



Radiochemical technique optimization to measure uranium and thorium by α -spectrometry

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Abstract

A common advanced radiochemical technique is the use of the AG® 1-X8 anion exchanger, Cl^{2-} form (from Bio Rad), to separate uranium and/or thorium from a sample by ion exchange. This method is used to separate elements by chemical elution from an ion exchange column via a precipitate of substances (co-precipitation), with Nd^{3+} as a thin layer of smooth fluoride particles on a membrane filter, then using α -spectrometry to measure uranium and thorium. The obtained data showed that the column could be reused, at least twelve times, safely in separating uranium and thorium from environmental samples, before observing any change in the performance of the exchanger.

Keywords AG® 1-X8 anion exchanger · Uranium · Thorium · Radiochemical technique · α -spectrometry

Abbreviations

Th	Thorium
U	Uranium
HNO_3	Nitric acid
HCl	Hydrochloric acid
pCi	Picocurie
TiCl_3	Titanium (III) chloride
HF	Hydrofluoric acid

Introduction

Appropriate management of radioactive wastes and their subsequent effect both on nature and on human welfare requires analytical procedures for delicate and reliable identification and determination of a wide assortment of radionuclides in a wide assortment of sample matrices. Other researchers have developed methodologies for isolating, precipitating, and mounting actinides for α -spectrometry [1–3], either separately or mixed, as either fluorides or hydroxides [4, 5]. In these methods, actinides were isolated from all other components of the sample and from each other by chromatography of ion exchange, co-precipitated with

Nd^{3+} as fine fluoride particles, and mounted on membrane filters for α -spectrometry [6–8].

Since ion exchange columns are only used once, it is common for many of organic ion exchangers to be expended in these studies. An anion exchanger (AG1-X8, chloride form, 100–200 mesh, from Bio-Rad) is routinely used in radio-analytical techniques in analyzing uranium, thorium, and plutonium radionuclides in different types of environmental samples [1, 2, 6, 7, 9–11]. Large quantities of ground water samples are typically received for investigation. Radionuclides of uranium and radium, in addition to radon-222, are the main radionuclides of interest in ground water [12–15] and the use of the exchanger is mainly due to the routine work of uranium analysis in ground water [16–18]. In the experimental, the equal amounts of the same sample were used in each run of the same column, and a blank sample was added to wash the exchanger after every three sample runs in the same renewal column to prepare it for measurement by using α -spectrometry. The performance of the washed exchanger was examined by examining changes in the sample recovery and the blank sample counting rate. In a similar experiment to determine the suitability of this method for separating thorium, we used the same level of aqueous solutions using 8 M HNO_3 media; the column could be reused at least 12 times without degradation of the measurement for U and Th.

The aim of the present article is to study the possibility of renewing the exchanger and reusing the column, with the

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goal of reducing the resin consumption rate and reducing cost.

Low-level samples require 24 h of counting time [4, 19–21]. In the experimental setup described means that only 8 samples can be counted per day, even though more samples may be prepared. This leads investigators to store samples for some time while waiting for counting. Storing samples in a dry atmosphere may lead to changes in the physical properties of the fluoride particles of the thin source, and hence may result in spectrum degradation [8, 22, 23]. However, the stability of the fine fluoride particles with time is also tested in this work.

Methodology and experiments

Standard reference materials

For this study, we used ^{232}U and ^{229}Th standard reference materials, purchased from the National Bureau of Standards, USA, under the code numbers STM 4324 and STM 4328, respectively. The activities for ^{232}U and ^{229}Th are 0.1557209291 Bq/ml (reference date 14/2/2002), and 0.332834375 Bq/ml (reference date 7/5/1984) respectively. The reference materials were diluted and used as a spiking tracer for analyzing uranium and thorium standard solutions [24, 25].

Uranium and thorium standard solutions

Standard radioactive solutions are used for chemical yield determinations during the chemical separation process [27]. They are usually supplied in a form of 5 g aqueous solutions, composed of the radionuclide salt in an acidic medium contained in glass ampule. Uranium and thorium standard solutions were prepared in the laboratory from uranyl chloride and thorium nitrate salts, respectively [28, 29]. For quality control, aliquots of the prepared standard solutions were spiked with the respective radiotracer and analyzed by α -spectrometry, which is shown in Fig. 1.

Uranium samples

In a 100 mL measuring flask, we combined 5 mL of seawater, an aliquot of uranium standard (13.5 pCi ^{238}U), and enough concentrated HCl to get 10 M, and diluted it to volume with distilled water. This solution contained almost 2.7 pCi of $^{238}\text{U}/20$ mL of 10 M HCl; it was designated U-I. The second uranium solution was prepared exactly as U-I, except that 28 pCi ^{238}U were added instead of 13.5 pCi. This solution contained almost 5.6 pCi $^{238}\text{U}/20$ mL of 10 M HCl and was designated U-II. The fixed amount of seawater was added to each solution to bring ions in solution comparable

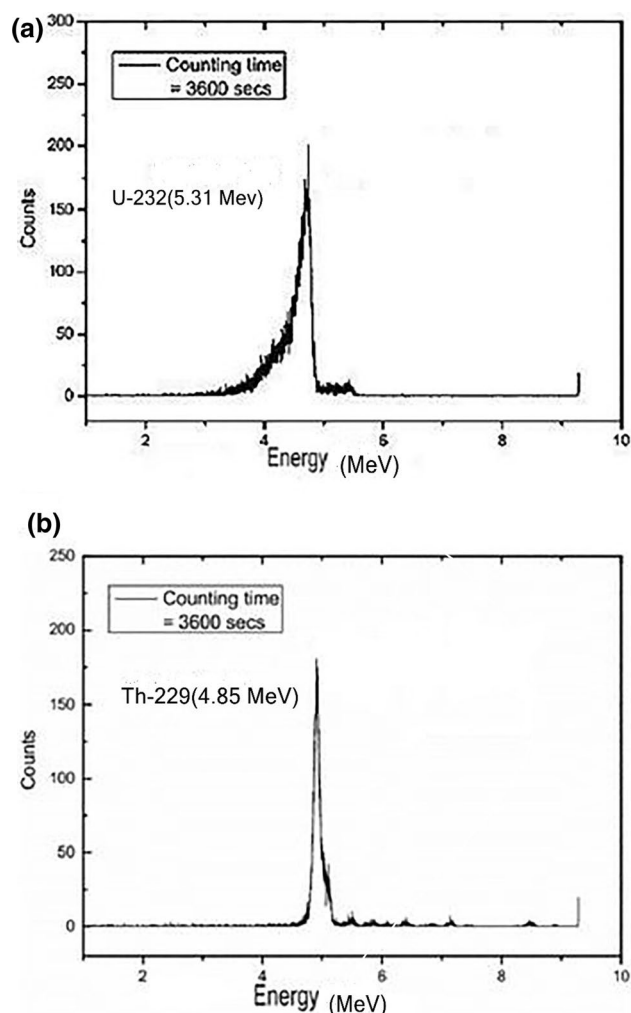


Fig. 1 a Alpha Spectrum of ^{232}U isotope measured by α -spectrometry, b Alpha Spectrum of ^{229}Th isotope measured by α -spectrometry.

to those in the environmental samples. Seawater does add a constant amount of natural uranium and thorium to all the samples; however, this amount of activity is negligible compared to the concentration of uranium or thorium in the prepared samples.

Thorium samples

Two thorium solutions (2.5 and 5.1 pCi ^{232}Th in 20 mL of 8 M HNO_3 , respectively) were prepared in the same manner as the uranium solutions except that ^{232}Th and HNO_3 were used instead of ^{238}U and HCl, respectively. These solutions were respectively designated Th-I and Th-II.

Apparatus

For this project, we used an ORTEC Octete Plus high resolution α -spectrometry system from ORTEC. The device was

connected to a vacuum pump and contained eight 450 mm² silicon surface barrier detectors situated in isolated chambers. The background count rate ranged from 0 to 2 counts within 18 h under the energy peaks of ²³⁸U or ²³⁴U, producing an ultra-low detection limit of " $< 0.01/\text{Bq/L}$ ". The efficiency of the detectors ranged from 20 to 21.5%.

Analysis

Uranium and thorium were analyzed by chemical separation and co-precipitation as a thin fluoride sources for α -spectrometry according to the method described by Moghissi (1969) [6], which is shown in Fig. 2.

Briefly, in water samples, aliquots were first spiked with the radiotracer. Next, the solution evaporated to reach dryness. Then, the resulting salt was transformed into the suitable form.

To isolate uranium, the material in the chloride structure, which was spiked with ²³²U radiotracer (1 cpm/mL), was loaded in 20 mL 10 M HCl. A 10 mL sample was placed in the separation column (from Bio Rad), filled with AG® 1-X8 anion exchanger (5 mL bed volume); 20 mL of 10 M HCl was passed to precondition the column. Next, the uranium was washed with another 20 mL of 10 M HCl and eluted from the column by passing 20 mL of 0.1 M HCl. To prepare the uranium source, 50 μL of Nd³⁺ solution (1 mg Nd³⁺/mL) were added to the isolated uranium (the eluted sample), followed by an additional measure of TiCl₃ (15%), drop by drop, to change the solution color to purple; at that point an additional 1 mL was added to keep uranium in the tetravalent state. The next step was to add the HF solution (5 mL of 40% of HF) to the sample and leave it for 30 min before filtering it with a 0.1 μL polypropylene membrane filter. The precipitate was washed with 3 mL of an 80% ethanol solution. Finally, the sample was dried at 50° C for five minutes, placed on stainless steel disc, and measured using α -spectrometer [3, 6, 26].

The thorium was isolated in the same manner as the uranium except that 8 M and 1 M HNO₃ was used in loading and eluting the thorium instead of the 10 M and 0.1 M HCl used with the uranium, respectively. The source of thorium was also prepared as the uranium was, except there was no need for the addition of a TiCl₃ solution as shown in Fig. 2.

Results and discussion

Equal fractions of 20 mL of each of the uranium and thorium solutions (U-I, U-II, Th-I, and Th-II) were repeatedly applied to each of four fixed columns (numbered I, II, III, and IV, respectively) packed with AG® 1-8X anion exchanger, 100–200 mesh, Cl²⁻ form. In other words, equal

fractions of the same sample were applied in each run for the same column.

As mentioned above, dilute acid was used to elute the retained uranium or thorium and regenerate the column for the next run. The eluted fraction was prepared for counting by α -spectrometry. Twenty-two runs were carried out through each column with the same solution. The column was regenerated between runs, and a blank sample was applied to each column after every three successive sample runs to follow the change in counting rate of the blank samples due to repeated column reuse. The performance of the column could be evaluated by following the change in the chemical yield of the eluted uranium or thorium fractions, in addition to the change in the counting rate of the eluted fraction of the blank sample.

The change in chemical yield with repeated column reuse is illustrated in Figs. 3 and 4. Two different concentrations were tested for uranium and for thorium to evaluate the effect of concentration on the performance of the reused column. The Figures showed that the chemical yield was almost the same along all 22 runs in the four columns (90.8 ± 6.2 % and (81.4 ± 6.2) % for the U-I and U-II solutions, respectively. For both thorium solutions (Th-I and Th-II), the chemical yield was almost equal (87.4 ± 10.5 %). This means that the ion exchange was unaffected, although the resin may suffer from contact with the reused concentrated mineral acids.

Results of the counting rate of the blank samples are given in Tables 1 and 2. It can be concluded that the slight increase in count rate appeared after run number 15, indicating slight contamination.

The background level was measured for each detector after every five sample runs (Tables 3 and 4). This was to test whether the slight change in counting rate of the blank sample was due to column contamination or detector recoil contamination. The results showed a negligible recoil contamination. Accordingly, these results indicated that the columns can be regenerated at least 12 times for safe reuse.

The resolution of the resultant α -spectrometry is similar to that obtained by electrodeposition onto cleaned steel plates; however, the technique discussed here is much quicker, more reliable, and generally gives a higher chemical yield [15].

Due to the possibility of storing the prepared sample sources in covered Petri dishes for days or weeks before counting, or of needing to recount older samples after some period, the physical properties of the fluoride particles (such as porosity, surface area, or particle size) may change with time due to the dry atmosphere of the laboratory, resulting in spectrum degradation. However, the stability of the prepared uranium or thorium sources were tested by repeated counting of two sources on the same detectors occasionally over a 100-day period to examine

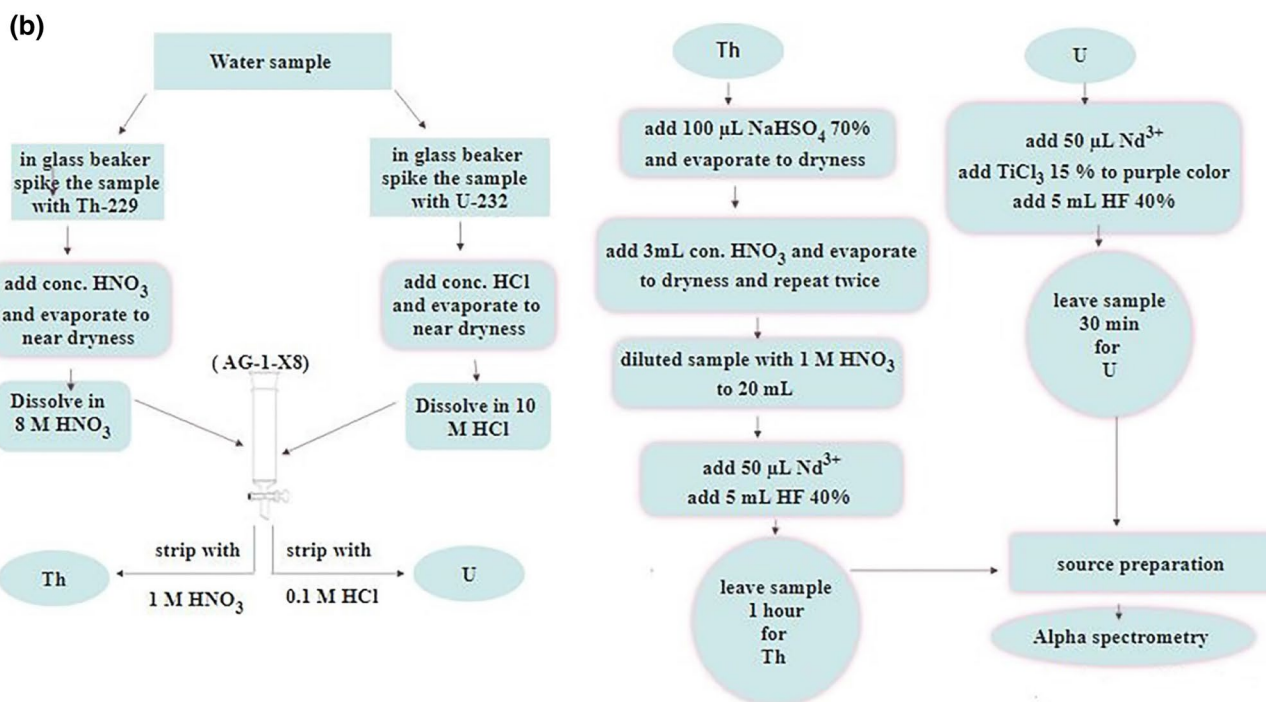
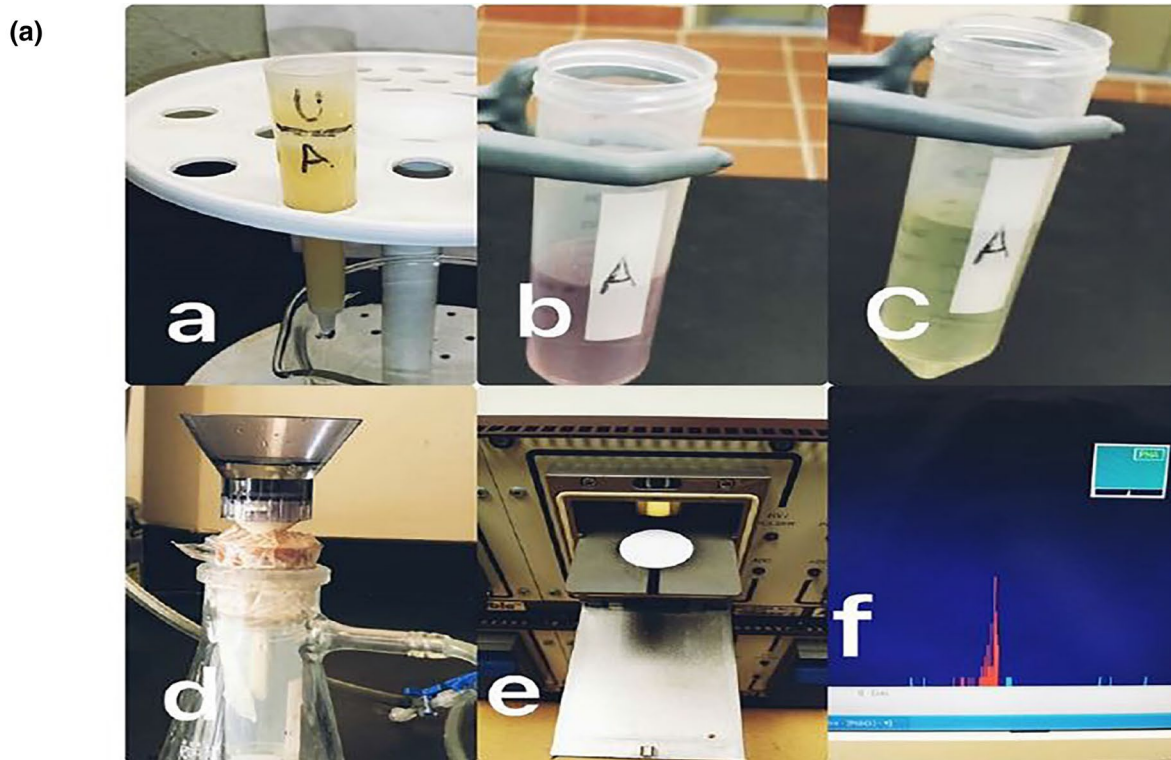


Fig. 2 (a) **a** separation column filled with AG® 1-X8 anion exchanger; **b** TiCl_3 (15%) added drop by drop, to change the solution color to purple; **c** HF solution (5 mL of 40% of HF) added to the sample and leave it for 30 min before filtration; **d** filtering sample

with a 0.1 μL polypropylene membrane filter; **e** placing the sample on stainless steel disc; **f** Spectrum shows ^{232}U and ^{229}Th measured using α -spectrometer. (b) A flowchart showing the main procedure to determine U and Th isotopes

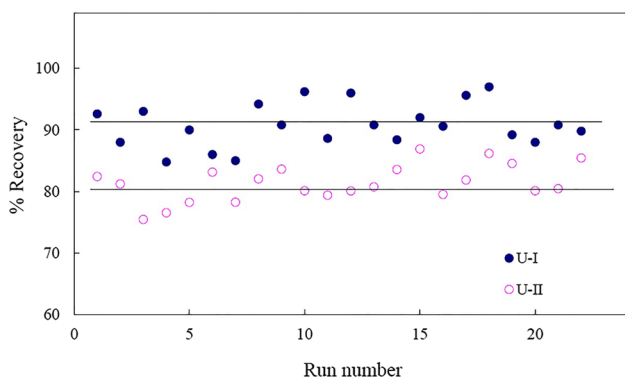


Fig. 3 Effect of repeated regeneration of the uranium columns on the chemical yield

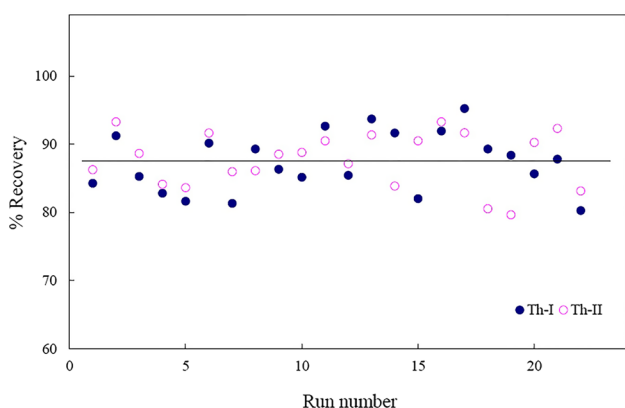


Fig. 4 Effect of repeated regeneration of the thorium columns on the chemical yield

Table 1 The counting rate of the blank samples under the ^{238}U and ^{234}U energy peaks

Run No	Counting rate, Counts/18 h			
	U-I		U-II	
	^{238}U	^{234}U	^{238}U	^{234}U
After run 3	0	1	2	0
After run 6	1	1	2	2
After run 9	1	2	4	2
After run 12	1	2	3	2
After run 15	10	4	5	1
After run 18	8	4	6	3
After run 21	9	5	12	4

the change in resolution of the α -spectrometry peaks with time, which are shown Fig. 5. The results showed that the resolution of the Spectra peaks was almost constant over the studied period.

Table 2 The counting rate of the blank samples under the ^{232}Th and ^{228}Th energy peaks

Run No	Counting rate, Counts/18 h			
	Th-I		Th-II	
	^{232}Th	^{228}Th	^{232}Th	^{228}Th
After run 3	2	0	0	2
After run 6	1	1	2	3
After run 9	1	2	2	5
After run 12	3	4	5	5
After run 15	6	9	11	15
After run 18	8	9	11	14
After run 21	19	14	13	21

Table 3 Background count rate of the detectors under ^{238}U and ^{234}U energy peaks

Run No	Counting rate, Counts/18 h			
	U-I		U-II	
	^{238}U	^{234}U	^{238}U	^{234}U
Before run 1	1	1	2	1
After run 5	1	1	2	1
After run 10	1	1	2	1
After run 15	0	1	0	0
After run 21	2	1	1	1

Table 4 Background count rate of the detectors under ^{232}Th and ^{228}Th energy peaks

Run No	Counting rate, Counts/18 h			
	Th-I		Th-II	
	^{232}Th	^{228}Th	^{232}Th	^{228}Th
Before run 1	2	0	0	2
After run 5	2	0	0	2
After run 10	1	2	1	4
After run 15	3	3	3	4
After run 21	2	3	2	3

Conclusion

An AG® 1-X8 anion exchanger was used to separate uranium or thorium from all other components of a sample by ion exchange chromatography, a commonly used radiochemical technique.

The concept of renewing the exchanger for column reuse was tested, with the goal of reducing the costs in mind. The obtained data showed that the column could be regenerated safely at least 12 times for reuse before observing any change in the performance of the exchanger.

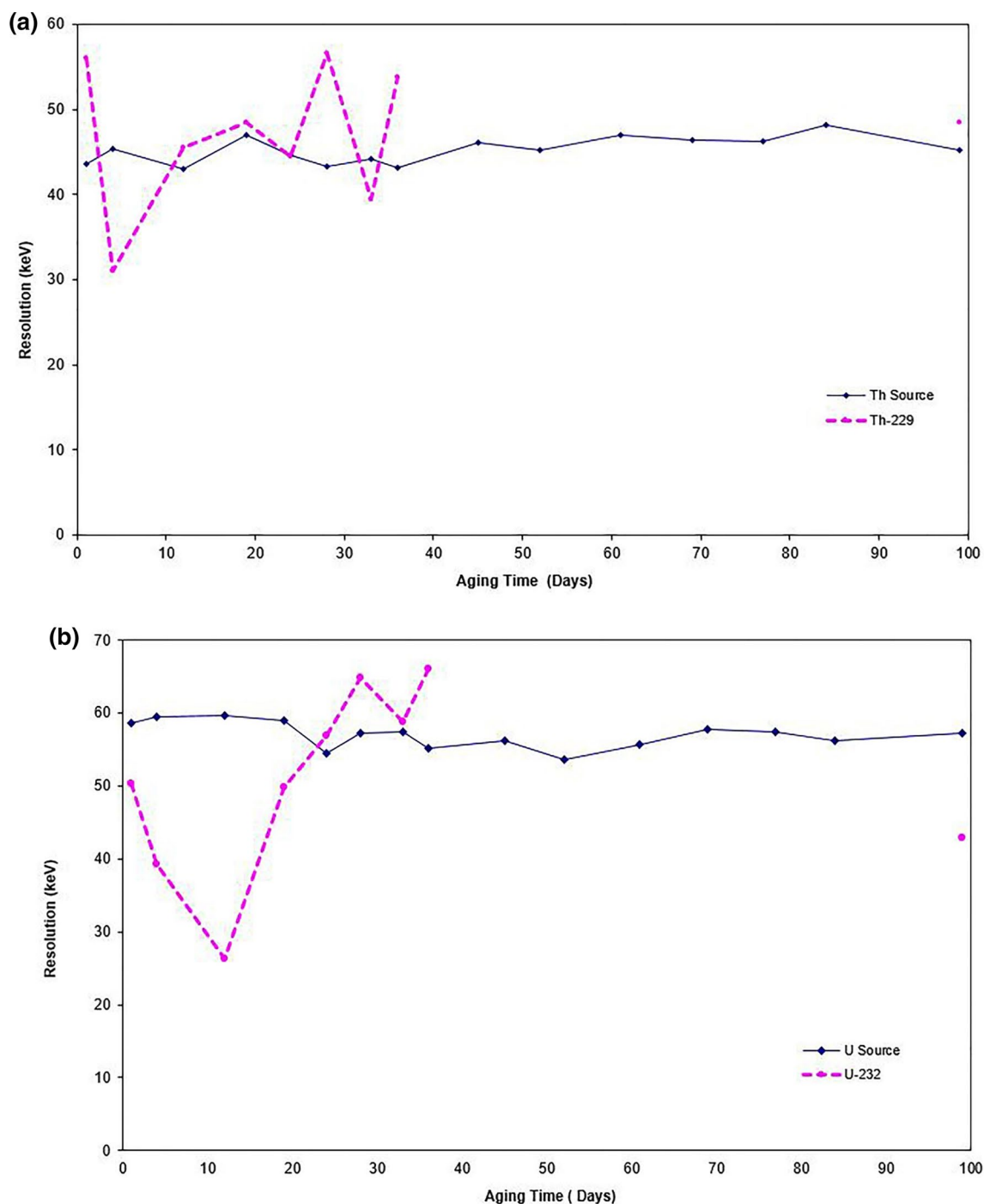


Fig. 5 **a** Effect of aging time on the resolution of the spectra of the prepared thorium source. **b** Effect of aging time on the resolution of the spectra of the prepared uranium source

The stability of the uranium or thorium fluoride sources that were prepared for counting by α -spectrometry were also tested by constructing peak resolution–aging time curves. The data obtained showed that even after 100 days of storage, the resolution of the source peaks is virtually unaffected with time.

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Authors' contributions O. Fallatah will oversee the overall objectives of the article at radiochemical analysis laboratory in Radiation Protection & Training Centre, King Abdul-Aziz University. He's responsible for the supervision of organizing and overall management of the components of the research activities, ordering required materials, calibration of the Alpha spectrometer, and also be responsible for publication and presentation of results. M. M. T. Qutub carried out analysis, chemical separation, and measurement of results by using α -spectrometry.

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Availability of data and materials All the experiments were carried out at radiochemical analysis laboratory at the center of Radiation Protection & Training, King Abdul-Aziz University. The data were measured by using α -spectrometry and all data saved in the system, which are available at Nuclear Engineering Department. All the data are available from the corresponding author (Dr. O. Fallatah) of this manuscript.

Declarations

Conflict of interest There is no conflict of interest.

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