

Solvent extraction behavior of Zr and Hf with 2-furoyltrifluoroacetone as model experiments for rutherfordium (element 104)

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Our group has been investigating the solvent extraction behavior of zirconium (Zr) and hafnium (Hf) with chelating agents such as 2-thenoyltrifluoroacetone (HTTA) and di-2-ethylhexylphosphoric acid (HDEHP) as model experiments for the heavier homolog, rutherfordium (Rf).^{1–3} In our previous study, we extracted Zr and Hf (extractant: HDEHP) with a rapid extraction apparatus by using a flow injection analysis (FIA) technique.³ Although the distribution ratio (D) of Zr and Hf increased more rapidly than those in the batch method, it took more than several minutes to reach the extraction equilibrium of Zr and Hf with the apparatus. An experiment with HTTA using the apparatus showed almost the same result; therefore, we planned to employ another chelate extractant having faster extraction kinetics for the short-lived Rf experiment. In this study, we used 2-furoyltrifluoroacetone (HFTA), which is a β -diketone like HTTA, for extraction experiments of Zr and Hf. This extractant has lower distribution constant (K_d) and acid dissociation constant (pK_a) values than HTTA.⁴ Because lower K_d and pK_a values lead to a higher concentration of the coordinating anion, FTA^- , in the aqueous phase, HFTA may show faster kinetics than HTTA. The extraction kinetics and mechanism for Zr and Hf with HFTA were investigated by the batch method. In addition, an extraction experiment using the FIA apparatus was conducted.

Long-lived radionuclides of ^{88}Zr ($T_{1/2} = 83.4$ d) and ^{175}Hf ($T_{1/2} = 70$ d) were produced in the $^{89}\text{Y}(d, 3n)^{88}\text{Zr}$ and $^{nat}\text{Lu}(d, xn)^{175}\text{Hf}$ reactions, respectively, by using the RIKEN K70 AVF cyclotron. These produced radiotracers were separated and purified by an anion exchange and a solvent extraction method. In the batch extraction experiment, 600 μL of 1 M HNO_3 solution containing ^{88}Zr and ^{175}Hf tracers was mixed with the same volume of 0.008–0.021 M HFTA/toluene solution. The mixture was mechanically shaken at 25°C and then centrifuged. After the separation of each phase, the samples of aqueous and organic phases were subjected to γ -ray spectrometry using a Ge detector. In the FIA experiment, aqueous (1 M HNO_3) and organic (0.018 M HFTA/toluene) phases were pumped with syringe pumps at the same flow rate of 30–100 $\mu\text{L}/\text{min}$. These two phases were mixed in an extraction coil (Teflon capillary) with an inner diameter of 0.17 mm and a length of 1–10 m. The aqueous and organic solutions eluting from the extraction coil were collected in a sample tube. After centrifugation, both phases were

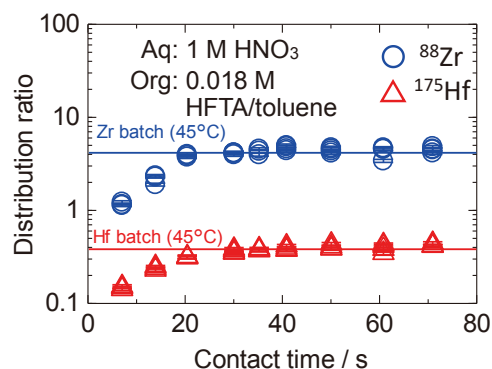


Fig. 1. Dependence of the D values of Zr and Hf on contact time in the extraction coil (inner diameter: 0.017 mm) of the FIA apparatus at 45°C.

separated by pipetting into other sample tubes. The samples were then subjected to γ -ray spectrometry using a Ge detector. The D values of Zr and Hf were calculated from the following equation:

$$D = A_o/A_a,$$

where A denotes the radioactivity of either ^{88}Zr or ^{175}Hf and the subscripts a and o refer to the aqueous and organic phase, respectively.

In the batch extraction experiment, the extraction equilibrium of Zr and Hf with HFTA was attained in 3–4 min, showing faster kinetics than HTTA which required approximately 1 h for attaining equilibrium.⁵ The plots of $\log D$ of Zr and Hf against $\log[\text{HFTA}]$ showed linear relations with slopes of approximately 4 for both Zr and Hf. The slope indicates the number of HFTA molecules involved in the extraction reaction, and therefore, the extracted species would be $\text{Zr}(\text{FTA})_4$ and $\text{Hf}(\text{FTA})_4$.

Figure 1 shows the dependence of the D values of Zr and Hf on contact time in the extraction coil of the FIA apparatus. The experiment in Fig. 1 was conducted at an increased temperature (45°C) because the acceleration of the extraction reaction by using the FIA apparatus at 25°C was insufficient. The result showed that the extraction equilibrium of Zr and Hf with HFTA using the FIA apparatus was attained in 30–40 s. This is a promising result for the extraction experiment of the short-lived ^{261}Rf ($T_{1/2} = 68$ s) isotope. In the future, an on-line extraction experiment of Zr and Hf with the FIA apparatus coupled to a gas-jet transport system will be conducted.

References

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