Algerian Journal of Engineering and Technology

Journal homepage: https://jetjournal.org/index.php/ajet

Original Article

Gamma spectrometry for natural radioactive nuclides in Spa waters in some areas in north Algeria

Tarek Azli[a], Faiza Zidouni[b], Mohammed Messaoudi[c,*], Besma Mesbout[d], Abderezzak Hadri [a], Samir Begaa[c]

[a] *Nuclear Research Centre of Draria CRND, / COMENA. Algiers, Algeria*

[b] *LMFTA Laboratory, Faculty of Physics, University of Sciences and Technology- USTHB, Algiers, Algeria*

[c] *Reactor Chemistry Department, Nuclear Research Centre of Birine. P.O. Box 180. Ain Oussera. 17200 Djelfa. Algeria*

[d] *Faculty of Physics, University of Blida, Algeria*

ARTICLE INFO

Article history:
Received 28 September 2021
Revised 21 October 2021
Accepted 22 October 2021

Keywords:
Natural Radioactive;
Spa waters;
Gamma spectrometry;
Radium 226;
Potassium 40;
Algeria.

ABSTRACT

The work aims to determine the radioactivity levels of Algeria thermal waters which have been used permanently in spas for therapeutic intentions. Eight Spas waters in north Algeria analysis was performed to determine their radioactivity concentration for ^{226}Ra, ^{232}Th, ^{235}U and ^{40}K, using a high-resolution HPGe γ-spectrometry system. Water is imbedded in a Marinelli beakers tightly sealed for 28 days to achieve secular equilibrium between ^{226}Ra and its short-lived daughter products before analyzing by gamma ray spectrometry. The average activity concentrations for spa waters from study areas were 0.045 to 2.077 Bql^{-1} for ^{226}Ra; 0.17to 3.416 Bql^{-1} for ^{232}Th; 0.085to 7,235 Bql^{-1} for ^{235}U and 1.402 to 15.156 Bql^{-1} for ^{40}K. This study would be useful for used and official authorities for the assessment of radiation exposure risk due to usage of the considered spa waters.

1. Introduction

A thermal water is a natural mineral water, it having a set of characteristics which are likely to give it properties favorable to health, It contains minerals, salts, gases and sludge, likely to act effectively on health, also is clearly distinguished from other water intended for human consumption by its nature, such as the content of minerals, trace elements or other constituents, by its effects and by its original purity, these characteristics having been preserved intact due to the underground origin of this water thus kept away from any risk of pollution [1–6].The thermal establishments are spaces for relaxation, body care, well-being as well as therapeutic purpose. According to indications, hydrotherapy involves a range of methods and techniques to facilitate thermoregulatory reactions or fitness, his hot waters contain significant amounts of salts in solution (calcium carbonate or sulfate, sodium chloride, iron, magnesium, sulfides, traces of trace elements, including lithium) [7–9]. Some of them are gaseous: the hydrogen sulfide content is mostly low, while carbon dioxide is often abundant (effervescent waters). Those waters may also contain natural radioactive elements with variable concentrations according to the types of rock from which the soils originate and mainly depend on geological and geographical conditions [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

* *Corresponding author.*
E-mail address: *messaoudi2006@yahoo.fr ; m.messaoudi@crnb.dz*
Peer review under responsibility of University of El Oued.

http://dx.doi.org/10.5281/zenodo.5600855

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. Also, Radon inhalation is another important source of internal exposition in the spa, particularly for the staff [2]. Rémy and Lemaître 1990 [17] found that this natural exposition is two to three times higher in the granitic areas than in the sedimentary basins.

Directive 96/29 / Euratom [18], setting the basic standards relating to the protection of the population and workers against the ionizing radiation hazards, has identified hydrotherapy as a professional activity during which workers are exposed to natural radiation sources such as radon or thoron progeny.

Therefore, the objective of this work aims to assess the activity of radionuclides in eight-spa water from north Algeria using gamma spectrometry and to evaluate their radiological implications on the population used these waters.

2. Materials and Methods

2.1 Sample collection methodology

Sampling was carried out on March 2020. Samples locations are shown in Fig. 1 and their detailed coordinates are presented in Table 1.

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

The samples were collected in 1.5-liter plastic bottle at the eight spas. We collected the water by dropping the sampling bottles as close as possible to the spring discharge point to avoid any contamination from the surface. As the waters are completely clear, filtering of samples was not necessary.

Fig 1. Map showing samples location

2.2 Sample preparation

Waters from the spas studied were tightly sealed in Plastic Marinelli beaker of 450cm^3 volume using 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 step is necessary to make sure that radon gas is confined within the volume and the daughter product will remain in the sample.

2.3 Analytical methods of radioactivity

The detector of GeHP gamma spectrometer has an attractive ability to use bulk samples that mostly doesn't require any radiochemical preparation. 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. The detector element is enclosed in a 100 mm thick lead shield to reduce the natural external background radiation. The absolute efficiency response curve of a HPGe detector have been established in the energy range 60–1836 keV by measuring the absolute efficiencies using gamma-emitting radionuclide source supplied by the IAEA. 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. These radionuclides are packed within a resin matrix in a Marinelli beaker of 450cm^3 volume (Fig.2).

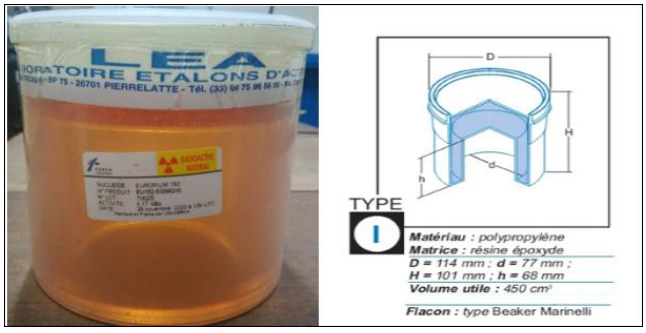

Fig 2. Gamma Source Embedded resin and Marinelli beaker

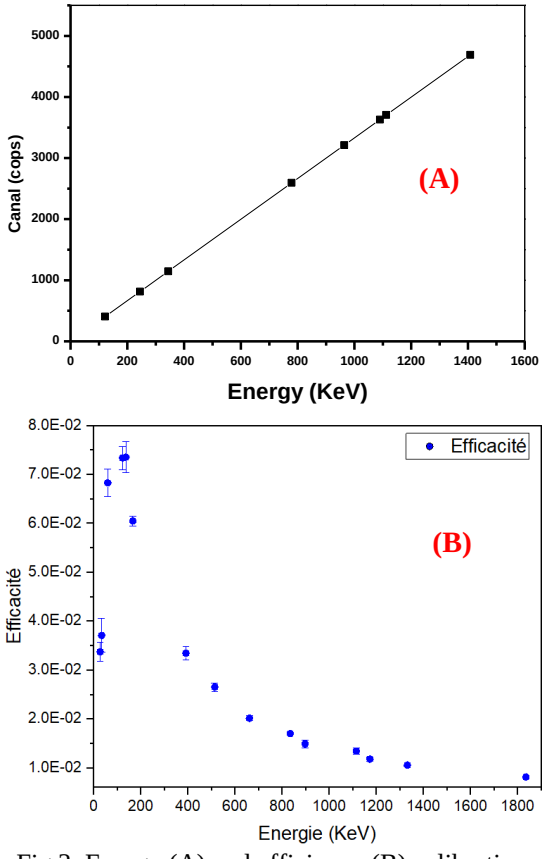

Fig 3. Energy (A) and efficiency (B) calibration

The advantage of using mono-energetic calibration sources is that they are free from decay-scheme effects and hence are best used for both absolute and total efficiency measurements. A suitable fitting function for the measured efficiencies is performed to enable the interpolation at other energies of interest and to improve the experimental estimates (Fig.3).The energy and efficiency calibrations of the spectrometer were carried out using standard sources of ^{252}Eu embedded in a resin matrix. The energy spectra emits in a range from 30 up to 1500 keV to cover all gamma energies of radionuclides of interest.

2.4 Background measurement

The background measurement is essential for present study because the measured activities from the samples are relatively low. The unsubtraction of the background from the measured activities may lead to an overestimation of the measurements. In order to keep the same measurement conditions, the background spectrum emanating from the detector environment was determined using deionized water sample poured in a Marinelli type I container during 24 hour of acquisition time. The background spectrum in the Figure 4, reveals the presence of radionuclides of the uranium and thorium series.

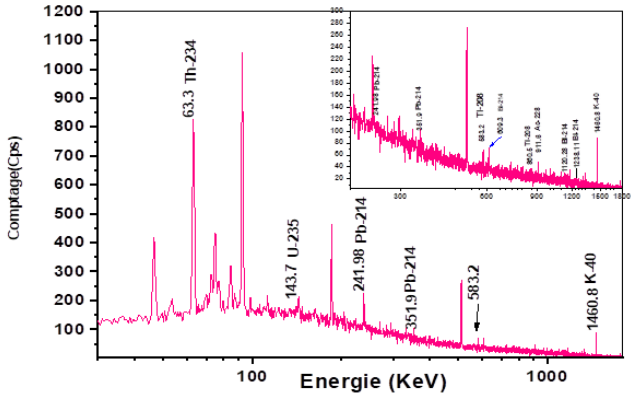

Fig 4. Background spectrum from deionized water.

2.5 Minimum Detectable Activity (MDA) Measurement

The low-level radioactivity measurements in environmental samples leads to a likely obtain an inappropriate ray. This fact is due to the important random statistical fluctuation of the background count rate. In such cases, we have to determine the achievable lowest activity, MDA, for each considered gamma rays. It is a specific energy measure of the activity required to identify a source within a statistical certainty (95% in this case).

According to Curie equation, Table 2 summarizes the MDA given for each considered energy

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

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

3. Results and discussion

Most of the measurement data were presented by their mean ± the standard deviation due to statistical analysis using Gamma Vision and the efficiency calculation. Firstly in the Table 3, we have presented the results of the radionuclides counts obtained by GeHP gamma spectrometer detector.

A set of measurements was made using gamma spectrometry over 24 hours for all samples in order obtain an activity with reliably low incertitude (see fig.5).

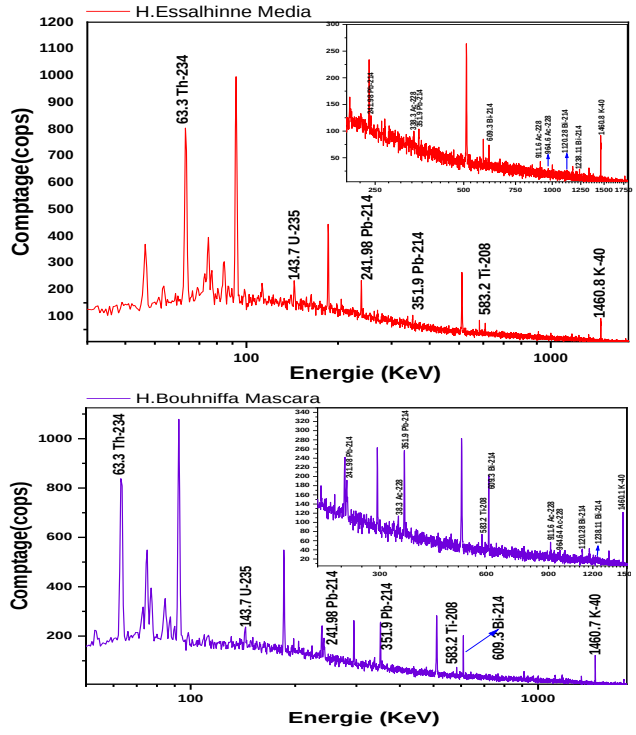

Fig 5. The spectrum of γ radiation emitted by the sample of hammam Essalhinne Media and Bouhniffa respectively.

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 ^{226}Ra activity is then deduced from equation (01), as represented in fig.6.

$$A_{^{226}\mathrm{Ra}}\,(Bq/kg)=\frac{A_{^{214}Bi}+A_{^{214}Pb}}{2} \qquad (01)$$

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 Radioactivity in thermal water samples maybe depends on some factors, like as the interaction between water and the solid phases, therefore, the result show the concentrations of radionuclides in the various types of water samples vary over a large range.

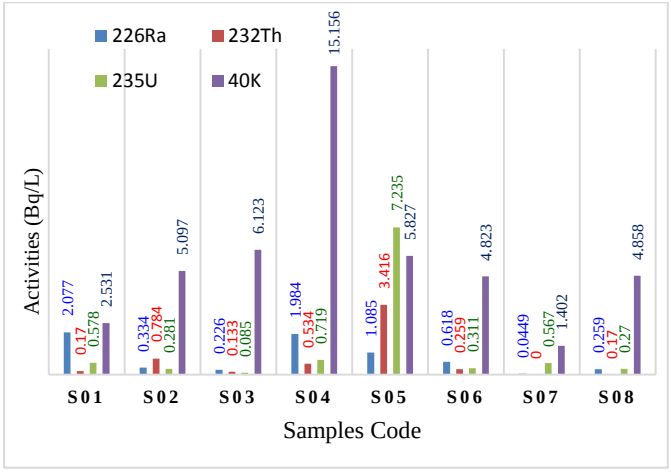

Fig 6. Radionuclide Activity Concentration for different thermal spring samples

For radiological consideration, the ^{226}Ra 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}Rn 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	$^{214}_{82}$Pb	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
	$^{214}_{83}$Bi	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	$^{228}_{89}$Ac	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	$^{235}_{92}$U	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
^{40}K		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
^{226}Ra		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 those results obtained in this work, we can note that with the exception of H. Essalhine-Media thermal water, which has an activity below at all the remain thermal water samples analyzed are unfit for everyday consumption, but maybe used just for short time corresponding to the cure duration because of the risk to a human being during his whole lifetime.

4. 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 investigated. These values obtained in this work are considered to be very important for Algerian public health as these thermal water supplies are mainly used for therapy and/ or consumption purposes unconsciously since people.

Depending on the radioactive properties of these thermal waters examined, they can cause problems when using therapeutic treatments for a long time, in addition, this thermal water cannot be used for drinking purposes.

Conflict of Interest

The authors declare that they have no conflict of interest.

Acknowledgements

This work has been carried out at NUR Research reactor (CRND). The authors thanks all the members of the Department of Neutron Activation Analysis for the technical assistance.

References

1. Duran SU, Kucukomeroglu B, Damla N, Taskin H, Celik N, Cevik U, Ersoy H. Radioactivity measurements and risk assessments of spa waters in some areas in Turkey. *Isotopes in Environmental and health Studies*. 2017;53(1):91-103.
2. Karakaya MÇ, Doğru M, Karakaya N, Kuluöztürk F, Nalbantçılar MT. Radioactivity and hydrochemical properties of certain thermal Turkish spa waters. *Journal of water and health*. 2017;15(4):591-601.
3. Salahel Din K, Ali K, Harb S, Abbady AB. Natural radionuclides in groundwater from Qena governorate, *Egypt. Environmental Forensics.* 2021;22(1-2):48-55.
4. Ahmad N, Khan A, Ahmad I, Hussain J, Ullah N. Health implications of natural radioactivity in spring water used for drinking in Harnai, Balochistan. *International Journal of Environmental Analytical Chemistry*. 2021;101(9):1302-1309.
5. Donné Z, Rasolonirina M, Djaovagnono HC, Kall B, Rabesiranana N, Rajaobelison J. Study of water radioactivity transfer from telluric origin in the Amber Mountain, Antsiranana, *Madagascar. Scientific African*. 2021:e00902.
6. Mourad S, Ayoub GM, Al Hindi M, Zayyat RM. Occurrence and hazard assessment of natural radioactivity in drinking water in South Lebanon. *Environmental Monitoring and Assessment*. 2021;193(6):1-22.
7. Goldscheider N, Mádl-Szőnyi J, Erőss A, Schill E. Thermal water resources in carbonate rock aquifers. *Hydrogeology Journal*. 2010;18(6):1303-1318.
8. Dvorjetski E. Leisure, Pleasure and Healing: Spa culture and medicine in ancient eastern Mediterranean. Brill; 2007.
9. Chowdhury RS, Islam MD, Akter K, Sarkar MA, Roy T, Rahman ST. Therapeutic Aspects of Hydrotherapy: A Review. *Bangladesh Journal of Medicine*. 2021;32(2):138-41.
10. Akiko Tanigava P. Natural radioactivity in Brazilian bottled mineral waters and consequent doses. *Journal of Radioanalytical and nuclear chemistry.* 2001;249(1):173-176.
11. Milena-Pérez A, Piñero-García F, Benavente J, Expósito-Suárez VM, Vacas-Arquero P, Ferro-García MA. Uranium content and uranium isotopic disequilibria as a tool to identify hydrogeochemical processes. *Journal of Environmental Radioactivity*. 2021;227:106503.
12. Bignall ON, Caldwell T. Radon (222Rn) Concentration in Fresh and Processed Coconut Water Using a RAD7 Detector. *Natural Science*. 2021;13(9):425-436.
13. Pintilie-Nicolov V, Georgescu PL, Iticescu C, Moraru DI, Pintilie AG. The assessment of the annual effective dose due to ingestion of radionuclides from drinking water consumption: calculation methods. *Journal of Radioanalytical and Nuclear Chemistry*. 2021;327(1):49-58.
14. Sánchez AM, Tomé FV, Quintana RO, Escobar VG, Vargas MJ. Gamma and alpha spectrometry for natural radioactive nuclides in the spa waters of Extremadura (Spain). *Journal of environmental radioactivity*. 1995;28(2):209-220.
15. Arabi AE, Ahmed NK, Salahel Din K. Natural radionuclides and dose estimation in natural water resources from Elba protective area, Egypt. *Radiation protection dosimetry*. 2006;121(3):284-292.
16. Ben Fredj A, Hizem N, Chelbi M, Ghedira L. Quantitative analysis of gamma-ray emitters radioisotopes in commercialised bottled water in Tunisia. *Radiation protection dosimetry*. 2005;117(4):419-424.
17. Remy ML, Lemaitre N. Radioactivity in mineral waters. *Hydrogeologie*. 1990:267-278.
18. Directive C.: 96/29/Euratom of 13 May 1996 laying down basic safety standards for the protection of the health of workers and the general public against the dangers arising from ionizing radiation. *Official Journal of the European Communities L*. 1996:159; 10.
19. Knoll GF. Radiation detection and measurement. John Wiley & Sons; 2010.
20. Salehipour A, Eslami A, Mirzaee M, Bolori F, Saghi MH, Bahmani Z, Hashemi M. Spatial distributions of natural radionuclide concentrations of bottled mineral water: doses estimation and health risk assessment. *Environmental Health Engineering and Management Journal*. 2020;7(2):107-17.
21. Nuccetelli C, Rusconi R, Forte M. Radioactivity in drinking water: regulations, monitoring results and radiation protection issues. *Annali dell'Istituto superiore di sanità*. 2012;48:362-373.
22. EPA U. United States Environmental Protection Agency, National primary drinking water regulations: In Radionuclides Rule. *Federal Register.* 2001:76708-76753.

Recommended Citation

Azli T, Zidouni F, Messaoudi M, Mesbout B, Hadri A, Begaa S. Gamma spectrometry for natural radioactive nuclides in Spa waters in some areas in north Algeria. *Alger. J. Eng. Technol. 2021*, 5:43-48. http://dx.doi.org/10.5281/zenodo.5600855