dowex 1, X-4 (100 - 200 mesh) at a rate of 3 to 6 drops per minute.
5. Rinse reservoir above column with several drops of 8.0 M $HNO_3$. Allow rinse to pass through column. Again rinse reservoir thoroughly with 8.0 M $HNO_3$ several times, discarding these rinses by drawing off with vacuum.
6. Pass from 15 to 20 ml 4.5 M $HNO_3$, 0.1 M semicarbazide, 0.01 M ferrous sulfamate through column at flow rate of 3 to 6 drops per minute.
7. Pass 2 ml 8.0 M $HNO_3$ through the column to remove semicarbazide and ferrous sulfamate.
8. Elute the neptunium with 2 ml 0.005 M ceric sulfate in 0.25 M $HNO_3$, catching eluate in a 2 ml volumetric. Note 2.
9. Mount an aliquot on a platinum disc for total alpha counting and alpha energy analysis. The yield is determined by comparative counting the 0.24 Mev gamma from neptunium-239 on the disc with that of a standard neptunium-239 disc.

### Notes

1. For Redox samples, the procedure is varied by adding a sufficient excess of 3.0 M ferrous sulfamate to reduce the sodium dichromate or other oxidizing agents present.

2. For samples with a neptunium-to-plutonium ratio greater than $10^4$, an added wash is inserted after step 6. Pass from 1 to 2 ml 12 M HCl through the column to remove $NO_3^-$. Then pass from 4 to 5 ml 0.1 M $NH_4I$ - 12 M HCl through the column (apply vacuum to maintain a flow rate of 3 to 6 drops per minute). Omit step 7 and 8 above. The neptunium is eluted with 2 ml 6.5 M HCl - 0.004 M HF.

UC-4, Chemistry-General
(TID-4500, 14th Ed.)

## INTERNAL DISTRIBUTION

| Copy Number | |
|---|---|
| 1 | L. A. Berry |
| 2 | F. P. Brauer |
| 3 | R. J. Brouns |
| 4 | R. E. Burns |
| 5 | E. W. Christopherson |
| 6 | V. R. Cooper |
| 7 | G. B. Hansen |
| 8 | K. M. Harmon |
| 9 | O. F. Hill - G. J. Alkire |
| 10 | H. H. Hopkins |
| 11 | J. W. Jordan |
| 12 | R. L. Moore |
| 13 | J. M. Nielsen |
| 14 | W. H. Reas |
| 15 | D. L. Reid |
| 16 | F. P. Roberts |
| 17 | D. M. Robertson |
| 18 | R. W. Stromatt - F. A. Scott |
| 19 | E. E. Voiland |
| 20 | A. J. Waligura |
| 21 | M. T. Walling, Jr. |
| 22 | 300 Files |
| 23 | Record Center |
| 24 - 27 | G.E. Technical Data Center, Schenectady, N. Y., Attn: A. Cohen |
| 28 - 30 | Extra |