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Lawrencium Chemistry: No Evidence for Oxidation States Lower than 3+ in Aqueous Solution

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Abstract

Lawrencium (3-min ^{260}Lr) together with other actinides, was produced in the bombardment of a ^{249}Bk target with ^{18}O ions. There was no sign of a reduction of Lr^{3+} in dilute hydrochloric acid by V^{2+} or Cr^{2+}, although in the same experiments, Md^{3+} was reduced to Md^{2+} ($E^\circ = -0.2$ V). The resulting limit for the reduction potential of the $Lr^{3+}/Lr^{1(2)+}$ couple is $E^\circ < -0.44$ V.

Introduction

Lawrencium, element 103, is the last member of the 5f actinide series and its chemistry should be similar to that of its light lanthanide homolog, lutetium. One would then expect that the ionization would stop with the $5f^{14}$ core intact, giving rise to a stable trivalent oxidation state of Lr in aqueous solution. Again by analogy, Lr^0 was expected to have a $5f^{14}6d7s^2$ electronic configuration [1]. Because of relativistic effects, Brewer has predicted a $5f^{14}7s^27p_{1/2}$ configuration [2]. Multiconfigurational relativistic Dirac–Fock calculations [3] predict the same electronic ground state configuration which arises from a strong relativistic stabilization of the $7p_{1/2}$ orbital. Furthermore, it has been suggested [4] that the $7s^2$ closed shell might be sufficiently stabilized by relativistic effects to make it an 'inert core' so that only the $7p_{1/2}$ (or 6d) electron may be removed under reducing conditions, thus producing monovalent Lr.

Silva *et al.* [5] used 26-s ^{256}Lr to show that Lr^{3+} is the most stable oxidation state in aqueous solution by comparing the extraction behaviour of ^{256}Lr with several tri- and tetravalent actinide ions and with divalent Ba, Ra, and No. Thenoyltrifluoroacetone in methyl isobutyl ketone was used to extract the tracer ions from aqueous solutions at different pH values. The extraction behaviour of Lr was found to be identical to that of the 3+ actinides and distinctly different from that of the 2+ and 4+ ions studied.

More recently, Hoffman *et al.* [6] performed chemical studies using the 3-min, 8.03 MeV α activity produced by the ^{249}Bk(^{18}O, α3n) reaction and previously assigned [7] to ^{260}Lr. In these studies, the assignment of this 8.03 MeV α activity to an isotope of element 103 was confirmed. An attempt to reduce Lr^{3+} by treatment with hydroxylamine hydrochloride for 20 s at 80 °C was unsuccessful.

In the present work, ^{260}Lr and other actinides (including ^{254}Md, ^{255}Md and ^{250}Fm–^{255}Fm) were produced in ^{18}O + ^{249}Bk bombardments. We tried to produce Lr with an oxidation state lower than 3+ in aqueous solution using vanadous (V^{2+}) and chromous (Cr^{2+}) ion solutions, as well as zinc and hydroxylamine, as reductants. We used extraction chromatography with di(2-ethylhexyl)orthophosphoric acid (HDEHP) as the stationary phase and dilute acid solutions as the mobile phase [8] because this system is ideally suited for the separation of 3+ ions from lower (or higher) oxidation states. In these experiments two fractions were collected. After being treated with the reductant, the 'reducible' actinides, *i.e.* ions which exist as mono- or divalent ions under reducing conditions and as 3+ ions under non-reducing or weakly oxidizing conditions, were eluted from an HDEHP column in 0.3 M HCl. This fraction contained, as expected [9], the Md activities which were produced together with the Lr. The second, or 'non-reducible' actinide fraction, characterized by strong absorption on HDEHP in 0.3 M HCl and rapid elution in 4 M HCl, contained the ions which

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remained in the 3+ oxidation state under both the reducing and slightly oxidizing conditions. This fraction contained most of the 3+ actinide activities produced in the bombardment, notably the ^{250}Fm–^{255}Fm activities. Both fractions were free of metal ions with oxidation states greater than 3+.

Experimental

Bombardments of a ^{249}Bk target with ^{18}O ions were performed at the Lawrence Berkeley Laboratory 88-inch cyclotron to produce 3-min ^{260}Lr by the compound nucleus, α3n reaction and to produce other actinides by transfer reactions. The 117 MeV $^{18}O^{5+}$ beam of 5×10^{12} particles per second passed through a 1.8 mg/cm^2 HAVAR window, a volume of nitrogen cooling gas (0.2 mg/cm^2), and the target substrate (3.06 mg/cm^2 Be) before passing through the ^{249}Bk target material with an energy of 100–101 MeV. The target was prepared as the oxide with a ^{249}Bk thickness of 836 μg/cm^2 by electrodeposition of the nitrate from an isopropanol solution directly onto the Be substrate [10]. At the time of the experiments, the target consisted of 769 μg/cm^2 ^{249}Bk and 67 μg/cm^2 ^{249}Cf. Products from the heavy-ion reaction recoiled into a volume of He gas at 1.3 bar saturated with a KCl aerosol. The He gas and the activity-bearing aerosols were transported by a capillary (i.d. 1.2 mm) to the head of an Automated Rapid Chemistry Apparatus, ARCA [11]. There the KCl clusters, together with the transported radionuclides, were collected on the surface of a quartz frit through which the transport gas was sucked by a pump. In the present experiments, ARCA consisted of three chemically inert HPLC pumps (Latek, Heidelberg) that pumped the various solutions through teflon tubing (i.d. 0.5 mm) to the quartz frit and/or to the columns. Flow rates and times as well as the operation of the pneumatic slider valves were controlled by a microcomputer. The collected activity was processed batchwise after 9 min accumulations of the aerosol. The aerosol was dissolved from the frit at room temperature in 0.3 M HCl containing the reducing agent 0.01 M V^{2+}, 0.01 M Cr^{2+}, or 0.1 M NH_3OH^+, respectively.

A schematic flow diagram of the chemical separations is given in Fig. 1. In the reduction experiments with V^{2+} or Cr^{2+} ions the 0.3 M HCl solution containing the reducing agent and the radionuclides dissolved from the collection frit was passed first through a 2 mm × 60 mm column heated to 80 °C and filled with finely grained Zn(Hg) amalgam. The solution was subsequently pumped through the first HDEHP column (1.75 mm × 40 mm) at 80 °C. In the experiments with hydroxylamine the Zn(Hg) amalgam was replaced by an inert powder (Celite 535 from Johns Manville) kept at 100 °C. The Zn(Hg) amalgam or Celite column was used to provide an increased contact time and to provide for heating of the radionuclides with the reductant. The contact time of the radionuclides with the heated section was 15 s, except for the reduction experiments with hydroxylamine where it was increased to 60 s.

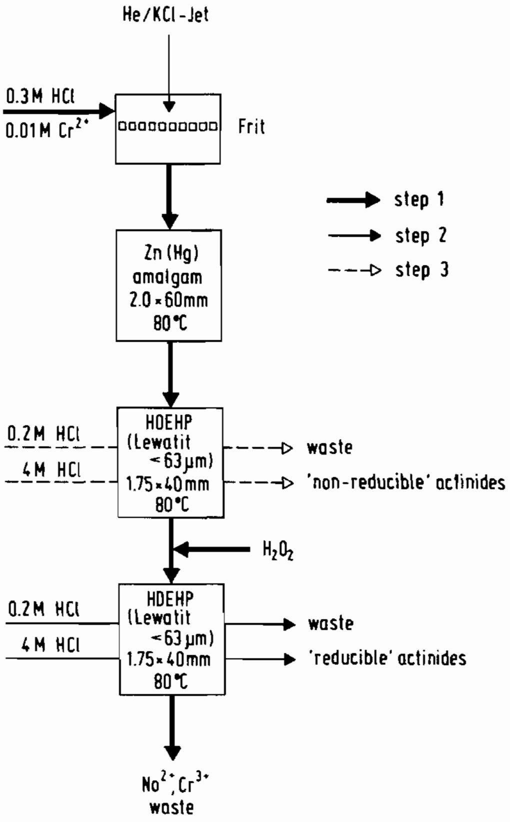

Fig. 1. Schematic flow diagram of the reduction chemistry for Lr^{3+} ions by Cr^{2+}. Step 1 involves the dissolution of the collected activity from the quartz frit, and the transport of the solution through Zn(Hg) amalgam and subsequently through two HDEHP columns. Steps 2 and 3 involve washing of these columns and the elution of the trivalent actinides.

The HDEHP columns contained LEWATIT-OC 1026® from Bayer Leverkusen, consisting of porous polystyrene beads coated with undiluted HDEHP (diameter < 63 μm). An aliquot (1.25 ml) of the reducing 0.3 M HCl solution was pumped over the first HDEHP column. This volume was sufficient to quantitatively elute monovalent or divalent ions, as previously demonstrated with Cs^{1+}, Ba^{2+} and Eu^{2+} tracer activities. This volume was much too small to elute trivalent lanthanide (or actinide) ions as demonstrated with Eu^{3+}. The effluent from the first HDEHP column, see Fig. 1, was mixed through a 'T joint' with hydrogen peroxide at room temperature by simultaneously pumping a 6% solution of H_2O_2 into the 'T' by pump 2, producing together a 0.2 M HCl solution with the reduced actinides (except for No^{2+})

reoxidized to the trivalent oxidation state. This solution was pumped through the second HDEHP column (1.75 mm X 40 mm) where the reoxidized trivalent actinides were extracted while the No^{2+}, the Cr^{3+} and the oxidized vanadium species (presumably VO_2^+) passed through and were carefully removed by a subsequent washing of the column with 0.2 M HCl. The No fraction was discarded. The second HDEHP column was then stripped with 4 M HCl and two fractions of ten drops each were collected on tantalum disks that were heated from below by contact with a hot plate. To substantially speed up the evaporation, a flow of heated He gas was directed downward onto the liquid. After evaporation, the Ta disks were flamed and inserted into the counting system. Counting of the 'reducible' actinides started 150–210 s after the end of bombardment.

Immediately after the stripping of the second HDEHP column ('reducible' actinides) the first HDEHP column, after a rinse with 0.2 M HCl to remove the reductant, was stripped too with 4 M HCl and another two portions of ten drops each were collected and dried on Ta disks. Counting of these 'non-reducible' actinides started 210–270 s after the end of bombardment.

After stripping of the columns with 4 M HCl was complete, they were reconditioned by washing with water and 0.2 M HCl. The first HDEHP column was also conditioned with 0.3 M HCl containing the reducing agent. By the end of this reconditioning of ARCA another 9-min collection of the aerosol was completed and the separation was automatically carried out again. The HDEHP columns were replaced by new ones after every six separations.

The chromous or vanadous ion solutions were prepared in an inert-atmosphere (Ar) glove box by dissolving VCl_2 or $CrCl_2$ in 0.3 M HCl. These solutions were stored over a bottom layer of Zn(Hg) amalgam (3% Hg) in a vessel that allowed excess pressure from the produced hydrogen to be released without opening the system to the atmosphere. It was possible to connect these vessels directly via teflon tubing to the HPLC pump.

The technical realization of the above separation scheme is indicated in Fig. 2, which, as an example, shows ARCA in the situation immediately after the end of the collection time. The jet has just been switched to the exhaust line so that the frit can be washed with the reducing 0.3 M HCl solution pumped by pump P1. With this solution the dissolved activity passes the Zn(Hg) amalgam column and column 1 (C1). The effluent from column 1 is mixed with H_2O_2 pumped by P2, and the mixture passes column 2 (C2) so that No^{2+} and the reoxidized chromium or vanadium metal ions are pumped through valve 8 into the waste. Next, valve 6 is switched so that C1 is disconnected from C2. The rotary valve at P2 is switched, and P2 pumps 0.2 M HCl washing solution through valve 7, C2, and valve 8, into the waste. Then, the rotary valve at P2 selects the connection to the 4 M HCl container, valve 8 is switched, and P2 pumps 4 M HCl through C2 until 2 X 10 drops are collected at the exit of valve 8. Correspondingly, washing and stripping of C1 is performed by P3 through valves 5, 6 and 8.

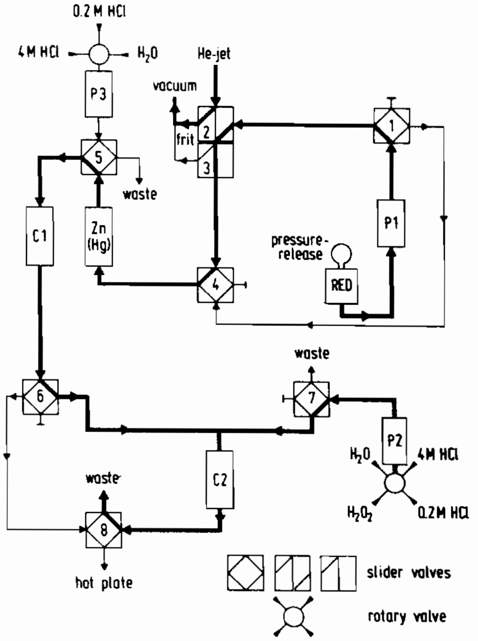

Fig. 2. Schematic diagram of the microprocessor-controlled HPLC-system ARCA [11]. The system consists of three pumps, P1, P2 and P3, two HDEHP columns, C1 and C2, and pneumatically operated slider valves and rotary valves.

In order to provide (nominally) more powerful reducing agents, two more series of experiments were carried out. In one series, mixed column beds of LEWATIT-OC 1026® and fine Zn grains ($E° = -0.76$ V) were used as C1, and the dissolution and transport of the activities from the frit to this column were performed in 0.3 M HCl, with no added reducing agents. All other details were the same as in the reduction experiments with V^{2+} or Cr^{2+}. Finally, in another series, a 0.1 M solution of hydroxylamine hydrochloride ($E° = -1.87$ V) in 0.3 M HCl was used to dissolve the aerosol and to transport the activity to C1. In these experiments the Zn(Hg) amalgam column in Fig. 1 was replaced by a Celite column which was kept at 100 °C.

The detection of the ^{260}Lr and the other actinides was performed by α-particle spectroscopy with a series of 300-mm^2 Si(Au)-surface barrier detectors. The energies, detector identifications and times of all α particles detected with energies between 5.0 and 10.0 MeV were recorded on magnetic tape for later analysis. The typical α-particle energy resolution of 35 keV was more than sufficient to distinguish the 8.03 MeV α-activity of ^{260}Lr from the other actinide activities. The activities of ^{253,254,255}No might have been a serious interference because of their similar half-lives and α-decay energies. Therefore, No was separated from the 'reducible' actinides, after their reoxidation, on the second HDEHP column and discarded, as described above.

Results and Discussion

Figure 3 shows the sum of the α-particle spectra from 20 experiments with Cr^{2+} as the reducing agent. Spectrum 1 is associated with the 'non-reducible' actinides as collected in two 10-drop fractions from the first HDEHP column. The prominent α activities can be assigned to the following Fm isotopes: 20-h ^{255}Fm, 25-h ^{252}Fm, 3.2-h ^{254}Fm, and 30-min ^{250}Fm. In addition, by γ-ray counting, isotopes of Bk and Es, most intensively ^{250}Bk, and/or ^{250}Es, were detected in this fraction. The insert in spectrum 1 which magnifies the energy region from 7.0 to 8.5 MeV shows an α group at 8.0 MeV consisting of 11 events which we assign to the decay of ^{260}Lr. As also observed elsewhere[§] this group is possibly composed of two peaks, one at 7.96 MeV (3 events), and the other at 8.03 MeV (8 events). The time distribution of these events is consistent with the 3.0 ± 0.5 min half-life measured by Eskola *et al.* [7]. In 22 accumulation and separation cycles, a total of 13 decays of ^{260}Lr were observed in the 'non-reducible' actinide fractions, while no single 8 MeV α-particle was observed in the 'reducible' actinide fractions, see spectrum 2 of Fig. 3. When using the production cross-section of 8.3 ± 1.7 nb [6] and a detector geometry of 30%, the observed ^{260}Lr events indicate a combined gas-jet and chemical yield of about 45%. This is in agreement with independent measurements of the transport efficiency and the chemical yield, the latter being determined with various lanthanide tracer activities. As can be seen from spectrum 2 in Fig. 3, the 'reducible' actinide spectrum contains pure Md. The main activities are 27-min ^{255}Md, and 3.24-h ^{254}Fm, the electron-capture decay daughter of ^{254}Md. In agreement with the standard reduction potential of Md^{3+} of about −0.2 V [9, 12, 13] we find from spectra 1 and 2 that the reduction of Md^{3+} by Cr^{2+} occurred almost quantitatively in our experiments. Bk, Es and Fm were not reduced in agreement with their reduction potentials [9] for the III → II half reaction of −2.5 V, −1.55 V and −1.15 V, respectively. For comparison, the Cr^{3+}/Cr^{2+} potential is −0.41 V, and that for the V^{3+}/V^{2+} potential is −0.26 V [14].

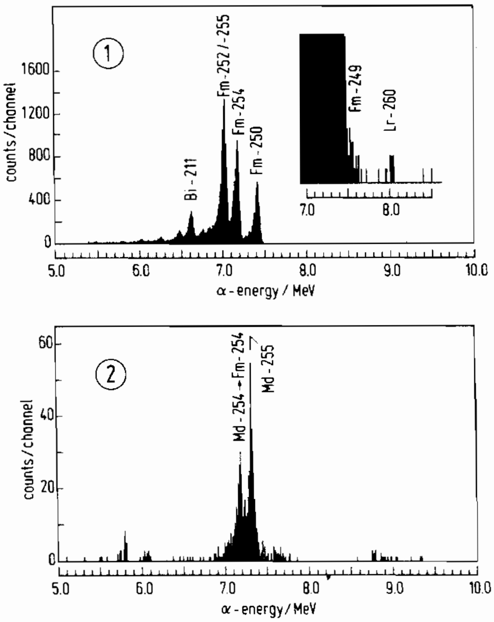

Fig. 3. α-Particle spectra in the reduction experiments with Cr^{2+}. Spectrum 1 is associated with the 'non-reducible' actinides, spectrum 2 with the 'reducible' actinides. The activities at 6.06 and 8.78 MeV are due to ^{212}Bi which recoiled onto the detectors from a ^{212}Pb (^{212}Bi–^{212}Po) α-energy calibration source. The peak at 5.81 MeV is due to ^{249}Cf target material on the detectors from previous experiments. The peak at 6.62 MeV in spectrum 1 is due to ^{211}Bi produced by transfer reactions with Pb target impurities.

The distribution of the Lr ions with 13 events in the 'non-reducible' fractions and no single event in the 'reducible' actinide fractions in the experiments with Cr^{2+} can be used to calculate an upper limit for the standard reduction potential for a possible $Lr^{3+} + e^- \rightarrow Lr^{2+}$ half reaction or for the $Lr^{3+} + 2e^- \rightarrow Lr^{+}$ half reaction. Although there is better theoretical justification [4] for the existence of the Lr^{1+} ion, the reduction to Lr^{2+} is included in the discussion below because the chemical separations did not differentiate between the Lr^{1+} and Lr^{2+} ions.

The following equilibrium can be written for the reduction of Lr^{3+} to Lr^{1+} by chromous ion.

$$2Cr^{2+} + Lr^{3+} = 2Cr^{3+} + Lr^{1+}$$

In equilibrium the potentials E for the two half reactions must be equal such that

$$E^{\circ}_{\mathrm{Lr\,III-I}} = E^{\circ}_{\mathrm{Cr\,III-II}} + (RT/2F)\ln\frac{[Cr^{3+}]^2[Lr^{1+}]}{[Cr^{2+}]^2[Lr^{3+}]} \quad (1)$$

where the brackets indicate activities of these ions. In order to determine the ratio of Lr ion activities in the above equation ($[Lr^{1+}]/[Lr^{3+}]$), we use the thirteen ^{260}Lr events found in the 'non-reducible' fractions; no ^{260}Lr events were observed in the 'reducible' fractions, but we assume a maximum of three events to

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[§] A lower energy α group for ^{260}Lr was possibly also observed in ion exchange studies performed concurrently with this work.

be compatible with a 95% confidence level. The $[Cr^{3+}]/[Cr^{2+}]$ ratio was determined in two ways: (i) via the degree of reduction of Eu^{3+} ions, reduction potential $E^\circ = -0.35$ V [15], observed in experiments under similar conditions with tracer amounts of $^{152,154}Eu$; and (ii) by using chromium metal ion solutions of similar composition via the measurement of absorption spectra.

Because it is more conservative we start with estimate (i). The equation for the oxidation–reduction reaction is

$$Cr^{2+} + Eu^{3+} = Cr^{3+} + Eu^{2+}$$

The associated equilibrium constant

$$K = ([Cr^{3+}][Eu^{2+}])/([Cr^{2+}][Eu^{3+}])$$

is related via the Nernst equation to the difference between the standard potentials $E^\circ_{\mathrm{Eu\,III-II}}$ and $E^\circ_{\mathrm{Cr\,III-II}}$ as

$$-0.35 + 0.41 = 0.06 = (RT/F) \ln K$$

so that $K = 7.31$.

From the measured ratio $[Eu^{2+}]/[Eu^{3+}]$ which was $\gg 9$[†] under the conditions of the present experiments, we can then conclude that the ratio $[Cr^{3+}]/[Cr^{2+}]$ must have been $\ll 0.8$. We know from the light sky-blue color of the chromous solution that the actual admixture of chromic ion (green) present in the Lr reduction experiments must have been much less than the 45% indicated by the above (conservative) estimate. Inserting the above estimate for the chromic–chromous ratio of $\ll 0.8$ into eqn. (1) results in an upper limit for the standard reduction potential for the Lr(III)–Lr(II) couple of

$$E^\circ \ll -0.44 \text{ V}.$$

Similarly, for the Lr(III)–Lr(II) couple, the following equilibrium

$$Cr^{2+} + Lr^{3+} = Cr^{3+} + Lr^{2+}$$

leads to the following equation.

$$E^\circ_{\mathrm{Lr\,III-II}} = E^\circ_{\mathrm{Cr\,III-II}} + (RT/F) \ln \frac{[Cr^{3+}][Lr^{2+}]}{[Cr^{2+}][Lr^{3+}]} \qquad (2)$$

Solving as before gives an upper limit for the standard reduction potential of the Lr(III)–Lr(II) couple as $E^\circ \ll -0.46$ V. Therefore a very conservative estimate for the standard reduction potential for reduction of Lr^{3+} to the divalent or monovalent state is more negative than -0.44 V.

For the less conservative estimate (ii) after the foregoing experiments, chromous solutions of similar composition as well as pure chromic solutions in 0.3 M HCl were examined by absorption spectroscopy (chromic ion solutions show two absorption maxima at 430 nm and at 600 nm, while chromous solutions do not absorb at these wave lengths). We found that, reproducibly, only 4% of the chromous ion was oxidized, resulting in a $[Cr^{3+}]/[Cr^{2+}]$ ratio of 0.04 and a standard potential for reduction of Lr^{3+} of $E^\circ \ll -0.53$ V. Because it is not known whether the chromous solution used in the actual Lr experiments was of exactly the same quality we prefer the more conservative estimate of $E^\circ \ll -0.44$ V.

We also conducted a few experiments with V^{2+} as the reductant. The reduction potential for the $V^{3+} + e^- = V^{2+}$ reaction is less negative, $E^\circ = -0.26$ V, and is much closer to the Md^{3+}/Md^{2+} potential ($E^\circ = -0.2$ V [9]). Nevertheless, complete reduction of Md^{3+} has been previously observed [13], and in the present experiments, when V^{2+} was used as the reducing agent, we again found Md in the 'reducible' actinide fractions.

Additional attempts to reduce Lr^{3+} (i) by zinc in the mixed Zn/LEWATIT-OC 1026® column beds, and (ii) by hydroxylamine hydrochloride, failed. In these experiments, even Md^{3+} was not reduced to the divalent state. In case (i), it is conceivable that the reducing surface was too small and the contact time too short to achieve reduction. In case (ii), the time was probably insufficient for the reduction to proceed to an appreciable extent. Oxidation of hydroxylammonium ion involves several steps and requires reactions of hydroxylamine with its own partially oxidized descendants such as nitrosyl [14]. Even though partial oxidation to N_2 (without) progressing to the nitrous or nitric ion) is associated with the impressive potential $E^\circ = -1.87$ V, the multi-step nature of the oxidation of hydroxylamine makes for a very slow kinetics, incompatible with the requirements of the present experiments.

Further searches for the 1+ state of Lr are of prime importance. In aqueous solutions electrochemical methods [16–19] appear to be promising even though these methods have not so far been applied to isotopes as short-lived as 3-min ^{260}Lr. Non-aqueous ion exchange or extraction systems may have to be used to avoid limitations due to the reduction of water. Reduction–cocrystallization experiments in molten salts [20] have provided valuable information on standard potentials for Me^{3+}/Me^{2+} couples within the lanthanide and actinide series. However, the time required for such cocrystallization experiments is too long for a serious consideration of this method for the reduction of 3-min ^{260}Lr. Use of the recently discovered [21], longer-lived $^{261,262}Lr$ might permit more extensive chemical studies.

[†] The ratio is based on the overall yields of Eu^{2+} in tracer studies with ARCA without correction for its chemical yield (typically $\gg 90\%$). Therefore, the ratio of the true equilibrium activities Eu^{2+}/Eu^{3+} must have been larger than 9.

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