Nucl. Sci. and Tech., Vol.8, No. 3 (2018), pp. 29-35

Nuclear Science and Technology

Journal homepage: https://jnst.vn/index.php/nst

Using a delayed coincidence counting system to determine ^{223}Ra, ^{224}Ra in seawater sample

Vo Thi Mong Tham, Phan Son Hai, Nguyen Van Phuc, Nguyen Minh Dao, Phan Quang Trung, Le Xuan Thang, Nguyen Thi Huong Lan

Nuclear Research Institute, 01 Nguyen Tu Luc Street, Dalat, Vietnam
Email: vothimongtham@gmail.com

Abstract: A Radium Delayed Coincidence Counter (RaDeCC) includes 3 channels (^{223}Ra channel, ^{224}Ra channel, and total channel). It has been newly designed and assembled at Nuclear Research Institute. To determine ^{223}Ra and ^{224}Ra in seawater samples, the system efficiency at all 3 channels were investigated and calibrated. The research results showed that the RaDeCC operates stably and reliably with high efficiency of 26%. In this project, a procedure for measuring short half-life radium isotopes was established with a low detection limit (LOD (^{223}Ra) = 0.002 Bq; LOD (^{224}Ra) = 0.01 Bq), good reproducibility, and high precision. The technique is suitable for qualitative analysis of ^{223}Ra, ^{224}Ra in seawater samples at low concentration. The 11 coastal water samples were collected in a coastal of Ninh Thuan province. The analytical data of short-lived radium isotopes concentration in seawater at Ninh Thuan coastal area are $11.2 \times 10^{-3} \div 45.5 \times 10^{-3}$ mBq/L for ^{223}Ra, and $34.7 \times 10^{-2} \div 21.9 \times 10^{-1}$ mBq/L for ^{224}Ra.

Keywords: *Radium Delayed Coincidence Counter, ^{223}Ra and ^{224}Ra, seawater samples, efficiency calibration, limit of detection.*

I. INTRODUCTION

Natural radium isotopes have been used very effectively to study the dynamic parameters of coastal waters such as residence time, oceanic processes, vertical and horizontal diffusion coefficients, process of mixing groundwater with seawater, etc. [1-6]. Radium isotopes are proved to be ideal tracers for quantifying fluxes of dissolved components across the continental shelf (Moore, 2000). Radium isotopes have been applied to study residence time of coastal water, mixing factors of coastal water with ocean *(Bourquin, M. et al., 2008; Beek P. van et al., 2008; Moore W.S. et al., 2008; Rapaglia J. et al., 2010; Souza T.A. et al., 2010; HequanGu et al., 2012)*. ^{226}Ra and ^{228}Ra are suitable for studies in regional level owing to their long half-lives. Short-lived nuclides ^{223}Ra ($T_{1/2}$ = 11.44 d) and ^{224}Ra ($T_{1/2}$ = 3.66 d) are appropriate for the investigation of the submarine groundwater discharge and its pathway [1-7].

There are some techniques for analyzing radium isotopes such as Alpha spectrometry, Gamma spectrometry, Liquid Scintillation Counting, Inductively Coupled Plasma-mass Spectrometry, Thermal Ionisation Mass Spectrometry, and Accelerator Mass Spectrometry, etc. However, analysis of ^{223}Ra and ^{224}Ra radioactive in sea water is difficult due to the following reasons: (i) Activities of ^{223}Ra and ^{224}Ra in seawater samples is very low (e.g. 0.5 ÷ 5.0 mBq/L); (ii) The half-lives of 2 radium isotopes are very short, so all current

https://doi.org/10.53747/jnst.v8i3.71
Received 03 January 2018, accepted 20 November 2018

analytical methods require pre-enrichment and radium separation to eliminate disturbance factors [4, 8-10].

A newly analytical technique has been developed to quickly and easily identify ^{223}Ra and ^{224}Ra radionuclides in seawater by radium delayed coincidence counter system [3]. This technique was successfully applied by many research groups around the world [7-8, 10-13].

This study is aimed at: (i) Calculating the efficiency of RaDeCC, calibrating the efficiencies at 3 channels; (ii) Establishing the limit of detection with good reproducibility, and high precision; (iii) Establishing the procedure for analyzing shorted-lived radium isotopes in seawater samples; (iv) Applying this technique to an in-situ research at Ninh Thuan coastal area to evaluate the ability of the method.

II. EXPERIMENTS

A. Theory of RaDeCC

Radium in seawater is adsorbed on a cartridge filled with MnO_2 fiber (called Mn-fiber). The RaDeCC system monitors alpha decays of short-lived Rn which recoil from the Mn-fiber. The principle of the method is based on the measurement of alpha radiation, produced by radioactive decay of the Ra daughter, Rn, in a scintillation (or Lucas) cell coated in the inside with silver-activated ZnS. When an alpha particle collides with the ZnS surface, it produces a light signal which is detected by a photomultiplier tube which translates the photon into an electrical count. Rn produced by the decay of Ra on the Mn-fiber is transported to a scintillation cell where it decays to Po. As alpha decay of Rn occurs, it produces an electronic signal which opens the gate to a delayed coincidence circuit. The counts are displayed on a computer by Labview [10, 12].

A closed circulation system to pump radon to the detector is described in Fig. 1. It consists of (1) a pump with 0-14 L/min flow rate; (2) flow rate meter; (3) cartridge, filled with Mn-fiber; (4) compressed helium tank; and (5) alpha detector.

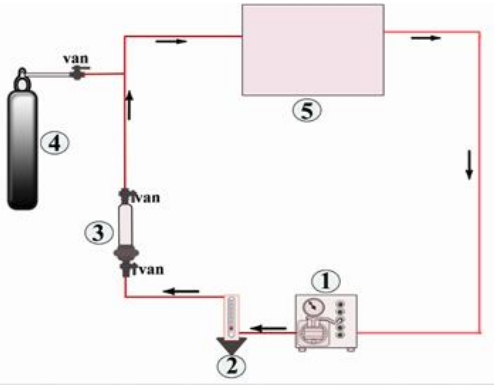
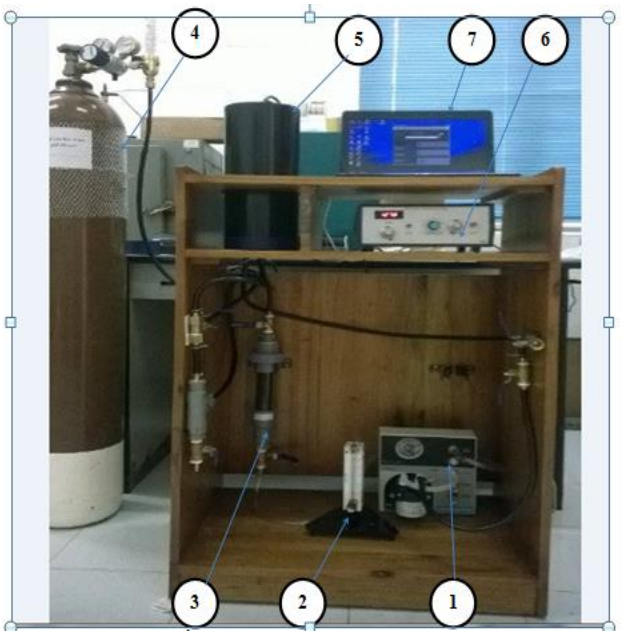


Fig. 1. Schematic diagram of radon circulation system [10].

Prior each measurement, Helium gas was pumped into the chamber to carry radon close to detector. In this chamber, the delayed coincidence signals generated by the decay of these radon isotopes (^{220}Rn, ^{219}Rn) to a short-lived polonium isotope (^{216}Po, ^{215}Po) are measured.

B. Method of experiment

In the project, Manganese dioxide impregnated acrylic fiber (Mn-fiber) was prepared for pre-concentrating radium in seawater. One gram of this Mn-fiber could retain 100% of radium and other elements in 8 L of seawater.



Notes:

(1) Air pump has flow rate of 7 L /min;
(2) Flow meter to measure airflow from air pump;
(3) PVC cartridges were filled with 35g of Mn-fiber (diameter 3.5cm, length 30cm);
(4) Helium gas cylinders with purity of 99.99%;
(5) A cylinder chamber was made of plexiglass with a volume of 1.6 L; photomultiplier tube (R877) with an amplifier of Hamamatsu;
(6) To power supply amplifier and delay circuit;
(7) Computer has installed the Labview software.

Fig. 2. RaDeCC system at NRI.

1. Selecting optimal factors for the RaDeCC

Selecting an optimal high voltage: By investigating the dependence of count rate on high voltage using standard alpha sources, the optimal high voltage was chosen.

Choosing an optimal amplification factor: A suitable amplification factor at which the ratio of real signal to the noise signal is largest was selected. The procedures are as follows:

+ Use a piece of dark paper to cover detector surface and then change the value of amplification to investigate the variance of a noise signal.

+ Use a standard alpha source to investigate the variance of count rate with an amplification factor. From these data, optimal amplification factor was determined.

2. Investigating the background of the RaDeCC system

Helium gas has been pumped into the chamber. The background of the system was counted for 12h.

3. Investigating the efficiency of the RaDeCC system

The efficiency of the RaDeCC system was determined by using ^{223}Ra and ^{224}Ra standard sources. The ^{223}Ra standard source was prepared from a ^{227}Ac standard solution supplied by Eckert & Ziegler Analytics. The ^{224}Ra standard source was prepared by digesting standard Thorium ore No. AMD/Phy/Std-7/76 with (0.360 ± 0.003) % ThO_2 in content.

Fig. 3. Picture of the fully assembled cartridges.

4. Development of analytical method for ^{223}Ra and ^{224}Ra

- *Preparation of standard sources:* ^{223}Ra standard source and ^{224}Ra standard source were prepared from the ^{227}Ac standard solution and the standard thorium ore, respectively.

- *Sample preparation:* 200 ÷ 300 L of seawater were passed through a cartridge filled with 35 g of Mn-fiber at flow-rate of 2 ÷ 3 L/min. Then 10 L of deionized water were continuously passed through this cartridge at above flow-rate to remove salt. Fiber in the cartridge was dried by air flow until the ratio of water to dry weight of Mn-fiber was about 50 ÷ 80%. Two valves of the cartridge were closed tightly in order to grow Radon inside the cartridge and attain radioactive equilibrium with Ra.

- *Measurement*: To determine ^{223}Ra and ^{224}Ra, each sample was counted for 4 hours twice. The first measurement and the second one had been conducted within 1-3 days and 7-17 days since the radon confinement, respectively.

- *Calculation:* ^{223}Ra and ^{224}Ra activities were calculated based on ^{219}Rn and ^{220}Rn net count rates of samples and those of standard that were corrected for chance coincidence events as well as reciprocal interferences between ^{219}Rn and ^{220}Rn channels.

-*Sensitivity, Accuracy and Repeatability:* These factors were estimated by using standard sources.

5. Analysis of ^{223}Ra and ^{224}Ra isotopes

- *Sample collecting:* 11 surface sea water samples in a coastal of Ninh Thuan province were collected. Sampling distances are from 1.5 to 15.5 km from shore. Sampling depth was 3 m from sea surface.

- *Radium preconcentration and analysis:* Radium in seawater was pre-concentrated by pumping 300 L of seawater through a cartridge filled with 35 g of Mn-fiber at the flow rate of 2 ÷ 3 L/min. After that, 5 ÷ 10 L of deionized water were passed through the cartridge at the same flow rate to remove salt on the fiber. The cartridge was then dried by air pump to make the ratio of water to dry weight fiber reaching 50 ÷ 80%. Short-lived nuclides ^{223}Ra and ^{224}Ra were measured directly on RaDeCC.

III. RESULTS AND DISCUSSION

High voltage: Based on the investigation of variation in counts with high voltage, the optimal high voltage was selected to be 1250 V for this system.

Amplification factor: The optimal amplification factor at which the ratio of real signal to noise reaches the maximum for this system signal as follows: Coarse gain = 3; Fine gain = 6.

A. Background

The most advantage of RaDeCC is its low background. Background measurement results are significant parameters for calculating the efficiency of the system. These data were used for calculating number of sample's count, correcting the results and uncertainties. Because it is performed before every sample count and used for correction of the results and uncertainties.

Background count rates for ^{219}Rn and ^{220}Rn channels were 0.01cpm (Stdev = 0.001) and 0.13 cpm (Stdev = 0.05), respectively.

However, by consecutively measuring samples in the same counter the subsequent backgrounds may increase due to decay products remaining in the counting cell. In order to clear the system of these residual isotopes, ambient air is circulated through the open system for at least 30 mins.

B. Efficiency

^{223}Ra (0.57 ± 0.11 Bq) and ^{224}Ra (1.37 ± 0.01 Bq) standard material adsorbed on Mn-fiber are measured at the same sample geometry, air flow rate, and optimal factors to calibrate the RaDeCC's efficiency (Fig. 4).

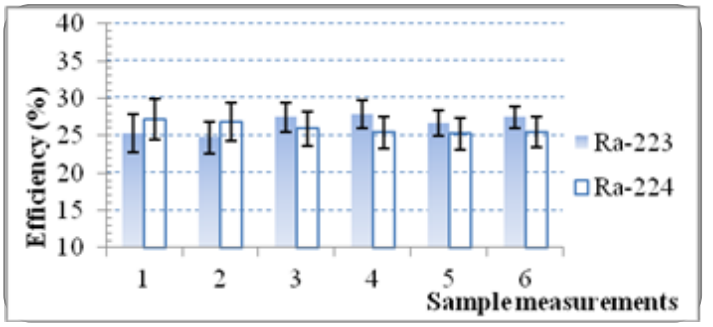


Fig. 4. Efficiencies of ^{223}Ra, ^{224}Ra channels.

Based on the results from 6 times of measurements, efficiency of ^{223}Ra changed from 24.75 to 27.88 percent and from 25.25 percent to 27.18 percent for ^{224}Ra channel.

Mean counting efficiencies (%) at ^{219}Rn and ^{220}Rn channels were 26.6 ± 2.0 and 26.0 ± 2.3, respectively.

C. Development of an analytical method for ^{223}Ra and ^{224}Ra:

- *Limit of detection:* Based on background count rates and standard sample count rates, limit of detection (LOD) was estimated to be 0.002 Bq for ^{223}Ra and 0.01 Bq for ^{224}Ra.

In this study, 300L of sea water needed to be collected to determine ^{223}Ra and ^{224}Ra on the RaDeCC.

- *Accuracy of the method:* Results from analyzing standard samples showed that analytical values and certified values agreed to each other in a maximum deviation of 3.5%.

Table I. The results of standard analysis (measurement time: 2 400 s).

Isotopes	RaDeCC Analysis (dpm)	Activity on the Mn-fiber standard (dpm)	Deviation (%)
^{223}Ra	35.2 ± 2.4	34.0 ± 6.8	-3.5
^{224}Ra	80.7 ± 7.4	82.1 ± 0.7	1.7

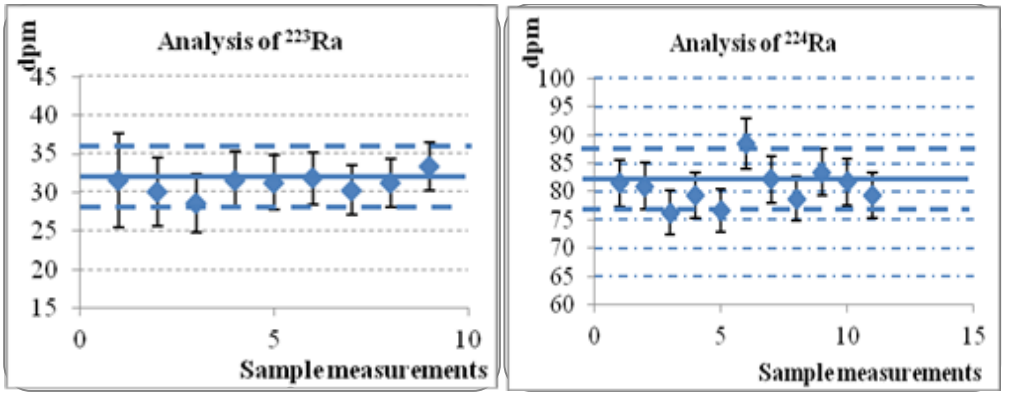


Fig.5. The results of standard measurement.

- *Repeatability of the method:* Results from repeated analyzing of standard samples showed that all analytical values were within 95% confidence level of certified value.

D. Concentrations of ^{223}Ra and ^{224}Ra isotopes in seawater samples:

The concentrations of short-lived radium isotopes in Ninh Thuan coastal area, which range from 11.2 × 10^{-3} mBq /L to 45.5 × 10^{-3} mBq /L for ^{223}Ra and from 34.7 × 10^{-2} mBq /L to 21.9 × 10^{-1} mBq /L for ^{224}Ra, are shown in Table II. In comparisons with some previous studies, the results of radium concentration of Ninh Thuan sea are seem to be in good agreement with the range of radium concentration at other areas in the world.

Table II. A concentration of ^{223}Ra and ^{224}Ra isotopes of 11 seawater samples.

Sample	^{223}Ra (mBq/L)	^{224}Ra (mBq/L)
PD_A1	45 × 10^{-3} ± 1.8 × 10^{-3}	218 × 10^{-2} ± 7 × 10^{-2}
PD_A2	188 × 10^{-4} ± 3 × 10^{-4}	121 × 10^{-2} ± 3 × 10^{-2}
PD_A3	272 × 10^{-4} ± 6 × 10^{-4}	124 × 10^{-2} ± 3 × 10^{-2}
PD_A4	269 × 10^{-4} ± 6 × 10^{-4}	119 × 10^{-2} ± 2 × 10^{-2}
PD_A5	308 × 10^{-4} ± 8 × 10^{-4}	110 × 10^{-2} ± 1.4 × 10^{-2}
PD_A6	198 × 10^{-4} ± 3 × 10^{-4}	103 × 10^{-2} ± 1.0 × 10^{-2}
PD_A7	329 × 10^{-4} ± 9 × 10^{-4}	102 × 10^{-2} ± 1.3 × 10^{-2}
PD_A8	112 × 10^{-4} ± 1.1 × 10^{-4}	680 × 10^{-3} ± 4 × 10^{-3}
PD_A9	116 × 10^{-4} ± 1.2 × 10^{-4}	469 × 10^{-3} ± 2 × 10^{-3}
PD_A10	164 × 10^{-4} ± 2 × 10^{-4}	347 × 10^{-3} ± 1.4 × 10^{-3}
PD_A11	204 × 10^{-4} ± 4 × 10^{-4}	406 × 10^{-3} ± 1.2 × 10^{-3}

IV. CONCLUSIONS

The project has been completely implemented and following main results were achieved:

- A procedure for preconcentration and analysis of short-lived radium isotopes ^{223}Ra and ^{224}Ra using delayed coincidence counting system was developed. This procedure is fairly simple, easy to operate, capable of providing analytical data in a short time.

- The analytical method has high sensitivity (^{223}Ra: 0.002 Bq; ^{224}Ra: 0.01Bq), accuracy (uncertainty <5%), and repeatability. This procedure meets the requirement for rapid analysis of ^{223}Ra and ^{224}Ra in sea water.

- The preliminary results showed that this new technique is absolutely applicable to determination of ^{223}Ra and ^{224}Ra at low level in Vietnam coastal area.

REFERENCES

[1]. Beek, P. van et al., "*Radium isotopes to investigate the water mass pathways on the Kerguelen Plateau (Southern Ocean)*". Deep-Sea Research II (55), pp. 662-637, 2008.

[2]. Gu, H. et al., "*Using radium isotopes to estimate the residence time and the contribution of submarine groundwater*

discharge (SGD) in the Changjiang effluent plume, East China Sea". Continental Shelf Research (35), pp. 95-107, 2012.

[3]. Moore, W.S., "*Fifteen years experience in measuring ^{224}Ra and ^{223}Ra by delayed-coincidence counting*". Marine Chemistry (109), 188 – 197, 2008.

[4]. GuogangJia, Jing Jia, "*Determination of radium isotopes in environmental samples by gamma spectrometry, liquid scintillation counting and alpha spectrometry: a review of analytical methodology*". Journal of Environmental Radioactivity (106), pp. 98-119, 2012.

[5]. Rapaglia, J. et al., "*Investigation of residence time and groundwater flux in Venice Logoon: Comparing radium isotope and hydrodynamical models*". Journal of Environmental Radioactivity (101), pp. 571-581, 2010.

[6]. Souza, T.A. et al., "*Use of multitracers for the study of water mixing in the Paraiba do Sul River estuary*". Journal of Environmental Radioactivity (101), pp. 564-570, 2010.

[7]. Bourquin, M. et al., "*Comparison of techniques for pre-concentrating radium from seawater*". Marine Chemistry 109, pp. 226-237, 2008.

[8]. Souza, T.A. et al., "*Use of multitracers for the study of water mixing in the Paraiba do Sul River estuary*". Journal of Environmental Radioactivity (101), pp. 564-570, 2010.

[9]. Moore. WS., Arnold, R., "*Measurement of ^{223}Ra and ^{224}Ra in coastal waters using a delayed coincidence counter*". J. Geophys. Res. (101), 1321-1329, 1996.

[10]. E. Garcia-Solsona et al., "*Uncertainties associated with ^{223}Ra and ^{224}Ra measurements in water via a Delayed Coincidence Counter (RaDeCC)*". Marine Chemistry (109), 198 – 219, 2008.

[11]. Guebuem Kim, "*Measurement and Application of Radium and Radon in the Environment*". Journal of Analytical Science & Technology 2 (Supply A), A115-A119, 2011.

[12]. Giffin, C., A. Kaufman, and W. S. Broecker, "*Delayed coincidence counter for the assay of action and thoron*". J. Geophys.Res., (68), 1749-1757, 1963.

[13]. Moore, W.S., Reid, D.F., "*Extraction of radium from natural waters using manganese-impregnated acrylic fibers*". J. Geophys.Res. 78 (36), 8880-8885, 1973.