

1 LOG NUMBER OF PAPER: 190

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Journal of Radioanalytical and Nuclear Chemistry

19

Revised Version Submitted: July 31, 2012

20 **A new method for the determination of low-level actinium-227 in geological samples**

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31 **Abstract:**

32 We developed a new method for the determination of ²²⁷Ac in geological samples. The method uses
33 extraction chromatographic techniques and alpha-spectrometry and is applicable for a range of natural matrices.
34 Here we report on the procedure and results of the analysis of water (fresh and seawater) and rock samples. Water
35 samples were acidified and rock samples underwent total dissolution via acid leaching. A DGA (N,N,N',N'-tetra-n-
36 octyldiglycolamide) extraction chromatographic column was used for the separation of actinium. The actinium
37 fraction was prepared for alpha spectrometric measurement via cerium fluoride micro-precipitation. Recoveries of
38 actinium in water samples were 80±8 % (number of analyses n=14) and in rock samples 70±12 % (n=30). The
39 minimum detectable activities (MDA) were 0.017-0.5 Bq kg⁻¹ for both matrices. Rock sample ²²⁷Ac activities ranged
40 from 0.17 to 8.3 Bq kg⁻¹ and water sample activities ranged from below MDA values to 14 Bq kg⁻¹ of ²²⁷Ac. From
41 the analysis of several standard rock and water samples with the method we found very good agreement between our
42 results and certified values.

43 **Keywords:** actinium-227, extraction chromatography, water, rock, alpha-spectrometry

44 **Introduction**

45 Actinium-227 is a member of the naturally occurring ^{235}U decay series (Fig. 1). It is a beta-emitter with a
46 half-life of $T_{1/2}=21.77$ years. The concentration of ^{227}Ac in natural samples is extremely low, in seawater the
47 reported activities range from 0.83 mBq m^{-3} to 90 mBq m^{-3} [1], in some basalts, assuming equilibrium with ^{231}Pa ,
48 the expected range can be as low as <0.1 to 5 Bq kg^{-1} [2]. Actinium-227 is used as an oceanographic tracer for
49 studies of deep-ocean mixing and upwelling [1, 3], and it has the potential to be used as a tracer for geochemical
50 characterization of rocks and other geological material. Some already existing techniques for ^{227}Ac analysis include
51 separation on ion exchange columns followed by measurement of its daughters ^{227}Th and ^{223}Ra by alpha-
52 spectrometry [4, 5]. The disadvantage of the ion exchange columns is that chemical recoveries tend to be lower
53 ($\sim 50\text{-}60\%$) and may not be well suited for actinium separation from complex matrices. Another popular method
54 uses a radium delayed coincidence counting (RaDeCC) system [6]. Actinium-227 in water samples is quantitatively
55 sorbed on a MnO_2 -coated acrylic fiber and allowed to sit for 90 days for ^{223}Ra ingrowth. The fiber is then measured
56 by the RaDeCC system in which the ^{219}Rn - ^{215}Po pair is counted. This technique works well for seawater analysis for
57 example [6], but is impractical for rock samples.

58 We adapted a single-column extraction chromatographic technique (DGA column), which simplifies the
59 separation step, reduces analysis time and the amount of reagents needed. The use of this technique assures clean
60 separation of actinium from other elements and leads to close to quantitative chemical recoveries from diverse
61 geological matrices. Here we report on its use for ^{227}Ac separation from freshwater, seawater, and rock samples.

62 **Experimental**

63 *Experimental design*

64 A commercially available extraction chromatographic resin containing N,N,N',N'-tetra-n-
65 octyldiglycolamide sorbed on 50-100 μm particle size Amberchrom^R CG-71 (DGA column manufactured by
66 Eichrom Technologies, Inc [7]) was chosen for separation of actinium from other actinides and the sample matrix.
67 This resin has high adsorption capacity for rare earth elements and actinides (0.086 mmol/mL of Eu) and various
68 concentrations of acidic solutions allow a sequential elution of individual elements. The separation sequence for Ac

69 was selected based on distribution coefficients of actinides and common ions on DGA derived by Horwitz et al. [7]
70 using batch experiments for 1-hour contact time of solutes with DGA at 22°C. Figure 2 illustrates k' for Ac, Th, Fe
71 and alkaline earth cations in each separation and rinsing step on the column. K' is defined as the volume distribution
72 ratio of the element between the stationary extractant phase and the mobile aqueous phase times the ratio of the
73 volumes of the stationary and mobile phases in a slurry packed column. We used 4M HCl as load solution for which
74 the k' of Ac is 20, of Th, U and Am is >1,000, of Ba, Sr, Ca and Ra is 1-5, and of Fe is 1,000. Based on these k'
75 values, actinides and iron are well retained on the column with a 4 M HCl load solution while radium and other
76 alkaline earth elements have no affinity and pass through the column without retention. We used 3 M HNO₃ to rinse
77 any leftover alkaline earth elements and iron from the column. In 3 M HNO₃ the k' of iron drops to <2, while all
78 actinides including Ac have $k' >1,000$. In the next step we eluted actinium with 2 M HCl, which is efficient for Ac
79 but leaves Th and other actinides retained on the DGA column. If needed for further analysis, thorium (²²⁸Th for
80 ²²⁸Ac or ²²⁷Th analysis) can be stripped from the column using dilute nitric acid [7]. We tested the procedure using
81 an aliquot of NIST certified ²²⁹Th/²²⁵Ac standard solution (Fig. 1), which offered an ideal opportunity to demonstrate
82 good separation between actinium and thorium on the DGA column. Consistent with the findings of Horwitz et al.
83 [7] we observed that the presence of iron in the load solution positively affects the actinium uptake on DGA due to
84 the salting out effect. Therefore, each load solution was spiked with 1 mg of iron as FeCl₃.

85 *Chemical procedure*

86 Rock samples were crushed to <1 mm and then dissolved completely by a series of digestions using HF and
87 HNO₃, followed by HNO₃ + H₃BO₃ and HClO₄ to decompose fluorides [8]. In the final stage they were dissolved
88 and stored in 4 M or higher HCl + sat. H₃BO₃ until analysis. Freshwater and seawater samples were acidified to pH
89 1. All samples were spiked using a NIST certified ²²⁹Th/²²⁵Ac tracer.

90 While it is possible for water samples to be evaporated, dissolved in 4 M HCl and loaded to the column
91 directly, the high amount of salts in dissolved rock samples required a pre-concentration step. We used a PbSO₄ co-
92 precipitation technique after Martin et al. [4]. All sample volumes were reduced to 100 mL. We added 1 mL of 98%
93 H₂SO₄ to each sample after which 2 g of K₂SO₄ were added and dissolved. While stirring, 1 mL of 0.24 M Pb(NO₃)₂
94 solution was added to the sample drop-wise. The sample was then heated and the precipitation was allowed to settle.
95 The supernatant was decanted and the precipitate was washed using 20 mL of 0.1 M K₂SO₄+0.2 M H₂SO₄. The

96 precipitate was then easily dissolved in 20 mL of 4 M HCl. Some precipitates required heating and the addition of
97 higher volumes of 4 M HCl; we tested the method with up to 50 mL of load solution for which we still achieved
98 quantitative recoveries. A 1 mg Fe in solution was added to the solution prior to loading on the DGA column. The
99 column was attached to a vacuum box (Eichrom Technologies, Inc.), which was used to achieve flow rates of 1
100 mL/min. The beaker was rinsed with 2x5 mL of 4 M HCl, which was loaded on the column. The DGA was then
101 rinsed using 10 mL of 3 M HNO₃ and the eluate, which contained iron and any leftover alkaline earth elements was
102 discarded. Actinium was eluted using 20 mL 2 M HCl while Th and other actinides were retained on the DGA
103 column.

104 The Ac fraction was saved and an alpha-source was prepared using CeF₃ micro-precipitation [9]. 100 µg of
105 Ce carrier in solution was added to the Ac fraction, stirred and 2 mL of concentrated HF were added while stirring.
106 The solution rested for 30 minutes and then the precipitate was filtered using 0.1 µm polypropylene, 25 mm
107 diameter 0.1 µm polypropylene Resolve™ filters (Eichrom Technologies, Inc.). The filters were dried and mounted
108 on steel planchets.

109 *Alpha-spectroscopy*

110 The samples were counted using silicon surface barrier alpha detectors (Ortec, 450 mm) that were
111 calibrated by a NIST certified ²⁴¹Am solution prepared in the same geometry as the samples. The source detector
112 distance was 10 mm and in this geometry the detector efficiencies ranged from 19.3 to 20.9%. After source
113 preparation the samples were stored for 15-20 minutes for the ingrowth of the ²²⁵Ac daughters ²²¹Fr (T_{1/2}=4.8 min)
114 and ²¹⁷At (0.3 sec). The sample was then counted immediately to obtain the highest count rate due to the 10-day
115 half-life of ²²⁵Ac. From this measurement, counts from the region of ²¹⁷At at 7.06 MeV (Fig. 3a) were used to
116 calculate the chemical recovery of ²²⁵Ac and therefore also ²²⁷Ac. A second measurement was performed after 90
117 days of sample preparation, which allowed for the decay of ²²⁵Ac and the ingrowth of ²²⁷Th and ²²³Ra from ²²⁷Ac
118 (Fig. 3b). Counts from the energy region of 5.38 – 6.10 MeV originating from ²²⁷Th and ²²³Ra (99.4 %) were used to
119 calculate ²²⁷Ac. Any leftover ²²⁵Ac still present was subtracted from this region.

120 The ²²⁷Ac activity was calculated using the count-rate in the 7.06 MeV peak of ²¹⁷At for yield
121 determination and in the 5.38 – 6.10 MeV originating from ²²⁷Th and ²²³Ra minus any decay corrected leftover

122 counts from the ^{225}Ac spike [4]. Actinium-227 at the time of separation $A_{227\text{Ac}}$ was then calculated using the
 123 branching ratios for ^{227}Ac of 98.2% by beta-decay to ^{227}Th and 1.38% by alpha-particle emission to ^{223}Fr , while 100
 124 % of ^{227}Th and 99.4% of ^{223}Ra decay via alpha-particle emission:

$$125 \quad A_{227\text{Ac}} = \frac{A_{227\text{Th}+223\text{Ra}}}{0.9862I_{227\text{Th}} + 0.994I_{223\text{Ra}}},$$

126 where $A_{227\text{Th}+223\text{Ra}}$ is the measured $^{227}\text{Th} + ^{223}\text{Ra}$ activity, and $I_{227\text{Th}}$ and $I_{223\text{Ra}}$ are the calculated ingrowth
 127 fractions of ^{227}Th and ^{223}Ra at the time of separation [4].

128 Minimum detectable activities (MDA) were calculated for a confidence limit of $\alpha=0.05$, 3-day counting
 129 times and one sigma standard deviation of the counts from the $^{227}\text{Th} + ^{223}\text{Ra}$ region of background spectra according
 130 to the method described by Currie [10].

131 Results and Discussion

132 We tested the procedure with $^{229}\text{Th}/^{225}\text{Ac}$ spike in de-ionized water. As suggested by Horwitz [7], in our
 133 test solutions the chemical recovery increased from 70% ($^{229}\text{Th}/^{225}\text{Ac}$ solution in de-ionized water) to 100 % with
 134 the addition of Fe ($^{229}\text{Th}/^{225}\text{Ac}$ in de-ionized water with 50 mg Fe). Increasing Fe concentrations did not have further
 135 beneficial effects on the Ac sorption, the chemical recovery dropped to 70% when we added up to 1 g of iron (Fig.
 136 4). During these test runs we observed good separation of ^{229}Th from the ^{225}Ac fraction. One way to check the
 137 performance of our chemical separation was to evaluate the alpha-spectra for radium, polonium and thorium.
 138 Radium-226 (4.8 MeV), ^{222}Rn (5.49 MeV) and ^{218}Po (6.00 MeV) counts in the spectrum would be an indication of
 139 ^{226}Ra impurity, ^{210}Po has a peak at 5.30 MeV and finally ^{228}Th and its daughters can be detected via the ^{212}Po peak at
 140 8.78 MeV. All our spectra including seawater and rock samples were free of these or only had minor interferences
 141 indicating that the extraction chromatography procedure reliably removes any interferences and impurities from the
 142 Ac fraction.

143 The analyzed water samples included de-ionized water, seawater and tap water spiked with ^{227}Ac . The
 144 analysis of the de-ionized water sample was considered as blank and resulted in zero net counts in the $^{227}\text{Th} + ^{223}\text{Ra}$

145 region after background correction. Our analysis of a certified ^{227}Ac standard (AEA Technology supplied by the
146 IAEA [11]) resulted in $(333 \pm 16) \text{ Bq kg}^{-1}$ and was in good agreement with the IAEA value of $(329 \pm 16) \text{ Bq kg}^{-1}$
147 [11]. Actinium recoveries of water samples were $80 \pm 8 \%$ (number of analyses $n=14$; where the standard deviation of
148 the average of the 14 analyses is 8%). The average minimum detectable activity for water samples for ~4 day
149 counting time was 0.017 Bq kg^{-1} . The sample activities ranged from below MDA values to 14 Bq kg^{-1} of ^{227}Ac .

150 The weights of analyzed rock samples were between 0.3 and 5.4 grams and we analyzed various basalts
151 and USGS and U-series community rock standards (BCR-2 [12], BHVO-1 [13], Hawaiian basalt (HK) [2], Samoan
152 basalt (SAV) [14]). No certified value for ^{227}Ac exists for these standards but assuming equilibrium through the
153 decay chain (all basalts were over 100 years old) and a closed system we can compare ^{227}Ac to ^{231}Pa [2] (Table 1).
154 There is a good agreement for ^{227}Ac and ^{231}Pa , for all samples the $^{227}\text{Ac}/^{231}\text{Pa}$ ratio is within 5% of secular
155 equilibrium. For the 24 rock analyses the chemical recoveries were $70 \pm 12 \%$ ($n=24$). The lower recoveries were the
156 results of 1) an incomplete PbSO_4 precipitation because some rock samples could not be held dissolved unless kept
157 in high acidity solution, 2) a high iron content ($>1\text{g}$) remaining in the samples even after the PbSO_4 precipitation
158 negatively affects the Ac sorption on DGA (Fig. 4); and 3) the presence of significant amount of lanthanides which
159 negatively affects the co-precipitation of actinium by PbSO_4 [4].

160 The minimum detectable activities for rock samples averaged 0.05 Bq kg^{-1} for 3-day counting and MDAs
161 for individual sample measurements were in the range of $0.017\text{-}0.5 \text{ Bq kg}^{-1}$. Sample activities ranged from $0.17 -$
162 8.3 Bq kg^{-1} .

163 Uncertainties were derived from counting statistics of the ^{217}At (usually 3% error) and $^{227}\text{Th} + ^{223}\text{Ra}$
164 (ranged from 3-10 %) region peaks and error propagation. Uncertainties of all analysis were $<10\%$. Overall the
165 DGA separation method performed well, providing actinium fractions without interferences in alpha-spectrometry
166 and resulting in high chemical recoveries. Our results agree well with certified values for water and ^{231}Pa values for
167 rock samples.

168 **Conclusions**

169 The advantages of extraction chromatographic techniques over ion exchange columns in general are a
170 shorter analysis time and less acid waste produced. The method developed here has a high sensitivity due to the low

171 backgrounds on the alpha-detectors and because of the use of the double-peak of ^{227}Th and ^{223}Ra , which doubles the
172 counts and lowers the counting error [15]. Additional advantage of the DGA method is its possible extension to the
173 analysis of thorium isotopes. Our typical 2σ errors were 5% which are much higher than those usually obtained for
174 example by mass spectrometric analysis (ICP-MS, TIMS) of other isotopes, however due to the low abundance of
175 ^{227}Ac MS methods are currently not sensitive enough for its analysis. For comparison, in units of fg g^{-1} used for MS
176 techniques, our method has a limit of detection of 0.02 fg g^{-1} .

177 **Acknowledgement**

178 We would like to acknowledge Phil Horwitz and William Burnett for their advice on the extraction
179 chromatographic techniques. Ken Sims' lab at the Woods Hole Oceanographic Institution performed the rock
180 dissolution procedures and Ken Buesseler (WHOI) provided the counting equipment for the alpha-spec analysis. Jan
181 Scholten from the IAEA provided the actinium standard and spiked seawater samples.

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211 ^{238}U - ^{230}Th - ^{226}Ra - ^{210}Pb - ^{210}Po , ^{232}Th - ^{228}Ra , and ^{235}U - ^{231}Pa constraints on the ages and petrogenesis of Vailulu'u and
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214 exchange and alpha-spectrometry. *J Radioanal Nucl Chem* 115(1): 23-37

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216

217
 218 Table 1: ^{227}Ac activities in selected standard water and basalt samples (BCR-2 [12], BHVO-1 [13], Hawaiian basalt
 219 (HK) [2], Samoan basalt (SAV) [14]) analyzed by DGA-column followed by alpha-spectrometry. All of the basalt
 220 rock samples analyzed are older than 100 years and ^{231}Pa and ^{227}Ac are expected to be in secular radioactive
 221 equilibrium.

Standard	^{227}Ac by DGA	Certified ^{227}Ac	$^{227}\text{Ac}_{\text{DGA}}/^{227}\text{Ac}_{\text{cert}}$	Chemical recovery
Water:	Bq/kg	Bq/kg		
AEA Technology-IAEA	333 ± 16	329 ± 16	1.01	75%
Rocks (basalts):		$^{231}\text{Pa}^*$	$^{227}\text{Ac}_{\text{DGA}}/^{231}\text{Pa}$	
BCR-2	0.955 ± 0.083	0.967	0.99	83%
BHVO-1	0.299 ± 0.017	0.283	1.05	71%
HK-018	0.965 ± 0.009	0.948	1.02	86%
HK-019	0.962 ± 0.073	0.966	0.99	91%
HK-021	0.559 ± 0.055	0.572	0.98	80%
HK-022	0.887 ± 0.080	0.862	1.03	68%
SAV B6	0.677 ± 0.067	0.680	1.00	66%

222 *2 σ uncertainty of ^{231}Pa <0.8%

223

224 Figures:

225 Figure 1: Decay schemes of a) ^{235}U including ^{227}Ac and its daughters ^{227}Th - ^{223}Ra , and b) the ^{229}Th - ^{225}Ac pair used
226 as a yield tracer. The vertical arrows indicate alpha decays and the tilted arrows represent transformations via beta
227 decay. Half-lives are indicated below each isotope.

228

229 Figure 2: Resin capacity factor k' for Ac, Th, Fe and alkaline earth cations in each separation and rinsing step on the
230 DGA column derived using batch experiments for 1-hour contact time of solutes with DGA at 22°C [7]. The higher
231 the k' the higher the fraction of the element in the stationary extractant phase.

232

233 Figure 3: Alpha-spectrum of the actinium fraction of a seawater sample a) counted immediately after source
234 preparation showing peaks of ^{225}Ac , ^{221}Fr and ^{217}At ; and b) the same source counted 90-days after preparation when
235 ^{225}Ac has mostly decayed and daughters ^{227}Th and ^{223}Ra are almost in equilibrium with ^{227}Ac .

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237 Figure 4: Actinium recoveries from a $^{229}\text{Th}/^{225}\text{Ac}$ spiked de-ionized water solution without and with the addition of
238 variable amounts of iron.

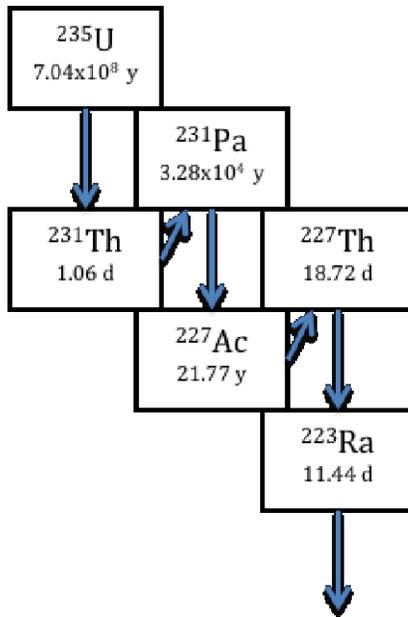
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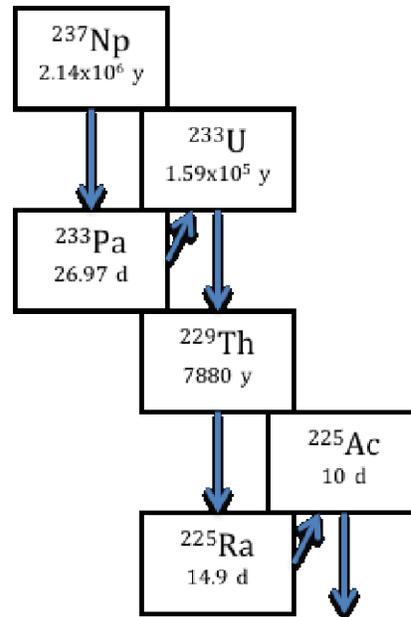
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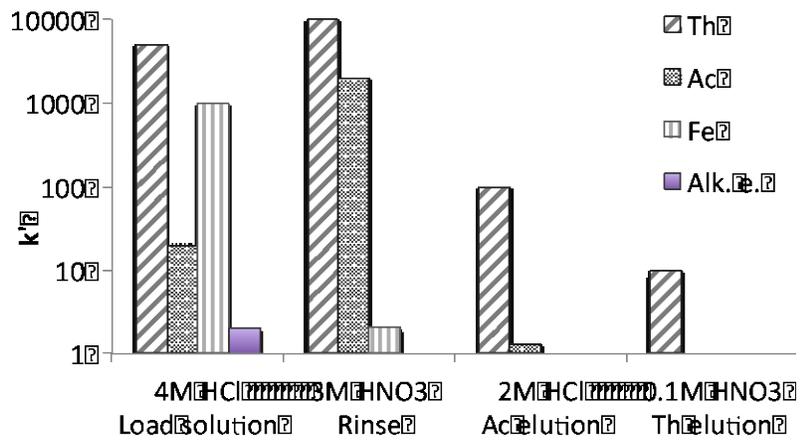
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Figure 1

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Figure 2

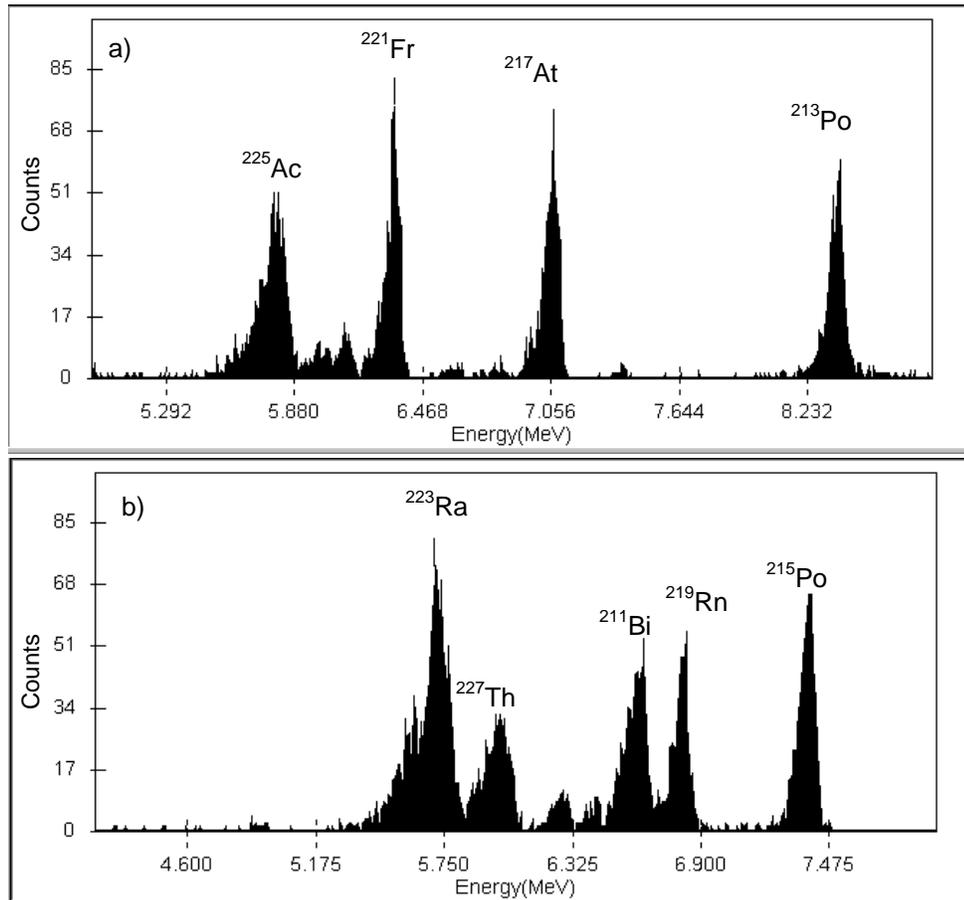
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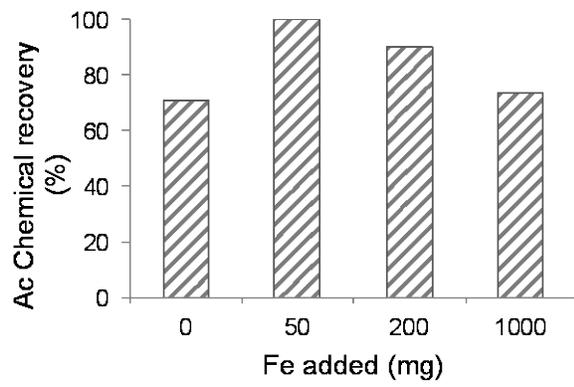
268 **Figure 3**

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273 **Figure 4**