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ATOM-AT-A-TIME RADIOCHEMICAL SEPARATIONS OF THE HEAVIEST ELEMENTS:  
LAWRENCIUM CHEMISTRY

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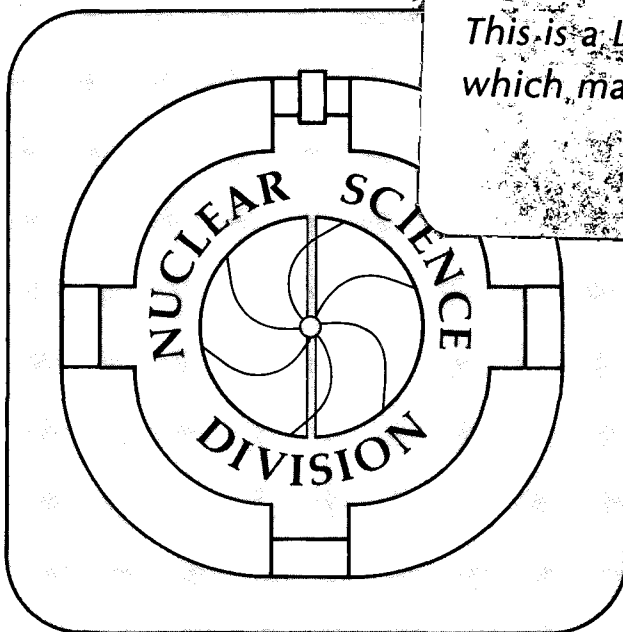
## ATOM-AT-A-TIME RADIOCHEMICAL SEPARATIONS OF THE HEAVIEST ELEMENTS: LAWRENCIUM CHEMISTRY

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H.L. Hall, D.M. Lee, M.J. Nurmi, S. Cai,  
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Atom-at-a-Time Radiochemical Separations of the Heaviest  
Elements: Lawrencium Chemistry

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ATOM-AT-A-TIME RADIOCHEMICAL SEPARATIONS OF THE HEAVIEST  
ELEMENTS: LAWRENCIUM CHEMISTRY

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The isotope  $^{260}\text{Lr}$  produced in reactions of  $^{18}\text{O}$  with  $^{249}\text{Bk}$  was used to perform chemical experiments on lawrencium to learn more about its chemical properties. These experiments involved extractions with thenoyl trifluoroacetate (TTA), ammonium alpha-hydroxyisobutyrate (HIB) elution from a cation exchange resin column, and reverse-phase chromatography using hydrogen di(2-ethylhexyl)orthophosphoric acid (HDEHP) to investigate the chemical properties of Lr. The results from the HIB elutions also give information about the ionic radius of Lr(III) which was found to elute very close to Er. An attempt to reduce Lr(III) was also made.

## I. INTRODUCTION

Studies of the chemical properties of the elements above fermium are very difficult because these elements must be produced at accelerators and must be performed with isotopes having very short half-lives and available in quantities of only a few atoms at a time. This necessitates devising very fast and efficient radiochemical procedures. In addition, if reliable information concerning chemical properties is to be obtained, methods in which each of the available

atoms is equilibrated rapidly through many reactions are normally required.<sup>1</sup> Techniques such as ion exchange, solvent extraction, and gas chromatography can often be used. A classic example of such a study is the determination<sup>2</sup> of the No(II)-No(III) potential by Silva et al. The 3-minute <sup>255</sup>No isotope produced from the <sup>244</sup>Pu(<sup>16</sup>O, 5n) reaction was used. The distinction between No(II) and No(III) was made on a few atoms at a time basis by using a column chromatographic technique. The standard potential was estimated from a comparison of the behavior of nobelium with the behavior of tracer quantities of other radionuclides of known standard potentials.

Studies of the chemical properties of the heaviest actinides and comparison with the properties of the lanthanides are of particular interest because they help assess the influence of relativistic effects.<sup>3</sup> These cause a stabilization of the s and p orbitals in the actinides. By analogy with lutetium, the last of the lanthanide series, which has an electronic structure of [Xe]4f<sup>14</sup>5d<sup>1</sup>6s<sup>2</sup>, the structure of lawrencium would be expected to be [Rn]5f<sup>14</sup>6d<sup>1</sup>7s<sup>2</sup>. However, because of relativistic effects, Brewer<sup>3</sup> predicted the configuration would be [Rn]5f<sup>14</sup>7s<sup>2</sup>7p<sup>1</sup> and Dirac-Fock calculations<sup>4</sup> confirm this prediction. Furthermore, the 7s<sup>2</sup> might be stabilized to the extent that only the 7p<sub>1/2</sub> electron could be removed in the presence of suitable reducing agents, resulting in the production of Lr in the 1<sup>+</sup> oxidation state.

Recently, we have undertaken experiments to deduce the ionic radius of lawrencium (element 103) by determining its elution position from a cation-exchange resin column relative to the trivalent rare earths and other trivalent actinides for which the ionic radii<sup>5-7</sup> are known. Earlier extraction studies<sup>8</sup> using the 26-s <sup>256</sup>Lr have shown that Lr(III) is the most stable oxidation state in aqueous solution and that

Lr completes the actinide series as predicted by Seaborg<sup>9</sup> in 1945. The elution positions from cation exchange resin columns with ammonium alpha-hydroxyisobutyrate (HIB) have also been determined<sup>10,11</sup> for the trivalent rare earths and for the actinides through mendelevium (element 101). These elements are eluted in order of their ionic radii, those with the smallest radii being eluted first. Although  $^{260}\text{Lr}$ , an 8.03-MeV alpha-emitting isotope with a half-life of  $3.0 \pm 0.5$  m, was discovered by Eskola et al.<sup>12</sup> in 1971, no further chemical experiments were performed on Lr until our present studies.

## II. EXPERIMENTAL

### A. Production of $^{260}\text{Lr}$

The 3-m  $^{260}\text{Lr}$  was produced via the reaction  $^{249}\text{Bk}(^{18}\text{O}, \alpha 3n)$  at the LBL 88-Inch Cyclotron. Targets of  $\text{Bk}_2\text{O}_3$  containing about  $0.9 \text{ mg/cm}^2$  of  $^{249}\text{Bk}$  were prepared by electrodeposition<sup>13</sup> with a diameter of 6 mm on  $2.75 \text{ mg/cm}^2$  Be foil. They were irradiated with 117-MeV  $^{18}\text{O}^{5+}$  projectiles resulting in incident energies on target of 102-MeV with intensities of about 0.5  $\mu\text{A}$ . A stream of helium was passed over crystalline KCl kept at about  $650 \text{ C}^\circ$  in a quartz tube before being fed into the target recoil chamber where the pressure of He was about 1.3 bar. The recoiling reaction products attach to the KCl aerosol and are transported via the pressurized He gas system through a capillary to a collection chamber several meters away where they are collected on a metallic foil. Typically, reaction products were collected for 6 to 10 minutes and then chemically processed.

### B. Chemical procedures

In order to verify that the 3-m activity was indeed properly assigned to Lr, extractions with 0.1 M thenoyl trifluoroacetate (TTA) in methylisobutyl ketone (MIBK) were performed. The KCl deposit was

dissolved in a buffer solution of monochloroacetic acid or acetic acid adjusted to pH ranges of 1.86 to 5.5. Extractions with TTA from buffer solutions of different pH were performed. The organic phase was dried on a Pt plate and alpha counted. The entire procedure required about three minutes.

Reduction of Lr was also attempted. A reverse-phase chromatographic column<sup>14</sup> (2-mm i.d. x 5-cm long) consisting of hydrogen di(2-ethylhexyl)orthosphosphoric acid (HDEHP) on hydrophobic celite (50-75 micron diameter particles) was used to sorb trivalent and higher oxidation state species from 0.3 M HNO<sub>3</sub>. The lower valent species and Ac<sup>3+</sup> were completely removed by washing with 0.3 M HCl. In the reduction experiments, 0.06 M NH<sub>2</sub>OH·HCl in 0.3 M HCl was passed through the column at a temperature of about 80°C in an attempt to reduce Lr<sup>3+</sup> to a lower oxidation state which would then be removed from the column. Trivalent actinides can be quickly eluted from the column with 3 M HCl leaving tetravalent and higher oxidation state species on the column. Thus appropriate combinations of these separations can be used to distinguish between 1<sup>+</sup> or 2<sup>+</sup>, 3<sup>+</sup>, and 4<sup>+</sup> oxidation states of heavy actinides.

In other experiments, the reaction products, together with the appropriate rare earth tracers, were taken up in 0.05 M HCl and sorbed on a 2-mm i.d. x 4.5-cm long, 10 micron particle size, Dionex cation exchange resin column. The actinides and lanthanides were eluted with 0.05 M ammonium alpha-hydroxyisobutyrate adjusted to pH 4.47. The fractions were collected dropwise on Pt foils, evaporated to dryness, flamed, and alpha counted. The plates were later subjected to gamma-spectral analysis to determine the elution positions of the added rare earth tracer pairs, Yb and Er, and Tm and Ho. About 6 minutes were required for separation before alpha spectroscopic measurements could begin.



### C. Data analysis

Alpha spectra were measured with 300 mm<sup>2</sup> Si(Au) surface barrier detectors. Data acquisition and analysis were performed using our Realtime data Acquisition and Graphics System (RAGS). The signals from the ADC's are taken into a Standard Engineering CAMAC interface to a Digital Equipment Corporation LSI 11/73 computer and the detector number, time, and channel number (energy) for each event are stored on magnetic tape. This list mode storage allows versatile off-line data analysis, including histogramming and time-correlation analysis. Using this system we can search for alpha-time correlations from successive alpha decays between mother, daughter, etc., in a genetic sequence. In this way, 8.03-MeV alphas arising from decay of 2.2-m <sup>223</sup>Ac (produced from reactions of <sup>18</sup>O with possible traces of <sup>208</sup>Pb in the target) via the decay chain shown in Fig. 1 could be distinguished from the 8.03-MeV alphas from <sup>260</sup>Lr. However, the data were all examined for time correlations characteristic of the <sup>223</sup>Ac decay chain and its contribution was found to be negligible.

In order to correct for gas jet yield, chemical yield, detector efficiency, beam intensity, and other possible variables, the yield of <sup>260</sup>Lr was obtained relative to the amounts of 30-m <sup>250</sup>Fm, 3.2-h <sup>254</sup>Fm, or 25-h <sup>252</sup>Fm produced in each run. The yields of these Fm isotopes were determined from separate one-hour irradiations carried out just before or after the fast chemistry runs and under the same conditions. The recoiling products were caught in 1-2 mg/cm<sup>2</sup> Au foil. The experimental arrangement is described in a previous paper.<sup>15</sup> The Au foil was dissolved in conc. HCl and a few drops of HNO<sub>3</sub> containing <sup>241</sup>Am tracer for yield determination. The resulting solution was passed

through an anion exchange resin column to remove the Au and then electroplated.<sup>16</sup> Alpha spectroscopic measurements were performed to measure the production cross sections of the Fm isotopes.

### III. RESULTS AND DISCUSSION

Recoiling reaction products were extracted with TTA from buffer solutions of pH 1.86, 2.33, 2.67, 3.00, 3.15, 3.5, 4.0, 4.5, 5.0, and 5.5. The number of events of  $^{260}\text{Lr}$  produced per experiment can be calculated relative to the observed production of  $^{250}\text{Fm}$ ,  $^{254}\text{Fm}$ , or  $^{252,255}\text{Fm}$  whose effective cross sections for the target composition were determined for the conditions of these experiments. (The contribution from  $^{249}\text{Cf}$  must be considered since  $^{249}\text{Bk}$  decays with a 330-d half life to  $^{249}\text{Cf}$ .) In about one hundred 6- to 10-minute collections and separations, 27 events attributable to  $^{260}\text{Lr}$  were detected. Neither the 3-m  $^{260}\text{Lr}$  nor the Fm isotopes was extracted at pH 1.86. The extraction of the 8.03-MeV, 3-m activity was nearly complete by pH 3.15. This shows that it exhibits the same extraction behavior as observed<sup>8</sup> previously for 28-s  $^{256}\text{Lr}$  and the trivalent heavy actinides Am, Cm, Cf, and Fm. Its behavior differs from that extraction of divalent No whose extraction does not begin until pH 4 and is not complete until about pH 5. The fact that no 8.03-MeV, 3-m alpha events were extracted at pH 1.86 shows that  $^{260}\text{Lr}$  is not in a tetravalent oxidation state. From these experiments, we conclude that the chemistry of the 3-m, 8.03-MeV alpha emitter is consistent with that of Lr in the trivalent oxidation state.

The cross section for production of  $^{260}\text{Lr}$  via the  $^{249}\text{Bk}(^{18}\text{O}, \alpha 3n)$  reaction at 101 MeV was measured in similar TTA extractions conducted at a pH of 2.9 to avoid possible contamination from No. About 45 alphas from  $^{260}\text{Lr}$  were detected. The yield for the

procedure was obtained from the Fm isotopes and a cross section of  $8.3 \pm 1.7$  nb was calculated for  $^{260}\text{Lr}$ . The half-life for these events was consistent with the  $3.0 \pm 0.5$ -m half-life reported by Eskola et al.<sup>12</sup>

The attempts to reduce Lr(III) to a lower oxidation state with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  were unsuccessful. In a series of 24 experiments, no events attributable to  $^{260}\text{Lr}$  were observed in the 0.3 M HCl/0.06 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  fraction from the HDEHP column which contained the species with lower oxidation states. Four events attributable to  $^{260}\text{Lr}$  were observed in the 3 M HCl fraction containing the heavy trivalent actinides. Although the potential for the oxidation of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  to  $\text{N}_2$  is -1.87 V, the kinetics are known to be slow. A check of our data showed that  $^{254,255}\text{Md}$  was not reduced even though its standard reduction potential<sup>17</sup> is only -0.1 to -0.2 V, thus confirming that a time of 20 s at  $80^\circ\text{C}$  was insufficient to accomplish the reduction. Other strong reducing agents whose kinetics are faster will have to be used, or perhaps studies with the recently discovered<sup>18</sup> longer-lived isotopes  $^{261,262}\text{Lr}$  can be performed.

In the initial HIB elutions from cation exchange resin columns, Yb and Er tracers were used and it was found that the 3-m  $^{260}\text{Lr}$  eluted nearly with the Er tracer. In order to avoid any possible problems due to the finite (about 0.1  $\mu\text{g}$ ) mass of the Er tracer, a series of elution experiments was conducted using only Tm and Ho tracers to bracket the Er (Lr) position. In 18 such experiments, seven alpha events attributable to 3-m  $^{260}\text{Lr}$  were detected. (The most probable half-life for these 8.03-MeV alpha events is  $2.7^{+1.7}_{-0.9}$  m, consistent with the value of  $3.0 \pm 0.5$  m reported earlier by Eskola et al.<sup>12</sup>.) The elution position of each of these 8.03-MeV alpha events was compared with the elution positions of the Tm and Ho tracers. (See Fig. 2.) From this infor-

mation, an ionic radius was calculated for each Lr event, and the average Lr radius was found to be  $0.0005 \pm 0.0003$  nm larger than that of Er. If the ionic radius of Er is taken to be 0.0881 nm as measured by Templeton and Dauben<sup>5</sup>, then the ionic radius of Lr is  $0.0886 \pm 0.0003$  nm.

Other experiments have shown that Md (101) elutes very close to the Ho position, implying that the ionic radius of Md is similar to that of Ho, or about 0.0894 nm. This gives a difference between the  $\text{Md}^{3+}$  radius and the  $\text{Lr}^{3+}$  radius of only 0.001 nm, comparable with the usual difference between ionic radii of adjacent lanthanide or actinide elements, even though there is a difference of 2Z between Md and Lr. This is much smaller than the 2Z separation of 0.0021 nm for the analogous lanthanide ions,  $\text{Tm}^{3+}$  and  $\text{Lu}^{3+}$ , at the end of the lanthanide series. Due to these apparently very close values for the ionic radii of the last three actinides, it becomes especially important to measure the ionic radius of the  $\text{No}^{3+}$  ion. Because No is most stable in aqueous solution in the divalent state, the HIB method cannot be used as it will not work under the strongly oxidizing and acidic conditions necessary to keep No in the 3+ state. Perhaps the HDEHP chromatographic column technique can be adapted for obtaining information about the ionic radius of No(III) based on its elution position relative to other actinides and the lanthanides.

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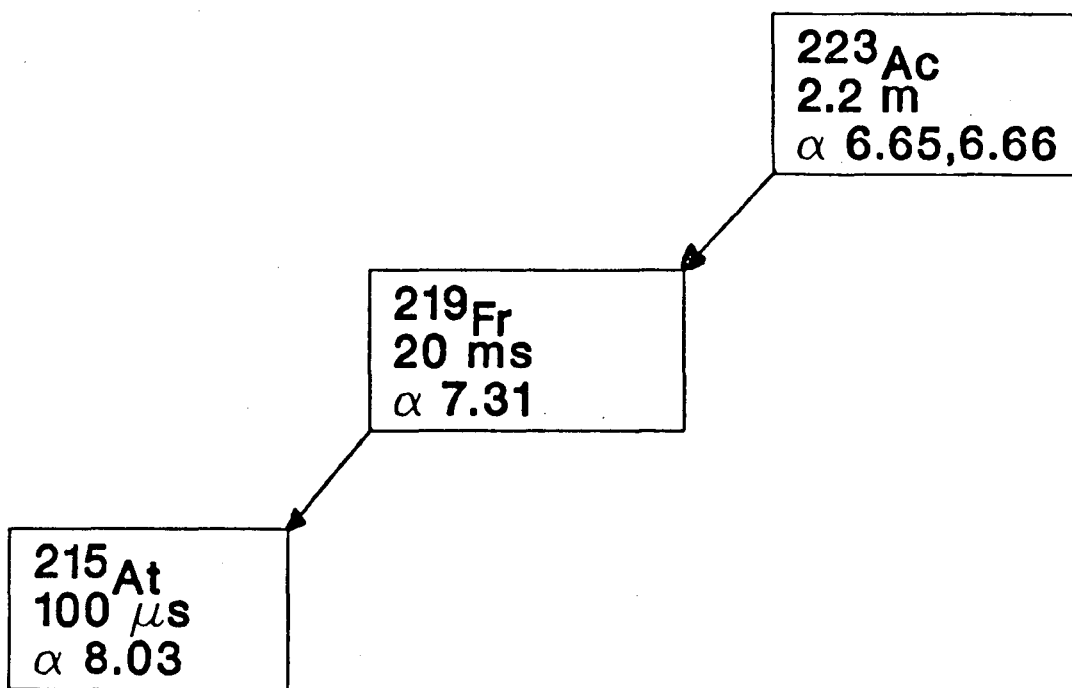
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Figures

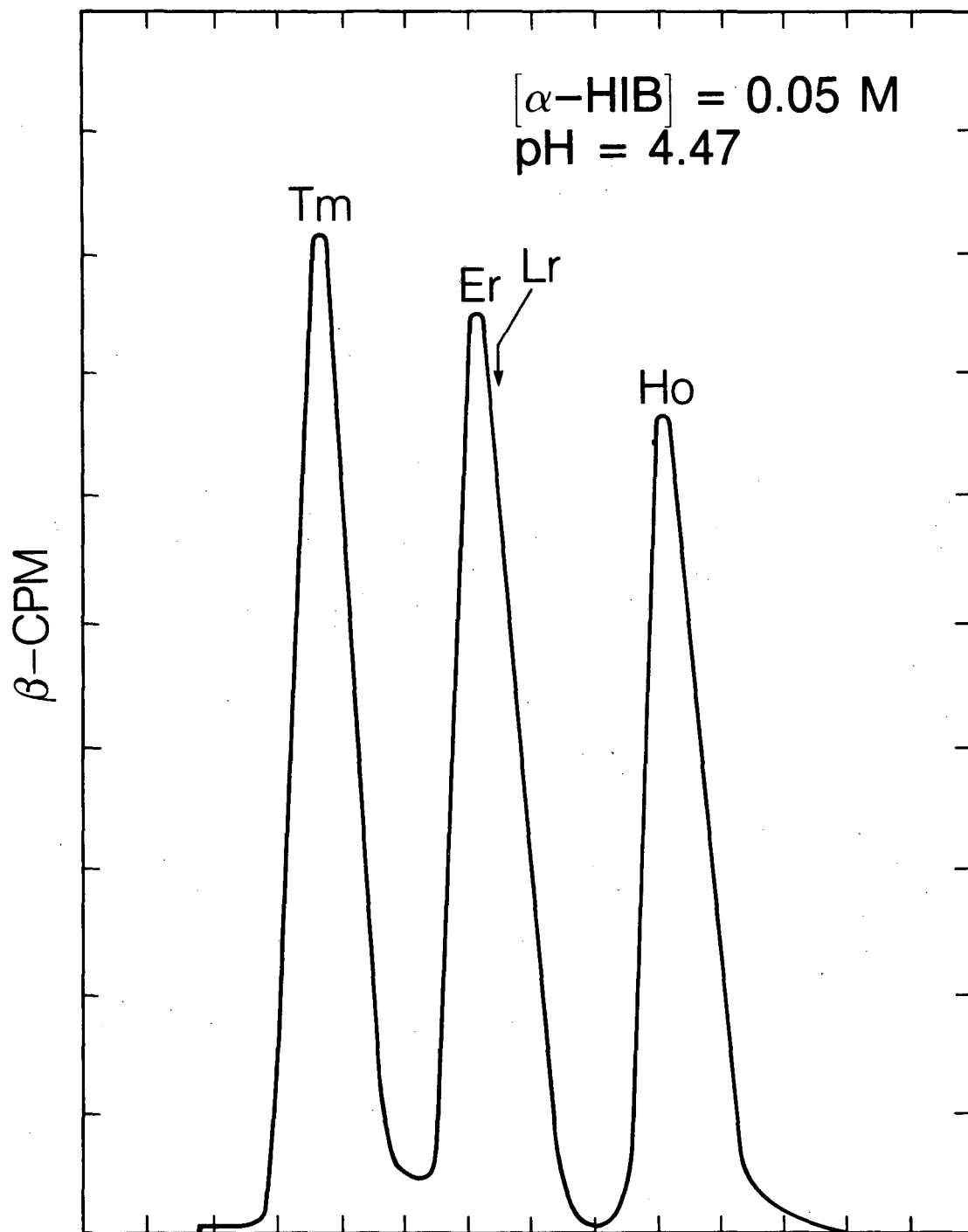
Figure 1. Decay sequence from  $^{223}\text{Ac}$ .

Figure 2. Schematic of HIB elution showing Lr position.



XBL 874-1766

Fig. 1. Decay sequence from  $^{223}\text{Ac}$



XBL 873-1270

Fig. 2. Schematic of HIB elution showing Lr position



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