GAMMA AND ALPHA SPECTROMETRY AND EMANATION OF THERMOMINERAL WATERS OF TUNISIA

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(Soumis en avril 2000, accepté en janvier 2001)

ABSTRACT : In Tunisia, 22 out of 60 registered thermomineral springs are being used either for therapeutic purposes or commercial waters. This study identifies and quantifies natural radioelements in thermal and mineral waters in Tunisia, using analytical methods which include γ-ray spectrometry, α-particle spectrometry and ^{226}Ra by the emanation method. Radioactivity is essentially due to potassium, radium, uranium and thorium. The results show that the activities of these waters are lower than the maximum concentrations allowed by the International Commission of Radiological Protection (ICRP) for drinking water, and seem to satisfy the recommendations of the World Health Organisation (WHO). Consumption of these waters does not represent any hazard to public health.

Keywords : Radioactivity, mineral water, thermal water, radioisotopes

RESUME : En Tunisie, 22 sources thermominérales sont exploitées, parmi les 60 recensées. Elles sont soit utilisées à des fins thérapeutiques en établissement thermal, soit commercialisées en tant qu'eau de boisson. Cette étude, porte sur l'analyse radioactive des sources thermominérales tunisiennes par les techniques appropriées de la spectrométrie γ, de la spectrométrie α et la méthode dite d'émanation. L'étude a consisté à identifier et à quantifier les radioéléments naturels présents dans ces eaux. Leur radioactivité est due essentiellement au potassium, au radium, à l'uranium et au thorium. Les résultats obtenus montrent que la radioactivité dans ces eaux est faible. Les activités volumiques mesurées sont inférieures aux concentrations maximales admissibles retenues par la Commission Internationale de Protection Radiologique (CIPR) pour l'eau potable et en accord avec les directives de la qualité pour l'eau de boisson de l'Organisation Mondiale de la Santé (OMS). La consommation des eaux étudiées ne présente pas de risque sanitaires.

Mots clés : Radioactivité, eau minérale, eau thermale, radioisotopes

I. INTRODUCTION

When passing through various deep geological layers, thermomineral waters carry away radioactive elements belonging to natural radioactive families [1]. This radioactivity had always

been considered beneficial. However, since adverse biological effects of radioactivity have become known, much research has been devoted to health aspect of these waters by analysis of their radioactivity [2,3]. There have been no prior studies in Tunisia on the radioactivity of our thermomineral sources. Thus, as a first step, we have conducted a survey of radioactive elements in 12 wells in one area northeaster Tunisia (Ben Arous, Nabeul and Zaghouan). The source at Aîn Oktor is the only cold mineral spring among the set.

II. EXPERIMENTAL PROCEDURE

II.1- Gamma spectrometry

The outstanding advantage of γ-ray spectrometry is its ability to measure γ-ray emitters in a sample without the need for chemical separations. γ-ray spectrometry allows both qualitative identification and quantitative determination of radionuclides [4]. This method can be used to determine γ-emitting radionuclides with energies ranging from 60 to 2000 keV in a large variety of samples.

II.1.1- Materials and methods

The instrumentation used for the γ-ray spectrometry consists of a high-purity, high-resolution germanium semiconductor detector, associated with an amplification system and a multichannel analyser.

γ spectrometry needs an energy and efficiency calibration. Energy calibration is performed using an uranium standard of a certified activity of 3700 Bq. The uranium spectrum presents several peaks that are easily identifiable and that cover a wide energy range. Efficiency calibration is performed using mixte standard in 2L Marinelli beaker geometry containing the following isotopes (^{241}Am, ^{109}Cd, ^{57}Co, ^{139}Ce, ^{51}Cr, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{60}Co, ^{88}Y).

For the γ-ray spectrometry, the sample was measured directly in a Marinelli beaker (2L). The activities of the samples were relatively low, so the statistical significance of the results was improved by setting the counting time at 24 hours.

To check the precision of each result, the samples were analysed twice on the same detector at the *Centre National de Radioprotection* (CNRP) in Tunis and a third time by in an intercomparison with the *Office de Protection contre les Rayonnements Ionisants (OPRI)* in France.

II.1.2- Gamma-ray Results and Discussion

The spectrum for each sample includes several peaks which cover the same energy range as the calibration source.

The activity of ^{40}K is determined through the 1460 keV γ-ray and the activity of ^{235}U is determined through the 143 keV γ-line. ^{226}Ra activity is determined using the count rate from the 186 keV peak after subtracting the contribution de ^{235}U of the same peak.

The results of the γ-ray measurements are shown in Table I. They are given with uncertainties of 2σ.

The most important contribution to the total radioactivity of these waters comes from ^{40}K.
Among the waters studied, the richest in potassium are those of Jebel Oust and Hammam Jedidi, with respectively 6.2 and 5.9 Bq/L. For the other springs the activities are lower, and often below the limit of detection.
Compared to some French springs like Marie-Christine Nord with 6.3 Bq/L of ^{40}K or Preuschdorf with 13.7 Bq/L of ^{40}K [5,6], the ^{40}K activity of most of the Tunisian waters is low. These values are lower than those found in seawater (14.8 Bq/L).

TABLE I : Gamma-ray activities of radioelements in 12 thermomineral springs in Tunisia (Bq/L)

Spring	^{40}K	^{226}Ra	^{228}Th	^{235}U
Aîn El Bey	4. 2 ± 1.9	< 4.6	< 0.80	< 0.28
Aîn El Ariane	3.9 ± 1.8	< 3.3	< 0.66	< 0.20
Aîn Oktor	< 2.6	< 2.9	< 0.49	< 0.26
Aîn Sbia	2.7 ± 1.8	< 3.3	0.89 ± 0.40	< 0.20
Aîn Echfa	3.0 ± 1.8	< 3.2	< 0.56	< 0.19
Aîn Arraka	< 4.1	< 3.3	< 0.83	< 0.20
Aîn Fakroun	< 3.3	< 4.8	< 0.74	< 0.29
Aîn El Atrous	< 3.2	< 3.3	< 0.54	< 0.20
Aîn Kalaa Srira	3.4 ± 1.8	< 3.7	0.74 ± 0.40	< 0.22
Hammam Jedidi	5.9 ± 2.0	< 3.3	< 0.49	< 0.20
Jebel Oust	6.2 ± 1.9	n.d	0.90 ± 0.40	n .d
Hammam Zriba	< 3.6	< 4.0	< 0.54	< 0.24

n.d : not detected

II.2-Alpha spectrometry

The thorium and uranium isotope analyses were performed by α-particle spectrometry in a gridded ionisation chamber after chemical separation of these elements. The chemical protocol used was that of the radiochemical laboratory at OPRI in France. All the reagents used were analytical grade.

II.2.1- Materials and methods

The instrumentation used for the α-particle spectrometry is composed of a detector (gridded ionisation chamber), a pneumatic circuit, an amplification system and a multichannel analyser.

As for γ spectrometry, α spectrometry also needs an energy and efficiency calibration. This was accomplished using a mixte alpha standard of ^{238}U, ^{234}U, ^{239}Pu, ^{241}Am.
Spectra were collected over a sufficient time to obtain good statistics.

*** Uranium α-particle spectrometry**

At first sampling, a quantity of internal standard (^{232}U) was added. The solution was dissolved in 40 mL of 4% sodium diethyldithiocarbamate and 6 mL of 40% ammonium thiocyanate.
The uranium was precipitated by adding 12 mL methyl purple.

After stirring for 30 min, the solution was filtered. Filters were washed with a few mL of water. After ashing at 560°C for 20 h, the residue was dissolved with 5 mL of 2.5 M HNO_3 and heated in a boiling water bath for 1 h. After centrifugation and decantation, 2 ml of this solution was taken and added to 6 mL of doubly distilled water and 4 mL of ammonium oxalate. The uranium was electrodeposited onto a stainless steel disc which was counted for α-particles using the gridded ionisation chamber.

*** Thorium α-particle spectrometry**

The radiochemical protocol adopted for the thorium separation is summarised as follows [7].
An internal standard (^{229}Th) was added at the start of the chemical preparation. It was dissolved in 100 mL of conc. HNO_3 and dried. The residue was redissolved with 30 mL of conc. HNO_3 and 10 mL 30% H_2O_2 and then dried. This was repeated three times. The residue was dissolved with 100 mL of 1 M HNO_3 and 5 mL of $Fe(NO_3)_3$ at pH 7.
The precipitate containing the thorium was separated by centrifugation and dissolved in approximately 100 mL of 7 M HNO_3. The thorium fraction was obtained by passing this solution through an anion exchange column (BIO-RAD. AG 1X4 50-100 mesh) prepared with 100 mL of 7 M HNO_3. The thorium was retained and the americium fraction was eluted with 100 mL of 7 M HNO_3. The purified thorium fraction was finally eluted with 100 mL of 9 M HCl . It was dried, and the residue was dissolved with 50 mL of 0.2 M HCl, stirring for 30 min. The pH was adjusted to 1.9, 1 mL of LaO_2 and 1 mL of 40% HF were added. After stirring for 20 min, the solution was filtered through a 0.22 µm Millipore membrane. These filters were counted in the gridded ionisation chamber where the signal strength was directly proportional to the energy of the particles emitted by the sample.

Chemical yield is about 70 to 80%.

II.2.2- Results and discussion

The spectra consisted of a series of irreguliar peaks, with a tailing on the low-energy side due to α-particle energy loss in the source which was not always thin enough, and to diffusion in the deposit and on the walls of the chamber.

Generally, uranium activities in these waters were very low (see Table II). In spite of the higher values of 0.08 Bq/L for ^{234}U and 0.04 Bq/L for ^{238}U measured for the Jebel Oust spring, the activities of the whole set of waters were low. In Finland, for example, some waters have activities above 1,5 Bq/L in uranium, which means a high uranium concentration in the subterranean rocks [5]. Among French springs, those of the *Massif Central* often contain uranium. The most remarkable instance is the Badoit water with 0.9 Bq/L of ^{238}U and 2.5 Bq/L of ^{234}U [5,6]. This activity is not considered dangerous because the maximum allowed concentration of uranium is 20 times higher than the activity found in the Badoit water [8].

Thorium is less abundant in these waters. It may disappear by adsorption on solid particles. Activities of ^{232}Th are below the lower limit of detection of our measuring system, but they are significant for ^{230}Th and the ^{228}Th counts with however, a large uncertainty (Table III).
The values range from 3.8 to 10.8 mBq/L for ^{230}Th and from < 3.7 to 29.6 mBq/L for the ^{228}Th.
The low values of activities of thorium generally found in the thermomineral waters is consistent with its low solubility (Figure 1).
Isotopic analysis has show an important disequilibrium in terms of exces ^{234}U with respect to ^{238}U which can be explained by various means [3].

II.3- Emanation procedure for ^{226}Ra

^{226}Ra was measured indirectly by scintillation counting of the emanation of its first daughter (^{222}Rn) by the method proposed by Lucas [9] .

II.3.1- Materials and methods

Radium in solution can be determined by transferring its radon daughter into a scintillation vessel for measurement. The technique is specific and can be applied to almost any material which can be converted to a homogeneous solution. The radon is transferred by bubbling an inert gas through the solution after equilibrium with ^{226}Ra has been established. The lower detection limit is 30 mBq/L of ^{226}Ra for a 250 mL test sample.

II.3.2- Results and discussion

Values for concentrations (mBq/L) are presented in Table IV.

If we compare activities of ^{226}Ra in Tunisian waters studied with those in waters from other countries, in France for example, we find that among the most radioactive in ^{226}Ra are those of Saint-Alban and Bourbonne-les-Bains with respectively 1.8 and 2.7 Bq/L. In Central Europe, Mondorf has 15 Bq/L and Aditos, 4.8 Bq/L [6]. We notice that the majority of Tunisian waters have a comparatively low radioactivity.

The most radioactive water in radium is that of Jebel Oust with 3.9 Bq/L, which is still low, since the maximal concentration allowed by the ICPR for drinkable water is 8.5 Bq/L [8]. For the other springs, the activities satisfy the quality recommendations for potable water of the WHO.

TABLE II : Activities of the uranium isotopes in 12 thermomineral Springs in Tunisia by alpha spectrometry (mBq/L)

Spring	^{238}U	^{234}U	^{235}U
Aîn El Bey	5.1 ± 20%	11.6 ±15%	< 1.5
Aîn El Ariane	3.4 ± 27%	10.3± 17%	< 3.0
Aîn Oktor	1.9 ± 33%	3.8 ± 27%	< 2.5
Aîn Sbia	21.0 ± 12%	31.1± 12%	< 2.5
Aîn Echfa	1.6 ± 41%	2.3 ± 34%	< 1.4
Aîn Arraka	3.8 ± 23%	5.3 ± 21%	< 1.9
Aîn Fakroun	3.4 ± 31%	4.3 ± 26%	< 1.3
Aîn El Atrous	1.5 ± 39%	1.1 ± 36%	< 1.6
Aîn Kalaa Srira	2.5 ± 32%	4.3 ± 24%	< 1.9
Hammam Jedidi	8.4 ± 29%	17.0± 19%	< 3.7
Jebel Oust	42.7± 17%	82.2± 6%	< 4.0
Hammam Zriba	8.9 ± 2 3%	21.0± 16%	< 1.8

N.B : Statistical counting error 2σ

TABLE III : Activities of the thorium isotopes in 12 thermomineral springs in Tunisia measured by α-particle spectrometry (mBq/L)

Spring	^{232}Th	^{230}Th	^{228}Th
Aîn El Bey	< 4.5	3.8 ± 43%	8.1 ± 23%
Aîn El Ariane	< 4.6	6.8 ± 26%	2.1 ± 15%
Aîn Oktor	< 2.9	4.5 ± 31%	2.3 ± 38%
Aîn Sbia	< 4.3	6.0 ± 26%	2.9 ± 13%
Aîn Echfa	< 4.0	10.8± 19%	20.0 ± 15%
Aîn Arraka	< 3.2	6.7 ± 20%	21.4 ± 12%
Aîn Fakroun	< 2.7	6.6 ± 21%	12.1 ± 15%
Aîn El Atrous	< 3.7	7.1 ± 20%	7.8 ± 19%
Aîn Kalaa Srira	< 3,0	4,1 ± 29%	13,1± 15%
Hammam Jedidi	< 3.4	8.0 ± 23%	10.2± 19%
Jebel Oust	< 3.4	7.6 ± 20%	29.6± 12%
Hammam Zriba	< 3.1	5.2 ± 28%	< 3.7

N.B : Statistical counting error 2σ

TABLE IV: Activities of the ^{226}Ra in 12 thermomineral springs in Tunisia (mBq/L)

Spring	^{226}Ra
Aîn El Bey	551 ± 26
Aîn El Ariane	110 ± 3
Aîn Oktor	< 34
Aîn Sbia	603 ± 26
Aîn Echfa	757 ± 33
Aîn Arraka	478 ± 24
Aîn Fakroun	599 ± 28
Aîn El Atrous	761 ± 33
Aîn Kalaa Srira	436 ± 22
Hammam Jedidi	1101 ± 66
Jebel Oust	3903 ± 21
Hammam Zriba	272 ± 26

N.B : Statistical counting error 2σ

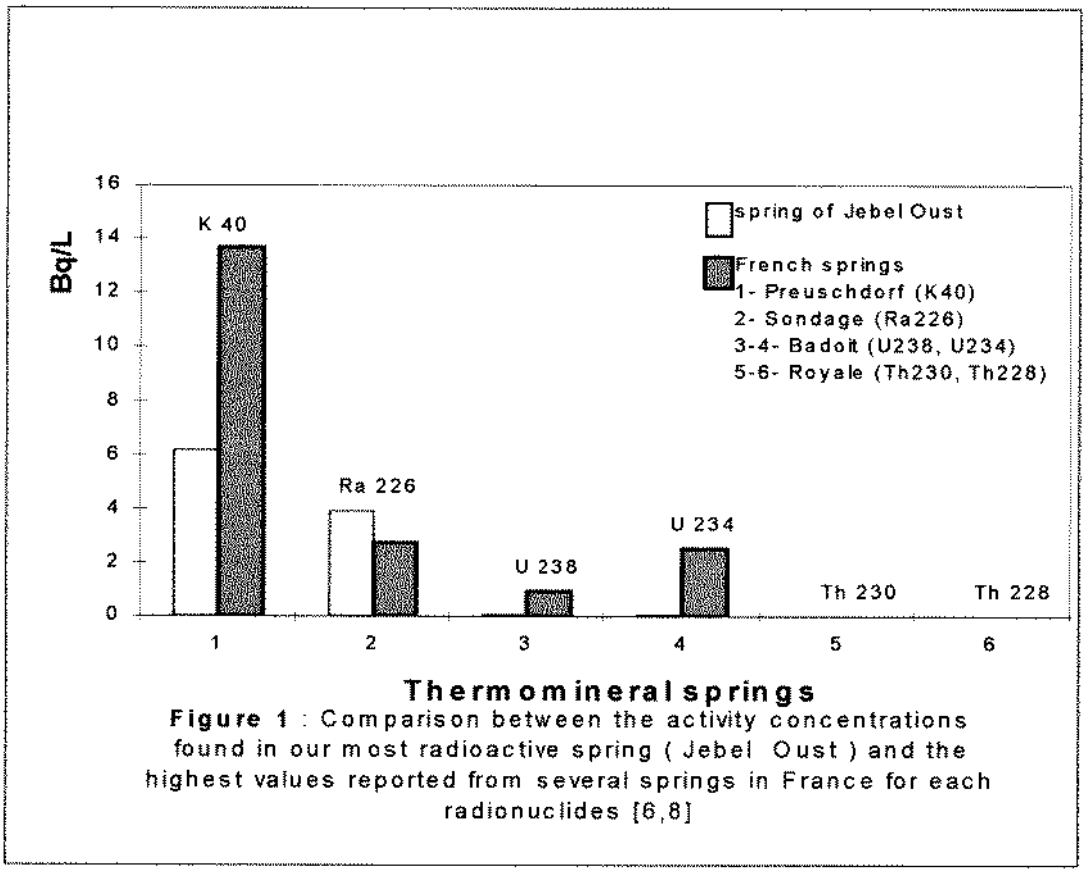

Figure 1 : Comparison between the activity concentrations found in our most radioactive spring (Jebel Oust) and the highest values reported from several springs in France for each radionuclides [6,8]

III. CONCLUSION

This study identifies the naturally-occurring radioelements in 12 thermomineral springs in Tunisia and measures their activities using different methods. The results show that the activities of measured radioelements which are related to the kind of geological strata crossed by the water are lower than the maximum concentration levels allowed by the ICRP for potable water and in general satisfy WHO recommendations [10].

The activity is essentially due to potassium, to radium and, at a lower level, uranium and thorium. Comparison of our results with those from other countries reported in literature shows that thermomineral waters in Tunisia have a lower radioactivity level, and the consumption of any of these waters does not present any hazard for public health.

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