Chemical Studies of Rutherfordium (Rf) and Nobelium (No) on an Atom-at-a-time Scale

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Hexafluoro comlexation of rutherfordium (Rf) and successful oxidation of the divalent state of nobelium (No) recently carried out at JAEA are reviewed. The ^{261}Rf and ^{255}No isotopes were produced in the ^{248}Cm(^{18}O, $5n$) and ^{248}Cm(^{12}C, $5n$) reactions, respectively, at the JAEA tandem accelerator. Anion-exchange behavior of Rf in HF and HNO$_3$ (HF/HNO$_3$) mixed solution was studied together with short-lived Zr and Hf isotopes using an automated chemistry apparatus to characterize anionic fluoride species of Rf and to evaluate its formation constants. It was found that the hexafluoro complex of Rf is present in the HF/HNO$_3$ solutions under the given conditions where the same complexes of Zr and Hf are existing. The formation constant of the Rf complex was evaluated to be at least one order of magnitude smaller than those of Zr and Hf, which suggests a larger ionic radius of Rf^{4+} than those of Zr^{4+} and Hf^{4+}. Oxidation experiments of No^{2+} were conducted in 0.1 M α-hydroxyisobutyric (α-HIB) acid using a newly developed electrolytic column chromatography apparatus on a single atom scale. The result clearly demonstrated that stable No^{2+} is successfully oxidized to the trivalent state, No^{3+}, which is held in the α-HIB solution.

1. Introduction

Chemistry of the transactinide elements with atomic numbers (Z) ≥ 104 is one of the most fascinating and challenging subjects in the research field of nuclear and radiochemistry. At present, the elements up to element 118 are reported to be produced in heavy-ion-induced nuclear reactions.[1, 2] The position of these elements at the Periodic Table is of fundamental importance. Pioneering chemical works performed with a few of atoms have thus far experimentally verified to place the transactinide elements on respective positions at the Periodic Table (see Figure 1). Rutherfordium (Rf) through hassium (Hs)[3, 4] and copernicium (Cn)[5] are arranged on the groups 4 to

8 and 12 in the newly appearing 6d transition series, respectively. Very recently, chemical behavior of element 114 was reported to deviate from the systematic trend in that of lighter group-14 elements although further confirmation is necessary.[6]

It is of special interest to study chemical properties of the transactinide elements in detail to elucidate the influence of increasingly strong relativistic effects. Relativistic mass increase of electrons due to its velocity approaching to the speed of light enforces the contraction and stabilization of s and p$_{1/2}$ orbitals. The increased screening by these contracted orbitals for a positive nuclear charge makes outer p$_{3/2}$, d, and f orbitals expanded and destabilized. Relativistic contribution also comes from the spin-orbit splitting of electron orbitals

Figure 1. Periodic Table of the elements.

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with angular moment > 0. These three effects change approximately as Z^2 for the valence shells down a column of the Periodic Table. The ground state electronic configuration of the transactinide elements has drastic rearrangement due to strong relativistic effects,[7-9] and accordingly, their chemical properties cannot be anticipated simply from systematic trends in those of lighter homologues. Detailed chemical characterization of these elements is, therefore, necessary to allow thorough comparison of their properties with those of lighter homologues, which provides a unique opportunity to examine modern relativistic quantum-chemical treatments.[10-12]

Because of the short half-lives ($T_{1/2}$) and the extremely low production rates of the transactinide nuclides, chemical experiments must be carried out with single atoms. One needs to conduct chemical experiments giving the same results between a macro amount and single atoms. For single atoms, the classical law of mass action is no longer valid because the single atom cannot exist in different chemical forms taking part in chemical equilibrium at the same time. It is suggested that the concept of the chemical equilibrium is replaced by the equivalent expression of finding probabilities of the single atoms in one phase or the other measured in repetitive experiments.[13, 14] Partition methods such as ion exchange, solvent extraction, and gas chromatography are often employed for single atoms.

In the last decade, great progress was made in aqueous chemistry of the transactinide elements. Precisely measured chemical quantities such as a distribution coefficient (K_d) of the heaviest elements enabled quantitative interpretation for complex formation and redox (oxidation – reduction) reactions, which are the most fundamental chemical properties of ions in aqueous solution. At JAEA, chemical properties of Rf was systematically explored in acidic solutions using AIDA (the Automated Ion-exchange separation apparatus coupled with the Detection system for Alpha spectroscopy).[15] Chloride, nitrate, fluoride, and sulfate complexation of Rf was thoroughly investigated.[16-22] Redox studies of the heaviest elements by a novel electrochemical technique were also successfully carried out using a flow electrolytic chromatographic column apparatus.[23, 24]

In this account, hexafluoro complex formation of Rf and oxidation of No^{2+} conducted at JAEA are presented as examples to elucidate the influence of strong relativistic effects through the determination of an ionic radius and a redox potential. First of all, production of ^{261}Rf and ^{255}No with a ^{248}Cm target at the JAEA tandem accelerator is presented. Then, fluoride complexation of Rf with anion-exchange chromatography using AIDA is showed.[19] The formation constants of the anionic fluoride-complexes of Rf are experimentally obtained from the measurement of its K_d values. An ionic radius of Rf^{4+} is evaluated from the formation constants and is compared with theoretical predictions. Our newly developed electrochemistry technique for single atom chemistry using a flow electrolytic chromatography apparatus[23] is, thereafter, introduced. This unique technique is successfully applied to the oxidation of No^{2+} to No^{3+} on a single atom scale,[24] which demonstrates the capability of the technique to perform redox experiments of the transactinide elements. Finally, prospects of aqueous chemistry of the heaviest element at JAEA are briefly considered.

2. Production of ^{261}Rf and ^{255}No

The heaviest elements are produced at accelerators using nuclear reactions of heavy-ion beams with heavy target materials. A ^{248}Cm target was used to produce neutron-rich and relatively long-lived isotopes in hot-fusion reactions at the JAEA tandem accelerator. Rutherfordium-261 ($T_{1/2}$ = 78 s)[25] and ^{255}No ($T_{1/2}$ = 3.1 min)[25] were produced in the ^{248}Cm(^{18}O, 5n) and ^{248}Cm(^{12}C, 5n) reactions with production rates of approximately 2 and 30 atoms per minute, respectively, under typical experi-

mental conditions.

Gadolinium isotopes were mixed into the ^{248}Cm target to simultaneously produce short-lived isotopes of respective lighter homologues Hf and Yb which were used for monitoring their chemical behavior and yields during repetitive chromatographic experiments of Rf and No, respectively. This is an important experimental manner to guarantee reproducibility of the experimental cycles. We also produced short-lived isotope pairs of Zr/Hf and Yb/Sr for the Rf and No experiments, respectively, to establish chromatographic behavior of these lighter elements. These pairs were simultaneously produced by irradiating mixed Ge/Gd targets with the same beams as those for the Rf and No production.

These reaction products recoiling out of the target were attached to KCl aerosols seeded in a helium gas stream and are continuously transported to the chemistry laboratory through a thin Teflon capillary at a typical gas flow rate of 2.0 L min^{-1}. The transport efficiency of the He/KCl gas-jet system was estimated to be 35%.[26]

3. Hexafluoro complex formation of Rf

Fluoride complexation of Rf has been reported to be quite different from that of its lighter homologues Zr and Hf.[27-30] Strub *et al.* systematically studied the adsorption of Rf on the cation- and anion-exchange resin in the 0.0001 - 1 M HF/0.1 M HNO$_3$ solution and reported that the adsorption behavior of Rf is remarkably different from that of Zr and Hf.[29, 30] Haba *et al.* then examined the anion-exchange behavior of Rf, Zr, and Hf in 1.9 - 13.9 M HF using AIDA.[17] The result showed that the adsorption probabilities of Rf are much smaller than those of Zr and Hf and suggested that the different fluoride species between Rf and the homologues are present in the HF solution.[17] To further understand the characteristic behavior of Rf and to assess its ionic radius from the behavior, it is essentially important to study the formation of anionic fluoride complexes of Rf quantitatively. In the present study, we systematically measured K_d values of Rf as well as those of its homologues Zr and Hf as a function of the concentrations of F$^-$ and NO$_3^-$ which acted as a counter ion competing with anionic complexes on the binding site.[31] Anionic fluoride species of Rf in HF/HNO$_3$ was clearly identified by a slope analysis with the NO$_3^-$ counter-ion on anion-exchange resin. Then formation constants of anionic fluoride-complexes of Rf was evaluated by analyzing variation of the K_d value against the concentration of the F$^-$ ion. An ionic radius of Rf^{4+} was discussed based on the formation constants.

In the experiment, two different-sized chromatographic columns of 1.6 mm i.d. × 7.0 mm long and of 1.0 mm i.d. × 3.5 mm long were employed to study chromatographic behavior of Rf in a wide range of HF/HNO$_3$ concentrations. The transported products by the gas-jet method were collected on the deposition site of AIDA for 2 min. After collection, the products were dissolved with HF/HNO$_3$ and were subsequently fed onto an anion-exchange column at a flow rate of 740 μL min^{-1}. Remaining products on the resin were stripped with 4.0 M HCl at a flow rate of 1000 μL min^{-1}. The effluents were collected on Ta discs as fractions 1 and 2, respectively. These samples were separately evaporated to dryness with hot He gas and a halogen heat lamp to prepare dried samples for α-spectrometry. The two discs were then transferred to the α-spectrometry station of AIDA equipped with 600 mm^2 passivated implanted planar silicon (PIPS) detectors. The detection efficiency and energy resolution was 35% and approximately 70 keV FWHM, respectively. After the α-particle measurement, γ-ray of ^{169}Hf was monitored using Ge detectors for every third or fourth pair of the Ta discs to determine its adsorption probability and the chemical yield. These experiments were repeated in a 2-min cycle. The elution behavior of Zr and Hf was also examined to

Chemical studies of rutherfordium (Rf) and nobelium (No) on an

*J. Nucl. Radiochem. Sci.*, Vol. 12, No. 1, 2012 **A3**

investigate their chromatographic behavior under the identical conditions. The elution behavior was established by assaying effluent samples in plastic tubes with γ-ray spectrometry.

From a total of 3788 separation cycles of the anion-exchange experiments, 334 α-particles of ^{261}Rf and ^{257}No including 46 time-correlated α-particle pairs from ^{261}Rf and ^{257}No were observed. In Figure 2, variation of K_d values for Zr, Hf, and Rf in the constant [F$^-$] of 3.0×10^{-3} M is shown as a function of [NO$_3^-$]. Concentrations of dissociated ions in HF/HNO$_3$ were evaluated applying the law of mass action to chemical equilibria of H$^+$ + F$^-$ ⇌ HF and HF + F$^-$ ⇌ HF$_2^-$.[32] The K_d values of ^{85}Zr and ^{169}Hf by the column chromatography are in good agreement with those of ^{88}Zr and ^{175}Hf measured in separate batch experiments under static conditions. It indicates that the chemical reactions in the rapid chromatography reach equilibrium. The K_d values of Zr and Hf are identical with each other, and the slopes in the logK_d vs. log[NO$_3^-$] plot are -2.0 ± 0.1 as indicated by the dashed line. We deduced K_d values of Rf from its adsorption probabilities by assuming that the chemical reactions of Rf in the anion-exchange chromatography are as fast as those of Zr and Hf.[17-19] As shown in Figure 2, the K_d values of Rf are much smaller than those of Zr and Hf, and the slope is -2.2 ± 0.2 depicted by the solid line. In Figure 3(a), variation of the K_d values for ^{261}Rf, ^{88}Zr and ^{175}Hf is shown as a function of [F$^-$]. Curves are results of the theoretical calculation discussed later. The K_d values of ^{88}Zr and ^{175}Hf start to increase at around [F$^-$] = 1×10^{-5} M, gradually reaching constant values between 10^{-4} and 10^{-3} M, and decrease beyond [F$^-$] = 5×10^{-3} M. In contrast to this behavior, the K_d values of Rf begin to increase at [F$^-$] = 5.0×10^{-4} M. In Figure 3(b), variation of the slopes for Rf, Zr and Hf in the logK_d - log[NO$_3^-$] plot is shown as a function of [F$^-$]. The slope for ^{261}Rf is taken from Figure 2. The slopes for Zr and Hf are approximately -2 in the [F$^-$] range of 10^{-5} M to 10^{-2} M.

The variation of the K_d values is calculated based on anion-exchange reactions and formation reactions for fluoride complexes of the group-4 elements. An exchange reaction between an anionic complex A^{c-} and a counter ion L$^-$ [31] on the anion-exchange resin R is described as

$$A^{c-} + c\text{RL} \rightleftarrows R_c A + c\text{L}^-. \qquad (1)$$

The consecutive formation of the fluoride complexes of Zr and Hf is represented[31-35] as

$$[\text{MF}_{n-1}]^{4-(n-1)} + \text{F}^- \rightleftarrows [\text{MF}_n]^{4-n} \qquad (n = 1 - 6) \qquad (2)$$
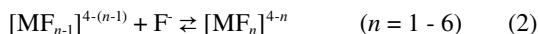
where M indicates Zr or Hf and n denotes the coordination number in the products. From these chemical equilibria, the K_d value is derived as

$$\log K_d = \log D_2 - 2\log \frac{[\text{L}^-]}{[\text{RL}]} + \log \frac{\beta_6 [\text{F}^-]^6}{1 + \sum_{n=1}^{6} \beta_n [\text{F}^-]^n}. \qquad (3)$$

The symbols β_n ($n = 1 - 6$) show the stability constants represented as $\beta_n = \prod_{i=1}^{n} K_i$ and D_2 is the equilibrium constant for Eq. (1); see ref. 17 for details. The -2 slope shown in Figure 3(b) demonstrates that a hexafluoro complex [MF$_6$]$^{2-}$ is the dominant species for these elements. In Figuer 3(a), calculated K_d values for Zr and Hf with Eq. (3) are shown by the dotted and broken curves, respectively, where the logK_n ($n = 1 - 6$) values from refs. 34 and 35 are used. The calculation with Eq. (3) well reproduces the experimental data of these elements.

Assuming that Rf forms fluoro complexes according to Eq. (2), its hexafluoro complex [RfF$_6$]$^{2-}$ is identified from the -2 slope shown in Figure 2. Increasing formation of [RfF$_6$]$^{2-}$ in the HF/HNO$_3$ solution with an increase of [F$^-$] in Figure 3 (a) is also verified. Formation constants of the anionic fluoride-complexes of Rf, K_5 and K_6, in addition to its D_2 value were
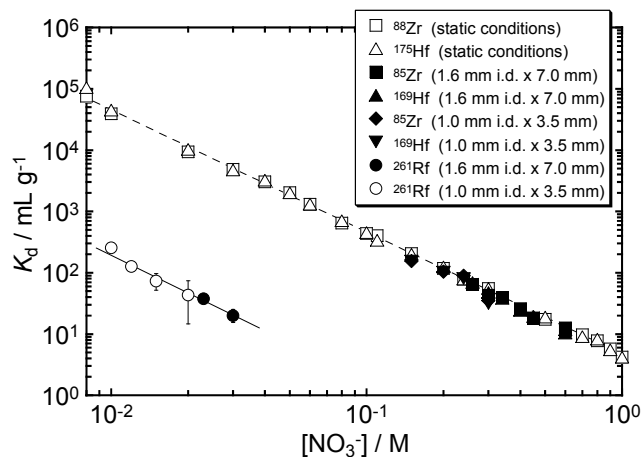

Figure 2. Variation of the K_d values of ^{88}Zr and ^{175}Hf under static conditions and those of ^{85}Zr, ^{169}Hf and ^{261}Rf from column chromatography as a function of [NO$_3^-$] at the constant [F$^-$] of 3.0×10^{-3} M. The K_d values of ^{88}Zr and ^{175}Hf obtained in the batch experiments are plotted by open squares and open triangles, respectively. The values of ^{85}Zr, ^{169}Hf, and ^{261}Rf with the column chromatography are shown by closed symbols. Linear relationships of the logK_d vs. log[NO$_3^-$] for Rf and Zr/Hf are indicated by the solid and dashed lines, respectively. Adapted from ref. 19.
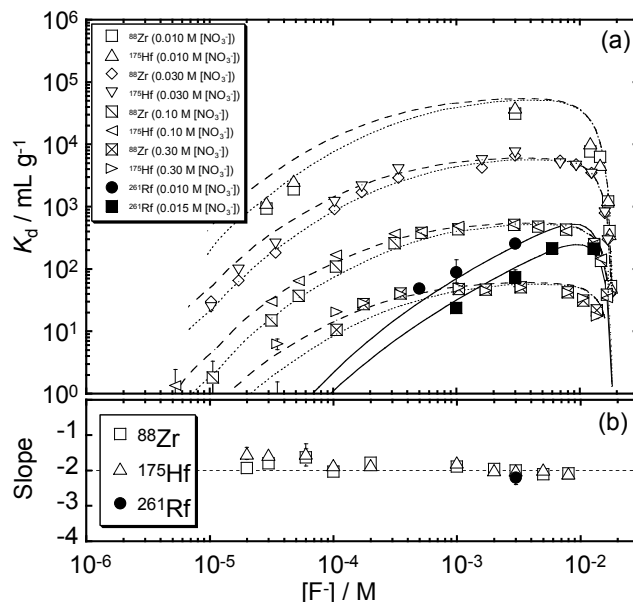

Figure 3. (a) Variation of the K_d values of ^{88}Zr and ^{175}Hf in static conditions and of ^{261}Rf in the column chromatography as a function of the F$^-$ concentration. The K_d values of ^{88}Zr under static conditions at [NO$_3^-$] of 0.010 M, 0.030 M, 0.10 M and 0.30 M are represented by open squares, open diamonds, open squares with diagonal line, and open squares with cross, respectively, and those of ^{175}Hf are shown by open triangles, open inverted triangles, open left-facing triangles, and open right-facing triangles, respectively. K_d values for ^{261}Rf at [NO$_3^-$] of 0.01 M and 0.015 M are depicted by closed circles and closed squares, respectively. The solid, broken, and dotted curves are results of the theoretical calculation for the K_d values of ^{261}Rf, ^{88}Zr, and ^{175}Hf, respectively. (b) Variation of the slopes for Zr, Hf and Rf in the logK_d - log[NO$_3^-$] plot as a function of [F$^-$]. Adapted from ref. 19.

evaluated on the basis of Eq. (3) to be $> 1 \times 10^3$, $< 1 \times 10^2$, $> 1 \times 10^4$, respectively, with the assumptions of $K_n > 10^4$ ($n = 1 - 4$). The K_5,[34] K_6,[34] and D_2 value of Zr are 3.2×10^4, 1.9×10^3, 5×10^5, respectively, and those of Hf[35] are 5.0×10^4, 3.2×10^3, 5×10^5, respectively. It is found that the maximum possible value of the K_6 value of Rf is at least one order of magnitude smaller than K_6 of the homologues. As an example, the results of the calculation for the K_d of Rf using the values of $K_5 = 4 \times 10^3$, K_6

= 2, and $D_2 = 5 \times 10^5$ are shown as solid lines in Figure 3(a).

An ionic radius of Rf^{4+} is evaluated to be larger than those of Zr^{4+} and Hf^{4+} based on the inverse trend between stabilities of the fluoride complexes and crystallographic ionic radii due to the predominant electrostatic interaction between the metallic ion and fluoride ligands. This was also confirmed by our cation-exchange experiment of Rf with comparison with the behavior of Zr, Hf, and Th.[20, 21] The larger ionic radius of Rf^{4+} is consistent with the early theoretical calculation.[36] This calculation predicts that the ionic radius of Rf^{4+} is 79 pm with the coordination number of 6 and is larger than those of Zr^{4+} (72 pm[37]) and Hf^{4+} (71 pm[37]) with the same coordination number by the comparison of the maxima of the charge density in the outermost p orbitals for Ti, Zr, Hf, and Rf to the measured ionic radii of Ti^{4+}, Zr^{4+}, and Hf^{4+}. This is explained due to the orbital expansion of the 6p orbital.[11, 12]

The modern prediction with the fully relativistic density-functional theory showed the trend of Zr > Hf > Rf[38] which is consistent with the observed sequence in the K_6 values, although the theory is assuming hydrolysis to happen in the pH-range where the experiment was performed. In this calculation, free energy changes of the complex formation reactions for fluoride-complexes and hydrolyzed complex are considered. The bond lengths of Rf complexes were taken to be 5 pm larger than those of Hf.[38]

4. Electrolytic oxidation of No

It is quite difficult to investigate the redox properties of the heaviest elements by ordinary electrochemical methods utilized on a macro-amount scale because these elements must be treated with on a single atom scale. Redox reactions of the heaviest elements in aqueous solution have been so far studied using column chromatography with some kinds of oxidizing or reducing agents. Hulet *et al.*[39] and Maly *et al.*[40] determined the redox potential of Md in HCl with V^{2+}-V^{3+} and Ti-TiO_2 couples, respectively. Silva *et al.* showed the oxidation of No^{2+} to No^{3+} and their separation by column chromatography in oxidizing solutions such as H_5IO_6.[41] These methods are, however, time-consuming and complicated, and in some cases have slow kinetics. In this study, therefore, we have developed a rapid and efficient electrochemical approach to determine redox potentials with controlling oxidation states in a chromatographic process.[23] This electrochemistry method was successfully applied to the oxidation of No^{2+} to No^{3+} in 0.1 M α-hydroxyisobutyric (α-HIB) acid solution.[24]

In the experiment, transported products were deposited on a collection site of AIDA[15] for 10 min. After collection, the products were dissolved with 0.1 M α-hydroxyisobutiric acid (α-HIB) (pH 3.9) and were subsequently fed through a thin Teflon tube into a column-type working electrode which was made of glassy carbon fibers modified by Nafion perfluorinated ion-exchange resin.[23] A cross sectional view of the flow electrolytic column apparatus that is based on the ones by Kihara *et al.*[42] is shown in Figure 4. The potential applied to the working electrode was adjusted to 0.2 to 1.2 V referred to a Ag/AgCl electrode in 1.0 M LiCl. The effluent from the column electrode was consecutively collected with a volume of 180 μL on 6 separate Ta discs. The remaining products in the column were stripped with 360 μL of 3.0 M HCl and collected on another 2 Ta discs. The 8 samples were evaporated to dryness using hot helium gas and halogen heat lamps and were then transferred to an α-spectrometry station of AIDA. Counting efficiencies and energy resolution of the detectors were 35% and 100 keV FWHM, respectively. After the α-particle measurement of No, the Ta discs were assayed by γ-ray spectrometry with a Ge detector to monitor elution behavior of ^{162}Yb ($T_{1/2} = 18.9$ min)[25] as the representative trivalent ion and its chemical yields. Prior to the experiment of No and Yb, elu-

tion behavior of ^{81}Sr ($T_{1/2} = 22.1$ min)[25] and ^{162}Yb with 10^6 atoms was investigated to establish a clear separation between the divalent (Sr^{2+}) and trivalent (Yb^{3+}) ions under the identical conditions as those with No and Yb using the present system, the Sr^{2+} expressing the anticipated behavior of No^{2+}. The effluents from the column electrode were collected in plastic tubes and were assayed with γ-ray spectrometry.

Figures 5(a) and 5(b) show the elution behavior of ^{255}No and ^{162}Yb under the applied potentials of (a) 0.2 V and (b) 1.2 V, respectively, while the elution of ^{81}Sr and ^{162}Yb in the separate experiment is depicted in Figure 5(c). From the reference run with ^{81}Sr and ^{162}Yb, the clear separation between the trivalent and divalent ions is obvious; $^{162}Yb^{3+}$ is eluted with 0.1 M α-HIB, while $^{81}Sr^{2+}$ is present in the subsequent strip fraction of 3.0 M HCl. The elution positions of ^{81}Sr and ^{162}Yb are almost

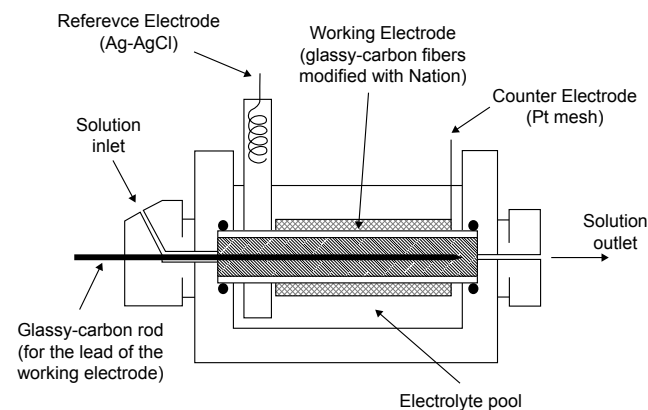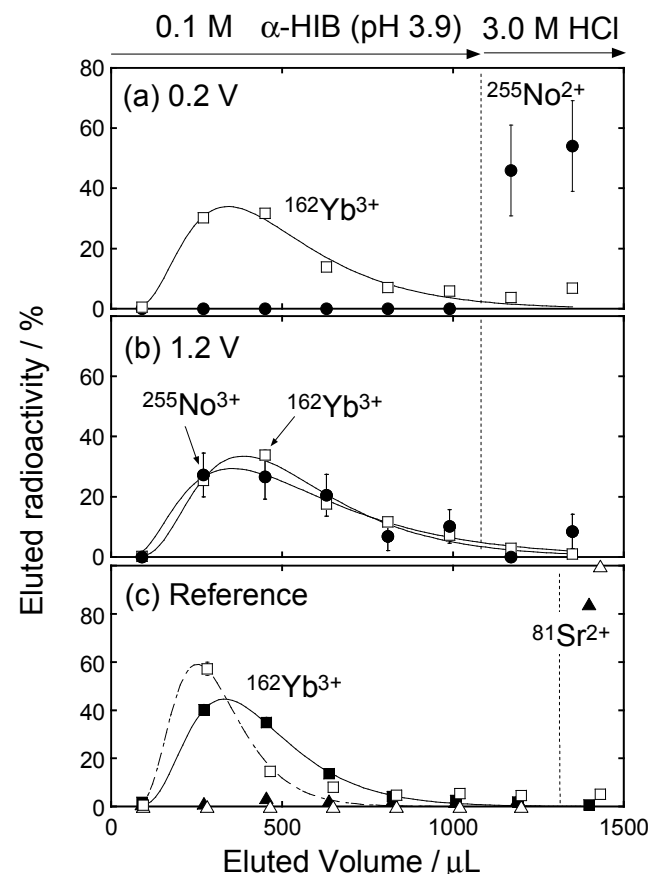**Figure 4.** Schematic view of the electrochemistry apparatus. Adapted from ref. 23.

Figure 5. Elution behavior of ^{255}No and ^{162}Yb at the applied potentials of (a) 0.2 V and (b) 1.2 V. (c) Elution of the typical trivalent $^{162}Yb^{3+}$ and the divalent $^{81}Sr^{2+}$ in the reference experiment: close symbols at 0.2 V, open symbols at 1.2 V. Adapted from ref. 24.

Chemical studies of rutherfordium (Rf) and nobelium (No) on an

J. Nucl. Radiochem. Sci., Vol. 12, No. 1, 2012 **A5**

independent of the applied potentials in the studied range of 0.2 - 1.2 V. At 0.2 V, ^{255}No is detected in the 3.0 M HCl fraction while the monitored ^{162}Yb^{3+} is eluted earlier with α-HIB as shown in Figure 5(a). The adsorption of ^{255}No is the same as that of ^{81}Sr^{2+}, clearly indicating that No is bound in its stable divalent state, which is consistent with the early cation-exchange study.[43] On the other hand, the elution of ^{255}No in the 0.1 M α-HIB fraction is unambiguously observed at 1.2 V at the position of ^{162}Yb^{3+}. This behavior demonstrates that No^{2+} is successfully oxidized to No^{3+} and the trivalent state is complexed in the α-HIB solution with the present apparatus.

Figure 6 shows the oxidation probability of No as a function of the applied potential, that probability defined as 100 × [No^{3+}] / ([No^{2+}] + [No^{3+}]), where [No^{2+}] and [No^{3+}] represent the radioactivities of ^{255}No measured in the 3.0 M HCl and 0.1 M α-HIB fractions, respectively. The oxidation reaction begins at around 0.7 V and is complete by 1.0 V. The formal redox potential of the No^{3+} + e$^-$ ⇄ No^{2+} reaction corresponding to a half of the oxidation probability is evaluated to be approximately 0.75 V under the present conditions. This novel technique has a great potential for investigating redox reactions of transactinide elements in queous solutions.

5. Summary and perspectives

The hexafluoro complex of Rf [RfF$_6$]$^{2-}$ was clearly identified by the slope analysis with the anion-exchange in the HF/HNO$_3$ solutions. The formation constant of the hexafluoro complex of Rf was evaluated to be at least one order of magnitude smaller than those of Zr and Hf. An ionic radius of Rf^{4+} was evaluated to be larger than those of Zr^{4+} and Hf^{4+}, which is in good agreement with the theoretical predictions. The electrolytic column chromatography apparatus was newly developed for the redox studies on a single atom scale. Oxidation experiments of No^{2+} were conducted in 0.1 M α-HIB acid solution using the apparatus. The stable No^{2+} was successfully oxidized to No^{3+} which is held in the α-HIB solution.

In application with a developed technique of the electrolytic column chromatography, an ionic radius of No^{3+} which is a key to understand the contraction of the ionic radii at the end of the actinide series[44] will be determined. Elution position of No^{3+} from a column electrode in α-HIB will be measured by comparison with those of trivalent lanthanides and actinides.

For the elucidation of relativistic effects on stabilities of valence electron orbitals of the transactinide elements, a reduction of Sg will be investigated with the isotope ^{265}Sg produced in the ^{248}Cm(^{22}Ne, 5n) reaction. A flow electrolytic-column apparatus combined with a continuous extraction apparatus of SISAK [45, 46] will be utilized to overcome experimental difficulty due to the short half-life (~15 s) and the extremely small production yield (~1 atom/h).
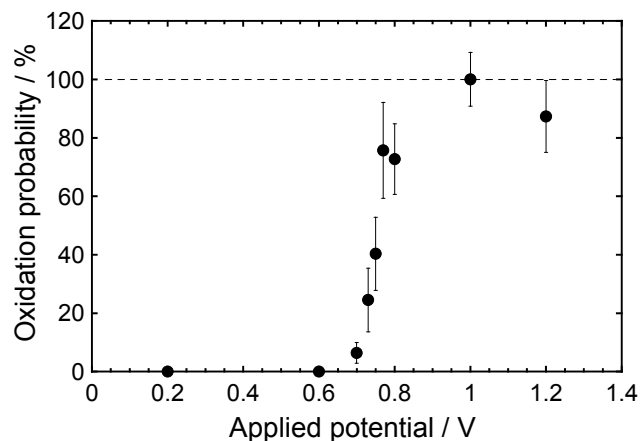
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Figure 6. Oxidation probability of ^{255}No vs. applied potentials. Adapted from ref. 24.

in Research and Development in the Field of Ion Beam Application.

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