

Solvent extraction of Zr and Hf from HCl by Aliquat 336 using a flow-type extraction apparatus toward online chemical studies of element 104, rutherfordium[†]

Y. Kasamatsu,^{*1} N. Kondo,^{*1} K. Nakamura,^{*1} Y. Kuboki,^{*2,*3} H. Ninomiya,^{*1} Y. Shigekawa,^{*1} E. Watanabe,^{*1} Y. Yasuda,^{*1} K. Toyomura,^{*1} M. Nagase,^{*1} T. Yokokita,^{*1,*3} Y. Komori,^{*1,*3} H. Haba,^{*3} T. Yoshimura,^{*4} H. Itabashi,^{*5} and A. Shinohara^{*1}

Chemical studies of the transactinide (superheavy) elements with atomic numbers $Z \geq 104$ are imperative for systematic understanding of all the elements in the periodic table. In particular, the influence of relativistic effects on orbital electrons of superheavy elements could cause their unique chemical properties. For chemical experiments on superheavy elements which can be produced only by nuclear reactions, repetitive or flow-type rapid chemistry apparatus connected with a gas-jet system which rapidly transports the nuclear reaction products from the accelerator room to the chemistry laboratory (“online” experiment) is required. The chemical properties of heavy elements are discussed on the basis of comparison of their behaviors with those of the corresponding homologues.

We plan to apply a flow-type solvent extraction apparatus, having a chemical reaction unit which shortens the time required for equilibrium, to transactinide chemistry in order to obtain equilibrium D values for short-lived transactinide elements. Thus, we developed such a solvent extraction apparatus for the online transactinide chemistry and determined the conditions to rapidly obtain equilibrium D values for Zr and Hf toward the extraction of ²⁶¹Rf. In addition, we carried out the online extraction experiment as a model experiment for Rf using the developed apparatus.

First of all, we carried out the solvent extraction of Zr and Hf by the conventional shaking (batch) method to obtain the equilibrium D values using ⁸⁸Zr and ¹⁷⁵Hf tracers. The D values were determined from the concentration ratio of the tracers between organic and aqueous solutions.

Then, we developed an online flow-type solvent extraction apparatus: flow Injection Solvent Extraction apparatus for heavy elements (ISE) for rapid solvent extraction and phase separation toward the extraction of 68-s ²⁶¹Rf. The developed extraction apparatus is equipped with a reactor tube filled with PTFE chips to mix aqueous and organic solutions thoroughly (extraction unit; EU).¹⁾ By this unit, the diffusion length of metal complexes between the aqueous and organic solutions decreases, which is expected to aid the rapid achievement of equilibrium in the extraction reactions.

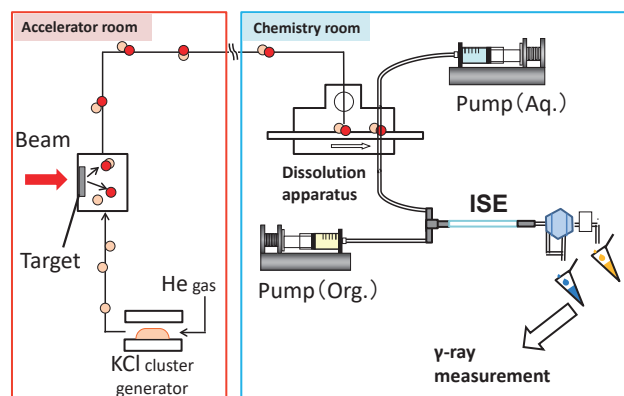


Fig. 1. Schematic diagram of online solvent extraction experiment for heavy elements.

For rapid phase separation between aqueous and organic solutions, a flow-type phase separation unit (PSU) using a PTFE membrane filter (pore size: $0.8 \mu\text{m}$) is set downstream of the EU.²⁾ The online extraction experiment employing the ISE was carried out using the ^{89g,m}Zr and ¹⁷³Hf nuclides produced at the AVF cyclotron in RCNP as shown schematically in Fig. 1.

The D values obtained with ISE in 7.8 M HCl are clearly lower than the equilibrium D values, suggesting that the equilibrium D values cannot be obtained in 7 M HCl. When the extraction was carried out in 9.3 and 11.2 M HCl using a 30-cm-long EU packed with 250–500 μm PTFE chips, the D values obtained with ISE are all equivalent with the equilibrium values, indicating that the extraction reactions rapidly reach equilibrium state under these conditions. It was also found that the elution of almost all the isotopes from PSU was accomplished within 55 s. Based on this time information, the time taken for extraction and evaporation for α measurements in Rf experiment can be estimated to be <2 min, which is sufficiently fast in comparison with the previous experiment of ²⁶¹Rf (~ 100 s).

A linear relationship was observed between the logarithm of D value and the logarithm of Aliquat 336 concentration for both Zr and Hf, suggesting that the extracted chloride complex determined from the slopes (net charge) could be $[\text{MCl}_6]^{2-}$. Similar discussion can be made for Rf, which will help to understand the chloride complexation of Rf.

References

- 1) H. Itabashi, Y. Mesuda, *J. Flow Inj. Anal.* **20**, 193 (2003).
- 2) S. Motomizu, M. Oshima, *Analyst* **112**, 295 (1987).

[†] Condensed from the article in *Solvent Extr. Ion Exch.* **38**, 318 (2020)

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

^{*2} National Institute of Technology, Ibaraki College

^{*3} RIKEN Nishina Center

^{*4} Radioisotope Research Center, Osaka University

^{*5} Faculty of Engineering, Gunma University