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Analysis of ^{226}Ra, ^{228}Ra and ^{40}K in the Egyptian Bottled Mineral Water by γ- Ray Spectroscopy Technique

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Abstract The activity level concentrations of ^{226}Ra, ^{228}Ra and ^{40}K have been analyzed nondestructively by γ- ray spectrometry (HPGe- detector) in bottled mineral waters, explored from four regions of different origins, namely: Siwa oasis, El Sadat, El Giza, and Beilbeis cities. The study covered eight types of mineral water used for drinking. The results showed that, concentrations up to 184 ± 10, 156 ± 30 and 1700 ± 99 mBq l^{-1} were observed for ^{226}Ra, ^{228}Ra and ^{40}K, respectively, in one type of the mineral water explored from Siwa oasis. The lowest activity concentration of ^{226}Ra and ^{228}Ra was found in one type of the mineral water explored from El Sadat region. The activity concentration of ^{40}K was found within the background range in the water types from El Sadat, El Giza and Beilbeis regions. The committed effective doses are reached up to 1.9×10^{-2} and 3.9×10^{-2} mSv yr^{-1} for ingestion of ^{226}Ra and ^{228}Ra, respectively. An apparent relation was found between the total activity content and both pH and TDS.

Introduction

The natural radioactiviy in waters comes mainly from the primordial radionuclides of ^{238}U, ^{235}U and ^{232}Th- series and ^{40}K. The risk to the human body caused by the ingestion of radioactivity from drinking water has become one of the most important sources concerning environmental radiation scientists[1]. Since ^{226}Ra (^{238}U-series) has similar chemical properties to calcium (Ca), it is accumulated in the human body for a long time due to its long half life time ($t_{1/2}$.1622 yr) [2]. Higuchi[3] reported that, the harmfulness of ^{226}Ra dissolved in drinking water is ~ 40 times that of ^{90}Sr.

It is also known that, ^{226}Ra contribution to the equivalent dose from water intake is higher than that from ^{137}Cs even near nuclear power plants[4].

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Therefore, knowledge of ^{226}Ra activities in drinking water is very important because an appreciable fraction of ^{226}Ra is deposited in human bone, with the corresponding contribution to the internal dose[5]. The recommendations of the guidelines for drinking water quality, published by the World Health Organization (WHO) can be used to guide the competent authorities in determining whether the water is of an appropriate quality for human consumption. According to this guideline[6]:

a. the reference level of committed effective dose is 0.1 mSv y^{-1}, below reference level of dose, the drinking water is acceptable for human consumption.

b. the reference level of gross alpha activity (including ^{226}Ra) should not exceed 100 mBq l^{-1} and gross beta (^{228}Ra and/or ^{40}K) should not exceed 1000 mBq l^{-1} .

Recently, Somlai et al.[7], determined activity levels of ^{226}Ra in almost all types of bottled mineral water commercially available in Hungary. He found that few samples contain ^{226}Ra with a level which exceed the permissible level (100 mBq l^{-1}), while most samples are the lower levels. Also, the gross alpha and beta activities in bottled waters sold in the Mexican market[8], were studied to assess its radiological quality. It was found that all water samples have values of beta activity less than the limit for potable drinking water, while three brands surpassed the limit of alpha activity. The present work is directed to analyze the important natural radionuclides of ^{226}Ra ($t_{1/2}$. 1622 y), ^{228}Ra ($t_{1/2}$. 6.7 y) and ^{40}K ($t_{1/2}$. 1.28×10^9 y) in the bottled mineral waters explored from four regions of different origins in Egypt. The corresponding committed effective absorbed dose (mSv y^{-1}) due to ingestion of ^{226}Ra and ^{228}Ra are also estimated and assessed.

Experimental

Mineral Water in Egypt

In the past few years, due to the increase in the living standards, the demand to use bottled mineral water for drinking also increased. Most tourists coming to Egypt during the year consume large amounts of the mineral water. Therefore, many of the investment companies in Egypt drilled many wells on far depths more than 1000 m to explore the water. The water is packed in sterilized bottles to be available for the consumers in the markets as bottled mineral water.

Collection of Water Samples

In this work, 57 samples covering eight brands (A, B, C, …and H) of the mineral water were collected from different super markets, for the radiometric investigation. All the water samples have volume of 1500 ml and expiry date during 2002. The samples are explored from different 4 regions I, II, III and IV, presented in Table 1 with their pH and the corresponding total dissolved solids content (TDS).

Table 1. Regions, trade markets, date of collection, pH values and total dissolved solids (TDS) content of the studied brands of the bottled mineral water.

Region	Trade mark (code)	n	pH	TDS (mg l^{-1})	Collection date
I. Siwa oasis	Aqua siwa* (A)	7	7.10	170	15 . 05 . 2002
	Hayat (B)	8	7.32	185	19 . 05 . 2002
	Safi (C)	6	7.61	194	26 . 05. 2002
II. El Sadat	Aqcwatab (D)	6	7.52	253	01 . 06 . 2002
	Delta (E)	6	7.68	260	06 . 06 . 2002
	Schweppes (F)	7	7.48	240	11 . 06 . 2002
III. El Mansoura	Baraka (G)	9	7.50	430	15 . 06 . 2002
VI. Beilbeis	Mineral (H)	8	7.18	300	21 . 06 . 2002

n = number of samples from each type, and * = well on depth more than 1,300 m.

These regions are: region I is located in Siwa oasis in Matrouh Governorate. From this region, three brands of mineral waters explored and sold under different trade markets: Aqua Siwa (A), Hayat (B) and Safi (C). Region II, is located in El Sadat city in west of El Monofya Governorate. Three brands of mineral waters with trade mark Aqcwatab (D), Delta (E) and Schweppes (F) are produced. Region III is located in Kafr El Arbein near El Mansoura city in El Dakahlia Governorate. One brand of mineral water is produced under trade market Baraka (G). Region IV is located in Beilbeis desert in El Sharkia Governorate, one type of water is produced under trade market Mineral (H).

Sample Preparation

Each water sample was filtered off through a filter of pore size 8 μm to separate any undissolved solids, then pH was measured using a pH meter with an accuracy of ± 0.01. The sample was acidified by adding 2.5 ml of concentrated nitric acid (65%) to pH< 2 to prevent adsorption of radionuclides on the container walls and prevent growth of microorganisms[9,10]. 1500 ml of water sample was preconcentrated to 100 ml by evaporation at ~ 95 ^{o}C. This allows also to driven off the dissolved ^{222}Rn gas. Then, the water sample is carefully packed in polyethylene bottle (150 cm^{3}), closed tightly, sealed using molten wax and stored for seven half lives of radon-222 (3.84 days) before gamma ray measurement[11]. All steps for sample preparation till measurements are summarized in Fig. 1.

Gamma Ray Measurements

The prepared water samples were analyzed nondestructively by γ- ray spectrometry, using HPGe- detector with relative efficiency of 20% and resolution of 2 keV at 1.33 MeV for ^{60}Co. Sealed point sources (0.1 μCi) of ^{22}Na, ^{60}Co, ^{133}Ba and ^{137}Cs were used for energy calibration, while 100 ml of standard solution containing 200 Bq of ^{228}Ra and ^{224}Ra (^{232}Th-series) dissolved in 1% acidic media, was used for efficiency calibration.

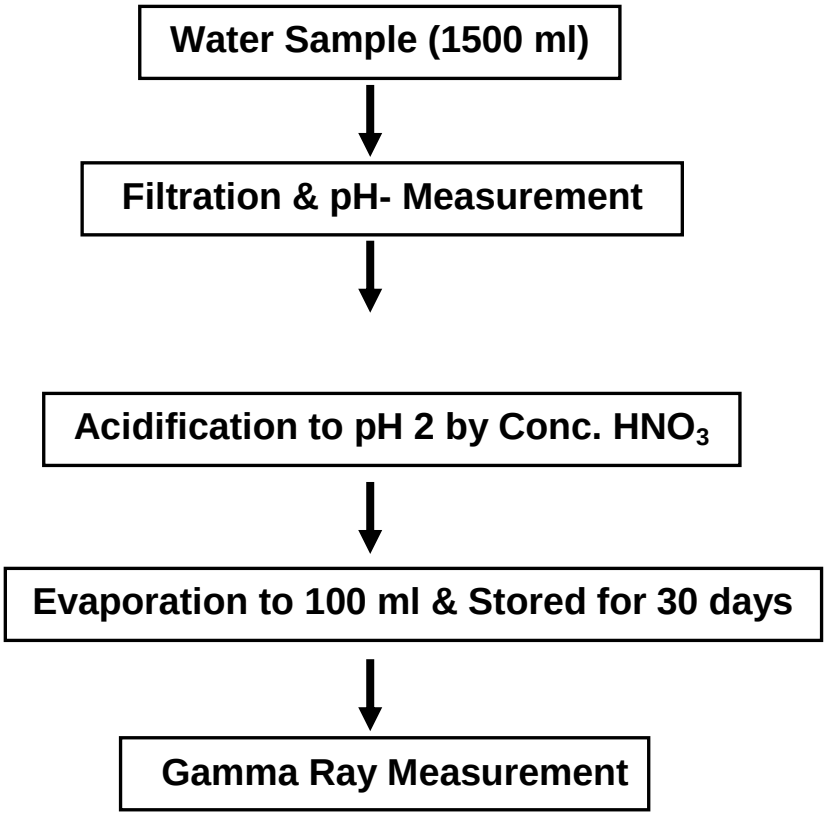

Fig. 1. Preparation of water samples for radiometric analysis.

The activity levels of the different radionuclides are measured from γ-energy lines of their respective decay progenies, as shown in Table 2. ^{226}Ra is determined from average activities of ^{214}Pb and ^{214}Bi, whereas^{228}Ra is determined from average activities of ^{228}Ac at different γ- energies and ^{40}K is determined directly from its γ- energy at 1460.8 keV, Table 2. The minimum detectable activity (MDA) during counting for 86 400 second (24 hrs) is 38, 70 and 525 mBq l^{-1} for ^{226}Ra, ^{228}Ra and ^{40}K, respectively.

Estimation of the Committed Effective Dose

In this concern, assuming a person consumes one liter of bottled mineral water per day, the committed effective dose (D) can be calculated by the activity annually ingested as follows[12,13]:

$$D\ (mSv\ yr^{-1}) = R \times A \times C$$

Table 2. The measured progenies used in determination of ^{226}Ra, ^{228}Ra and ^{40}K.

Radionuclide	Measured progeny ($t_{1/2}$)	Energy (keV)	Intensity (%)
^{226}Ra	^{214}Pb (27 m)	295.2	18.7
		351.9	35.8
	^{214}Bi (20 m)	609.3	45
		1120.3	14.9
		1764.5	16.1
^{228}Ra	^{228}Ac (6.2 h)	338.6	12.3
		911.1	29
		968.9	17.5
^{40}K	^{40}K (1.28×10^9 yr)	1460.8	10.7

m = minute, h = hour, yr = year

Where R, A and C are the annual consumption rate (liter yr^{-1}), activity level concentration of the radionuclide (mBq l^{-1}) and the dose conversion coefficient (Sv Bq^{-1}) for adult up to 70 years, respectively. The dose conversion coefficients due to ingestion of ^{226}Ra and ^{228}Ra are taken from recommendations of IAEA[12] and ICRP[13]. The values of these coefficients are 2.8×10^{-7} and 6.9×10^{-7} Sv Bq^{-1} for ^{226}Ra and ^{228}Ra, respectively.

Results and Discussion

Evaluation of water Quality

As shown in Table 1, it is observed that the pH values of all water brands (A, B, …H) have a slight basic values in the range 7.10-7.61. All these values are acceptable for the drinking water quality, since this range lies within pH limits (6.5 - 9.5) according to recommendations of the World Health Organization (WHO)[14]. It is known that, the limits of total dissolved solids (TDS) required for drinking water quality is in the ranges 400-500 mg l^{-1} as recommended by WHO[14] and 300 - 400 mgl^{-1} according to recommendations

of Egyptian standards[15]. It is clear that, TDS content for all water brands analyzed is in the range 170 - 430 mg l^{-1}, Table 1. Therefore, these values are lower and acceptable as compared with the limits of WHO and the local standards.

Figure 2 represents the relation between the pH of the water brands and the corresponding TDS content. It is clear that, there is a relative increase in the pH values with the TDS content in case of water brands from Siwa oasis and El Sadat regions. This can be explained by presence of soluble carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) of alkaline cations, e.g. Na^+, K^+, Ca^{2+} and Mg^{2+}. It is also noticed that, although the TDS content in cases of mineral water G and H brands explored from Beilbeis and El Mansoura is relatively higher than the other brands, the corresponding pH values are less than the maximum pH values of the other brands. These variations can be attributed to differences in the chemical composition of each region.

Radioactivity in Water Samples

The concentrations of ^{226}Ra, ^{228}Ra and ^{40}K in the mineral water brands under investigation determined and presented in Table 3. Activity level concentrations of ^{226}Ra, ^{228}Ra and ^{40}K are varied in the ranges 42-198, 69-206 and 530-1862 mBq l^{-1}, respectively. The higher activity levels is observed in the mineral water samples of B brand (Hayat) explored from Siwa oasis region, while the lowest level is in the E brand (Delta) explored from El Sadat region. ^{40}K activity is found in all brands of mineral water explored from Siwa oasis region, while its activity in the other brands was within the background level.

No good correlation was observed between ^{226}Ra and ^{228}Ra activities, since $^{226}R/^{228}Ra$ ratio is varied between 0.64 in mineral water of A (Aqua Siwa) brand from Siwa oasis region and 1.74 in water of H brand from Beilbeis region. It is also found that ^{226}Ra and ^{228}Ra have nearly the same activity in the mineral water of C (Safi) and G (Baraka) brands from Siwa oasis and El Mansoura regions, respectively. This can be mainly attributed to the geological nature of each region. Also, the distribution of ^{226}Ra and ^{228}Ra in water is a function of the U and Th contents in the aquifer, the geological properties of the dissolution of aquifer solids, and the half live of each isotope.

Table 4 lists the activity concentration of ^{226}Ra in mineral water in different countries components the range of ^{226}Ra in eight brands of the mineral water used in Egypt. It is observed that, the concentration of ^{226}Ra in most brands of the Egyptian mineral water used for drinking, is higher than that found in Taiwanian mineral waters either the local or the imported brands, as reported by Kuo et al.[2], and some types used in Morocco[16]. It is also found that, the higher concentrations of ^{226}Ra determined in the present work is less than the higher ^{226}Ra in some brands of the mineral water used in Hungary[7], Spain[1], Mexico[8] and Morocco[17].

Table 3. The activity concentrations (mBq l^{-1}) of ^{226}Ra, ^{228}Ra and ^{40}K, and the $^{226}Ra/^{228}Ra$ ratio in samples of the bottled mineral water

Region	Type	n*	^{226}Ra (mBq l^{-1})		^{228}Ra (mBq l^{-1})		$^{226}Ra/^{228}Ra$	^{40}K (mBq l^{-1})	
			Range	Mean ± sd	Range	Mean ± sd		Range	Mean ± sd
I. Siwa oasis	A	7	73 - 107	91 ± 11	120 - 166	143 ± 15	0.64	530 - 628	576 ± 31
	B	8	167 - 198	184 ± 10	109 - 206	156 ± 30	1.18	1545 - 1862	1700 ± 99
	C	6	137 - 184	167 ± 16	116 - 185	149 ±26	1.12	652 - 839	738 ± 65
II. El Sadat	D	6	115 - 152	137 ± 12	136 - 141	138 ± 2	0.99	N.f	N.f
	E	6	42 - 105	69 ± 21	69 - 74	71 ± 2	0.97	N.f	N.f
	F	7	92 - 125	108 ± 10	147 - 166	156 ± 7	0.69	N.f	N.f
III. El Mansoura	G	9	122 - 192	166 ± 22	134 - 173	152 ± 12	1.09	N.f	N.f
IV. Beilbeis	H	8	117 – 179	150 ± 20	78 - 96	85 ± 6	1.74	N.f	N.f

Notes:

maximum and minimum values are bolded,

sd = standard deviation at confidence level 95% (1σ) , * = number of the analyzed samples, and

Nf = not found

Table 4. Activity concentration (mBq l^{-1}) of ^{226}Ra in mineral water in different countries.

Country	No. of types	^{226}Ra (mBq l^{-1})	Reference
Taiwan	6 [a]	Bkgd - 4.3	2
	6 [b]	Bkgd - 28.1	2
Spain	1	264 - 270	1
Morocco	3	9.1 - 1248	17
	2	< 25	16
Mexico	21	> 100 [c]	8
Hungary	28	<10 - 2922 [d]	7
Egypt	8	69 - 184	*This work*

a = local types, b = imported types, c = three types higher than 100 mBq l^{-1}, while 18 less than 100 mBq l^{-1} (Mexico) and d = six types higher than 100 mBq l^{-1}, while 22 less than 100 mBq l^{-1} (Hungary)

Based on the above mentioned results, an average concentration of ^{226}Ra as a source for alpha activity in A and E brands from Siwa oasis and El Sadat regions, respectively, is less than the maximum permissible level (100 mBq l^{-}) required for the acceptable quality of drinking water as recommended by WHO[(6)] and US EPA[(18)]. In the other six brands of water, theaverage concentration of ^{226}Ra is above the recommended limits by WHO and US EPA, and reached to 184 mBq l^{-1} in water samples of B brand (Hayat) from Siwa oasis. An average concentration of ^{228}Ra as source of beta activity in all brands of the mineral water is less than the permissible safe limit (1000 mBq l^{-1}) as recommended by WHO. Concentration of ^{40}K as a source for beta activity is only higher than the permissible safe limit (1000 mBq l^{-1}) as recommended by WHO[(6)], in mineral water samples of B brand from Siwa oasis region.

Relation between total Radium Content, pH and TDS

The relation between total activity concentration due to total radium (^{226}Ra + ^{228}Ra) in the different water brands with the corresponding pH, is represented in Fig. 3. It is clear that, there is a relative increase in total radium content with pH of water environment in most brands. This is expected since radionuclides of radium isotopes generally tend to precipitate with the decrease in pH values[19]. This behavior is not noticed, however in case of water samples of brand E explored from El Sadat region. The variation between total radium content and acidity of water brands from site and/or region to another, can be due to differences in geological composition and chemical medium in each site for water exploration.

On the other hand, the relation between total radium content in the different water brands with the corresponding total dissolved solids (TDS) is shown in Fig. 4. In most brands of mineral water explored from Siwa oasis, El Sadat and Beilbeis regions, there is a relative decrease in total radioactivity

due to radium (^{226}Ra + ^{228}Ra) with TDS content. This relation is opposite to that found between the radioactivity and mineral salts content in the Mexican mineral water[8]. The mineral water of G (Baraka) brand explored from El Mansoura region has higher TDS, although its total radium is almost equals to that found in mineral water of B (Hayat) and C (Safi) brands from Siwa oasis. This difference can be attributed to geological considerations.

Assessment of the Committed Effective Doses

When humans ingest radium, about 20% is absorbed into the bloodstream[20]. The absorbed radium is initially distributed in soft tissues and bone, its retention is mainly in growing bone. Based on the activity level concentrations determined in different eight brands of the mineral water commonly used for drinking in Egypt, the committed effective dose was evaluated for ^{226}Ra and ^{228}Ra ingestion. The dose was estimated by assuming a daily consumption of one liter mineral water and the arithmetic mean of activity level concentration for each water brand[12]. The estimated committed effective doses of all the investigated water types are given in Table 5.

The results showed that, the highest committed effective doses is observed in case of mineral water of B brand from Siwa oasis region, while the lowest doses is found in water samples of E brand from El Sadat region. For instance, a person consuming one liter in a day of the mineral water, is exposed to an annual committed effective dose of 1.9×10^{-2} and 3.9×10^{-2} mSv y^{-1} as a result ingestion of ^{226}Ra and ^{228}Ra , respectively, while the total dose was 5.8×10^{-2} mSv y^{-1}, Table 5. It is clear that, all the estimated values of the committed effective dose in all water brands due to ingestion of ^{226}Ra and ^{228}Ra, and the total dose value are less than the permissible dose level (0.1 mSv y^{-1}), when a person consumes only 1 liter or even 1.5 liter per day. For comparison, the estimated committed effective doses in the present work are lower than that observed in many brands of the Hungarian bottled mineral water. (7)

Table 5. Expected committed effective doses (mSv y^{-1}) due consumption of the bottled mineral water.

Region	Brand	Committed effective doses (mSv yr^{-1})		
		^{226}Ra	^{226}Ra	total dose
I	A	9.3×10^{-3}	3.6×10^{-2}	4.5×10^{-2}
	B	1.9×10^{-2}	3.9×10^{-2}	5.8×10^{-2}
	C	1.7×10^{-2}	3.7×10^{-2}	5.4×10^{-2}
II	D	1.4×10^{-2}	3.5×10^{-2}	4.9×10^{-2}
	E	7.0×10^{-3}	1.8×10^{-2}	2.5×10^{-2}
	F	1.1×10^{-2}	3.9×10^{-2}	5.0×10^{-2}
III	G	1.7×10^{-2}	3.8×10^{-2}	5.5×10^{-2}
IV	H	1.5×10^{-2}	2.1×10^{-2}	3.6×10^{-2}

maximum and minimum values are bolded

Conclusion

Activity concentration of ^{226}Ra, ^{228}Ra and ^{40}K was determined in eight brands of the bottled mineral waters commercially available in Egypt. The higher average concentrations were observed in the mineral water of brand B (Hayat) explored from Siwa oasis region. The corresponding total committed

effective doses due to ingestion of ^{226}Ra and ^{228}Ra was less than the permissible dose level (0.1 mSv y^{-1}) recommended by the World Health Organization (WHO).

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