

Cation-Exchange Separation of Group V Elements: Model Experiments on Isolation and Chemical Identification of Db

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Received April 5, 2007

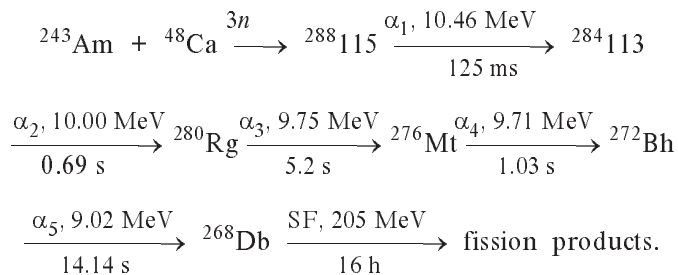
Abstract—A cation-exchange procedure was developed for separating Nb from Ta, Pa from Ta, and Nb, Pa, and Ta from Zr, Hf, and lanthanides in dilute HCl/HF solutions. The stability of the fluoride complexes of Group IV and V elements decreases in the following order: Nb ≈ Pa > Zr > Hf > Ta. This procedure can be used in experiments on synthesis of superheavy nuclei for isolation of Db from the reaction products and for its chemical identification.

PACS numbers: 82.30.Hk

DOI: 10.1134/S1066362208030132

Chemical identification and study of chemical properties of transactinide elements (TAEs) received recently a special attention. Relatively long life of the new radionuclides produced by reactions with ⁴⁸Ca and of their decay products open the possibilities for not only on-line (directly in heavy ion beams during continuous isolation of the reaction products) but also off-line (relatively prolonged irradiation of targets with subsequent isolation of the radionuclides) experiments. The first such experiment on chemical identification of Db, the final decay product of element 115, was performed in 2004 in FLNR [1, 2].

The isotope of element 115 with an atomic weight of 288 was synthesized for the first time by the nuclear reaction ⁴⁸Ca + ²⁴³Am → ²⁸⁸115 + 3n using a gas-filled separator of the reaction products [3]. The nuclide underwent five successive α-decays to form ²⁶⁸Db which decayed by spontaneous fission:



The total time of 5 α-decays is approximately 20 s. The half-life of ²⁶⁸Db estimated from the three observed events [3] is 16₋₆⁺¹⁹ h.

Fifteen events of spontaneous fission of ²⁶⁸Db were detected in the course of the chemical experiment. The ²⁶⁸Db half-life (*T*_{1/2} = 29 h) was refined, and the energy of the fission products and the number of neutrons emitted during fission were determined from the time distribution of the events [4]. The results of the “chemical” experiment proved independently formation of elements 115 and 113 by the reaction ⁴⁸Ca + ²⁴³Am.

The off-line experiment is of interest not only for chemical identification but also for study of chemical properties of Db. For this purpose, it is appropriate to use for producing the long-lived isotope ²⁶⁸Db the procedure similar to that in [1]. More selective procedures that would allow not only isolation of Group V elements but also their separation (a more complex problem) should be used in the next steps. The aim of this study was to develop a cation-exchange procedure for isolating and separating Group V elements.

This procedure was developed taking into account the results of the on-line experiments on the study of chemical properties of dubnium.

Extraction of Nb, Ta, Pa, and Db from HF, HCl, and HBr solutions with aliphatic amines was studied

in [5–9]. The stability of Group V metal halide complexes was shown to decrease in the following order: $F^- > Cl^- > Br^-$. However, the results of these studies do not provide sufficient information to compare unambiguously the stability of halide complexes of Db with that of the complexes of its homologs Nb and Ta and pseudohomolog Pa.

Pershina [10, 11] studied the hydrolysis and complexation of Group V elements (Nb, Ta, and Pa) in hydrogen halide solutions. Based on the results of quantum chemical calculations, she suggested that hydrolysis decreased in the order $Ta > Db > Nb > Pa$ and the competing complexation with halide anions decreased in the reverse order: $Pa \gg Nb > Db > Ta$.

Sorption of Group IV and V elements on an anion exchanger from fluoride solutions was studied previously [12, 13]. Caletka and Krivan [12] showed that, in a wide range of HF concentrations, the sorption of these elements decreased in the order $Ta > Hf \approx Zr > Pa$. At the HF concentration lower than 0.3 M, the sorption decreased in the order $Ta > Hf \approx Zr > Pa > Nb$ [13].

Previously we studied complexation of Group IV and V elements in aqueous solutions with different HF concentrations. Zr complexes formed in dilute HF solutions are sorbed on the cation-exchange resin, and the negatively charged Nb complexes remain in the solution. We showed that anionic Nb fluoride complexes were formed in 0.1 M HCl solutions containing 10^{-3} – 10^{-5} M HF. At $[HF] < 5 \times 10^{-4}$ M, neutral and cationic Nb species appear.

Thus, the strongest difference in the behavior of Group V and IV elements should be observed in dilute HCl/HF solutions.

EXPERIMENTAL

Carrier-free tracers were produced by (α, xn) and (n, γ) reactions and by the fission reaction $(p; xn, yp, f)$ on the U-200 cyclotron, MT-25 microtron (FLNR, JINR), and F synchrocyclotron (Laboratory of Nuclear Problems, JINR), respectively. The half-lives and production reactions of the isotopes used in this study are given below.

Isotope	Production reaction	Half-life
^{233}Pa	$^{232}\text{Th}(n, \gamma)^{233}\text{Th} \rightarrow ^{233}\text{Pa}$	27.0 days
^{92m}Nb	$\text{natY}(\alpha, xn)^{92m}\text{Nb}$	10.15 days
^{177}Ta	$\text{natLu}(\alpha, xn)^{177}\text{Ta}$	56.6 h
^{88}Zr	$\text{natSr}(\alpha, xn)^{88}\text{Zr}$	83.4 days
^{175}Hf	$\text{natYb}(\alpha, xn)^{175}\text{Hf}$	70 days
^{87m}Sr	$\text{natRb}(\alpha, xn)^{87}\text{Y} \rightarrow ^{87m}\text{Sr}$	2.81 h
^{173}Lu	$\text{natTa}(p; xn, yp, f)^{173}\text{Lu}$	1.37 years

Chemical isolation of Pa, Nb, and Ta was performed as follows.

^{233}Pa production. A set of thorium foils of different thicknesses and total weight of 0.9 g was placed in a cylindrical plastic container and was irradiated with thermal neutrons using a U–Be converter of the MT-25 microtron [neutron flux $10^8 \text{ n cm}^{-2} \text{ s}^{-1}$] for 10 h. After irradiation completion, the foils were allowed to stand for 3 days and were then dissolved in 11.3 M HCl (10 ml) containing 2 M HF (1–2 drops) to facilitate the dissolution. The resulting solution was passed through an 8×40 mm anion-exchange column packed with AG 1×8 resin (10–200 mesh). Then the column was washed with 8 M HCl (9 ml). Pa was eluted with 2 M HCl (6 ml). Approximately 95% of Pa was isolated.

^{92m}Nb (^{177}Ta) production. Yttrium (lutetium) nitrate applied to an aluminum support was calcined. The resulting rare-earth oxide Y_2O_3 (Lu_2O_3) (100–130 mg/10 cm²) was irradiated on the U-200 accelerator with α -particles (32–33 MeV) for 10 h (6 h) at an average current of 10 μA (7 μA). After irradiation completion, the sample was allowed to stand for 100 h. Then the oxide layer was dissolved in concentrated HNO_3 (10 ml). The solution was evaporated to dryness, and the dry residue was dissolved in HNO_3 . YF_3 (LuF_3) was precipitated by the addition of HF to the composition of 0.5 M HNO_3 + 1–1.5 M HF. Then the mixture was centrifuged for 5 min (4000 rpm), and the solution was decanted and evaporated to dryness. The dry residue was dissolved in 3 M HF (100 μl). The resulting solution was passed through an anion-exchange column (2×50 mm) packed with Dowex 1×8 resin (200–400 mesh). Nb (Ta) was eluted with 0.5 M HNO_3 + 1.5% H_2O_2 .

Isolation of Lu, Zr, Hf, and Sr was described in detail in our previous papers [2, 16, 17].

The solutions of the examined radioisotopes were mixed, and the carrier of the corresponding isotope (1 μg) and La (1 mg) in the form of $\text{La}(\text{NO}_3)_3$ were added. The lanthanum amount was determined by the procedure for separating reaction products from the target material, described in [1]. The solution was evaporated with a few drops of aqua-regia and then was evaporated to dryness.

The dry residue was dissolved in 0.2 M HCl (0.5 ml). The resulting solution was applied to a 6×30 -mm column containing Dowex 50×8 resin (100–200 mesh). The elements were separated by washing of the column with mineral acid solutions of

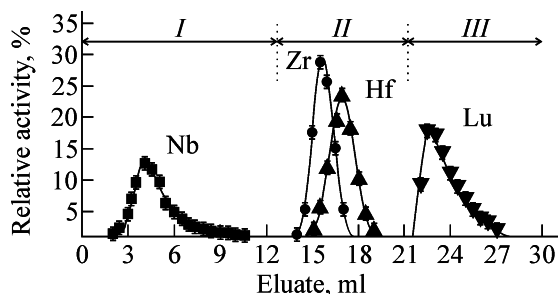


Fig. 1. Cation-exchange separation of Nb, Zr, Hf, Ta, and Lu (Dowex 50×8, 100–200 mesh, 6×30 mm). Eluent: (I) 0.2 M HCl + 5×10^{-4} M HF, (II) 0.2 M HCl + 2×10^{-3} M HF, and (III) 6 M HCl.

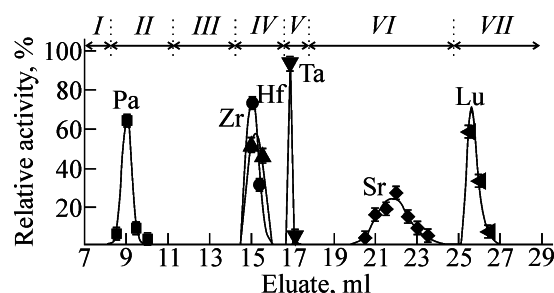


Fig. 2. Cation-exchange separation of Pa, Zr, Hf, Sr, and Lu (Dowex 50×8, 100–20 mesh, 6×30 mm). Eluent, M: (I) 0.2 M HCl + 5×10^{-4} M HF, (II) 0.2 M HCl + 7.5×10^{-4} M HF, (III) 0.2 M HCl + 1×10^{-3} M HF, (IV) 0.2 M HCl + 5×10^{-3} M HF, (V) 1 M HF, (VI) 2 M HNO₃, and (VII) 6 M HCl.

different concentrations. The element fractions were analyzed on a γ -ray spectrometer with a Ge detector (ORTEC) by the standard procedure.

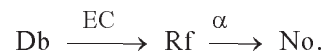
The conditions of sorption of the examined elements on the cation-exchange resin (0.2 M HCl) were estimated using the Speciation software (IUPAC SC-Database/Academic Software) [18].

RESULTS AND DISCUSSION

First we studied cation-exchange separation of Nb, Zr, Hf, and Lu on Dowex 50×8 resin (Fig. 1). Niobium was eluted first, with 0.2 M HCl + 5×10^{-4} M HF; then Group IV elements (Zr and Hf) were eluted with 2 M HCl + 2×10^{-3} M HF; and finally Lu was eluted with 6 M HCl. It should be noted that separation of Nb from Zr and Hf confirms the correct choice of the initial separation conditions. The behavior of the elements being separated supports the results of the on-line separation of Nb and Zr on a SISAK unit [14]. It should be noted that, since the Zr/Hf separation factor $\alpha_{Zr/Hf}$

is about 1.1, separation of these elements under similar conditions is possible. Group IV and V elements were also separated from actinides simulated by Lu.

The aim of next step was to study the behavior of Pa (Db pseudohomolog) and Ta under these conditions. In these experiments, ^{87m}Sr , a chemical analog of No, was introduced into the mixture to be separated. No can be formed by the following reaction:



The separation results are shown in Fig. 2. Pa was eluted with 0.2 M HCl + 7.5×10^{-4} M HF. Then, Group IV elements (Zr, Hf) were eluted with 0.2 M HCl + 5×10^{-3} M HF; Ta, Sr, and Lu were eluted with 1 M HF, 2 M HNO₃, and 6 M HCl, respectively.

Since Ta is eluted after Group IV elements, the location of the Ta band on the chromatogram is of interest. Presumably, the stability constant of the Ta fluoride complex is significantly lower than that of the related complexes of the other examined elements. Our first experimental results showed that the elution peaks of Pa and Nb are close.

In addition, as seen from the chromatogram, in the case of No formation by the above scheme, this procedure allows complete separation of Group IV and V elements from Sr (No analog) and Lu (an analog of trivalent actinides). Thus, the decontamination factor of the examined elements from actinides is as high as $\sim 10^4$.

Thus, a cation-exchange procedure was developed for the separation of Nb from Ta, Pa from Ta, and also of Nb, Ta, and Pa from Zr, Hf, and lanthanides in dilute HCl/HF solutions. The behavior of the Pa + Nb system under these conditions requires additional study.

Our results show that the stability of the fluoride complexes of Group IV and V elements decreases in the following order: Nb \approx Pa > Zr > Hf > Ta. The behavior of these elements in the examined solutions is consistent with results of the previous studies and theoretical calculations.

Thus, the developed procedure allows selective separation of Group V elements from their analogs Rf (Zr, Hf) and from heavy actinides (Cm, Cf) and nuclear-physical analysis of several fractions obtained in the course of the study of chemical properties of Db and its identification.

ACKNOWLEDGMENTS

The authors are grateful to T.V. Shishkina for assistance in radiochemical separation and to Ts.N. Piperov for theoretical calculations.

This study was financially supported by the Russian Foundation for Basic Research (project nos. 04-03-32047 and 07-03-00430).

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