

## Two Methods for the Isolation of Tracer Amounts of Plutonium

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Two new methods have been devised for the isolation of plutonium from uranium samples, which have been irradiated with slow neutrons for about 1 year and have cooled for about 3 months. The number of moles,  $\beta$ - and  $\gamma$ -activity of the products obtained in these samples have been calculated.

The complex formation between organic ligands and some lanthanide and actinide elements has been studied for several years by a group at this institute <sup>1,2</sup>. For a long time it has been our aim to extend these studies to include some transuranium elements. Due to the generosity of the Dutch-Norwegian Joint Establishment for Nuclear Energy Research (J.E.N.E.R.), we have been allowed to irradiate uranium samples in the pile at Kjeller, Norway. Some transuranium isotopes and a number of fission products are formed during this irradiation. This paper describes two methods, which have been found useful for the isolation of plutonium from these samples.

### PRODUCTS OBTAINED IN NEUTRON IRRADIATED URANIUM

The radioactivity  $I_1$  (dis./sec.) of an isotope produced by the irradiation of a thin sample by particles of a certain energy can be calculated from the equation

$$I_1 = f \sigma N A_0^{-1} a_0 (1 - e^{-\lambda_1 T}) e^{-\lambda_1 t} = I_0 \cdot e^{-\lambda_1 t} \quad (1)$$

where  $f$  is the particle flux (particles  $\times$  cm<sup>-2</sup>  $\times$  sec<sup>-1</sup>),  $\sigma$  the reaction cross section (cm<sup>2</sup>),  $N$  the Avogadro number,  $a_0$  the number of grams of the irradiated isotope of the atomic weight  $A_0$  ( $N \cdot A_0^{-1} \cdot a_0$  is the number of bombarded atoms),  $\lambda_1$  the disintegration constant of the product nucleus (half-life  $\tau_1 = 0.693 \lambda_1^{-1}$ ),  $T$  the irradiation time, and  $t$  the time between the end of the irradiation and the measurement (cooling time). This equation is valid as long as no macroscopic changes takes place in the target ( $a_0 = \text{constant}$ ), and nuclear reactions with the product isotope can be neglected. For very long half-lives ( $\tau \gg T+t$ ) equation (1) reduces to  $I_1 = I_0 \lambda T$ .

If the decay products are also radioactive, their activity can be calculated from the formula first given by Bateman <sup>3</sup>

$$I_n = I_0 (C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t} + \dots + C_n e^{-\lambda_n t}) \quad (2)$$

where

$$C_1 = \frac{\lambda_1 \cdot \lambda_2 \dots \lambda_{n-1}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1) \dots (\lambda_n - \lambda_1)}$$

$$C_2 = \frac{\lambda_1 \cdot \lambda_2 \dots \lambda_{n-1}}{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2) \dots (\lambda_n - \lambda_2)}$$

$$C_3 = \frac{\lambda_1 \cdot \lambda_2 \dots \lambda_{n-1}}{(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3) \dots (\lambda_n - \lambda_3)}$$

etc. which is valid for  $n > 1$ .

Tables and methods to simplify the solution of these equations have recently been given by Flanagan and Senftle <sup>4</sup>, and by Kirby and Kremer <sup>5</sup>.

The mass  $a_i$  in grams of a particular isotope produced is given by

$$a_i = I_i A_i / \lambda_i N \quad (3)$$

In combining eqn (1) with eqn (3) it should be noted that  $A_0$  in eqn. (1) is the mass number of the bombarded nucleus, while  $A_i$  in eqn. (3) is the mass number of the product nucleus. In most nuclear reaction  $A_i \approx A_0$ . All time should be given in seconds in eqns. (1)–(3).

Equations (1)–(3) have been used to calculate the composition of the products formed in 20 g  $UO_3$  samples, which have been irradiated with  $9 \times 10^{18}$  thermal neutrons per  $cm^2$  ( $f \cdot T$ ) for about a year ( $T$ ), and have cooled for about 3 months ( $t$ ). The results are given in Table 1.

Table 1. Main products in 20 g  $UO_3$ , which has been subjected to slow neutron irradiation;  $f = 3 \cdot 10^{11}$  neutrons  $\times cm^{-2} \times sec^{-1}$ ,  $T = 1$  year,  $t = 3$  months.

Isotopes	Amount	Radioactivity
$U^{238} + U^{234}$	16.6 g	$2.5 \cdot 10^7$ $\alpha$ -dpm
$Np^{237}$	$< 10^{-6}$ g	600 $\alpha$ -dpm
$Pu^{239}$	$0.42 \cdot 10^{-3}$ g	$6.0 \cdot 10^7$ $\alpha$ -dpm
$Th^{234}$ ( $UX_1$ )	$< 10^{-6}$ g	$1.2 \cdot 10^7$ $\beta$ -dpm
$Pa^{235}$ ( $UX_2$ )	$< 10^{-6}$ g	$1.2 \cdot 10^7$ $\beta$ -dpm
Fission products	$0.57 \cdot 10^{-3}$ g	$5 \cdot 10^{11}$ $\beta$ -dpm *
		$3 \cdot 10^{11}$ $\gamma$ -particles/min **

\* 0.23 curie.

\*\*  $\gamma$ -energy  $\geq 0.1$  MeV.

The relative amounts and fractions of  $\beta$ - and  $\gamma$ -activity of each fission product has also been calculated, and the results are given in Table 2. Since the fine structure for only one of the peaks <sup>6</sup> of the fission yield curve was available, the calculations have been based on the smooth fission yield curve <sup>7</sup>.



## EXPERIMENTAL

Depending on the activity of the samples, the chemical experiments were carried out either in an iron-lead shielded box <sup>16</sup>, in a dry-box or in well-ventilated fume hoods.

All chemicals used were of p.a. quality.  $UO_2$  of high purity was obtained from A. B. Atomenergi; it decomposed partly during the pile irradiation.

The  $\alpha$ -samples were prepared by the evaporation of  $\leq 0.10$  ml of solution on Pt-dishes, placed on aluminium rings on a hot plate. In order to obtain thin and smoothly spread layers of the samples in the presence of visible amounts of salts, the samples were slurried with glycerol and slowly dried at 250° C. The solid matter of the samples never exceeded 0.3 mg/cm<sup>2</sup>, so that the self-absorption of  $\alpha$ -particles in the samples could be neglected <sup>27</sup>.

All measurements were made with a gas-flow (90 % A, 10 %  $CH_4$ ) proportional counter (Nuclear Measurements Corp., Indianapolis); the samples and the Al-foils used in the absorption experiments were measured inside its hemi-spherical ionization chamber (radius 3 cm).

## THE ISOLATION OF PLUTONIUM

The object of the isolation may either be to obtain chemically pure or radioactively pure plutonium. For tracer chemical work with plutonium, the latter object is usually more important; it will generally also provide a sufficient chemical purity of the product.

The most common laboratory method used in the isolation of plutonium from neutron irradiated uranium is the "lanthanum fluoride cycle" <sup>17</sup>. However, a great number of cycles (five to ten <sup>18</sup>) have to be carried out to obtain radioactively pure plutonium. The use of highly corrosive HF is a further drawback of the method.

Many other methods have been, and can be devised, which involve fewer steps and no HF. The two methods, which are described below, give radioactively pure plutonium in relatively few steps. These methods do not appear to have been described previously.

## Separation method I

The "zirconium phosphate cycle" devised for the isolation of neptunium <sup>19</sup> has been modified to suit the isolation of plutonium. Instead of zirconium, bismuth is used as a carrier for the phosphate precipitates. Some of the advantages of this change are that the bismuth phosphate is easier to filter and to dissolve than the zirconium phosphate. Depending on the conditions in the solution, the bismuth phosphate can be made to carry either the +3 and +4 valency states of the actinides together, or only the +4 valency state.

As a final purification step, an extraction with the chelating agent thenoyl-trifluoroacetone is used.

Extraction processes with chelating agents have the advantage that very high decontamination factors can be achieved. Thus it can be shown <sup>20</sup> that the distribution ratio of Th(IV) between 0.3 M thenoyltrifluoroacetone in benzene and 0.2 M  $HNO_3$  is about  $10^{12}$  times greater than the distribution of La (III) between the solvents. Though it is usually not possible to separate the phases with so great a precision that the quotient between the distribution ratios will become equal to the decontamination factor, a factor  $> 10^4$  is easily reached.

With the symbols used in the preceding paper<sup>21</sup> the separation flow-sheet consist of the following unit processes: V46, V66, S34, V36, S34, V46, S4.

1. The uranium sample is dissolved in hot, conc.  $\text{HNO}_3$  and kept at  $90^\circ \text{C}$  for 30 minutes, giving a solution of U(VI) and Pu(IV)<sup>22</sup>. (V46.)
2. The solution is diluted to 5 M in  $\text{HNO}_3$  and solid  $\text{NaBiO}_3$  is added to oxidize plutonium to the +6 valency state. (V66.)
3. The solution is made 0.1 M in  $\text{HNO}_3$  (if it becomes turbid,  $\text{HNO}_3$  is added until the solution is clear) and 0.1 M in phosphate. The  $\text{BiPO}_4$  precipitate is centrifuged off. This precipitate carries most of the fission products, and especially those with a chemistry similar to Pu(IV). (S34.)
4. The supernatant solution containing Pu(VI) is made 1 M in  $\text{HNO}_3$ , 0.05 M in  $\text{N}_2\text{H}_4$  and 0.005 M in  $\text{Fe}^{3+}$ . In this solution plutonium is rapidly reduced to Pu(III). (V36.)
5. The solution is diluted to 0.1 M in  $\text{HNO}_3$  and made 0.1 M in phosphate.  $\text{Bi}^{3+}$  is then added (1 drop 0.1 M  $\text{Bi}^{3+}$  for each ml solution) to precipitate  $\text{BiPO}_4$ , which carries all the plutonium. The precipitate, which is usually contaminated with some uranium, is centrifuged off and washed. (S34.)
6. The phosphates in the precipitate are converted into hydroxides by treating with warm  $\sim 10 \text{ M}$  KOH. After centrifuging, the solution is drawn off, and the precipitate washed and dissolved in hot, conc.  $\text{HNO}_3$ . (V46.)
7. After some hours at room temperature, the solution is diluted to 1 M  $\text{HNO}_3$ , and extracted with an equal volume of 0.3 M thenoyltrifluoroacetone in benzene. This gives a pure Pu(IV) solution in the benzene phase, leaving the rest of the uranium and the fission products in the aqueous phase (see also steps 5 and 6 in separation method II, below). (S4.)

The plutonium yield of the preliminary experiments with this method in our laboratory has been better than 60 %. No  $\beta$ - $\gamma$ -activity above background could be detected in the final plutonium sample, when measured through a  $10 \text{ mg/cm}^2$  Al-absorber.

### Separation method II

From Table 2 of the fission products it is seen that there is a great number of elements to the right of Nb, which can appear in many different oxidation states, so that it may be difficult to predict their behavior in a certain separation scheme. However, most of these elements have sulfides, which are insoluble in fairly strong acids<sup>23</sup>. The other elements to the right of Nb either form anions or gaseous products when dissolved in strong  $\text{HNO}_3$ , and can thus be separated from the cations to the left of Nb by relatively simple methods. It was therefore felt that many troublesome fission products could be removed with a sulfide precipitate in  $\text{HNO}_3$ , provided that a suitable carrier is used.

It is seen from Table 2 that Zr and Nb constitute about 35 % of the total  $\beta$ -activity and about 60 % of the total  $\gamma$ -activity of the fission products. Since Zr in many respects behaves chemically like Pu(IV), the separation of Zr from Pu is one of the most important steps in the purification of plutonium.

In experiments with tracer Zr and Nb it was found that a considerable amount of these elements was adsorbed on glass surfaces. This adsorption depends upon the acid used, and varies with the concentration of the acid. Fig. 1 shows the adsorption of a mixture of  $\text{Zr}^{95}$  and  $\text{Nb}^{95}$  on a silica gel column as a function of acid concentration. No attempt to separate Zr and Nb were made in these experiments. Since plutonium does not adsorb in such a column at  $\text{HNO}_3$  concentrations above 2 M, a  $\text{SiO}_2$ -adsorption step was incorporated in the separation procedure.

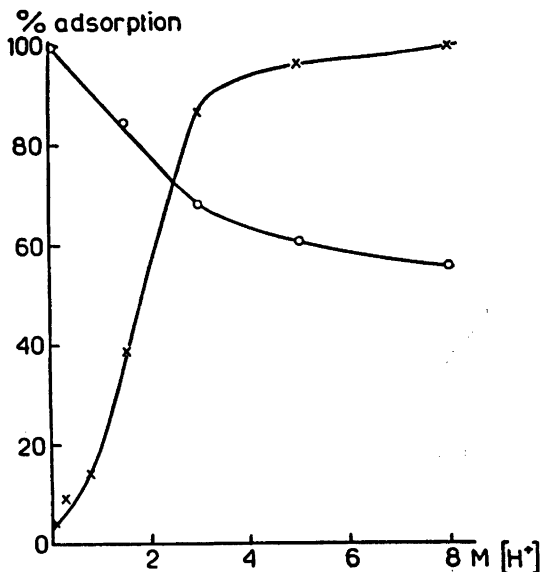


Fig. 1. The adsorption of tracer Zr + Nb on a silica gel column 10 cm long and 0.8 cm wide as a function of HCl (O) and HNO<sub>3</sub> (x) concentration.

As a final purification step, the thenoyltrifluoroacetone extraction process was used.

With the symbols used in the previous paper <sup>21</sup>, the flow-sheet consists of the following processes: V46, Sx, V46, S4.

1. The UO<sub>3</sub> sample is dissolved in hot, conc. HNO<sub>3</sub> and kept at 90°C for 30 minutes, giving a solution of U(VI) and Pu(IV) <sup>22</sup>. (V46.)
2. The acidity of the cooled solution is adjusted to 6 M in HNO<sub>3</sub>, and the solution is run through two columns of SiO<sub>2</sub> gel. This removes most of the Zr and Nb. The columns have a diameter of 0.8 cm and a length of 10 cm. (Sx.)
3. Cu<sup>2+</sup>, La<sup>3+</sup> and ZrO<sup>2+</sup> (1 drop 0.1 M carrier for each ml of solution) are added to the solution, and it is then diluted to 0.5 M in HNO<sub>3</sub>. On the addition of H<sub>2</sub>S, CuS precipitates and carries most of the fission products with sulfides insoluble in 0.5 M HNO<sub>3</sub>. The precipitate is centrifuged off. (Sx.)
4. The solution is evaporated almost to dryness and then kept for 30 minutes in hot ~10 M HNO<sub>3</sub>. This removes H<sub>2</sub>S and restores the Pu(IV) valency state. (V46.)
5. The solution is diluted to 1 M in HNO<sub>3</sub> and extracted with an equal volume of 0.3 M thenoyltrifluoroacetone in benzene. During these conditions practically only Pu(IV) and Zr(IV) are extracted, leaving uranium, thorium (UX<sub>1</sub>) and the rest of the fission products in the aqueous phase <sup>20, 24</sup>. (S4.)
6. After a two-fold dilution of the organic phase with benzene, Pu(IV) can be extracted back into an aqueous phase with 10 M HNO<sub>3</sub> or HClO<sub>4</sub>. This provides an additional purification from Zr <sup>20</sup>. In practice it has not proved necessary to use this step.

The plutonium yield of this procedure was about 90 % in the preliminary experiments performed in this laboratory. The decontamination from β-γ-radiation of the fission products is approximately 10<sup>6</sup> (see also below).

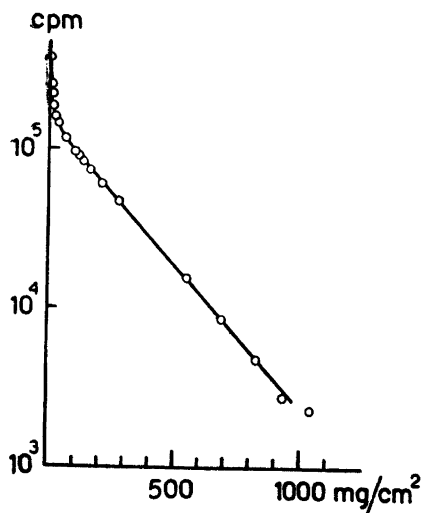


Fig. 2. Measured radioactivity (cpm) from neutron irradiated uranium sample as a function of aluminium absorber thickness (mg/cm<sup>2</sup>).

#### ABSORPTION MEASUREMENTS

The purity of the samples was checked by measuring the absorption of the radiation through aluminium foils.

The absorption curve obtained for the original, neutron irradiated  $\text{UO}_3$  sample is shown in Fig. 2, and Fig. 3 gives the absorption curve for the isolated plutonium sample (*i. e.* the benzene phase of step 5 in separation method II, above) \*. The activity of the Pu-sample measured without an adsorber was  $7\,600 \pm 80$  cpm (counts per minute). Both curves are taken on the  $\beta$ -plateau of the proportional counter. The  $\alpha$ -activity of the Pu-sample (measured on the  $\alpha$ -plateau of the proportional counter) was  $1\,220 \pm 10$  cpm. The difference between these two activities,  $6\,380 \pm 90$  cpm, is most probably due to soft  $\beta$ -radiation. The range of this radiation is about  $7\text{ mg/cm}^2$ , corresponding <sup>25</sup> to a maximum  $\beta$ -energy of about 70 keV. The range also corresponds <sup>26</sup> to an  $\alpha$ -energy roughly equal to that of Pu <sup>239</sup>, but the ratio between the activities measured on the  $\beta$ -plateau and the  $\alpha$ -plateau excludes the possibility that the absorption curve in Fig. 3 is only due to the  $\alpha$ -particles. In addition the sample contains some  $\gamma$ -radiation. The ratio between the  $\alpha$ -,  $\beta$ - and  $\gamma$ -activities measured in the ionization chamber is about 1:5:0.01. From Table 1 and Figs. 2 and 3 it can be found that the final plutonium sample contains less than  $1:10^6$  of the fission products with a  $\beta$ -energy  $>0.07$  MeV.

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\* The ordinate values of the curves are not comparable.

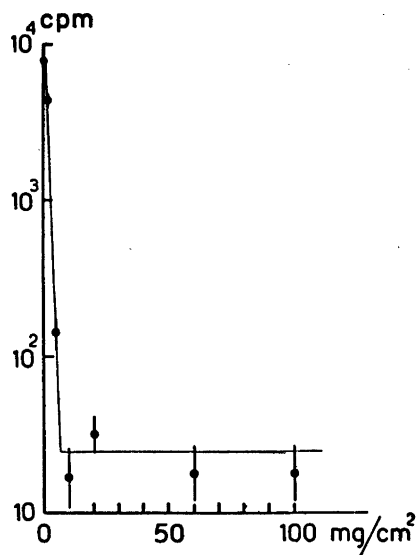


Fig. 3. Measured radioactivity (cpm) from the isolated plutonium sample as a function of aluminium absorber thickness ( $\text{mg}/\text{cm}^2$ ).

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\* N.N.E.S. = *National Nuclear Energy Series*, published by McGraw-Hill Book Company, New York.



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