Asian Journal of Chemistry Vol. 19, No. 2 (2007), 1035-1044

Measurement Ratio of $^{226}Ra/^{228}Ra$ in Marine Samples Using The Cation Exchange Resin and Gross α/β Spectrometry

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A method for determine activity of ^{226}Ra and ^{228}Ra in seawater samples by Gross α/β spectrometry was developed, where the Ba(Ra) was purified using a cation exchange resin column in warm temperature (70ºC). The $Ba(Ra)SO_4$ salts were wrapped on the plastic disc and counted using the gross α/β spectrometry after remain standing for three months. In order to certify the validation of this method, sediment reference materials have been analyzed and provided a good agreement between the analytical results and recommended values with the recovery values of 105.2 and 108.5% for ^{226}Ra and ^{228}Ra, respectively. This radiochemical procedure was also applied on the marine environment samples collected from Pulau Redang, Terengganu, such as seawater and suspended particulate matter. The analytical results for ^{226}Ra and ^{228}Ra in seawater were varied from 2.08 ± 0.19 mBq L^{-1} to 12.43 ± 0.47 mBq L^{-1} and 5.92 ± 0.93 mBq L^{-1} to 33.53 ± 2.03 mBq L^{-1}, respectively. Meanwhile, the activities of ^{226}Ra and ^{228}Ra in suspended particulate matter were also varied in the range of 4.32 ± 0.37 Bq g^{-1} to10.29 ± 0.59 Bq g^{-1} and 5.12 ± 0.46 Bq g^{-1} to 9.82 ± 0.47 Bq g^{-1}, respectively.

Key Words: $^{226}Ra/^{228}Ra$, Gross α/β spectrometry, Marine samples.

INTRODUCTION

Radium has four naturally occurring isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra) with the half-life vary from a few days until 1600 years. Studies on particular aqueous system may lead to understanding of various mobilization processes occurred in the ocean. Furthermore, studies on the isotopic concentration ratios in the ocean are useful to provide information on

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mixing processes[1-5]. Meanwhile, determination of radium isotopes in environmental samples is not always easy due to its low activity contents. Therefore, there has been much interest to develop methods for ^{226}Ra and ^{228}Ra determination in particular matrix samples.

The most common methods for determining radium isotopes are performed by α spectrometry, liquid scintillation counting (LSC) and gamma spectrometry. α Spectrometry is the most sensitive technique and allows simultaneous measurement of α-emitting radium isotopes. However, it is difficult to isolate the radium from other alkaline earth metals[6-8]. A rapid and convenient method to measure ^{226}Ra and ^{228}Ra isotopes is using γ-ray energy directly. However, the probability of γ-emission is relatively low due to low counting sensitivity in γ-Spectrometry and is liable to interference from ^{235}U[6,9,10]. In contrast, LSC provides high detection efficiency up to 100 % for unquenched samples. But, the α-background count rate of LSC is slightly too high. Furthermore, the sample mixture with a cocktail is usually stated in unstable condition during counting using the LSC. This may lead to loss of radon resulting from the volatilization of toluene[10,11].

In this work, the simultaneous analysis of ^{226}Ra and ^{228}Ra in marine samples by gross α/β spectrometry method with isolation of $BaSO_4$ co-precipitate using a cation exchange resin column was carried out.

EXPERIMENTAL

Analytical grade reagents and high purity of deionized distilled water (EASYPureUV) were used throughout this work. Stock solution of ^{226}Ra (20 dpm/mL) was prepared in 100 mL of 1 M HCl. Standard reference material from the International Atomic Energy Agency (IAEA) was used for validation of the analytical procedures. Marine samples such as seawater and suspended particulate matter were collected at Pulau Redang, Terengganu were analyzed. The activities of ^{226}Ra and ^{228}Ra were then measured by the gross α/β spectrometry (LB5 100-W, Tennelec).

The analytical procedure was performed *via* an inter-comparison exercise and analysis of reference material supplied by the IAEA. In this work, three sets of standard reference material sample (SRM) IAEA-300 had been analyzed.

About 0.5 to 1.0 g of SRM was weighed and 20 mg of Ba^{2+} carrier was spiked in the sample as a chemical yield and leached with 20 mL of 8 M HCl at 100 - 110ºC for 3 h. The sample was filtered after digestion and the filtrate was heated on the hot plate until dryness. The residue was then dissolved with 50 mL of 1 % $HClO_4$ and the aqueous part was poured into the cation resin column (Fig. 1).

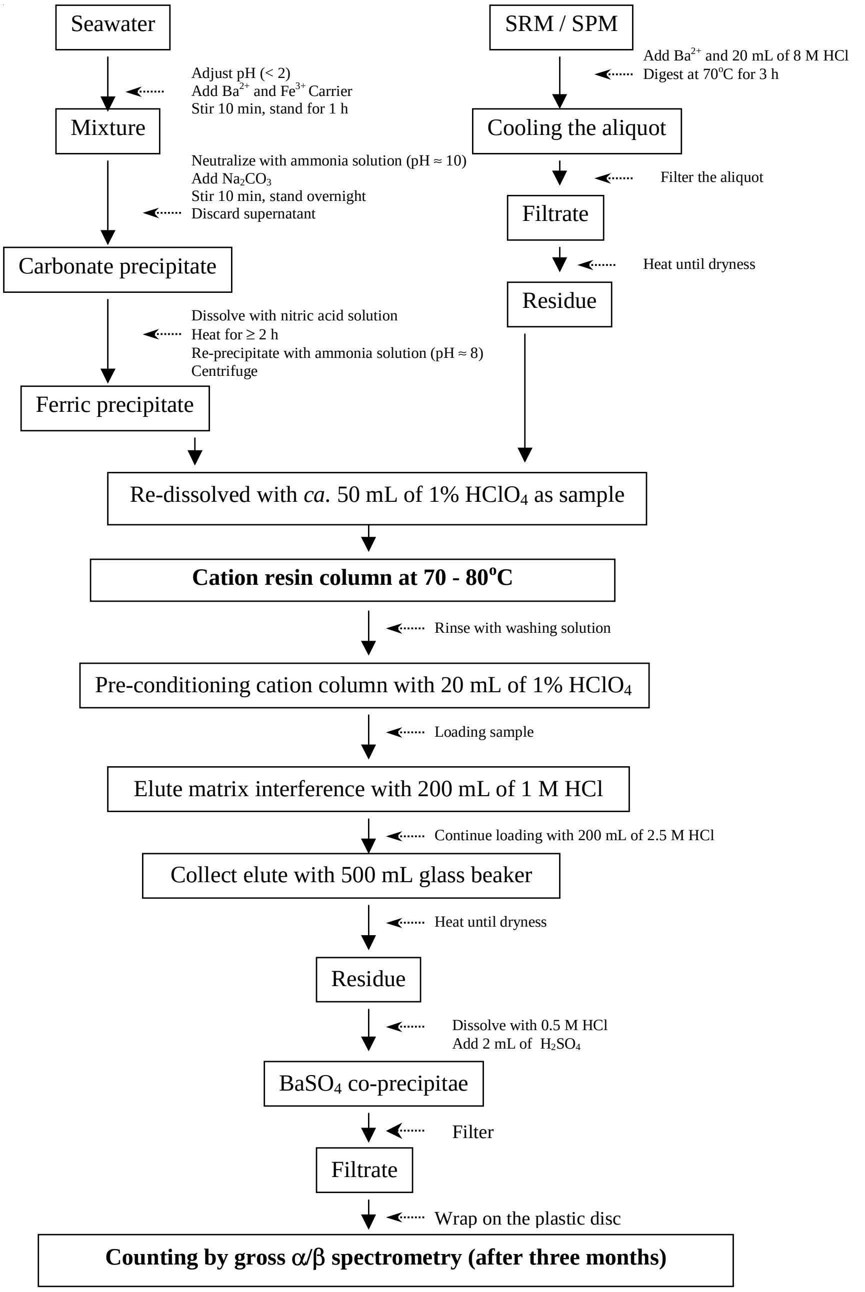

Fig. 1. Analytical procedures of ^{226}Ra and ^{228}Ra

Preparation efficiency curves and calculation

The efficiency curve for α-emitter was used to calculate the actual activity of ^{226}Ra in the analyzed samples. The efficiency curve for α-emitter was prepared based on the α-emitter of ^{226}Ra for different weights of Ba^{2+} carrier (Fig. 2). Trace containing α-emitter (*ca*. 1 mL), such as ^{226}Ra tracer (20 dpm/mL) and 10 mg of Ba^{2+} carrier were spiked into a glass beaker containing 50 mL of 1 M HCl, and were heated on the hot plate until dryness. The residue was re-dissolved with 20 mL of 0.5 M HCl and 2 mL of concentrated H_2SO_4 were then added to produce the $Ba(Ra)SO_4$ salts. The $Ba(Ra)SO_4$ was filtered through the pre-weighed 25 mm diameter of GF/C filter paper and dried up in an oven at 60ºC and wrapped on the 25 mm diameter plastic disc. The similar procedure was applied on the different weight of Ba^{2+} carrier as from 20 to 70 mg.

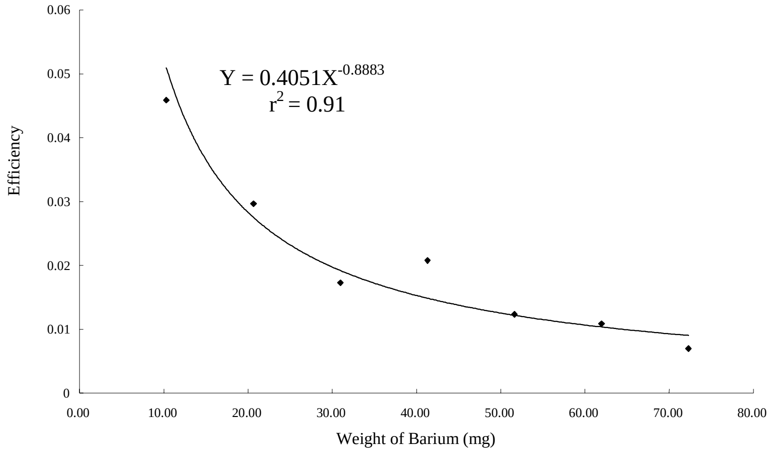

Fig. 2. Counting efficiency of alpha emitter caused by ^{226}Ra obtained from the gross α/β spectrometry

Meanwhile, the actual activity of ^{228}Ra as a beta emitter was also calculated from the beta efficiency curve. The efficiency curve for β emitter was also prepared from various weigh of potassium chloride (Fig. 3). About seven samples of KCl with different weigh from 10 to 70 mg were prepared. The KCl salt was attached on the 25 mm diameter of GF/C filter paper using glue and acetone (1:25) and dried in an oven at 60ºC and wrapped on the 25 mm diameter plastic disc for the gross α/β spectrometry counting.

Purification of barium(radium) by cation exchange column

During experiment, all solutions such as acids and samples and cation column were operating in warm temperature which is between 70-80ºC. Approximately about 35 mL of Bio-Rad AG 50 W-X4 resin with 200-400 mesh size were added into the glass column and rinse with the order of washing solution before applied to the actual samples: (1) 100 mL of de-ionized distilled water, (2) 20 mL of 1 % $HClO_4$, (3) 20 mL of mixing solution (containing 4 g of boric acid, 18 mL of $HClO_4$, 2 mL of HF dissolved in 1000 mL of de-ionized distilled water), (4) 10 mL of 1 % $HClO_4$, (5) 50 mL of 10 % tartaric acid, (6) 20 mL of 1 % $HClO_4$, (7) 200 mL of 4 M HCl, (8) 250 mL of 2 M H_2SO_4 and (9) 100 mL of de-ionized distilled water.

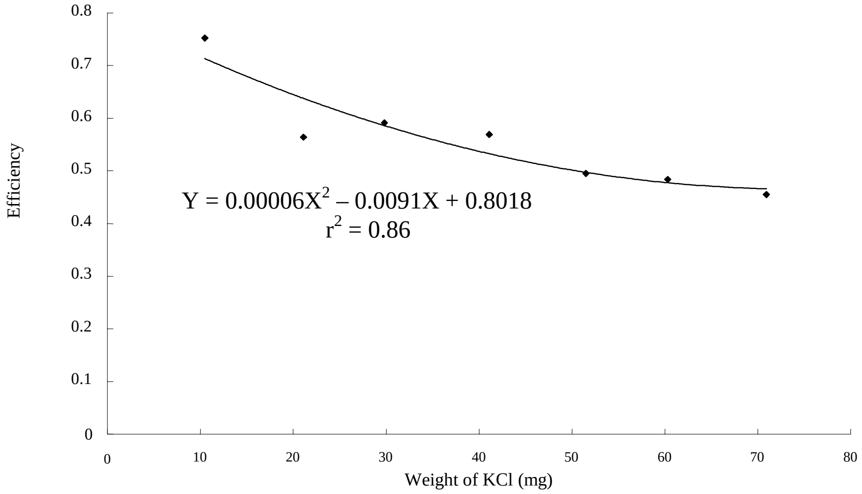

Fig. 3. Counting efficiency of beta emitter caused by potassium obtained from the gross α/β spectrometry.

The purpose of using washing solutions is to remove all the matrixes or interferences combined in the cation resin column. The cation resin column was pre-conditioned with 20 mL of 1 % $HClO_4$ and continued pour with a sample solution at the effluent rate is about 4-5 mL/min. After all the aqueous of sample were discharged from the column, about 200 mL of 1 M HCl were poured into the column to elute lead, iron, uranium and all undesired elements. About 200 mL of 2 M HCl was then poured again into the column to elute Ba(Ra) from the resin and was collected into the glass beaker for further analysis.

The Ba(Ra) solution was heated on the hot plate until dryness. The residue was dissolved with 50 mL of 0.5 M HCl and spiked with 1-2 mL of H_2SO_4 to obtain the $Ba(Ra)SO_4$ salts. The $Ba(Ra)SO_4$ was then filtered with 25 mm diameter of GF/C filter paper and dried at 60ºC until constant weight. The dried $Ba(Ra)SO_4$ salts on the filter paper was weighed to calculate their yield and to determine the content activities of ^{226}Ra and ^{228}Ra on the $Ba(Ra)SO_4$ after stand for more then three months to ensure the equilibrium occurs between the isotopes of radium with its progenies.

Application on marine samples

About 15 L of seawater samples were colleted using Van Dorn water sampler surrounding Pulau Redang on 27 July 2003 to 31 July 2003 (Fig. 4) and brought to the laboratory for further analyses. The *in situ* parameters, such as salinity, pH, dissolved oxygen were also determined using the calibrated portable meter (Model: YSI-SCT 6810).

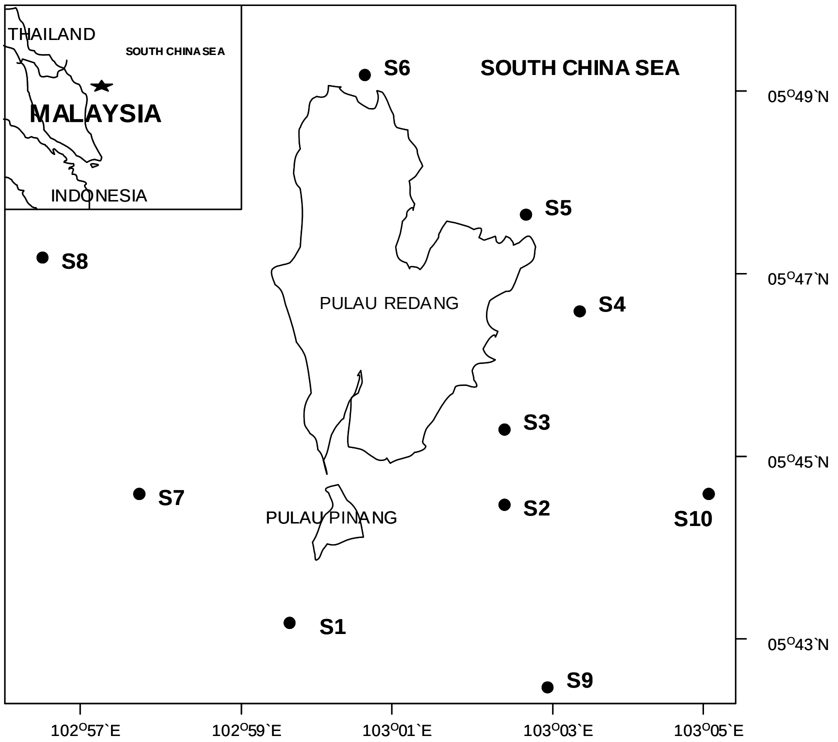

Fig. 4. Map showing the location of sampling sites around Pulau Redang, Malaysia

In the laboratory, seawater samples were filtered with 45 mm diameter of pre-weighed membrane filter paper (0.45 µm pore size) as described by Theng and Mohamed[12]. Briefly, the filtered seawater was acidified with HNO_3 (pH < 2) and spiked with 25 mg/mL of Fe^{3+} and 20 mg/mL of Ba^{2+} carriers. The ferric precipitation was centrifuged on 5000 rpm for 5 min and the supernatant was discarded. Ferric precipitate was then re-dissolved with 50 mL of 1 % $HClO_4$ and poured into the cation column.

Meanwhile, the suspended particulate matter (SPM) were dried in an oven at 60ºC until constant weight and undergone the same analyses as SRM samples.

Activity calculation

The actual activity of ^{226}Ra in analyzed sample was calculated based on the calibrated efficiency curve of ^{226}Ra (Fig. 2). The measurement of ^{226}Ra activity in analyzed samples took about one month after separation from the cation column due to the establishment of the equilibrium secular between ^{226}Ra to its progenies and also reducing the interferences of ^{223}Ra and ^{224}Ra activities. The equation suggested by Godoy[13] was also used to calculate the actual activity of radium in the analyzed samples as follows:

$$A(^{226}\text{Ra}) = \frac{\text{cpm}^{226}\text{Ra}}{Y_{ch} \cdot Y_{eff} \cdot [1 + 3(1 - e^{-\lambda t})]} \quad (1)$$

where; A(^{226}Ra) = ^{226}Ra activity (dpm), cpm ^{226}Ra = counts of ^{226}Ra activity in one min (cpm), Y_{ch} = chemical yield, Y_{eff} = counting efficiency of ^{226}Ra activity, λ = decay constant for ^{222}Rn (day) and t = time intervals between date of running cation exchange column until date of counting (day).

The actual activity of ^{228}Ra in analyzed samples is calculated from the calibrated efficiency curve of ^{228}Ra (Fig. 3). Through the previous study, the ^{228}Ac progenies would emitted the high energy of β-ray which interfered during the counting activity of ^{228}Ra. Then, to avoid this interference, the counting samples were measured after remain standing for three months, where the equilibrium is established between ^{228}Ra and ^{228}Ac:

$$A(^{228}\text{Ra}) = \frac{\text{cpm}^{228}\text{Ra} - (Y_{ch} \cdot Y_{eff} \cdot A(^{226}\text{Ra})(1 - e^{-\lambda t})}{Y_{ch} \cdot Y_{eff\,(^{228}\text{Ra})}} \quad (2)$$

where; A (^{228}Ra) = ^{228}Ra activity (dpm), Y_{ch} = chemical yield, Y_{eff} = counting efficiency for gross α, Y_{eff} (^{228}Ra) = counting efficiency for gross β, cpm ^{228}Ra = counts of ^{228}Ra in 1 min, A (^{226}Ra) = ^{226}Ra activity (dpm), λ = decay constant for ^{222}Rn and t = time interval between date of running column and counting (day).

RESULTS AND DISCUSSION

The counting efficiencies of ^{226}Ra and ^{228}Ra were calculated from the efficiency curves of α and β emitter, respectively (Figs. 2 and 3) as follows:

$$Y(^{226}\text{Ra}) = 0.401\ (\text{Ba})^{-0.8883} \quad (3)$$

$$Y(^{228}\text{Ra}) = 0.00006\ (\text{Ba})^2 - 0.0091\ (\text{Ba}) + 0.8018 \quad (4)$$

where; Y(^{226}Ra) = counting efficiency for ^{226}Ra (cpm/dpm), Y(^{228}Ra) = counting efficiency for ^{228}Ra (cpm/dpm) and Ba = weight of barium carrier (mg).

In order to confirm the validation of this procedure, three sets of standard reference material samples IAEA-300 were analyzed and the activities of ^{226}Ra and ^{228}Ra were measured simultaneously by gross α/β spectrometry after remain standing for three months, where the equilibrium occur between parents and daughters. The recoveries of ^{226}Ra and ^{228}Ra activities were 105.2 and 108.5 %, respectively (Table-1).

The method described above has been applied to determine the activities of ^{226}Ra and ^{228}Ra in seawater and suspended particulate material around Pulau Redang, Terengganu. The activities of dissolved ^{226}Ra and ^{228}Ra varied from 2.08 ± 0.19 mBq L^{-1} to 12.43 ± 0.47 mBq L^{-1} and 5.92 ± 0.93 mBq L^{-1} to 33.53 ± 2.03 mBq L^{-1}, respectively (Fig. 5a). Meanwhile, the activities of ^{226}Ra and ^{228}Ra in SPM varied ranging from 4.32 ± 0.37 Bq g^{-1} to10.29 ± 0.59 Bq g^{-1} and 5.12 ± 0.46 Bq g^{-1} to 9.82 ± 0.47 Bq g^{-1}, respectively (Fig. 5b). The activities of ^{226}Ra and ^{228}Ra are almost similar with previous studies by different researchers as shown in Table-2. This means that the developed method using cation column and measuring the activity of radium with the gross α/β spectrometry was successful.

TABLE-1
ACTIVITIES OF ^{226}Ra AND ^{228}Ra IN THE REFERENCE MATERIAL SAMPLES OF IAEA-300

Replicate	^{226}Ra (Bq kg^{-1} ± σ)	^{228}Ra (Bq kg^{-1} ± σ)
1	58.1 ± 12.7	203.1 ± 10.7
2	67.5 ± 14.76	181.1 ± 11.8
3	52.6 ± 13.6	232.2 ± 13.2
Mean	59.5 ± 7.8	205.5 ± 6.9
Recommended value	56.5	189.3
Confidence interval	54.4-60.2	182.1 – 193.9
Recovery (%)	105.2	108.5

TABLE-2
COMPARISON OF RADIUM ACTIVITIES IN SEAWATER MEASURED DURING THIS STUDY

Location	^{226}Ra (mBq L^{-1})	^{228}Ra (mBq L^{-1})	Reference
Redang Island	2.08 ± 0.19 – 12.43 ± 0.47	5.92 ± 0.93 – 33.53 ± 2.03	This study
Bengal Bay	5.4 ± 2.4 – 19.0 ± 8.3	3.0 ± 2.0 – 7.6 ± 3.7	Ghose[9]
Bengal Bay	2.0 – 19.0	0.3 – 44.2	Moore[14]
Chao Phraya River	2.1 ± 0.2 – 4.3 ± 0.2	2.4 ± 0.6 – 18.4 ± 1.1	Nozaki[15]
Yeoja Bay	1.5 – 4.8	–	Hwang[16]
South China Sea	1.30 ± 0.03	2.98 ± 0.93	Nozaki[17]
Strait of Malacca	2.52	8.97	Nozaki[17]
East China Sea	1.67 – 3.3	4.16 – 10.0	Nozaki[18]
Ulsan Bay	1.40 – 5.40	4.49 – 19.9	Lee[19]

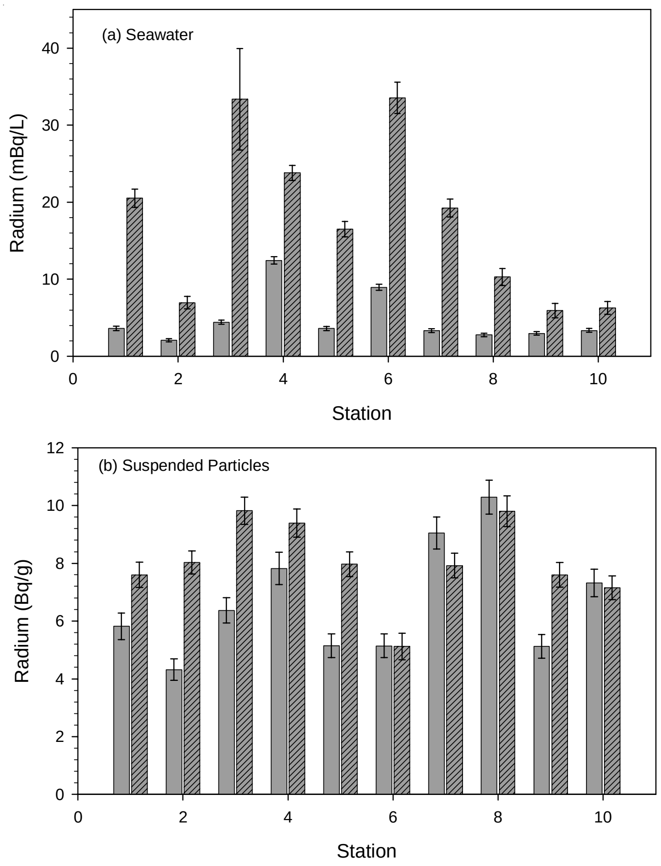

Fig. 5. Activities of ^{226}Ra (open) and ^{228}Ra (closed) in dissolved (5a) and suspended particle material (5b) phases in Pulau Redang

Conclusion

Method described using Bio-Rad AG 50 W-X4 resin (200-400 mesh size) and running in warm temperature including all chemicals is agreeable with the recommended values of International Atomic Energy Agency and marine samples.

ACKNOWLEDGEMENTS

This research was supported by the IRPA Grant 09-02-02-0045-EA141. The authors would like to thank the Laboratory Assistant from Universiti Kebangsaan Malaysia and Malaysian Institute Nuclear Technology for their help during sampling and sample analysis.

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(*Received*: 8 October 2005; *Accepted*: 21 August 2006) AJC-5052