

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,*3} Y. Komori,^{*3} H. Haba,^{*3} 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.

Radiotracers of ⁸⁸Zr ($T_{1/2} = 83.4$ d) and ¹⁷⁵Hf ($T_{1/2} = 70$ d) were produced in the ⁸⁹Y(d, 3n) and ¹⁷⁵Lu(d, 2n) reactions, respectively, using the RIKEN K70 AVF cyclotron. Metal foils of Y (150 μ m thickness) and Lu (100 μ m thickness) were used as targets. Incident energy of the deuteron beam was 24 MeV. The produced radiotracers 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 μ L) containing ⁸⁸Zr and ¹⁷⁵Hf radiotracers 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 μ L 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:

$$D = A_o/A_a, \quad (1)$$

where A_a and A_o 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 (M^{4+}) with TTA, the extraction reaction is usually described by the following equation:



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 $Zr(TTA)_4$ and $Hf(TTA)_4$ 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 $ZrOH^{3+}$ and $HfOH^{3+}$. Thus, an experimental condition suitable for extraction of Rf(TTA)₄ 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) technique³⁾ will be performed for the Rf experiment.

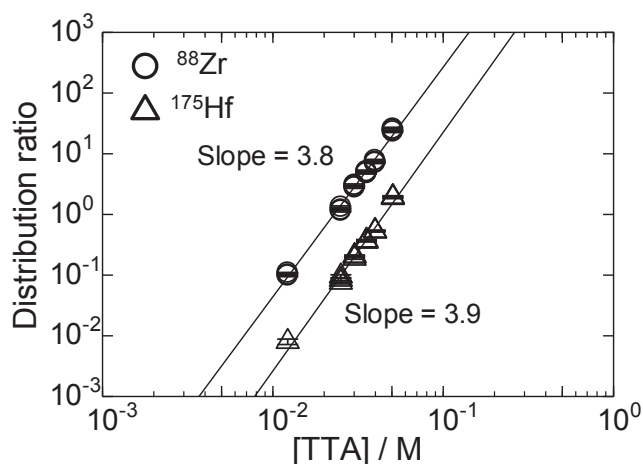


Fig. 1. Dependence of distribution ratios of ⁸⁸Zr and ¹⁷⁵Hf from 3 M HNO₃ on TTA concentration in toluene.

References

- 1) H. Haba et al.: J. Nucl. Radiochem. Sci. **3**, 143 (2002).
- 2) H. Haba et al.: J. Am. Chem. Soc. **126**, 5219 (2004).
- 3) T. Koyama et al.: 5th Asia-Pacific Symposium on Radiochemistry'13 (APSORC 13), "Development of a rapid solvent extraction technique with flow injection analysis for superheavy element chemistry" 25-NCP-05.

*1 Institute of Science and Technology, Niigata University

*2 Research Center for Electron Photon Science, Tohoku University

*3 RIKEN Nishina Center

*4 Faculty of Science, Niigata University