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3 Title: Development of a ²¹²Pb and ²¹²Bi generator for homolog studies of flerovium and
4 moscovium

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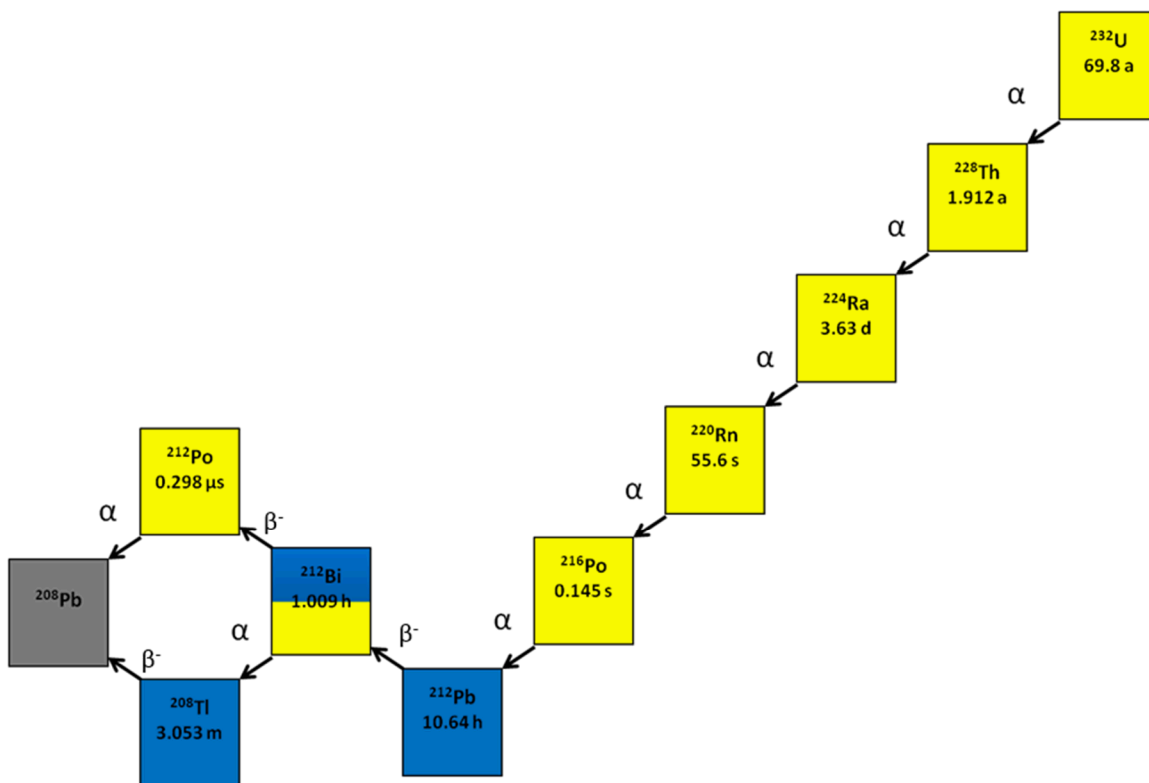
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37 Chemical investigations of superheavy elements ($Z \geq 104$) are very challenging. Due
38 to their short half-lives and small production cross-sections (\sim pb) these elements need to
39 be studied one-atom-at-a-time. Their chemical properties are ascertained through
40 systematic studies of their chemical groups [1]. For flerovium, Fl, $Z=114$, and
41 moscovium, Mc, $Z=115$, (residing in Group 14 and 15 of the Periodic Table,
42 respectively) their direct chemical homologs are Pb and Bi. To develop an aqueous
43 chemical system for future studies of Fl and Mc, a readily available source of Pb and Bi
44 as no-carrier-added (NCA) radioisotopes is required. This can be achieved using
45 radionuclide generators based on the natural U and Th decay chains.

46 For the specific application to Fl homolog chemistry various generator systems have
47 been proposed by Guseva *et al.* for generation of $^{211}\text{Pb}/^{211}\text{Bi}$ and $^{212}\text{Pb}/^{212}\text{Bi}$ from
48 generators using the parent nuclides ^{227}Ac and ^{228}Ra , respectively. For these generators
49 HCl/CH₃OH and HBr eluents were chosen [2-4]. This method is undesirable for future Fl
50 homolog experiments due to the need to change matrices. It was desired to make a
51 generator which could be eluted and used for long durations of time from an HCl matrix.
52 The Guseva *et al.* experiments also do little to mention the very long-term use of the
53 generator. A simple method for isolation of $^{212}\text{Pb}/^{212}\text{Bi}$ from HCl matrices was described
54 in [5] showing elution of the aforementioned Pb and Bi isotopes from a ^{228}Th parent;
55 however, no discussion on how long a generator of this type could last based on that
56 simple procedure was presented. A similar separation scheme is also described in [6], in
57 this case ^{212}Pb and ^{207}Bi were eluted and seen to behave as described in this paper.

58 Legacy material at Lawrence Livermore National Laboratory (LLNL) of ^{232}U
59 containing all of its naturally occurring daughters (including ^{228}Th) was used to develop

60 and characterize a $^{212}\text{Pb}/^{212}\text{Bi}$ generator for studies of Fl and Mc homologs. The decay
61 chain resulting in the isotopes $^{212}\text{Pb}/^{212}\text{Bi}$ is shown in Fig. 1.



62

63 **Fig. 1.** ^{232}U decay chain, with half-lives from Ref. [7].

64 Experiments on the long-term stability of this generator as well as possible breakthrough
65 of the parent radionuclides were performed to establish the use of such a generator for a
66 long-term heavy element research program.

67 **Experimental**

68 **Reagents and Materials**

69 Acids were prepared from trace-metal grade acids and de-ionized water (18 $\text{M}\Omega\cdot\text{cm}$). AG
70 50Wx8 (100-200 mesh) cation exchange resin was used for preparation of the generators.

71 The resin was cleaned based on the procedure given in [8]. The ^{232}U was LLNL legacy
72 material with all daughters in secular equilibrium.

73 **Activity Measurements**

74 Activity measurements were performed on a high purity germanium (HPGe) gamma-ray
75 spectrometer coupled with a multi-channel analyzer (DSPEC, Ortec). Spectral files were
76 analyzed with Maestro spectral software (Ortec). The spectral lines with the highest relative
77 yield were chosen for determining the activity of each radionuclide (Table 1) [7].

78 **Table 1** Photon energies selected for activity determination [7].

| Radionuclide (half-life) | Energy (intensity, %) |
|--|------------------------------|
| ^{212}Pb ($t_{1/2} = 10.64$ h) | 238.6 keV (43.3%) |
| ^{212}Bi ($t_{1/2} = 60.55$ m) | 727.3 keV (6.58%) |
| ^{224}Ra ($t_{1/2} = 3.66$ d) | 240.9 keV (4.10%) |

79

80 All samples were maintained in the same 1 mL or 0.5 mL geometry so efficiency
81 calibrations were not needed. All samples were counted for 120 s to 600 s to obtain at least
82 1000 counts per analyzed radionuclide.

83 **Generator Set up**

84 An initial generator was prepared on May 30th, 2014 and has been used for experiments
85 detailed in [9, 10], with a final elution performed for longevity studies presented in this
86 work on April 18th, 2017. To prepare this generator (Gen1), a ^{232}U sample (approximately
87 10 μCi) was evaporated and reconstituted in 1 mL of 0.4 M HCl. A 2.5 mL AG 50Wx8
88 (100-200) mesh column was prepared by gravity flow and preconditioned with 3 mL
89 portions of 2 M and 0.4 M HCl alternating the two acids three times before the resin was

90 left in 0.4 M HCl. The ^{232}U was loaded onto the column followed by a 10 mL rinse with
91 0.4 M HCl, and allowed to sit for three days to allow for > 99% of ^{212}Pb to reach
92 equilibrium (74.5 hr, approximately 7 half-lives of ^{212}Pb gives > 99% equilibrium with
93 parent). A second generator (Gen2) was prepared for repeated elution curve analysis by the
94 same method mentioned above except with only 0.5 μCi of ^{232}U stock in 0.5 mL of 0.4 M
95 HCl, and with 2 mL of AG 50Wx8.

96 **Breakthrough Study**

97 After allowing Gen1 to sit for three days it was eluted with 10, 1 mL fractions of 2 M HCl,
98 each collected in 15 mL centrifuge tubes (same geometry as the stock solution). These
99 solutions were monitored by HPGe gamma spectroscopy to determine the elution behavior
100 of ^{212}Pb from the generator. Under these conditions, ^{212}Bi also elutes and ^{228}Th has its
101 lowest distribution ratio. The solutions were stored for one month, allowing any ^{228}Th
102 present to have its daughters obtain secular equilibrium before being recounted to look for
103 ^{228}Th breakthrough.

104 **Repeat Elution Study**

105 Using Gen2, three elutions approximately one week apart (4/4, 4/10 and 4/18/17) were
106 performed to isolate ^{212}Bi and ^{212}Pb from the column. For each elution, 10, 0.5 mL 0.4 M
107 HCl fractions were collected, followed by 10, 0.5 mL fractions of 2 M HCl and finally 3
108 fractions of 0.4 M HCl were collected at the end before 0.5 mL of 0.4 M HCl was left
109 above the resin bed for storage. All fractions were collected in 5 mL centrifuge tubes (same
110 geometry as initial stock solution for direct comparison). Each sample was counted by
111 HPGe gamma spectroscopy and compared to the stock solution to determine elution
112 profiles of ^{212}Pb and ^{212}Bi . Each elution fraction was counted a second time a week later to

113 ensure ^{212}Pb had decayed away, an indication of no breakthrough of the parent
114 radionuclides.

115

116 **Long Term Stability Study**

117 Using Gen1 the same elution conditions described in the Repeat elution study was run and
118 samples counted by HPGe gamma spectroscopy. This experiment was performed on
119 4/18/2017 almost three years after Gen1 was initially prepared.

120 **Results and discussion**

121 **Breakthrough and Long Term Stability Study**

122 Under the operating conditions of the generator, the ^{232}U will eventually bleed off the
123 column; however, ^{228}Th and its daughters with Z higher than ^{212}Pb remain strongly
124 sorbed on the column, Table 2.

125

126 **Table 2.** Distribution ratios for elements in the ^{212}U decay chain for various
127 concentrations of HCl on AG 50Wx8 [11].

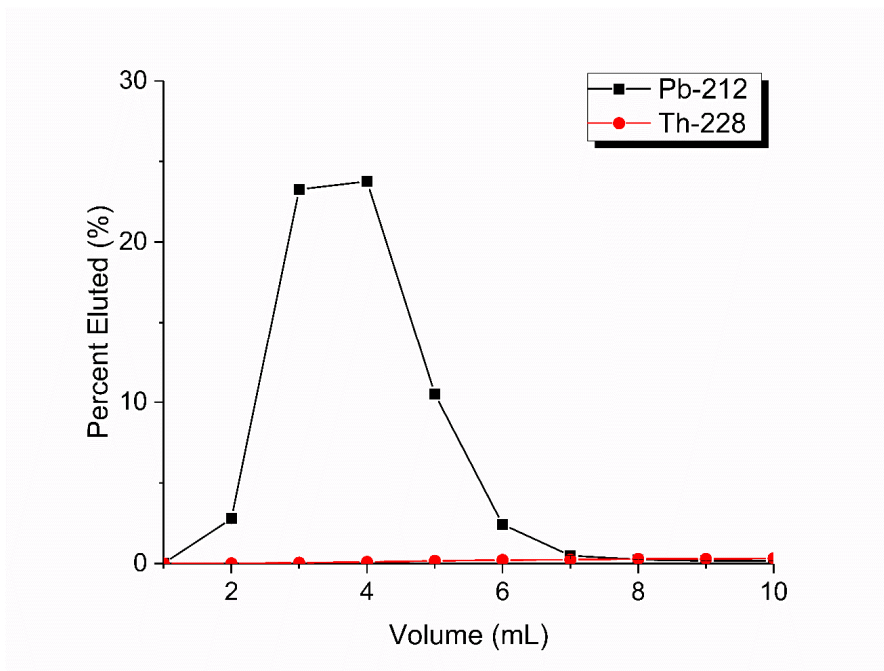
| Element | 0.2 M HCl | 0.5 M HCl | 1.0 M HCl | 2.0 M HCl |
|---------|-----------|-------------|-----------|-----------|
| U | 860 | 102 | 19.20 | 7.3 |
| Th | $>10^5$ | $\sim 10^5$ | 2049 | 239 |
| Pb | 1420 | 183 | 35.66 | 9.8 |
| Bi | Ppt. | <1 | 1 | 1 |

128

129

130 Bleeding of the ^{232}U present will not allow detectable amounts of ^{212}Pb to grow into
131 solution over the approximately 3 hour experimental time frames (due to the long 69.8
132 year half-life of ^{232}U and the 1.912 year half-life of ^{228}Th). However, if ^{228}Th were to

133 breakthrough, the generator would slowly degrade and detectable amounts of ^{212}Pb would
134 grow into the experimental solutions during the 3 hour time frames of which experiments
135 are performed.



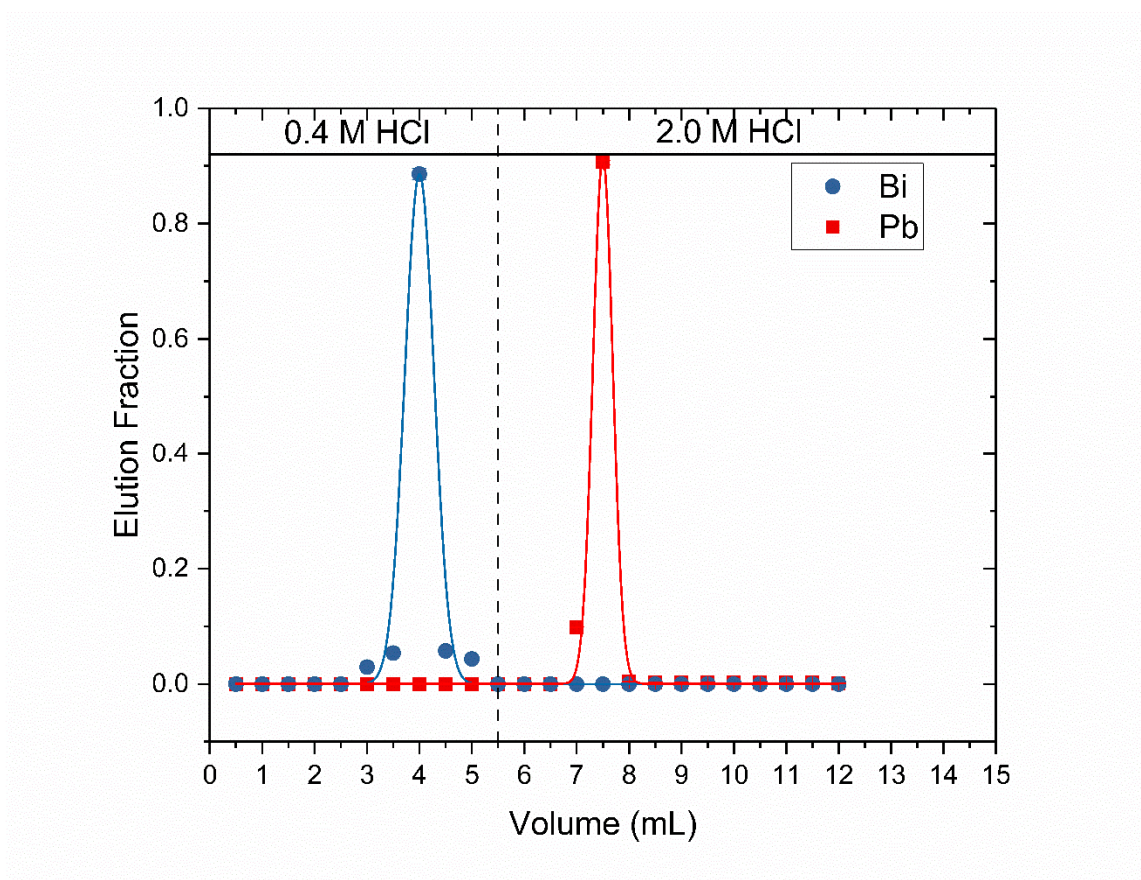
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137 **Fig. 2.** Elution of ^{212}Pb with 2 M HCl with ^{228}Th breakthrough (from counting the same
138 samples one month later). Lines presented to guide the eye only. Errors are from counting
139 statistics (error bars are inside the points).

140

141 From Fig. 2, it can be seen that initial counts of a ^{212}Pb elution show as an expected
142 elution curve. By counting these same solutions one month later and looking for the ^{212}Pb
143 gamma-lines, any detectable ^{212}Pb would be due to ^{228}Th bleeding through the column.
144 As seen in Fig. 2 no ^{212}Pb was detected one month later, indicating no detectable
145 breakthrough of ^{228}Th . Periodically over the three year usage time of the generator
146 (during experiments described in [9, 10]) the original eluted ^{212}Pb stock solutions were
147 recounted a month later and in each case no detectable ^{212}Pb was seen, indicating a very
148 stable generator that can be used for greater than three years without issue. This is further

149 strengthened by the clean separation of ^{212}Pb from ^{212}Bi performed three years later as
150 part of the long term stability study, Fig. 3. The percent eluted for this generator was
151 normalized to 1, due to the fact the exact amount of ^{232}U that was loaded onto the column
152 several years ago was not recorded as this generator was just intended as a ^{212}Pb cow.



153

154 **Fig. 3.** Elution of Gen1 after three years of continual use. Lines intended to guide the eyes
155 only. Errors shown are counting errors and are inside the points.

156

157 As can be seen in Fig. 3, and as confirmed by gamma spectroscopy there is no detectable

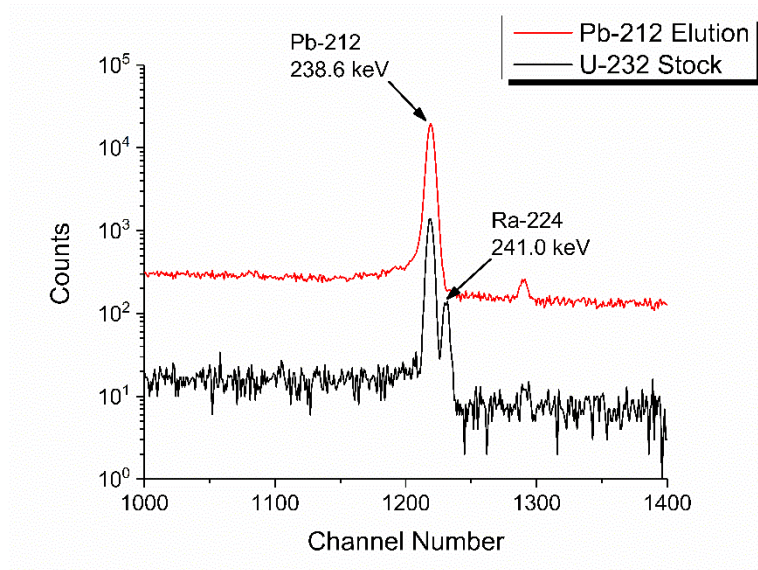
158 ^{212}Bi in the ^{212}Pb elution showing a good stability of the generator over its three year usage

159 timeline. The 3.63-day half-life of the ^{224}Ra parent of ^{212}Pb is the most important element

160 to retain on the column during ^{212}Pb elutions. If this isotope was to elute with ^{212}Pb , a large

161 amount of ^{212}Pb would grow into the stock solution during the experimental time frames.

162 The presence of ^{224}Ra is easy to detect via its 241.0 keV gamma-line, and each ^{212}Pb elution
163 was checked for ^{224}Ra , Fig. 4.



164

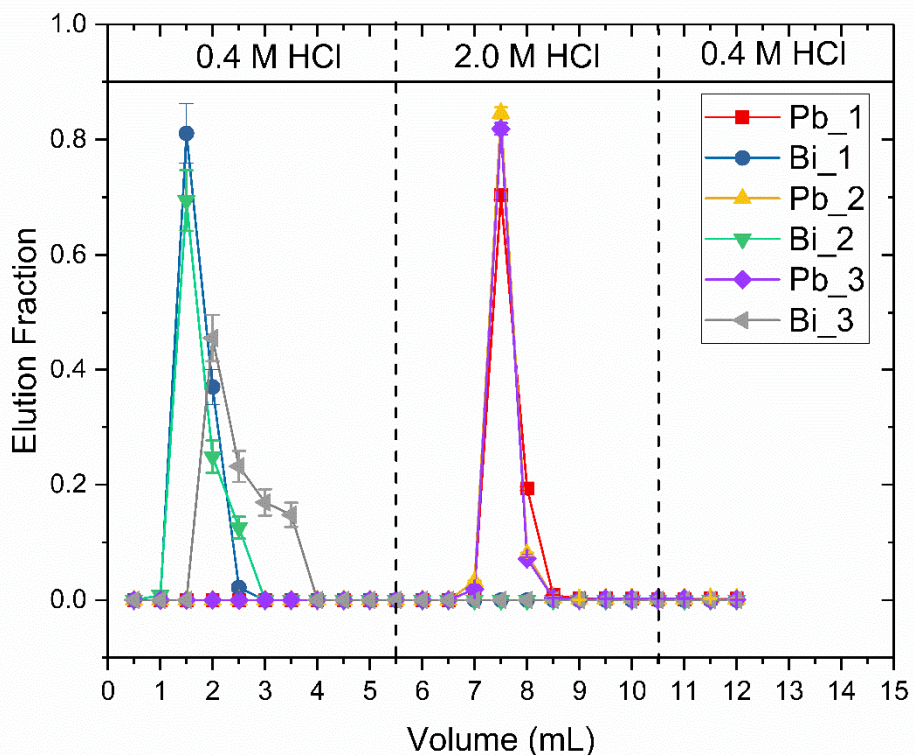
165 **Fig. 4.** Gamma spectrum showing the ^{212}Pb and ^{224}Ra gamma lines for the ^{232}U stock
166 solution and an eluted ^{212}Pb fraction.

167

168 As seen in Fig. 4 there is no detection of the ^{224}Ra gamma-line in the ^{212}Pb elution,
169 indicating ^{224}Ra is retained by the column during ^{212}Pb elution. This is confirmed by
170 counting the ^{212}Pb solution a few weeks later to obtain a background spectrum.

171 **Repeat Elution Study**

172 The Gen2 generator was eluted three times after allowing enough time for ^{212}Pb and ^{212}Bi
173 to reach secular equilibrium with their parents. The elution profiles for ^{212}Pb and ^{212}Bi are
174 shown in Fig. 5.



175

176 **Fig. 5.** The elutions of Gen2 performed after enough time was allowed for secular
 177 equilibrium to be re-established. The first elution was on 4/4/17, second on 4/10/17 and
 178 third on 4/18/17. Lines intended to guide the eye only. Errors presented are counting errors.
 179

180 As can be seen from Fig. 5, in each elution (also confirmed by gamma spectroscopy) no
 181 detectable amount of ^{212}Bi was seen in the ^{212}Pb fractions. The ^{212}Pb and ^{212}Bi elution bands
 182 show good reproducibility, even more so when compared to the result in Fig. 3 with Gen1
 183 three years after preparation. Results are also consistent with Pb and Bi elution profiles
 184 presented in Ref. [6]. In each case the counts done one week after elution were at
 185 background indicating no breakthrough of a parent radionuclide. The Bi₃ elution, while
 186 within the desired volume range, shows a slight tail and shift to its elution profile when
 187 compared to that of the previous elutions. This can be attributed to the longer duration of

188 time with this generator sitting in a state where Bi is not retained by the resin. Table 3
189 shows the percent yeilds for Gen2.

190 **Table 1.** Percent yields for each elution of Gen2.

| Elution | ²¹² Pb Percent Yield (%) | ²¹² Bi Percent Yield (%) |
|---------|-------------------------------------|-------------------------------------|
| 1 | 94.0 ± 1.6 | 120.2 ± 8.8 |
| 2 | 97.7 ± 1.8 | 107.7 ± 10.0 |
| 3 | 92.3 ± 1.6 | 101.0 ± 11.1 |

191
192 Decontamination factors are not calculated due to limited counting durations. However, as
193 was mentioned each elution fraction was counted multiple times, and nuclides decayed
194 with expected half-lives and no detectable amount of either ²¹²Bi or ²¹²Pb was seen in each
195 others respecitve fractions. The reasons for the high ²¹²Bi yields, as seen in Table 3, is due
196 to decay of ²¹²Pb during elutions constantly producing more ²¹²Bi. Due to slight differences
197 in flow rates, this accounts for the slightly different ²¹²Bi yields. In either case the yields
198 for both ²¹²Bi and ²¹²Pb are high for each subsequent elution.

199 **Conclusions**

200 A ²¹²Pb and ²¹²Bi generator system based on simple HCl matrices and cation-exchange
201 resin has been established for continual elution of Pb and Bi from ²³²U legacy material and
202 its first daughter ²²⁸Th. This generator system was tested for breakthrough of the parent
203 ²²⁸Th as well as longevity over the span of three years. A second generator was set up to
204 check reproducibility of elution profiles, and demonstrated that this generator system is
205 very reproducible.

206 The results presented provide a path to obtain NCA ^{212}Pb and ^{212}Bi , which can be
207 used to approximate atom-at-a-time chemistry. The generator system gives the direct
208 homolog of Fl and Mc for preparatory experiments to fully characterize these homologs for
209 a future aqueous study of Fl and Mc.

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215 **References**

- [1] Schädel M, Shaughnessy DA (eds) (2014) The chemistry of the super heavy elements. Springer, Heidelberg
- [2] Guseva LI, Tikhomirova GS (2002) A ^{211}Pb generator as a methodical approach to studying the chemistry of element 114 in solutions. *Radiochem* 44:167-170
- [3] Guseva LI, Tikhomirova GS, Dogadkin NN (2004) An ^{227}Ac - ^{211}Pb generator for test experiments of solution chemistry of element 114. *J Radioanal Nucl Chem* 260:167-172
- [4] Guseva LI (2007) A study of the ion-exchange behavior of Pb in dilute HBr solutions *Radiochem* 49:92-96
- [5] Hyde EK (1959) The radiochemistry of thorium. Subcommittee on Radiochemistry, National Academy of Sciences-National Research Council, Washington D. C.
- [6] Kmak KN, Despotopulos JD, Shaughnessy DA (2017) Separation of Pb, Bi and Po by cation exchange resin. *J Radioanal Nucl Chem* 314:985-989
- [7] National Nuclear Data Center "NNDC" (2017) Brookhaven National Laboratory, [Online]. Available: <http://www.nndc.bnl.gov/>. Accessed 19 Dec 2017

- [8] Rieman W, Walton HF (1970) Ion exchange in analytical chemistry. Pergamon Press, Oxford
- [9] Despotopulos JD, Kmak KN, Gharibyan N, Henderson RA, Moody KJ, Shaughnessy DA, Sudowe R (2016) Characterization of the homologs of flerovium with crown ether based extraction chromatography resins: studies in hydrochloric acid. *J Radioanal Nucl Chem* 310:1201-1207
- [10] Despotopulos JD, Kmak KN, Gharibyan N, Henderson RA, Moody KJ, Shaughnessy DA, Sudowe R (2017) Characterization of the homologs of flerovium with crown ether based extraction chromatography resins: studies in nitric acid. *J Radioanal Nucl Chem* 311:649-653
- [11] Strelow FWE (1960) An ion exchange selectivity scale of cations based on equilibrium distribution coefficients. *Anal Chem* 32:1185-1188