**Application of modified analytical procedure for the determination of 226Ra in sea water samples**

**Wafaa.F.Bakr and Heba A. Anis**

Egyptian nuclear and radiological regulatory authority, Nasr City-11762, Cairo, Egypt, B.O.Box7551

**Received:** 26 December 2018**; Revised:** 17 January 2019; **Accepted:** 28 January 2019

**Abstract:** A minor modification of the radio-chemical determination of 226Ra by alpha spectrometry in water samples was carried out to overcome the effect of high salinity in sea water samples. Adjustment steps were applied to the radio-analytical procedure by using calcium phosphate co-precipitation and the addition of isopropanol. Method validation of the modified steps was carried using IAEA reference samples and spiked standard solutions. The modified procedure was applied in the determination of 226Ra in sea water samples collected from the North coast of Egypt.

**Key words**: radium isotopes, radiochemical separation, radioactivity

**INTRODUCTION**

Radium-226 is an alpha-emitting radionuclide. It is a daughter of the naturally occurring 238U- decay series, and the direct progeny of 230Th. Generally, Radium is determined in environmental samples using both high resolution gamma spectrometry and alpha spectrometry techniques1-3. A comparative study of different methodologies for the determination of 226Ra in water was carried out and concluded that there is a good agreement was found in the results obtained from different methods (gamma spectrometry, alpha spectrometry and liquid scintillation technique)4. The pre-concentration and separation are the main steps in the determination of radium in water samples. The most frequently applied pre-concentration method is co-precipitation. Ion exchange chromatography, extraction chromatography (solid phase extraction), and solvent extraction are typically methods for separation5. There are several methods dealing with radium co-precipitation and source preparation for alpha spectrometry measurements 6-8.

In advanced procedure for the determination of 226Ra in sea water, the [radium](https://www.sciencedirect.com/topics/earth-and-planetary-sciences/radium) is pre-concentrated with hydrous [titanium oxide](https://www.sciencedirect.com/topics/earth-and-planetary-sciences/titanium-dioxide) (HTiO) and is purified by combined anion/cation exchange column chromatographic separation. BaSO4 micro-precipitation step to prepare a thin-layer counting source to determine the activities 226Ra by alpha [spectrometry](https://www.sciencedirect.com/topics/earth-and-planetary-sciences/spectroscopy)9.

In this study, 226Ra was determined using the method described by Nour S. *et.al*.10. In this approach, radium isotopes and 133Ba tracer are co-precipitated with MnO2, dissolved in 2M HCl, and loaded into a Diphonix resin column. The collected Ra/Ba fraction was precipitated using BaSO4 micro-precipitation. The aim of this study is reaching to the most probable thin layer of Ra-Ba co-precipitate after the eliminating the effect of high salinity in the selected sea water samples.

**MATERIALS AND APPARATUS**

Radium extraction was carried out using Diphonix Resin (50-100 and 100-200 mesh), supplied from Triskem International, 35170 Bruz, France. Standard reference solutions of 226Ra were supplied by the National Institute of Standards and Technology (NIST), (SRM 4967A, SRM 4339B). The 133Ba standard solution was supplied by North American Technical Services (NATS) (EZ-83879-767). Bio Rad columns of 0.9 cm diameter were backed with the selected cation exchanger.

The measurements of 133Ba yield is determined through its gamma lines 276, 302and 384 keV by the measurements of the samples on gamma spectrometry based on HPGe coaxial detector with relative photo-peak efficiency of 40% for the 1332 keV line of 60Co. The alpha spectrometric analysis for 226Ra were carried out using a Canberra Alpha Analyst, with a chamber containing a passive implanted planar silicon (PIPS) detector with an active area of 450 mm2. All chemicals used in this study were of analytical grade.

**Interference and method adjacent:** Due to the high salinity of the collected samples, formation of white BaSO4 precipitate was observed during the barium sulphate micro-precipitation. In the current procedure described by Nour et.al, 226Ra was analyzed by alpha spectrometry after micro-precipitation with BaSO4. This is done by evaporating the load/rinse solution from the column to near dryness, adding of 50 mg Ba carrier, and precipitation of BaSO4 by addition of Na2SO4, a few drops of acetic acid, and 100 ml of a BaSO4 ‘‘seeding suspension’’ to ensure fast kinetics and small crystallites. Slightly variation in these conditions for source preparation in our case to avoid the white precipitates formed during the co-precipitation steps is carried out by canceling the addition of Ba carrier and adding 2-propanol prior to adding sodium sulphate and BaSO4 seeding suspension. When adding barium carrier in barium high contents water (e.g. sea water), native barium, which can adversely affect alpha spectrometry resolution, cannot be removed11, so cancelling the step of adding barium carrier is preferred in source preparation of Ba/Ra co-precipitate in sea water samples. The 2-propanol acts as surfactant to minimize the adhering properties of the barium sulphate precipitate7.

**Validation of modified steps:** Three spiked water samples with standard concentration of 226Ra and IAEA standard water samples are used for the method validation of the adjusted procedure. In order to more closely to the selected seawater samples which contain high concentrations of divalent alkaline earth ions (Ca+2, Mg+2,etc.) that competes with radium, the reference samples (IAEA-425, IAEA-426, IAEA-430 and IAEA-431) and spiked standard solution were enriched with 74% CaCl2, 23% MgCO3 and 55% NaCl solutions.

**Sea water samples collection and preparation:** Seven sea water samples were collected from different locations from Mediterranean coasts. The samples were collected from the surface, at a distance of 30 meters from the shore. Five liters from each sample were collected, filtered out through a membrane of diameter = 0.45µ, acidified with 11 M HCl solution transferred to polyethylene bottles and transferred to laboratory.

**RESULTS AND DISCUSION**

**Results of method validation:**Applications of the modified procedure on the spiked standard solution of 226Ra (6.28 Bq/L) was carried out three times and the average concentration is recorded and compared with the standard prepared value. The procedure was applied also on the certified reference samples IAEA-425, IAEA-426, IAEA-430 and IAEA-431. **Table (1)** and **figure (1)** represent the results of these analyses

**Table (1**): Activity concentration of 226Ra in certified IAEA reference samples and spiked standard solutions.

|  |  |
| --- | --- |
| Sample Code | Activity of 226Ra (Bq/L) |
| Reference Values | Measured Values |
| IAEA-425 | 0.31±0.12 | 0.30±0.17 |
|  IAEA-426 | 6.50±2.7 | 6.12±0.34 |
| IAEA-430 | 2.92±0.046 | 2.82±0.17 |
| IAEA-431 | 23.9±0.38 | 22.8±1.5 |
| Spiked standard solution |  6.28±0.03 |  6.23±0.17 |

Figure (1): The Measured and standard 226Ra values (Bq/L) in the selected samples

**Measuring 226Ra in sea water samples:** The activity concentrations of 226Ra in sea water samples collected from the coastal area of the Mediterranean sea are determined using the adjusted procedure. The results of 226Ra activities in the selected samples were illustrated in **Table (2) and figure (2).**

**Table 2:** The activity concentrations of 226Ra in the selected sea water samples

|  |  |  |
| --- | --- | --- |
| Locations | TDS (g/L) | 226Ra Activity (mB/L) |
|  |  |  |
| I- The Mediterranean |
| Rasheed | 32.4 | 293.5±12.7 |
| Borollos | 36.4 | 58.2±4.1 |
| Balteem | 33.9 | 129.0±9.0 |
| Gamasa | 37.1 | 108.5±7.3 |
| Dametta | 35.1 | 69.5±4.9 |
| Ras Al- Barr | 30.3 | 328.6±16.4 |
| Port Said | 40.7 | 180.3±12.6 |
| Average |  | 166.8±9.6 |

**Fig. 2:** The activity concentrations 226Ra in the selected seawater samples

Analysis of the natural radioactivity contents in the Egyptian coastal water was carried out by S.M.Sefien *et al.12*. The investigations have been carried out monthly for one year period. The analysis is based on the determinations of gross α, ß and γ activities (due to the resolved activities of 226Ra, 232Th and 40K) in sea water samples. The averaged values the determined gross alpha, beta and gamma activities in the collected sea water samples have been found to be ranged from (0-61, 3-77 and 13-381) ×10-3 Bq.L-1 for α, β and γ respectively. The data showed that, the lowest values are at Matrouh and Marina while the highest one corresponds to Rashid.

**CONCLUSION**

Determination of 226Ra by alpha spectrometry required a comprehensive determination of thin film for counting step which is found to be the main problem in the selected analytical procedure. Minor adjustment of the procedure to enhance the BaSO4 precipitation by adding isopropanol during the precipitation process and avoid the adding off Ba carrier were done and the method validated through inter-comparison methodology with certified IAEA reference samples and a known spiked standard solution of 226Ra. It is concluded that the analytical method for 226Ra used by Nour S. *et al* .10 is valid for sea water samples after minor adjustment in the preparation of Ba/Ra precipitate as described in this paper.

**REFERENCES**

1. E. Garcia-Torano; Current status of alpha-particle spectrometry, Appl.Radiat.Isot.2006, 64. 1273-1280
2. R. Rihs, M. Condomines, An improved method for Ra isotope (226Ra, 228Ra, 224Ra) measurements by gamma spectrometry in natural waters: application to CO2-rich thermal waters from the French Massif Central, Chem. Geol.2002, 182, 409-421.
3. R.A. Tinker, J.D. Smith, M.B. Cooper, An assessment of the selection criteria for an analytical method for radium-226 in environmental samples, J. Radioanal. Nucl Chem., 1995, 193, 329-336.
4. A. B. Ibrahim F. Al-Hamarneh, Fahad I. Almasoud, A comparative study of different radiometric methodologies for the determination of 226Ra in water, Nuclear Engineering and Technology 50 , 2018,159-164.
5. IAEA analytical quality in nuclear applications series no. 19, Analytical methodology for the determination of radium isotopes in environmental samples, IAEA, Vienna, 2010.
6. C. Sill; Determination of radium-226 by high resolution alpha spectrometry,1983, Report CONF-830695-Y.
7. R. Bojanowski, Z. Radecki, K. Burns, Determination of radium and uranium isotopes in natural waters by sorption on hydrous manganese dioxide followed by alpha-spectrometry, J. Radioanal. Nucl. Chem., 264 (2), 437-443.
8. , Y.J. Kim, C.K. Kim, C.-S. Kim, J.Y. Yun, B.-H. Rho, Determination of 226Ra in environmental samples using high-resolution inductively coupled plasma mass, spectrometry, J. Radioanal. Nucl. Chem.,1999, 240, 613-618

1. [Lijuan Song](https://www.sciencedirect.com/science/article/pii/S0265931X16307330%22%20%5Cl%20%22%21), [Yonggang Yang](https://www.sciencedirect.com/science/article/pii/S0265931X16307330#!), [Maoyi Luo](https://www.sciencedirect.com/science/article/pii/S0265931X16307330#!), [Yan Ma](https://www.sciencedirect.com/science/article/pii/S0265931X16307330#!) And [Xiongxin Dai](https://www.sciencedirect.com/science/article/pii/S0265931X16307330#!), Rapid determination of radium-224/226 in seawater sample by alpha spectrometry, [Journal of Environmental Radioactivity](https://www.sciencedirect.com/science/journal/0265931X), [Volume 171](https://www.sciencedirect.com/science/journal/0265931X/171/supp/C),  2017, 169-175.
2. S. Nour, A. El-Sharkawy, W.C. Burnett And E.P. Horwitz, Radium-228 determination of natural waters via concentration on manganese dioxide and separation using diphonix ion exchange resin, Applied Radiation and Isotopes, 2004, 61, 1173–1178.
3. Maxwell S. L. and Culligan B. K., Rapid determination of 226Ra in environmental samples, Journal of Radio-analytical and Nuclear Chemistry, 2012, 293 (1), 149-156.
4. S.M.Sefien, W.E.Abdel Malik, A.S.Ibrahim and S.K.Yousef, Activity concentrations of radionuclides in sea water in some coastal Egyptian regions and their public health impacts, The Second All African IRPA Regional Radiation Protection Congress 22-26 April 2007, Ismailia, Egypt.

**\* Corresponding author: *Wafaa F. Bakr***

Egyptian nuclear and radiological regulatory authority, Nasr City-11762, Cairo, Egypt, B.O.Box7551; Email : wdbakr75@gmail.com, *Email:* *bupdiv@yahoo.fr*

**On line publication Date: 28.01.2019**