Reports of the Academy of Sciences of the USSR

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1960

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1960. Volume 134, No. 5

CHEMISTRY

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ISOLATION OF WEIGHABLE AMOUNTS OF PURE PROTACTINIUM-231

Despite the intensive development of work on the chemistry of protactinium carried out over the last decade in a number of countries, this element remains one of the least studied, which is explained by the difficulty of isolating weighable amounts of its long-lived isotope, Pa^{231}, the most convenient for chemical investigations.

Various wastes from uranium production serve as raw material for obtaining protactinium-231; their large reserves make it possible to obtain kilogram quantities of the element. However, the technological procedures described in the literature for processing them are distinguished by complexity and by a multistage character, including operations of coprecipitation with a carrier, extraction, and ion exchange (1–6). The absence of a single method suitable for the various raw-material sources of the element is connected with the fact that the behavior of protactinium, whose concentration in uranium wastes is 10^{-6}–10^{-5} wt. %, is strongly affected by the influence of accompanying elements, while the nature of the latter depends on the composition of the starting ore and on the method of the main technology.

To concentrate protactinium from uranium-production wastes, we used its ability to be sorbed from nitric-acid solutions on a precipitate of manganese dioxide (7), as a result of which a high degree of purification from the principal macrocomponents of the starting material—aluminum, iron, and calcium—is achieved. In this way a concentrate of the following composition was obtained: MnO_2 81%; SiO_2 4.1%; Fe_2O_3 2.4%; Al_2O_3 0.9%; TiO_2 0.4%; ZrO_2 0.3%; CaO 0.03%; P_2O_5 1.5%; As_2O_5 2.9%. The protactinium content, determined by the method of (8), was $2.5 \cdot 10^{-4}$%, which was 100 times higher than the concentration in the starting material.

When the concentrate was treated with hydrochloric acid, the silicic acid contained in it separated as a gel, while the protactinium was distributed between the solution and the precipitate. The character of the distribution depended on the acidity of the solution and on the completeness of coagulation of the silicic acid.

The silicic acid gel obtained on dissolving the concentrate in 1 N HCl with addition of $NaNO_2$ contained all the protactinium present in the concentrate. The main impurities in it were Fe, P, As, Mn, Ti, Zr, and Nb.

After removal of the silicic acid by alkaline treatment or by distillation with hydrofluoric acid and dissolution of the residue in hydrochloric acid, the protactinium separated with the precipitate of phosphates of zirconium, titanium, and niobium, the predominant component of which was zirconium. It should be noted that the indicated elements are chemically related to protactinium and usually accompany it in concentration processes. Their separation constitutes the principal difficulty in obtaining pure protactinium-231.

The methods of fractional crystallization and fractional precipitation ([1,9]), used by a number of investigators to achieve this goal, require multiple repetition of individual operations, are very labor-consuming, and are inefficient. The applicability of the recently proposed method for purifying protactinium by extraction with diisobutylcarbinol ([10]) is limited by the scarcity of this extractant.

The separation of protactinium from other elements by means of anion exchange in concentrated HCl solutions or in mixtures of HCl and HF is the subject of works (11–15). In the cited studies, the separation involved microamounts of protactinium, niobium, zirconium, and titanium, or the separation of amounts not exceeding 1–2 mg. We developed a method for purifying milligram amounts of protactinium from impurities of niobium, titanium, and zirconium whose amounts exceeded the protactinium content by tens and hundreds of times.

Table 1

Dependence on pH of the distribution coefficients of protactinium and niobium between MnO_2 and a 0.5 N NH_4F solution

pH	K_p(Pa)	K_p(Nb)	Ratio K_p(Nb) : K_p(Pa)
5.48	19.8	560.0	28.3
5.23	16.0	380.4	24.0
4.97	11.0	232.0	21.4
4.65	6.1	110.0	18.0
3.90	5.1	26.7	6.3
2.91	4.3	17.1	4.6
1.62	3.7	14.8	4.0
1.00	3.4	14.6	4.3
0.50	3.5	13.3	3.8

Note: The pH measurements were made on a P-4 potentiometer with quinhydrone and calomel electrodes.

Study of the possibility of separating the indicated elements on domestic anion exchangers of the AB-16, AB-17, and AN-2F grades under conditions described in the literature as optimal for Dowex-1 resin (use of 7 N HCl) did not give the desired result. The use of manganese dioxide proved to be more effective. Sorption of protactinium from a 10 N HNO_3 solution on a column with MnO_2 makes it possible to separate it from large amounts of zirconium and titanium, which are held more weakly by this sorbent and can be completely removed from the column by washing with 10 N nitric acid. The analogous behavior of protactinium and niobium under these conditions makes it necessary to consider specially the possibility of their separation. For this purpose, a study was carried out of the dependence of the distribution coefficients (K_p) of protactinium and niobium between manganese dioxide and a 0.5 N NH_4F solution on pH, using solutions of protactinium-233 and niobium-95 (Table 1). The distribution coefficients were determined as the ratio of the activity of 1 g of sorbent to the activity of 1 ml of solution. The Nb^{95} used in the work was a standard commercial isotope; Pa^{233} was obtained by neutron irradiation of thorium nitrate and purified from impurities by the method (16,17). Identification of the isolated Pa^{233} and checking of its radiochemical purity were carried out by determining the half-life and the maximum energy of the β-radiation. The values found for these quantities ($T = 27.2$ days; $E_{\beta\,\max} = 0.57$ MeV) agree with the literature data (18).

The sharper dependence of K_p on the pH of the solution for niobium than for protactinium leads to an increase in the ratio $K_p(\mathrm{Nb}) : K_p(\mathrm{Pa})$ as the concentration of hydrogen ions decreases. However, the high absolute values of the distribution coefficients in the region pH > 4.5 account for the slowness of washing out protactinium and niobium sorbed on a column with manganese dioxide and make it necessary to work in the acidic region, despite the fact that $K_p(\mathrm{Nb}) : K_p(\mathrm{Pa})$ at low pH becomes less favorable.

The use of acidic NH_4F solutions for eluting protactinium and niobium made it possible to achieve complete separation of these elements sorbed on a column with manganese dioxide. Fig. 1 shows the elution curve of protactinium-233 and niobium-95 with a solution of 0.5 N HNO_3 + 0.2 N NH_4F. The column diameter was 0.4 cm, the height of the manganese dioxide layer 30 cm, the grain size 0.17–0.25 mm, and the rate of solution passage 0.1 $\mathrm{ml \cdot cm^{-2} \cdot min^{-1}}$. The manganese dioxide for filling the column was prepared by oxidizing $MnSO_4$ in a neutral medium with a $KMnO_4$ solution (19). The precipitate obtained was dried at 110–120°, after which the required fraction was sieved out.

The method developed on model solutions for separating protactinium from zirconium, titanium, and niobium was applied for concentrating

protactinium-231 present in the precipitate of zirconium, titanium, and niobium phosphates. The indicated product was boiled with a 10% NaOH solution, and the hydroxides obtained were treated with HNO_3. The nitric-acid solution was passed through a column with manganese dioxide, after which titanium and zirconium were removed by washing with 10 N nitric acid. Protactinium was separated from niobium by elution with a solution of 0.5 N HNO_3 + 0.2 N NH_4F.

In the course of elution of protactinium, an insignificant amount of manganese passed into the eluate (several μg/ml); to remove it, the solution was passed through a column with KU-2 resin. Protactinium, forming a stable negatively charged complex with fluoride ions, was not sorbed by the resin and passed into the filtrate; manganese remained on the column.

Fig. 1. Elution of protactinium and niobium with a solution of 0.5 N HNO_3 + 0.2 N NH_4F

Fig. 2. Spectrum of the α-radiation of the obtained protactinium-231 preparation

As a result of carrying out the operations described, milligram quantities of protactinium were obtained from several kilograms of the initial concentrate. The chemical purity of the product was established by spectral analysis of a sample containing 1.5 μg of protactinium. When the spectrograph was focused on the 2500–3000 Å region, the lines characteristic of protactinium were observed: 2732.2; 2743.9; and 2755.9 Å. Lines of other elements were not found in this region.

Additional identification of the isolated element was carried out by the method of isotope dilution and by the energy of the α-radiation. In the isotope dilution method, the behavior of the isolated protactinium-231 was compared with that of protactinium-233 during coprecipitation with certain carriers. Before precipitation or before the introduction of the prepared carrier into the solution, the mixture of Pa^{231} and Pa^{233} was heated and kept for 2 days to attain isotopic equilibrium. The content of each isotope was determined by successive measurement of a disk with a portion of the solution deposited on it, first on a B-2 type apparatus with a T-25-BFL end-window counter, which recorded the β-radiation of Pa^{233}, and then on the "Floks" apparatus, which recorded the α-radiation of Pa^{231} by means of a scintillation counter. The results obtained are given in Table 2.

Table 2

Behavior of a mixture of Pa^{231} and Pa^{233} during precipitation on carriers

Carrier	Medium	Degree of coprecipitation, % of initial	Ratio of activities Pa^{233} and Pa^{231}: initial solution	Ratio of activities Pa^{233} and Pa^{231}: solution above precipitate	Ratio of activities Pa^{233} and Pa^{231}: precipitate
MnO_2	10 N HNO_3	53.1	3.1	–	3.1
Nb_2O_5	6 N HNO_3	66.0	20.3	20.8	–
CaF_2	4 N HNO_3	56.2	3.4	3.2	–
Zirconium mandelate	6 N HCl	15.0	9.6	–	10.0
Zirconium phosphate	3 N HCl	91.0	17.7	16.4	–

The preservation of a constant value of the ratio of the activities of Pa^{233} and Pa^{231} during distribution between two phases indicates analogous behavior of both isotopes in various coprecipitation processes and, consequently, their chemical identity.

A study of the nature of the radiation of the isolated product* showed (Fig. 2) that its nuclear properties correspond to the literature data for protactinium-231 ([18]), and established the radiochemical purity of the preparation obtained.

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Received
22 VI 1960

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* The study of the radiation of the Pa^{231} sample was carried out by S. A. Baranov and Yu. F. Rodionov in the Laboratory of Nuclear Spectroscopy of the I. V. Kurchatov Institute of Atomic Energy, Academy of Sciences of the USSR.