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Determination of Radium, Uranium and 222Rn in groundwater Samples from Different Regions in Saudi Arabia

KEYWORDS: groundwater, radium, uranium, radon, Saudi Arabia, gamma spectrometry, alpha spectrometry.

A.Al-Muqrin
Princess Nora University, College of Science, department of Physics, Riyadh, KSA

H. Al-Ghamdi
Princess Nora University, College of Science, department of Physics, Riyadh, KSA

A.El-Sharkawy
Nuclear and radiological Regulatory Authority, Cairo, Egypt.

ABSTRACT *Surveillance monitoring in different regions of the Saudi Arabian Kingdom (KSA) has been carried out to determine the activity levels of radium isotopes (226Ra and 228Ra), 222Rn and uranium isotopes (234U and 238U) in groundwater samples collected from selected wells. Several techniques were exploited in the radioanalysis methods; the radon-222 was measured through its daughter Po-218, with a silicon alpha detector (RAD-7), the activity concentrations of 234U and 238U isotopes were determined using a surface barrier alpha detector, preceded by a radiochemical separation of both isotopes using extraction chromatography. The radium isotopes were measured by gamma spectrometry using high purity germanium detectors, after radiochemical separation of the isotopes with ion-exchange chromatography using a strong cation exchange resin. Quality assurance and methods validation were established through the efficiency calibration of the detectors, the estimation of uncertainties, the use of blanks, the analysis of standard reference samples and the intercomparison with other international laboratories. The average activity concentrations of 226Ra and 228Ra were 6.3 and 6.9 pCi/L respectively, and the relatively higher values of radium activities were found in Qaseem, Hail and Tabouk. The average activity concentration of Rn-222 was 182.0 pCi/L, which is below the maximum contaminant level proposed by EPA for drinking water (300 pCi/L). The average activity concentration of 234U and 238U were 48.8 and 36.0 mBq/L respectively. The uranium activity ratio (234U/238U) in the investigated samples had an average value of 1.6. The data obtained from the activity concentrations of the investigated radioisotopes are comparable to the results reported in literature for radium, uranium and radon in the Kingdom of Saudi Arabia, and can be used to establish a radiological baseline radioactivity map for uranium, radium and radon radioactivity levels in groundwater of these regions.*

1. INTRODUCTION

Groundater is a very important natural resource related directly to the survival of all living organisms and its quality, therefore cannot be compromised. Groundwater sources of drinking water may contain naturally occurring radionuclides from the uranium-238, uranium-235 and thorium-232 series, especially uranium, radium, and radon. The occurrence of radionuclides in groundwater depends on several factors, one of them is the presence of this radionuclide or its parent nuclides in the aquifer matrix [1]. The existence of radium in groundwater is controlled by many factors, including the decay of the dissolved parent isotopes, the desorption from aquifer surface, the alpha recoil and the water chemical composition [2]. Contrary to radium, uranium is more mobile under oxidizing conditions. In its reduced form, it is quite insoluble. The dominant process for moving ^{238}U into the groundwater is mineral dissolution. Uranium is transported in groundwater as the uranyl ion, most commonly complexed by carbonate and phosphate ions or adsorbed on surfaces of ferric oxyhydroxides, clays and organic matter [3]. The concern over exposure of humans to radioactivity is an important driving factor behind the studies of environmental radiation and natural radioactivity levels in groundwaters. These radioisotopes in groundwaters enable us to understand their distribution in the environment and the resulting health consequences. Therefore, it is necessary to manage and protect the natural surface and groundwaters. Several studies have been carried out to evaluate the radioactivity content in shallow and deep wells in Saudi Arabia. The ^{226}Ra and ^{228}Ra activities were estimated in lower Wajid and Saq aquifers in Saudi Arabia [4]. Shabana and Hobaib measured the ^{226}Ra, ^{228}Ra activities and the $^{234}U/^{238}U$ activity ratios in ground water wells of two selected regions in Saudi Arabia [5]. Tap water and drinking water including natural mineral water have been investigated for their radon concentrations in Jeddah, Saudi Arabia. It was observed that the radon concentration in natural mineral water samples is the highest 9.9 Bq/L, compared with that in tap water 1.7 Bq/L [6]. Afaf et al reported that the concentrations of ^{238}U ranged from <0.001 to 0.17 Bq/l, with an average of 3.5 ppb, ^{226}Ra series values ranged from LDL to 2.5 Bq/l and ^{228}Ra ranged from LDL to 3.3 Bq/l in water samples from Jeddah and Tabouk, Saudi Arabia [7]. In groundwater samples from Mecca province, Shabana et al reported that the ^{222}Rn concentrations ranged from 10-100 Bq/L with an average value of about 40 Bq/L. The uranium concentration, in samples of gross activity levels exceeding the national guideline value, ranged from 9 to 55 µg/L and the levels of ^{226}Ra and ^{228}Ra were below the detection limit of the counting system in all samples [8]. The purpose of this study is to analyze groundwater samples for concentrations of U, Ra, and Rn in different regions of Saudi Arabia, to ensure that the radioactivity levels in these regions are within the naturally occurring levels, and may serve as a reference or baseline radiological map in case of any future studies.

2. METHODOLOGY

2.1 Sampling

Water samples were collected from 124 local wells in Riyadh, Qaseem, Hail, Tabouk, Al-Jouf, Al-Madinah, Mecca, Dammam, Khobar and Jazan. The detailed sampling sites are represented in table 2.1 and map 2.1.

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Map 2.1 : Sampling sites

Location	Radium samples	Radon samples	Uranium samples
Riyadh	12	12	5
Qaseem	9	1	2
Hail	14	13	9
Tabouk	12	11	7
Al-Jouf	9	-	3
Mecca	10	10	5
Al-Madinah	14	14	10
Al-Sharqyah	36	36	12
Al-Baha	4	4	-
Gazan	4	2	-
Total number	124	103	53

These wells were selected to represent groundwater in each aquifer. Groundwater samples from each well were analyzed for radioactive and chemical constituents. The water sampling was carried out according to the IAEA-295 technical report [9]. The water was allowed to run in a continuous flow for a short period to eliminate any contamination from the pipes, and have a representative samples. For radioactivity measurements, water samples were collected from the continuous flow, filtered with 0.45µ membrane filter, acidified with 11 M HCl 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 and the growth of micro-organisms, and transferred to polyethylene bottles. Also, from this continuous flow, a radon sample was collected into a submerged glass bottle, and radon-222 was measured directly using a radon detector (RAD-7).

2.2 Materials and Apparatus

Radium extractions were carried out using Purolite C-100 strong acid cation exchange resin. A package of 30 kg of the resin, in the Na form, was supplied by Veolia Water Company, Riyadh, KSA. Radium separation was conducted in a column mode using BIORAD Glass Econo columns of 0.9-cm diameter, together with polypropylene funnels and Teflon end fittings connected with plastic taps. Standard reference solutions of ^{226}Ra and ^{228}Ra were supplied by the National Institute of Standards and Technology (NIST), (SRM 4967A and SRM 4339B). Uranium isotopes were separated from other actinides using extraction chromatography resin UTEVA supplied by Triskem International Co., France. All gamma radioactivity measurements were carried out using a Canberra HPGe coaxial detector Model (GC4020) with relative photo-peak efficiencies of 40% for the 1332 keV line of ^{60}Co. The germanium detector was connected to a Digital Spectrum Analysis model DSA-1000. 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 radon measurements were carried out using a silicon semiconductor detector (RAD7) supplied by Durridge Co. All other acids and reagents used in this study were of analytical grade.

2.3 Radioanalyses and Measurements

Water samples were analyzed for radium isotopes (^{226}Ra and ^{228}Ra) following the procedure described by A.El-Sharkawy et al, 2013 [10], where 4 liters of the water samples were allowed to pass through a strong cation exchange resin. The resin was transferred to standard counting containers and 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) measurements was carried out using standard resin 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 an identical matrix with a known activity, and all other conditions were followed typically (flow rate, resin volume, counting time, 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.

Uranium extractions from water were carried out following Eichrom method ACW-01, where the ^{234}U and ^{238}U were determined by the radiochemical separation of the isotopes using calcium phosphate co-precipitation to concentrate and remove actinides from aqueous samples. Uranium isotopes were separated from other actinides using extraction chromatography, and followed by the electrochemical deposition of those isotopes on a stainless steel disc using a specially designed electrodeposition cell. Finally, the samples were counted using an alpha detector. A ^{232}U tracer was used to monitor chemical recoveries and correct results to improve precision and accuracy [11, 12].

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:

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

2.4 Quality Assurance

For quality assurance and validation purpose, reference water samples were determined using the same analysis and measurement protocol, and were compared against their certified values to test the closeness of the measured samples to its reference values. Also, proficiency tests were carried out with the International Atomic Energy Agency, IAEA-CU-2010, IAEA-TEL-2011-03, IAEA-TEL-2014-03. Errors were propagated due to nuclear counting statistics, tracer and volume.

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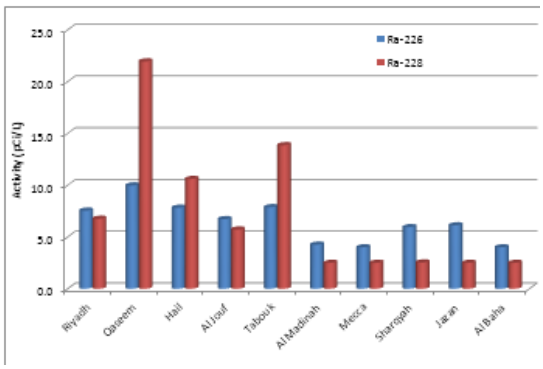
3. RESULTS AND DISCUSSION

Fig.(3-1) : Activity concentrations of Ra-226 and Ra-228 in some groundwater wells from different regions in KSA

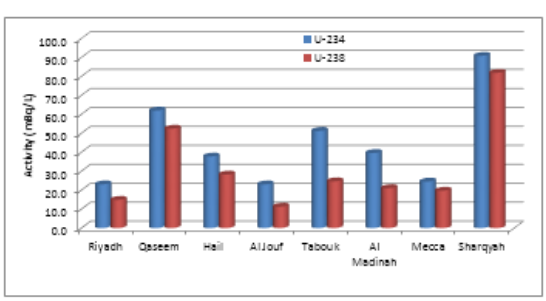


A.Al-Muqrin et al.,Fig.(3-1)

The average activity concentrations of ^{226}Ra and ^{228}Ra in the selected regions are represented in fig. (3-1). As shown in figure, the average activity concentration of ^{226}Ra is 6.3 pCi/L, ranging from 4.0 to 34.3 pCi/L, while the average activity concentration of ^{228}Ra is 6.9 pCi/L, ranging from 2.5 to 41.6 pCi/L.

Some water samples have shown a relatively higher ^{228}Ra activity in Qaeem, Hail and Tabouk. High radium anomalies were recorded in the confined zone of the Saq aquifer in these regions, where the reducing conditions are prevailed, which is the prohibited condition for radium to be released from rock into groundwater. On the other hand, the activity concentration of radium ^{228}Ra increases sharply in the confined part of Saq aquifer, where high negative values of oxidation reduction potential is prevailed (Minatome, 1984) [13]. The relatively higher ^{226}Ra activities in some Qaseem samples are probably related to the occurrence of phosphatic levels on top of Saq aquifer in this region, providing uranium and radium to groundwater by dissolution [14].

Fig.(3-2) : Activity Concentrations of 234U and 238U in groundwater samples from different regions in KSA
A.Al-Muqrin et al.,Fig.(3-2)



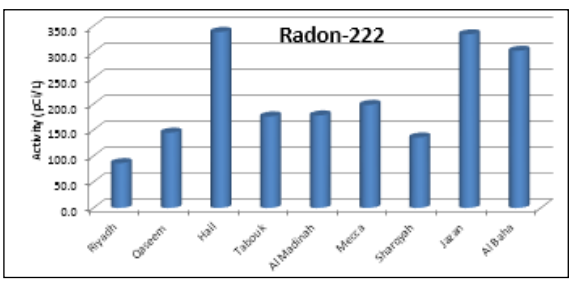
3.2 Uranium Isotopes in Water Samples

The average activity concentrations of ^{234}U and ^{238}U in the selected regions are represented in fig. (3-2). The average activity concentration of ^{234}U is 48.8 mBq/L, ranging from 3.2 to 136.2 mBq/L, while the average activity concentration of ^{238}U is 36.0 mBq/L, ranging from 1.2 to 130.7 mBq/L.

The obtained results showed a relatively maximum values of both isotopes in the eastern Province (Sharqyah). These wells generally tap Tertiary Formations such as Dammam or Um El Radhuma, which are generally limestones. The uranium activity ratio (^{234}U/^{238}U) in the investigated samples had an average value of 1.6. Groundwater is often found to have ^{234}U/^{238}U ratios greater than unity indicates that ^{234}Uatoms are easier leached from rocks than ^{238}U nuclei, as a result of some processes which include selective leaching which involves the preferential mobilization of ^{234}U relative to ^{238}U, and the increased solubility [15].

3.3 Radon in Water Samples

Fig.(3-3) : Activity of Rn-222 in groundwater samples from different regions in KSA



The average activity concentration of Rn-222 is 182.0 pCi/L, ranging from 10.0 to 684.0 pCi/L. Nearly 16% of water samples have values exceed the maximum contaminant level proposed by EPA for drinking water (300 pCi/l) [16]. Radon concentrations in groundwater are highly variable, where there are many factors affect the presence of ^{222}Rn in groundwater, such as the uranium and radium content in the aquifer rock.

4. CONCLUSION

Surveillance monitoring in different regions of the Saudi Arabian Kingdom has been carried out to determine the activity levels of radium isotopes (^{226}Ra and ^{228}Ra), ^{222}Rn and uranium isotopes (^{234}U and ^{238}U) in groundwater samples collected from 124 different wells in Riyadh, Qaseem, Hail, Tabouk, Al-Jouf, Al-Madinah, Mecca, Dammam, Khobar and Jazan. The average activity concentration of ^{226}Ra is 6.3 pCi/L, ranging from 4.0 to 34.3 pCi/L, while the average activity concentration of ^{228}Ra is 6.9 pCi/L, ranging from 2.5 to 41.6 pCi/L. The relatively higher values of radium activities were found in Qaseem, Hail and Tabouk, which may be explained by the nature and properties of the aquifers. The average activity concentration of ^{222}Rn is 182.0 pCi/L, ranging from 10.0 to 684.0 pCi/L. Nearly 16% of water samples have values exceed the maximum contaminant level proposed by EPA for drinking water (300 pCi/l). The average activity concentration of ^{234}U is 48.8 mBq/L, ranging from 3.2 to 136.2 mBq/L, while the average activity concentration of ^{238}U is 36.0 mBq/L, ranging from 1.2 to 130.7 mBq/L. The uranium activity ratio (^{234}U/^{238}U) in the investigated samples had an average value of 1.6. The data obtained may serve as a reference or baseline radiological map for the natural radioactivity levels in these regions in case of any future studies.

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