Development of new methods for aqueous chemistry on element 104, rutherfordium: Batch-type solid-liquid extraction and coprecipitation

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Rapid chemical experiment targeting single atoms combined with identification via alpha-particle measurement is required for superheavy element chemistry. Herein, successful development of two types of experimental methods of superheavy element chemistry: solid-liquid extraction and precipitation, is presented. The chemical behaviors of Zr and Hf (homologues of element 104, Rf), and Th (pseudo homologue) were investigated using carrier-free RI tracers. Through these studies, rapid chemical reaction systems were found and the comparative data to discuss the chemical properties of Rf were obtained. In addition, automated chemistry apparatuses for extraction and precipitation were developed and their performance was evaluated using the short-lived isotopes of Zr and Hf, which were transported online from the nuclear reaction chamber in the accelerator room by a He/KCl gas-jet system. From those results, the newly developed methods were both found to be applicable to [261]Rf experiments, and suitable experimental conditions to study the chloride complexation (solid-liquid extraction) and hydroxide complexation (coprecipitation) of Rf were determined.

1. Introduction

The elements with the atomic numbers $Z \geq 104$; namely, beyond actinide elements, are called superheavy elements (SHEs) or transactinide elements. The SHEs are relatively new elements for us and major part of their chemical properties is unknown. Because the influence of relativistic effects on electron orbital shells becomes significant for heavy elements, the chemical properties of the SHEs are expected to deviate from the periodicity of the lighter homologues in the periodic table.[1,2] Thus, it is important and interesting to clarify their chemical properties. Some kinds of chemical studies on the SHEs have been conducted since 1970's.[1,2] Because of the extremely low production rates and short half-lives (within a few min) of these heavy nuclides, chemical evaluations of the SHEs must be conducted on a one-atom-at-a-time basis,[3] and must be rapidly completed. These difficulties limit the variety of chemical investigation of SHEs. Indeed, simple chemical behaviors such as adsorption and extraction have been mainly investigated. In these experiments, the chemical separations were repeated hundreds or thousands of times under identical conditions to observe the chemical behavior of SHEs existing as single atoms. This approach requires two types of apparatuses: an online system having the capability for rapid transport of nuclear reaction products from the reaction chamber (in the accelerator room) to the chemistry laboratory, and a rapid chemistry apparatus equipped with a radiation detection system.[1,2] Additionally, for unambiguous identification of superheavy elements (single atoms), it is necessary to measure the energies and lifetimes of α or sometimes spontaneous fission decays. Thus, it is difficult to clarify various chemical properties of SHEs. In this paper, two types of newly developed experimental methods to study chemical properties of SHEs are presented; one is the method to study time dependence of the solid-liquid extraction behavior (observation of

the equilibrium of the chemical reactions) for SHEs,[4] and the other is that to study coprecipitation behaviors of SHEs with Sm hydroxide.[5,6]

In solution chemistry for SHEs, extraction behaviors to solid phase or organic solution have been mainly investigated on the lightest transactinide elements, rutherfordium (Rf, $Z = 104$) and dubnium (Db, $Z = 105$).[1,2,7–20] From the viewpoint of the similarity of the extraction behavior of SHE to its homologues, chemical properties of the SHE were discussed. On the other hand, equilibrium of the chemical reactions has not been confirmed for the short-lived SHEs, although this confirmation is important to investigate the detailed chemical properties of these elements such as complex formation. In the fluoride complexation studies,[11,13,15–17,19] the equilibrium distribution ratios were obtained for the lighter homologues in online experiments, and an interesting result for Rf was found; the K_d values of Rf obtained in the ion-exchange chromatography in hydrofluoric acid (HF) and HF/HNO$_3$ mixture solutions were clearly different from those of Zr and Hf.[11,13,15,19] Investigation of the complex formation of Rf with other ligands is very important for an understanding of its chemical properties. However, sufficiently fast chemical reaction systems for the fast chemical apparatus such as ARCA (AIDA)[21,22] seem to be very limited. Thus, a new apparatus allowing a longer contact time between the two phases, AMBER, was developed,[4] which is introduced herein. With this chemical apparatus, the distribution behavior of Rf in equilibrium would be observed to allow a discussion of the complex formation of Rf with various ligands. Furthermore, the time dependence of the distribution behavior for the SHEs is expected to be observed for the first time.

On the other hand, a novel method to study chemical properties of SHEs is desirable to expand the research region of SHE chemistry. Recently, the coprecipitation method using Sm hydroxide was developed for SHE chemistry.[5,6] It was suggested that the formation of hydroxide and ammine complexes of various elements would be investigated through the coprecipitation yields with Sm hydroxide.[5]

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To establish the experimental methods for SHE chemistry, three steps of preliminary experiments using homologue samples are needed. First, the chemical behaviors of homologues are investigated by conventional method using carrier-free RI tracers. From these experiments, fast chemical reaction system is searched and suitable experimental conditions to study objective chemical properties of the elements (homologues and SHEs) are determined. The distribution ratios in two phases at equilibrium are also obtained in this experiment by using long-lived RI tracers of the homologues. In the next step, the rapid chemistry apparatus for "online" use is developed and its performance is evaluated using RI tracers. Finally, "online" chemical experiment of homologues is performed using the developed apparatus, accelerator, and the gas-jet transport system of nuclear reaction products. In the "online" experiment, consistent data with those obtained by conventional method must be obtained. Through those results, suitable conditions for online experiment of SHE are determined.

2. Batch-type solid-liquid extraction

As a preliminary experiment of SHE chemistry, various solvent extraction and ion-exchange (solid-liquid extraction) experiments with the homologues of objective SHEs have been performed.[23–32] Some works also tried to develop the new chemistry apparatuses.[24,25] Solid-liquid extraction experiment of Zr, Hf, and Th in the TIOA/HCl system is described below, which was applied to the online extraction experiment using AMBER.[4]

2.1. Solid-liquid extraction for Zr, Hf, and Th. In the solid-liquid extraction experiment by conventional batch method, the 18–57 wt% TIOA resin and 6.2–10.9 M HCl containing the ^{88}Zr ($T_{1/2}$ = 83.4 d), ^{175}Hf ($T_{1/2}$ = 70.0 d), and ^{234}Th ($T_{1/2}$ = 24.1 d) tracer solution were used. These were mixed in a polypropylene (PP) tube and the mixture was shaken for 2–120 min at 25 ± 1 °C with a vortex mixer. Then, the samples were subjected to γ-ray spectroscopy using a Ge semiconductor detector. In all solid-liquid extraction experiments, control experiments without the resin were performed to determine the radioactivity of the control solution. The R values were determined from the following eq 1,

$$R = \frac{A_r V_s}{A_s w_r} = \frac{(A_c - A_s)V_s}{A_s w_r} \qquad (1)$$

where A_r and A_s are the radioactivities on the resin and in the solution, respectively, V_s is the volume (mL) of the solution, and w_r is the mass (g) of the dry resin. A_c denotes the radioactivity of the control solution. The R value in equilibrium is described as the K_d value in this solid-liquid extraction experiment.

As a result, the K_d values were determined from the dependences of the R values on the shaking time. The chemical reactions were found to be fast in the TIOA/HCl extraction when using TIOA resins with weight concentrations above 30 wt%.[4] The dependences of the K_d values of Zr, Hf, and Th on the HCl concentration are shown in Figure 1 together with the results obtained in the online experiment. The results indicate that the abundances of the anionic chloride complexes of Zr and Hf increase with higher HCl concentrations, and that these complexes assemble with protonated TIOA ions as $(R_3NH)_2[MCl_6]$ to be extracted into the solid phase,[26] while the species of the pseudo homologue Th dominantly exist in HCl solutions. Formation of the anionic chloride complexes of the group 4 elements was able to be investigated based on the solid-liquid extraction behaviors in the TIOA/HCl system. As the solid (organic) phase, 30–60 wt% TIOA resin and 7–11 M HCl as the aqueous phase were proposed for the Rf experi-
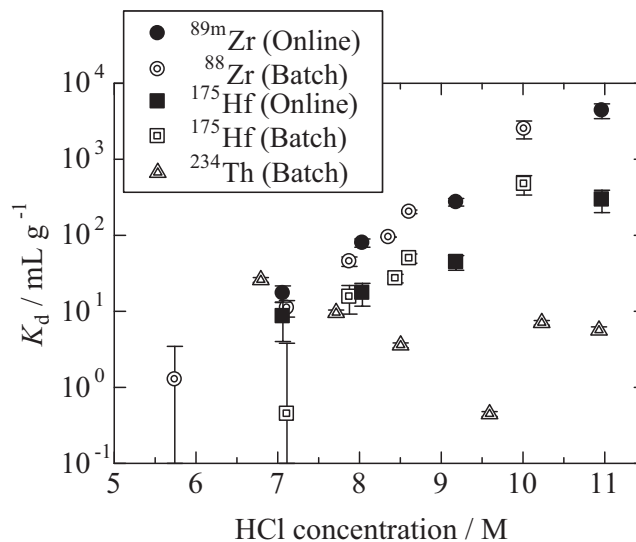

Figure 1. The K_d values of Zr (circles) and Hf (squares) obtained by online experiment with AMBER as a function of HCl concentration at 31 wt% of the TIOA resin and those obtained in offline batch experiments with 10-min shaking (double circles and squares) together with the K_d values of Th (double triangles).[4]

ment.

2.2. Development of the solid-liquid extraction apparatus. An AutoMated Batch-type solid-liquid Extraction apparatus for Repetitive experiments of transactinides (AMBER) was developed, and a schematic diagram of AMBER is shown in Figure 2.[4] Automated Slider-type dissOlution equipment (ASO) was based on the dissolution section of ARCA[21,22]. Compressor supplies compressed air through a buffer tank to air cylinders and chemical reaction containers. A compact-DAQ device and LabVIEW software from National Instruments were used for operations of the valves and air cylinders, and all the operations were controlled with fixed time intervals in online extraction experiments. Polytetrafluoroethylene (PTFE) tubes were used in all the passage ways for solution. Because the PTFE tubes used downstream of the dissolution apparatus had an internal diameter of 0.17 mm, the dead volume in these tubes was negligibly small. Chemical reaction containers, in which the solution sample and resin were mixed to extract the reaction products to the resin phase, were made of polychlorotetrafluoroethylene (PCTFE), and the inner volume of the container was about 0.6 mL. At the bottom of the container, a PTFE filter with a pore size of 5 or 10 μm was set to push out only the solution with compressed air after the extraction. By this method, separation between the solution and resin phases was accomplished within 10 s automatically.

2.3. Online solid-liquid extraction for Zr and Hf. In the online experiment, the ^{89g,m}Zr ($T_{1/2}$ = 3.27 d, 4.18 min) and ^{175}Hf nuclides were produced in the ^{89}Y(p, n)^{89g,m}Zr and ^{175}Lu(p, n)^{175}Hf reactions, respectively, using the K70 AVF cyclotron at RIKEN. The product nuclides were transported by the gas-jet system to the chemistry laboratory and deposited on a collection site of ASO for 60 s. Then, the deposited sample was dissolved in 160–230 μL of 6–11 M HCl. The solution passed through the valves, and then entered the chemical reaction container containing the 31 wt% TIOA resin. After shaking the container with a vortex mixer for 10–120 s, only the liquid phase was pushed out of the container by the compressed air at 0.5 MPa, and was assayed by γ-ray spectroscopy. The residual Zr and Hf species adsorbed on the resin were stripped by washing the resin three times with about 220 μL of a mixture solution of 5.1 M HNO$_3$ and 0.01 M HF. The first two fractions of the stripping solution were analyzed γ-ray spectro-
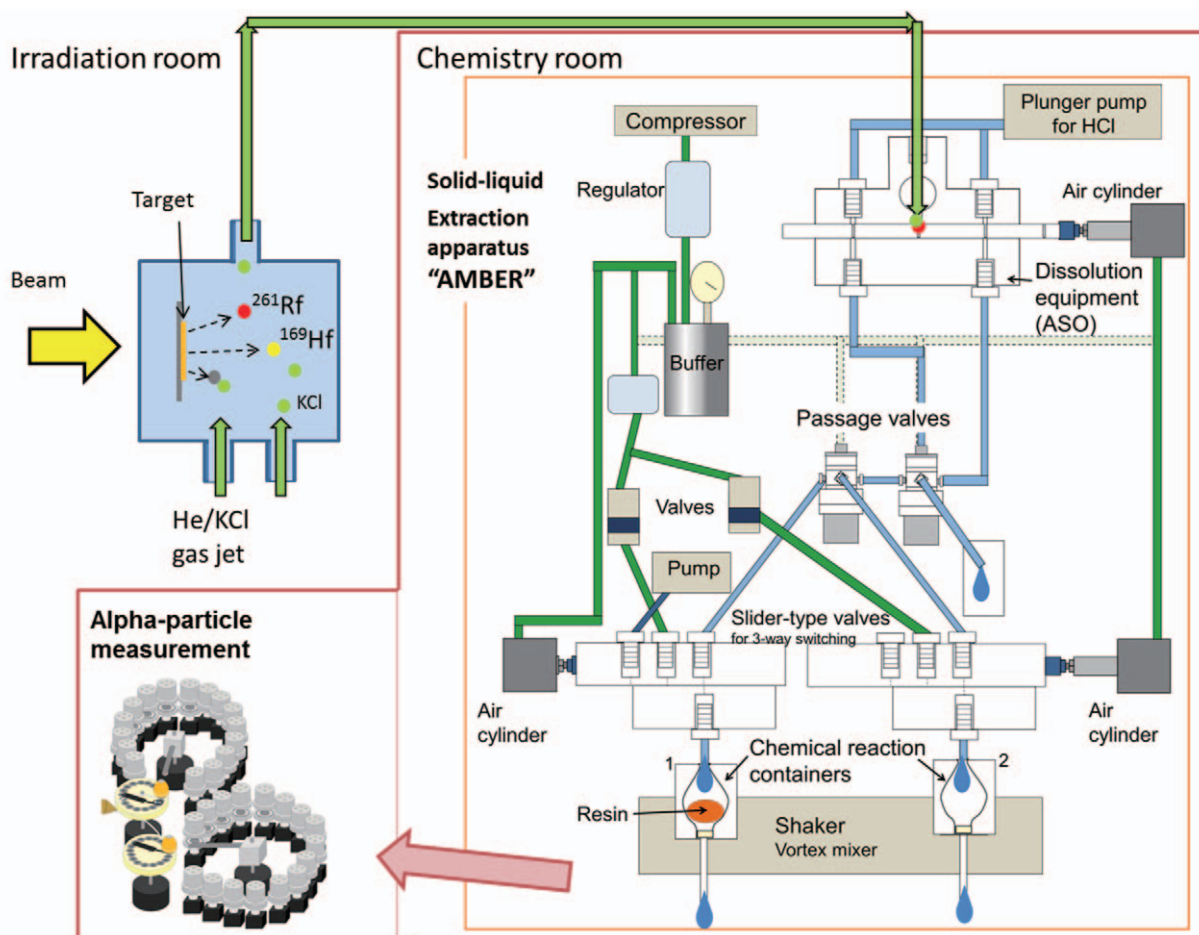
Figure 2. Schematic diagram of the online extraction experiment using the batch-type solid-liquid extraction apparatus AMBER.[4] The nuclear reaction products are continuously transported to the dissolution equipment in AMBER located in chemistry room. Eluate from the dissolution equipment goes through two passage valves and a slider-type valve into a chemical reaction container. After the extraction, only the solution is pushed out from the container.

scopically. A control extraction experiment without the resin was also performed.

The online solid-liquid extraction experiment was successfully performed using AMBER. The *R* values of Zr and Hf obtained with shaking times of 10–120 s were approximately constant; very rapid achievement of the equilibrium of the chemical reactions within 10 s was observed in the present extraction system. The averaged *R* value at each HCl concentration was consistent with the K_d values obtained in the offline batch experiment in 7–11 M HCl as shown in Figure 1. Consequently, it was found that the K_d values of Zr and Hf were able to be obtained in the online rapid experiment with AMBER. In the extraction using AMBER with shaking for 10 s, the solution sample for measurement was prepared about 35 s from the start of the dissolution of the products transported by the gas-jet system. This result suggests that the present extraction experiment is applicable to the 68-s [261]Rf experiment. Indeed, solid-liquid extraction experiment of [261]Rf with AMBER at RIKEN was recently achieved and interesting results were reported.[33]

3. Coprecipitation with Sm hydroxide

The precipitation property is one of the important chemical properties and coprecipitation technique using carrier elements has been widely used for chemical separation and so on in radiochemical researches.[34] In 2009, a simple and rapid coprecipitation method with Sm hydroxide, which facilitates alpha spectrometry with high energy resolution, was established.[35] For the application of this method to SHEs, the

coprecipitation experiments of various elements including homologues of SHEs and development of the suction filtration apparatus for online use were conducted.[5,6]

3.1 Establishment of the experimental method of coprecipitation with Sm hydroxide for SHEs

To establish a new methodology for superheavy element chemistry, the coprecipitation behaviors of 34 elements with Sm hydroxide were investigated using multitracer (multiple radionuclide source).[5] The multitracer was produced by irradiating [nat]Ta targets (2-μm thickness × 30 foils) with [14]N[7+] ions accelerated to 135 MeV per nucleon by the RIKEN ring cyclotron for 40 h. The beam current was ~1.6 electric μA. Various nuclides, namely various elements, with $Z \leq 73$ (Ta) were produced by nuclear spallation reactions. Only the nuclear reaction products recoiling out of the target foils were transported from the nuclear reaction chamber to the chemical laboratory by a He/KCl gas-jet system through a PTFE capillary tube.[36] The transported products were collected on glass filter paper, and were dissolved in 1 mL of 0.01 M HCl.

In a PP beaker, 20 μL of Sm standard solution (1000 mg L^{−1}, 1 M HNO₃) was added into 220 μL of the prepared multitracer solution. The solution was stirred, and then, 2 mL of the basic solution (dilute and concentrated aqueous NH₃, and 0.10, 1.0, 6.0, or 12 M NaOH solutions) was added. The solution was stirred for 10 s or 10 min at room temperature. Then, the solution containing the precipitate was filtrated by suction with a PP membrane filter (eichrom, Resolve® Filters 0.1 μm). Both the precipitate and filtrate were dried using a heater at 100 °C. The precipitate, filtrate, and PP beaker used were subjected to

γ-ray spectrometry with Ge semiconductor detectors. The standard activities of the radiotracers were also determined. The precipitation yields, *Y*, were evaluated from these radioactivities according to eq 2.

$$Y = \frac{A_{ppt}}{A_{std}} \times 100 \qquad (2)$$

In the above equation, A_{ppt} represents the radioactivity of the precipitate and A_{std} represents the standard radioactivity.

The product nuclides were identified based on their characteristic γ-ray energies and corresponding half-lives. In total, 34 elements containing more than 60 nuclides were identified as follows: [24]Na, [42]K, [82m]Rb, [127,129]Cs {group 1}, [28]Mg, [47]Ca, [128,(131)]Ba {group 2}, [44,47,48]Sc, [(86),87g,(m)]Y {group 3}, ([132]La), [132,135]Ce, [145,146,(147)]Eu, [146,147,149]Gd, [149-153,155]Tb, [152,155,157]Dy, ([160m]Ho), [161]Er, [165,(166),167]Tm, [166,(169)]Yb, [169,(170),171,172]Lu {group 3 (lanthanides)}, [(86,87)89]Zr, [170,173]Hf {group 4}, [90]Nb, [176]Ta {group 5}, [93m]Mo {group 6}, [96]Tc {group 7}, [99m,100,(101m)]Rh {group 9}, [65]Zn {group 12}, ^{67}Ga, [110,111]In {group 13}, [71,72]As, [118m,120m]Sb {group 15}, [73]Se, and [119m]Te {group 16}. The nuclides listed in parentheses are ones for which the coprecipitation yields could not be determined. Various elements belonging to various groups in the periodic table (including the homologues of nine SHEs (groups 4–18)) were found in the prepared multitracer sample.

The coprecipitation yields of radionuclides of groups 1–7, 9, 12, 13, 15, 16 elements with Sm hydroxide were determined and shown in Tables 1 and 2 with the stirring time of 10 s and

10 min, respectively. The variation of the yields for the prepared basic solutions qualitatively reflects the ordinary hydroxide precipitation properties (formation of ammine and hydroxide complexes) of the elements in macro amounts. For example, the coprecipitation yields of group 1 elements, Na, K, Rb, and Cs, were lower than 1.5% under all the conditions studied. This result indicates that these elements do not form coprecipitates with Sm hydroxide, which is consistent with the fact that group 1 elements in macro amounts hardly form precipitates in basic aqueous solutions, including NH_3 and NaOH.[37] In addition, the coprecipitation yields of group 3 elements are almost 100% when using aqueous NH_3 and 0.10 and 1.0 M NaOH solutions. These behaviors are consistent with the well-known properties of these elements, i.e., hydroxide precipitation in basic solutions.[35] The yields of some elements were low when using 6.0 and 12 M NaOH, and it was found that these elements form hydroxide complex ions such as $[M(OH)_4]^-$ (M^{3+} = metal ions) in high $[OH^-]$ solutions.[38] See ref. 5 for details. Anyway, the observed consistency between the coprecipitation yields of various elements with Sm hydroxide and their individual hydroxide precipitation properties suggests that the coprecipitation behavior of an element whose chemical properties are unknown can be investigated using the present coprecipitation method and from the coprecipitation behaviors, general hydroxide precipitation properties of the elements can be discussed. Additionally, the chemical reactions for the majority of the elements in the multitracer are sufficiently fast to reach equilibrium within 10 s of stirring.

TABLE 1: Coprecipitation yields, *Y*, with stirring time of 10 s.[5]

Nuclide	dil. NH₃		conc. NH₃		0.10 M NaOH		1.0 M NaOH		6.0 M NaOH		12 M NaOH	
	Y (%)	error	Y (%)	error	Y (%)	error	Y (%)	error	Y (%)	error	Y (%)	error
[24]Na	9.0E-04	3.E-05	1.11	0.93	9.0E-04	3.E-05	9.0E-04	3.E-05	1.34	1.41	1.07	0.94
[42]K	1.0E-03	1.E-04	1.0E-03	1.E-04	1.0E-03	1.E-04	1.0E-03	1.E-04	1.0E-03	1.E-04	1.0E-03	1.E-04
[82m]Rb	1.9E-03	2.E-04	1.9E-03	2.E-04	1.9E-03	2.E-04	1.9E-03	2.E-04	1.9E-03	2.E-04	1.9E-03	2.E-04
[127]Cs	1.9E-04	1.E-05	1.9E-04	1.E-05	1.9E-04	1.E-05	1.9E-04	1.E-05	1.9E-04	1.E-05	1.9E-04	1.E-05
[28]Mg	6.1E-03	4.E-04	13.8	5.9	109	11	101	11	17.8	8.0	7.8	3.6
[47]Ca	58.0	9.0	58.0	11.4	86.1	12.7	72.5	16.0	88.4	13.7	116	12
[128]Ba	1.2E-03	2.E-04	69.6	17.0	36.0	5.6	1.2E-03	2.E-04	1.2E-03	2.E-04	1.2E-03	2.E-04
[48]Sc	92.4	6.0	89.1	6.0	83.7	6.3	83.8	6.2	63.2	4.6	26.9	3.0
[87]Y	98.1	4.0	96.8	4.5	100	4	98.1	3.7	86.0	3.1	42.1	1.7
[132]Ce	83.2	5.9	91.5	8.1	88.2	14.7	98.6	16.0	101	17	84.5	7.5
[145]Eu	100	5	97.0	4.0	101	3	95.0	5.0	92.9	4.5	85.5	3.0
[146]Gd	98.0	17.4	99.0	16.4	101	16	101	16	97.3	14.9	83.1	12.2
[150]Tb	94.3	5.7	96.6	6.2	104	6	97.0	9.1	102	8	73.8	6.0
[152]Dy	91.1	9.0	98.6	7.7	96.4	9.2	92.5	11.5	87.4	11.3	54.6	8.5
[161]Er	94.4	1.6	97.0	1.6	103	2	101	3	91.8	2.9	47.5	1.8
[165]Tm	96.3	5.8	102	4	100	4	101	4	77.4	3.5	40.0	2.1
[166]Yb	94.1	5.6	89.3	5.5	89.7	5.5	88.3	5.7	66.5	4.7	31.3	1.7
[169]Lu	102	6	97.0	6.3	99.3	6.4	95.3	6.6	71.4	4.3	37.0	3.0
[89]Zr	97.3	3.7	95.9	3.7	99.9	3.4	95.5	3.5	40.5	2.1	32.6	1.3
[173]Hf	90.6	5.4	90.4	5.3	88.9	5.1	98.3	8.0	34.4	2.9	24.0	1.6
[90]Nb	98.4	6.4	91.0	6.5	94.4	6.4	88.5	6.3	97.1	7.0	77.8	11.2
[176]Ta	93.1	8.0	74.2	7.0	65.8	6.6	60.3	6.5	56.0	6.7	52.1	6.7
[93m]Mo	74.2	7.3	26.8	5.4	9.9	4.7	0		0		0	
[96]Tc	1.8	1.9	0		0		0		0		0	
[99m]Rh	101	7	71.0	5.3	79.8	6.3	55.1	6.0	43.4	4.3	15.4	2.8
[65]Zn	200	90	3.2E-02	3.E-03	120	60	91	47	58	32	36	7
[67]Ga	21.3	6.3	24.8	3.5	29.7	4.7	22.9	5.2	16.8	3.2	17.7	1.5
[111]In	96.6	10.5	91.1	8.6	96.0	8.9	93.5	8.6	48.9	5.3	24.2	2.4
[71]As	99.0	7.5	97.8	6.9	61.0	4.8	35.8	2.9	46.0	5.4	22.4	2.4
[118m]Sb	101	16	66.3	13.8	24.4	9.8	15	13	3.8	13.9	27.1	9.6
[73]Se	50.2	13.0	21	12	2.4E-04	3.E-05	2.4E-04	3.E-05	2.4E-04	3.E-05	2.4E-05	3.E-06
[119m]Te	101	9	104	9	57.1	5.9	43.5	5.4	51.4	5.4	42.8	3.8

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TABLE 2: Coprecipitation yields, *Y*, with stirring time of 10 min.[5]

| Nuclide | Added basic solution | | | | | | | | | | | |
| | dil. NH₃ | | conc. NH₃ | | 0.10 M NaOH | | 1.0 M NaOH | | 6.0 M NaOH | | 12 M NaOH | |
	Y (%)	error	Y (%)	error	Y (%)	error	Y (%)	error	Y (%)	error	Y (%)	error
²⁴Na	4.9E-04	2.E-05	4.9E-04	2.E-05	4.9E-04	2.E-05	4.9E-04	2.E-05	4.9E-04	2.E-05	3.6	1.4
⁴²K	4.9E-03	6.E-04	4.9E-03	6.E-04	4.9E-03	6.E-04	4.9E-03	6.E-04	4.9E-03	6.E-04	4.9E-03	6.E-04
⁸²ᵐRb	7.2E-04	5.E-05	7.2E-04	5.E-05	7.2E-04	5.E-05	7.2E-04	5.E-05	7.2E-04	5.E-05	7.2E-04	5.E-05
¹²⁷Cs	6.7E-05	1.E-06	6.7E-05	1.E-06	6.7E-05	1.E-06	6.7E-05	1.E-06	6.7E-05	1.E-06	6.7E-05	1.E-06
²⁸Mg	3.1E-03	2.E-04	38.6	4.8	93.9	10.2	79.3	9.4	22.5	5.3	3.1E-03	2.E-04
⁴⁷Ca	48.2	5.1	90.1	10.3	92.3	12.3	40.9	7.2	53.1	8.5	68.9	9.5
¹²⁸Ba	18.8	1.4	106	6.0	36.3	3.6	6.7E-04	3.E-05	6.7E-04	3.E-05	12.4	0.9
⁴⁸Sc	80.4	6.6	96.0	7.7	85.5	8.2	100	8	61.9	6.1	36.2	4.5
⁸⁷Y	86.3	2.4	96.9	3.0	99.8	3.2	102	3	92.1	2.6	81.9	2.6
¹³²Ce	73.3	1.9	87.2	2.3	103	2	102	2	113	2	98.7	2.2
¹⁴⁵Eu	83.9	3.1	92.2	3.7	93.6	3.8	96.7	4.0	107	4	93.9	3.8
¹⁴⁶Gd	84.1	4.5	95.7	4.4	100	5	96.3	4.6	107	5	95.4	4.5
¹⁵⁰Tb	86.4	5.8	94.4	6.6	108	8	109	10	112	8	101	9.0
¹⁵²Dy	77.3	2.8	88.8	3.3	91.6	3.8	90.5	3.6	94.3	4.1	84.6	3.8
¹⁶¹Er	77.5	4.0	86.4	4.5	98.8	6.4	101	7	97.8	6.3	84.5	6.7
¹⁶⁵Tm	91.0	2.6	97.1	2.6	104	2	102	2	78.9	1.9	62.6	2.1
¹⁶⁶Yb	93.7	6.2	94.6	7.3	99.4	8.1	93.3	6.3	75.0	4.8	60.2	4.0
¹⁶⁹Lu	103	5	107	9	112	13	104	5	81.4	3.6	52.3	7.8
⁸⁹Zr	88.4	2.8	96.4	3.6	102	4	93.3	3.3	44.4	1.8	9.06	0.93
¹⁷³Hf	77.9	8.3	80.1	8.1	97.3	11.2	63.4	6.8	38.1	3.6	6.9	1.4
⁹⁰Nb	106	6	88.3	4.9	104	6	94.6	5.4	99.6	5.2	19.0	1.6
¹⁷⁶Ta	74.6	7.2	75.5	7.8	68.5	7.6	76.3	8.3	84.7	7.7	18.3	9.2
⁹³ᵐMo	1.1E-03	1.E-04	1.1E-03	1.E-04	1.1E-03	1.E-04	1.1E-03	1.E-04	1.1E-03	1.E-04	1.1E-03	1.E-04
⁹⁶Tc	4.1E-03	2.E-04	4.1E-03	2.E-04	4.1E-03	2.E-04	4.1E-03	2.E-04	4.1E-03	2.E-04	4.1E-03	2.E-04
⁹⁹ᵐRh	84.9	7.3	52.0	4.5	107	9	99.2	7.2	63.8	5.3	37.3	3.1
⁶⁵Zn	60.7	11.5	35	18	68.7	18.3	49.7	11.8	60.7	5.7	110	13
⁶⁷Ga	16.6	2.7	15.5	2.3	25.9	4.2	26.3	4.3	29.9	4.0	53.7	14.7
¹¹¹In	85.7	5.0	84.3	5.3	96.2	5.6	95.7	5.6	52.9	3.4	4.58	0.84
⁷¹As	85.7	7.3	87.3	8.0	47.7	6.4	30.0	5.3	28.2	4.4	52.5	8.8
¹¹⁸ᵐSb	77.1	8.9	85.0	9.7	17.9	5.6	3.1E-03	2.E-04	20	15	3.1E-03	2.E-04
⁷³Se	17	11	1.1E-03	1.E-04	1.1E-03	1.E-04	1.1E-03	1.E-04	1.1E-03	1.E-04	1.1E-03	1.E-04
¹¹⁹ᵐTe	81.9	4.4	85.0	6.3	48.9	4.6	42.4	4.2	44.4	2.3	16.4	4.6

These results indicate that the present coprecipitation method with Sm hydroxide is applicable to SHE chemistry. Note that, for actual SHE chemistry, detailed preliminary experiment using the homologues of the objective SHE and search for suitable conditions are necessary.

3.2. Coprecipitation experiment for Zr, Hf, and Th with Sm hydroxide. For coprecipitation experiment of Rf, detailed coprecipitation experiment with Sm hydroxide was performed with ⁸⁸Zr, ¹⁷⁵Hf, and ²²⁸Th ($T_{1/2}$ = 1.91 y) tracers.[6] Coprecipitated samples with Sm hydroxide were prepared using various basic solutions: dilute and concentrated aqueous NH₃ and 0.1, 1.0, 6.0, and 12.0 M NaOH solutions. A 20 µL aliquot of the Sm standard solution was added into 220 µL of an aqueous solution (~0.4 M HCl) containing the radiotracers in a PP beaker. The solution was stirred and 2 mL of the basic solution was then added to produce the precipitate. After aging the precipitate for 10 s or 10 min at 25 °C, the precipitate sample was subjected to suction filtration with a PP membrane filter. The obtained sample was dried on a heater at 100 °C, and was subjected to γ-ray and α-particle measurements. The radioactivities of the filtrate and PP beakers used were also measured. The standard radioactivities of ⁸⁸Zr, ¹⁷⁵Hf, and ²²⁸Th were determined at the same detection efficiency. Precipitation yields, *Y*, were determined from these radioactivities. The errors in the yields were determined by taking into account the standard deviation in each γ or α count and in the variation of the precipitation yield.

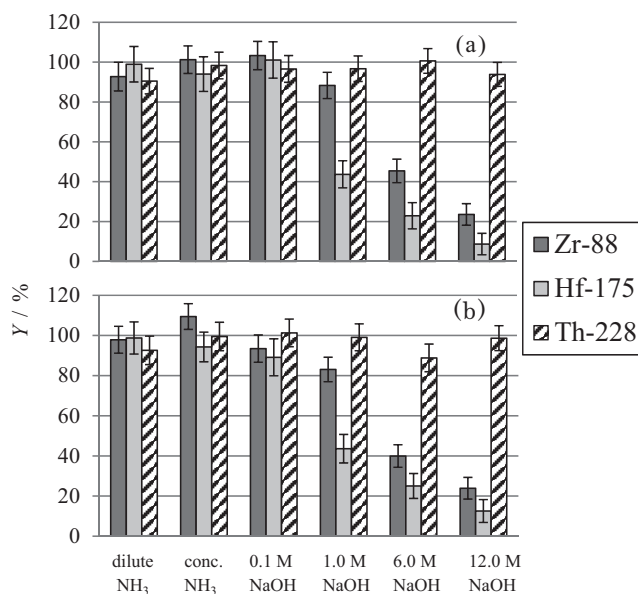The coprecipitation yields of Zr, Hf, and Th when 10-min

Figure 3. Coprecipitation yields of Zr, Hf, and Th based on the addition of various basic solutions. Yields obtained with stirring for 10 min are shown in (a) and for 10 s in (b).[6]

aging was employed are shown in Figure 3(a), and those obtained with 10-s aging are displayed in Figure 3(b). Figures 3(a) and 3(b) demonstrate that the yields obtained with 10-min and 10-s aging are in good agreement with each other. This
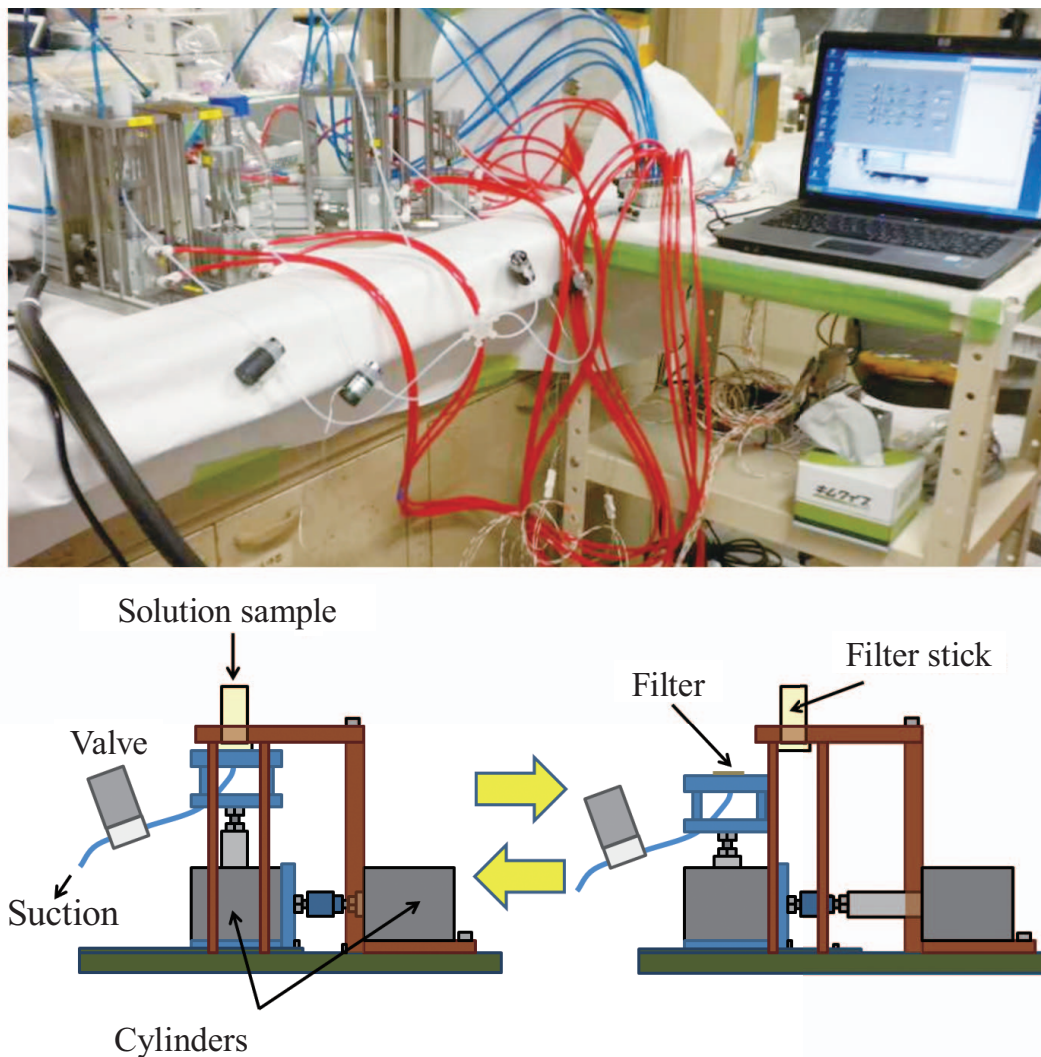
Figure 4. A photograph of CHIN (upper) and schematic illustration of the filtration section of CHIN (lower).[6]

result suggests that the chemical reactions during coprecipitation of Zr, Hf, and Th are fast, and the present conditions are suitable for evaluating the coprecipitation behavior of 68-s ^{261}Rf.

Almost complete coprecipitation of Zr and Hf with Sm hydroxide was achieved when aqueous NH$_3$ solutions and 0.1 M NaOH were used. These results are consistent with those obtained for multitracer (Tables 1 and 2) and with the inherent properties of these elements, i.e., hydroxide precipitation in basic solutions.[39,40] With the use of more highly concentrated NaOH solutions, the yields of Zr and Hf decreased as the OH$^-$ concentration increased, whereas the Th yields were constant at ca. 100%. These behaviors are attributed to the fact that Zr and Hf form hydroxide complex ions such as [M(OH)$_5$]$^-$ (M^{4+} = Zr^{4+} and Hf^{4+})[38,41] in solutions with high hydroxide concentration. The yields of Hf were consistently lower than those of Zr in the same solutions. These results are qualitatively consistent with the larger solubility product of [Hf(OH)$_5$]$^-$ (logK_{s5} = −3.2) than that of [Zr(OH)$_5$]$^-$ (logK_{s5} = −3.6).[41] In addition, the highest yields of Th compared with those of Zr and Hf is consistent with the smallest solubility product of Th (logK_{s5} = −5.8).[41] The ~100% coprecipitation yields of Zr, Hf, and Th with the use of aqueous NH$_3$ indicate that the ammine-coordinated complex ions, which dissolve in aqueous solution (e.g., Zn, Cu, and Ag hydroxide dissolve in concentrated NH$_3$ solutions), are not dominantly formed even in concentrated NH$_3$ solution. The obtained results indicate that the hydroxide and ammine complexation properties of group 4 elements can be

qualitatively investigated through their coprecipitation behaviors with Sm hydroxide under the present experimental conditions.

In addition, it was found in this study[6] that well-resolved alpha spectra can be obtained for coprecipitated samples without compromising the yield by aging the hydroxide precipitate for only 10 s at 25 °C.

3.3. Development of the apparatus and online coprecipitation experiment. A computer-controlled suction filtration apparatus for the preparation of precipitated samples of heavy elements, CHIN, was developed using cylinders operated by compressed air, valves operated by on/off operation of 24 V DC power and so on as shown in Figure 4.[6] This apparatus enables rapid and repetitive filtration. Filter sticks were fabricated using PTFE to prevent the adsorption of the radiotracers on the wall of the stick, and the stick was washed after each usage.

The online experiment using CHIN was performed with relatively short-lived nuclides ^{89m,g}Zr and ^{173}Hf ($T_{1/2}$ = 23.6 h) produced using the AVF cyclotron at the Research Center of Nuclear Physics (RCNP).[6] These nuclides produced in the reactions of ^{nat}Sr(α,xn)^{89m,g}Zr and ^{nat}Yb(α,xn)^{173}Hf were rapidly and continuously transported from the nuclear reaction chamber to the chemistry laboratory using the He/KCl gas-jet system. The products were collected on the collection site of the dissolution apparatus, ASO. After dissolution by 200 μL of dilute HCl for 12 s, the precipitate samples were prepared at

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room temperature in a manner similar to that used in the tracer experiment described above, with stirring for 10 s. The samples were filtered with the CHIN, and were subsequently dried on a heater under hot air. The coprecipitation yields were determined from the γ-ray radioactivity of the precipitated sample relative to the total radioactivity of the precipitated and filtrate samples.

The coprecipitation yields obtained in the online experiments are shown in Figure 5. The yields in Figure 5 and their dependence on the composition of the added basic solution approximately correspond with those in Figure 3(b); this online experiment using CHIN well demonstrated the coprecipitation experiment of Rf. In this online experiment, the time required for the sample preparation from the start of the dissolution was 80–120 s, which represents applicability for [261]Rf experiment, except in the case employing 12 M NaOH. With the use of 12 M NaOH, more than 4 min was required for the suction filtration because of the high viscosity of the solution; consequently, the use of 12 M NaOH is unsuitable for Rf experiment. Through this online experiment, the suitable conditions in suction filtration, sample drying, etc., for rapid preparation of the precipitated samples were determined.

4. Conclusion

In the present paper, two types of newly developed experimental methods for SHE chemistry are introduced. In both the studies, preliminary chemical experiments using the homologues of [104]Rf and development of the apparatuses are achieved, and substantial applicability for Rf experiment was indicated. Feasibility to study the chloride complexation of Rf was represented through the solid-liquid extraction in the TIOA/HCl system using the apparatus AMBER. This methodology also has a possibility of the first observation of the equilibrium of the chemical reactions for SHE.[33] In coprecipitation study, the coprecipitation method was proposed to investigate the hydroxide and ammine complexation of SHEs as a quite new method for SHE chemistry. In addition, good energy resolution in alpha spectroscopy was confirmed for precipitated samples.

It is very difficult to clarify the chemical properties of new elements (SHEs) owning to their characteristics such as short life, low production rate, and single atom situation. For the breakthrough in the research field of SHE chemistry, developments of various new experimental methods would be necessary. It is hoped that the methods introduced herein will provide such valuable findings.

Figure 5. Coprecipitation yields of Zr and Hf obtained in the online experiment.[6]

References

(1) *The Chemistry of Superheavy Elements, 2nd ed.*, edited by M. Schädel and D. Shaughnessy (Springer, Heidelberg, 2014).

(2) M. Schädel, Angew. Chem. Int. Ed. **45**, 368 (2006).

(3) R. Guillamont, J. P. Adloff, A. Peneloux, and P. Delamoye, Radiochim. Acta **54**, 1 (1991).
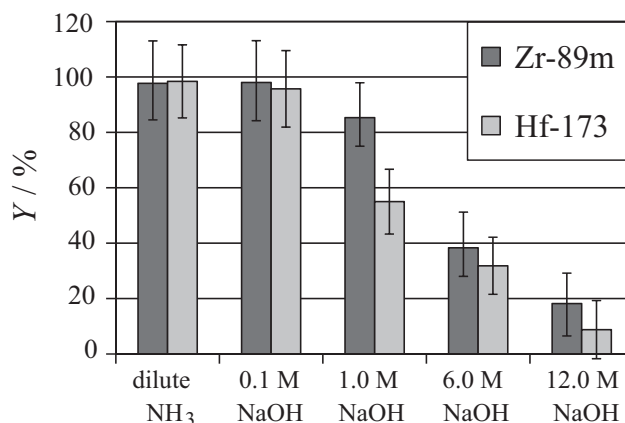
(4) Y. Kasamatsu, A. Kino, T. Yokokita, K. Nakamura, Y. Komori, K. Toyomura, T. Yoshimura, H. Haba, J. Kanaya, M. Huang, Y. Kudou, N. Takahashi, and A. Shinohara, Radiochim. Acta **103**, 513 (2015).

(5) Y. Kasamatsu, T. Yokokita, K. Toyomura, Y. Shigekawa, H. Haba, J. Kanaya, M. Huang, Y. Ezaki, T. Yoshimura, K. Morita, and A. Shinohara, Appl. Radiat. Isot. **118**, 105 (2016).

(6) Y. Kasamatsu, K. Toyomura, N. Shiohara, T. Yokokita, Y. Komori, A. Kino, T. Yoshimura, N. Takahashi, H. Haba, Y. Kudou, H. Kikunaga, T. Mitsugashira, T. Ohtsuki, K. Takamiya, and A. Shinohara, J. Nucl. Radiochem. Sci. **14**, 7 (2014).

(7) K. R. Czerwinski, K. E. Gregorich, N. J. Hannink, C. D. Kacher, B. A. Kadkhodayan, S. A. Kreek, D. M. Lee, M. J. Nurmia, A. Türler, G. T. Seaborg, and D. C. Hoffman, Radiochim. Acta **64**, 23 (1994).

(8) K. R. Czerwinski, C. D. Kacher, K. E. Gregorich, T. M. Hamilton, N. J. Hannink, B. A. Kadkhodayan, S. A. Kreek, D. M. Lee, M. J. Nurmia, A. Türler, G. T. Seaborg, and D. C. Hoffman, Radiochim. Acta **64**, 29 (1994).

(9) C. D. Kacher, K. E. Gregorich, D. M. Lee, Y. Watanabe, B. Kadkhodayan, B. Wierczinski, M. R. Lane, E. R. Sylwester, D. A. Keeney, M. Hendricks, N. J. Stoyer, J. Yang, M. Hsu, D. C. Hoffman, and A. Bilewicz, Radiochim. Acta **75**, 127 (1996).

(10) R. Günther, W. Paulus, J. V. Kratz, A. Seibert, P. Thörle, S. Zauner, W. Brüchle, E. Jäger, V. Pershina, M. Schädel, B. Schausten, D. Schumann, B. Eichler, H. W. Gäggeler, D. T. Jost, and A. Türler, Radiochim. Acta **80**, 121 (1998).

(11) E. Strub, J. V. Kratz, A. Kronenberg, A. Nähler, P. Thörle, S. Zauner, W. Brüchle, E. Jäger, M. Schädel, B. Schausten, E. Schimpf, Li Zongwei, U. Kirbach, D. Schumann, D. Jost, A. Türler, M. Asai, Y. Nagame, M. Sakama, K. Tsukada, H. W. Gäggeler, and J. P. Glatz, Radiochim. Acta **88**, 265 (2000).

(12) H. Haba, K. Tsukada, M. Asai, S. Goto, A. Toyoshima, I. Nishinaka, K. Akiyama, M. Hirata, S. Ichikawa, Y. Nagame, Y. Shoji, M. Shigekawa, T. Koike, M. Iwasaki, A. Shinohara, T. Kaneko, T. Maruyama, S. Ono, H. Kudo, Y. Oura, K. Sueki, H. Nakahara, M. Sakama, A. Yokoyama, J. V. Kratz, M. Schädel, and W. Brüchle, J. Nucl. Radiochem. Sci. **3**, 143 (2002).

(13) H. Haba, K. Tsukada, M. Asai, A. Toyoshima, K. Akiyama, I. Nishinaka, M. Hirata, T. Yaita, S. Ichikawa, Y. Nagame, K. Yasuda, Y. Miyamoto, T. Kaneko, S. Goto, S. Ono, T. Hirai, H. Kudo, M. Shigekawa, A. Shinohara, Y. Oura, H. Nakahara, K. Sueki, H. Kikunaga, N. Kinoshita, N. Tsuruga, A. Yokoyama, M. Sakama, S. Enomoto, M.

Schädel, W. Brüchle, and J. V. Kratz, J. Am. Chem. Soc. **126**, 5219 (2004).

(14) H. Haba, K. Tsukada, M. Asai, A. Toyoshima, Y. Ishii, H. Toume, T. Sato, I. Nishinaka, T. Ichikawa, S. Ichikawa, Y. Nagame, W. Sato, K. Matsuo, Y. Kitamoto, Y. Tashiro, A. Shinohara, J. Saito, M. Ito, T. Ikezawa, M. Sakamaki, S. Goto, H. Kudo, H. Kikunaga, M. Arai, S. Kamataki, A. Yokoyama, K. Akiyama, K. Sueki, Y. Oura, M. Schädel, W. Brüchle, and J. V. Kratz, Radiochim. Acta **95**, 1 (2007).

(15) A. Toyoshima, H. Haba, K. Tsukada, M. Asai, K. Akiyama, S. Goto, Y. Ishii, I. Nishinaka, T. K. Sato, Y. Nagame, W. Sato, Y. Tani, H. Hasegawa, K. Matsuo, D. Saika, Y. Kitamoto, A. Shinohara, M. Ito, J. Saito, H. Kudo, A. Yokoyama, M. Sakama, K. Sueki, Y. Oura, H. Nakahara, M. Schädel, W. Brüchle, and J. V. Kratz, Radiochim. Acta **96**, 125 (2008).

(16) K. Tsukada, H. Haba, M. Asai, A. Toyoshima, K. Akiyama, Y. Kasamatsu, I. Nishinaka, S. Ichikawa, K. Yasuda, Y. Miyamoto, K. Hashimoto, Y. Nagame, S. Goto, H. Kudo, W. Sato, A. Shinohara, Y. Oura, K. Sueki, H. Kikunaga, N. Kinoshita, A. Yokoyama, M. Schädel, W. Brüchle, and J. V. Kratz, Radiochim. Acta **97**, 83 (2009).

(17) Y. Kasamatsu, A. Toyoshima, M. Asai, K. Tsukada, Z. Li, Y. Ishii, H. Toume, T. K. Sato, T. Kikuchi, I. Nishinaka, Y. Nagame, H. Haba, H. Kikunaga, Y. Kudou, Y. Oura, K. Akiyama, W. Sato, K. Ooe, H. Fujisawa, A. Shinohara, S. Goto, T. Hasegawa, H. Kudo, T. Nanri, M. Araki, N. Kinoshita, A. Yokoyama, F. Fan, Z. Qin, Ch. E. Düllmann, M. Schädel, and J. V. Kratz, Chem. Lett. **38**, 1084 (2009).

(18) A. Toyoshima, Y. Kasamatsu, K. Tsukada, M. Asai, Y. Ishii, H. Toume, I. Nishinaka, T. K. Sato, Y. Nagame, M. Schädel, H. Haba, S. Goto, H. Kudo, K. Akiyama, Y. Oura, K. Ooe, A. Shinohara, K. Sueki, and J. V. Kratz, J. Nucl. Radiochem. Sci. **11**, 7 (2010).

(19) Y. Ishii, A. Toyoshima, K. Tsukada, M. Asai, Z. Li, Y. Nagame, S. Miyashita, T. Mori, H. Suganuma, H. Haba, S. Goto, H. Kudo, K. Akiyama, Y. Oura, A. Shinohara, M. Schädel, V. Pershina, and J. V. Kratz, Bull. Chem. Soc. Jpn. **84**, 903 (2011).

(20) Z. Li, A. Toyoshima, M. Asai, K. Tsukada, T. K. Sato, N. Sato, T. Kikuchi, Y. Nagame, M. Schädel, V. Pershina, H. Liang, Y. Kasamatsu, Y. Komori, K. Ooe, A. Shinohara, S. Goto, H. Murayama, M. Murakami, H. Kudo, H. Haba, Y. Takeda, M. Nishikawa, A. Yokoyama, S. Ikarashi, K. Sueki, K. Akiyama, J. V. Kratz, Radiochim. Acta **100**, 157 (2012).

(21) M. Schädel, W. Brüchle, E. Jäger, E. Schimpf, J. V. Kratz, U. W. Scherer, and H. P. Zimmermann, Radiochim. Acta **48**, 171 (1989).

(22) Y. Nagame, K. Tsukada, M. Asai, A. Toyoshima, K. Akiyama, Y. Ishii, T. Kaneko-Sato, M. Hirata, I. Nishinaka, S. Ichikawa, H. Haba, S. Enomoto, K. Matsuo, D. Saika, Y. Kitamoto, H. Hasegawa, Y. Tani, W. Sato, A. Shinohara, M. Ito, J. Saito, S. Goto, H. Kudo, H. Kikunaga, N. Kinoshita, A. Yokoyama, K. Sueki, Y. Oura, H. Nakahara, M. Sakama, M. Schädel, W. Brüchle, and J.

V. Kratz, Radiochim. Acta **93**, 519 (2005).

(23) Z. J. Li, A. Toyoshima, K. Tsukada, and Y. Nagame, Radiochim. Acta **98**, 7 (2010).

(24) D. Hild, K. Eberhardt, J. Even, J. V. Kratz, N. Wiehl, P. Löb, B. Werner, and C. Hofmann, Radiochim. Acta **101**, 681 (2013).

(25) Y. Kasamatsu, Y. Kikutani, A. Kino, Y. Komori, T. Yokokita, T. Yoshimura, N. Takahashi, and A. Shinohara, Radiochim. Acta **101**, 515 (2013).

(26) R. Sudowe, M. G. Calvert, Ch. E. Düllmann, L. M. Farina, C. M. Folden III, K. E. Gregorich, S. E. H. Gallaher, D. C. Hoffman, S. L. Nelson, D. C. Phillips, J. M. Schwantes, R. E. Wilson, P. M. Zielinski, and H. Nitsche, Radiochim. Acta **94**, 123 (2006).

(27) A. Kino, Y. Kasamatsu, T. Yokokita, T. Yoshimura, Y. Komori, Y. Kikutani, N. Takahashi, and A. Shinohara, Solvent Extr. Res. Dev. Jpn. **22**, 127 (2015).

(28) T. Yokokita, Y. Kasamatsu, T. Yoshimura, N. Takahashi, and A. Shinohara, Solvent Extr. Ion Exch. **33**, 472 (2015).

(29) T. Yokokita, Y. Kasamatsu, K. Ooe, T. Yoshimura, N. Takahashi, Y. Komori, and A. Shinohara, J. Radioanal. Nucl. Chem. **301**, 751 (2014).

(30) Y. Kasamatsu, A. Toyoshima, H. Toume, K. Tsukada, M. Asai, H. Haba, and Y. Nagame, J. Nucl. Radiochem. Sci. **13**, 9 (2013).

(31) Y. Kasamatsu, A. Toyoshima, H. Haba, H. Toume, K. Tsukada, K. Akiyama, T. Yoshimura, and Y. Nagame, J. Radioanal. Nucl. Chem. **279**, 371 (2009).

(32) T. Yokokita, K. Ooe, Y. Kasamatsu, T. Yoshimura, N. Takahashi, N. Shiohara, K. Takamiya, Y. Komori, Y. Kikutani, A. Kino, and A. Shinohara, J. Radioanal. Nucl. Chem. **303**, 1091 (2015).

(33) T. Yokokita, Y. Kasamatsu, A. Kino, H. Haba, Y. Shigekawa, Y. Yasuda, K. Nakamura, K. Toyomura, Y. Komori, M. Murakami, T. Yoshimura, N. Takahashi, K. Morita, and A. Shinohara, Dalton Trans. **45**, 18827 (2016).

(34) M. Maly, T. Sikkeland, R. Silva, and A. Ghiorso, Science **160**, 1114 (1968).

(35) H. Kikunaga, Y. Kasamatsu, K. Takamiya, T. Ohtsuki, H. Yuki, A. Yokoyama, T. Nakanishi, and T. Mitsugashira, Appl. Radiat. Isot. **67**, 539 (2009).

(36) H. Haba, D. Kaji, Y. Kanayama, K. Igarashi, and S. Enomoto, Radiochim. Acta **93**, 539 (2005).

(37) *Analytical Chemistry, Volume I Qualitative Analysis*, edited by W. T. Hall and F. P. Treadwell (John Wiley & Sons, Inc., New York, 1937).

(38) *The Hydrolysis of Cations*, C. F. Baes, Jr. and R. E. Mesmer (Wiley, New York, 1976).

(39) H. Bilinski, M. Branica, and L. G. Sillen, Acta Chem. Scand. **20**, 853 (1966).

(40) J. Ueda and M. Takagi, Bull. Chem. Soc. Jpn. **63**, 544 (1990).

(41) *Stability Constants of Metal-Ion Complexes, Special Publication No.17*, edited by L. G. Sillen and A. E. Martell (the Chemical Society, London, 1964).