7-1 Analyzing Supherheavy Atoms on an Atom-at-a-Time Scale — Oxidation of Nobelium with Flow Electrolytic Chromatography—

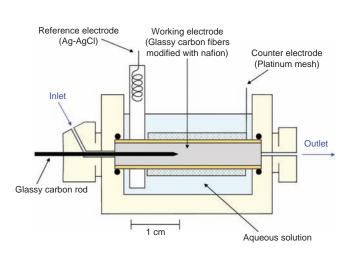


Fig.7-3 Flow electrolytic chromatograph apparatus Single atoms injected from the inlet pass through the columntype working electrode modified with Nafion cation-exchanger, where single ions are electrolyzed and chemically separated.

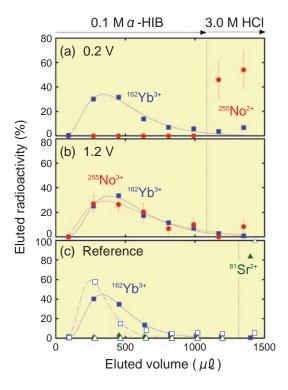


Fig.7-4 Elution behavior of No, Sr^{2*} , and Yb^{3*} Elution behavior of No(\bigcirc) and $Yb^{3*}(\bigcirc$) at the applied potentials of (a) 0.2 V and (b) 1.2 V. (c) Behavior of Sr^{2*} (0.2 V: \triangle , 1.2 V: \blacktriangle) and Yb^{3*} (0.2 V: \bigcirc , 1.2 V: \bigcirc).

The electron configuration of superheavy elements placed at the uppermost end of the periodic table is predicted to be intensely affected by strong relativistic effects. Redox properties sensitive to the electron configuration are, therefore, important in elucidating the influence of the relativistic effects. Because an atom-at-a-time scale is used with these elements, however, their redox properties had not been studied previously. Here we report the oxidation of element 102, nobelium (No), using flow electrolytic chromatography on an atom-at-a-time scale.

We produced nobelium - 255 (²⁵⁵No) with a half-life of ~3 min in a nuclear reaction of carbon-12 (¹²C) and curium-248 (²⁴⁸Cm) at the JAEA tandem accelerator. No was dissolved with 0.1 M α -hydroxyisobutyric acid (α -HIB) and was then injected into the flow electrolytic chromatography apparatus shown in Fig.7-3. The No²⁺ ion passed through a column-type working electrode composed of thin carbon fibers modified with Nafion cation-exchanger where No²⁺ is electrolyzed to No³⁺ and these ions are separated from each other. After elution with α -HIB, adsorbed ions on the electrode were stripped with 3.0 M HCl.

In Figs.7-4(a) and (b), the elution behavior of No and Yb³⁺ are shown, while that of Sr²⁺ and Yb³⁺ are plotted as a reference in Fig.7-4(c). Quite different behavior between Sr²⁺ and Yb³⁺ indicates clear separation between +2 and +3 ions under the given conditions. At the applied potential of 0.2 V, No is not eluted with α -HIB and is stripped with 3.0 M HCl. This behavior is quite similar to that of Sr²⁺, showing that No is bound in a stable +2 state. On the other hand, at 1.2 V, No is eluted with α -HIB at the position of Yb³⁺, which unambiguously indicates that No is oxidized to the +3 state. These results demonstrate successful electrochemical oxidation on an atom-at-a-time scale for the first time.

In the future, we will clarify the redox properties of other superheavy elements by applying this newly developed electrochemistry approach.

Reference

Toyoshima, A. et al., Oxidation of Element 102, Nobelium, with Flow Electrolytic Column Chromatography on an Atom-at-a-Time Scale, Journal of the American Chemical Society, vol.131, no.26, 2009, p.9180-9181.