Anion exchange of Zr, Hf, and Th by the automated extraction apparatus: toward the chemical study of $_{104}$Rf in HNO_3

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Chemical elements with $Z \geq 104$ are called superheavy elements (SHEs). The chemical properties of SHEs are almost unknown because they must be synthesized by heavy-ion-induced nuclear reactions using accelerators with very low cross sections and have very short half-lives ($T_{1/2} \leq 1$ min). There are some chemical experiments on $_{104}$Rf in solution chemistry; however, its chemical properties are not sufficiently understood due to limited experimental methods. Further systematic experimental studies are needed. In our previous work, we developed the automated batch-type solid-liquid extraction apparatus (AMBER) and investigated the anion-exchange behavior of Rf in HCl and H_2SO_4 to obtain the distribution coefficients (K_d) of Rf under chemical equilibrium conditions.[1,2]

In this study, we focus on the formation of the Rf nitrate complexes. Indeed, the clear difference between the complexation of Th (pseudo homologue of Rf) and those of Zr and Hf (homologues) in HNO_3 is known; Th forms an anionic complex with large coordination numbers of 10 and/or 12, while Zr and Hf do not. We previously found that anion-exchange reactions using Adogen 464 resin (anion exchanger) in HNO_3 reach the chemical equilibrium in 60 s for Th, and this resin is promising for ^{261}Rf ($T_{1/2} = 68$ s) experiments. Toward the anion-exchange experiments of Rf in HNO_3 using AMBER, herein, we determined the experimental conditions for washing the resin and its repetitive use.

We produced the ^{88}Zr and ^{175}Hf isotopes in the ^{89}Y$(d, 3n)$ and ^{nat}Lu(d, xn) reactions, respectively, by using the RIKEN AVF cyclotron. ^{234}Th was separated from ^{238}U (α-decay mother nuclide). These radionuclides were purified by an anion-exchange method.

0.3 mL of 8 M HNO_3 including ^{88}Zr, ^{175}Hf, and ^{234}Th was injected into the chemical reaction container in AMBER, containing 3 mg of the Adogen 464 resin, and the container was shaken for 60 s (anion-exchange part). After only the solution phase was discharged from the container passing through a PTFE filter with compressed air, the Zr, Hf, and Th adsorbed on the resin were washed out by injecting 0.1 M HNO_3 or 0.1 M HCl into the container (back extraction part). In the same manner as above, the washing solution was discharged from the container. This part was repeated until all of Zr, Hf, and Th were excluded from the resin. The recovery rate until the m-th back extraction was determined from the following equation:

$$R(m) = \sum_i^m A_i / \sum_i^n A_i, \quad (1)$$

where A_i is the radioactivity of the solution in the i-th back extraction, and n is the total number of back extraction.

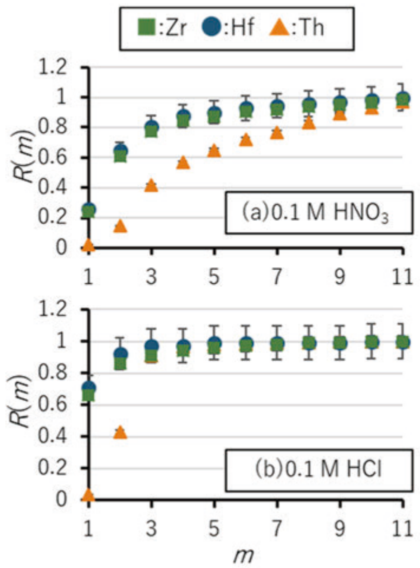

Fig. 1. Recovery rate $R(m)$ of Zr, Hf, and Th using 0.1 M HNO_3 and 0.1 M HCl as the back extractant.

Figure 1 shows the behavior of $R(m)$ as a function of m. This graph shows that 9 or 10 times of back extractions are required to wash out all of the Zr, Hf, and Th adsorbed on the resin in 0.1 M HNO_3 (a), while 3 or 4 times are enough in 0.1 M HCl (b). This difference results in different experimental times for one cycle (the total time of anion-exchange part, back extraction part, and conditioning part); 5 min for 0.1 M HNO_3 (9 back extractions), and 3 min for 0.1 M HCl (3 back extractions). We decided to use 0.1 M HCl as the solution for back-extraction since the experiments for ^{261}Rf should be performed in shorter cycles.

We performed about 100 cycles of the following sequence; 60 s of anion exchange with 8 M HNO_3, followed by 4 back extractions with 0.1 M HCl, and then 2 iterations of conditioning with 8 M HNO_3. The K_d values of Zr, Hf, and Th in the anion exchange were constant in 100 consecutive runs using AMBER, and this result indicates that the Adogen 464 resin has sufficient durability to conduct a repetitive anion-exchange experiment of ^{261}Rf.

In the near future, an on-line experiment of Zr and Hf will be conducted as a model experiment for Rf under the experimental conditions determined in this study.

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References
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