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Application of modified analytical procedure for the determination of ^{226}Ra in sea water samples

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Abstract: A minor modification of the radio-chemical determination of ^{226}Ra 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 ^{226}Ra 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 ^{238}U- decay series, and the direct progeny of ^{230}Th. Generally, Radium is determined in environmental samples using both high resolution gamma spectrometry and alpha spectrometry techniques[1-3]. A comparative study of different methodologies for the determination of ^{226}Ra 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 separation[5]. 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 ^{226}Ra in sea water, the radium is pre-concentrated with hydrous titanium oxide (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[9].

In this study, ^{226}Ra was determined using the method described by Nour S. *et.al*.[10]. In this approach, radium isotopes and ^{133}Ba tracer are co-precipitated with MnO_2, dissolved in 2M HCl, and loaded into a Diphonix resin column. The collected Ra/Ba fraction was precipitated using $BaSO_4$ 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 ^{226}Ra were supplied by the National Institute of Standards and Technology (NIST), (SRM 4967A, SRM 4339B). The ^{133}Ba 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 ^{133}Ba 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 ^{60}Co. The alpha spectrometric analysis for ^{226}Ra 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 mm^2. 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 $BaSO_4$ precipitate was observed during the barium sulphate micro-precipitation. In the current procedure described by Nour et.al, ^{226}Ra was analyzed by alpha spectrometry after micro-precipitation with $BaSO_4$. This is done by evaporating the load/rinse solution from the column to near dryness, adding of 50 mg Ba carrier, and precipitation of $BaSO_4$ by addition of Na_2SO_4, a few drops of acetic acid, and 100 ml of a $BaSO_4$ ‘‘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 $BaSO_4$ 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 removed[11], 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 precipitate[7].

Validation of modified steps: Three spiked water samples with standard concentration of ^{226}Ra 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% $CaCl_2$, 23% $MgCO_3$ 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 ^{226}Ra (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 ^{226}Ra in certified IAEA reference samples and spiked standard solutions.

Sample Code	**Activity of ^{226}Ra (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

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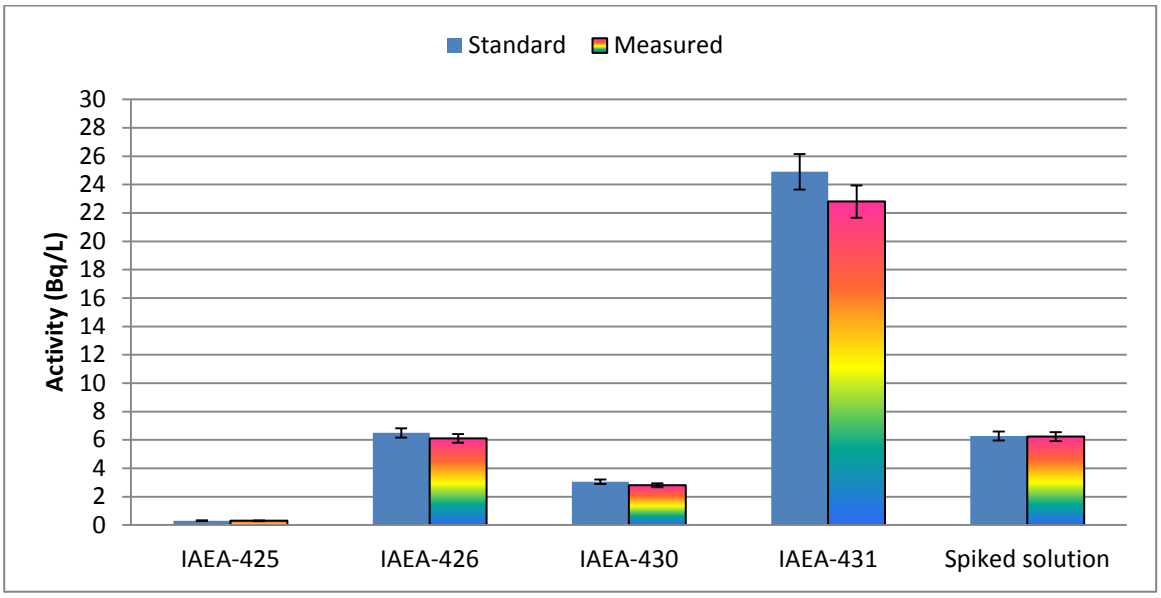

Figure (1): The Measured and standard ^{226}Ra values (Bq/L) in the selected samples

Measuring ^{226}Ra in sea water samples: The activity concentrations of ^{226}Ra in sea water samples collected from the coastal area of the Mediterranean sea are determined using the adjusted procedure. The results of ^{226}Ra 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)	^{226}Ra 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

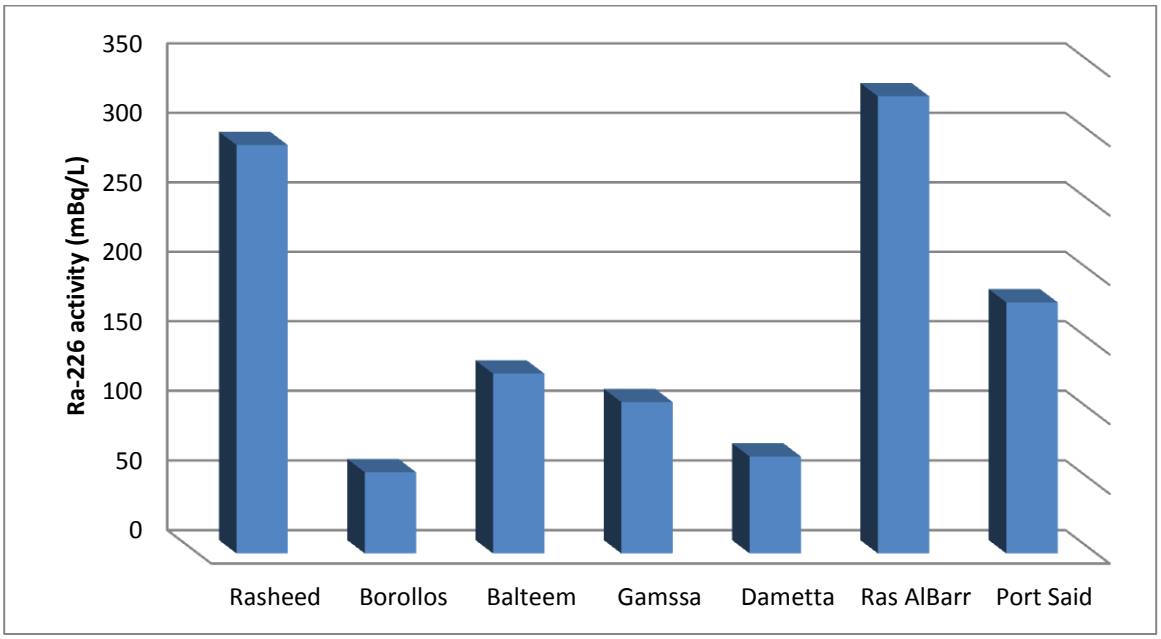

Fig. 2: The activity concentrations ^{226}Ra in the selected seawater samples

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 ^{226}Ra, ^{232}Th and ^{40}K) 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 ^{226}Ra 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 $BaSO_4$ 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 ^{226}Ra. It is concluded that the analytical method for ^{226}Ra 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 (^{226}Ra, ^{228}Ra, ^{224}Ra) measurements by gamma spectrometry in natural waters: application to CO_2-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 ^{226}Ra 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 ^{226}Ra in environmental samples using high-resolution inductively coupled plasma mass, spectrometry, J. Radioanal. Nucl. Chem.,1999, 240, 613-618
9. Lijuan Song, Yonggang Yang, Maoyi Luo, Yan Ma And Xiongxin Dai, Rapid determination of radium-224/226 in seawater sample by alpha spectrometry, Journal of Environmental Radioactivity, Volume 171, 2017, 169-175.
10. 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.
11. Maxwell S. L. and Culligan B. K., Rapid determination of ^{226}Ra in environmental samples, Journal of Radio-analytical and Nuclear Chemistry, 2012, 293 (1), 149-156.
12. 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.

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