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**MODIFIED CHROMATOGRAPHIC SEPARATION
OF A SUM OF SPALLATION LANTHANIDES**

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Модифицированное хроматографическое разделение суммы спалогенных лантаноидов

Элементы ряда лантаноидов (Ln) представляют большой научный интерес, поскольку находятся в переходной области ядерной деформации. Начиная с 1960-х гг. разрабатывались методы их разделения. Один из наиболее удачных методов разработан Н. А. Лебедевым в ОИЯИ для ускоренного отделения спалогенных лантаноидов от облученной Та-мишени энергией 660 МэВ. Продукты данных облученных мишеней используются в научных исследованиях, медицинской терапии и диагностике. Необходимым требованием к радиоизотопам Ln является более длительный период полураспада. Метод Лебедева переоценивается и модифицируется: добавляется колонка UTEVA, которая очищает Ln от изотопов Hf и Zr, применяемых в исследованиях. Дальнейшее разделение отдельного Ln осуществляется с использованием смолы Aminex A6 и смеси (MIX- α -HIB) α -гидроксиизобутирата аммония (NH_4 - α -HIB) с α -гидроксиизобутировой кислотой (α -HIBA) (с регулируемым pH). Полученные чистые элементные фракции использовались также для исследований ферритов и вольфраматов методом $\gamma\gamma$ -ВУК.

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Modified Chromatographic Separation of a Sum of Spallation Lanthanides

The elements of the lanthanide (Ln) row being in the transitional region of nuclear deformation are of great scientific interest. Since the 1960s, the Ln series has been researched and methods for the separation of these elements have been developed. One of the most successful separation methods has been developed by N. A. Lebedev at the Joint Institute for Nuclear Research (JINR) for the accelerated separation of spallation lanthanides from irradiated Ta target at 660 MeV. The products from such targets are used in scientific research, medical therapy and diagnostics. Nowadays, the need is for Ln radioisotopes with longer half-lives. Thus, the method developed by N. A. Lebedev is reevaluated and modified: the UTEVA column is added, facilitating the purification from Hf and Zr isotopes used in different scientific research. The further separation of individual Ln is carried out with the use of Aminex A6 resin and a mixture (MIX- α -HIB) of ammonium α -hydroxyisobutyrate (NH_4 - α -HIB) with α -hydroxyisobutyric acid (α -HIBA) (with regulated pH). The obtained elementally pure fractions were further used in $\gamma\gamma$ -TDPAC measurement of ferrites and tungstates.

The investigation has been performed at the Dzhelepov Laboratory of Nuclear Problems, JINR.

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INTRODUCTION

From nuclear physics point of view, the isotopes of the lanthanides are researched actively because they are in the transitional region of nuclear deformation. At the Joint Institute for Nuclear Research (JINR), an intensive study of these nuclei with nuclear spectroscopy methods began in the 1960s. Therefore, in order to obtain a wide range of lanthanides, N. A. Lebedev has developed a special technique [1]. The lanthanide production has been carried out by irradiation of the tantalum target with 660-MeV protons at the Phasotron at the Laboratory of Nuclear Problems, followed by the dissolution and separation of the lanthanides from tantalum by co-precipitation with lanthanum, and finally the separation of all consecutive lanthanides with chromatographic methods at heightened temperature and pressure. All the steps of the methodology were well-developed and established, so they formed the basis for an integral technological process for obtaining short-lived isotopes of lanthanides. This process has been carried out on a unique equipment manufactured at the experimental production facility of the Laboratory of Nuclear Problems based on Lebedev's model. Thus, the data for the lanthanide isotopes have made it possible to get a number of unique results. Using this method for separation of lanthanides, pure isotopes can be obtained, such as ^{177}Lu , which is a radiotherapeutic radionuclide used for treatment of patients [2].

Numerous methods for the separation of rare earth elements (REE) have been researched and used over the years [3–14]. The most commonly applied methods are based on liquid–liquid extraction [3, 5, 6, 8, 10, 12, 13, 15–18]. However, the liquid–liquid extraction needs a large amount of solutions in order to obtain results. Therefore, the focus for the separation of REE has been directed towards extraction and ion-exchange chromatography. The method using a mixture (MIX- α -HIB) of ammonium α -hydroxyisobutyrate (NH_4 - α -HIB) with α -hydroxyisobutyric acid (α -HIBA) (with regulated pH) with cation-exchange resin has been developed and applied by researchers since the 1960s. This method is a great way to separate the lanthanides [19]. To study the separation of REE, a Ta target must be irradiated with high-energy protons.

The α -HIBA method has been focused on the separation of short-lived radionuclides, thus it has been an accelerated method for the separation of lanthanides. Today, research is focused on the separation of radionuclides with half-life from 1 day up to a couple of years and their following use [8, 17, 18, 20, 21]. After the irradiation of a metallic Ta target with a high-energy proton beam it is expected that other isotopes besides the ones of the lanthanides (Ln) are to be produced, such as Hf, Y, Ba, W, etc. The first (precipitation) step of the method includes the precipitation of Ln and Y for their separation from all other elements.

The element in the largest amount in the dissolved target solution is Ta, followed by Hf, Ba, and W. The precipitation of Ln is not 100%, therefore there is a certain amount of Ln that remains in the initial solution.

Usually the work with the Ln isotopes is done with the precipitated fraction. The remaining radioisotopes in the solution could be further purified and used as well. The separation of Hf from Ln in the solution is of high significance, for the purification of the Ln also gives the possibility for the further use of pure Hf isotopes, for example, in ^{172}Hf - ^{172}Lu generators, or scientific research with $\gamma\gamma$ -TDPAC [22, 23].

In the present study, a new way for the processing of an irradiated Ta target is applied with the use of the UTEVA resin and different concentrations of HNO_3 [16, 24]. Furthermore, the method for the separation of Ln has been modified and simplified.

1. EXPERIMENTAL

1.1. Materials. In this research we used concentrated HF and different concentrations of HNO_3 , saturated H_3BO_3 with 0.5 M HNO_3 , and 0.5 M NH_4NO_3 from Chimmed and Sigmatec (Moscow Region, Russia), bi-distilled water and La^{3+} solution in 6 M HCl. Initial solution of α -HIBA 1.72 M was titrated to pH = 4.7 with the concentrated NH_4OH solution. It should be taken into account that the MIX- α -HIB solution contains $[\text{MIX-}\alpha\text{-HIB}] = [\text{NH}_4\text{-}\alpha\text{-HIB}] + [\alpha\text{-HIBA}]$. For the proton irradiation, a 4 g metallic Ta target (20×19×0.6 mm) was used. Three types of resins were applied: the extraction chromatographic resin UTEVA (100–150 μm) (Triskem International, Bruz, France) and cation-exchange resins Aminex A6 (15.5–19.5 μm) (BioRad) and Dowex 50×8 (200–400 mesh in H^+ form) (Sigma-Aldrich Co. LLC).

For work with HF, 50 ml plastic test tubes and plastic chromatographic columns were used. Standard UTEVA column (with $d = 6.68$ mm and 700 mg of resin) (Triskem International, Bruz, France) was used in this research. For the α -HIBA separation of Ln a glass column ($h = 100$ mm, $d = 2.2$ mm) is used. For the collection of the fractions in the α -HIBA separation a fraction collector

designed at JINR was used. All used chemicals were of analytical grade from Chimmed, Sigmatec (Moscow Region, Russia) and Sigma-Aldrich Co. LLC.

To analyze the radionuclides, an ORTEC γ -ray spectrometer with an HPGe detector system and Samar software was used. The dead time of the detector was always kept below 7% [25].

1.2. Methods. First, a Ta metallic target ($20 \times 19 \times 0.6$ mm) is irradiated with a proton beam with energy $E_p = 650\text{--}660$ MeV at the Phasotron (JINR). The reaction at such high energies can be given as $p, xp\ yn$, where the higher E_p is, the higher the relative emission of neutrons. After a cooling period of one month the Ta target is dissolved, during this time all short-lived radionuclides decay fully (Fig. 1). The dissolution is made by using the ratio of concentrated HF (5 ml/g Ta) to concentrated HNO_3 (0.6 ml/g Ta). To the resulting solution is then added 2 mg of La^{3+} as a carrier, and 1 g of resin Dowex 50×8 (200–400 mesh in H^+ form) is added to form a suspension in the solution. After a day, the solution with all suspended particles is loaded into a plastic column containing 2 g of cation-exchange resin Dowex 50×8 (200–400 mesh in H^+ form) (Fig. 1, step 1). After loading, the column is washed with concentrated HF (Fig. 1, step 2). At these two steps a large amount of dissolved Ta and W is fully separated from the REE products. The column is additionally washed with 0.5 M HNO_3 (Fig. 1, step 3). The column is then washed with a solution of saturated $\text{H}_3\text{BO}_3 + 0.5$ M HNO_3 for the conversion of the precipitated products into ion form, followed by washing with 0.5 M HNO_3 to remove the boric ions (Fig. 1, steps 4 and 5). The sorbed ions are then eluted with 8 M HNO_3 from the Dowex 50×8 resin and loaded into a standard UTEVA column preconditioned in 8 M HNO_3 (Fig. 1, step 6). The UTEVA column is washed with 8 M HNO_3 , where Ln and Y elute together (Fig. 1, step 6.1). With 3 M HNO_3 any residual Hf is eluted from the UTEVA column (Fig. 1, step 6.2). Next, an elution with 1 M HCl is applied for the elution of Zr (Fig. 1, step 6.3).

The next method describes the procedure for the separation of individual Ln. As the initial sample was the final solution containing Ln from the previous procedure (Fig. 1, step 6). The 8 M HNO_3 solution was dried to wet salts and then diluted with 0.1 M HNO_3 .

For this separation method, a glass column ($h = 100$ mm, $d = 2.2$ mm) (see Fig. 2) filled with Aminex A6 resin was used; the column was pre-conditioned with 4 M HNO_3 followed by bi-distilled water. The 0.1 M nitric solution was loaded into the column in four portions of 250 μl and collected in one fraction of 1 ml. The pH within the column volume was regulated up to 5 by washing the resin with 0.5 M NH_4NO_3 . For the separation of Ln the column was washed with MIX- α -HIB in different concentrations from 0.07 to 0.5 M, where the Ln elute consecutively starting with Lu and ending with La. After completion of the Ln separation, the column was washed with 4 M HNO_3 .

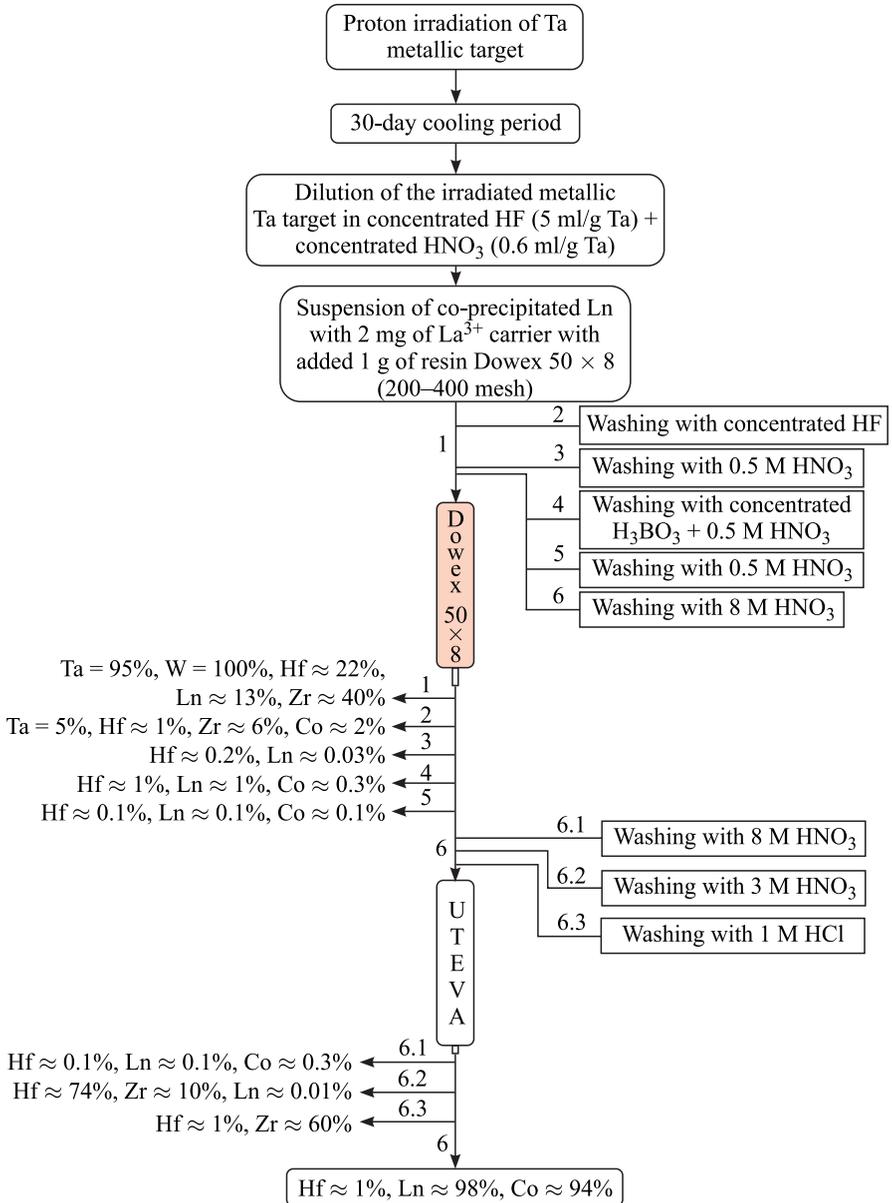


Fig. 1. Separation scheme of Ln from proton-irradiated Ta target. Plastic column with 2 g of resin Dowex 50 × 8 (200–400 mesh) (upper column) and UTEVA filled plastic column with 700 mg of resin 100–150 μm (lower column)

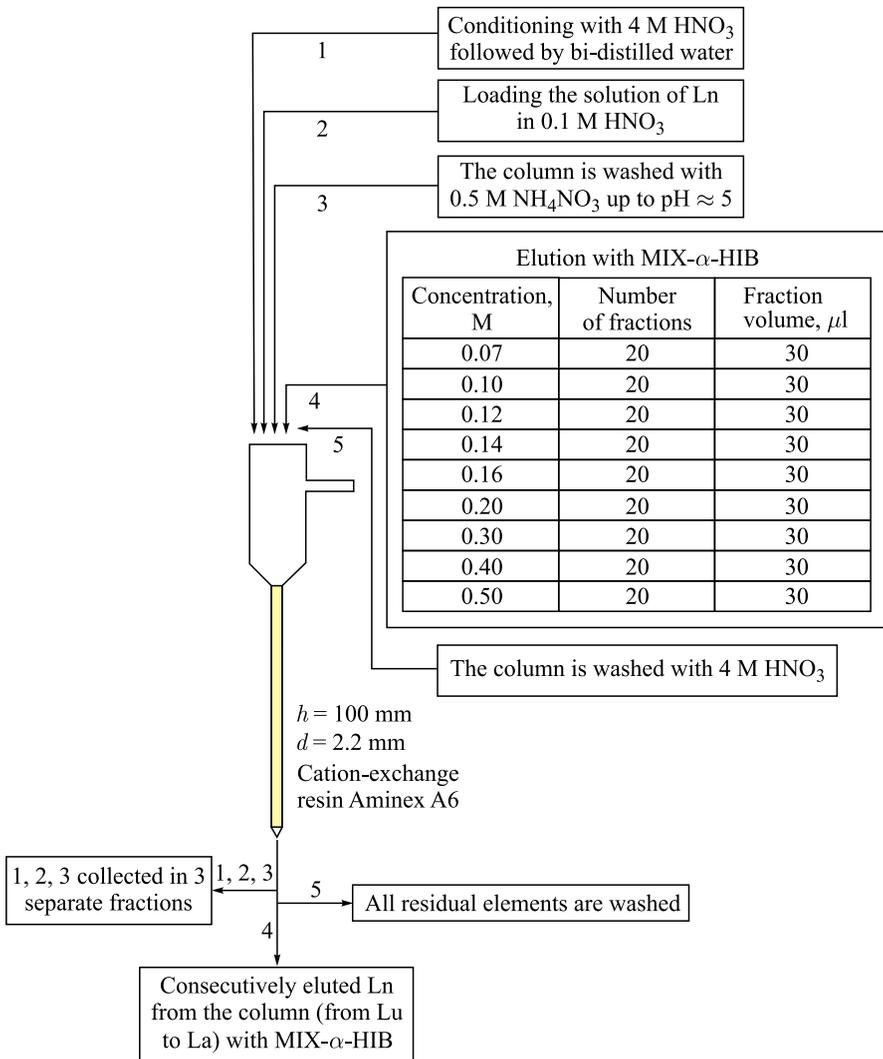


Fig. 2. Scheme of the consecutive elution of Ln, using column filled with Aminex A6 resin ($h = 100$ mm, $d = 2.2$ mm, $d_{\text{particles}} = 17 \pm 2 \mu\text{m}$)

2. RESULTS AND DISCUSSION

The results obtained using the scheme from Fig. 1 are presented in Fig. 3, where the separation of Ln from all other elements is given. As the bulk of the target is Ta, the separation of Ln from it is one of the most important tasks. Thus,

the target is dissolved in concentrated HF and cation-exchange resin is added to the solution together with 2 mg of La^{3+} as a carrier. This way the Ln in the solution are co-precipitated. Remaining in the solution are mostly non-Ln. In the first fraction eluted from the cation-exchange column (loaded with 2 g of Dowex 50×8 , 200–400 mesh) the dissolved elements are almost fully eluted except for Hf, thus a few more fractions are collected by washing the resin with concentrated HF. Then the column is washed, as described in Fig. 1, with 0.5 M HNO_3 and with saturated $\text{H}_3\text{BO}_3 + 0.5 \text{ M HNO}_3$ in order to change the Ln into ionic form. After washing with few more milliliters of 0.5 M HNO_3 , the UTEVA column is added to the system consecutively to the Dowex column. The Ln are eluted with 8 M HNO_3 from the cation-exchange resin through the UTEVA column and collected. Then the UTEVA column is washed with 3 M HNO_3 and 1 M HCl for the elution of the sorbed Hf and Zr (Fig. 3). The estimate for the REEs

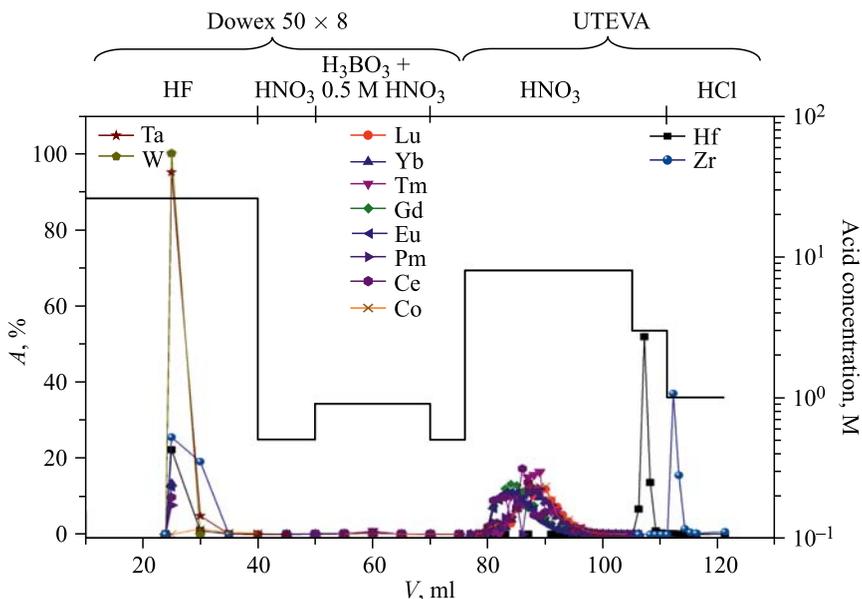


Fig. 3. Separation of Ta target after dissolution. Percentage activity ($A, \%$) to the eluted volume (V, ml) using different acids and concentrations. Up to the 75th ml the elution is only through cation-exchange column (resin 2 g of Dowex 50×8 , 200–400 mesh). After the 75th ml the UTEVA column (700 mg of resin 100–150 μm) is added consecutively to the cation-exchange column

sorption on the resin is made based on published data for UTEVA [16]. The four valent Hf and Zr strongly retain in HNO_3 with concentrations above 6 M on the UTEVA resin [24]. The lanthanides have next to no sorption in concentrations

of HNO_3 up to 10 M, in higher concentrations the heavy REE have low sorption on the resin. In 3 M HNO_3 Hf and Zr have lower sorption but Zr, having higher distribution coefficient, retains better; therefore, Hf is fully eluted, and Zr has to be eluted with 1 M HCl where it has its lowest value for the distribution coefficient.

The following separation with α -HIBA with adjusted $\text{pH} = 4.7$ by addition of NH_4OH is schematically illustrated in Fig. 2 and graphically in Fig. 4. The illustrated separation shows the separation of Ln with the gradual exponential increase in concentration from 0.07 to 0.5 M MIX- α -HIB. The main advantage of this method is that it is performed at room temperature with low pressure up to 2 bar.

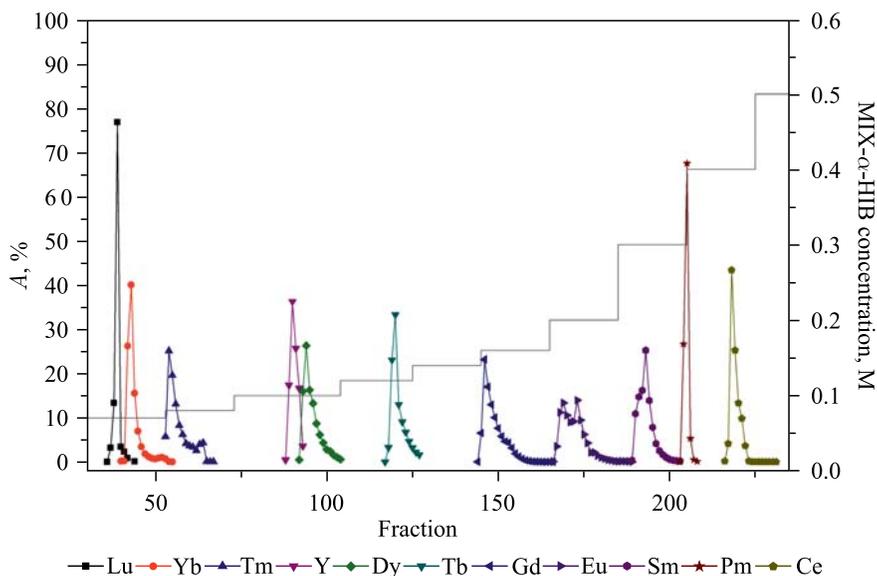


Fig. 4. Percentage activity ($A, \%$) to collected fraction ($\approx 28 \mu\text{l}$) for the separation of lanthanides with exponential increase in MIX- α -HIB concentration ($\text{pH} = 4.75$) through a glass column ($h = 100 \text{ mm}$, $d = 2.2 \text{ mm}$) Aminex A6 ($15.5\text{--}19.5 \mu\text{m}$)

For the first separation (Figs. 1 and 3) the high values of the eluted Ta, W, Hf and Zr show that the larger amount of these elements pass with the solution and having low sorption on the resin [26]. The fact that Hf and Zr retain with the lanthanides is due to the co-precipitation method used to separate the lanthanides. Research on the co-precipitation with La has presented that there are two main reasons for Hf and Zr to retain: first is the time of precipitation and the second is the amount of La added as a carrier [27].

For the final separation of Hf and Zr from the lanthanides, the UTEVA column separation is conducted, where the lanthanides elute in 8 M HNO₃, while Hf and Zr retain. Hf and Zr are then subsequently eluted with 3 M HNO₃ and 1 M HCl.

As for the second separation, there is no published data for conducting it at room temperature and close to normal pressure. Thus, in this research a modified separation of lanthanides is presented (Figs.2 and 4). Following the increase in MIX- α -HIB concentration, the lanthanides are eluted consecutively from heavy to light.

These methods allow a successful separation of pure radionuclides of the REE from a Ta target in only two separation stages. The other elements can be further purified and used as well. This way, for example, the ¹⁷²Hf isotope is used in generator systems to get pure ¹⁷²Lu, which is applied in other scientific research using nuclear spectroscopic methods like TDPAC.

CONCLUSIONS

The original method for the separation of Ln using a mixture (MIX- α -HIB) of ammonium α -hydroxyisobutirate (NH₄- α -HIB) with α -hydroxyisobutiric acid (α -HIBA) (with regulated pH) was modified. In the present research the methodology is adapted to be more accessible for use in close to standard conditions. One of the main advantages of the researched elutions is that they enable the separation of Hf from REE from irradiated Ta target, allowing the direct use of the obtained pure elements.

As Zr and Hf have similar properties, at the first stage both elements are eluted from Dowex 50 \times 8 and retained on the UTEVA resin with concentrated HNO₃. The specific selectivity of the UTEVA resin allows for the separation of Zr and Hf from each other by elution with different acid solutions with lower concentrations. The first stage allows the simultaneous elution of REE and their following separation to individual elements at the second one.

The second separation is an excellent way to produce pure elements of the lanthanide row and Y. The most important thing is the successful separation of the individual elements at room temperature and pressure no higher than 2 bar by the use of low concentrations of ammonium α -hydroxyisobutirate in small volume.

In the end, the pure individual lanthanides can be used for various research purposes. The elements can be easily transferred from MIX- α -HIB solution to any other due to small volume and low concentrations of the collected fractions.

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