

Production of Plutonium-236 Tracer with Irradiation of Natural Uranium by 18 MeV Protons

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The production of ²³⁶Pu by the reaction $^{238}\text{U}(\text{p},3\text{n})^{236\text{m}}\text{Np} \xrightarrow{\beta^-} ^{236}\text{Pu}$ using the Åbo Akademi 103 cm AVF cyclotron (MGC-20) was carried out. Plutonium of nanogram quantities was isolated from the irradiated natural uranium target with a chemical method including two separation steps: anion exchange with DOWEX 1 resin and extraction chromatography with TRU-Spec. resin. High decontamination plutonium from uranium, neptunium and fission products was achieved.

KEYWORDS: *proton induced nuclear reactions, natural uranium, plutonium 236 tracer, plutonium 238, chemical separation, extraction chromatography*

I. Introduction

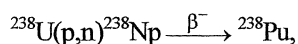
The alpha-emitter ²³⁶Pu ($T_{1/2} = 2.858 \text{ y}^{(1)}$) is mainly used as a tracer for the control of ^{238,239,240}Pu released into the environment from the nuclear fuel cycle. ²³⁶Pu is not formed in the nuclear fuel cycle in the significant amount and it has suitable decay characteristics such as the energy of alpha emission, about 5.77 MeV, that is essentially higher than for any usual fuel plutonium isotopes.

Production of ²³⁶Pu has been earlier carried out mainly by means of the reaction ⁽²⁻⁶⁾:



where ^{236m}Np is the short-lived isomeric state of ²³⁶Np with $T_{1/2} = 22.5 \text{ h}^{(1)}$.

This reaction is one of the most productive at the proton energy lower than 30 MeV ⁽²⁻⁶⁾. However, in addition to the mentioned reaction, another reaction occurs simultaneously producing an admixture of ²³⁸Pu:



where ²³⁸Np decays to ²³⁸Pu with $T_{1/2} = 2.117 \text{ d}^{(1)}$.

It is very important that the produced ²³⁶Pu contains minimum amounts of other plutonium isotopes formed in the nuclear fuel cycle such as ²³⁸Pu. Therefore, the goal of the present work has been the production of ²³⁶Pu with the optimal combination of amount and radionuclide purity of ²³⁶Pu. In order to achieve this goal, it is necessary to use an efficient chemical separation method for the purification of ²³⁶Pu from uranium, neptunium and fission products.

II. Experimental

1. Irradiation of uranium target

The uranium target was a 0.17 mm thick natural uranium foil having the weight of 460 mg. The uranium target was irradiated with the external beam of the Åbo Akademi 103 cm AVF cyclotron (MGC-20). The irradiation was carried out with 18.5 MeV protons at an intensity of about 4 μA for 2 h.

After the cooling time of one day the irradiated target was transported from Åbo Akademi University, in Turku to Department of Chemistry, Laboratory of Radiochemistry in Helsinki for chemical separation of plutonium from uranium, neptunium and fission products (FP). The time of the chemical separation was chosen as 4 days after the end of bombardment so that maximum amount of ²³⁶Pu with minimum one of ²³⁸Pu was obtained ⁽⁹⁾.

2. Chemical separations

Uranium target was dissolved in 4 ml of concentrated nitric acid under heating. Then the solution was evaporated to dryness.

The chemical separation of plutonium from the irradiated uranium target included two procedures: anion exchange with DOWEX 1 resin and extraction chromatography with TRU-Spec. resin.

(1) Anion-exchange separation.

The anion-exchange column was filled with the resin DOWEX 1x8 100 – 200 mesh, NO_3^- form. Dimensions of the glass column were 9 cm length by 1.2 cm diameter

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(free column volume, FVC, 6.7 cm^3). The anion exchange column was conditioned with 5 FVC of 7.2 M HNO_3 . The scheme of the anion exchange procedure included the following steps (Fig. 1):

- (a) Dissolution of the dry residue in 5 ml of 7.2 M HNO_3 .
- (b) Adjustment of plutonium in tetra-valence state:
 - Adding 0.1 ml of $\sim 50\%$ $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$ into the solution.
 - Heating the sample solution at $95 - 98^\circ \text{C}$ on a hot plate until the complete decomposition of $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$.
 - Heating again the sample solution for 5 minutes.
- (c) Loading the sample solution into the column.
- (d) Rinsing the column with 15 FVC of 7.2 M HNO_3 to remove uranium, neptunium and fission products.

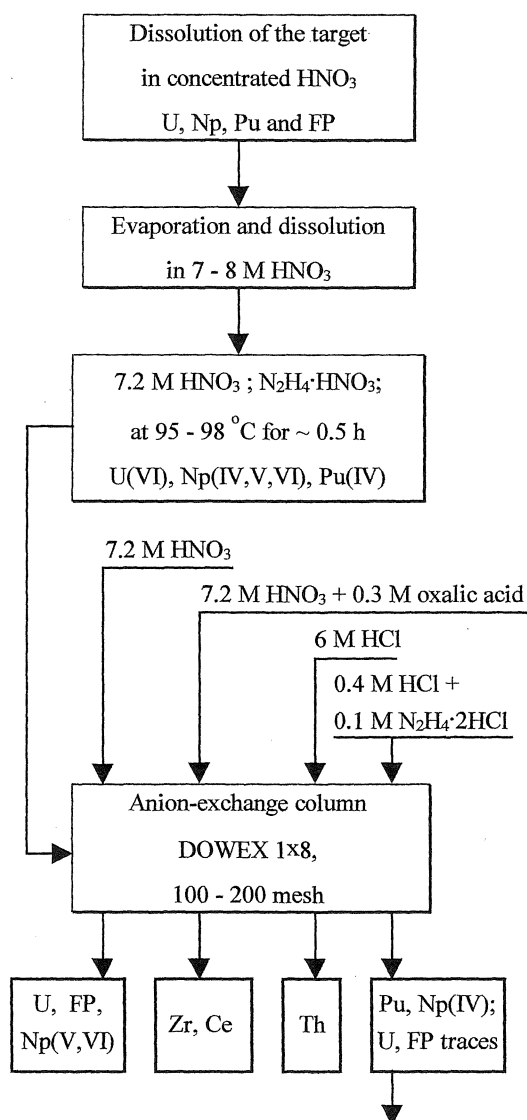


Fig. 1 Scheme of anion-exchange separation.

- (e) Rinsing the column with 4.5 FVC of 7.2 M HNO_3 + 0.3 M $\text{H}_2\text{C}_2\text{O}_4$ to remove zirconium and cerium.
- (f) Rinsing the column with 4.5 FVC of 6 M HCl to remove thorium.
- (g) Desorbing plutonium with 7.5 FVC of 0.4 M HCl + 0.1 M $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ (plutonium fraction).

Because the plutonium fraction contained about 90% of the total amount of neptunium an additional purification of plutonium from neptunium was necessary.

(2) Extraction chromatography separation.

The extraction chromatography column was filled with TRU-Spec resin. The extraction chromatography procedure was carried out mainly according to the scheme described in the work of Horwitz *et al.*⁷⁾. The bed height of the column was 5 cm and i.d. 7.6 mm (2.26 cm^3 bed volume, FVC 1.6 cm^3). The extraction chromatography column was conditioned with 5 FVC of 2 M HNO_3 . The scheme of the extraction chromatography procedure consisted of the following steps (Fig. 2):

- (a) The plutonium fraction from the anion-exchange separation was evaporated to dryness.
- (b) Treating the dry residue with concentrated HNO_3 to destroy hydrazine chloride and evaporating again.
- (c) Dissolution of the dry residue with 3 ml of 2 M HNO_3 .
- (d) Adjustment of Pu and Np in tetra-valence state:
 - Adding 0.5 ml of 1M ferrous sulfamate solution.
 - Adding dropwise 0.8 M ascorbic acid until the blue colour does not appear any more.
 - Adding 50 mg of sodium nitrite.
- (e) Loading the sample solution into the column.
- (f) Rinsing the column with 20 ml of 2 M HNO_3 to remove rest of fission and activation products.
- (g) Rinsing the column with 3.4 ml of 9 M HCl to convert the column to the chloride form.
- (h) Elution of lanthanides (Ln) and some fission products (so-called americium fraction) with 20 ml of 4 M HCl .
- (i) Elution of plutonium fractions with 20 ml of 4 M HCl + 0.1 M hydroquinone.
- (j) Elution of neptunium fractions with 20 ml of 1.0 M HCl + 0.03 M oxalic acid.

3. Gamma and alpha measurements

The activities of ^{237}U , $^{236\text{m}}\text{Np}$, ^{238}Np and ^{239}Np were determined from the spectra measured with a HPGe-detector in the Laboratory of Radiochemistry. Energy resolution was 1.8 keV at 1332 keV. These spectra were analyzed by the SAMPO 90 computer program⁸⁾.

Alpha-spectrometry samples were made by transferring drops of solution on stainless steel plate and then heated to dryness. The alpha spectrum was measured with a surface-barrier silicon detector (Fig. 3) with a sensitive area of 300 mm^2 and an energy resolution of 25 keV at

5767 keV. Total alpha activity was measured with a liquid scintillation counter.

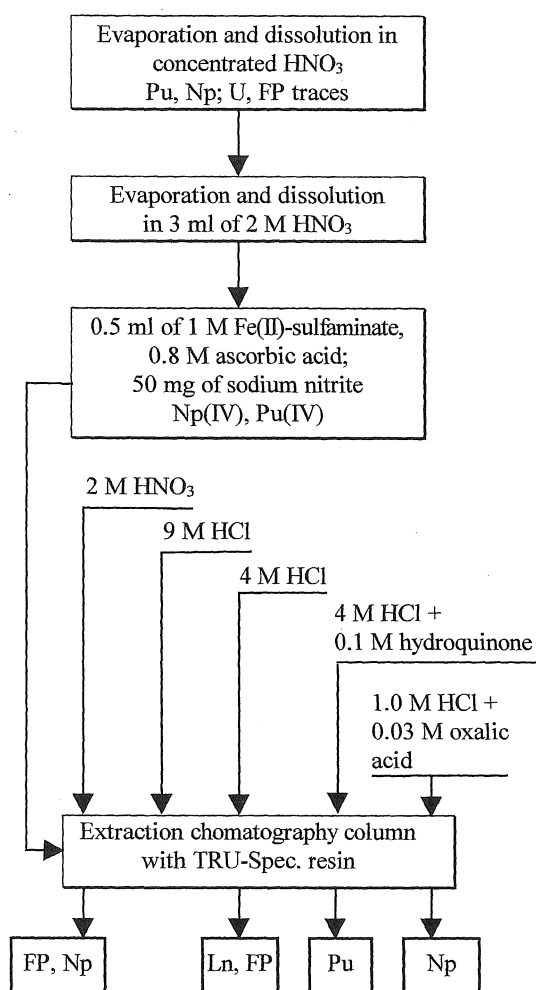


Fig. 2 Scheme of the extraction-chromatography separation.

III. Results and Discussion

It is known plutonium and neptunium are characterized for a complex chemical behavior in aqueous solution, especially in the case of the trace amounts. In order to obtain their quantitative separation and good purification it is very important to stabilize the valences of these elements through the chemical procedure. It is also known that the distribution coefficient for Pu(IV) in anion-exchange resin in 7–8 M nitric acid is $\sim 3 \cdot 10^3$, for Np(IV) $\sim 2 \cdot 10^3$ and for U(VI) ~ 8 . Therefore, it was desired to stabilize plutonium in valence state Pu(IV) before the start of the anion-exchange separation to make the best conditions for the removal of uranium and fission products without losing plutonium. The

stabilization of plutonium in the valence state Pu(IV) was carried out using hydrazine-nitrate under heating. During the decomposition of $N_2H_4 \cdot HNO_3$ plutonium turns into the valence state Pu(III). After the complete decomposition of hydrazine nitrate (the bubbles stop to arise) the nitric acid turns Pu(III) very quickly and wholly into Pu(IV). The neptunium does not stabilize in one valence state and occurs as Np(IV,V,VI). The valence states Np(V,VI) were removed by washing the column with 7.2 M HNO_3 . The valence state Np(IV) remained in the column was desorbed with 0.4 M HCl + 0.1 M $N_2H_4 \cdot 2HCl$ together with plutonium. In the anion-exchange procedure the yield and activity of ^{236}Pu were 98 % and 20 kBq, respectively. The ^{236}Pu solution contained 92 % of the initial amount of neptunium which was determined with photopeaks of ^{238}Np . Because ^{238}Np is the mother nucleus of ^{238}Pu an additional purification of plutonium from neptunium was necessary.

The extraction chromatography with TRU-Spec. resin was chosen to isolate plutonium from neptunium. The extraction chromatography procedure was carried out mainly according to the scheme described in the work of Horwitz *et al.*⁷⁾ The yield of plutonium after the extraction chromatography was 98 %. The purification factor of plutonium from neptunium was more than 10^4 . The yield and purification factor obtained in the present work were essentially better than those obtained by using the di-2-ethyl-hexyl-phosphoric-acid chromatography column⁶⁾ (84% and 200, respectively). In the present work the purification factor of plutonium from uranium was more than 1500.

The activity of ^{236}Pu was 19.5 kBq. Alpha spectrum of the stock solution sample is presented in Fig. 3. The contribution of ^{238}Pu activity was 2.4% of the ^{236}Pu activity.

Acknowledgments

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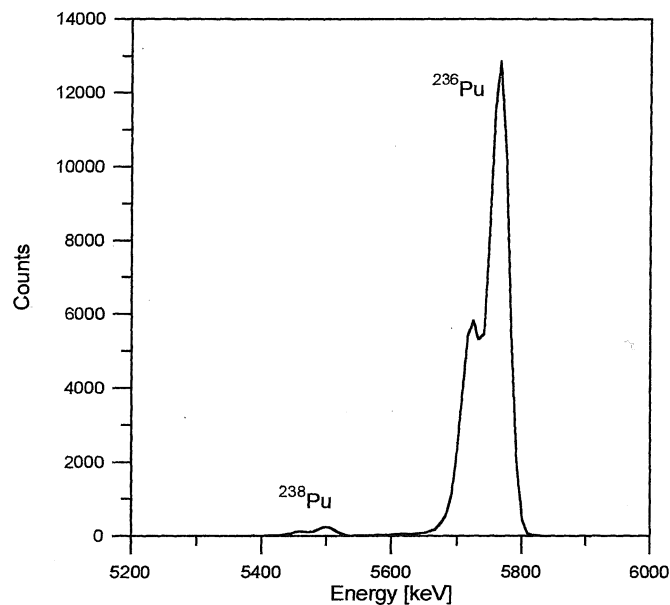


Fig. 3 Alpha-spectrum of the sample made from the stock solution of ^{236}Pu . Other alpha-peaks were not observed in the spectrum. Photopeaks of ^{237}U , $^{236\text{m}}\text{Np}$, ^{238}Np and ^{239}Np were not observed in the gamma-spectrum of the stock solution.