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Measurement of the Md^{3+}/Md^{2+} Reduction Potential Studied with Flow Electrolytic Chromatography

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Supporting Information

ABSTRACT: The reduction behavior of mendelevium (Md) was studied using a flow electrolytic chromatography apparatus. By application of the appropriate potentials on the chromatography column, the more stable Md^{3+} is reduced to Md^{2+}. The reduction potential of the $Md^{3+} + e^- \rightarrow Md^{2+}$ couple was determined to be -0.16 ± 0.05 V versus a normal hydrogen electrode.

Relativistic effects are strongly affecting the ground-state electron configurations of the heaviest elements.[1−4] For the actinides, theoretical calculations predict that, in addition to f-shell effects, the relativistic expansion of the inner 5f orbital contributes to the actinide contraction. A decreased shielding of the central nuclear charge leads to shrinkage of the outer valence orbitals.[5−7] Up to 50% of the actinide contraction is caused by relativity.[7] These changes of the relativistic origin influence the binding energies of valence orbitals and the stabilities of electron configurations of the actinide atoms. It is, however, difficult to directly measure energetic levels of the heaviest actinides with atomic number >100 by any spectroscopic method because these elements are not available in macro amounts. For the actinides, redox reactions between the divalent and trivalent oxidation states are related to the third ionization potential and to the energies of the electron transitions between the $5f^n7s^2$ and $5f^{n-1}6d7s^2$ states.[8,9] This indicates that the redox potentials of actinides help to provide information on the relative stabilities of the 5f orbital and other electron configurations.

Mendelevium (Md), atomic number 101, is one of the heaviest actinides. Nugent et al. predicted the oxidation potentials of heavy actinides between divalent and trivalent ions.[9] The potential for the $Md^{2+} \rightarrow Md^{3+} + e^-$ couple, which has $5f^{13}$ and $5f^{12}$ electron configurations,[10,11] respectively, was predicted to be 0 ± 0.2 V versus a normal hydrogen electrode (NHE).[9] Bratsch and Lagowski predicted the reduction potential of Md to be -0.2 V versus a NHE using an empirical model with parameters of standard formation enthalpies and ionization potentials of lanthanides and lighter actinides.[10] Experimentally, Hulet et al. first studied the reduction of Md^{3+} to Md^{2+} with reducing agents in 0.1 M HCl.[12] They demonstrated that the behavior of Md^{2+} is different from that of its neighbors Es^{3+} and Fm^{3+} in a $BaSO_4$ coprecipitation separation and is similar to that of Eu^{2+} in bis(2-ethylhexyl)orthophosphoric acid (HDEHP) extraction. They deduced the reduction potential of the $Md^{3+} + e^- \rightarrow Md^{2+}$ couple to be ~ -0.2 V versus a NHE based on the result with a V^{2+}/V^{3+} reducing couple. Maly and Cunningham also carried out the reduction of Md with reducing agents, which was followed by coprecipitation with $BaSO_4$ in sulfuric acid.[13] They suggested the reduction potential of Md to be ~ -0.1 V versus a NHE from the result with a Ti^{3+}/TiO^{2+} couple; for more information, see also refs 14a,b and references cited therein. However, reduction potentials deduced with reducing agents depend on the given experimental conditions such as the temperature and reaction time. In addition, their radiation measurement for spontaneous fission of its daughter nucleus did not allow the direct identification of Md.[12,13] Thus, it is essential to precisely determine the reduction potential of Md by an electrochemical method.

Very recently, we have developed a novel method of electrolytic column chromatography available for single ions.[15] Carbon fibers modified with a Nafion perfluorinated ion-exchange resin were employed as a working electrode as well as a cation exchanger. This technique was successfully applied to the oxidation of nobelium (No).[16] In the $No^{2+} \rightarrow No^{3+} + e^-$ reaction, performed in 0.1 M α-hydroxyisobutyric acid, No^{3+} was clearly separated from No^{2+}. In the present study, the reduction potential of Md was determined with similar electrolytic column chromatography.

The isotope ^{255}Md (half-life $t_{1/2} = 27$ min) was produced in the bombardment of a ^{248}Cm target with ^{11}B beams at a JAEA tandem accelerator. Nuclear reaction products, recoiling out of the target, were transported to a chemistry laboratory attached to tiny KCl particles in a helium gas stream. All transported products were deposited on the collection site of a chemistry apparatus for 10 min.[17] After collection, trivalent actinide ions including Md were chemically separated from KCl with a chromatographic HDEHP column in 0.1 M HCl.[18] Subse-

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quently, a dried sample was dissolved with 22 μL of 0.10 M HCl. This solution was then fed with 0.10 M HCl into a Nafion electrode column at a flow rate of 800 μL min^{-1}. Potentials between −0.3 and −0.9 V versus a Ag/AgCl reference electrode (SSE) in 1.0 M LiCl were applied. In this study, 1.0 M LiCl was used as the electrolyte in the SSE. We measured a potential of 0.271 V for this SSE versus NHE including a liquid junction potential between the SSE and the working solution. To avoid dissolved oxygen in 0.10 M HCl, the solution had first passed through another flow electrolytic column at a potential of −1.5 V versus a SSE. In each experiment, a fresh Nafion electrode was used and was preconditioned by applying sweeping potentials between 0 and −1.5 V versus a SSE for 4 min and then introducing electrolyzed HCl for 3 min. To determine the elution position of Md, the effluent from the Nafion electrode was collected on eight tantalum (Ta) disks with a volume of 240 μL on each disk. The remaining products were then stripped with 600 μL of 3.0 M HCl and were collected on two Ta disks. After collection, 10 samples were evaporated to dryness. α-Particle measurements started ~12 min after the end of the last KCl collection and were performed with 10 passivated implanted planar silicon detectors for ~90 min. The counting efficiency and energy resolution was ~30% and ~60 keV full width at half-maximum, respectively. After α-particle measurement, γ-rays of ^{250}Bk, present in the samples as a byproduct of the nuclear reaction and used as a reference trivalent actinide, were measured with germanium (Ge) detectors. The chemical yield of ^{255}Md was approximately 12%.

Prior to the Md experiments, we examined the elution behavior of ^{139}Ce^{3+}, ^{146}Gd^{3+}, ^{169}Yb^{3+}, ^{85}Sr^{2+}, and ^{146}Eu^{3+} in 0.10 M HCl using the same apparatus to verify the reduction of Eu^{3+} to Eu^{2+} and the separation of divalent ions (Sr^{2+} and Eu^{2+}) from the trivalent ones (Ce^{3+}, Gd^{3+}, Yb^{3+}, and Eu^{3+}). Carrier-free radiotracers produced at the RIKEN Ring Cyclotron were utilized. A total of 20 μL of the radiotracers stored in 0.10 M HCl was fed into the electrode in ~2000 μL of electrolyzed 0.10 M HCl. The potential applied to the electrode was adjusted between −0.2 and −0.9 V versus a SSE. The effluent from the electrode was collected in 13 plastic vials. The adsorbed ions were then stripped from the electrode with 3.0 M HCl at −0.2 V. The effluent was collected with 2 vials. These samples were then analyzed by γ spectrometry using a Ge detector. Chemical yields of these radiotracers were >90%.

Parts a and b of Figure 1 show the typical elution behavior of Sr^{2+}, Ln^{3+} (Ce^{3+}, Gd^{3+}, and Yb^{3+}), and Eu in 0.10 M HCl measured at applied potentials of −0.2 and −1.0 V, respectively. At both potentials, divalent Sr ions are eluted with 0.10 M HCl, while the trivalent ions of Ln^{3+} are stripped with 3.0 M HCl. This shows that divalent ions can be separated from trivalent ions under the given conditions. At −0.2 V, Eu is not eluted with 0.10 M HCl and is stripped with 3.0 M HCl. This behavior is the same as that of Ln^{3+}, showing that Eu exists as Eu^{3+} in solution. At −1.0 V, Eu is eluted with 0.1 M HCl, similar to the elution of Sr^{2+}. This demonstrates that Eu^{3+} ions are completely reduced to Eu^{2+} at this potential.

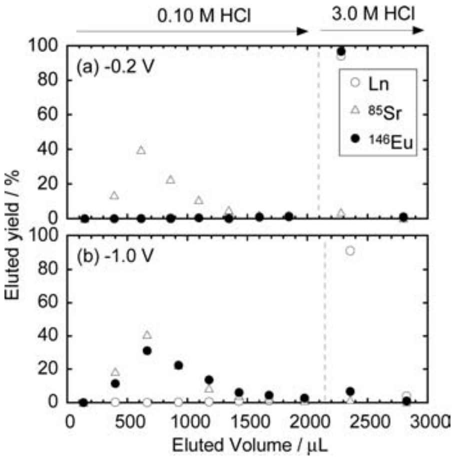

Figure 1. Elution behavior of Ln (Gd, Ce, and Yb), Sr, and Eu in 0.10 M HCl at applied potentials of (a) −0.2 and (b) −1.0 V. Gd, Ce, and Yb are depicted with an open circle as Ln as they show a similar behavior.

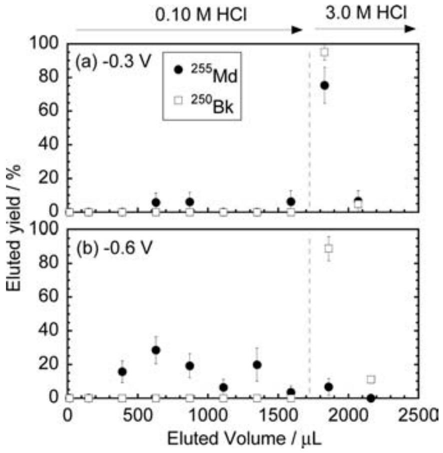

Figure 2. Elution behavior of Md and Bk at applied potentials of (a) −0.3 and (b) −0.6 V.

Parts a and b of Figure 2 show the elution behavior of ^{255}Md and ^{250}Bk at applied potentials of −0.3 and −0.6 V, respectively. Bk is not eluted with 0.10 M HCl and is stripped with 3.0 M HCl at both potentials. This is typical for trivalent ions, as shown in Figure 1 for lanthanides. Small amounts of Md are eluted with 0.10 M HCl at −0.3 V. As shown in Figure 1, a clear separation between divalent and trivalent ions was achieved under these conditions. It is, therefore, found that a small fraction of Md^{3+} is reduced to Md^{2+} at −0.3 V. In comparison, at −0.6 V, ^{255} Md is almost completely eluted with 0.1 M HCl. This clearly demonstrates that Md^{3+} is reduced to Md^{2+}, which is eluted with 0.10 M HCl like Sr^{2+}.

In Figure 3, reduction ratios of Md and Eu are shown as closed circles and open squares, respectively, as a function of the applied potential. The reduction ratio (% Red) is defined by the equation % Red = $100 \times A_1/(A_1 + A_2)$, where A_1 and A_2 are the amounts of Md and Eu observed in 0.1 and 3.0 M HCl fractions, respectively.

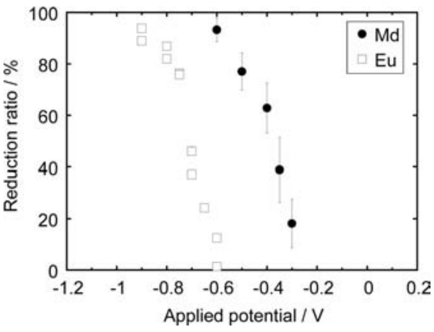

Figure 3. Reduction ratios of Md and Eu in 0.10 M HCl. Error bars are ±1σ values from counting statistics.

The reduction ratios for both elements sharply increase with decreasing applied potential. From 50% reduction ratio values, the formal reduction potentials of the $Md^{3+} + e^- \rightarrow Md^{2+}$ and $Eu^{3+} + e^- \rightarrow Eu^{2+}$ couples were evaluated to be −0.40 ± 0.03 and −0.70 V versus a SSE, respectively. The error limits of the Md value include a 1σ error from counting statistics and a systematic error from the scattering of the data in evaluating the 50% reduction ratio. Applying the above-mentioned value of 0.271 V for the SSE versus NHE relationship, we obtain −0.13 ± 0.03 and −0.43 V versus a NHE for the reduction potential of Md and Eu, respectively.

The present Eu value of −0.43 V agreed with that in our separately performed cyclic voltammetry (CV) measurement with 0.010 M Eu in 0.1 M HCl using the same apparatus. This value is, however, lower than its standard potential of −0.35 V versus a NHE.[19] We, therefore, compared our formal reduction potentials of Eu^{3+}/Eu^{2+}, V^{3+}/V^{2+}, W^{6+}/W^{5+}, and Cu^{2+}/Cu^{+}, measured with CV using the same apparatus, to literature data of standard reduction potentials.[19,20] Figure 4 shows a linear correlation between the measured formal potentials and the referred standard potentials.[19,20] Thus, a correction was made for the observed potential value of Md using this linear relationship, yielding −0.16 ± 0.05 V versus a NHE. The error includes 1 standard deviation of the fitting in Figure 4 in addition to the above-mentioned error limits of the Md value.

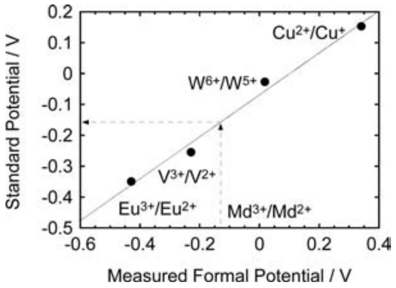

Figure 4. Relationship between measured formal potentials from CV measurements using the present apparatus and the reference standard reduction potential values.

Our result of −0.16 ± 0.05 V for the Md^{3+}/Md^{2+} reduction potential provides a much more precise value compared with ∼−0.2 V and ∼−0.1 V previously reported by Hulet et al.[12] and Maly and Cunningham,[13] respectively. The predicted value of −0.2 ± 0.2 V by Bratsch and Lagowski[10] is much closer to the experimental value compared to 0.0 ± 0.2 V given by Nugent et al.[9] The present result helps to validate and improve empirical models, and it provides an opportunity to test model calculations based on modern relativistic quantum-chemical treatments.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and complete ref 17. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The experiments were performed by all authors. A.T. analyzed the data. A.T. and Y.N. prepared the manuscript. M.S. and H.H. commented on the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Pershina, V. *Chem. Rev.* **1996**, *96*, 1977−2010.
(2) Dyall, K. G.; Faegri, K. *Relativistic Quantum Chemistry*; Oxford University Press: Oxford, U.K., 2007.
(3) Reiher, M.; Wolf, A. *Relativistic Quantum Chemistry*; Wiley: New York, 2009.
(4) Autschbach, J. *J. Chem. Phys.* **2013**, *136*, 150902−1−15.
(5) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563−594.
(6) Küchle, W.; Dolg, M.; Stoll, H. *J. Phys. Chem. A* **1997**, *101*, 7128−7133.
(7) Laerdahl, J. K.; Fægri, K., Jr.; Visscher, L.; Saue, T. *J. Chem. Phys.* **1998**, *109*, 10806−10817.
(8) Worden, E. F.; Blaise, J.; Fred, M.; Trautmann, N.; Wyart, J.-F. Spectra and Electronic Structures of Free Actinide Atoms and Ions. In *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Morss, L. R., Edelstein, N. M., Fuger, J., Eds.; Springer: Dordrecht, The Netherlands, 2006; Chapter 16, pp1859−1860.
(9) Nugent, L. J.; Baybarz, R. D.; Burnett, J. L.; Ryan, J. L. *J. Phys. Chem.* **1973**, *77*, 1528−1539.
(10) Bratsch, S. G.; Lagowski, J. J. *J. Phys. Chem.* **1986**, *90*, 307−312.
(11) Cao, X.; Dolg, M. *Coord. Chem. Rev.* **2006**, *250*, 900−910.
(12) Hulet, E. K.; Lougheed, R. W.; Brady, J. D.; Stone, R. E.; Coops, M. S. *Science* **1967**, *158*, 486−488.
(13) Maly, J.; Cunningham, B. B. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 445−451.
(14) (a) Silva, R. J. Fermium, Mendelevium, Nobelium, and Lawrencium. In *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Morss, L. R., Edelstein, N. M., Fuger, J., Eds.; Springer: Dordrecht, The Netherlands, 2006; Chapter 13, pp1635−1636. (b) Edelstein, N. M.; Fuger, J.; Katz, J. J.; Morss, L. R. Summary and Comparison of Properties of the Actinide and Transactinide Elements. In *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Morss, L. R., Ed.; Springer: Dordrecht, The Netherlands, 2006; Chapter 15, p 1779.
(15) Toyoshima, A.; Kasamatsu, Y.; Kitatsuji, Y.; Tsukada, K.; Haba, H.; Shinohara, A.; Nagame, Y. *Radiochim. Acta* **2008**, *96*, 323−326.
(16) Toyoshima, A.; Kasamatsu, Y.; Tsukada, K.; Asai, M.; Kitatsuji, Y.; Ishii, Y.; Toume, H.; Nishinaka, I.; Haba, H.; Ooe, K.; Sato, W.; Shinohara, A.; Akiyama, K.; Nagame, Y. *J. Am. Chem. Soc.* **2009**, *131*, 9180−9181.
(17) Nagame, Y.; et al. *Radiochim. Acta* **2005**, *93*, 519−526.
(18) Horwitz, E. P.; Bloomquist, C. A. A. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 753−759.
(19) In *Standard Potentials in Aqueous Solution*; Bard, A. J., Parsons, R., Jordan, J., Eds.; Marcel Dekker: New York, 1985.
(20) Pershina, V.; Johnson, E.; Fricke, B. *J. Phys. Chem. A* **1999**, *103*, 8463−8470.