Liquid-liquid extraction of zirconium and hafnium with 2-thenoyltrifluoroacetone for chemical studies of element 104, rutherfordium

A. Tanaka,1 K. Ooe,1 H. Kikunaga,2 M. Murakami,1,5 Y. Komori,1 H. Haba,2 S. Goto,1 and H. Kudo*4

Chemical studies of element 104, rutherfordium (Rf), in aqueous solutions have been carried out mainly using column chromatography.1,2) In these column chromatographic experiments, inorganic ligands such as fluoride and chloride ions were used, and inorganic complex formation of Rf was investigated. However, little has been reported regarding the complex formation of Rf with organic ligands such as a chelating agent. In the present study, liquid-liquid extraction of zirconium (Zr) and hafnium (Hf), which are lighter homologs of Rf, was performed to find suitable experimental conditions for complexation studies of Rf with organic ligands. 2-thenoyltrifluoroacetone (TTA), which is often used as a chelate extractant in analytical chemistry and separation techniques, was applied in this experiment.

Radioisotopes of 88Zr (T1/2 = 83.4 d) and 175Hf (T1/2 = 70 d) were produced in the 58Y(d, 3n) and 172Lu(d, 2n) reactions, respectively, using the RIKEN K70 AVF cyclotron. Metal foils of Y (150 µm thickness) and Lu (100 µm thickness) were used as targets. Incident energy of the deuterium beam was 24 MeV. The produced radioisotopes were chemically separated from the target materials through the anion exchange method and stored in 3 M HNO3 solution. Aqueous solution of 3 M HNO3 (600 µL) containing 88Zr and 175Hf radioisotopes was mixed with an equal volume of TTA in toluene solution in a polypropylene tube, and the mixture was mechanically shaken for 15 hours at 25 °C. After equilibration, the mixture was centrifuged for 30 seconds, and a 420 µL aliquot from each phase was separately transferred into a polypropylene tube. The radioactivity of each phase was measured by a Ge detector, and the distribution ratio (D) was calculated by the following equation:

\[
D = A_o / A_i, \tag{1}
\]

where \(A_o\) and \(A_i\) denote the radioactivities of either of 88Zr and 175Hf in aqueous and organic phases, respectively.

Figure 1 shows the dependence of D values of 88Zr and 175Hf from 3 M HNO3 on the TTA concentration in toluene. The D value of 88Zr was approximately 10 times that of 175Hf. It is well-known that the chemical behavior of Zr is remarkably similar to that of Hf and mutual separation between these two elements is very difficult. Therefore, the present result shows that TTA has extraction selectivity for Zr, and it is very interesting to investigate extraction behavior of Rf with TTA.

In the extraction of tetravalent metal ions (MIV) with TTA, the extraction reaction is usually described by the following equation:

\[
M^{4+} + 4\text{HTTA}_{\text{aq}} \rightleftharpoons M(\text{TTA})_{4\text{aq}} + 4\text{H}^+. \quad (2)
\]

From eq. (2), it is expected that the log D vs. log [TTA] plot shows linear relation with the slope of 4 and the value of the slope indicates the number of TTA molecules involved in the extraction reaction. A least-squares fit to the present data showed a straight line with a slope of 3.8 for 88Zr and 3.9 for 175Hf. Therefore, this result suggests that the main extracted species of Zr and Hf would be Zr(IIIA4) and Hf(IIIA4) from 3 M HNO3. The slope value of the log D vs. log [TTA] plot was closer to 3 for both Zr and Hf, in not greater than 2 M HNO3. This might be caused by the effect of hydrolysis of Zr and Hf: formation of ZrOH2+3 and HfOH3+. Thus, an experimental condition suitable for extraction of Rf(IIIA4) is determined to be 3 M HNO3 solution.

In the future, liquid-liquid extraction experiments of Zr and Hf with a rapid extraction apparatus using flow injection analysis (FIA) technique5 will be performed for the Rf experiment.

Fig. 1. Dependence of distribution ratios of 88Zr and 175Hf from 3 M HNO3 on TTA concentration in toluene.

References