INVESTIGATION OF THE BUILDUP OF ISOTOPES OF PROTOACTINIUM AND URANIUM WHEN Th\(^{230}\) AND Th\(^{232}\) ARE IRRADIATED BY THERMAL NEUTRONS


When Th\(^{230}\) and Th\(^{232}\) are irradiated in a reactor by thermal neutrons, the isotopes Pa\(^{231}\), Pa\(^{233}\), U\(^{232}\), and U\(^{233}\) are formed by the reactions:

\[
\begin{align*}
\text{Th}^{230} & \rightarrow \text{Th}^{231} \\
\text{Th}^{232} & \rightarrow \text{Th}^{233} \\
\text{Pa}^{231} & \rightarrow \text{Pa}^{233} \\
\text{Pa}^{233} & \rightarrow \text{Pa}^{235} \\
\text{U}^{232} & \rightarrow \text{U}^{233}
\end{align*}
\]

The thermal neutron capture cross section for Th\(^{230}\), according to recent data [1], is approximately 56.8 barn, and therefore even in the case of brief irradiation of Th\(^{230}\) in a reactor by a high density neutron flux, considerable quantities of Pa\(^{231}\) and U\(^{233}\) can be produced. The first experiments to obtain protoactinium from samples of thorium oxide enriched in Th\(^{230}\) by neutron irradiation were described in [2].

The aim of the present work is determination of the buildup of isotopes of protoactinium and uranium and also the burn-up of thorium isotopes in irradiation of preparations with a ratio of the isotopes Th\(^{230}\)/Th\(^{232}\) = 1.462 in a thermal neutron flux of 1.10\(^{15}\) neutrons/cm\(^2\).sec.

EXPERIMENTAL

The scheme for separating thorium from uranium ore and purification of the thorium sample, and also data from mass-spectrographic analysis on the isotopic composition of the sample and impurity content, were presented in a previously published paper [1]. The thorium sample in the form of nitrate containing 9.2 mg Th\(^{230}\) and 13.45 mg of Th\(^{232}\) was placed in an aluminum ampoule and irradiated in a reactor for ten effective days. The total neutron flux during irradiation was 0.925.10\(^{21}\) neutrons/cm\(^3\). Seventy-six days after irradiation, the sample was dissolved with heating in 20 ml of 8 N HF. The total weight of solution of the sample was 20.3 g and the total \(\alpha\)-activity was 5.22.10\(^9\) imp/min.

In order to extract the protoactinium and separate it from isotopes of uranium, thorium, fission products, and daughter products from decay of U\(^{233}\), silica gel was used with the following characteristics: specific pore volume 0.933 cm\(^3\)/g, specific surface 264/388 m\(^2\)/g. This method has been described previously in [3]. The entire experiment was carried out in a Teflon or polyethylene vessel.

An aliquot part of the original solution (1.07 g) was diluted with 8 N HNO\(_3\) to a volume of 5 ml and passed at the rate of 0.5 ml/min through a chromatographic column, 10 cm high and 0.5 cm diameter, filled with silica gel (granulation 0.25-0.5 mm; volume 2 ml).

After passage of the main bulk of the solution, the column was washed with 20 ml of 6 N HNO\(_3\). The filtrate and wash water were combined for further determination of the uranium and thorium isotopes. The protoactinium was extracted with a solution of 40 ml of 0.5 M H\(_2\)C\(_2\)O\(_4\).

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Taken after irradiation</th>
<th>Isotope</th>
<th>Taken after irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th(^{230})</td>
<td>9.2</td>
<td>Pa(^{233})</td>
<td>6.04</td>
</tr>
<tr>
<td>Th(^{232})</td>
<td>13.45</td>
<td>Pa(^{235})</td>
<td>6.0063</td>
</tr>
<tr>
<td>Pa(^{231})</td>
<td>6.32</td>
<td>Pa(^{237})</td>
<td>6.1428</td>
</tr>
</tbody>
</table>

The α-radiation spectrum of the protoactinium fraction was examined by means of an alpha-spectrometer with a silicon detector. An α-scintillation counter was used for determining the Pa$^{231}$ concentration. Targets were prepared by a gravimetric method. The Pa$^{233}$ content was determined by γ-spectrometric analysis. Additional monitoring of the filtrate and washings for protoactinium content was carried out also by the γ-spectrometric method, by recording $E_γ = 0.311$ MeV from the Pa$^{233}$.

In order to separate the uranium from the thorium, the fission and daughter products from the decay of U$^{232}$, extraction with a solution of 1-phenyl-3-methyl-4-benzoylpyrazolon-5 (PhMBP) in benzene was used. The extraction of thorium with PhMBP has been described previously by us in [4]. Solutions of PhMBP were prepared by accurate weighing of the reagent (AR quality), purified by double recrystallization from heptane. The filtrate and wash water after passage of the original solution through silica gel were evaporated to dryness, the dry residue was treated twice with 2 ml of 0.1 N HCl, with heating, and dissolved in 10 ml of 0.1 N HCl. The solution was transferred to a separating funnel, 10 ml 0.2 M PhMBP in benzene were added and the uranium and thorium were extracted over 10 min. The impurities present in the sample remained in the aqueous phase. The uranium was reextracted with 10 ml of 2 N HCl, the extract was washed with benzene and the U$^{232}$ and U$^{233}$ content was determined by the isotopic dilution method on the MI-1311 mass-spectrometer, using U$^{238}$ as a tracer. Thorium was recovered from the extract with 6 N H$_2$SO$_4$. The determination of thorium can be carried out on the mass-spectrometer directly from the filtrate after separation of protoactinium and without preliminary removal of uranium.

**RESULTS AND DISCUSSION**

In the process of passing the solution to be analyzed through the silica gel column, the protoactinium was separated completely from the accompanying elements and was then recovered quantitatively with a solution of oxalic acid. The presence in the spectrum of the oxalate fraction (Fig. 1) of only one group of α-particles with energies 5.01, 4.94, and 4.69 MeV confirm the radiochemical purity of the separated Pa$^{231}$ isotope, Fig. 2 shows the γ-spectrum of protoactinium. It was determined that the Pa$^{231}$ content in the original solution was 0.32 mg and the Pa$^{233}$ was 0.014 mg. Protoactinium was not detected by the γ-spectrometric method in the filtrate and washings. According to Fig. 3, U$^{232}$ (5.22 and 5.34 MeV), Th$^{231}$ (4.67 MeV), isotopes of bismuth (6.25 MeV) etc., were contained in the filtrate.

The greatest difference in behavior of the intercomplex compounds of uranium and thorium with PhMBP was observed in 2 N HCl and fission products and daughter products from U$^{232}$ decay were separated from them in 0.1 N HCl. The uranium, in the presence of macroquantities of thorium, is 90% extracted over 10 min from the 0.1 N HCl with a solution of 0.2 M PhMBP in benzene. On subsequent reextraction with 2 N HCl, the uranium is transferred completely to the aqueous phase and 98% of the thorium remains in the organic phase. The radiochemical purity of the uranium separated by this procedure was confirmed by data from α-spectrometric analysis. Using the isotopic dilution method, it was found on the mass-spectrometer that the contents of the isotopes U$^{232}$ and U$^{233}$ were 0.0503 and 0.1426 mg respectively. After irradiation, the Th$^{230}$ content was 8.5 mg and that of Th$^{232}$ was 13.25 mg. Table 1 shows the composition of the thorium sample after irradiation.

Thus, when a thorium sample with isotopic ratio Th$^{230}$/Th$^{232} = 1.462$ is irradiated for 10 effective days with a thermal neutron flux of $1 \cdot 10^{15}$ neutrons/cm$^3$-sec, 3.5% of the initial Th$^{230}$ was transformed into Pa$^{231}$. The