



## Rapid determination of radium-224/226 in seawater sample by alpha spectrometry



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### ABSTRACT

A new radiochemical separation method has been developed for rapid determination of alpha-emitting radium isotopes in seawater samples. This method can be applied for the measurement of  $^{226}\text{Ra}$  in seawater samples when  $^{224}\text{Ra}$  is used as tracer for chemical recovery correction. Likewise,  $^{226}\text{Ra}$  can also be added as tracer for the determination of  $^{224}\text{Ra}$  in seawater sample. In the method, radium is first pre-concentrated with hydrous titanium oxide (HTiO) and is purified by combined anion/cation exchange column chromatographic separation. The radium in the eluate is then co-precipitated with HTiO, dissolved in 9 M  $\text{H}_2\text{SO}_4$ , and followed through a  $\text{BaSO}_4$  micro-precipitation step to prepare a thin-layer counting source to determine the activities of  $^{224}\text{Ra}/^{226}\text{Ra}$  by alpha spectrometry. Replicate spike and blank samples were measured to evaluate the performance of the procedure. The minimum detectable activity concentration was determined to be  $0.5 \text{ mBq} \cdot \text{L}^{-1}$  for  $^{226}\text{Ra}$  and  $0.4 \text{ mBq} \cdot \text{L}^{-1}$  for  $^{224}\text{Ra}$  in 1 L of seawater sample with a counting time of 48 h. The method is a promising candidate for rapid measurement for alpha-emitting Ra isotopes in a large population of environment water samples.

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### 1. Introduction

The determination of radium isotopes is important in environmental studies and for the protection of public health. Radium has four naturally occurring isotopes: three of them are alpha emitters ( $^{226}\text{Ra}$  in the uranium decay series,  $^{224}\text{Ra}$  in the thorium series and  $^{223}\text{Ra}$  in the actinium series) and one is beta emitter ( $^{228}\text{Ra}$  in the thorium series). Radium isotopes in seawater are mainly supplied by diffusion from deep-sea and continental shelf sediments. The Ra activity in seawater decreases with increasing distance from the source, as a result of dilution (mixing) and radioactive decay. Due to their widely ranging half-lives ( $^{226}\text{Ra}$ ,  $T_{1/2} = 1600 \text{ y}$ ;  $^{228}\text{Ra}$ ,  $T_{1/2} = 5.75 \text{ y}$ ;  $^{223}\text{Ra}$ ,  $T_{1/2} = 11.4 \text{ d}$ ;  $^{224}\text{Ra}$ ,  $T_{1/2} = 3.66 \text{ d}$ ), these radium isotopes have been widely used as geochemical tracers for a variety of oceanographic process studies (e.g., large scale ocean mixing, diffusion, horizontal and vertical eddy mixing, water-mass and particulate residence time) (Koczy, 1958; Moore and Santschi, 1986;

Rutgers van der Loeff et al., 1995; Rama and Moore, 1996) and for estimation of chemical fluxes to the ocean (e.g., riverine inputs, sediment inputs and submarine groundwater discharge) (Moore, 2000; Charette et al., 2007; Burnett et al., 2008; Moore and Oliveira, 2008). These studies often require sensitive, accurate and rapid determination of radium isotopes in a large population of seawater samples, particularly when short-lived  $^{224}\text{Ra}/^{223}\text{Ra}$  isotopes need to be analyzed.

As a large quantity of low level radioactive wastes or by-products containing long-lived Ra nuclides ( $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ ) can be produced from the phosphate industry, mining and processing of uranium and rare earth elements as well as coal and oil mining and combustion, the release of these Ra-containing wastes to the environment has been a serious concern for radiation protection and environmental protection. Similar to other alkaline earth metals (Ca, Sr and Ba), Ra can be incorporated into bone and is highly radiotoxic to human health. Consumption of water and food with elevated concentration of Ra isotopes could lead to a significant increase of the total annual effective radiation dose to the public, especially in the areas with high natural radioactivity background. Therefore, the determination of Ra isotopes in environmental samples including water samples is of interest to radiation protection (Bassam et al., 2004).

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A variety of decay-counting or mass spectrometric techniques have been reported for the determination of radium isotopes in water samples, including gamma-ray spectrometry (Rihs and Condomines, 2002; Jia and Jia, 2012),  $^{222}\text{Rn}$  emanation (Broecker et al., 1976; Ku and Lin, 1976), liquid scintillation counting (Higuchi et al., 1984), radium delayed coincidence counting (RaDeCC) (Moore and Arnold, 1996), direct (Hancock and Martin, 1991) or indirect (Eikenberg et al., 2001) alpha spectrometry, as well as thermal ionization mass spectrometry (TIMS) (Cohen and O'Nions, 1991; Volpe et al., 1991) and multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) (Lariviere et al., 2003).

Gamma spectrometry has been successfully used to measure high activities of  $^{228}\text{Ra}$  and  $^{226}\text{Ra}$  in coastal seawater samples (Schmidt and Reys, 1996; Charette et al., 2001; Kim et al., 2003; Van Beek et al., 2007). However, very large volume (20–100 L) of seawater would need to be processed due to poor detection efficiency and high background of the most commonly used high purity germanium (HPGe) detectors. LSC methods can provide high sample throughput, and acceptable sensitivity for  $^{228}\text{Ra}$  (Repinc and Benedik, 2001); but it is not possible for resolving the activities of three alpha-emitting Ra isotopes in the same sample due to its poor energy resolution. The RaDeCC system utilizes closely spaced decays of the progeny nuclides to measure short-lived  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$  with excellent background reduction (Moore and Arnold, 1996). This technique can also be used to measure long-lived  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  by storing the samples (e.g. scavenged on a  $\text{MnO}_2$ -fibre) to allow for the in-growth of  $^{222}\text{Rn}$  and  $^{228}\text{Th}$ . However, it would require long-term storage of samples at appropriate moisture levels to ensure good detection efficiency. Mass spectrometric methods provide good sensitivity and high precision for long-lived  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  with relatively shorter measuring time (<1 h) than those decay counting techniques. But it suffers from isobaric and poly-atomic interferences, tailing interferences, and sample matrix effects etc (Zorij et al., 2005). Mass spectrometric techniques are also not sufficiently sensitive for the measurements of short-lived  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$  nuclides. Alpha spectrometry can provide excellent sensitivity and adequate energy resolution for simultaneous determination of alpha-emitting Ra isotopes (ie.,  $^{226}\text{Ra}$ ,  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$ ) in a single sample. However, it is necessary to prepare a thin-layer sample source so that the counting of alpha particles would not be compromised.

In this study, a new procedure for rapid determination of radium isotopes in seawater samples by alpha spectrometry was described. Replicate spike and blank samples were analyzed for validation of the procedure, and the results are summarized and discussed.

## 2. Experimental

### 2.1. Reagents and standards

The resins employed in this work are AG-1x8 anion resin ( $\text{Cl}^-$  form, 100–200 mesh), AG-50wx8 cation exchange resin ( $\text{H}^+$  form, 100–200 mesh) and AGMP-1M macro-porous anion exchange resin ( $\text{Cl}^-$  form, 100–200 mesh). All these ion exchange resins were purchased from Bonna-Agela Technologies (Tianjin, China). Other chemicals used in the experiments were purchased as analytical purity or the highest purity available, and were used without any further treatment. All solutions were prepared using ultra-pure water (UPW) with a conductivity of  $>18 \text{ M}\Omega \text{ cm}^{-1}$ , produced from a Milli-Q Reference water purification system.

The  $^{226}\text{Ra}$  standard was obtained from the National Institute of Standards Technology (NIST Gaithersburg, MD, USA), and the  $^{232}\text{U}$  standard was supplied by the National Physical Laboratory (NPL, UK).

### 2.2. Experimental procedure

#### 2.2.1. Sample preparation

The procedural blanks, seawater blanks and seawater spike samples were prepared to examine the performance of the present method. The seawater used in this study was collected from Shandong Peninsula coast ( $36^\circ 56' 46.0'' \text{ N}$ ,  $122^\circ 35' 19.8'' \text{ E}$ ) and the salinity of the seawater was measured to be about 3.0%. The procedural blanks consisted of 1 L ultra-pure water, while the seawater blanks were aliquots of 1 L unspiked seawater. The spike samples were prepared by adding known amounts of the  $^{226}\text{Ra}$  standard or the  $^{232}\text{U}$  standard (in secular equilibrium with its daughter nuclides  $^{228}\text{Th}$  and  $^{224}\text{Ra}$ ) to 1 L of seawater. Prior to analysis, all the blank and spike samples were acidified with concentrated  $\text{HNO}_3$  to 0.1 M. A known activity ( $\sim 40$ – $50 \text{ mBq}$ ) of  $^{232}\text{U}$  standard (in equilibrium with  $^{224}\text{Ra}$ ) was added as tracer for chemical recovery monitoring and correction for the analysis of  $^{226}\text{Ra}$ . Similarly,  $^{226}\text{Ra}$  can also be used as tracer for the determination of  $^{224}\text{Ra}$  in seawater sample.

#### 2.2.2. Preconcentration

By adding  $\sim 2 \text{ mL}$  7%  $\text{TiOCl}_2$  solution, then adjusting the pH to 8–9 with concentrated  $\text{NH}_4\text{OH}$ , Ra was co-precipitation with the formation of hydrous titanium oxide. The sample was centrifuged and the supernatant was discarded. The  $\text{HTiO}$  precipitate was dissolved in 0.5 mL of 12 M HCl and diluted to 40 mL with UPW.

#### 2.2.3. Column purification of radium

The column purification was performed very similarly to that conducted in the reference (Dai et al., 2012), and the specific steps are described as follows. A sequence of three ion exchange columns was used for separating and purifying the Ra from the pre-concentrated samples. All the columns were prepared by loading the resin with UPW onto 2-mL empty cartridges (purchased from Bonna-Agela Technologies, Tianjin, China). The inner diameter of the cartridge was 1.0 cm and the loading height of the resin was  $\sim 2.5 \text{ cm}$ . The resin columns were pre-conditioned in batches: the  $1 \times 8$  anion resin was pre-conditioned with 10 mL of 0.2 M HCl; the 50wx8 cation resin with 10 mL of 8 M  $\text{HNO}_3$ , followed by 10 mL of 0.2 M HCl; the AGMP-1M macro-porous anion resin with 10 mL of 8 M  $\text{HNO}_3$ .

The sample was first passed through a  $1 \times 8$  anion column stacked on top of a 50wx8 cation column at a rate of  $\sim 1 \text{ mL} \cdot \text{min}^{-1}$ , and Ra was extracted onto the cation resin. The columns were then rinsed with 5 mL of 0.2 M HCl, and the anion column was removed and discarded. After further rinse with 10 mL of 0.2 M HCl, residual Ca was effectively removed from the cation resin with 80 mL of 1.5 M HCl.

The cation column was then resembled on top of the pre-conditioned AGMP-1M column. By passing 15 mL of 8 M  $\text{HNO}_3$  through the two columns, radium was eluted from the cation resin into a 50-mL centrifuge tube. Any  $^{228}\text{Th}$  that was stripped off the cation resin would be immediately captured by the downstream AGMP-1M column and separated efficiently from radium.

#### 2.2.4. Secondary HTiO co-precipitation

A secondary  $\text{HTiO}$  co-precipitation step was carried out to convert the eluate from 8 M  $\text{HNO}_3$  to sulfuric medium for the preparation of a thin-layer alpha counting source in the subsequent step. After diluting the eluate sample to 30 mL with UPW,  $\sim 0.5 \text{ mL}$  of 7%  $\text{TiOCl}_2$  was added and the pH was adjusted to  $>9$  with concentrated  $\text{NH}_4\text{OH}$ . The Ra was co-precipitated with  $\text{HTiO}$ , and the precipitate was centrifuged. The precipitate was rinsed with UPW, centrifuged again, dissolved in 1.25 mL of 9 M  $\text{H}_2\text{SO}_4$ , and diluted to a total volume of 15 mL with UPW.

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