

## Elution Curve of Rutherfordium (Rf) in Anion-Exchange Chromatography with Hydrofluoric Acid Solution

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An elution curve of element 104, rutherfordium (Rf), in anion-exchange chromatography has been obtained for the first time on an atom-at-a-time basis. The distribution coefficient in 5.4 M hydrofluoric acid solution has been determined to be  $28 \pm 6$  mL/g from the observed peak volume of the elution curve.

### 1. Introduction

In the study of aqueous chemistry of the transactinide elements, partition experiments, such as liquid-liquid extraction, ion-exchange chromatography, and reversed-phase extraction chromatography, are generally performed on an atom-at-a-time scale.<sup>1,2</sup> The chromatographic systems with fast kinetics are ideally suited for the dynamic partition of single atoms between the stationary and mobile phases through rapid and multiple sampling of chemical species of interest. To determine thermodynamic equilibrium constants of the transactinide elements, quantitative data on chemical equilibria such as distribution coefficients ( $K_d$ ) are required. Because of the short half-lives and low production yields of the transactinide elements, however, reliable  $K_d$  values of those elements are little available at present.

A few attempts have been made to determine the  $K_d$  values of element 104, Rf, by using the ion-exchange chromatographic methods. Pfeiffer et al.<sup>3</sup> showed via the retention time with the multi-column technique that the  $K_d$  values of Rf on an anion-exchange resin in mixed 0.27 M HF/0.1 M HNO<sub>3</sub> and 0.27 M HF/0.2 M HNO<sub>3</sub> were identical with those of the lighter homologue Hf. The  $K_d$  values of Rf in HF/HNO<sub>3</sub> were also measured by the rapid ion-exchange separation method as a ratio of specific radioactivities of Rf in the solid and liquid phases, in which the significant differences in the  $K_d$  values between Rf and Hf were observed.<sup>4</sup> The measurement of the  $K_d$  values of Rf in the reversed-phase extraction chromatography from 8 M HCl into tributylphosphate (TBP) was carried out and the extraction sequence among Rf, Zr, and Hf was established through the  $K_d$  values.<sup>5</sup> In our previous report,<sup>6</sup> the anion-exchange behavior of Rf was studied together with its lighter homologues, Zr and Hf, as a function of HF concentration in 1.9–13.9 M. The  $K_d$  values of Rf were deduced from the relationship between adsorption probability and the  $K_d$  values of Zr and Hf by assuming that the kinetics in the fluoride complexation and the ion-exchange processes of Rf is the same as those of the homologues, Zr and Hf. However, no  $K_d$  values of Rf directly measured from elution curves in chromatographic

experiments have not been reported yet.

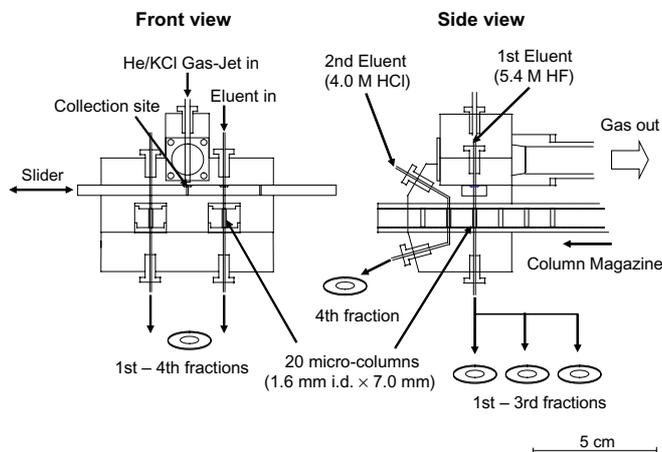
In this paper, we present the first observation of the elution curve of Rf in anion-exchange chromatography with 5.4 M HF on an atom-at-a-time basis. The  $K_d$  values of Rf was directly determined from the peak volume.

### 2. Experiment

The isotope 78-s <sup>261</sup>Rf (Ref. 7) was produced in the <sup>248</sup>Cm(<sup>18</sup>O, 5n) reaction with a 94-MeV <sup>18</sup>O<sup>6+</sup> beam delivered from the Japan Atomic Energy Research Institute (JAERI) tandem accelerator. The <sup>248</sup>Cm target of 610 μg/cm<sup>2</sup> in thickness was prepared by electrodeposition of Cm(NO<sub>3</sub>)<sub>3</sub> in 2-propanol onto a 2.4-mg/cm<sup>2</sup>-thick beryllium backing foil. The beam intensity was 250–300 particle nA. The production cross section of <sup>261</sup>Rf through the reaction was 13 nb,<sup>8</sup> resulting in a production rate of about 2 atoms/min under the given condition. The target included 36-μg/cm<sup>2</sup> enriched <sup>152</sup>Gd (the isotopic composition was: 39.3% <sup>152</sup>Gd, 5.9% <sup>154</sup>Gd, 16.7% <sup>155</sup>Gd, 13.8% <sup>156</sup>Gd, 7.7% <sup>157</sup>Gd, 10.0% <sup>158</sup>Gd, and 6.6% <sup>160</sup>Gd) to simultaneously produce the short-lived <sup>169</sup>Hf isotope ( $T_{1/2} = 3.24$  min) via Gd(<sup>18</sup>O, xn) that was used for monitoring on-line elution behavior of the homologue Hf under strictly identical experimental condition. Reaction products recoiling out of the target were stopped in a volume of He gas (~1 bar) which had been loaded with KCl aerosols generated by sublimation from the surface of KCl powder at 640°C. The products attached to the aerosols were swept out of the recoil chamber with the He gas flow (2.0 L/min) and were transported through a Teflon capillary (2.0 mm i.d., 20 m long) by a He/KCl gas-jet system to a rapid chemical separation apparatus. The transport efficiency of the products through the gas-jet system was estimated to be approximately 35%.<sup>8</sup>

To perform fast and repetitive anion-exchange chromatography of Rf, we employed an apparatus AIDA (Automated Ion-exchange separation apparatus coupled with the Detection system for Alpha spectroscopy)<sup>9,10</sup> that consists of a modified ARCA (Automated Rapid Chemistry Apparatus)<sup>11</sup> which is a miniaturized computer controlled liquid chromatography system and an automated on-line α-particle detection system. In the present study, AIDA was used to collect consecutive 4 effluent fractions as schematically shown in Figure 1. The

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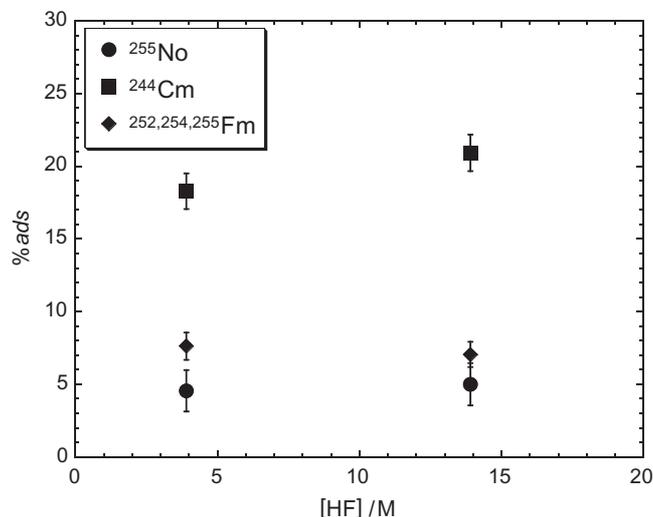


**Figure 1.** Schematic diagram of the AIDA.

nuclear reaction products transported by the gas-jet system were deposited on the collection site of AIDA. After collection for 182 s, the site was mechanically moved onto the microcolumn packed with an anion-exchange resin, MCI GEL CA08Y, Mitsubishi Chemical Corporation. The resin, a strongly basic quaternary-amine polymer with a particle size of  $22 \pm 2 \mu\text{m}$  in a chloride form, was converted to a fluoride form by washing in a column with 26 M HF, washed thoroughly by the batch method with pure water and dried to a constant weight at  $80^\circ\text{C}$  in a vacuum oven.

The collected products were dissolved with 5.4 M HF and were fed onto the  $1.6 \text{ mm i.d.} \times 7 \text{ mm}$  anion-exchange column at a flow rate of 0.8 mL/min. The effluent from the column was consecutively collected on three separate Ta disks with a volume of 170, 130, and 130  $\mu\text{L}$  as fraction 1, 2, and 3, respectively. Then, the remaining products in the column were eluted with 260  $\mu\text{L}$  of 4.0 M HCl at a flow rate of 1.4 mL/min through the second path after one-step forward movement of the column magazine (see Figure 1). The effluent was collected on the other Ta disk as fraction 4. Each fraction was evaporated to dryness with hot He gas and halogen heat lamps. These 4 Ta disks were in turn subjected to  $\alpha$ -spectroscopy with eight  $600 \text{ mm}^2$  passivated ion-implanted planar silicon (PIPS) detectors. The counting efficiency of each detector was 35% and its  $\alpha$ -particle energy resolution was 110–200 keV FWHM. All events were registered event-by-event together with time information. After the  $\alpha$ -particle measurement, the 493 keV  $\gamma$ -ray of  $^{169}\text{Hf}$  was measured with Ge detectors for every third or fourth set of the samples to monitor the elution behavior of Hf and its chemical yield. Counting durations for the  $\alpha$ -particle and  $\gamma$ -ray measurements were 222 s and 297 s, respectively. The chemical yield of Hf including deposition and dissolution efficiencies of the aerosols was 55% on the average.

In order to evaluate the contribution of “primordial  $^{257}\text{No}$ ”<sup>3,4</sup> formed from the  $\alpha$  decay of  $^{261}\text{Rf}$  between the start of the collection at AIDA and the end of the 5.4 M HF elution to the eluted radioactivities of  $^{261}\text{Rf}$  in anion-exchange chromatography, adsorption behavior of No on the same anion-exchange resin was examined using  $^{255}\text{No}$ , because the  $\alpha$ -particle energies of  $^{261}\text{Rf}$  ( $E_\alpha = 8.28 \text{ MeV}$ ) and of its daughter  $^{257}\text{No}$  ( $E_\alpha = 8.22, 8.27, 8.32 \text{ MeV}$ ) are indistinguishable.<sup>13</sup> The isotope 3.1-min  $^{255}\text{No}$  was produced in the 77-MeV  $^{12}\text{C}$ -induced reaction of  $^{248}\text{Cm}$  through  $^{248}\text{Cm}(^{12}\text{C}, 5n)$  with the cross section of about 500 nb.<sup>14</sup> The reaction products recoiling out of the target were transported by the He/KCl gas-jet system to the collection site of AIDA. After deposition for 300 s, the products were dissolved with 270  $\mu\text{L}$  of 3.9 and 13.9 M HF solution and were fed onto the  $1.6 \text{ mm i.d.} \times 7 \text{ mm}$  chromatographic column filled with the anion-exchange resin, MCI GEL CA08Y, at a flow rate of 1.0 mL/min. The effluent collected on a Ta disk as fraction 1 was evaporated to dryness with hot



**Figure 2.** Percent adsorption (%ads) of No, Cm, and Fm on the anion-exchange resin CA08Y as a function of HF concentration, [HF].

He gas and a halogen heat lamp. The remaining products in the column were eluted with 250  $\mu\text{L}$  of 4.0 M HCl. The effluent was collected on another Ta disk and was evaporated to dryness as fraction 2. The pair of Ta disks were assayed by  $\alpha$ -spectroscopy with the eight  $600\text{-mm}^2$  PIPS detectors. The  $\alpha$ -decay events were accumulated for 937 and 904 s for the first and second fractions, respectively.

### 3. Results and Discussion

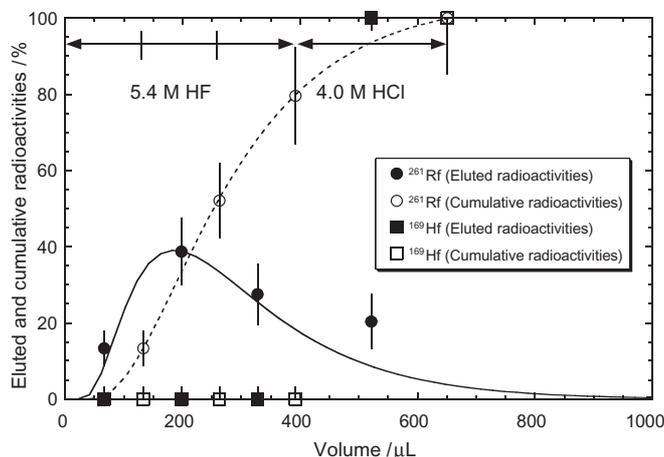
The adsorption on the anion-exchange resin of  $^{255}\text{No}$  together with that of  $^{244}\text{Cm}$ , recoil products of the target (the  $^{248}\text{Cm}$  target contains 1.12%  $^{244}\text{Cm}$  and 1.31%  $^{246}\text{Cm}$ ) and of  $^{252,254,255}\text{Fm}$  produced in the nucleon transfer reactions is shown in Figure 2. The ordinate indicates the percent adsorption expressed as, %ads =  $100 A_2 / (A_1 + A_2)$ , where  $A_1$  and  $A_2$  are the eluted radioactivities observed in fractions 1 and 2, respectively. It has been found that the %ads values of  $^{255}\text{No}$  are almost independent of the HF concentration. The %ads values of Cm and Fm were approximately 20% and 7%, respectively.

The results on the elution behavior of  $^{261}\text{Rf}$  and  $^{169}\text{Hf}$  are summarized in Table 1, where the fraction number, the elapsed time  $T$  from the end of aerosol collection at AIDA to the start of the  $\alpha$ -particle measurement, the volume of eluted solutions, the number of observed  $\alpha$  particles ( $\alpha$ ) of  $^{261}\text{Rf}$  and of its daughter 25-s  $^{257}\text{No}$  and correlated  $\alpha$  particle pairs ( $\alpha$ - $\alpha$ ) of  $^{261}\text{Rf}$  and  $^{257}\text{No}$ , and the relative eluted radioactivities of  $^{261}\text{Rf}$  and  $^{169}\text{Hf}$  are listed. From the 511 cycles of the anion-exchange experiments, a total of 48  $\alpha$  events from  $^{261}\text{Rf}$  and  $^{257}\text{No}$  were registered in the energy range of 8.00–8.36 MeV, including 6  $\alpha$ - $\alpha$  time-correlated  $\alpha$  pairs of  $^{261}\text{Rf}$  and  $^{257}\text{No}$ . The expected event ratio between  $\alpha$  singles and  $\alpha$ - $\alpha$  correlations is to be 45 : 5 evaluated by taking into account the counting efficiency of the detectors (35%), the recoil effect of  $^{257}\text{No}$  and the decay of

**TABLE 1: Relative Eluted Activities of  $^{261}\text{Rf}$  and  $^{169}\text{Hf}$  in Each Fraction**

Fraction No.	$T/s^*$	Volume/ $\mu\text{L}$	$\alpha$ ( $\alpha$ - $\alpha$ ) count	Relative activity of $^{261}\text{Rf}/\%$	Relative activity of $^{169}\text{Hf}/\%$
1	68.5	$133 \pm 12$	8 (1)	$13 \pm 5$	0
2	81.6	$130 \pm 9$	20 (1)	$39 \pm 9$	0
3	95.5	$129 \pm 10$	12 (3)	$28 \pm 8$	0
4	108.3	$259 \pm 12$	8 (1)	$20 \pm 8$	100

\*Elapsed time from the end of aerosol collection at AIDA to the start of the  $\alpha$ -particle measurement.



**Figure 3.** Elutions of  $^{261}\text{Rf}$  and  $^{169}\text{Hf}$  with 5.4 M HF. Closed circles and squares are the relative eluted radioactivities for  $^{261}\text{Rf}$  and  $^{169}\text{Hf}$ , respectively. The open symbols show the cumulative ones. The dashed line is the fitted curve by the Glueckauf equation<sup>15</sup> and the solid line indicates the integral curve (see text).

$^{261}\text{Rf}$  and  $^{257}\text{No}$ , that is reasonably consistent with the experimental ratio (48 : 6) within the counting statistics. Relative eluted radioactivities of  $^{261}\text{Rf}$  in Table 1 were corrected for the decay of  $^{261}\text{Rf}$  and the contributions from the background and from “primordial  $^{257}\text{No}$ ”. The average background count in each fraction was estimated as 0.36. The contribution of “primordial  $^{257}\text{No}$ ” to the relative eluted radioactivity of  $^{261}\text{Rf}$ , which was taken into consideration on the basis of the standard equations of growth and decay and the adsorption behavior of No (Figure 1), is evaluated to be less than 5% for the 1st fraction and is negligible for the others in the present experimental condition.

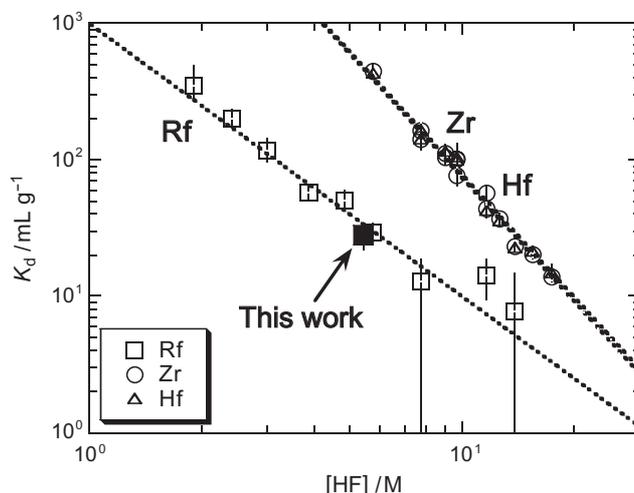
In Figure 3, the relative eluted radioactivities of  $^{261}\text{Rf}$  and  $^{169}\text{Hf}$  are plotted by closed circles and closed squares, respectively, as a function of the half volume of each effluent, while the cumulative radioactivities of  $^{261}\text{Rf}$  and  $^{169}\text{Hf}$  are indicated by open circles and open squares, respectively, against the cumulative eluted volume. As shown in Figure 3, the peak volume of the elution curve for  $^{261}\text{Rf}$  is observed at around 200  $\mu\text{L}$  while the isotope  $^{169}\text{Hf}$  was eluted only in the 4th fraction, indicating that the  $K_d$  value of Rf is much smaller than that of Hf. The present result is consistent with the previous results that the adsorption of Rf is much weaker than those of Zr and Hf at the same concentration of HF.<sup>6</sup>

The elution curve of  $^{261}\text{Rf}$  is analyzed by the Glueckauf model<sup>15</sup> which is based on the theoretical plate concept assuming a continuous flow and local equilibrium. The eluted radioactivity  $A(v)$  with the effluent volume  $v$  is represented as

$$A(v) = A_{\max} \exp \left\{ - \frac{N}{2} \left( \frac{v_p - v}{v_p v} \right)^2 \right\} \quad (1)$$

where parameters  $A_{\max}$ ,  $N$ , and  $v_p$  are the maximum peak height, the number of theoretical plates, and the peak volume, respectively. The values of  $v$  and  $v_p$  are corrected for the dead volume of 40  $\mu\text{L}$ . The dashed line shows the integrated curve of eq 1 to fit the experimental cumulative yields of  $^{261}\text{Rf}$  except for the data of the 4th fraction (4.0 M HCl) with  $v_p = 186 \pm 35 \mu\text{L}$  and  $N = 2.6 \pm 1.5$ . The solid line in Figure 3 is the differential curve of the dashed line, i.e., the theoretical fit of the eq 1. The smaller value of  $N = 2.6 \pm 1.5$  for Rf than that for Zr and Hf ( $4.8 \pm 0.5$ )<sup>6</sup> would be due to low statistics of the present experiment. Although the statistics of Rf acquired in this study is not enough to determine the details of the elution curve, such as a peak width and a peak height, the peak volume can be roughly obtained.

In the chromatographic system, the  $K_d$  value is described as,



**Figure 4.** The distribution coefficient  $K_d$  of  $^{261}\text{Rf}$  on the anion-exchange resin at 5.4 M HF is shown in the  $\log K_d$  vs.  $\log [\text{HF}]$  plot by a closed square. For comparison, dependence of the  $K_d$  values of Rf and those of Zr and Hf evaluated in Reference 6 are also depicted.

$$K_d = \frac{v_p}{m_r} \quad (2)$$

where  $m_r$  is the mass of the dry resin. The  $K_d$  value of Rf in anion-exchange chromatography with 5.4 M HF was determined to be  $28 \pm 6 \text{ mL/g}$  with  $m_r = 6.6 \pm 0.3 \text{ mg}$ . In Figure 4, the  $K_d$  value of Rf in this study is plotted together with those of Rf, Zr, and Hf evaluated in our previous study.<sup>6</sup> It is found that the previously deduced  $K_d$  values<sup>6</sup> agree well with the present one obtained from the peak volume.

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## References

- (1) J. V. Kratz, *Liquid-Phase Chemistry, The Chemistry of Superheavy Elements*, ed. M. Schädel, Kluwer Academic Publishers, Dordrecht, 2003, p159.
- (2) J. V. Kratz, *Chemistry of Transactinides, Handbook of Nuclear Chemistry, Vol. 2, Elements and Isotopes*, ed. A. Vértes, S. Nagy, and Z. Klencsár, Kluwer Academic Publishers, Dordrecht, 2003, p323.
- (3) G. Pfrepper, R. Pfrepper, D. Krauss, A. B. Yakushev, S. N. Timokhin, and I. Zvara, *Radiochim. Acta* **80**, 7 (1998).
- (4) E. Strub, J. V. Kratz, A. Kronenberg, A. Nähler, P. Thörle, S. Zauner, W. Brüchle, E. Jäger, M. Schädel, B. Schausten, E. Schimpf, Li Zongwei, U. Kirbach, D. Schumann, D. Jost, A. Türler, M. Asai, Y. Nagame, M. Sakama, K. Tsukada, H. W. Gäggeler, and J. P. Glatz, *Radiochim. Acta* **88**, 265 (2000).
- (5) R. Günter, W. Paulus, J. V. Kratz, A. Seibert, P. Thörle, S. Zauner, W. Brüchle, E. Jäger, V. Pershina, M. Schädel, B. Schausten, D. Schumann, B. Eichler, H. W. Gäggeler, D. T. Jost, and A. Türler, *Radiochim. Acta* **80**, 121 (1998).
- (6) H. Habu, K. Tsukada, M. Asai, A. Toyoshima, K. Akiyama, I. Nishinaka, M. Hirata, T. Yaita, S. Ichikawa, Y. Nagame, K. Yasuda, Y. Miyamoto, T. Kaneko, S. Goto, S. Ono, T. Hirai, H. Kudo, M. Shigekawa, A. Shinohara, Y. Oura, H. Nakahara, K. Sueki, H. Kikunaga, N. Kinoshita, N. Tsuruga, A. Yokoyama, M. Sakama, S. Enomoto, M. Schädel, W. Brüchle, and J. V. Kratz, *J. Am. Chem. Soc.* **126**, 5219 (2004).
- (7) B. Kadkhodayan, A. Türler, K. E. Gregorich, P. Baisden, K. R. Czerwinski, B. Eichler, H. W. Gäggeler, T. M. Hamilton,

- D. T. Jost, C. D. Kacher, A. Kovacs, S. A. Kreek, M. R. Lane, M. F. Mohar, M. P. Neu, N. J. Stoyer, E. R. Sylwester, D. M. Lee, M. J. Nurmia, G. T. Seaborg, and D. C. Hoffman, *Radiochim. Acta* **72**, 169 (1996).
- (8) Y. Nagame, M. Asai, H. Haba, S. Goto, K. Tsukada, I. Nishinaka, K. Nishio, S. Ichikawa, A. Toyoshima, K. Akiyama, H. Nakahara, M. Sakama, M. Schädel, J. V. Kratz, H. W. Gäggeler, and A. Türler, *J. Nucl. Radiochem. Sci.* **3**, 85 (2002).
- (9) H. Haba, K. Tsukada, M. Asai, S. Goto, A. Toyoshima, I. Nishinaka, K. Akiyama, M. Hirata, S. Ichikawa, Y. Nagame, Y. Shoji, M. Shigekawa, T. Koike, M. Iwasaki, A. Shinohara, T. Kaneko, T. Maruyama, S. Ono, H. Kudo, Y. Oura, K. Sueki, H. Nakahara, M. Sakama, A. Yokoyama, J. V. Kratz, M. Schädel, and W. Bröchle, *J. Nucl. Radiochem. Sci.* **3**, 143 (2002).
- (10) Y. Nagame, H. Haba, K. Tsukada, M. Asai, K. Akiyama, M. Hirata, I. Nishinaka, S. Ichikawa, H. Nakahara, S. Goto, T. Kaneko, H. Kudo, A. Toyoshima, A. Shinohara, M. Schädel, J. V. Kratz, H. W. Gäggeler, and A. Türler, *Czech. J. Phys. Suppl.* **A53**, 299 (2003).
- (11) M. Schädel, W. Bröchle, W. Jäger, E. Shimpf, J. V. Kratz, U. W. Scherer, and H. P. Zimmermann, *Radiochim. Acta* **48**, 171 (1989).
- (12) A. Toyoshima, K. Tsukada, H. Haba, M. Asai, S. Goto, K. Akiyama, I. Nishinaka, S. Ichikawa, Y. Nagame, and A. Shinohara, *J. Radioanal. Nucl. Chem.* **255**, 485 (2003).
- (13) R. B. Firestone, and V. S. Shirley, *Table of Isotopes, 8th ed.* (John Wiley and Sons, New York, 1996).
- (14) T. Sikkeland, A. Ghiorso, and M. Nurmia, *Phys. Rev.* **172**, 1232 (1968).
- (15) E. Glueckauf, *Trans. Faraday Soc.* **51**, 34 (1955).