DETERMINATION OF NEPTUNIUM-239 FROM FALLOUT SAMPLES.

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ABSTRACT

An analytical procedure is described for the separation of neptunium-239 from fallout samples. Neptunium is separated from uranium, plutonium and fission products by solvent extraction method. Np (IV) is extracted from 1 M nitric acid by shaking with equal volume of 0.5 M thenoyl-tri-fluoro acetone (T.T.A.) solution in xylene and back-extracted with 8 M nitric acid. Finally, Np is co-precipitated with zirconium mandelate, and counted in a low background beta-counting set-up. The average chemical recovery by this procedure is 82.6% Under the conditions described, very good separation of neptunium is effected from aluminium, iron, fission products, thorium, uranium and plutonium.

1. Introduction

NEPTUNIUM-239 is one of the important isotopes in the early fallout from the nuclear weapon tests. It is produced by the interaction of neutrons with the uranium used in the weapon, by (n, γ) reaction. The neutron capture cross-section for this reaction is fairly large and therefore the Np^{239} is present in large quantities in the fresh fallout. The rapid determination of Np^{239} in the presence of fission products, uranium and plutonium, requires a quantitative chemical separation from these elements, and generally solvent extraction methods are advantageous for such analyses.

Magnusson et al.1 studied the extraction of neptunium from hydrochloric acid solution by thenoyl-tri-fluoro acetone (T.T.A.) and determined the distribution coefficients for neptunium as a function of acidity and valence state. Moore² demonstrated the possibility quantitative extraction of Np (IV) with T.T.A. from nitric acid solution. The procedure described by Moore was tried for the fallout samples but it did not give consistent This was chemical recovery of Np^{239} . presumably due to incomplete reduction of neptunium to the fourth valence state or due to a change in the sample matrix. For a complete reduction of neptunium to the fourth valence state a combination of hydroxylamine hydrochloride and ferrous sulphamate was found more suitable. Fallout samples contain varying amounts of silica and iron, and as these elements interfere in the extraction of neptunium, one has to take special care during the chemical analysis.

Present paper gives the analytical procedure for the separation of Np²³⁹ from fallout samples. The separated neptunium is completely free from uranium and fission products.

2. EXPERIMENTAL

Sample Preparation.—(i) The high altitude dust samples are collected from the surfaces of commercial aircrafts. The various parts of the aircraft are swiped with cotton wool soaked in white petrol. After gamma-spectral analysis, the samples are leached with a mixture of 3 M hydrochloric acid and 0·1 M hydrofluoric acid. More than 95% radioactivity gets leached by this leaching mixture. The leached solution is made to a definite volume and known amounts of inactive carriers like Sr, Cs. Zr, Ce and Ru are added to it.

- (ii) Rain-water samples are evaporated to dryness and the residue is leached in the same way as swipe samples.
- (iii) Air filter samples are leached directly with the same leaching mixture as above.

Chemical Procedure and Results.—A suitable aliquot of the leached solution is taken for the neptunium analysis with 5 mg. of iron carrier. 1.0 gm. of hydroxylamine hydrochloride, boric acid + nitric acid mixture are added to the solution. The solution is then warmed and ammonium hydroxide is added slowly to the solution to precipitate hydroxides. The hydroxide precipitate is dissolved in dilute nitric acid and the solution is evaporated to dryness. (If silicic acid appeared while evaporating, it should be centrifuged in the presence of hot concentrated nitric acid to avoid the losses of neptunium due to adsorption on silicic acid. Silicic acid also interferes in the extraction of neptunium in the next steps.) The residue is then dissolved in 15 ml. of 1 N nitric acid and 0.25 gm. of hydroxylamine hydrochloride are added to it. The solution is warmed for ten minutes and 2 ml. of 3 M ferrous sulphamate are added to it. After cooling to room temperature the solution is transferred to a 50 ml.

separating funnel. Neptunium is extracted from this solution by shaking with equal volume of 0.5 M thenoyl-tri-fluoro acetone (T.T.A.) in xylene for ten minutes. The two layers are allowed to separate and the aqueous phase is transferred to another separating funnel and neptunium is extracted in the same way. Both the organic phases are collected together in another 100 ml. separating funnel and scrubbed with an equal volume of 1M nitric acid for one minute. Neptunium is back-extracted from the organic phase by shaking it with equal volume of 8 M nitric acid for four minutes. The phases are separated. The aqueous phase is evaporated to dryness and the residue is taken in 10 ml, of 1 M HNO₃. 2 ml, of ferrous sulphamate are added to the solution with 5 mgm, of inactive zirconium carrier. solution is kept for five minutes and then neptuco-precipitated with zirconiumnium mandelate by adding mandelic acid to the solution is kept for five minutes and then neptu-20 mm. diameter filtering stick, and the precipitate is mounted on special perspex planchet for counting in a low background beta-counter.

The procedure is checked by tracer experiments in which known amounts of Np²³⁹ tracer were added to old fallout samples. These samples were analysed for neptunium, using the above procedure to determine the chemical recovery and also the radiochemical purity of neptunium. Table I gives the percentage recovery of neptunium. The data in Table I

TABLE I
Recovery of Np²³⁹ from fallout samples

| No. | d.p.m. of Np ²³⁹ added | d.p.m. of Np ²³⁹ recovered | % | recovery |
|-----|---|---|-----|----------|
| 1 | 770 | 642 | | 83.4 |
| 2 | 770 | 623 | | 86.9 |
| 3 | 770 | €54 | | 84.9 |
| 4 | 185 | 151 | | 81.6 |
| 5 | 185 | 152 | | 82.2 |
| | | | | |
| | | | Av. | 82.6 |

show that there is not much variation in the chemical recovery of neptunium. The average chemical yield is 82.6%. Figures 1 and 2 respectively show the decay curve and gammaray spectrum of neptunium-239, separated from the fallout debris collected after a recent Chinese nuclear test (10th Chinese test). The above figures show that the radiochemical purity of separated neptunium is excellent.

In some cases where concentrations of Np^{239} in the sample is small and that of Zr^{95} is high,

a small quantity of radio-zicronium may follow the neptunium in the final stripping solution (i.e., 8 M HNO₃). This small amount of radio-zirconium in the final stripping solution can be removed by performing a five minutes extraction of stripping solution with equal volume of 0.5 M T.T.A. in xylene. Neptunium remains quantitatively in aqueous phase.

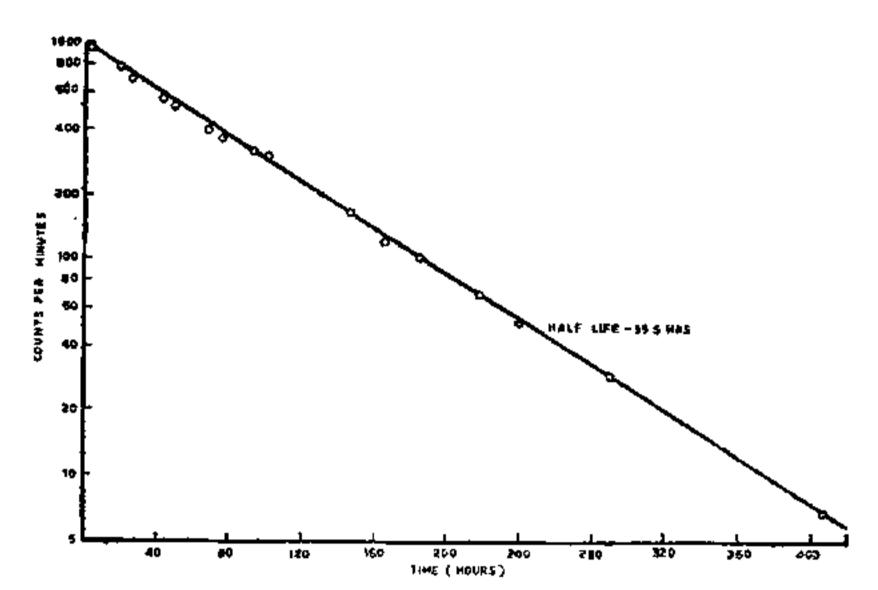


FIG. 1. Decay curve of negtunjum-239 separated from fallout debris collected after the tenth Chinese Nuclear Test.

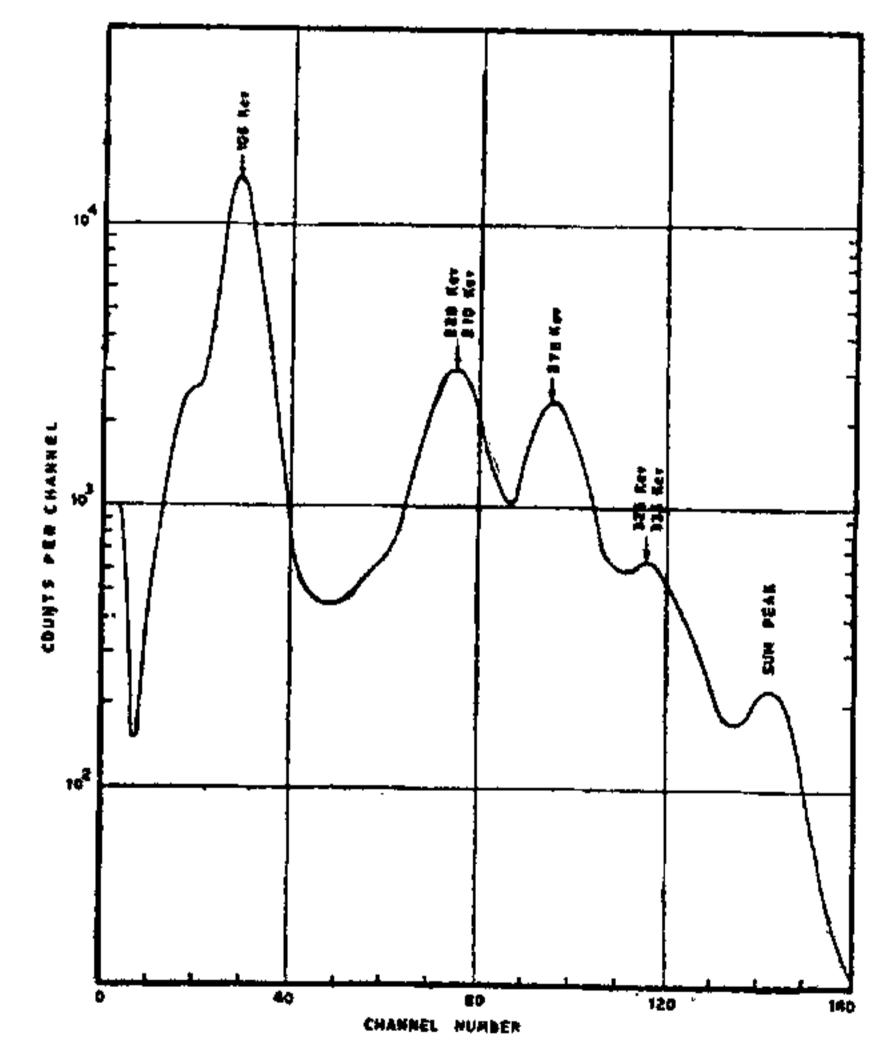


Fig. 2. Gamma-spectrum of neptunium-239 from the sample collected after the teath Chinese Nuclear Test.

The co-precipitation of neptunium (IV) with zirconium mandelate is also studied using Np²³⁹ tracer. Data in Table II show that the co-precipitation of neptunium with zirconium mandelate is quantitative. The co-precipitation of Np (IV) with zirconium mandelate in the

final step is more convenient for counting the beta-activity of Np²³⁹.

Table II

Co-precipitation of Np^{239} with Zr-mandelate

| No. | c.p.m. of Np ²³⁸ added | c.p.m. of Np ²³⁹ cartied with Zr-mandelate |
|-----|--------------------------------------|---|
| 1 | 925 | 915 |
| 2 | 1063 | 1060 |
| 3 | 808 | 8 10 |
| 4 | 1320 | 1305 |
| | | |

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X-RAY PATTERNS OF MOLLUSC SHELLS FROM INDIAN WATERS

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1. MATERIALS

TT is well known that the shells of molluscs consist of layers of calcium carbonate interspersed with protein layers and that the calcium carbonate occurs mostly as calcite or aragonite, and more rarely as vaterite. Some studies have been made on this subject and are summarised by Jean Bouillon.2 These, however, appear to have been made on specimens obtained from the temperate latitudes. The author is not aware of any reports of X-ray studies of the nature of the inorganic component in mollusc shells occurring in Indian waters. A study was therefore made of the X-ray diffraction patterns of a number of typical specimens obtained from the beaches of Madras State. The specimens studied are listed serially in Table I giving their class,

TABLE I

List of the shells studied with their identifications

Class—Gastropoda Sub-class—Prosobranchia

(A) Order-Megagastropoda

(a) Series—Strombacea
Specimens 1 and 2 Str

Specimens 1 and 2 Strombidae, Strombus (A' (Two different species)

(b) Series Cypraeacea
Secimens 2 and 4 Cyr

(A)√

Specimens 3 and 4 Cypraeidae, Cypres (A) $\sqrt{\text{Two different species}}$

(c) Series—Cerithiacea
Specimen 5—Turritellidae, Turritella

TABLE I-Contd.

(B) Order—Stenoglossa
(a) Series—Buccinacea

Specimen 6— Volemidae. Hemisuscus(A)
Specimen 7—Fasciolariidae, Fasciolaria
(A)

(C) Order-Archaeogastropoda

(a) Series—Zeugobranchia

Specimen 8-Haliotidae, Haliotis (A)

(b) Series--Trochacea

Specimen 9—Trochidae, Trochus (A)

(c) Serie - Patellacea

Specimen 10—Patellidae, Patella (C)√

Class-Lamellibranchiata

(A) Order—Eulamellibranchiata Sub-Order—Heterodonta

(a) Series-Veneracea

Specimen 11—Veneridae, Meretrix (A)

Sub-Order—Schizodonta
(a) Series—Unionacea

Specimen 12—Unionidae, Unioninae.

Lamellidens (A)

(B) Order—Anisomyaria

(a) Series-Pectinacea

Specimen 13—Pectinidae, Spondilinae, Spondylus (C) V

Class—Cephalopoda
Sub-Class—Tetrabranch

Sub-Class—Tetrabranchiata

Order-Nautiloidea

Specimen 14-Nautilidas, Nautilus (A) V

(C)=Calcite; (A)=Aragonite; $\sqrt{}$ =Also listed in Ref. 2.

sub-class (if any), order, family and genus. A fair number of specimens contained in this list have also been studied by Jean Bouillon. These are indicated by a mark (1/) in Table I.