TECHNIQUE FOR RAPID ASSAY OF RADIUM ISOTOPES IN WATER
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Abstract

A rapid and direct method of measuring radium isotopes is described. After removing the ^{224}Ra from a ^{228}Th solution using anion column separation at CRPP, the ^{224}Ra spike mixed with a ^{226}Ra internal standard were electrodeposited onto a planchet and measured by α spectrometry. The results indicate that the separation procedure at CRPP is effective and the electrodeposition procedure, followed by α spectrometry, might open another scope for SNO to measure the natural radioactivity in its water system.

Introduction

Radium is an important member of the natural uranium decay series and is quite soluble in water. One of the conventional methods for radium measurement in water is based on the measurement of radon gas emanating from the water. This method is frequently used, but some undesirable aspects are associated with this method, such as time consuming, indirect, and lack of assessment of the quality of an individual analysis. In contrast to the radon gas emanation method, electrodeposition of radium has a number of advantages: (1) it is a direct determination, (2) small samples (1-10 pCi/L) can be handled, (3) the analysis and measurement can be performed in a timely manner on the order of 2-3 days, (4) it can determine all of the radium isotopes at one measurement.

In this work, electrodeposition of radium, followed by alpha spectrometry will be used to measure the activity of radium isotopes. The main goals are: (1) to determine the activity of the ^{224}Ra spike used in the salt extraction experiment on the 1 TTF at CRPP, and (2) to develop a possible tool for radium measurements at the SNO water system.

Experimental

Stock Solution Preparation

A standard solution of ^{226}Ra (4.4444 Bq/ml) was obtained from University of Guelph. From this standard, a 0.4444 Bq/ml of ^{226}Ra stock solution was prepared in 0.14 M HCl solution.

Two ^{224}Ra spikes eluted from a ^{228}Th-attached column were prepared at CRPP on June 9 and 22, 2000, separately [details refer to the report of ^{224}Ra spike]. By taking account of ^{228}Th decay and ^{224}Ra buildup during the sample preparation time, the activities for Spikes 1 and 2 were estimated as 9.45 ± 0.47 and 8.94 ± 0.45 Bq.

0.5 ml of Spike 1 and 1.5 ml of Spike 2 were diluted with 0.14 M HCl for further electrodeposition and α spectrometry.

Electrodeposition

1 ml of the 0.4444 Bq ^{226}Ra standard and 1 ml of the diluted ^{224}Ra spike were mixed in 15-ml electroplating solution of ammonium oxalate and hydrochloric acid and transferred into a plating cell containing a stainless steel disc as cathode. A platinum wire was used as the anode. After addition of soluble platinum, the volume in the cell

was brought to approximately 30 ml. ^{224}Ra and ^{226}Ra were electrodeposited simultaneously onto the disc by using 600 mA current for 60 minutes.

α-Spectrometry

After the electrodeposition was completed, the disc was removed from the cell, rinsed with distilled water, dried, and placed into a low-background counter using a surface-barrier solid-state detector coupled with multi-channel pulse height analyzer (ORTEC 920-8). The activities of radium isotopes were measured by alpha spectrometry. The detection limit for both ^{224}Ra and ^{228}Th was estimated as 0.001 Bq at one-week counting time and 10% counting efficiency.

In this work, the intensity of the ^{224}Ra spike was determined by comparing with that of the known ^{226}Ra internal standard. This ratio is independent of the electrodeposition and counting efficiencies.

Results and Discussion

The energy-resolved alpha spectra from 4 to 8 MeV for both spikes are shown in Figures 1a and 1b. A ^{212}Po peak was also observed at 8.78 MeV (100%), but not included in these spectra. Spike 1 [Figure 1] was started to count roughly one day after electrodeposition, while Spike 2 [Figure 2] was sent to the counter one hour after electrodeposition. The overall counting time for both spikes was roughly 1.6 days. The alpha peaks of ^{226}Ra, ^{224}Ra and their daughters are identified in both figures.

Two peaks observed at 4.60 MeV (5.5%) and 4.78 MeV (94.5%) correspond to ^{226}Ra. The signal at 5.69 MeV (94%) corresponds to ^{224}Ra. A multiplet observed from 5.4 to 5.5 MeV is composed of a ^{222}Rn peak at 5.49 MeV, a minor signal of ^{224}Ra at 5.45 MeV (5.5%), and possibly a background of ^{228}Th at 5.42 MeV. It should be noted that after subtracting the counts from ^{222}Rn and ^{224}Ra, the intensity of this possible ^{228}Th peak is less than 1% of that of ^{224}Ra peak at 5.69 MeV.

Radioactivity decay is a random process and is a function of the time of observation. The equation for activity decay after a period of time, t, is written as

$$A = A_o e^{-\lambda t}$$

This equation can be rearranged as a form of straight line by taking the natural logarithms

$$\ln[A] = \ln[A_o] - \lambda t$$

A plot of ln[A] against time gives a straight line with a slope of -λ and a y-intercept of ln[A_o].

Figure 2 shows the example of plot of ln[A] versus counting time for ^{224}Ra peak at 5.69 MeV in Spike 1. The slope and y-intercept were extracted from a least-squares linear fit of the plot. From the slope, the $t_{1/2}$ of ^{224}Ra is 3.40 ± 0.82 days, which is in an agreement with the literature-reported value of 3.64 days within 7%. The [A_o] obtained from the y-intercept was compared with the peak intensity of ^{226}Ra at 4.78 MeV and the activity of ^{224}Ra at the beginning of counting is then calculated as 0.246 ± 0.022 Bq. After the correction of ^{224}Ra decay since the elution of spike, the portion of original activity is 1.004 ± 0.092 Bq on June 9, 2000. A final summary for Spikes 1 and 2, including the date of preparation, extracted half-

life, and overall activity, is presented in Table 1.

The activities for Spikes 1 and 2 were experimentally determined as 21.09 ± 1.93 and 20.12 ± 0.61 Bq compared to the estimated values of 9.45 ± 0.47 and 8.94 ± 0.45 Bq. The experimental activities are consistent with a factor of 2.24 larger than that of estimation, which indicates that a further investigation of the spike intensity is necessary.

Another method to derive the intensities of ^{224}Ra and ^{226}Ra is by a reverse calculation from their daughter's peak intensities with known branching ratios. However, this method generally requires the radium-plating disc to be aged for a period of time (for example, it takes approximately a month for ^{226}Ra decay) for the daughters to reach equilibrium. From Figures 1a and 1b, the growth of daughter as a function of time was observed by the different intensities of radium daughters due to different sitting time of disc before the start of α counting.

It is interesting to know that, under the non-equilibrium condition, in Spike 1, the integrated peak areas for the ^{226}Ra, ^{222}Rn, ^{218}Po, and ^{214}Po all are still in an agreement within 10%. This indicates that the ^{222}Rn gas produced from ^{226}Ra is effectively trapped on the disc, regardless of the possibility of radon diffusion inside the counting chamber.

Conclusion

As mentioned earlier, the ^{224}Ra spikes were prepared from a ^{228}Th standard solution through an anion column separation method. From Figures 1a and 1b, the maximum intensity of ^{228}Th compared to that of ^{224}Ra is less than 1% (statistical error ~2%) for each spike, which indicates the non-existence of ^{228}Th and suggests that the purification method of removing ^{224}Ra from ^{228}Th at CRPP is very effective.

The results from this study demonstrate that the method of electrodeposition, followed by alpha spectrometry, is a fast, direct, and quantitatively reliable method for ^{224}Ra determination with the help of ^{226}Ra internal standard. On the other hand, with the known electrodeposition and counting efficiencies, the procedure without adding any standard radium isotope is achievable. The efficiencies can be learned simply by a standard or calibrated α source. Modification of this technique to allow sample preparation suitable for radium measurement in large aqueous matrices could also be readily accomplished in conjunction with other established procedures (e.g., MnOx column, co-precipitation, etc.). This offers another tool for SNO to measure the natural radioactivity in the water system to complement the established radon emanation method.

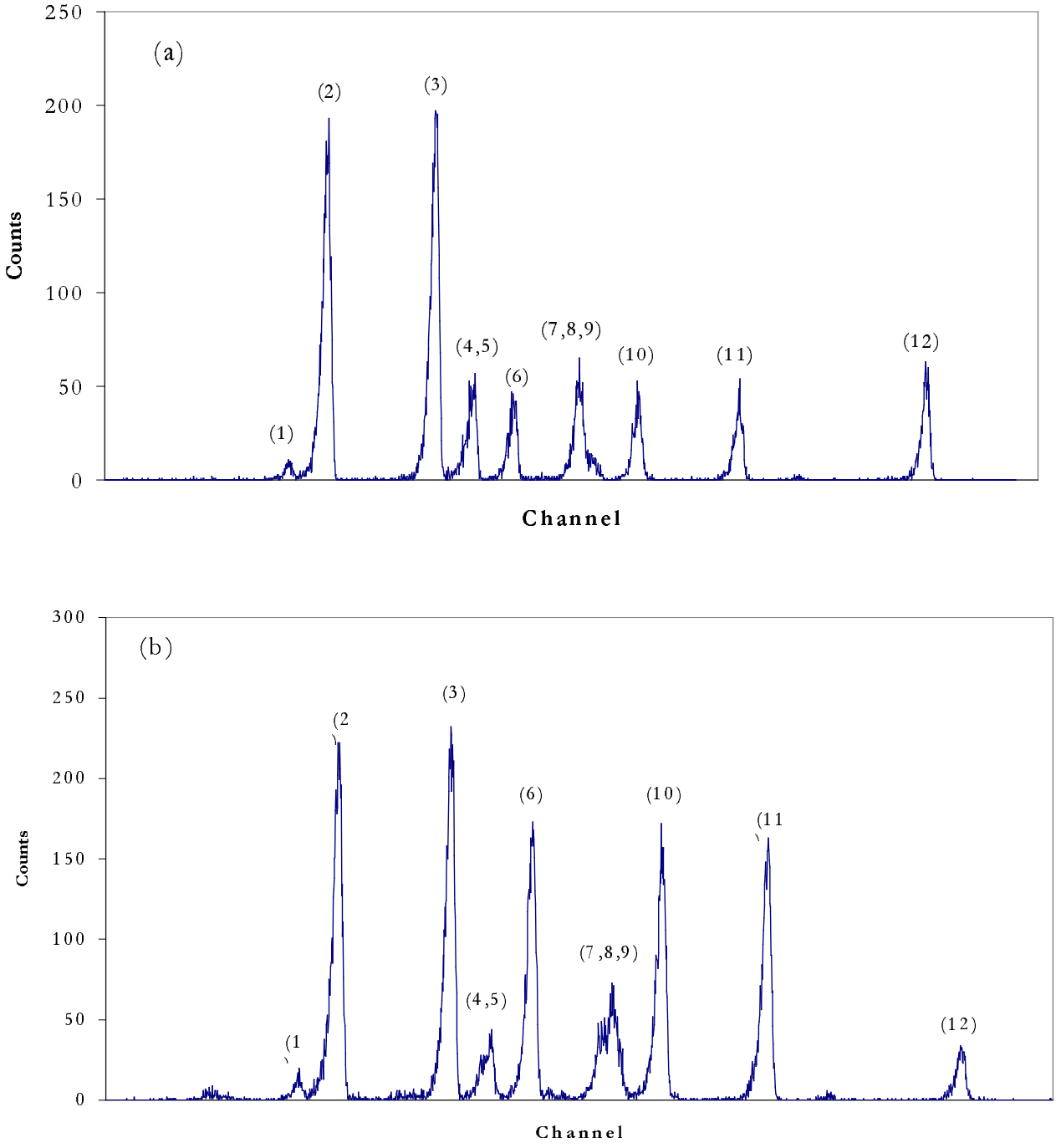

Figure 1a & 1b. The 4- to 8-MeV energy-resolution α spectra for spikes 1 and 2. (1) ^{226}Ra (4.598)- 5.5%, (2) ^{226}Ra (4.781)- 94.5%, (3) ^{210}Po (5.304)- 100%, (4,5) ^{222}Rn(5.486)- 100%, ^{224}Ra (5.447)- 5.5%, (6) ^{224}Ra (5.685)- 94.5%, (7,8,9) ^{218}Po (6.002)- 100%, ^{212}Bi (6.05)-70%, ^{212}Bi (6.09)- 27%, (10) ^{220}Rn (6.287)- 100%, (11) ^{216}Po (6.777)- 100%, (12) ^{214}Po (7.687)- 100%.

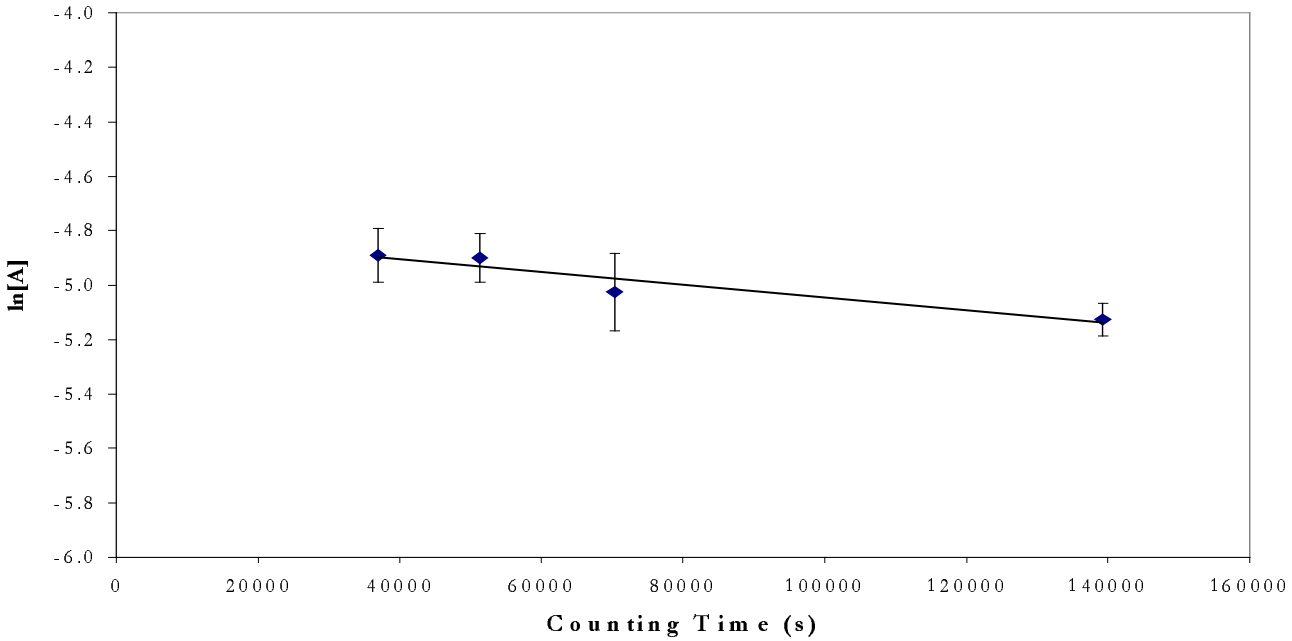

Figure 2. ln[*A*] versus counting time for ^{224}Ra peak at 5.69 MeV.

Table 1. A Summary for ^{224}Ra Spikes 1 and 2.

	Date of Preparation	$T_{1/2}$ [exp.] day	% for α Measurement	Activity at the Start of Counting (Bq)	Activity at the Day of Preparation (Bq)
Spike 1	June/9/2000	3.40 ± 0.82	4.76	0.246 ± 0.022	21.09 ± 1.93
Spike 2	June/22/2000	3.45 ± 0.55	20.19	1.499 ± 0.023	20.12 ± 0.61

Activity and the uncertainty were estimated from the least-squares linear fit of the plot of ln[A] vs. t.