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Sorption behaviour of rutherfordium and thorium from HCl/Hf containing aqueous solution

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Abstract

The sorption was studied of element 104 (rutherfordium, Rf) and thorium on the strongly acidic cation exchanger DOWEX 50×8. The experiments were carried out on-line. Rf is strongly retained on cation exchange resins from diluted HCl/HF solutions in a concentration range of 0.05 to 0.1 M HCl and HF concentrations up to 0.01 M. This behaviour is similar to its pseudohomologue thorium and very different from its lighter homologue hafnium which is desorbed from DOWEX 50×8 at HF concentrations above 10^{-3} M. The tested ion exchange system is suitable for fast on-line separation of element 106 (seaborgium, Sg) from all other contaminations and its decay product Rf. It, therefore, allows the indirect identification of Sg.

Keywords: Rutherfordium; Aqueous chemistry; Ion exchange; HCl/HF solution

1. Introduction

Diluted HCl/HF solutions were used for detailed sorption studies on cation and anion exchangers of group IV, V, and VI elements [1], and the pseudohomologues U(VI) and Th [2] aimed to develop suitable chemical systems for the isolation and identification of seaborgium. In these investigations it was observed that Zr and Hf desorbed from the cation exchanger DOWEX 50×8 at HF concentrations higher than 10^{-3} M in the presence of 0.05–0.1 M HCl, whereas U(VI) and Th were sorbed up to concentrations of 0.1 M HF. The group VI elements W and Mo show only slight sorption on the cation exchanger in this concentration interval. Based on these results, ion exchange on the cation exchanger AMINEX A6 with 0.1 M $HNO_3/5\times10^{-4}$ M HF solution as eluent was successfully applied in a first experiment to study the chemical properties of ^{265}Sg in aqueous solution using the ARCA apparatus [3]. Unfortunately, in this experiment the mother nuclide ^{265}Sg could not be detected directly due to its extremely short half-life [4]. Only correlated events from the α-decay products ^{261}Rf and ^{259}No were found. However, because Rf is proposed to behave similar to its lighter homologue Hf, it is expected to sorb on the cation exchange column. Under these conditions the detection of Rf and No events is evidence for the fact that Sg has passed through the chromatographic column. Therefore, detailed studies of the sorption of Rf under these conditions are of great interest. Earlier ion exchange experiments with 0.2 M HF solution showed that Rf is completely sorbed onto the anion exchanger DOWEX 1×8 due to the formation of stable anionic fluoride complexes [5]. More diluted solutions were not studied at all. We selected 0.1 M HCl/0.01 M HF solution as eluent and studied the sorption of Rf on the cation exchanger DOWEX 50×8. Additionally, batch experiments were carried out to investigate the sorption behaviour of the pseudohomologue ^{228}Th on the cation exchanger under similar concentration conditions. The results are compared with those for Hf obtained in earlier works [1,6].

2. Experimental

Rf was produced via the nuclear reaction

$$^{248}\mathrm{Cm} + {}^{18}\mathrm{O} \rightarrow {}^{261}\mathrm{Rf} + 5\mathrm{n}\ (97 - 99\ \mathrm{MeV})$$

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at the U-400 cyclotron of the FLNR (JINR Dubna, Russia). The target contained 1.01 mg cm^{-2} ^{248}Cm on 10 μm Be foil, covered by 200 mg cm^{-2} Gd (30% enriched in ^{152}Gd). The ^{18}O beam had an intensity of up to 0.5–0.7 pμA on target.

^{261}Rf ($T_{1/2}=78$ s [7,8], E_a: 8.29, 8.52 MeV [9]) and its daughter ^{257}No ($T_{1/2}=25$ s, $E_a=8.22$, 8.27, 8.32 MeV) were detected by α-measurement using four counting chambers with PIPS detectors (ORTEC, resolution 50 keV, counting time 4 min). No underground events were found in the energy window 8.0–8.7 MeV during a measure time of 24 h.

The slightly modified chemical apparatus that is described in [5] was used for the chromatographic experiments. After the transport from the target chamber to the chemical setup by use of a NaCl/Ar gas jet system, the activity was dissolved in the corresponding solution and continuously passed through a microcolumn filled with 50 mg DOWEX 50×8 (200–400 mesh) with a flow rate of 0.3 ml min^{-1}. The solution was collected onto a Ta backing for 1 min and evaporated to dryness by heating for another minute. During this time, the next sample was already collected so that one sample was prepared every minute for α-measurement. Columns were used for 1 h and then replaced by fresh ones. To control the behaviour of the simultaneously produced Hf isotopes, γ-measurements of the Ta backings and the columns were carried out with a GeLi detector 15 min after changing the column. The ion exchange resin of the column was transferred into a small vessel and then placed in front of the detector for measurement. All Ta discs on which the loading solution was evaporated during the use of one column were collected in a vessel and positioned in front of the detector.

A direct catch was also performed using 0.2 M HF solution without a column. Then DOWEX 50×8 columns were used for the separation using 0.1 M HCl/0.01 M HF solution.

For the batch experiments with ^{228}Th, 5 ml of the radioactive solution was contacted with 200 mg of ion exchange resin (DOWEX 50×8, 20–50 mesh) for 1 h. The results were obtained by separating the phases immediately after the experiments and determining the γ-activity of the decay products (mainly ^{212}Pb) after 1 month. The distribution coefficients were calculated as reported in [1].

Carrier-free ^{228}Th was obtained as an α-decay product of ^{232}U(VI) [10]. It was separated immediately before the experiments by adsorbing the ^{232}U(VI) on the anion exchange resin DOWEX 1×8 from 9 M HCl solution. The ^{228}Th passes through the column without sorption. This stock solution was diluted to the required concentration.

3. Results and discussion

In the direct catch without a column and 0.2 M HF solution, six single events were found in the energy window of 8.10–8.50 MeV during a time of 351 min (Fig. 1). In this spectrum a little contamination of ^{212m}Po can be seen (11.65 MeV (94%), $T_{1/2}=45.1$ s) which has also α-rays at 8.52 MeV (4.9%) and 9.08 MeV (1.0%). Therefore, the events with energies higher than 8.50 MeV were not taken into consideration. From this an average rate of 1.06 events per hour results for the direct catch. In the chromatographic experiment with DOWEX 50×8 and 0.1 M HCl/0.01 M HF solution as eluent, five single events were found in 582 min (0.52 events per hour) in the same energy window as above. The spectrum is shown in Fig. 2.

With these data, a log D value of 2.52 was calculated using the formula described in [1].

The γ-spectra of the simultaneously produced Hf iso-

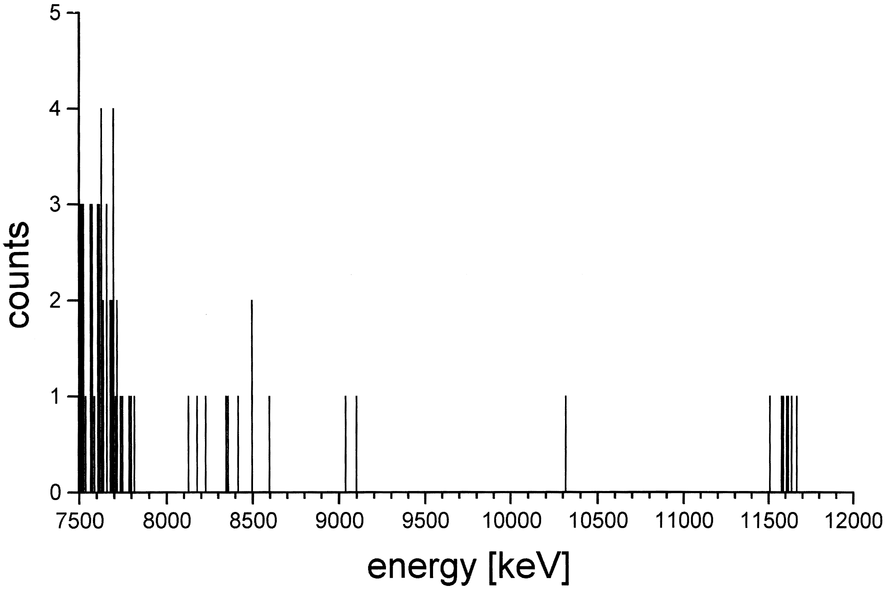

Fig. 1. Summarized α-spectrum of the direct catch without column, measure time 351 min, nuclear reaction $^{248}\mathrm{Cm}+{}^{18}\mathrm{O}\rightarrow{}^{261}\mathrm{Rf}+5\mathrm{n}$.

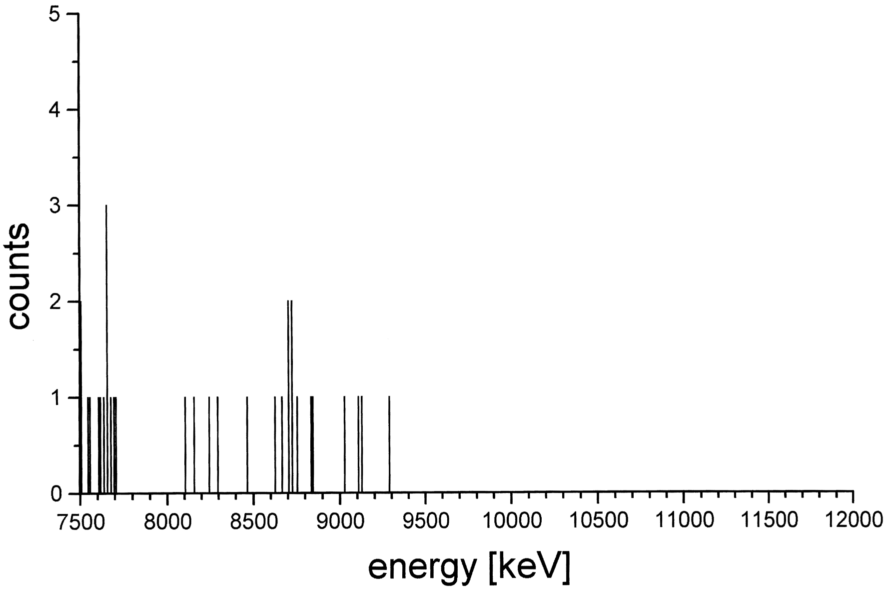

Fig. 2. Summarized α-spectrum after separation with 0.1 M HCl/0.01 M HF, measure time 582 min, nuclear reaction $^{248}Cm + ^{18}O \rightarrow ^{261}Rf + 5n$.

topes showed that Hf is not sorbed at all onto the cation exchange resin from 0.1 M HCl/0.01 M HF solution. Figs. 3 and 4 show the γ-spectra both of the column and the loading solution, respectively. For the understanding of these spectra the following must be explained: Since all γ-measurements were carried out off-line, only the long-lived Hf isotopes and the decay products of the short-lived Hf nuclides could be detected. Lu and Yb as β^+-decay products of Hf are known to sorb on the cation exchanger from diluted HCl/HF solutions [11]. The dead time of the separation system (including the time needed to pass the degasser unit and the column) is about 1 min, so that the isotopes ^{167}Hf ($T_{1/2} = 2.05$ min) and ^{169}Hf ($T_{1/2} = 3.25$ min) already partially decayed and their decay products Lu and Yb were found both on the cation exchange column and in the solution. On the contrary, ^{168}Hf ($T_{1/2} = 26$ min) and its decay products were only found in the spectra of the solution. From these results follows that Hf isotopes passed the cation exchange column without sorption as it was expected from earlier experiments [11].

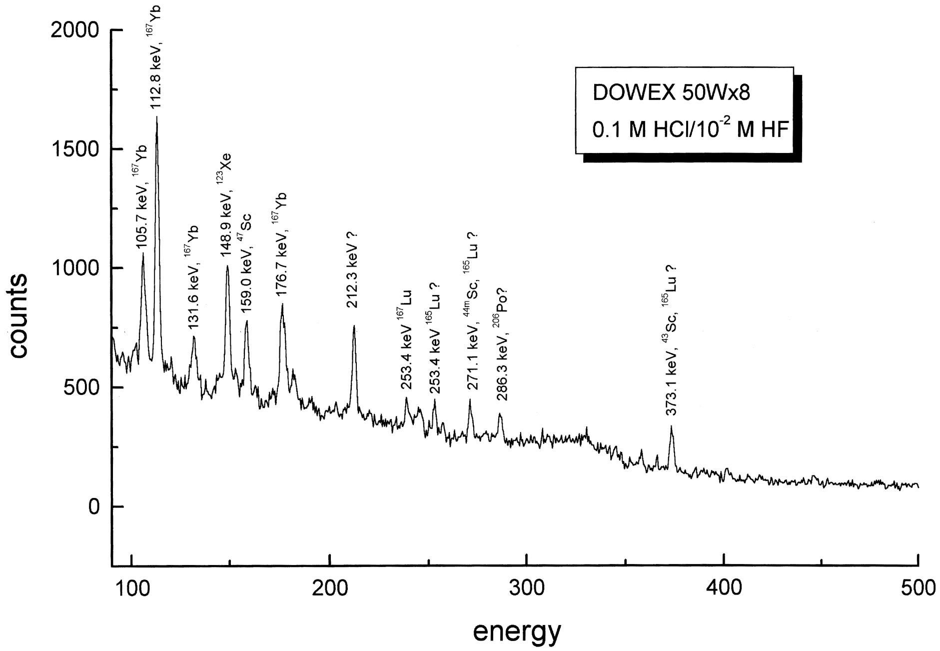

Fig. 3. γ-Spectrum of the DOWEX 50×8 column, eluted with 0.1 M HCl/0.01 M HF, flow rate 0.3 ml min^{-1}, collection time 1 h, nuclear reaction: $^{152}Gd + ^{18}O \rightarrow ^{(170-x)}W + xn$.

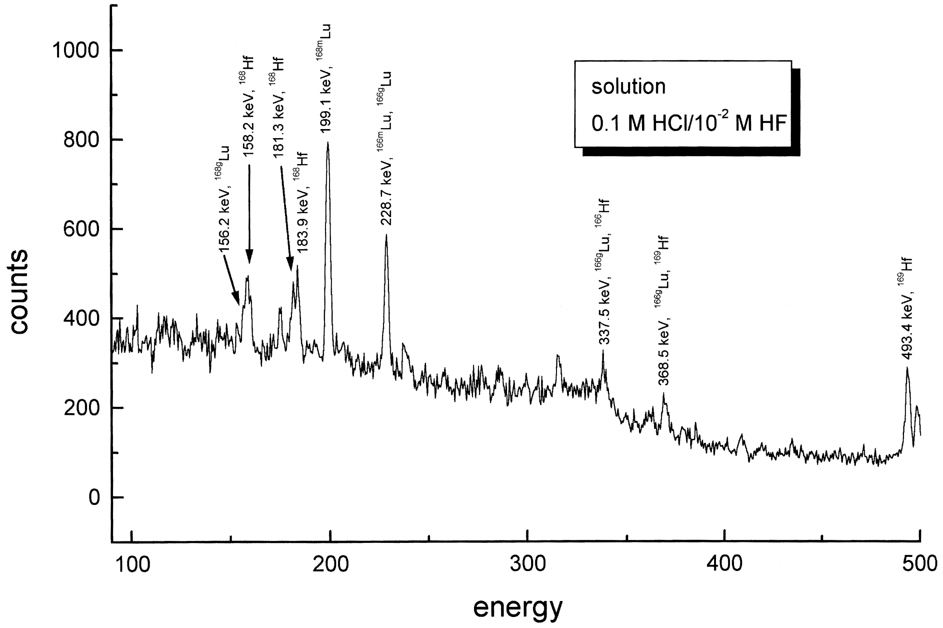

Fig. 4. γ-Spectrum of the evaporated solution (0.1 M HCl/0.01 M HF), flow rate 0.3 ml min^{-1}, collection time 1 h, ^{152}Gd+^{18}O→$^{(170-x)}$W+*x*n.

The results of the Th batch experiments are shown in Fig. 3. Th showed strong sorption on the cation exchanger over the hole investigated concentration range (10^{-5}–0.1 M HF, constant HCl concentration of 0.1 M). Only at 0.1 M HF a slight decrease is observed.

In Fig. 5, all results are compared with those of batch experiments [1] and earlier on-line studies with the ARCA apparatus [6]. It is evident that Rf shows under the described conditions a sorption behaviour different from that of its lighter homologue Hf, whereas similarities are found with the pseudohomologue Th. Th is not known to form anionic fluoride complexes [12]. The formation constants for Zr and Hf fluoride complexes decrease with increasing mass number [12]. Because Rf is known to form anionic fluoride complexes at 0.2 M HF concentration [5] the stability constants of fluoride complexes must lie between Hf and Th giving the following order of decreasing stability: Zr>Hf»Rf>Th.

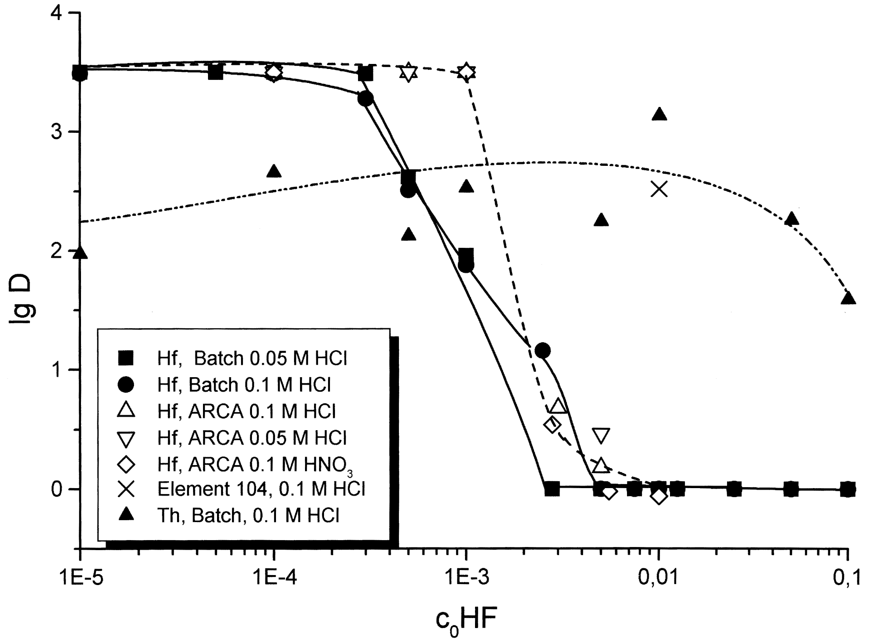

Fig. 5. Log *D* values of Hf, Th and Rf on DOWEX 50×8 as a function of the HF concentration at several constant HCl concentrations, data for Hf taken from [1,6].

4. Conclusions

This first result confirms the assumption that Rf can be strongly retained on cation exchange resins from diluted HCl/HF solutions in a concentration range of 0.05–0.1 M HCl and HF concentrations lower than 0.01 M. This makes the system suitable for fast on-line separation of Sg from all other contaminations and its decay product Rf, and, therefore, allows the indirect identification of Sg.

The normal trend of stability constants within the group IV is confirmed. However, to obtain better knowledge on the magnitude of the complex formation constants of rutherfordium fluoride complexes further investigation of its sorption behaviour in dependence on the HF concentration is necessary.

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