Oxidation of Element 102, Nobelium, with Flow Electrolytic Column Chromatography on an Atom-at-a-Time Scale

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Chemical studies of the heaviest elements are extremely interesting and challenging subjects in modern inorganic and nuclear chemistry.[1] A most important and fascinating aspect is the determination of the chemical properties of newly synthesized elements at the uppermost end of the periodic table and the elucidatation of the influence of relativistic effects on the valence electrons of these heavy elements.[2] The heaviest elements above element 100, fermium (Fm), however, must be produced at accelerators in heavy-ion-induced nuclear reactions and are available only as short-lived isotopes in quantities of a few atoms at a time. In addition, each available atom must be chemically equilibrated rapidly within its lifetime. Such restricted experimental conditions make it remarkably difficult to characterize the chemical properties of the heaviest elements.

The ionic radii of the trivalent actinide ions decrease with increasing atomic number. This behavior is known as the actinide contraction and is partly affected by relativistic effects.[3a,b] The determination of the ionic radii of the heaviest actinides is of particular interest to experimentally assess the magnitude of the contraction. The ionic radii of the heaviest actinides $_{100}Fm^{3+}$, $_{101}Md^{3+}$, and $_{103}Lr^{3+}$ have been measured[4] with a few tens of atoms on the basis of their elution positions in cation-exchange chromatography with α-hydroxyisobutyric acid (α-HIB) solution as a mobile phase that has high selectivity for trivalent metal cations. These elements were eluted in the sequence of their ionic radii, those with the smallest radii being eluted first.[5] Surprisingly, it has been reported that the elution position of the last actinide, Lr^{3+}, apparently deviates from the expected position deduced simply from the monotonically decreasing feature of the ionic radii from $_{98}Cf^{3+}$ to $_{101}Md^{3+}$;[6] the anomalously larger ionic radius for Lr^{3+} has been determined.[4,7a,b] However, no conclusive explanation for the sudden change of the contraction was obtained, although a comparison to theoretical calculations and the possibility of relatively less polarizability of the filled 5f orbital of Lr^{3+} were considered.[4] The measurement of the ionic radius of $_{102}No^{3+}$ is, therefore, of key interest to explore contractions of the ionic radii in the heaviest actinides. Because of the strong stability of the 5f electron shell, however, the divalent state is the most stable for No in aqueous solution. Though the pioneering studies by Maly et al.[8a] and Silva et al.[8b] demonstrated that No^{2+} can be oxidized to the trivalent state by some kinds of oxidants, the reported methods cannot be applied to the chromatographic separation with α-HIB to determine

the ionic radius of No^{3+} because α-HIB is not stable under strongly oxidizing and acidic conditions. Thus, an approach using a rapid and efficient electrochemical technique with α-HIB that can control oxidation states in a chromatographic process is mandated.

Very recently, we developed a new electrochemical apparatus based on flow electrolytic column chromatography.[9,10] Glassy-carbon fibers chemically modified with Nafion perfluorinated ion-exchange resin were employed as a working electrode as well as a cation-exchanger. An attempt was made to oxidize Ce^{3+} to Ce^{4+} using a radiotracer of ^{139}Ce (10^{10} atoms) in 0.1 M α-HIB solution. The oxidation of Ce^{3+} and the separation of the two states by holding Ce^{4+} on the column electrode above an appropriate applied potential were successfully conducted.[9] In the present study, we have applied this technique to the oxidation of No^{2+} by controlling the applied potential.

The isotope ^{255}No with a half-life ($T_{1/2}$) of 3.1 min was synthesized in a nuclear fusion reaction between ^{12}C ions and a ^{248}Cm target at the JAEA tandem accelerator with a typical production rate of 30 atoms/min. Nuclear reaction products recoiling out of the target were attached to potassium chloride (KCl) aerosols seeded in a helium gas stream and were then continuously transported to the chemistry laboratory through a Teflon capillary (2.0 mm i.d. × 25 m) within a few seconds. For 10 min, the transported products were deposited on a plastic plate of a rapid chemistry assembly.[11] After collection, the products were dissolved with 1080 μL of 0.1 M α-HIB (pH 3.9) and subsequently fed through a thin Teflon tube into the column-type working electrode composed of the glassy carbon fibers (11 μm in diameter) modified with Nafion at a flow rate of 600 μL/min.[9,10] The fibers were packed into a porous Vycol glass tube (4.8 mm i.d. × 30 mm). As a counter electrode, a Pt mesh was used to surround the glass tube in α-HIB solution.[9,10] The potential applied to the working electrode was adjusted to 0.2−1.2 V (vs 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 six separate Ta discs. The remaining products in the column were stripped with 360 μL of 3.0 M HCl and collected on another two Ta discs. The eight samples were evaporated to dryness using hot helium gas and halogen heat lamps and were then transferred to an α-spectrometry station equipped with eight 600 mm^2 passivated implanted planar silicon (PIPS) detectors[11] to identify ^{255}No through its α-decay energy. All events were registered event by event. The above procedures were accomplished within 3 min and repeated numerous times to obtain sufficient statistics for the α-decay counts of ^{255}No. The counting efficiency and energy resolution of the detectors were 35% and 100 keV fwhm, respectively. The ^{248}Cm target contained Gd to

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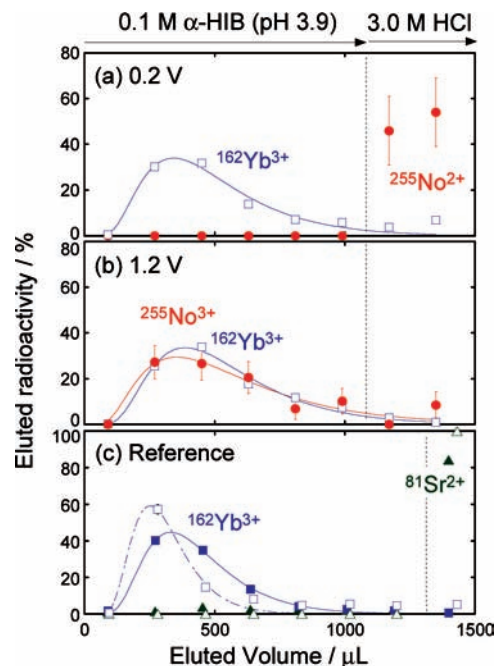[||] Tokyo Metropolitan University.

Figure 1. Elution behavior of ^{255}No and ^{162}Yb at applied potentials of (a) 0.2 and (b) 1.2 V. (c) Elution of the typical trivalent cation ^{162}Yb^{3+} and divalent ^{81}Sr^{2+} in the reference experiment, with solid symbols showing data at 0.2 V and open symbols data at 1.2 V.

simultaneously produce ^{162}Yb ($T_{1/2} = 18.9$ min) as the representative trivalent ion (nobelium is "eka-ytterbium") through the Gd(^{12}C, xn) reaction. After the α-particle measurement for No, the discs were assayed by γ-ray spectrometry with a Ge detector to monitor the elution behavior of ^{162}Yb^{3+} and its chemical yield. The chemical yield including the sample preparation was ∼50%. Prior to the experiments with No and Yb, the elution behavior of ^{81}Sr ($T_{1/2} = 22.2$ min) and ^{162}Yb with 10^6 atoms was investigated to establish a clear separation between divalent (Sr^{2+}) and trivalent (Yb^{3+}) ions in the present system, with the Sr^{2+} expressing the anticipated behavior of No^{2+}. The nuclides ^{81}Sr and ^{162}Yb were produced in the Ge(^{12}C, xn) and Gd(^{12}C, xn) reactions, respectively. The elution behavior was established by assaying effluent samples in plastic tubes with γ-ray spectrometry.

Figure 1a,b shows the elution behavior of ^{255}No and ^{162}Yb under applied potentials of 0.2 and 1.2 V, respectively, while the elution of ^{81}Sr and ^{162}Yb in the separate experiment is depicted in Figure 1c. From the reference run with ^{81}Sr and ^{162}Yb, the clear separation between the trivalent and divalent ions is obvious: ^{162}Yb^{3+} was eluted with 0.1 M α-HIB, while ^{81}Sr^{2+} was present in the subsequent strip fraction of 3.0 M HCl. The elution positions of ^{81}Sr and ^{162}Yb were almost independent of the applied potentials in the studied range of 0.2−1.2 V. At 0.2 V, ^{255}No was detected in the 3.0 M HCl fraction while the monitored ^{162}Yb^{3+} was eluted earlier with α-HIB, as shown in Figure 1a. The adsorption of ^{255}No was the same as that of ^{81}Sr^{2+}, clearly indicating that No was bound in its stable divalent state, which is consistent with the early cation-exchange study.[8a] On the other hand, the elution of ^{255}No in the 0.1 M α-HIB fraction was unambiguously observed at 1.2 V at the position of ^{162}Yb^{3+}. This behavior demonstrated that No^{2+} was successfully oxidized to No^{3+} and that the trivalent state was complexed in the α-HIB solution with the present apparatus.
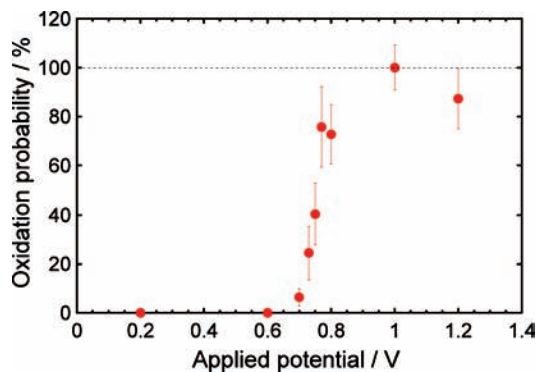

Figure 2. Oxidation probability of ^{255}No vs applied potential.

Figure 2 shows the oxidation probability of No as a function of the applied potential, where that probability is 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 began at ∼0.7 V and was complete by 1.0 V. The formal redox potential of the No^{3+} + e$^-$ ⇌ No^{2+} reaction corresponding to half of the oxidation probability was evaluated to be ∼0.75 V under the present conditions.

In conclusion, the most stable nobelium ion, No^{2+}, was successfully oxidized to the trivalent state, No^{3+}, which was held in the α-HIB solution by the newly developed flow electrolytic chromatography technique. It was found that the oxidation state of No on an atom-at-a-time scale is absolutely controlled by the employed apparatus. The present new approach will lead to the determination of the ionic radius of No^{3+}, which is a key to understanding the contraction of the ionic radii at the end of the actinide series.

Supporting Information Available: Supporting figures and complete ref 11. This material is available free of charge via the Internet at http://pubs.acs.org.

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