

Extraction behavior of rutherfordium as a cationic fluoride complex with a 2-thenoyltrifluoroacetone chelate extractant from HF/HNO₃ acidic solutions

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Recently, we developed a reversed-phase-chromatography technique with 2-thenoyltrifluoroacetone (TTA) as a chelate extractant to clarify chemical properties of a cationic fluoride complex of a superheavy element, rutherfordium (Rf). The resin containing a TTA *n*-octanol solution has been prepared for that purpose [1]. In this study, we have investigated chromatographic behavior of Rf with this technique in various HF/HNO₃ solutions.

Both of batch and on-line experiments were performed with Zr and Hf to determine experimental conditions suitable for Rf. For batch experiments, non-carrier tracers of Zr and Hf were used to examine distribution coefficient (K_d) values. As for on-line experiments, reversed-phase chromatography of the short-lived nuclides ^{89m}Zr and ¹⁶⁹Hf was performed with a micro-column in the same way as Rf experiment to obtain elution curves and percent adsorption values (%ads) as defined below.

In Rf experiments, nuclides of ²⁶¹Rf with a half-life of 68 s and ¹⁶⁹Hf were simultaneously produced in the ²⁴⁸Cm(¹⁸O, 5n)²⁶¹Rf and ^{nat}Gd(¹⁸O, xn)¹⁶⁹Hf reactions, respectively, with 109.3 MeV ¹⁸O beam at the RIKEN K70 AVF cyclotron. The reaction products were rapidly transported with a KCl/He gas-jet system to the chemistry laboratory and were deposited on the collection site of the on-line Automated Rapid Chemistry-Apparatus (ARCA) for chromatography experiments. The products were dissolved in HF/0.01 M HNO₃ solutions and were fed onto the micro-column (1.6 mmφ×7 mm) of ARCA at a flow rate of 0.1 mL/min. The resin containing 25 wt.% of TTA was filled in the column. The effluent from the column was collected on a Ta-disk as fraction 1. The remaining products in the column were then stripped with a 0.1 M HF/0.1 M HNO₃ solution and were collected on another Ta disk as fraction 2. These disks were then separately evaporated to dryness with a halogen heat lamp and heated He gas. The samples were assayed with a rapid α/SF detection system for studying the aqueous chemistry of superheavy elements at RIKEN.

The K_d values of Zr and Hf in the batch and on-line experiments were determined and compared in the wide range of F⁻ equilibrium concentration ($[F^-]_{eq}$) as shown in Fig. 1. The values of both Zr and Hf show sudden decreases

in the range of $[F^-]_{eq} > 4 \times 10^{-5}$ M in both the batch and on-line experiments. This indicates that fluoride complexation of Zr and Hf consecutively proceeds to form neutral or anionic species from cationic ones with the increase in $[F^-]_{eq}$. Therefore, differences in the formation of fluoride species between Rf and its homologues can be observed in these $[F^-]_{eq}$.

As a preliminary result, 160 α events including 21 time-correlated α-particle pairs (8.00-8.40 MeV) from ²⁶¹Rf and its daughter nuclide ²⁵⁷No were observed in 1001 cycles of the chromatography experiment. The %ads values of Rf were evaluated by using the following equation:

$$\%ads = \frac{100 \times Fr2}{Fr1 + Fr2'}$$

where Fr1 and Fr2 are the radioactivities observed in the fractions 1 and 2, respectively. The %ads values of Rf were constant at around 60% in the $[F^-]_{eq}$ range up to 5×10^{-4} M and then steeply decreased at $[F^-]_{eq} = 9 \times 10^{-4}$ M while those of Hf decreased significantly from 100% to a few percent around $[F^-]_{eq} = 1 \times 10^{-4}$ M. The latter data reproduced the results for Hf for the on-line experiments shown in Fig. 1. This suggests that the cationic fluoride complexes of Rf exist more stably than those of Hf at $[F^-]_{eq} > 1 \times 10^{-4}$ M.

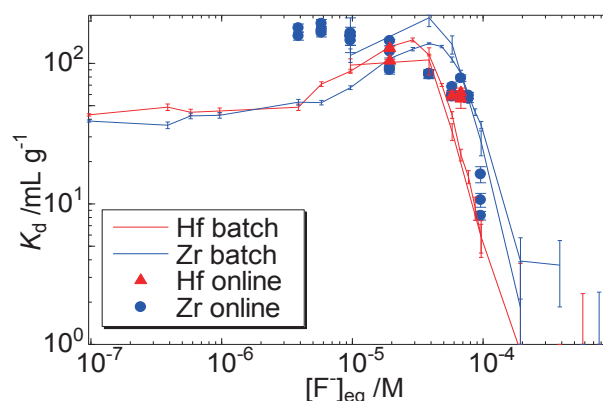


Fig. 1 Distribution coefficients, K_d , of Zr and Hf plotted as a function of $[F^-]_{eq}$ assayed by batch (solid lines) and on-line (closed symbols) experiments.

Reference

- 1) M. Araki, T. Nanri., Y. Takeda, M. Nishio, M. Nishikawa, Y. Kasamatsu, Y. Ezaki, Y. Kudou, H. Haba, and A. Yokoyama: RIKEN Accel. Prog. Rep. **43**, 271 (2010).

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