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ISOCRATIC ANION EXCHANGE SEPARATIONS
OF GROUP V ELEMENTS

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Настоящая работа выполнена в рамках экспериментов, направленных на исследование химических свойств долгоживущих изотопов дубния в водных растворах. Рассмотрено изократическое анионообменное разделение элементов группы V в растворах, содержащих HF. Показана принципиальная возможность разделения ниобия и тантала в системе HF/NH_4F. Проведена оптимизация параметров разделения гомологов дубния (Pa, Nb и Ta) в смешанных растворах HF/HNO_3. Предложена методика выделения и разделения элементов группы V из многокомпонентных систем.

Работа выполнена в Лаборатории ядерных реакций им. Г. Н. Флерова ОИЯИ.

The present study has been performed within the framework of experiments aimed at the investigation of chemical properties of long-lived Db isotopes in aqueous solutions. The isocratic anion exchange separations of group V elements in the solutions containing HF have been considered. A possibility in principle of niobium and tantalum separation in the system HF/NH_4F has been shown. Parameters of separation of dubnium homologues (Pa, Nb and Ta) in HF/HNO_3 mixed solutions have been optimized. The procedure of separation of group V elements from multicomponent system has been suggested.

The investigation has been performed at the Flerov Laboratory of Nuclear Reactions, JINR.

INTRODUCTION

Chemical identification of a decay chain product of a new nucleus is an alternative way of proving the synthesis of a superheavy element. The ^{268}Db isotope [1] recently discovered at the FLNR provides an excellent opportunity for the identification of superheavy Z-odd elements and for the study of dubnium chemical behavior in off-line experiments. Thus, the chemical identification of Db as a decay product of element 115 with mass number 288 (^{243}Am + ^{48}Ca reaction) was successfully performed [2, 3]. Until now 23 spontaneous fission events have been detected and the half-life of the ^{268}Db isotope has been estimated at a level of 28^{+11}_{-4} h [4].

In order to chemically characterize dubnium, new procedures for group V elements separation under the constant media content are required. It is well known that solutions containing fluoro-ions are the most usable for separation of the above-mentioned elements. Under these conditions one can expect the largest behavior differences between Nb, Ta and Pa. In our previous paper [5] a cation exchange separation of group V elements in dilute HF/HCl solutions was considered.

An anion exchange is also applied in the study of dubnium chemical properties since it forms well-sorbing fluoro-complexes [6, 7]. However, the separation of niobium and tantalum in the pure HF media with relatively small volumes of each fraction is highly difficult. That is why the behavior of these elements is investigated in mixed solutions containing F$^-$-ions, such as HF/NH$_4$F [8], HF/NH$_4$SCN [9], HF/HCl [10–14], HF/HNO$_3$ [15–17] and HF/H$_2$SO$_4$ [14, 16, 18].

The usage of solutions containing F$^-$-ions is justified for performing an isocratic anion exchange separation of group V elements. The aim of the present work is to propose a procedure for the off-line investigation of dubnium chemical properties using its long-lived isotopes.

EXPERIMENTAL

To develop the chemical separation procedures, the carrier-free tracers ^{91m,92m}Nb, ^{177}Ta, ^{175}Hf and ^{233}Pa (see Table 1) were produced via the (α, xn) reactions using the cyclotron U-200 at the FLNR (Dubna).

Table 1. Brief description of radioisotopes used in the work

Synthesis reaction	Isotope	Energy, keV (relative intensity, %)	$T_{1/2}$, days
^{nat}Y (α, xn)	^{91m}Nb	104.6 (0.5) 1204.8 (2.9)	60.9
	^{92m}Nb	934.5 (99.0)	10.15
^{nat}Lu (α, xn)	^{177}Ta	55.8 (41.8) 112.9 (7.2)	2.36
^{nat}Yb (α, xn)	^{175}Hf	343.4 (84.0)	70.0
$^{237}Np \xrightarrow{\alpha}$	^{233}Pa	312.2 (38.6)	27.0

The procedures of chemical isolations of Nb, Ta and Hf were described in papers [5, 19].

^{233}**Pa.** The production of the protactinium isotope is based on repeated elution of ^{233}Pa from the mother radionuclide ^{237}Np [20]. The creation of an isotopic generator with a strong acid cation exchanger and diluted HF solutions is based on the procedure described in [21].

Neptunium in the equilibrium with protactinium was adsorbed onto the top of a 4.7×57 mm column with Dowex 50×8 resin (100–200 mesh) from 0.1 M HNO$_3$. Protactinium was desorbed by means of HF sulutions with concentrations of less than < 0.01 M. Under these conditions protactinium forms anion complexes with F$^-$-ions and elutes in the first portions of eluent, whereas neptunium is retained by resin. The data of the HF concentration influence on Np and Pa distribution coefficients (K_d) are shown in Fig. 1. Evidently, the most usable range of HF solution concentrations for the pro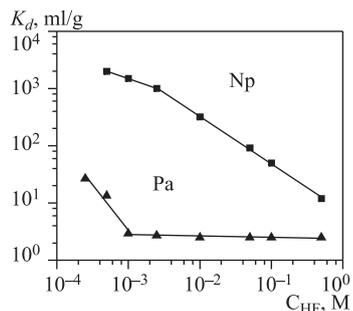tactinium elution is $1 \cdot 10^{-3}$–$2.5 \cdot 10^{-3}$ M because the maximal K_d values distinction of these elements is achieved. This allows us to elute repeatedly Pa with the minimal fraction volume, high specific activity ($> 90\%$ of the Pa activity is eluted in the first 2 ml) and the great separation factor. After the protactinium elution the column is washed with water and kept until next elution of accumulated Pa. This procedure is repeated from time to time until ^{237}Np activity is detected in the eluate. The presence of ^{237}Np isotope in the Pa-fraction was controlled by means of a LEGe-spectrometer. Spectra of the $^{237}Np/^{233}Pa$ initial solution aliquot and eluate fraction are shown in Fig. 2.

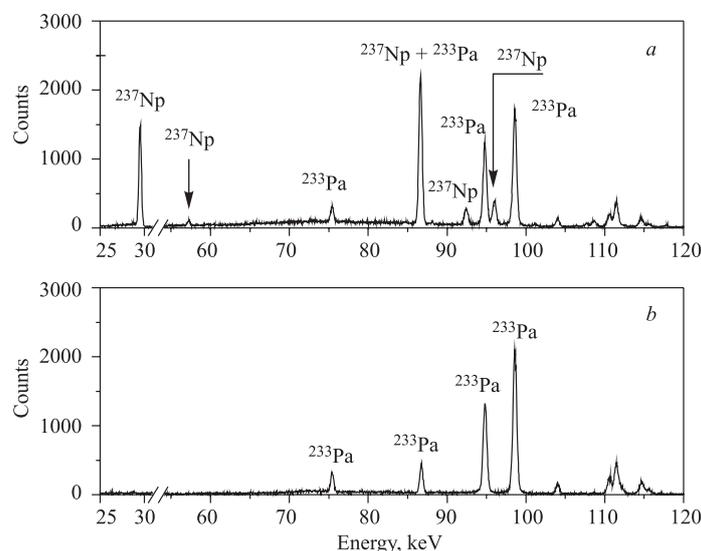Fig. 1. Distribution coefficients of Np and Pa between Dowex 50×8 resin and HF solutions of different concentrations [20]

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Fig. 2. Spectra: *a*) aliquot of ^{237}Np/^{233}Pa initial solution; *b*) Pa-fraction after elution from cation exchange column

Solutions, containing radioactive nuclides, were evaporated to dryness. The spot was dissolved in 0.2 ml of 1 M HF, and the prepared solution was adsorbed on a column with an anion exchanger.

To check procedures of isocratic separation of group V elements we used a copper beamstop of a target chamber [22] from the ^{242}Pu + ^{48}Ca experiment as a by-products catcher. The target was irradiated during 11 days. The ^{48}Ca-ion energy on the beamstop surface was around 235 MeV that corresponds to the projectile range of ~ 21 μm. The fluence of ^{48}Ca-ions was $2.1 \cdot 10^{18}$. The beamstop was kept in a lead container after the bombardment during 6.5 days. A thin layer of about 25–30 μm (corresponding to 100–120 mg of Cu) was removed from a catcher surface using a micro-lathe and in the form of copper chips was dissolved in concentrated HNO_3. For the spectrometric control of the procedure of isolation of the group V elements, we added into the solution the aliquots of the nitrates of the radionuclides ^{91m}Nb and ^{177}Ta.

The groups III–V elements were co-precipitated with La(OH)$_3$ from nitric acid by addition of 1 mg of La carrier and concentrated aqueous ammonia solution. Under these conditions, copper and most part of the groups VI–XIV elements remain in supernatant as complexes. This procedure was to be repeated twice to increase the separation efficiency. Afterwards the precipitate was dissolved in 0.5 ml of 0.2 M HCl and loaded onto the top of the first chromatography column.

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The cation exchange column (AG 50×8, 100–200 mesh, 6×30 mm) was used for the separation of the groups IV and V fraction from trivalent actinides (spattering and transfer reactions products) [3]. The groups IV and V fraction was eluted with 1 M HF in a volume of about 1–2 ml. Lanthanum, around 50% of scandium activity and heavy actinides were retained on the top of the column [21, 23].

For the separation of the group V elements on an anion exchange column the eluate from the previous step was used as a load solution. Then Nb and Ta were eluted separately with mineral acid (HNO_3, HF) mixtures.

Precisely separated element fractions were eluted exclusively with easy evaporable strong mineral acids of different types and concentrations. The amounts of described elements were finally determined by the γ-activity measurements of the corresponding tracers with a standard HPGe-spectrometer.

RESULTS AND DISCUSSION

Based on the analysis of literature data one can conclude that HF/NH_4F and HF/HNO_3 solutions are the most interesting media for the development of procedures for isocratic anion exchange separation of group V elements.

The Nb and Ta distribution coefficients in the mixed HF/NH_4F solutions decrease with an increase in both acid and ammonium fluoride concentrations [8]. Finally, K_d values allow one to separate niobium and tantalum and to obtain relatively small volume fractions of each element. Ranges of HF/NH_4F solution concentrations and corresponding minimal K_d values of groups III–V elements when Dowex 1×8 resin is used are given in Table 2. It is shown that Nb and Ta can be isolated and separated from each other by both component concentrations exceeding $\geqslant 3$ M.

Results of niobium and tantalum separations using 4 M HF / 3 M NH_4F solutions are shown in Fig. 3. Separation factors for these elements are: $\alpha_{Ta/Nb} \approx$ 1.3 (Fig. 3, a) and $\alpha_{Ta/Nb} \approx 1.4$ (Fig. 3, b). The latter factor value was achieved at the expense of optimizing the column and resin geometric parameters which will

Table 2. Ranges of HF/NH$_4$F solution concentrations and corresponding minimal K_d values of groups III–V elements when Dowex 1×8 resin is used [8]

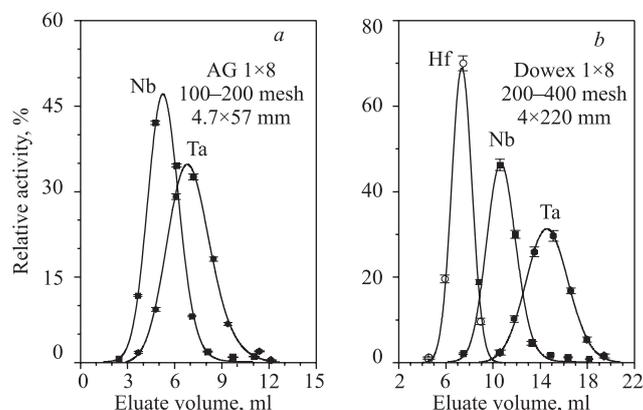| Element	K_d, ml/g	Concentration, M	
		HF	NH$_4$F
Nb	< 20	> 2	> 2
Ta		$\geqslant 3$	$\geqslant 3$
Pa	< 5		$\geqslant 2$
Hf	< 10	$\geqslant 0.2$	$\geqslant 7$
Sc	< 5		$\geqslant 1$

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Fig. 3. Separation of Nb, Ta (*a*) and Nb, Ta and Hf (*b*) by means of 4 M HF / 3 M NH$_4$F

be discussed below. However, this system has an essential disadvantage. The finite source for the α- and SF-measurement is prepared by evaporation of the corresponding fraction to dryness in a hot He jet. Under these conditions a mixture of NH$_4$F and NH$_4$HF$_2$ crystals is formed which means that the spectrometric measurements can be complicated. Moreover, the crystal sublimation will require heating up to 126 and 167 °C for ammonia fluoride and ammonia hydrofluoride, respectively. Due to this the thin polymeric film which is a bottom layer of the measurement source will be destroyed.

There are several fields of acid concentrations with relatively low values of distribution coefficients K_d of niobium and tantalum (Fig. 4) when a Dowex 1×8 exchanger is used [17]. In this system trends in the K_d value changing are of a different character. From this point of view the investigation of anion exchange behavior of Nb and Ta in the mixed HF/HNO$_3$ solutions with different content of each acid will allow one to get a deep understanding of chemical properties of the above-mentioned elements.

In Fig. 5 results of Nb, Ta and Hf separations are shown. Separation factors of niobium and tantalum are as follows: $\alpha_{\text{Ta/Nb}} \approx 3.4$ (Fig. 5, *a*) and $\alpha_{\text{Nb/Ta}} \approx 1.3$ (Fig. 5, *b*). An inversion of elution sequence of these elements is depicted. This fact can be explained by formation of [NbOF$_n$]$^{3-n}$ or [Nb(OH)$_2$F$_n$]$^{3-n}$ niobium complexes even at a high hydrofluoric acid concentration. The [NbF$_n$]$^{5-n}$ species can be formed at a HF concentration of > 10 M. In the case of tantalum, the complex anions [TaF$_n$]$^{5-n}$ can be expected [8]. Thus, mixed HF/HNO$_3$ solutions can be used for the separation of group V elements. Moreover, the contrary elution sequence of niobium and tantalum is an additional advantage which gives an opportunity to check the influence of relativistic effects on chemical properties of dubnium.
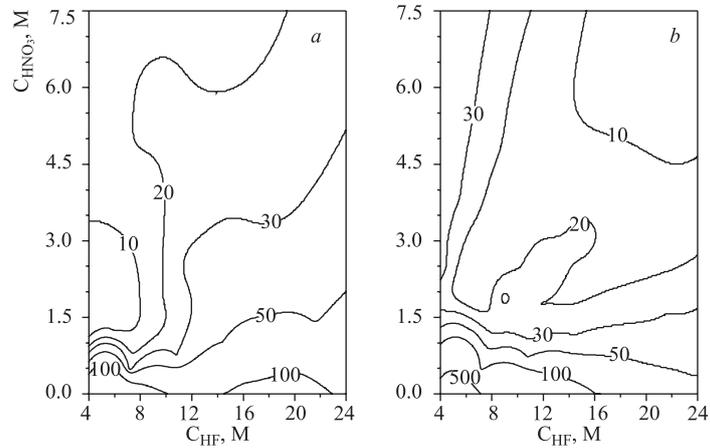
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Fig. 4. Distribution coefficients of Nb (*a*) and Ta (*b*) between Dowex 1×8 and HF/HNO$_3$ mixtures (compiled from [17])
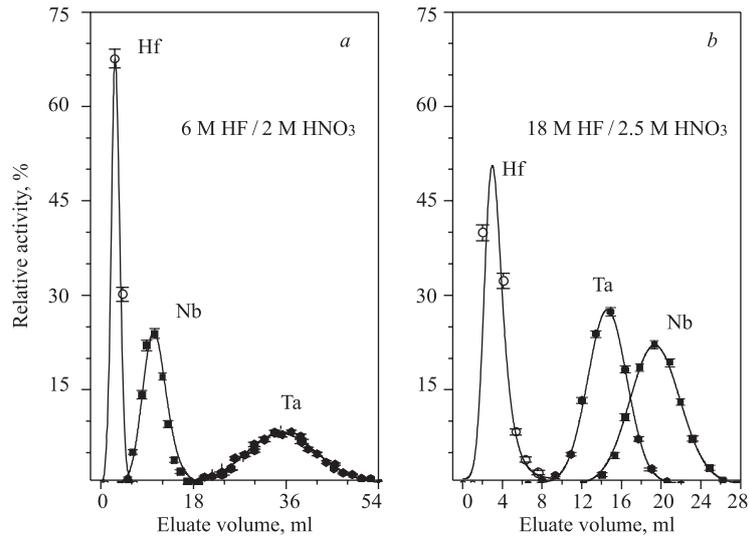

Fig. 5. Isocratic separation of Hf, Nb and Ta with the 4.7×57 mm column (AG 1×8, 100–200 mesh)

However, it is not convenient to use this system without preliminary optimization of the separation process. Relatively large volumes of each element fraction can be reduced by using resins with a smaller graining and content of divinylbenzene. For this purpose Dowex 1×2 and Dowex 1×4 resins with particle size of -400 mesh were used.
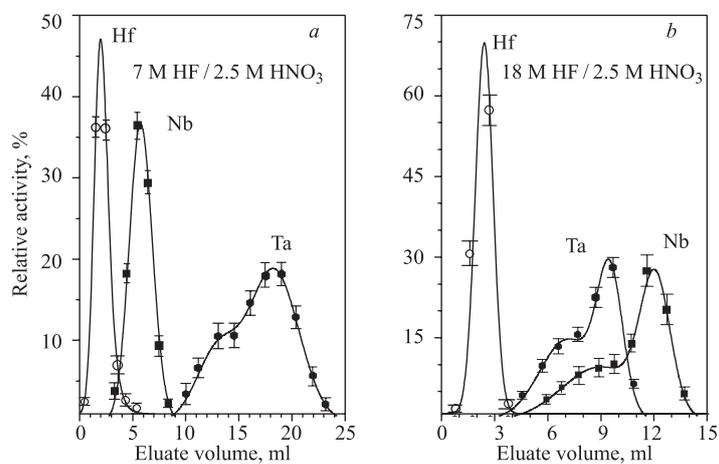
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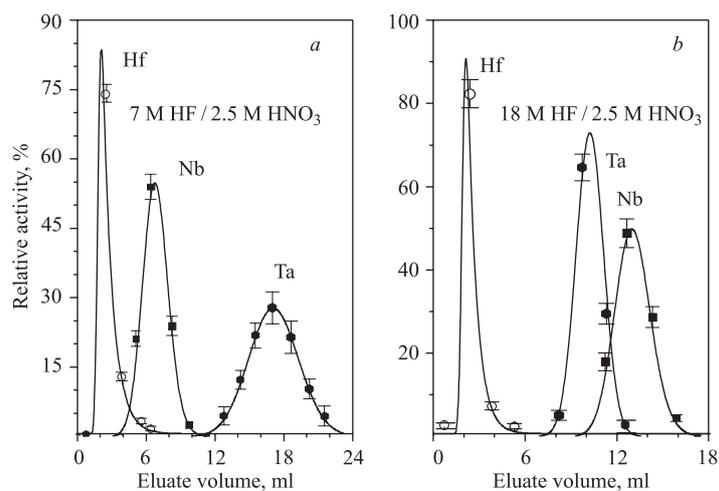Fig. 6. Separation of Nb, Ta and Hf by anion exchange with the 4.7×57 mm column (Dowex 1×2, -400 mesh)

Fig. 7. Separation of Nb, Ta and Hf by anion exchange with the 4.7×57 mm column (Dowex 1×4, -400 mesh)

Obviously, the usage of Dowex 1×2 resin is unacceptable because of interaction of Nb and Ta pure F^--complexes with the resin core (Fig. 6). The separations of Hf, Nb and Ta by Dowex 1×4 resin are shown in Fig. 7. The separation factors for niobium and tantalum are: $\alpha_{Ta/Nb} \approx 2.6$ (Fig. 7, *a*) and $\alpha_{Nb/Ta} \approx 1.3$ (Fig. 7, *b*). Both separations were carried out using the same nitric

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acid concentration that proves a major contribution of HF concentration changes to elution order of group V elements.

Variation of geometrical parameters of the columns and Glückauf's math model [24, 25] are required for further optimization of the separation procedures. The latter allows one to simulate the behavior of elements by ion exchange separation because it takes into account easily changeable parameters such as:

- height of exchanger in column;
- inner diameter of column;
- radius of resin particle;
- linear velocity of solution.

The task now is to fit the experimental data into the curve and to select the required parameters for achieving satisfactory separation.

Column parameters for the Nb and Ta separation according to the math model were selected in order to check such an approach. The goal was to calculate the height of the column with 4 mm i.d. and to achieve the same separation as we made using the 4.7×57 mm column at a 0.25 ml/min flow rate. Results of theoretical predictions and experimental data are shown in Fig. 8. It is shown that a 4×80 mm column allows one to achieve the necessary separation factor $\alpha_{Ta/Nb} \approx 2.1$. The same procedure was used for the column parameter optimization using different relationships of nitric and hydrofluoric acid concentrations. In the case of the 18 M HF/2.5 M HNO_3 solution the finite height of the column should be enough for the improved separation of Ta and Nb. And it can be realized with a 4×220 mm column.
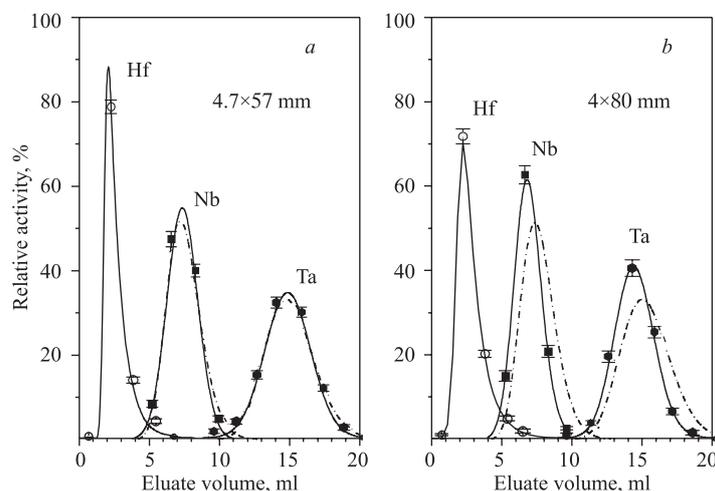

Fig. 8. Calculations (dash-dotted line) and separations of Nb and Ta by 6 M HF / 4 M HNO_3 solution with Dowex 1×4 (-400 mesh) resin and 0.25 ml/min flow rate
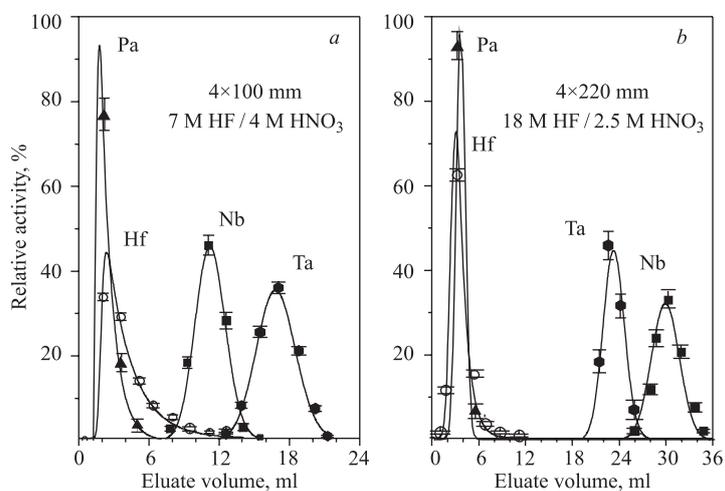
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Fig. 9. Separation of Nb, Ta, Pa and Hf by anion exchange (Dowex 1×4, -400 mesh)
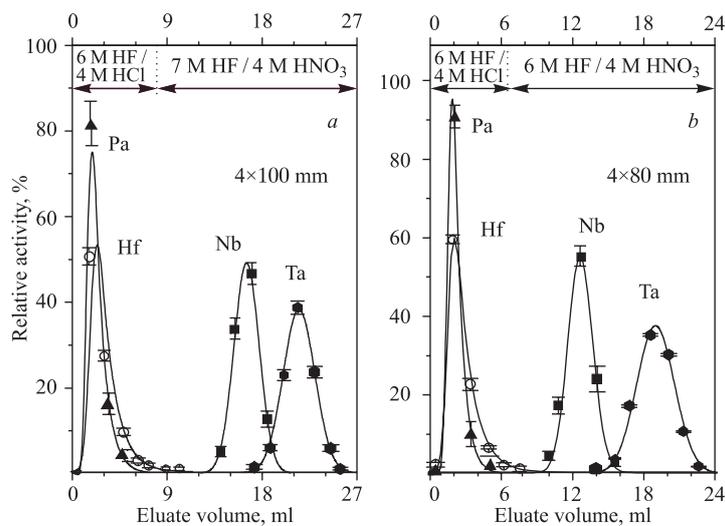

Fig. 10. Stepwise separation of Nb, Ta, Pa and Hf by anion exchange (Dowex 1×4, -400 mesh)

Besides, the behavior of protactinium is of interest under these conditions. It is shown in Fig. 9 that all three dubnium homologues were separated. The peak positions of Pa and Hf are close to each other. The separation factors of niobium

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and tantalum are: $\alpha_{Ta/Nb} \approx 1.5$ (Fig. 9, a) and $\alpha_{Nb/Ta} \approx 1.3$ (Fig. 9, b). In the case of the separation of Nb and Ta from Pa, separation factors are greater than 8.

Unfortunately, in Fig. 9, a niobium and hafnium peaks are overlapped. In this case the usage of HF/HCl solutions [13] can be useful in the fraction purification. Stepwise elutions are shown in Fig. 10. The scheme from Fig. 10, b has advantages because we achieved the better separation within the shorter time.

The efficiency of suggested procedures was checked experimentally. The scheme consists of consecutive stages such as lanthanum hydroxide precipitation for removing the catcher material (Cu), cation exchange for the purification of elements of interest from trivalent lanthanides and actinides, anion exchange for separating niobium and tantalum. In Fig. 11 spectra of the initial solution, Sc-, Nb- and Ta-fractions are shown. It is seen (Fig. 11, b) that Sc and Hf are eluted together. And all finite fractions don't contain any impurities. Chemical yields for niobium and tantalum in both separation procedures are given in Table 3. Obviously that proposed chemical system can be used in the study of dubnium properties in future off-line experiments.
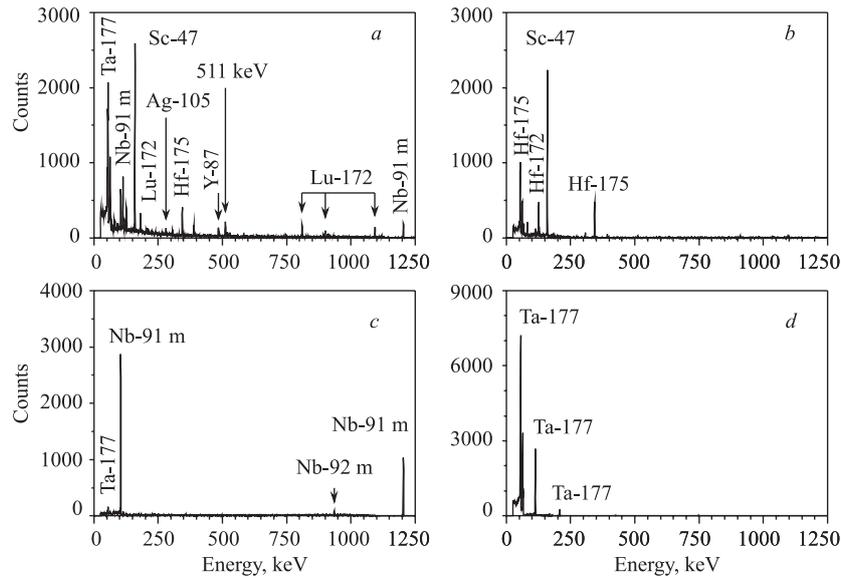

Fig. 11. Spectra: a) aliquot of the initial solution; b) Sc-fraction; c) Nb-fraction; d) Ta-fraction

Table 3. Yields of radioisotopes, %

Isotope	6 M HF / 4 M HNO$_3$		18 M HF / 2.5 M HNO$_3$	
	Nb-fraction	Ta-fraction	Ta-fraction	Nb-fraction
^{91m}Nb	84.5 ± 1.1	0.18 ± 0.05	1.96 ± 0.13	79.8 ± 0.8
^{177}Ta	1.27 ± 0.14	76.5 ± 1.2	72.9 ± 1.0	0.11 ± 0.08

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CONCLUSIONS

The isocratic anion exchange separations of dubnium homologues (Pa, Nb and Ta) in solutions containing F^--ions have been developed. A possibility in principle of niobium and tantalum separation in the system HF/NH_4F has been considered. The elution order of niobium and tantalum in HF/HNO_3 mixed solutions depends on the ratio of acids concentrations. This is an additional advantage which gives an opportunity to check the influence of relativistic effects on chemical properties of dubnium. A procedure of isolation and separation of group V elements from multicomponent system has been suggested. A combination of consecutive stages such as precipitation, cation and isocratic anion exchanges has been checked under real conditions. Chemical yields for elements of interest are around 80 per cent. Thus, this analytical procedure can be used in the study of dubnium chemical properties in future off-line experiments.

REFERENCES

1. *Oganessian Yu. Ts. et al.* // Phys. Rev. C. 2004. V. 69. P. 021601(R).
2. *Dmitriev S. N. et al.* // Mendeleev Commun. 2005. V. 15, No. 1. P. 1–4.
3. *Schumann D. et al.* // Radiochim. Acta. 2005. V. 93. P. 727–732.
4. *Stoyer N. J. et al.* // Nucl. Phys. A. 2007. V. 787, No. 1–4. P. 388c–395c.
5. *Tereshatov E. E. et al.* // Radiochemistry. 2008. V. 50, No. 3. P. 290–293.
6. *Trubert D. et al.* // Radiochim. Acta. 2002. V. 90. P. 127–132.
7. *Tsukada K. et al.* // Radiochim. Acta. 2009. V. 97. P. 83–89.
8. *Caletka R., Krivan V.* // J. Radioanal. Nucl. Chem. 1990. V. 142, No. 2. P. 359–371.
9. *Monroy-Guzman F., Trubert D., Le Naour C.* // J. Radioanal. Nucl. Chem. 2002. V. 254, No. 3. P. 431–437.
10. *Schumann D. et al.* // J. Radioanal. Nucl. Chem., Lett. 1994. V. 187, No. 1. P. 9–17.
11. *Schumann D. et al.* // Radiochim. Acta. 1996. V. 72. P. 137–142.
12. *Headridge J. B., Dixon E. J.* // Analyst. 1962. V. 87. P. 32–42.
13. *Kim J. I., Lagally H., Born H. -J.* // Anal. Chim. Acta. 1973. V. 64. P. 29–43.
14. *Caletka R., Hausbeck R., Krivan V.* // J. Radioanal. Nucl. Chem. 1989. V. 131, No. 2. P. 343–352.
15. *Huff E. A.* // Anal. Chem. 1964. V. 36, No. 10. P. 1921–1923.
16. *Danielsson L.* // Acta Chem. Scand. 1965. V. 19, No. 8. P. 1859–1874.

17. *Faix W. G., Caletka R., Krivan V.* // Anal. Chem. 1981. V. 53, No. 11. P. 1719–1721.
18. *Caletka R., Hausbeck R., Krivan V.* // J. Radioanal. Nucl. Chem. 1990. V. 142, No. 2. P. 383–391.
19. *Aksenov N. V. et al.* // Radiochemistry. 2008. V. 50, No. 4. P. 381–385.
20. *Guseva L. I., Tikhomirova G. S.* Application № 4850099/26. 1992. B. I. 44. P. 57.
21. *Guseva L. I., Tikhomirova G. S.* // Radiochemistry. 1993. V. 2. P. 103–110.
22. *Eichler R. et al.* // Nature. 2007. V. 447. P. 72–75.
23. *Ter-Akopian G. M. et al.* // Sov. J. Nucl. Phys. 1979. V. 29. P. 312–318.
24. *Marhol M.* Ion Exchangers in Analytical Chemistry. Prague: Academia, 1982. 261 p.
25. *Riemann W., Walton H. F.* Ion Exchange in Analytical Chemistry. Oxford-New York-Toronto-Sydney-Braunschweig: Pergamon press, 1970. 375 p.