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EXTRACTION OF RADIUM ISOTOPES FROM SOME COASTAL SEAWATER SAMPLES IN EGYPT METHOD VALIDATION

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ABSTRACT

A radiochemical separation of Ra isotopeswas carried out to determine the activity levels of radium (^{226}Ra and ^{228}Ra) in seawater samples, as well as providing a base-line data on background radiation in the investigated locations. Seawater samples were collected from selected sites along the coasts. The water samples were analyzed for radium isotopes (Ra-226 & Ra-228) using alpha and liquid scintillation detectors.Development steps were applied to the radioanalysis procedure by using calcium phosphate co-precipitation and the addition of isopropanol. Quality assurance and method validation of the developed procedure was carried out to assure the results. The obtained results were within the uncertainty level ± 5%. Quality control steps were applied through the efficiency calibration of the detectors, the estimation of uncertainties, the use of blanks and the comparison with other laboratories.For comparison, selected samples were measured by gamma spectrometry using high purity germanium detector, after radiochemical separation of the isotopes with ion-exchange chromatography using a strong cation exchange resin, and the activity concentrations of ^{228}Ra were comparable with those analyzed by the LSC. The average activity concentrations of ^{226}Ra and^{228}Ra in the Mediterranean seawater samples were found to be 166.8 and 500.6 mBq/L respectively, while in the Red seawater samples were 13.0 and 176.7 mBq/L respectively. The maximum value of radium activity was found at RasElBarr estuary, where the River Nile fresh water mixes with the coastal seawater. On the basis of the current results, we may conclude that the radium activities in the investigated seawater samples are well comparable to the corresponding reported values in literature.

Keywords: *radium, seawater, alpha spectrometry, method validation, Mediterranean.*

1. INTRODUCTION

Determination of radium in environmental water has become a matter of interest in public health because radium is one of the most hazardous elements with respect to internal exposure. Radium is of particular interest for oceanographers as it may lead to an understanding of various mobilization processes in the ocean, and studies of isotopic concentrations and ratios in the ocean can provide information about mixing processes and groundwater discharge into the ocean [1]. According to several investigators, the ^{226}Ra/ ^{228}Ra activity ratio in waters is extremely variable [2]. Several studies have shown that Ra isotope relationships are suitable for determination of fluxes and mixing rates of continental waters into the oceans and estuaries, and exchange between ground water and surface water [3].

The main feature of this northern coast is the presence of a large number of beaches and resorts. The Red Sea tourism is largely dependent on the surrounding environment such as sand, water quality, and coral reefs. On the Red Sea coast, there are oil exploration and production plants as well as phosphate ore mining and production, which are non-nuclear pollution sources that could have serious radiological impacts on the coastal environment of the Red Sea. Radionuclides are known to be associated with organic materials in nature. Therefore, oil, gas and oil field brines frequently contain radioactive materials, which may increase the risk of radiation exposure to the environment [4]. Phosphate deposits are generally characterized by enhanced radionuclide concentrations, consequently, the mining and processing of this phosphate ore redistribute radionuclides throughout the environment. Considering popularity of these beaches and the habits of the population and tourists to spend long hours on the beach, it was a useful approach to estimate the radioactivity in the seawater of these areas. Therefore, the aim of this study is to determine the activity concentrations of radium isotopes (^{226}Ra and ^{228}Ra) in selected locations along the Egyptian coastal areas of the Mediterranean and Red sea.

2. METHODOLOGY

Unless otherwise indicated, all references to water refer to deionized water (DDW).

2.1 Sampling

The collection of samples was performed at selected sampling points along the coasts. The selection of sampling sites was based primarily on the population existence at these beaches.

The seawater samples were collected from six locations along the Mediterranean coast from Rasheed to Port Said. For the red sea coast, nine samples were collected along the coast from Ain Sokhna to Hurghada,as shown in fig (1,2). The seawater 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 at the rate of 10 ml per liter of sample immediately.After filtration to avoid the adsorption of radionuclides on the walls of the container, transferred to polyethylene bottles and transferred to laboratory.

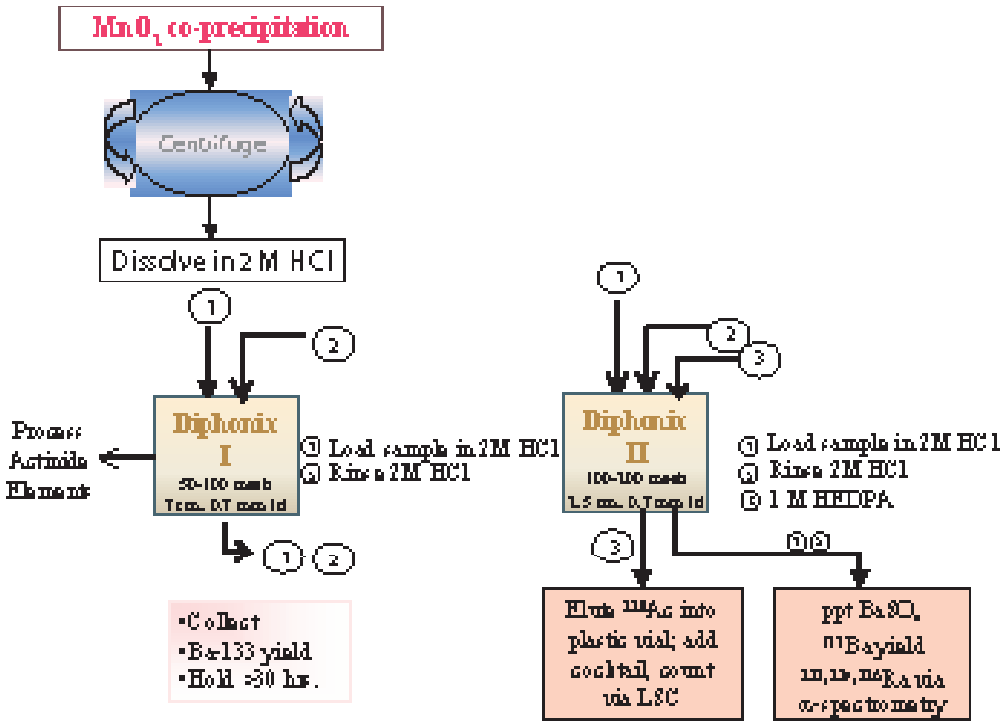
2.2 Materials and Apparatus

Radium extraction from water samples were carried out using Diphonix Resin (50-100 and 100-200 mesh), supplied from Triskem International, 35170 Bruz, France.Standard reference solutions of ^{226}Ra and ^{228}Ra were supplied by the National Institute of Standardsand Technology (NIST), (SRM 4967A, SRM 4339B). The ^{133}Ba standard solution was supplied by NorthAmerican Technical Services (NATS) (EZ-83879-767). The cation exchange resin was used in a column mode withBioRad Glass Econo columns of 0.9 cm diameter, together with polypropylene funnels and Teflon end fittings connected with plastic taps.All gamma radioactivity measurements were carried out using a Canberra HPGecoaxial detector with relative photo-peak efficiency of 40% for the 1332 keV line of ^{60}Co. The germanium detector was connected to a8192 multichannel analyzer with counting capacity of 228 counts per channel.The alpha spectrometric analysis were carried out using a Canberra Alpha Analyst, with a chamber containing a passivated implanted planar silicon (PIPS) detector with an active area of 450 mm^2. The efficiency of the detector was calibrated against a standard alpha multi-source (67970-121,Analytics Co.) using the certified activity of the measured radionuclides.The beta measurements of ^{228}Ac were carried out using Liquid Scintillation detector, Packard,model Tri-Carb 2770 TR/SL.All other chemicals used in this study, including $KMnO_4$, isopropanol, ammonium sulphate and different mineral acids were of analytical grade.

Fig.(2-1): The location of seawater samples along the Mediterranean and red sea coasts

2.3 Radioanalyses and Measurements

The radium isotopes (^{226}Ra and ^{228}Ra) were determined in the water samples following a combined alpha and beta spectrometric method described by S. Nour et al, 2004 [5]. In this approach, ^{226}Ra, ^{228}Ra and ^{133}Ba tracer are co-precipitated with MnO_2, dissolved in 2MHCl, loaded into a Diphonix resin column to eliminate other interfering radionuclides and is then kept for ^{228}Ac ingrowth period of two days, reloaded again into a second diphonix resin column. The collected Ra/Ba fraction was precipitated using $BaSO_4$ micro-precipitation.During the barium sulphate micro-precipitation, the formation of white $BaSO_4$ precipitate was observed. Development steps were carried out by using calcium phosphate co-precipitation and adding $(NH_4)_2SO_4$and isopropanol to the barium sulphate micro-precipitation in a tube, mixed well and allowed to stand in an ice bath for 30 min. before vacuum filtration[6], as shown in the flowchart.



The filter was mounted on a disk, counted by gamma for the ^{133}Ba recovery and the ^{226}Ra is assessed by alpha spectrometry. The ^{228}Ac, held in the column, was eluted with HEDPA (1M 1-Hydroxyethane–1,1– diphosphonic acid) in a LS vial, cocktail was added and the vial was counted. The chemical recovery was determined from the ^{133}Ba yield using the 276, 302 and 384 keV energy lines by gamma spectrometry.

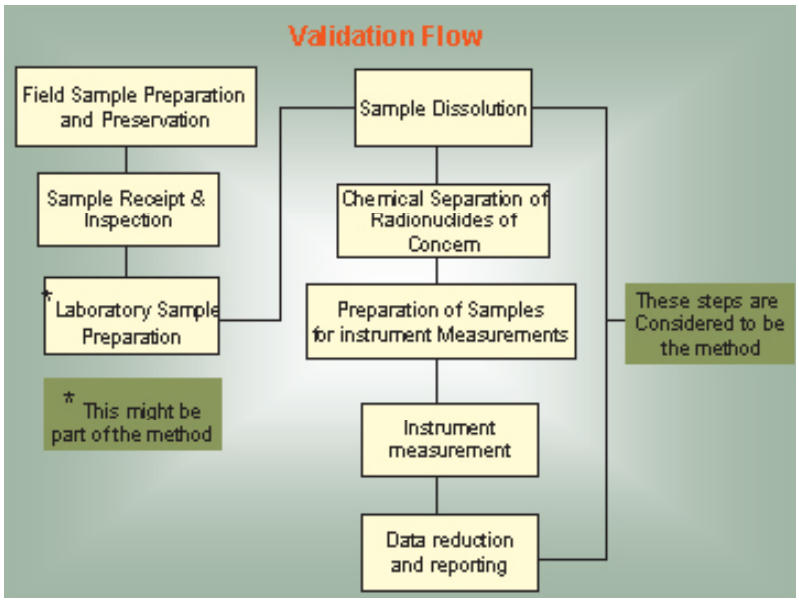
2.4 Quality Control and Method Validation

Validation steps

One of, or a combination of, the following:

- calibration using reference standards or reference materials;
- comparison of results achieved with other methods;
- interlaboratory comparisons;
- systematic assessment of the factors influencing the result;
- assessment of the uncertainty of the results based on scientific understanding of the theoretical principles of the method and practical experience.

For quality assurance and validation purpose, blank sampleswere prepared in the same manner as the corresponding samples, and measured for background estimation, and detection of any radioactive contamination. Reference water samples were determined using the same analysis and measure-



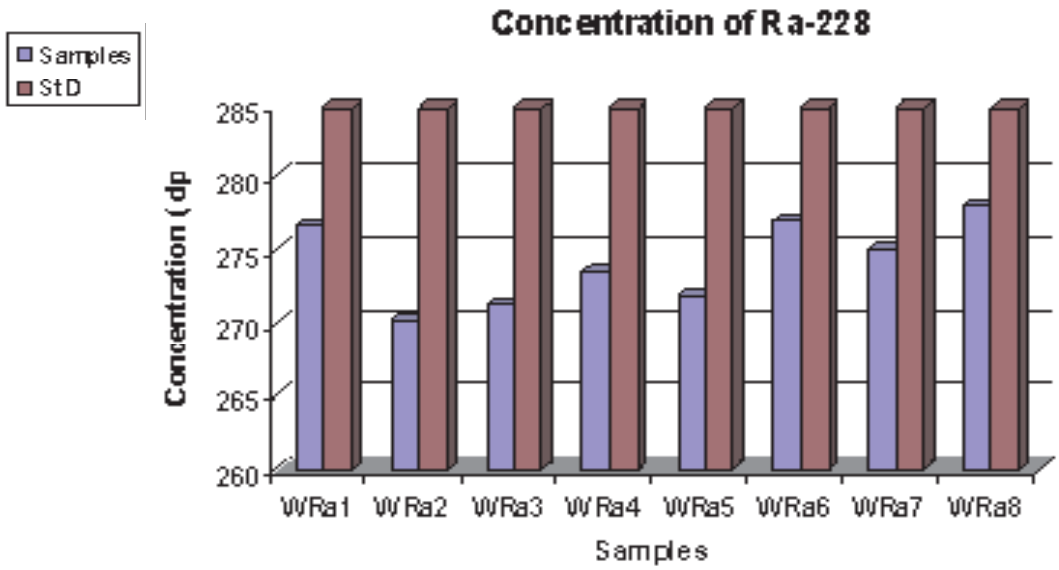


Fig. (2-2) : Activity concentrations of Ra-228 compared with the standard in the water samples

ment protocol, and were compared against their certified values to testthe closeness of the measured samples to its reference values. To verify the validity of the final results, spiked water samples were analyzed for ^{228}Ra by following the method described in flowchart to monitor any defects in the cali-

Table (2-1) : Results of Ba-133 yield, Ac-228 net cpm and Ra-228 activity

Samples	Ba yield as a fraction	Net cpm of Ac-228	Concentration of Ra-228 (dpm)	Chemical Recovery
WRa1	0.970	211.0	276.7 ± 1.6	97.0 %
WRa2	0.975	214.6	270.2 ± 1.2	94.8 %
WRa3	0.984	193.4	271.3 ± 0.9	96.2 %
WRa4	0.975	204.3	273.6 ± 1.0	96.0 %
WRa5	0.980	213.3	271.9 ± 1.4	95.4 %
WRa6	0.970	208.9	277.0 ± 1.6	97.2 %
WRa7	0.974	204.2	275.1 ± 1.3	96.5 %
WRa8	0.982	215.3	278.0 ± 1.5	97.5 %

brations, prepared solutions and measurements. Table (2-1) and fig.(2-2) represent the resulted ^{228}Ra activities.

Some selected samples were analyzed for radium isotopes (^{226}Ra and ^{228}Ra), the procedure described by A.El-Sharkawy et al, 2013 [7], where the seawater samples were allowed to pass through strong cation exchange resin(purolite) in a column mode withBioRad Glass Econo columns, the resin was transferred to standard counting containersand the containers were tightly sealed for four weeks to allow secular equilibrium between ^{226}Ra, ^{228}Ra and their decay products.The efficiency calibration of the germanium detector for the radium isotopes (Ra-226 and Ra-228) was carried out using standard samples. Known activity resins were prepared by spiking water (DDW) samples with known amounts of ^{226}Ra and ^{228}Ra. The spiked resin samples containing a known amount of the radionuclides of interest were used to provide a identical matrix with a known activity, and all other conditions were followed typically (flow rate, resin volume, counting time and geometry). The ^{226}Ra activities were determined via its daughters ^{214}Pb and ^{214}Bi through the gamma energy lines 295.22, 351.93 and 609.31 keV. The ^{228}Ra activities were determined through the gamma energy lines of 338.32 and 911.2 keV. The calculated specific activities were basically performed using a comparison method:

$$A_{unk} = \frac{A_{std}}{CR_{std}} . CR_{unk}$$

where;

$A_{unk}$is the calculated activity of the sample;

A_{std} is the activity of the standard resin;

CR_{std} is the counting rate for the standard resin; and

CR_{unk} is the counting rate of the unknown sample.

Validation through proficiency test

The validation was carried out through the participation in two proficiency testing exer-

Table (2-2) : Results of the IAEA water analysis

Sample code	Recovery	Combined standard uncertainty %	IAEA reference value (Bq / l)	Our values (Bq / l)
IAEA-423	88.0 %	0.78	8.4	6.8
IAEA-426	74.0 %	0.56	6.5	5.9
IAEA-427	90.0 %	0.70	65.0	63.1
IAEA-428	81.0 %	0.35	3.6	3.3
IAEA-431	90.0 %	2.4	23.9	22.8

Table 3-1:The radium activities in the Mediterranean and Red sea water samples

Locations	TDS	Ra-226		Ra-228	
I- The Mediterranean	g/L	mBq/L	±	mBq/L	±
Rasheed (W1)	32.4	293.5	12.7	766.4	28.2
Borollos (W2)	36.4	58.2	4.1	386.8	14.4
Balteem (W3)	33.9	129.0	9.0	564.2	28.2
Gamasa (W4)	37.1	108.5	7.3	195.1	8
Dametta (W5)	35.1	69.5	4.9	238.7	10.0
RasAlBarr (W6)	30.3	328.6	16.4	1156.4	64.8
Port Said (W7)	40.7	180.3	12.6	196.4	8.8
II- The Red sea					
Ain Sokhna1(A)	38.8	6.8	0.5	107.7	5.4
Ain Sokhna2 (H)	45.5	23.9	1.7	134.5	6.7
Zafarana (J)	43.1	12.1	1.0	102.0	5.1
Zafarana 2 (K)	45.5	11.9	0.8	211.2	9.7
RasGareb (L)	42.8	11.6	0.9	70.5	4.6
Rasshokair (O)	44.7	6.3	0.6	269.3	14.8
Gulf of Jimsah1 (P)	44	6.0	0.5	317.6	15.9
Gulf of Jimsah2 (R)	45.2	26.1	1.8	297.5	15
Hurghada (T)	41.5	12.7	0.8	80.3	4.9

cises.The results of the water analysis are summarized in Table (2-2). From the results, it is concluded that the applied method of analysis is "fit for purpose" to measure radium in various waters (low and very high salinity).

Errors were propagated due to nuclear counting statistics(σ_N), tracer(σ_S) and volume(σ_V), and the combined total uncertainty was calculated according to the following equation:

$$\sigma_T = \sqrt{(\sigma N)^2 + (\sigma V)^2 + (\sigma S)^2}$$

MDA: The minimum detectable activity at 95% confidence level is given by;

$$MDA = \frac{2.71 + 4.65\sqrt{B}}{T \times \text{eff} \times Y \times V}$$

Where,T : counting time
B : background counts
eff : efficiency
Y : Ba-133 yield
V : volume of samples in liters.

The minimum detectable activity (MDA) was calculated according to the equation presented by Currie, 1968 [8], and it was 6.6 mBq and 1.2 mBq for the beta and alpha measurements respectively.

3. RESULTS AND DISCUSSION

In the following section, the results of the radium levels in the Mediterranean and Red sea water samples will be represented.

Radium Isotopes in Water Samples

The activity concentrations of ^{226}Ra and ^{228}Ra in the Mediterranean and Red seawatersamples are represented in table 3-1.

The average activity concentration of ^{226}Ra in the Mediterranean water sample was 166.8mBq/L, (ranging from 58.2to 328.6mBq/L), while the average activity concentrationof ^{228}Ra was500.6mBq/L, (ranging from 195.1 to 1156.4mBq/L), as shown in figure 3-1.The activity concentrations of radium in the Mediterranean seawater samples obtained are comparable to those reported in literature. The Suez Canal water samples showed an average activity concentrations of 0.6 and 0.5 Bq/L for ^{226}Ra(^{238}U) series and^{228}Ra (^{232}Th series) respectively [9].

In a radiological survey along the Mediterranean coast from Alexandria to Rasheed, the activity concentrations of Ra-226 (U-series) and Ra-228(Th-232 series)in Rasheed coastal seawater were 1.9 and 0.5 Bq/L respectively [10].

The sample W6, which was collected from RasAlBarr estuary, showed relatively the maximum radium activity. This may be attributed to the desorption of radium from suspended particles and bottom sediments, as the River Nile fresh water meets and mixes with the coastal seawater [11, 12].

The average activity concentration of^{226}Ra in the Red Sea water sample was13.0mBq/L, (ranging from 6.0to 26.1 mBq/L), while the average activity concentration of ^{228}Ra was176.7mBq/L, (ranging from 70.5 to 317.6mBq/L), as shown in figure 3-2.

The sea water samples collected from RasShokair and GabalZait (O,P, R locations)

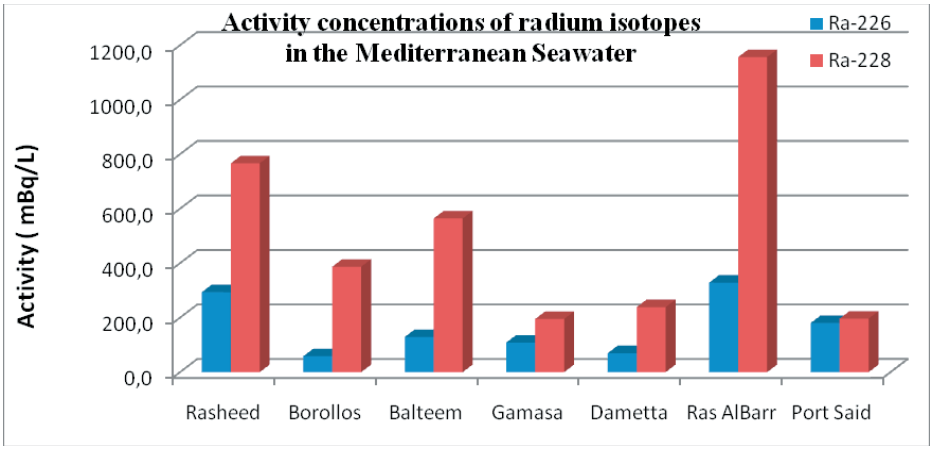


Fig 3-1 :Radium Concentrationsin the Mediterranean Seawater

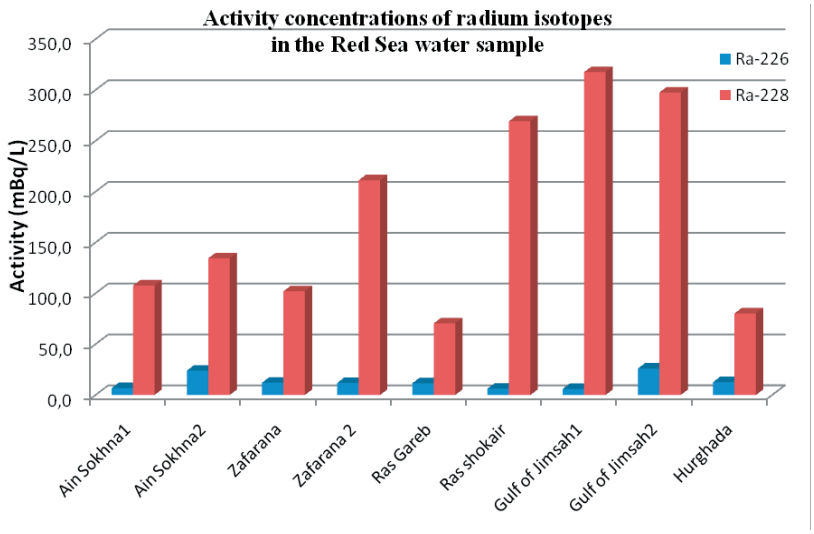


Fig 3-2 :Radium Concentrationsin the Red Seawater

Fig 3-3 :comparison of^{228}Ra activities by gamma and LSC

showed relatively the maximum radium activities, which may be explained by the presence of Rasel Behar field, one of the most important oil exploration and production-area along the Red Sea coast, at about few kilometers from their locations [13].

Selected samples were analyzed by gamma spectrometry for comparison with other laboratory, and the ^{226}Ra activity concentrations were within the low limit of detection of the germanium detector at the 609.3keV energy line (1.5 mBq/L). The^{228}Ra activity concentrations were comparable with those analyzed by LSC, as shown in fig.(3-3).

4. CONCLUSION

Surveillance monitoring along the Mediterranean and Red sea coasts has been carried out to determine the radium activity levels in sea water, and providing a base-line data on radium activities in the coastal seawaters. Radium isotopes (^{226}Ra and ^{228}Ra) were analyzed in theseawater samples from different locations, and the average activity concentrations were found to be 166.8 and 500.6mBq/L for ^{226}Ra and ^{228}Rarespectively

in the Mediterranean seawater samples, while the average activity concentrations of ^{226}Ra and^{228}Rain the Red seawater samples were 13.0 and 176.7 mBq/L respectively. The maximum value of radium activity was found at RasEl-Barr estuary, where the River Nile fresh water mixes with the coastal seawater.Some of the Red sea water samples were analyzed by different techniques using gamma spectrometry for comparison, and the activity concentrations of ^{228}Ra werecomparable with those analyzed by the LSC.On the basis of the current results, we may conclude that the radium activities in the investigated seawater samples are well comparable to the corresponding reported values in literature.

REFERENCES

[1] Ivanovich M., Latham A.G., and Ku T.L. Uranium-series disequilibrium applications in geochronology. In: Ivanovich M. and Harmon R.S. (eds.), Uranium-Series Disequilibrium: Applications to Earth, Marine, and Environmental Problems. Second Edition, Clarendon Press, Oxford, UK, Chapter 3, 62-94.(1992).

[2] Blanchard R. K., Hahne B., McCurdy D., Meller R.A., Moore M.S., and Sedlet J. Radiological sampling and analytical methods for national drinking water regulations. Health Physics, 48, 587-600.(1985).

[3] Moore W. S. High fluxes of radium and barium from the mouth of the Ganges-Bramaputra River during low river discharge suggest a large ground water source. Earth and Planetary Science Letters, 150, 141-150.(1997).

[4] Paschoa, A. S."NORM and petroleum origin".AppliedRadiation and Isotopes, 48, 1391-1396, (1997).

[5] NourS., El-SharkawyA., BurnettW.C. andHorwitzE. P.."Radium-228 Determination of Natural Waters via Concentration on Manganese Dioxide and Separation using Diphonix ion exchange Resin". Applied Radiation and Isotopes Vol.61, p.1173–1178, (2004).

[6] MaxwellS. L., CulliganB. K.."Rapid determination of 226Ra in environmental samples".Journal of Radioanalytical and Nuclear Chemistry, Vol. 293 (1), p.149-156, (2012).

[7]El-SharkawyA., EbaidY.Y., Burnett W.C.andAlDaihanS. K.."A rapid and inexpensive method for 226Ra and 228Ra measurements of high TDS groundwaters". ApplRadiatIsot. Vol.77: 89-93, (2013).

[8] Currie, L.A.,"Limits for qualitative detection and quantitative determination".Anal.Chem. 40 (3), 586–593, (1968).

[9]El-TahawyM.S., "Natural and artificial radionuclides in the Suez canal bottom sediments and stream water". Radiation Phy.and Chem., Vol.44, No.1/2, pp.87-89, (1994).

[10]Abeer A. El-Saharty. Radioactive survey of coastal water and sedimentsacross Alexandria and Rashid coasts.Egyptian Journal of Aquatic Research 39, 21–30,(2013).

[11]Elsinger, R.J. and Moore, W.S..226Ra behavior in the Pee Dee River-Winyah Bay Estuary.Earth Planet. Sc. Lett., 48:239-249, (1980).

[12]Yoshiyuki Nozakia, Yoshiyuki Yamamotoa,ToshikiManakaa , Hiroshi Amakawaa , AnondSnidvongs. Dissolved barium and radium isotopes in the Chao Phraya River estuarine mixing zone in Thailand. Continental Shelf Research 21, 1435–1448,(2001).

[13]Mahmoud A. Dar and Mahmoud I. El Saman.The interactions of some radioelements activitypatterns with some hydrographic parameters atthe petroleum and phosphate regions in the Red Sea, Egypt.Journal of Radiation Research and Applied Sciences, Vol.7, 292, (2014).