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UTILIZATION OF GAMMA SPECTROMETRY: QUANTIFYING RADIOACTIVE CONTENT OF EIGHT SPA WATER SAMPLES IN NORTHERN ALGERIA

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Abstract
Thermal waters at Algerian spas, used for centuries for medicine, will be tested for radioactivity. A high-resolution HPGe γ-spectrometry instrument was used to evaluate the radioactive concentration of eight Spas waters in north Algeria for ^{226}Ra, ^{232}Th, ^{235}U, and 40K. To achieve secular equilibrium between 226Ra and its short-lived daughter products before gamma spectrometry, water is embedded in Marinelli beakers and sealed for 28 days. Spa waters averaged 0.045–2.077 Bql^{-1} in ^{226}Ra activity, 0.17–3.416 in ^{232}Th activity, 0.085–7,235 in ^{235}U activity, and 1.402–15.156 in 40K activity. This research would assist users and government authorities in assessing radiation risks from spa bathing.

Keywords: gamma spectrometry, radioactive, water

Introduction

Natural mineral water called thermal water has been shown to provide health advantages owing to its chemical and physical properties. Its subsurface origin protects it from contamination and includes health-beneficial minerals, salts, gases, and sludge [1-6]. Its nature, such as minerals, trace elements, or other substances, effects, and cleanliness separate it from other drinking water. Thermal resorts provide relaxation, body care, and well-being. Hydrotherapy, which uses a variety of methods, can improve thermoregulation and fitness. His hot waters contain salts (calcium carbonate or sulphate, sodium chloride, iron, magnesium, sulphides, traces of trace elements, including lithium) [7-9]. Gaseous hydrogen sulphide is usually low, whereas carbon dioxide is commonly high. Water concentrations of natural radioactive elements vary by location and soil rock [10–13]. Indeed, these waters can originate from the rise to the surface, through faults in the geological structures, of rainwater infiltrated at great depth or the condensation of vapors emitted by volcanism, feeding hot springs or geysers [14], those Water sources may contain radionuclides such as ^{238}U, ^{232}Th, ^{40}K and ^{137}Cs [15, 16]. During the practices, (cure of drink, general and local showers, and the massages under the water) patients are exposed to the risk of natural radiation. Moreover, the spa staff is permanently exposed, this natural origin of radioactivity is principally due to the natural series of the ^{238}U, ^{232}Th, their respective progenies, and ^{40}K.

Radon inhalation is another major cause of spa staff exposure [2]. Rémy and Lemaître (1990)[17] found that granitic areas had two to three times more natural exposition than sedimentary basins. Hydrotherapy practitioners are exposed to natural radiation sources like radon or thoron progeny, according to Directive 96/29 / Euratom [18], which sets basic standards for protecting the population and workers from ionising radiation hazards. This paper uses gamma spectrometry to quantify the radioactive content of eight spa water samples in northern Algeria and assess the health concerns to the surrounding people.

Materials and Methods

March 2020 is when sampling was conducted Table 1 shows their coordinates.

Table 1. Geographic coordinates of thermal springs studied

Sample code	Thermal W. name	Province	Geographic coordinate
S01	Debagh	Galma	36°27'40.0"N 7°16'08.8"E
S02	Malouane	Blida	36°29'12.7"N 3°02'37.8"E
S03	Esaalihine	Bisakra	34°51'29.8"N 5°42'29.6"E
S04	Ouled Tebbane	Setif	35°48'33.1"N 5°06'27.1"E
S05	Bouhniffa	Mascara	35°18'50.7"N 0°03'00.5"W
S06	Boutrike	Ain daflla	36°22'54.7"N 2°24'00.0"E
S07	Essalihine	Media	36°10'04.4"N 2°58'19.6"E
S08	Ouled Djalale	Ouled Djalale	34°25'36.8"N 5°04'15.3"E

Eight spas gathered 1.5-liter plastic bottles of samples. To avoid surface pollution, we dropped sample bottles near the spring discharge site to gather water. Samples did not need screening because the waters are transparent. The spa waters were sealed in a 450cm3 Plastic Marinelli beaker with paraffin tape. It is worth noting that the containers are airproof and thick enough to avoid the radon permeation, so the pressure produced inside by ^{222}Rn of ^{226}Ra decay would not produce gas escape from the beaker. Prior to the gamma ray spectrometry analysis, the referenced waters were stored for 28 days to achieve secular equilibrium between ^{226}Ra and its short-lived daughter products. This process keeps radon gas in the volume and the daughter product in the sample. The GeHP gamma spectrometer detector has the advantage of using bulk materials without radiochemical pretreatment. In the present work,the activity concentrations of ^{226}Ra, ^{232}Th, ^{235}U and ^{40}K in the thermal water samples were determined using gamma-ray spectrometry with a high resolution provided by a high purity germanium (HPGe) vertical co-axial detector (Canberra, GC 2018-7500 model, series number 87063) coupled to a Canberra Multichannel Analyzer (MCA) computer system. To decrease ambient radiation, the detector element is shielded by 100 mm of lead. The absolute efficiency response curve of an HPGe detector in the energy range 60–1836 keV was determined using an IAEA-supplied gamma-emitting radionuclide source. The radionuclides recommended for the efficiency measurements ^{241}Am, ^{139}Ce , ^{109}Cd, ^{60}Co, ^{152}Cr, ^{137}Cs , ^{54}Mn ,^{85}Sr, ^{113}Sn, ^{88}Y and ^{65}Zn.

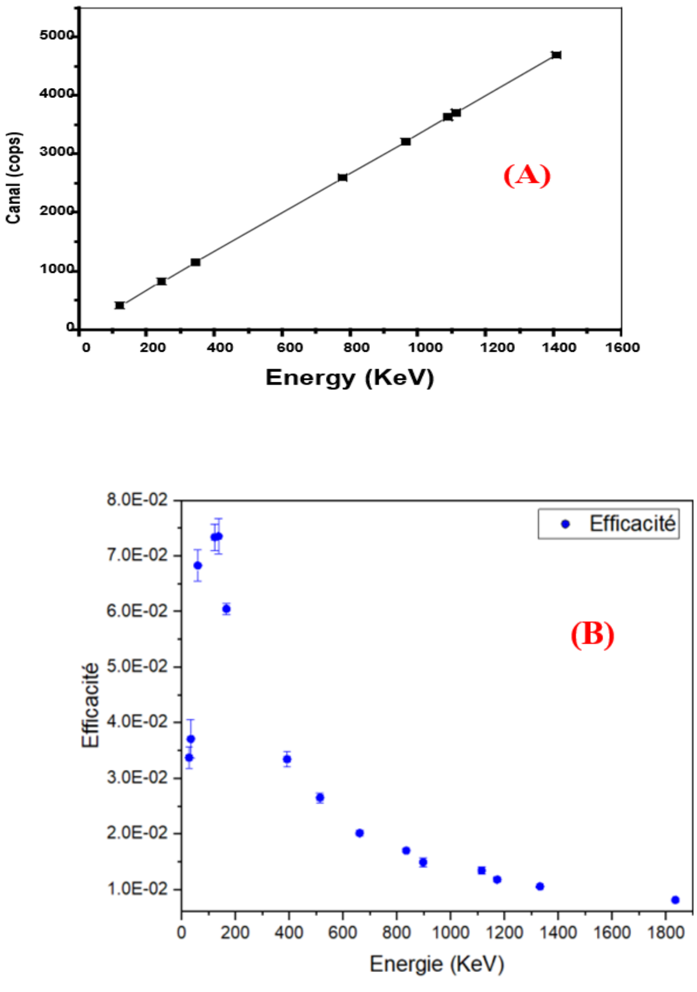


Fig 3. Energy (A) and efficiency (B) calibration

Mono-energetic calibration sources are optimal for absolute and total efficiency assessments since they have no decay-scheme effects. Using an appropriate fitting function for the observed efficiencies allows extrapolation at other energies and improves experimental estimations (Fig.2).Standard 252Eu sources in resin matrices were used to calibrate the spectrometer's energy and efficiency. For all radionuclide gamma energies, the energy spectra emits from 30 to 1500 keV.

Background measurement is necessary for this investigation since sample activities are low. Unsubtracting background from measured activity may overestimate measurements. The background spectrum from the detector surroundings was measured using deionized water poured in a Marinelli type I container for 24 hours to maintain the same measurement circumstances. Figure 4 shows uranium and thorium radionuclides in the background spectrum.

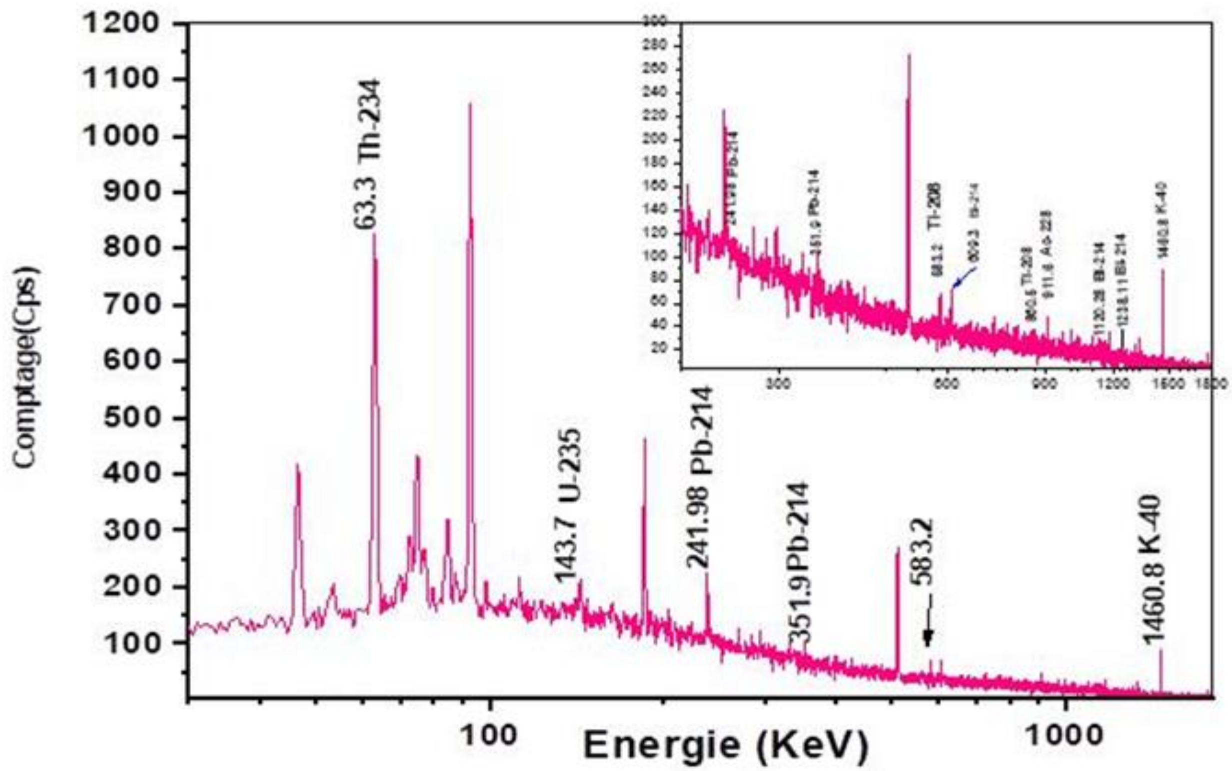


Fig 4. Background spectrum from deionized water.

Low-level radioactivity in environmental samples may provide an incorrect ray. Random stochastic fluctuations in the background count rate explain this. We must find the lowest activity, MDA, for each gamma ray. In this example, it measures the energy needed to identify a source with 95% accuracy. Table 2 shows the MDA for each energy using Curie equation.

$$MDA = \frac{LD}{\varepsilon_E V P_\gamma}$$

Where V is the mass of the sample per liter, ε is the detection efficiency, P_γ branching ratios and LD is the limit of the detection calculated using Curie formula

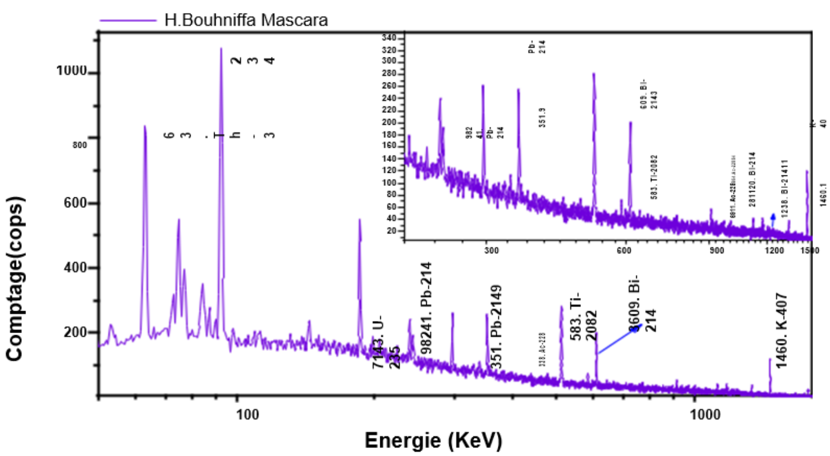
$$LD = 1{,}645\ (\sqrt{B/L_T})$$

B is the number of background counts under the considered energy peak and L_T is the corresponding real counting time. MDA takes a value "1" is assigned to MDA, [19]

Table 2. Detection Limit (Bq/kg)

Radio-nuclide	E (keV)	B (counts)	MDA(Bq/L)
214_{Pb}	351,9	159	0.0449
214_{Bi}	609.3	145	0.0567
228_{Ac}	911.6	110	0.1281
235_{U}	143,7	140	0.0722
40_{K}	1460	419	1.1501

Results and discussion



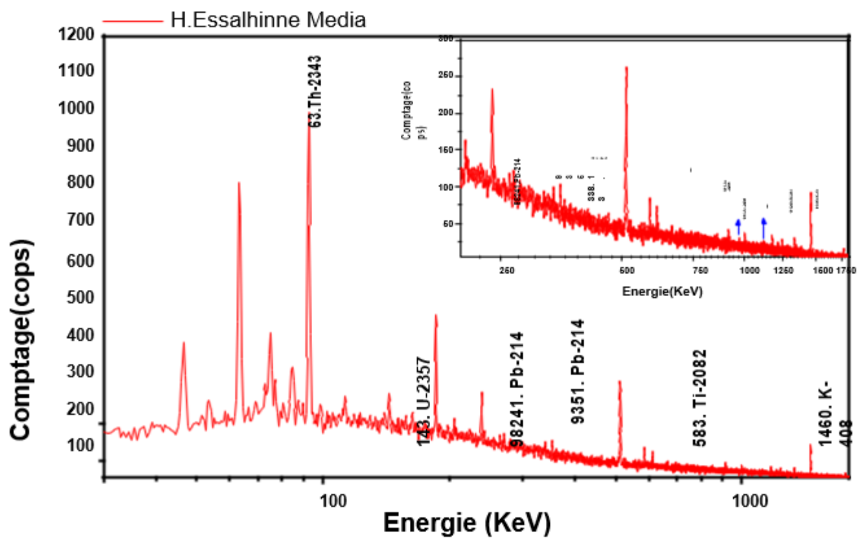


Fig 5. The spectrum of γ radiation emitted by the sample of hammam Essalhinne Media and Bouhniffa respectively.

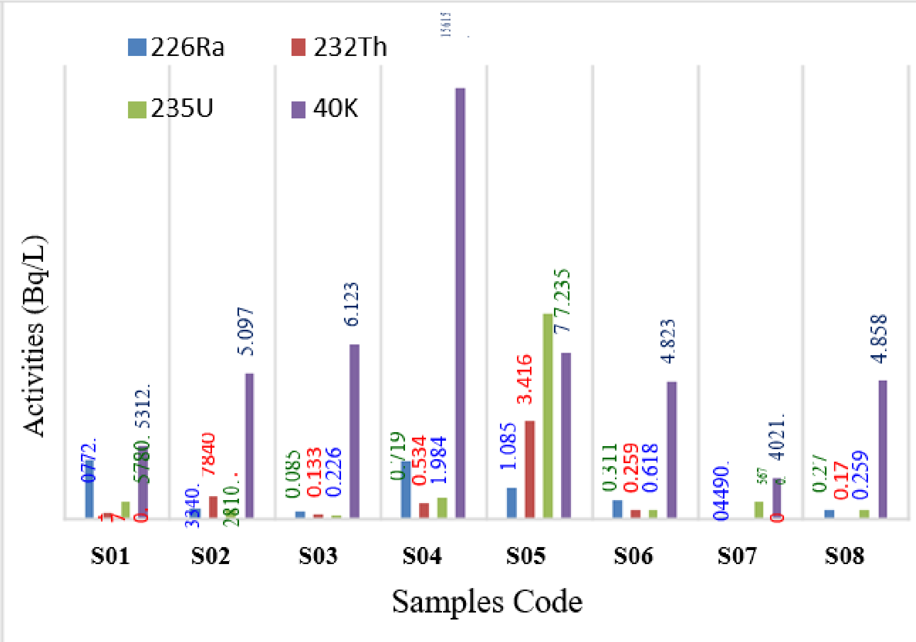


Fig 6. Radionuclide Activity Concentration for different thermal spring samples

Most measurement data were supplied as mean ± standard deviation for statistical analysis utilising Gamma Vision and efficiency calculations. First, we report GeHP gamma spectrometer detector radionuclide counts in Table 3. To establish an activity with minimal uncertainty, all materials were measured using gamma spectrometry for 24 hours (see fig.5).

The spectrum of γ radiation emitted by the sample of hammam Essalhinne Media and Bouhniffa respectively. Almost, all samples exhibit two peaks corresponding to ^{214}Pb and ^{214}Bi emissions emanating from ^{238}U. The similarity in the specific activities of ^{214}Pb from its gamma peak and ^{214}Bi from its gamma peak of 609.3 keV, shows a well-established secular equilibrium between ^{226}Ra and its progeny.

The measurement results of activity concentrations of thermal water for each sample are shown in Table 4, grouped in series: the activity concentration of the ^{238}U series was principally represented with its two concentrated elements: ^{214}Bi and ^{214}Pb where the activity rages from 0.02 to 2.08 Bq/L ^{214}Bi and from 0.01 à 1.9 Bq/L for ^{214}Pb. The ^{235}U series is predominant by its own peak (143.7 keV). Its activity ranged from 0.270 to 7.235 Bq/L. While the activity concentration of ^{40}K ranged from 2.531 to 15.153 Bq/L. However, the ^{232}Th series was represented by the ^{228}Ac with an activity ranging from 0.17 to 3.416 Bq/L. Those Radiation in thermal water samples may rely on parameters such water-solid phase interaction, therefore radionuclide concentrations vary widely.

For radiological consideration, the ^{226} is one of the most important element to assess because of its very long biological half-life and its high solubility in water. It can contaminate human body by ingestion when consuming thermal water or by inhalation of ^{222} during degassing in the internal atmosphere in the various spa areas. The ^{226}Ra activity for the different samples are within the range of 0.259 up to 2.077 Bq /L. Some studies reported nearly similar range in Iran , [20] (Ouled-Tebben hammam in Sétif (S01) and Debagh hammam in Guelma (S04) spas exhibit maximum activity in the order of 2.077 Bq/L and 1.984 Bq/L respectively, (see Figure 6). It worth to note that all the thermal water samples analyzed are not suitable for every day consumption, except S07 in Media province, which has an activity near the detection limit (LMD) equal to 0.018 Bq /L. Indeed, the measured activity of ^{226}Ra, for the latter, is much higher than the maximum admissible limit (LMA) equal to 185 mBq/L, established for drinking water by the American environmental protection agency, [21, 22].

Table 3. Detected radionuclides and counts

Element	Energy (keV)	Emission probability (%)	Efficiency	Back-ground (c/s)	(Count/s)							
					S 01	**S 02**	**S 03**	**S 04**	**S 05**	**S 06**	**S 07**	**S 08**
^{214}Pb	**351,9**	37.2	3.19E-02	159	406	345	228	624	1165	1062	167	270
^{214}Bi	**609.3**	46.3	1.94E-02	145	391	238	274	545	836	847	152	247
^{228}Ac	**911.6**	27.7	1.25E-02	110	145	216	111	156	133	182	96	128
^{235}U	**143,7**	10.5	6.60E-02	140	224	216	213	335	296	334	293	163
^{40}K	**1460,8**	10.67	7.04E-03	419	560	568	561	589	493	862	460	598

Table 4. Samples activities en (Bq/L) of each sample with pH and conductivity (µs/cm) at 25°C

Radio-nuclide		Activity (Bq/L)							
		S 01	**S 02**	**S 03**	**S 04**	**S 05**	**S 06**	**S 07**	**S 08**
^{238}U series		2.178± 0.244	0.402± 0.084	0.240± 0.056	1.968± 0.245	1.015± 0.144	0.534± 0.0840	0.07± 0.005	0.149± 0.041
		1.977± 0.243	0.266± 0.058	0.292± 0.067	2.008± 0.233	1.155± 0.192	0.703± 0.118	0.120± 0.005	0.369± 0.079
^{232}Th series		0.17± 0.080	0.784± 0.329	0.133± 0.070	0.534± 0.251	3.416± 1.711	0.259± 0.126	< MDA	0.17± 0.004
^{235}U series		0.578± 0.199	0.281± 0.075	0.085± 0.025	0.719± 0.237	7.235± 2.399	0.311± 0.085	0.567± 0.125	0.270± 0.134
		2.531± 0.792	5.097± 1.513	6.123± 1.811	15.156± 4.373	5.827± 1.735	4.823± 1.441	1.402± 0.440	4.858± 1.483
		2.077± 0.243	0.334± 0.071	0.226± 0.061	1.984± 0.239	1.085± 0.168	0.618± 0.101	0.0449± 0.0120	0.259± 0.065

pH at 25 °C	7.94	7.56	7.66	8.05	7.71	7.66	8.15	7.83
Conductivity (µs/cm) at 25°C	392.2	5627	1731	400.2	227.5	1394	237.3	447

Potassium (^{40}K) is present in the human body in constant amounts and does not concentrate like other isotopes. It is therefore not considered to be without risk to human health. However, it should be noted that all the samples of thermal waters turn out to be equally loaded with ^{40}K, whose activity in becquerel / liter fluctuates between 1 and 4, with the exception of the thermal water from the Ouled Tebben- hammam. Setif; which displays a very high activity equal to 16 Bq/L. The radionuclide ^{235}U is also present in all the samples analyzed with a very variable quantification. Based on these results, we can conclude that all thermal water samples analysed, except H. Essalhine-Media, are unfit for daily consumption and may only be used for the cure duration due to the lifetime risk to a human being.

Conclusions

In this study, the radioactivity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in spa waters in some areas in North Algeria were examined. Since individuals instinctively utilise thermal water supplies for therapy and consumption, these values are crucial for Algerian public health. These thermal waters can cause long-term therapeutic issues and cannot be drunk due to their radioactive characteristics.

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