

Co-precipitation behaviour of single atoms of rutherfordium in basic solutions[†]

Y. Kasamatsu,^{*1} K. Toyomura,^{*1} H. Haba,^{*2} T. Yokokita,^{*1} Y. Shigekawa,^{*1} A. Kino,^{*1} Y. Yasuda,^{*1} Y. Komori,^{*1} J. Kanaya,^{*2} M. Huang,^{*2} M. Murakami,^{*2} H. Kikunaga,^{*3} E. Watanabe,^{*1} T. Yoshimura,^{*4} K. Morita,^{*2} T. Mitsugashira,^{*5} K. Takamiya,^{*6} T. Ohtsuki,^{*6} and A. Shinohara^{*1}

In heavy atoms, the relativistic effects are strong, which would result in deviations of their chemical behaviours from those expected by simple extrapolation of the characteristics of the lighter homologues.¹⁾ It is very challenging to perform chemical experiments on the heavy elements, because their nuclides are produced with extremely low production rates and tend to decay rapidly; only one atom can be usually treated at a time. Thus, rapid transportation system of the nuclear reaction products and automated chemical separation apparatuses specialized for such elements are needed. Chemical studies of heavy elements have mainly been conducted by two-phase partition methods. In particular, the formation of fluoride, chloride, nitrate, and sulfide complexes of Rf has been investigated in solution chemistry.¹⁾

We focused on a precipitation approach to study heavy element chemistry. In a previous study, a co-precipitation method with Sm, 10–20 μg , was developed, and the method was applied to various elements using a multiple radiotracer source. The yields of co-precipitate formed in solutions with several concentrations of ammonia (NH_3) and sodium hydroxide (NaOH) were determined for elements from various groups in the periodic table.²⁾ From the consistent co-precipitation yields with their properties in hydroxide precipitation and ammine complexation, it was concluded that the hydroxide and ammine complexation of heavy elements can be qualitatively investigated on the basis of their co-precipitation behaviours with Sm. Based on these findings, the purpose of the present study is to investigate the co-precipitation behaviour of Rf with samarium hydroxide and get an insight into the properties of its hydroxide and ammine complex formation.

^{261}Rf was produced by the $^{248}\text{Cm}(^{18}\text{O}, 5n)$ reaction using the AVF cyclotron at RIKEN RIBF. ^{169}Hf was simultaneously produced to check the status of the online filtration apparatuses²⁾ by monitoring Hf behaviour. After dissolution of the transported nuclear reaction products in the dissolution apparatus, a basic

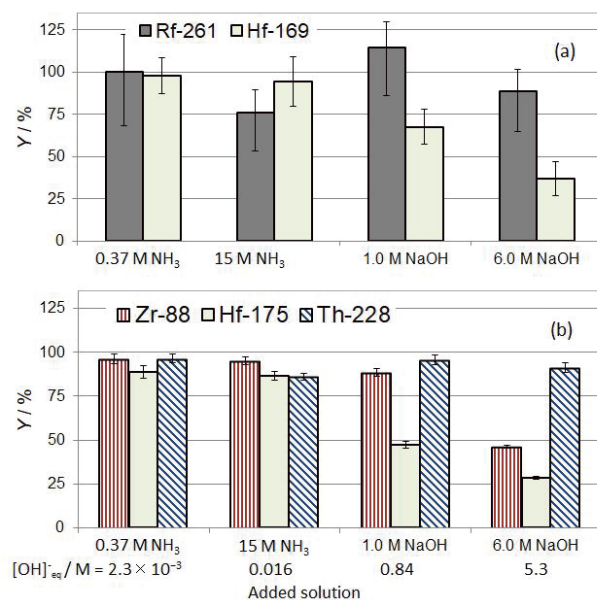


Fig. 1. The Y values of ^{261}Rf and ^{169}Hf (a) and those of ^{88}Zr , ^{175}Hf , and ^{228}Th (b).

solution (aq. NH_3 or NaOH) was added to produce the hydroxide precipitate. The co-precipitation yields, Y , were determined from the radioactivity of precipitate and total radioactivity.

The co-precipitation yields evaluated for ^{261}Rf and ^{169}Hf are shown in Fig. 1(a). The yields of ^{88}Zr , ^{175}Hf , and ^{228}Th previously obtained²⁾ are also shown in Fig. 1(b). The co-precipitation yields of ^{169}Hf determined in this study typically agreed with previously obtained values for ^{175}Hf , suggesting that the online experiment on ^{261}Rf was successful. In dilute OH^- solutions (aq. NH_3), the Y values of all the elements were high (76–100%), suggesting predominant precipitation. This indicates that the chemical properties of Rf allow for the formation of a hydroxide precipitate; namely, we extrapolate that Rf would form a hydroxide precipitate if in macro amounts. This behaviour is typical of the hydroxides of group 4 elements, precipitation as $\text{M}(\text{OH})_4$ (M^{4+} = metal ion of group 4 element). In addition, the yield of Rf in concentrated NH_3 solution was not markedly lower than the yields in other concentrations, suggesting that Rf does not strongly coordinate with NH_3 molecules, similar to its homologues. In concentrated OH^- solutions (NaOH), the Y values of Zr and Hf decreased with increasing

[†] Condensed from the article in Nature Chem. **13**, 226 (2021)

^{*1} Graduate School of Science, Osaka University

^{*2} RIKEN Nishina Center

^{*3} Research Center for Electron Photon Science, Tohoku University

^{*4} Radioisotope Research Center, Osaka University

^{*5} Institute for Material Research, Tohoku University

^{*6} Institute for Integrated Radiation and Nuclear Science, Kyoto University

OH^- concentration due to the formation of hydroxide complex ions such as $[\text{M}(\text{OH})_5]^-$ and $[\text{M}(\text{OH})_6]^{2-}$, whereas the yields of Rf and Th remained high. Indeed, the solubility products of $[\text{M}(\text{OH})_5]^-$ ($\log K_{s5} = [\text{M}(\text{OH})_5]^- / [\text{OH}]^-$) for Zr, Hf, and Th are -3.6 , -3.2 , and -5.8 , respectively, and this sequence is consistent with their Y values obtained with 6.0 M NaOH. We can deduce that $\log K_{s5}$ of Rf would be lower than those of Zr and Hf. It suggests a weaker tendency of Rf toward hydroxide complexation than those of Zr and Hf.

References

- 1) M. Schädel, Phil. Trans. R. Soc. A **373**, 20140191 (2015).
- 2) Y. Kasamatsu, J. Nucl. Radiochem. Sci. **18**, 24 (2018).