

## Development of an automated batch-type solid-liquid extraction apparatus and extraction of Zr, Hf, and Th by triisooctylamine from HCl solutions for chemistry of element 104, Rf<sup>†</sup>

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Online rapid chemical experiments on a “one-atom-at-a-time” basis using an accelerator are needed for the superheavy element chemistry. An apparatus for rapid and repetitive chemistry in online use is essential. So far, the pioneering works opened up the chemistry of new elements and revealed their properties as *d*-block metal elements in the periodic table.<sup>1)</sup> On the other hand, equilibration of the chemical reactions has not been confirmed for the short-lived superheavy elements, although this confirmation is important to investigate the detailed chemical properties of these elements such as complex formation. Only in the fluoride complexation studies, the equilibrated data were obtained for the lighter homologues in online experiments.<sup>1)</sup> The  $K_d$  values of Rf obtained in the ion-exchange chromatography under such conditions were clearly different from those of Zr and Hf. Investigation of the complex formation of Rf with other ligands is very important for an understanding of its chemical properties. However, it might be difficult to obtain well equilibrated data or to observe the time dependence of the distribution behaviors for superheavy elements.

In this work, we developed an automated batch-type solid-liquid extraction apparatus to study time dependence of extraction behavior, and performed the online extraction experiments of Zr and Hf in TIOA/HCl system. By comparing the results with those in “offline” extraction, applicability of the apparatus for Rf was investigated.

In the offline experiment, the 18–57 wt% TIOA resin and 6.2–10.9 M HCl containing the <sup>88</sup>Zr and <sup>175</sup>Hf tracer solution were mixed in a PP tube and the mixture was shaken for 2–120 min at 25 ± 1 °C. Then, we measured the sample  $\gamma$ -ray spectroscopically using a Ge semiconductor detector. In all solid-liquid extraction experiments, control experiments without the resin were performed to determine the radioactivity of the control solution. The  $R$  values were determined from the following equation:

$$R = A_r V_s / A_s w_r = (A_c - A_s) V_s / A_s w_r, \quad (1)$$

where  $A_r$  and  $A_s$  are the radioactivities on the resin and in the solution, respectively,  $V_s$  is the volume (mL) of the solution, and  $w_r$  is the mass of the dry resin (g).  $A_c$  denotes the radioactivity of the control solution. In this study, the  $R$  value in equilibrium is described as the  $K_d$  value in solid-liquid extraction.

An AutoMated Batch-type solid-liquid Extraction apparatus for Repetitive experiments of transactinides (AMBER) was developed. All the operations were controlled by PC with fixed time intervals in online extraction experiments.

In the online experiment, the <sup>89g,m</sup>Zr and <sup>175</sup>Hf nuclides were produced in the <sup>89</sup>Y(*p*, *n*)<sup>89g,m</sup>Zr and <sup>175</sup>Lu(*p*, *n*)<sup>175</sup>Hf reactions, respectively, using the K70 AVF cyclotron at RIKEN. The product nuclides were transported by the gas-jet system to the chemistry laboratory and deposited on a collection site of AMBER for 60 s. Then, the deposited sample was dissolved in 160–230  $\mu$ L of 6–11 M HCl. The solution passed through the valves, and then entered the chemical reaction container containing the 31 wt% TIOA resin. After shaking the container with a vortex mixer for 10–120 s, only the liquid phase was pushed out of the container by the compressed air at 0.5 MPa, and was assayed by  $\gamma$ -ray spectroscopy. The residual Zr and Hf species adsorbed on the resin were stripped by washing the resin three times with about 220  $\mu$ L of a mixture solution of 5.1 M HNO<sub>3</sub> and 0.01 M HF. We measured the first two fractions of the stripping solution  $\gamma$ -ray spectroscopically. A control extraction experiment without the resin was also performed.

In the offline experiment, the chemical reactions of Zr and Hf were found to be fast in the TIOA/HCl extraction when the TIOA concentrations were above 30 wt%. Based on these results, we determined the suitable experimental conditions for online experiment. By using the developed apparatus, we successfully performed an online solid-liquid extraction experiment with the AVF cyclotron at RIKEN. The  $R$  values of Zr and Hf obtained with shaking times of 10–120 s were approximately constant and the average value at each HCl concentration was consistent with the  $K_d$  values obtained in the offline experiment in 7–11 M HCl. This result suggests that the chemical reactions in the present extraction reach equilibrium within 10 s and the  $K_d$  values of Zr and Hf were obtained in the online experiment. In the extraction using AMBER with shaking for 10 s, the solution sample for measurement was prepared about 35 s from the start of the dissolution of the products transported by the gas-jet system. The present extraction experiment would be applicable to the 68-s <sup>261</sup>Rf experiment.

### Reference

- 1) M. Schädel and D. Shaughnessy: *The Chemistry of Superheavy Elements*, 2nd ed. (Springer, Heidelberg, 2014).

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