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STUDY ON ADSORPTION OF Zr, Hf AND Nb AS HOMOLOGUES OF SUPER-HEAVY ELEMENTS ON THE FILMS PREPARED OF SOME LIQUID ION EXCHANGERS ON THE SURFACE OF SOME FOILS

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Abstract
Sorption of Zr, Hf and Nb as homologues of super-heavy elements 104 (Rf) and 105 (Db) was studied on films of liquid ion exchangers covering one side of metal or plastic foils. Many tests with homologues of Rf and Db were carried out using Aliquat-336 and HDEHP, the anion and cation liquid exchangers. It was found that the examined nuclides were extracted with a high efficiency by Aliquat-336 from diluted solutions of hydrofluoric acid. It was also shown, that the examined metal ions are extracted by HDEHP with high extraction coefficients from diluted solutions of H_2SO_4 acid.

Streszczenie
Badano sorpcję Zr, Hf i Nb jako homologów superciężkich pierwiastków 104 (Rf) i 105 (Db) na błonkach ciekłych wymieniaczy jonowych pokrywających metalowe lub plastykowe folie. Badania prowadzono na anionowych i kationowych ciekłych wymieniaczach jonowych: Aliquat-336 i HDEHP. Stwierdzono, że badane nuklidy dobrze ekstrahują się z rozcieńczonych roztworów kwasu fluorowodorowego przy pomocy Aliquat'u 336 w postaci fluorkowej. Wykazano również, że badane jony dobrze ekstrahują się z rozcieńczonych roztworów H_2SO_4 za pomocą HDEHP.

Introduction

Syntheses of super-heavy elements [1-6] set the tasks of studying their properties, determining their place in the Mendeleev Periodic Table and answering the question, whether these elements obey the Periodic Law.

Until now, a number of elements, beginning from the element 109 up to 116 have been synthesized [7]. Because of great difficulties associated with short lifetimes and extremely small production cross-sections, the great majority of super-heavy elements are not yet available for direct chemical study. One of the authors of the present paper developed a method for fast and selective isolation of the element 104 (rutherfodium) [5] from the nuclear reaction products obtained in bombardment of the ^{248}Cm target by the ^{18}O ions on the U-400 cyclotron in the Laboratory of Nuclear Reactions at JINR in Dubna, Russia. On the ground of the performed experiments, he showed that in the hydrofluoric acid medium, similar to hafnium, rutherfordium forms the anion complexes which were sorbed by some anion exchange resins. Hafnium chemical property studies performed in a wide variety of chemical systems [8] showed that rutherfordium, in accordance with the Periodic Law, reveals similarity towards hafnium.

Discovering new elements generates a need for searching and developing some fast and selective methods for their isolation and chemical identification. Looking for the optimum conditions for Zr, Hf, and Nb isolation, the studies on their extraction from the diluted solutions of hydrofluoric acid by the Aliquat-336 in fluoride form were performed. With the same object in view studies of Zr, Hf and Nb extraction from the diluted solutions of sulfuric acid by HDEHP were also carried out. These studies were the starting point for performing some experiments on sorption of zirconium, hafnium and niobium on the films created by some liquid ion exchangers on the surface of metallic or plastic foils. Adsorption of the carrier free radionuclides on the surface of these films allows, in case of α-emitters, for obtaining a thin α-sources intended for α-spectrometry in the 2π-geometry. It is noteworthy, that sorption of nuclides on the films provides possibility of registration and identification of alpha–spectra with a high resolution.

Experimental

Extraction of Zr, Hf and Nb as homologues of super-heavy elements Rf and Db using the liquid ion exchangers: the cation exchanger - a di(2-ethylhexyl) phosphoric acid (HDEHP) and the anion exchanger – a methyltricaprylammonium fluoride (Aliquat-336)

was studied. The above mentioned extractants were used as pure substances. The films of the liquid ion exchangers were formed on the surface of the foils made of either metal or plastic, and then the examined nuclides were sorbed on them. Radioactivity of the studied samples was measured by a γ-spectrometer with the HPGe detector and the service program MAESTRO - 32. The isotopes: ^{181}Hf, ^{175}Hf, ^{95}Zr, ^{95}Nb were used as radionuclide tracers. A solution containing an examined isotope (20μl) was put on a foil coated by an extractant. The value of the extraction percent was calculated using the following expression:

$$E_{\%} = \frac{A_i}{A_e} \times 100$$

where: A_i – the initial activity, A_e – the end activity.

In the beginning, studies of hafnium extraction by Aliquat-336 from hydrofluoric acid solutions with concentrations ranging from 10^{-4}M to 10M were performed for determination of the maximum value of the distribution coefficient, K_d. Changes of the distribution coefficient as a function of acidity for the hafnium extraction are presented in Fig. 1.

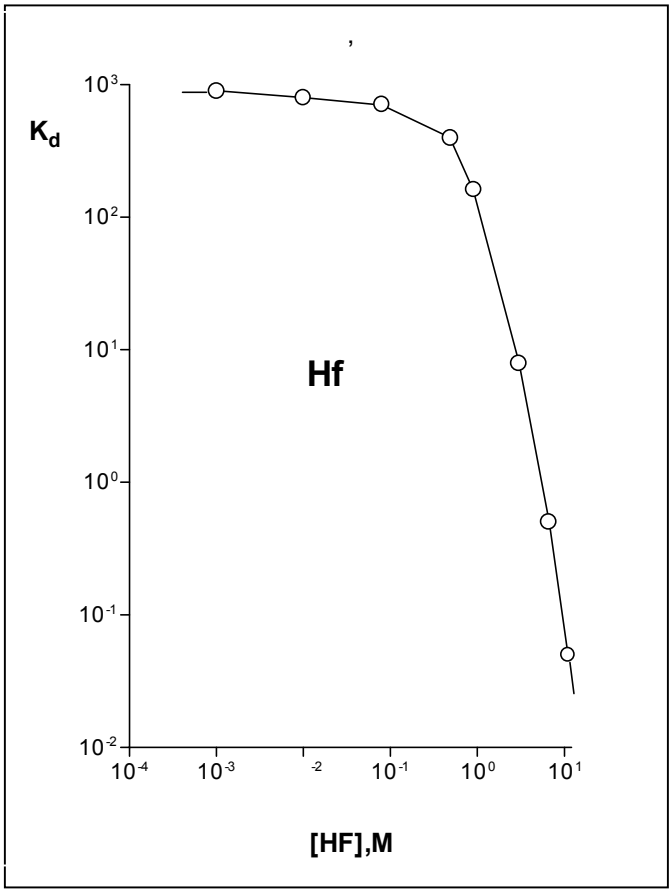

Fig. 1. Hafnium extraction by Aliquat –336 from the solutions of hydrofluoric acid.

As is seen in Fig. 1, the distribution coefficient has high values in the diluted acid solutions, but when the acid concentration is near the value of 10^{-1}M it reveals a sharp fall. On exceeding the acid concentration value of 0.1M, hafnium forms the complexes which display no extraction by Aliquat-336, and therefore Kd values sharply diminish.

In Table 1 are presented results of sorption of Zr, Hf and Nb on the Aliquat-336 films coating foils made of nickel, Maylar or PCV from the diluted hydrofluoric acid solution.

Table 1. Extraction of Hf, Zr and Nb from the 0.05M HF solution by Aliquat-336, that was coated on to a surface of foils.

Foil	Extraction, %		
	Zr	Hf	Nb
Ni	95	97	80
Mylar	94	98	75
PCV	96	95	82

The concentration of hydrofluoric acid was 0.05M. With this acid concentration, the optimum values of the distribution coefficient were obtained; these are in a good agreement with the results presented in Fig. 1. The results presented in Table 1 indicate that the values of the extraction percentage vary only slightly, whatever was the foil stuff. However, as regards niobium, the extraction percentage values are somewhat lower than those obtained for the other two elements.

Values of the distribution coefficient of some metals determined for their extraction by the liquid cation exchanger HDEHP from diluted solutions of two acids: HF and H_2SO_4 are given in Table 2.

Table 2. Distribution coefficients for Zr, Hf, Nb and Ce extracted by HDEHP from the HF and H_2SO_4 solutions.

Element	0.1M HF	0.05 M H_2SO_4
Zr	0.2	10^4
Hf	0.3	10^4
Nb	8	10^2
Ce	0.1	10^3

The data presented in Table 2 indicate that the examined elements are strongly extracted by HDEHP from sulfuric acid solution, whereas they practically are not extracted from a hydrofluoric acid solution. The similar results were obtained for hafnium, cerium, niobium and zirconium as well as for lutetium, neodymium and promethium which were sorbed on the cation exchange resin (DOWEX-50) from the diluted sulfuric acid solutions [**7**]. As well known [9], Zr has a higher affinity for fluor than for oxygen, and in the aqueous medium the bond Zr – F does not reveal tendency towards disruption. Due to this fact, zirconium and fluor are prone to formation of some anion complexes rather than cation ones, for instance, such as ZrF_7^{3-}, ZrF_6^{2-} i $ZrOF_4^{2-}$. The same behavior reveals hafnium [10]. It follows that, when extracted from the hydrofluoric acid medium by the cation exchanger HDEHP, zirconium and hafnium have very low values of the distribution coefficient, see Table 2. On the contrary, in the sulfuric acid medium zirconium and hafnium form some cation complexes, and therefore they are well extracted by HDEHP. It would be reasonable to suggest that the examined metals in the diluted solution of sulfuric acid may be present in the form of the following ion complexes: $ZrSO_4^{2+}$, $Zr(OH)_2^{2+}$, HfO^{2+}, $HfOOH^{+}$ i $Hf_2O_3^{2+}$. The high values for the distribution coefficients which were obtained for extraction of the studied elements by HDEHP indicate that these elements have to be strongly sorbed by the HDEHP films, as well. The preliminary results obtained have shown that HDEHP may be used for identification of both Zr, Hf and their homologues.

Studies on adsorption of Hf, Zr and Nb, as homologues of Rf and Db, on the surface of the metallic or plastic foils coated by the film of one of examined liquid ion-exchanger suggest that there is possibility to sorb them and to measure their activity on the foils prepared in such a way.

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