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Determination and evaluation of gross alpha and beta activity concentrations and metal levels in thermal waters from Ankara, Turkey

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Abstract: The gross α and β activity concentrations in the thermal waters of Karakaya-Ayaş, İçmece-Ayaş, Beypazarı (Dutluk-Tahtalı), Haymana, and Kızılcahamam spas in Ankara Province were measured by MPC-9604 multi-detector α/β counting system. Ranges of activity concentrations found were from 0.09 to 2.58 Bq L^{-1} for gross α and from 0.25 to 2.61 Bq L^{-1} for gross β. The ranges of minimum detectable concentrations for gross α (0.05–0.41 Bq L^{-1}) and for gross β (0.04–0.29 Bq L^{-1}) were obtained. Gross α and β activity concentrations found in samples were compared with the recommended guidelines of the World Health Organization and the Turkish Standards, and literature values. Na, K, Ca, Si, Mn, Ce, Te, Nd, Sm, Cs, W, La, U, and Th metal levels in these thermal ground waters were also determined by using wavelength dispersive X-ray fluorescence spectrometry (WDXRF).

Key words: Thermal waters, activity, gross α and gross β, WDXRF, spa

1. Introduction

Thermal waters coming from underground by drilling in spas (sanus per aquam) are important for human health, ecology, and the environment because of their consumptions by people and their ability to transport pollutants into the environment.[1−3] There are many spas in different parts of Turkey and 5 of them are the well-known Karakaya-Ayaş, İçmece-Ayaş, Beypazarı (Dutluk-Tahtalı), Haymana, and Kızılcahamam spas in Ankara Province. These spas are important recreation sites and health resorts. Thermal ground waters in these spas are consumed by people through drinking and taking baths and are used for the heating of buildings and irrigation of local fields. These waters may contain natural radioactivity related to gross α and gross β radiation, and metals such as Na, K, Ca, Th, and U. The presence of thorium and uranium in these water samples is particularly important because of their toxicity to the human body and the environment.[1−4] Th-232, U-235, U-238, and K-40 radionuclides are α and β emitters.[5] Natural radioactivity in water, particularly in ground water, mainly comes from these radionuclides in the earth's crust and in the environment.[3,6] Gross α is generally more important than gross β for natural radioactivity in water as it is related to the radioactivity of Th, U, and their decay products.[3] People using these spas are advised to be extra cautious about radioactivity because of the danger that the therapeutic water can be internally consumed by the bathers. Therefore,

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determinations of gross α and β activity concentrations in thermal waters of spas are important due to their potential health hazard to the population.

Measurements of natural radioactivity in drinking waters,[1,2] thermal waters used at spas,[7] natural mineral waters,[8] and waters of rivers and lakes[9] have been studied in various parts of the world for assessment of the activity levels of water consumed and for health risk. Water quality standards have been assessed by many countries to meet their national priorities, considering their economic, technical, social, cultural, and political needs.[1]

The evaluation of radioactivity concentrations in drinking waters with international recommended guideline activity concentrations is an important subject for human health. The activity concentrations in drinking waters recommended by the WHO[10] are 0.5 Bq L^{-1} for α and 1.0 Bq L^{-1} for β. Below these levels of gross activity, ground or drinking waters used for human consumption are acceptable and research is not necessary to reduce radioactivity.[9–11] In Turkey, according to the first guideline recommended by the Turkish standard,[12] gross α and β activity levels in drinking waters should be lower than 0.1 and 1.0 Bq L^{-1}, respectively. The second Turkish standard for natural mineral waters[13] has recommended that the gross α and β activity concentrations should be lower than 1.5 and 2.0 Bq L^{-1}, respectively. However, there has been no information about radioactivity measurements reported in thermal waters so far. If gross α or gross β activity concentrations in water samples exceed these guidelines, gross α and β activities or radionuclides have to be identified and their individual activities have to be measured.[1,14]

Determination of metals such as Th, U, and K in thermal spring waters is also important for investigating the origin of gross α and β radiations.[1,6] X-ray fluorescence (XRF) spectrometry is one of the most commonly used analytical techniques to determine the metals in all different materials in fields such as soil science, the food industry, mineralogy, geology, and environmental analysis of water samples and waste minerals.[15] XRF is a fast, accurate, and nondestructive method that usually requires a minimum sample preparation.

In the present study, gross α and gross β activity concentrations, heavy metals such as U and Th, and major elements (Na, K, and Ca) in the thermal ground waters of the Karakaya-Ayaş, İçmece-Ayaş, Beypazarı (Dutluk-Tahtalı), Haymana, and Kızılcahamam spas were determined. The relations between gross α and β activities and concentrations of U, Th, and K were investigated. The activity concentrations of gross α and β found were compared and evaluated according to the guidelines for drinking water quality recommended by the WHO, national guidelines, and previous studies on waters. The gross α and β activity concentrations found in these thermal waters will contribute to a radioactivity database in the future.

2. Experimental

2.1. Reagents and solutions

Nitric acid solution (1% v/v) was prepared by diluting HNO_3 (65% m/m, analytical grade, Merck, Darmstadt, Germany) with high purity deionized water (resistivity 18.3 MΩ cm) obtained by an ultrapure water system (Human power I^+, Human Corporation, Korea) and diluted to suitable concentrations throughout.

2.2. Collection and preparation of samples

In order to measure gross α and β activity values and perform the elemental analysis in thermal waters, samples were collected from the Karakaya-Ayaş, İçmece-Ayaş, Beypazarı, Haymana, and Kızılcahamam spas located in Ankara Province. The sampling sites are shown in the Figure. Three samples were taken from each site. Temperatures of samples measured at the sampling site using a thermometer were 31 °C, 52 °C, 50 °C, 44 °C, and 75 °C for Karakaya-Ayaş, İçmece-Ayaş, Beypazarı, Haymana, and Kızılcahamam, respectively. The pH values of all samples measured by a field pH-meter were from 5.0 to 8.0. The samples were collected in 2.5-L capacity polyethylene bottles that were previously cleaned with HNO_3 solution (1% v/v) and rinsed with the sample solution twice. Collected samples in bottles were immediately acidified with HNO_3 up to 1% v/v in situ to avoid the collection of organic materials and to prevent precipitation and adsorption of sample into the walls of the container.[2,9,14] Samples were taken to the laboratory for analysis.

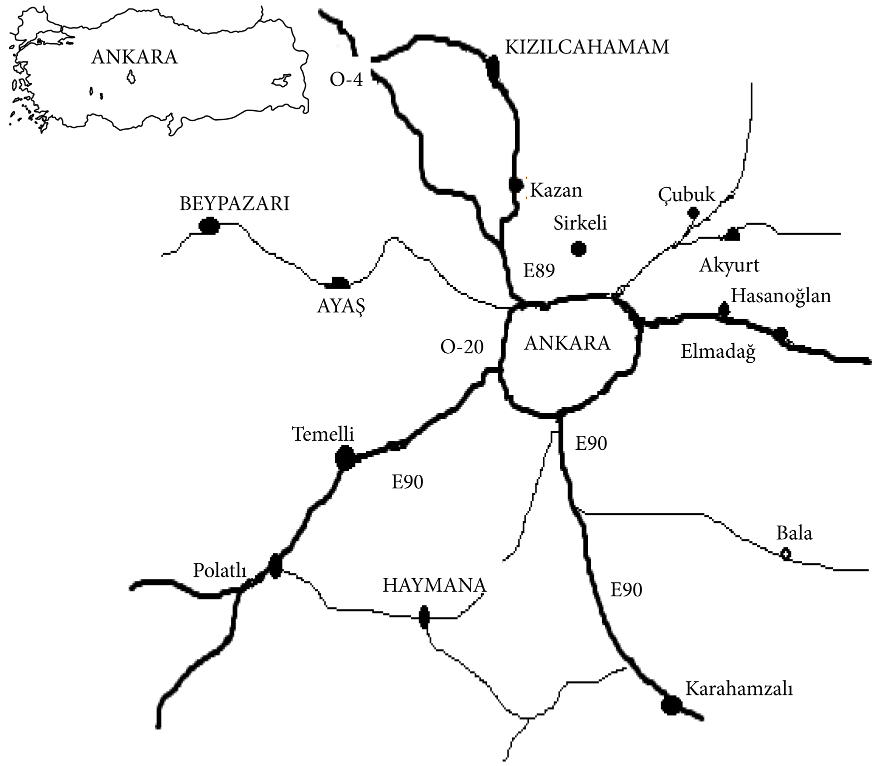

Figure. Map of the sampling sites.

Samples (20–100 mL portions) were slowly evaporated up to about 4 mL volumes (to avoid boiling) under an IR lamp. Then each sample was transferred into a stainless-steel planchette and dried until a solid precipitation was obtained. The sample precipitation was left at ambient temperature in a desiccator and was then weighed accurately.[16] Each precipitation in the planchette was directly applied to the α/β counting system.

For element analysis, thermal waters in 400-mL beakers were slowly evaporated without boiling under an IR lamp until dry precipitation occurred. The precipitate was pressed, weighed accurately, and applied to the XRF spectrometer.

2.3. Instrumentation

A multi-detector α/β counting system (MDS) (Protean Instrument Corporation, USA) consisting of one or more MPC-9604 units was used for the determinations of gross α and β activity concentrations in water samples. Each PIC-MPC-9604 unit contains 4 completely independent sample detectors, a guard detector, and lead shielding used to attenuate external radiation. The sample detectors have gas flow window-type counters equipped with an ultrathin window.[9] A gas mixture (10% methane and 90% argon) and stainless-steel planchettes were used for counting. The operating voltage on the detector was selected as 1515 V.

A PANalytical Advanced Axios Wavelength Dispersive X-Ray Fluorescence Spectrometer (WDXRF) equipped with an SST-mAX X-ray tube, which has 4 kW power output and 160 mA maximum emissions current, was used for the determination of metals.

2.4. Measurements of gross α and β activity concentrations in samples

The α and β energies of the α/β counting system were calibrated by preparing equal concentrations of ^{241}Am (913 Bq) and ^{90}Sr (931 Bq) standard samples, respectively. The counting times of the samples were selected as 900 min for gross α and β activities since the levels of radioactivity encountered in water samples were very low. Three samples were counted for each site. The background of the detector was determined by using a clean, empty planchette in the detector. Background counting times were 120 min for all samples. Efficiency and background data for the detector were collected, stored, and used for corrections in countings. Gross α and β activity concentrations (A(Bq L^{-1})) of samples and minimum detectable concentrations (MDC) for gross α or gross β were simply calculated by using the following equations:

$$A(Bq/L) = \frac{NetA}{AD \cdot \varepsilon\% \cdot AF \cdot V} \tag{1}$$

$$MDC(Bq/L) = \frac{\frac{3}{T_S} + 3.29 \cdot \sqrt{\frac{R_B}{T_S} + \frac{R_B}{T_B}}}{AD \cdot \varepsilon\% \cdot AF \cdot V \cdot 60} (\text{Brodsky method}) \tag{2}$$

where $NetA$ is the activity difference between sample and background in Bq, AD is activity divisor, $\varepsilon\%$ is the percent counting efficiency of the detector for gross α or gross β, AF is the efficiency attenuation factor of α or β or α to β for samples extracted from the calibration attenuation curves (attenuation factor is a ratio of the absolute attenuation factor extracted from the calibrated attenuation curve for the mass of the sample being analyzed and the absolute attenuation factor for the mass of the source used in the efficiency calculations), and V (in L) is the volume of sample. T_S and T_B are sample and background counting times (in minutes), respectively. R_B is the background counting rate for gross α or gross β per minute.

3. Results and discussion

3.1. Gross α and β activity concentrations in thermal waters

From the α/β counting system, AD, $\varepsilon\%$, AF, and MDC were obtained. AD was 1.00 for gross α or gross β. The $\varepsilon\%$, AF, and MDC found are given in Table 1.

By combining the instrumental parameters (AD, $\varepsilon\%$, AF and background counting time, etc.) and sample parameters (sample residual mass, volume, and sample counting time), the mean gross α and β activity concentrations (A) found for 3 samples taken from each sampling site were calculated and are given in Table 2.

The gross α and β activities found in thermal waters were compared with the maximum permissible values of the Turkish standards[12,13] and the WHO guidelines for drinking water quality.[10] It was explained that gross α and β activities recommended by the WHO[10] are for tap, well, and river waters, but thermal water is not in this range.[1] As shown in Table 2, the ranges of gross α and β activity concentrations in the sample solutions are from 0.09 to 2.58 Bq L^{-1} for gross α and from 0.25 to 2.61 Bq L^{-1} for gross β. Some of the α activity concentrations found in the samples were higher than the permissible values given by the WHO and Turkish standards. The large amounts of β activity observed in samples were in agreement with the permissible values given in the Turkish standard.[13]

Table 1. Parameters obtained from α/β counting system.

Sample name	α/β	Effiency (ε%)	Attenuation factor (AF)	MDC (Bq L^{-1})
Karakaya-Ayaş	α	12.1 ± 0.2	0.913	0.06
	α to β	30.8 ± 0.6	1.019	
	β	39.1 ± 0.7	1.000	0.05
İçmece-Ayaş	α	12.2 ± 0.2	0.964	0.05
	α to β	29.2 ± 0.6	1.008	
	β	40.8 ± 0.7	1.007	0.04
Beypazarı	α	12.3 ± 0.2	0.810	0.18
	α to β	29.0 ± 0.6	1.043	
	β	38.6 ± 0.6	0.985	0.16
Haymana	α	12.4 ± 0.2	0.698	0.41
	α to β	31.8 ± 0.7	1.074	
	β	38.5 ± 0.6	0.968	0.29
Kızılcahamam	α	12.2 ± 0.2	0.872	0.24
	α to β	28.4 ± 0.6	1.028	
	β	39.8 ± 0.7	0.994	0.22

Table 2. Comparison of gross α and β activity concentrations[a] found in thermal spring waters with some previous measurements obtained from spring waters.

Location of sample	Gross α (Bq L^{-1})	Gross β (Bq L^{-1})	Reference
Karakaya-Ayaş	0.09 ± 0.02	0.25 ± 0.02	Present study
İçmece-Ayaş	2.28 ± 0.06	0.47 ± 0.02	Present study
Beypazarı	1.53 ± 0.11	1.43 ± 0.07	Present study
Haymana	2.58 ± 0.22	1.82 ± 0.12	Present study
Kızılcahamam	1.85 ± 0.13	2.61 ± 0.10	Present study
Batman	3.91	2.097	1
Spain	$< 0.02 - 2.42$	$< 0.05 - 5.80$	4
Samsun	0.08	0.155	9
Villela, São Paulo, Brazil	0.002–0.428	0.120–0.860	11
Saratoga, USA	$< 0.04 - 31.0$	0.11–18.9	17
Emendre	0.37	0.390	18
Slovenia, spring and mineral waters	n.m.	0.033–4.758	16
Balatonfüred	1.75 ± 0.11	2.02 ± 0.15	16

[a]Mean of 3 replicate measurements with 95% confidence level, $\bar{x} \pm \frac{ts}{\sqrt{N}}$.

n.m.: Not measured.

The measured gross α and β activities were also compared with the results reported in previous studies. As seen in Table 2, maximum gross α activity concentration found for the Haymana thermal water (2.58 Bq L^{-1}) is smaller than the result given for Batman.[1] The range of gross α activity concentrations (0.09–2.58 Bq L^{-1}) is in agreement with the results given for spring waters in Spain[4] and Saratoga, USA.[17] The gross α activity concentrations found for 4 thermal waters (İçmece-Ayaş, Beypazarı, Haymana, and Kızılcahamam) are higher than the results given for the Villela, São Paulo, Brazil;[11] for Samsun;[9] and for Emendre.[18] The gross α activity concentrations found for the Beypazarı and Kızılcahamam thermal waters are in agreement with the result given for Balatonfüred.[16] The range of gross β activity concentrations (0.25–2.61 Bq L^{-1}) found for the samples is in agreement with the results given for spring waters in Batman;[1] Spain;[4] Saratoga, USA;[17] and Balatonfüred.[16] The gross β activity concentrations found in thermal waters of Beypazarı, Haymana, and Kızılcahamam are higher than the results given for spring waters in Samsun;[9] Villela, São Paulo, Brazil;[11] and Emendre;[18] and spring and mineral waters in Slovenia.[16]

As seen in Table 1, MDC ranges of gross α and gross β found for the samples were from 0.05 to 0.41 and from 0.04 to 0.29 Bq L^{-1}, respectively. They were in agreement with the results (0.03 Bq L^{-1} for gross α and 0.04 Bq L^{-1} for gross β) given in drinking water[19] and the results (0.13 Bq L^{-1} for gross α and 1.30 Bq L^{-1} for gross β) in sea water.[20]

3.2. Element analysis in samples by WDXRF

The dry residues obtained from samples were directly measured by wavelength dispersive X-ray fluorescence (WDXRF) spectrometry. Results of analytes found are given in Table 3. Major elements (Na, K, and Ca) in mg L^{-1} levels and heavy metals such as Th and U in μg L^{-1} levels were determined. The mean and standard deviations of triplicate measurements of each sample were found for each element. Main sources of gross α activity in thermal spring waters were uranium isotopes (^{234}U, ^{235}U, and ^{238}U) and ^{232}Th.[6,21] As for the β activity, it was probably caused by ^{40}K.[6,22] As seen in Tables 2 and 3, the gross α and β activity concentrations increased when concentration levels of U, Th, or K increased, but there was no linear relationship between them. The results of Ca, K, and Na found in sample solutions (Table 3) were compared with the recommended values given by the Turkish standard[11] (200 mg L^{-1} for Ca, 12 mg L^{-1} for K, and 175 mg L^{-1} for Na) and similar values were observed for Ca concentration. All K and Na (except Haymana) results were higher than the recommended values given by the Turkish standard.[12]

Table 3. Concentrations of elements in thermal waters.

	Concentration (μg L^{-1})[a]				
Element	Karakaya-Ayaş	İçmece-Ayaş	Beypazarı	Haymana	Kızılcahamam
Na (mg L^{-1})	1449 ± 38	1370 ± 32	515 ± 13	82 ± 3	586 ± 17
K (mg L^{-1})	34 ± 2	41 ± 3	54 ± 2	56 ± 4	64 ± 3
Si (mg L^{-1})	4.5 ± 0.2	7.3 ± 0.4	36 ± 2	54 ± 3	17 ± 1
Ca (mg L^{-1})	206 ± 17	182 ± 12	211 ± 11	88 ± 6	21 ± 2
Mn	10.2 ± 0.2	68 ± 5	23 ± 1	239 ± 15	4.6 ± 0.2
Te	12.8 ± 0.5	N. D.	156 ± 7	N. D.	N. D.
Ce	N. D[b]	N. D.	519 ± 28	N. D.	105 ± 5
Cs	1.2 ± 0.1	85 ± 5	N. D.	N. D.	N. D.
Nd	N. D.	N. D.	461 ± 22	78 ± 4	55 ± 3
Sm	N. D.	38 ± 2	N. D.	161 ± 9	N. D.
W	N. D.	17 ± 1	N. D.	N. D.	3.7 ± 0.2
La	30 ± 2	N. D.	N. D.	155 ± 8	N. D.
U	412 ± 25	651 ± 34	480 ± 28	514 ± 31	246 ± 12
Th	6.4 ± 0.4	43 ± 2	39 ± 3	73 ± 4	17 ± 1

[a] Mean of 3 replicate measurements with 95% confidence level, $\bar{x} \pm \frac{ts}{\sqrt{N}}$.

[b] N. D.: Not detected.

4. Conclusion

In this work, gross α and β activity concentrations and metal levels were determined in thermal ground waters of the Karakaya-Ayaş, İçmece-Ayaş, Beypazarı, Haymana, and Kızılcahamam spas. Some of the gross α and β results are higher than the guidelines given by the WHO for drinking water, but they are generally in agreement with the previously reported literature values. Gross α and β activity concentrations found were compared with the concentration levels of Th, U, or K in samples, but no linear relationship between them was observed. This detailed study may be the first on measurements of gross α and β activity concentrations and metal levels of thermal ground waters in Ankara and it may be used for the assessment of possible radioactivity changes in the future.

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