J Radioanal Nucl Chem
DOI 10.1007/s10967-012-2140-0

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

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Received: 31 July 2012
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Abstract We developed a new method for the determination of ^{227}Ac in geological samples. The method uses extraction chromatographic techniques and alpha-spectrometry and is applicable for a range of natural matrices. Here we report on the procedure and results of the analysis of water (fresh and seawater) and rock samples. Water samples were acidified and rock samples underwent total dissolution via acid leaching. A DGA (*N*,*N*,*N*′,*N*′-tetra-*n*-octyldiglycolamide) extraction chromatographic column was used for the separation of actinium. The actinium fraction was prepared for alpha spectrometric measurement via cerium fluoride micro-precipitation. Recoveries of actinium in water samples were 80 ± 8 % (number of analyses $n = 14$) and in rock samples 70 ± 12 % ($n = 30$). The minimum detectable activities (MDA) were 0.017–0.5 Bq kg^{-1} for both matrices. Rock sample ^{227}Ac activities ranged from 0.17 to 8.3 Bq kg^{-1} and water sample activities ranged from below MDA values to 14 Bq kg^{-1}of ^{227}Ac. From the analysis of several standard rock and water samples with the method we found very good agreement between our results and certified values.

Keywords Actinium-227 · Extraction chromatography · Water · Rock · Alpha-spectrometry

Introduction

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

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Journal : Large 10967 | Dispatch : 17-8-2012 | Pages : 5
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We adapted a single-column extraction chromatographic technique (DGA column), which simplifies the separation step, reduces analysis time and the amount of reagents needed. The use of this technique assures clean separation of actinium from other elements and leads to close to quantitative chemical recoveries from diverse geological matrices. Here we report on its use for ^{227}Ac separation from freshwater, seawater, and rock samples.

Experimental

Experimental design

A commercially available extraction chromatographic resin containing *N*,*N*,*N*′,*N*′-tetra-*n*-octyldiglycolamide sorbed on 50–100 µm particle size Amberchrom^{R} CG-71 (DGA column manufactured by Eichrom Technologies, Inc [7]) was chosen for separation of actinium from other actinides and the sample matrix. This resin has high adsorption capacity for rare earth elements and actinides (0.086 mmol/mL of Eu) and various concentrations of acidic solutions allow a sequential elution of individual elements. The separation sequence for Ac was selected based on distribution coefficients of actinides and common ions on DGA derived by Horwitz et al. [7] using batch experiments for 1-h contact time of solutes with DGA at 22 °C. Figure 2 illustrates k' for Ac, Th, Fe and alkaline earth cations in each separation and rinsing step on the column. K' is defined as the volume distribution ratio of the element between the stationary extractant phase and the mobile aqueous phase times the ratio of the volumes of the stationary and mobile phases in a slurry packed column. We used 4 M HCl as load solution for which 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' values, actinides and iron are well retained on the column with a 4 M HCl load solution while radium and other alkaline earth elements have no affinity and pass through the column without retention. We used 3 M HNO_3 to rinse any leftover alkaline earth elements and iron from the column. In 3 M HNO_3 the k' of iron drops to <2, while all actinides including Ac have k' >1,000. In the next step we eluted actinium with 2 M HCl, which is efficient for Ac but leaves Th and other actinides retained on the DGA column. If needed for further analysis, thorium (^{228}Th for ^{228}Ac or ^{227}Th analysis) can be stripped from the column using dilute nitric acid [7]. We tested the procedure using an aliquot of NIST certified ^{229}Th/^{225}Ac standard solution (Fig. 1), which offered an ideal opportunity to demonstrate good separation between actinium and thorium on the DGA column. Consistent with the findings of Horwitz et al. [7] we observed that the presence of iron in the load solution positively affects the actinium uptake on DGA due to the salting out effect. Therefore, each load solution was spiked with 1 mg of iron as $FeCl_3$.

Chemical procedure

Rock samples were crushed to <1 mm and then dissolved completely by a series of digestions using HF and HNO_3, followed by HNO_3 + H_3BO_3 and $HClO_4$ to decompose fluorides [8]. In the final stage they were dissolved and stored in 4 M or higher HCl + sat. H_3BO_3 until analysis. Freshwater and seawater samples were acidified to pH 1.

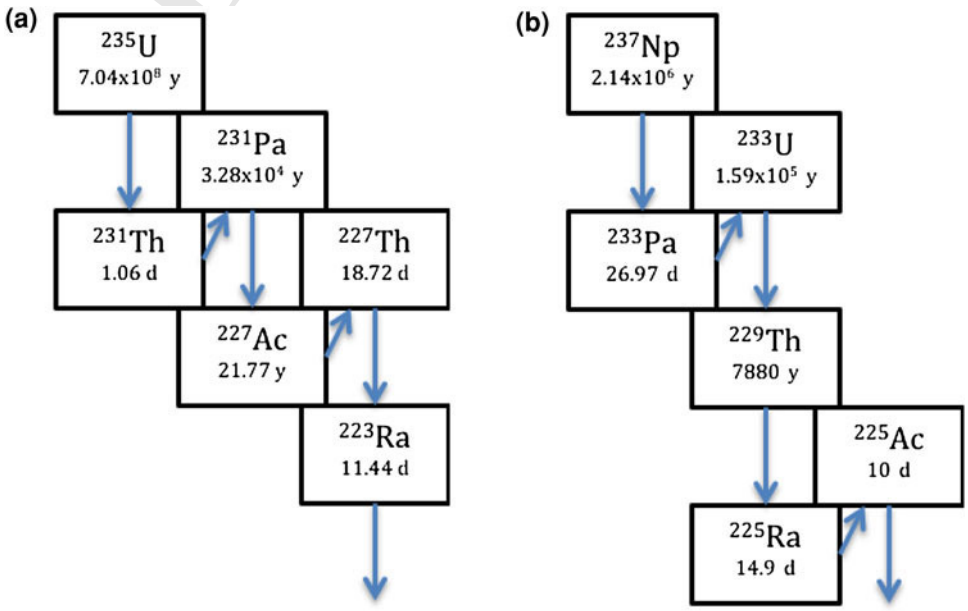

Fig. 1 Decay schemes of **a** ^{235}U including ^{227}Ac and its daughters ^{227}Th–^{223}Ra, and **b** the ^{229}Th–^{225}Ac pair used as a yield tracer. The *vertical arrows* indicate alpha decays and the *tilted arrows* represent transformations via beta decay. Half-lives are indicated below each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

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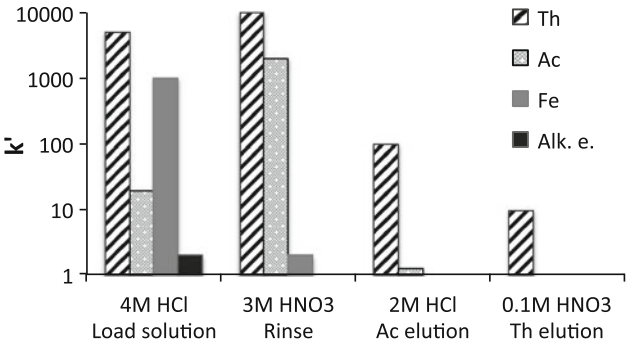

Fig. 2 Resin capacity factor k' for Ac, Th, Fe and alkaline earth cations in each separation and rinsing step on the DGA column derived using batch experiments for 1-hour contact time of solutes with DGA at 22 °C [7]. The higher the k' the higher the fraction of the element in the stationary extractant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

All samples were spiked using a NIST certified $^{229}Th/^{225}Ac$ tracer.

While it is possible for water samples to be evaporated, dissolved in 4 M HCl and loaded to the column directly, the high amount of salts in dissolved rock samples required a pre-concentration step. We used a $PbSO_4$ co-precipitation technique after Martin et al. [4]. All sample volumes were reduced to 100 mL. We added 1 mL of 98 % H_2SO_4 to each sample after which 2 g of K_2SO_4 were added and dissolved. While stirring, 1 mL of 0.24 M $Pb(NO_3)_2$ solution was added to the sample drop-wise. The sample was then heated and the precipitation was allowed to settle. The supernatant was decanted and the precipitate was washed using 20 mL of 0.1 M K_2SO_4 + 0.2 M H_2SO_4. The precipitate was then easily dissolved in 20 mL of 4 M HCl. Some precipitates required heating and the addition of higher volumes of 4 M HCl; we tested the method with up to 50 mL of load solution for which we still achieved quantitative recoveries. A 1 mg Fe in solution was added to the solution prior to loading on the DGA column. The column was attached to a vacuum box (Eichrom Technologies, Inc.), which was used to achieve flow rates of 1 mL/min. The beaker was rinsed with 2 × 5 mL of 4 M HCl, which was loaded on the column. The DGA was then rinsed using 10 mL of 3 M HNO_3 and the eluate, which contained iron and any leftover alkaline earth elements was discarded. Actinium was eluted using 20 mL 2 M HCl while Th and other actinides were retained on the DGA column.

The Ac fraction was saved and an alpha-source was prepared using CeF_3 micro-precipitation [9]. 100 µg of Ce carrier in solution was added to the Ac fraction, stirred and 2 mL of concentrated HF were added while stirring. The solution rested for 30 min and then the precipitate was filtered using 0.1 µm polypropylene, 25 mm diameter 0.1 µm polypropylene Resolve™ filters (Eichrom Technologies, Inc.). The filters were dried and mounted on steel planchets.

Alpha-spectroscopy

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

The ^{227}Ac activity was calculated using the count-rate in the 7.06 MeV peak of ^{217}At for yield determination and in the 5.38–6.10 MeV originating from ^{227}Th and ^{223}Ra minus any decay corrected leftover counts from the ^{225}Ac spike [4]. Actinium-227 at the time of separation $A_{^{227}Ac}$ was then calculated using the branching ratios for ^{227}Ac of

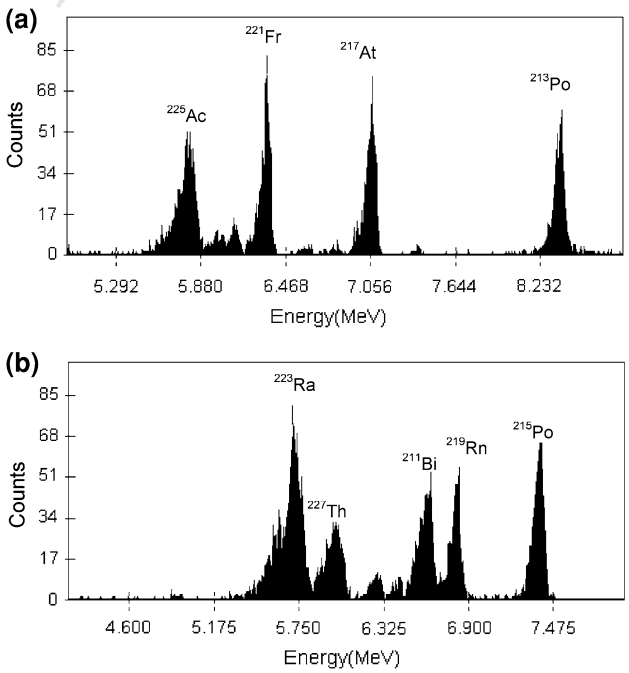

Fig. 3 Alpha-spectrum of the actinium fraction of a seawater sample **a** counted immediately after source preparation showing peaks of ^{225}Ac, ^{221}Fr and ^{217}At, and **b** the same source counted 90-days after preparation when ^{225}Ac has mostly decayed and daughters ^{227}Th and ^{223}Ra are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

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98.2 % by beta-decay to ^{227}Th and 1.38 % by alpha-particle emission to ^{223}Fr, while 100 % of ^{227}Th and 99.4 % of ^{223}Ra decay via alpha-particle emission:

$$A_{^{227}\mathrm{Ac}} = \frac{A_{^{227}\mathrm{Th}+^{223}\mathrm{Ra}}}{0.9862 I_{^{227}\mathrm{Th}} + 0.994 I_{^{223}\mathrm{Ra}}},$$

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

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

Results and discussion

We tested the procedure with ^{229}Th/^{225}Ac spike in de-ionized water. As suggested by Horwitz et al. [7], in our test solutions the chemical recovery increased from 70 % (^{229}Th/^{225}Ac solution in de-ionized water) to 100 % with the addition of Fe (^{229}Th/^{225}Ac in de-ionized water with 50 mg Fe). Increasing Fe concentrations did not have further beneficial effects on the Ac sorption, the chemical recovery dropped to 70 % when we added up to 1 g of iron (Fig. 4). During these test runs we observed good separation of ^{229}Th from the ^{225}Ac fraction. One way to check the performance of our chemical separation was to evaluate the alpha-spectra for radium, polonium and thorium. 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 ^{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 8.78 MeV. All our spectra including seawater and rock samples were free of these or only had minor interferences indicating that the extraction chromatography procedure reliably removes any interferences and impurities from the Ac fraction.

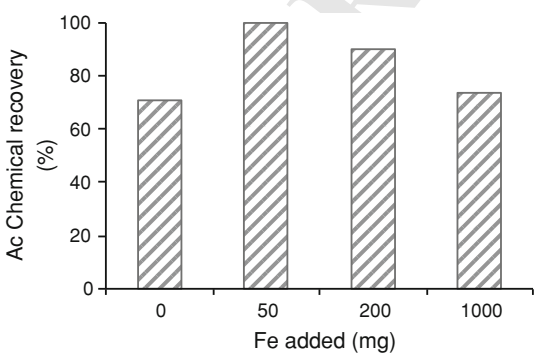

Fig. 4 Actinium recoveries from a ^{229}Th/^{225}Ac spiked de-ionized water solution without and with the addition of variable amounts of iron

The analyzed water samples included de-ionized water, seawater and tap water spiked with ^{227}Ac. The analysis of the de-ionized water sample was considered as blank and resulted in zero net counts in the ^{227}Th + ^{223}Ra region after background correction. Our analysis of a certified ^{227}Ac standard (AEA Technology supplied by the IAEA [11]) resulted in (333 ± 16) Bq kg^{-1} and was in good agreement with the IAEA value of (329 ± 16) Bq kg^{-1} [11]. Actinium recoveries of water samples were 80 ± 8 % (number of analyses $n = 14$; where the standard deviation of the average of the 14 analyses is 8 %). The average minimum detectable activity for water samples for ~4 day counting time was 0.017 Bq kg^{-1}. The sample activities ranged from below MDA values to 14 Bq kg^{-1}of ^{227}Ac.

The weights of analyzed rock samples were between 0.3 and 5.4 g and we analyzed various basalts and USGS and U-series community rock standards (BCR-2 [12], BHVO-1 [13], Hawaiian basalt (HK) [2], Samoan basalt (SAV) [14]). No certified value for ^{227}Ac exists for these standards but assuming equilibrium through the decay chain (all basalts were over 100 years old) and a closed system we can compare ^{227}Ac to ^{231}Pa [2] (Table 1). There is a good agreement for ^{227}Ac and ^{231}Pa, for all samples the ^{227}Ac/^{231}Pa ratio is within 5 % of secular equilibrium. For the 24 rock analyses the chemical recoveries were 70 ± 12 % ($n = 24$). The lower recoveries were the results of (1) an incomplete $PbSO_4$ precipitation because some rock samples could not be held dissolved unless kept in high acidity solution, (2) a high iron

Table 1 ^{227}Ac activities in selected standard water and basalt samples (BCR-2 [12], BHVO-1 [13], Hawaiian basalt (HK) [2], Samoan basalt (SAV) [14]) analyzed by DGA-column followed by alpha-spectrometry

Standard	^{227}Ac by DGA Bq/kg	Certified ^{227}Ac Bq/kg	$^{227}Ac_{DGA}/^{227}Ac_{cert}$	Chemical recovery (%)
Water				
AEA technology-IAEA	333 ± 16	329 ± 16	1.01	75
		^{231}Pa*	$^{227}Ac_{DGA}/^{231}$Pa	
Rocks (basalts)				
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

All of the basalt rock samples analyzed are older than 100 years and ^{231}Pa and ^{227}Ac are expected to be in secular radioactive equilibrium

* 2 σ uncertainty of ^{231}Pa < 0.8 %

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content (>1 g) remaining in the samples even after the $PbSO_4$ precipitation negatively affects the Ac sorption on DGA (Figs. 3, 4) the presence of significant amount of lanthanides which negatively affects the co-precipitation of actinium by $PbSO_4$ [4].

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

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

Conclusions

The advantages of extraction chromatographic techniques over ion exchange columns in general are a shorter analysis time and less acid waste produced. The method developed here has a high sensitivity due to the low backgrounds on the alpha-detectors and because of the use of the double-peak of ^{227}Th and ^{223}Ra, which doubles the counts and lowers the counting error [15]. Additional advantage of the DGA method is its possible extension to the analysis of thorium isotopes. Our typical 2 σ errors were 5 % which are much higher than those usually obtained for example by mass spectrometric analysis (ICP-MS, TIMS) of other isotopes, however due to the low abundance of ^{227}Ac MS methods are currently not sensitive enough for its analysis. For comparison, in units of fg g^{-1} used for MS techniques, our method has a limit of detection of 0.02 fg g^{-1}.

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

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