

## The Ionic Radius of $\text{No}^{3+}$

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Nobelium ( $^{259}\text{No}$ ,  $T_{1/2} = 58$  min) was produced in bombardment of  $^{248}\text{Cm}$  target with  $^{18}\text{O}^{5+}$  ions. Next, it was oxidised by  $\text{H}_5\text{IO}_6$  and loaded together with lanthanide tracers on a chromatographic column filled with cryptomelane  $\text{MnO}_2$ . In the  $\text{HNO}_3$  elution curve two peaks are observed. First one is related to the nonoxidized  $\text{No}^{2+}$  and the second corresponds to  $\text{No}^{3+}$  close to positions of elution peaks of  $\text{Ho}^{3+}$  and  $\text{Y}^{3+}$ . The ionic radius deduced from the elution position of  $\text{No}^{3+}$  is to be  $89.4 \pm 0.7$  pm.

### 1. Introduction

Studies of the heaviest actinides and comparison with the properties of lanthanides are interesting because they help to understand the influence of relativistic effects on the chemical properties. The relativistic effects influence the contraction of the 3+ lanthanides and actinides ionic radii by two ways: splitting of outermost  $p$  orbitals and stabilization of  $p_{1/2}$  orbitals, and expanding the  $f_{5/2}$  and  $f_{7/2}$  orbitals which results in less effective shielding of the nuclear charge. For the heaviest actinides these might result in ionic radii different from non-relativistic extrapolations. For example, in the case of  $\text{Fm}^{3+}$  the relativistic effect is responsible for 8 pm contraction of the ionic radius, while for  $\text{Er}^{3+}$  only 2.5 pm. The determination of the ionic radius of  $\text{No}^{3+}$  ion is of key interest, particularly since the ionic radius of  $\text{Lr}^{3+}$  has been determined.<sup>1</sup> This measurement would conclude the ionic radius determinations of the 3+ actinide ions.

The ground state electronic configuration of nobelium is  $[\text{Rn}]5f^{14}7s^2$ . Energy of  $5f_{7/2}$  orbitals in nobelium ( $-15.43$  eV) is more negative than  $4f_{7/2}$  orbitals in ytterbium ( $-14.67$  eV) (homologue in lanthanide series) which causes that nobelium as the only one among  $f$  electron cations is very stable in the oxidation state 2+. The redox potential of the  $\text{No}^{2+}/\text{No}^{3+}$  couple was determined to be  $1.4 \pm 0.2$  V.<sup>2</sup> This aspect of nobelium chemistry provides special problems for the determination of the  $\text{No}^{3+}$  ionic radius. In the determination experiment first  $\text{No}^{2+}$  must be oxidized to the  $\text{No}^{3+}$ . This can be accomplished with the use of strong oxidizing agent such as  $\text{KMnO}_4$  (1.5 V) or  $\text{H}_5\text{IO}_6$  (1.7 V). The second problem is to stabilize in the 3+ oxidation state during the determination experiment.

Ionic radii are usually obtained from X-ray diffraction data for oxides or fluorides. However, these techniques require weighable quantities of the compound. Unfortunately, elements heavier than fermium are produced in quantities of few atoms at a time, so that experimental structural data for these elements are not available. The values of ionic radii for  $\text{Md}^{2+}$ ,  $\text{Md}^{3+}$ ,  $\text{No}^{2+}$ , and  $\text{Lr}^{3+}$  were determined only by chromatographic methods.<sup>1,3,4</sup> The ionic radii of  $\text{Md}^{3+}$  and  $\text{Lr}^{3+}$  were determined by comparing their elution positions with the positions of rare earth tracers and of actinides of known ionic radii. The ionic radii of  $\text{Md}^{2+}$  and  $\text{No}^{2+}$  were determined by comparison with crystallographic radii of  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  (Ref. 3, 4).

For the determination of ionic radius of  $\text{No}^{3+}$ , Henderson<sup>5</sup> used ion exchange chromatography with  $\text{KMnO}_4$  and  $\text{H}_5\text{IO}_6$  as oxidizing agents and  $\alpha$ -HIB as eluent. Unfortunately, these strong oxidants decomposed both the  $\alpha$ -HIB and the ion exchange resin and, therefore, the determination of  $\text{No}^{3+}$  ionic radius could not be accomplished using this approach.

In our laboratory, samples of cryptomelane-type  $\text{MnO}_2$  inorganic ion exchanger were synthesized. This sorbent is known

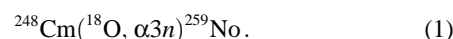
to possess interesting ion exchange properties. The cryptomelane  $\text{MnO}_2$  phase has a well-defined  $2 \times 2$  tunnel-framed structure with exchangeable hydrogen, alkali, or alkali earth cations.<sup>6</sup> The presence of exchangeable ions in the tunnels requires that some of the manganese atoms must be present in oxidation states lower than 4. The formulae could be represented by  $\text{HMn}^{\text{IV}}\text{Mn}^{\text{III}}\text{O}_{16}$  as postulated by Tsuji and Tamaura.<sup>7</sup> The average tunnel diameter is 0.28 nm so the selectivity of the sorbent is related to the steric effect in the tunnel structure.<sup>8</sup> Cryptomelane  $\text{MnO}_2$  has been demonstrated to show excellent ion-exchange selectivity towards cations with crystal ionic radii of 130–150 pm, e.g.  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ba}^{2+}$ , and  $\text{Ra}^{2+}$  (Ref. 6–8). For 3+ lanthanides and actinides the distribution coefficients are much lower, but strongly depend on the radius of cations. Additionally, in acidic solutions the sorbent exhibits both ion exchange and strong oxidizing properties, so  $\text{No}^{3+}$  should be stabilized in cryptomelane  $\text{MnO}_2$  phase. In the present work, cryptomelane-type  $\text{MnO}_2$  is used for the determination of  $\text{No}^{3+}$  ionic radius by chromatographic methods.

### 2. Experimental

**2.1. Synthesis of Cryptomelane Manganese Dioxide.** Manganese dioxide samples were synthesized according to the procedure used by Tsuji and Abe.<sup>9</sup> The precipitates were obtained by adding 250 cm<sup>3</sup> of 0.5 M  $\text{KMnO}_4$  in 1 M  $\text{H}_2\text{SO}_4$  to 250 cm<sup>3</sup> of 1 M  $\text{MnSO}_4$  solution containing 1 M of  $\text{H}_2\text{SO}_4$  at 60 °C. The precipitates were then aged overnight, filtered, and washed with water. The product was dried at ca 70 °C for three days, and then ground and sieved. The samples were transformed to the  $\text{H}^+$  form by percolating 6 M  $\text{HNO}_3$  solution.

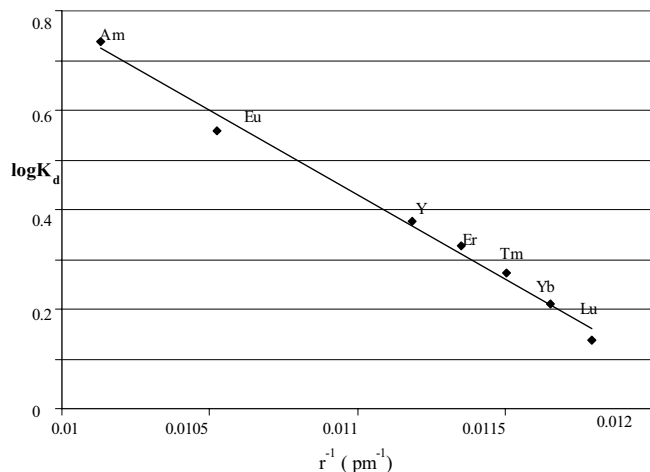
**2.2. Radioactive Tracers.** The radionuclides of  $^{89}\text{Sr}$ ,  $^{46}\text{Ca}$ ,  $^{90}\text{Y}$ ,  $^{177}\text{Lu}$ ,  $^{169}\text{Yb}$ ,  $^{170}\text{Tm}$ ,  $^{166\text{m}}\text{Ho}$ ,  $^{152}\text{Eu}$ , and  $^{241}\text{Am}$  were purchased from Isotope Products in Swierk, Poland. All tracers were stored in 6 M  $\text{HNO}_3$  solutions to prevent them from hydrolysis.

**2.3. Production of  $^{259}\text{No}$ .** The  $^{259}\text{No}$  ( $T_{1/2} = 58$  min) atoms were obtained by  $^{18}\text{O}$  irradiation of  $^{248}\text{Cm}$  target in reaction:



The experiments were carried out at Philips cyclotron at the Paul Scherrer Institute, Villigen (Switzerland). Target of 0.730 mg·cm<sup>-2</sup>  $^{248}\text{Cm}$  was irradiated for 2.5 h with  $^{18}\text{O}^{5+}$  ions. The beam energy on target was 99 MeV, and the beam intensity was  $1 \times 10^{12}$  particles per second. Under these conditions,  $^{259}\text{No}$  is produced with the cross section of about 30 nb. The target contained 10% of Gd thus producing simultaneously  $^{165,167}\text{Yb}$  and  $^{165,167}\text{Lu}$ . The reaction products recoiling out from the target were stopped in He gas and transported to the chemistry collection site by a KCl aerosol-seeded gas-jet system. The aerosol with reaction products was collected on a glass filter.

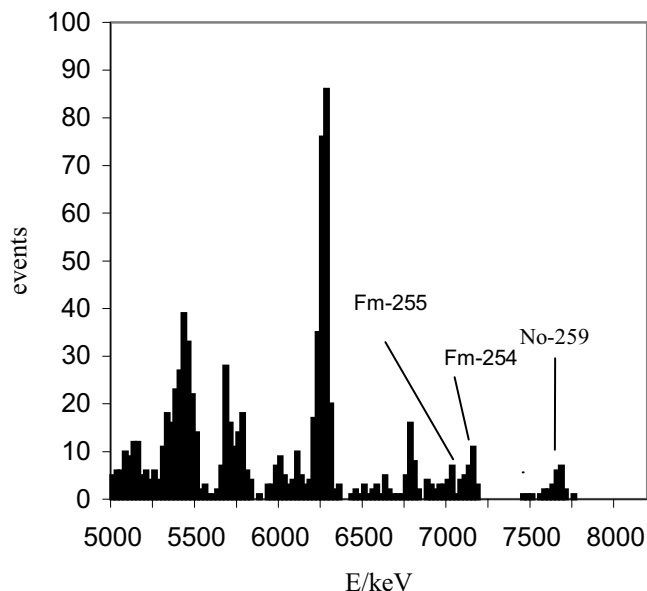
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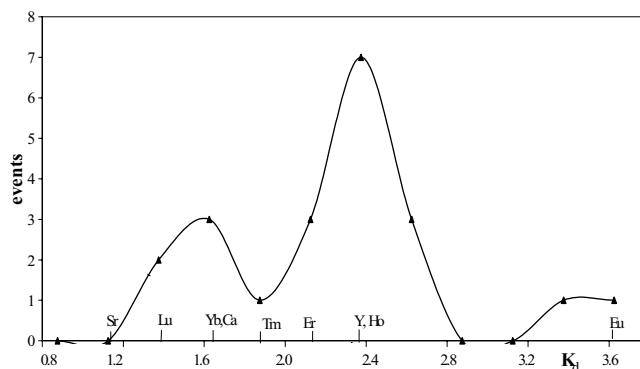
**Figure 1.** Dependence of logarithm of distribution coefficient on reciprocal crystal ionic radius for lanthanides, yttrium, and americium.

**2.4. Chromatographic Procedure.** A small glass column (3 mm × 5 cm) was filled with 0.5 g cryptomelane MnO<sub>2</sub> (0.01–0.05 mm) and preconditioned with solution of HNO<sub>3</sub>. The lanthanides and americium tracers were dissolved in 0.5 M HNO<sub>3</sub>, evaporated, and dissolved in 20 μL of 0.5 M HNO<sub>3</sub> and 0.05 M H<sub>2</sub>IO<sub>6</sub>. Next, the solution was placed on the top of the column. The radionuclides were subsequently eluted from the column with 0.5 M HNO<sub>3</sub> solution at a flow rate of 0.1 cm<sup>3</sup> min<sup>-1</sup>. Drop fractions from the column were collected and measured by γ spectrometry or by liquid scintillation counting (<sup>46</sup>Ca, <sup>90</sup>Y).

The same chromatographic procedure was used in nobelium experiments. The aerosol, together with the reaction products, was dissolved in 2 cm<sup>3</sup> of 0.5 M HNO<sub>3</sub>, evaporated, and dissolved in 20 μL of 0.5 M HNO<sub>3</sub> and 0.05 M H<sub>2</sub>IO<sub>6</sub>. The drops from the column were collected on stainless steel disc and evaporated on a hot plate. After evaporation the samples were inserted into the detector array for α spectroscopy, consisting 6 Si(Au)-surface barrier detectors, for 2.5 h measurement. The α events, together with the detector numbers and the associated time, were recorded. Spontaneous fission events were also recorded. Before α measurement the γ activity was measured by Ge(Li) detector for 1 min. The whole procedure, from the end of bombardment until the start of α spectroscopy, lasted about 40 min. The distribution coefficient ( $K_d$ ) between two phases in



**Figure 2.** Alpha particle spectrum of the elution fractions containing <sup>259</sup>No.



**Figure 3.** Sum of the elution curves from the experiments where <sup>259</sup>No was detected.

chromatographic system is defined as:

$$K_d = \frac{V_m - V_f}{V_s} \quad (2)$$

where  $V_m$  and  $V_s$  are the volumes of the mobile and the stationary phase, respectively, and  $V_f$  is the free column volume.

### 3. Results

The selectivity for the cations on cryptomelane MnO<sub>2</sub> strongly depends on the ionic radii of the exchanged cations. Because the diameter of the tunnel in the MnO<sub>2</sub> phase (280 pm) is similar to diameters of the metal cations, the selectivity of the sorbent is associated with the steric effect. The hydrated 3+ metal cations with diameter much larger than 280 pm must be dehydrated before entering the ion exchange phase. Therefore, the selectivity of the cryptomelane MnO<sub>2</sub> depends linearly on free energy of hydration,<sup>10</sup> which is also linearly related to the reciprocal of crystal ionic radius. The linearity of  $\log K_d$  on ionic radii for *f* electron cations was also found by Tsuji et al.<sup>11</sup> There are numerous data for ionic radii of the cations. The values commonly used are Shannon radii.<sup>12</sup> In case of heaviest actinides (Es<sup>3+</sup>, Fm<sup>3+</sup>, Md<sup>3+</sup>, and Lr<sup>3+</sup>) all available experimental ionic radii are given in the Templeton and Dauben<sup>13</sup> scale. In order to allow comparison we also used the Templeton and Dauben scale to present the ionic radii of the lanthanides and actinides cations studied. As mentioned earlier<sup>1</sup> it is known that the coordination number (CN) for the heavy trivalent lanthanides and actinides is 8. Although there is no experimental data on the CN of Md<sup>3+</sup>, No<sup>3+</sup>, and Lr<sup>3+</sup>, it is assumed that CN is also 8. Then, the  $\log K_d$  vs.  $(1/r)$  should be linear for the respective cations. A plot of  $\log K_d$  versus reciprocal crystal ionic radius for lanthanides, yttrium, and americium is shown in Figure 1. There is a good linear correlation for all the cations studied. The chromatographic columns calibrated previously for lanthanides tracers were used in experiments with nobelium. We performed 11 accumulation and chromatographic cycles during which we observed the decay of 22 atoms of <sup>259</sup>No. In Figure 2, the sum α spectra of all No fractions obtained in the elution processes are given. The analysis of <sup>259</sup>No α spectra is difficult since its α branch consists of five lines covering the energy range from 7.455 to 7.685 MeV.<sup>14</sup> The possible interference is only from <sup>250</sup>Fm (7.390 and 7.430 MeV). Other possible interfering nuclides decayed within experimental time (40 min). Taking into account the FWHM of the α spectra (25 keV) and the possible interference at 7.430 MeV, the events in the range 7.460–7.690 MeV were considered. From the γ-spectroscopy measurement the elution positions of <sup>165,167</sup>Yb and <sup>165,167</sup>Lu, produced in the <sup>nat</sup>Gd + <sup>18</sup>O reaction, were obtained to make sure that the column behaved as in the calibration runs, and to give markers in the elution so that all elutions could be compared on the same basis. During synthesis of <sup>259</sup>No also Fm, Es, and Cf nuclides were produced as transfer products. In collected fractions maximum of <sup>250</sup>Cf activity was found near Eu<sup>3+</sup> fraction and <sup>255</sup>Fm

close to  $\text{Dy}^{3+}$  so the elution positions of actinides are consistent with the elution positions of respective lanthanides.

The sum of the elution curves from the experiments where  $^{259}\text{No}$  was detected is presented in Figure 3. The elution curve is presented in the  $K_d$  scale because  $V_f$  and  $V_i$  of the column were not identical. As shown in the Figure 3 two maxima are observed. First — small one is probably related to the nonoxidized  $\text{No}^{2+}$  because it is seen between the fractions where cations  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  are eluted. The value of  $\text{No}^{2+}$  radius (105 pm) is between radii of the  $\text{Ca}^{2+}$  (100 pm) and  $\text{Sr}^{2+}$  (118 pm). The second maximum corresponds to  $\text{No}^{3+}$  and is eluted near the fraction where  $\text{Ho}^{3+}$  and  $\text{Y}^{3+}$  are eluted. The logarithm of distribution coefficient of  $\text{No}^{3+}$  was converted to an ionic radius from the slope and intercept of the line, yielding  $89.4 \pm 0.7$  pm in Templeton and Dauben scale or  $90.0 \pm 0.7$  pm in Shannon scale. The error limits on radius value represent the uncertainty in the elution positions as measured from separate experiments and the distribution of the observed No data points. Unfortunately, the uncertainty in the determination of  $\text{No}^{3+}$  radius is much larger than the error of determination in the case of  $\text{Md}^{3+}$  and  $\text{Lr}^{3+}$  radii ( $\pm 0.1$  pm).<sup>1</sup> This results from the slower kinetics observed on the cryptomelane  $\text{MnO}_2$  than on the ion exchange resin as well as from the lower selectivity of cryptomelane  $\text{MnO}_2$  to  $\text{M}^{3+}$  cations compared to the selectivity of complexation with  $\alpha\text{-HIB}$ . The  $\text{No}^{3+}$  radius value determined lies between radii of  $\text{Md}^{3+}$  and  $\text{Lr}^{3+}$ , closer to that of  $\text{Md}^{3+}$ .

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## References

- (1) W. Brüchle, M. Schädel, U. W. Scherer, J. V. Kratz, K. E. Gregorich, D. M. Lee, M. J. Nurmiä, R. M. Chasteler, H. L. Hall, R. A. Henderson, and D. C. Hoffman, *Inorg. Chim. Acta* **146**, 267 (1988).
- (2) R. J. Silva, T. Sikkeland, M. Nurmiä, A. Ghiorso, and E. K. Hulet, *J. Inorg. Nucl. Chem.* **31**, 3405 (1969).
- (3) R. J. Silva, W. J. McDowell, O. L. Keller, and J. R. Tarrant, *Inorg. Chem.* **13**, 3405 (1969).
- (4) L. I. Gusieva, G. S. Tikhomirova, G. V. Buklanov, Zen Zin Phar, I. A. Lebedev, N. V. Katargin, and B. F. Myasoedov, *J. Radioanal. Nucl. Chem. (Lett.)* **117**, 205 (1987).
- (5) R. A. Henderson, LBL-29568 (1990).
- (6) M. Tsuji, S. Komarneni, and M. Abe, *Solvent Extr. Ion Exch.* **11**, 143 (1993).
- (7) M. Tsuji and Y. Tamaura, *Solvent Extr. Ion Exch.* **18**, 187 (2000).
- (8) B. Bartoś, A. Bilewicz, R. Delmas, and C. Neskovic, *Solvent Extr. Ion Exch.* **15**, 533 (1997).
- (9) M. Tsuji and M. Abe, *Solvent Extr. Ion Exch.* **2**, 253 (1984).
- (10) R. Reichenberg, *Ion Exchange Selectivity, in Ion Exchange Ed., vol. 1*, edited by J. Marinsky (Marcel Dekker Inc, New York, 1966).
- (11) M. Tsuji, H. Kaneko, M. Abe, Y. Morita, and M. Kubota, *Radiochim. Acta* **69**, 93 (1993).
- (12) R. D. Shannon, *Acta Crystallorg. A* **32**, 751 (1976).
- (13) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.* **76**, 5237 (1954).
- (14) W. Westmeier and A. Merklin, *Catalog of Alpha Particles from Radioactive Decay* (Fachinformationszentrum Karlsruhe, 1985).