

# Solid-liquid extraction of $^{85}\text{Sr}$ and $^{133}\text{Ba}$ with DGA-resin towards the chemical study of element 102, nobelium

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Element 102, nobelium (No), is an actinide with unique chemical properties. No exhibits a +2 oxidation state in aqueous solutions, and its chemical behavior resembles that of group 2 elements, with an ionic radius intermediate between  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$ . However,  $\text{No}^{2+}$  may have a softer acidic nature, contrasting with the hard acid characteristics of group 2 metal ions. Further research is required to understand the chemical properties of No, which can be affected by relativistic effects. For a systematic chemical study of No, we propose extraction with diglycolamide (DGA) ligands, because they enable various structural modifications to tune extraction properties. For the chemical study of elements with  $Z > 100$ , rapid and automated experiments at accelerators are required, which are called “online experiments.”<sup>1)</sup>

This study aims to investigate the solid-liquid extraction of group 2 elements from nitric acid by DGA-resin towards an online experiment with  $^{255}\text{No}$ . For that, batch experiments with  $^{85}\text{Sr}$  and  $^{133}\text{Ba}$  radio-tracers were conducted, and quantum chemical calculations of the extracted M(II)-DGA complexes were performed.

Solid-liquid extraction was performed with the DGA-resin, normal (TODGA-resin), as the solid phase and  $^{85}\text{Sr}(\text{II})$  and  $^{133}\text{Ba}(\text{II})$  tracer solutions as the liquid phase in the range of the nitric acid concentration of  $0.2\text{--}4\text{ mol}\cdot\text{L}^{-1}$  and extraction time of 1–75 min.  $^{85}\text{Sr}$  and  $^{133}\text{Ba}$  were produced in the  $^{nat}\text{Rb}(d, xn)$  and  $^{133}\text{Cs}(d, 2n)$  reactions, respectively, at the RIKEN AVF cyclotron. Scalar-relativistic density functional theory (DFT) calculations of  $[\text{M}(\text{TEDGA})_3]^{2+}$  complexes with triple-zeta valence plus polarization basis functions were performed for geometry optimization (BP86) and single point calculations (B3LYP) using ORCA v5.0 program.

The nitric acid concentration dependencies of the weight distribution ratios ( $K_d$ ) of Sr(II) and Ba(II) extracted by DGA-resin are shown in Fig. 1. The  $K_d$  values of Sr(II) are higher than those of Ba(II). The  $K_d$  values obtained here in the batch extraction experiments agree with those reported for an extraction chromatography study using DGA-resin.<sup>2)</sup> Based on the slope analysis, it is suggested that Sr(II) and Ba(II) are extracted with two equivalents of  $\text{NO}_3^-$  ions for complex neutrality. The time required to reach extraction equilibrium for  $^{85}\text{Sr}$  and  $^{133}\text{Ba}$  extraction is evaluated to be  $<3$  min, which is sufficient for an on-

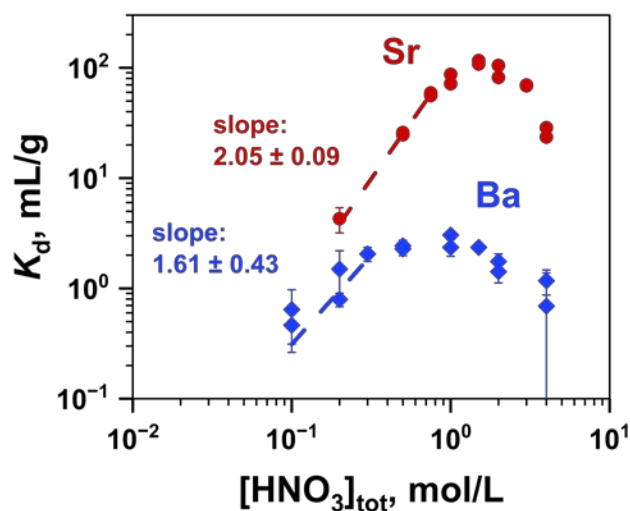


Fig. 1. Nitric acid concentration dependency for the weight distribution ratios of  $^{85}\text{Sr}(\text{II})$  and  $^{133}\text{Ba}(\text{II})$  in extraction by DGA-resin ( $T = 25^\circ\text{C}$ ).

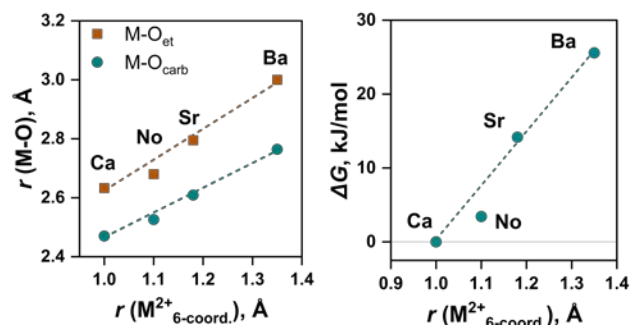


Fig. 2. DFT calculation results of  $[\text{M}(\text{TEDGA})_3]^{2+}$  complexes. A) Coordination bond lengths in the optimized structures. B) Relative stability of complexes.

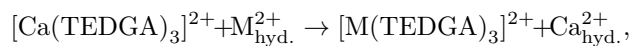
line experiment with  $^{255}\text{No}$  ( $T_{1/2} = 3.5$  min).

To support and validate extraction results, DFT calculations were conducted. Optimized geometries of  $[\text{M}(\text{DGA})_3]^{2+}$  complexes ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba},$  and  $\text{No}$ ) were obtained and bonding analyses were performed (Fig. 2A). The bond lengths of  $\text{M}^{2+}$  ( $\text{M} = \text{Ca}, \text{Sr},$  and  $\text{Ba}$ ) with the donor ether and carbonyl oxygen atoms ( $\text{O}_{\text{et}}$  and  $\text{O}_{\text{carb}}$ , respectively) of DGA ligand are in linear correlation with ionic radii, indicating an ionic interaction. The lengths of bonds formed by  $\text{No}(\text{II})$  were found to be shorter than expected by the linear trend, which suggests a stronger bonding ability

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of No(II). Next, the relative stability of the complexes was studied by calculating the Gibbs energy change of the following exchange reaction:



where  $\text{M}_{\text{hyd}}^{2+}$  states for  $[\text{M}(\text{H}_2\text{O})_8]^{2+}$ ,  $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ , and  $\text{No}$  (Fig. 2B). The stability of DGA complexes of group 2 metal ions decreases in the order  $\text{Ca(II)} > \text{Sr(II)} > \text{Ba(II)}$ , reproducing the trend of distribution ratios in extraction.<sup>2)</sup> As for the No(II) complex, it appears to be more stable than suggested by the almost linear trend of Ca(II)-Sr(II)-Ba(II), which is consistent with the bonding analysis.

#### References

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- 2) E. P. Horwitz *et al.*, *Solvent Extr. Ion Exch.* **23**, 319 (2005).