Measurement of Gross Alpha-Beta, Radionuclide Activity Concentration of Water of the Suleymanli Thermae and the Ekinozu Spa and Elemental Analysis in Kahramanmaras, Turkey

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ABSTRACT: The gross alpha and beta radioactivity concentrations and radionuclide activity concentrations in the water of the Suleymanli thermae and the Ekinozu spa have been measured. In addition, the elemental analysis has been done in the water of the Suleymanli thermae and The Ekinozu spa by using XRF. Samples taken from Ekinözü spa and the Suleymanli thermae have been stimulated both by ^{241Am} and ^{55}Fe radioactive source. We have found various concentrations of Ca, Fe, Sr and Ba by the analysis of the water samples taken from Ekinözü spa and we have found Ca, Sr, Ba and trace of Ag in samples from Süleymanlı thermae.

Keywords: *X-ray spectra, scintillation detectors, gross alpha and gross beta*

Süleymanlı Ilıcası ve Ekinözü İçme Sularında Toplam Alfa-Beta, Radyonüklid Aktivite Konsantrasyonlarının Ölçülmesi ve Elemental Analizleri

ÖZET: Süleymanlı ılıcası ve Ekinözü içmesinin sularında toplam alfa ve toplam beta radyoaktivite konsantrasyonları ve radyonüklid aktivite konsantrasyonları ölçüldü. Bunlara ek olarak, Süleymanlı ılıcası ve Ekinözü içmesinin sularının elemental analizleri XRF sistemi ile yapıldı. Ekinözü içmesinden ve Süleymanlı ılıcasından alınan numuneler, sırasıyla ^{241}Am ve ^{55}Fe radyoaktif kaynakları ile uyarıldı. Ekinözü içmesinden alınan su örneklerinin elemental analizlerinde Ca, Fe, Sr ve Ba bulunurken, Süleymanlı ılıcasından alınan su örneklerinin elemental analizlerinde Ca, Sr, Ba ve iz düzeyde Ag bulunmuştur.

Anahtar Kelimeler: *X-Işını spektrumu, sintilasyon detektörü, toplam alfa ve toplam beta*

1. INTRODUCTION

XRF (X-Ray Fluorescence) is an analytical method to determine the chemical composition of all kinds of materials. Those materials can be in from of soil, liquid, powder, filtered or others materials. XRF can also sometimes be used to determine the thickness composition of layers and coating. XRF method is the fast, accurate and non-destructive methods that usually require only a minimum of sample preparation. Applications of this method are very broad and include metal, cement, oil, polymer, plastic and food industries, along with mining, mineralogy and geology and environmental analysis of water and waste minerals. XRF is also an effective analysis technique in research and pharmacy [1].

There are a lot of thermae and spa in different parts of Turkey. Two of these are the Ekinözü spa and the Suleymanli thermae that they are located in Kahramanmaraş. The spa water is undoubtedly drunk by people who do not know whether it is useful for health or not. There seems to be a widespread impression that the radioactivity of all spa waters is high, but that is certainly not the case [2]. Natural radioactivity is always present in the environment. Water, especially ground water, is not free of radioactive isotopes from naturally decaying series of ^{235}U, ^{238}U, ^{232}Th and ^{40}K [3]. The international regulation for quality control with regards to limit values for gross alpha and beta radioactivity concentration in thermae and spa water are 0.5 Bq/L for alpha and 1.0 Bq/L for beta [4]. Natural radioactivity of spring water used at spas in Spain was measured by Ródenas et al. [5]. Potential health hazards from natural radionuclides in consuming water have been considered worldwide [4]. The recommendations for water quality by World Health Organisation (WHO) introduce to regular operational conditions of water supply systems when ground waters are used for public water supplies [6]. Gross alpha is generally more of a concern than gross beta for natural radioactivity in water as it refers

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to the radioactivity of Th, U, Ra as well as Rn and its decay products. A study related with radioactivity properties and trace element contents of mineral water in Gümüşhane, Turkey, vicinity have been done by Gültekin et al. [7]. In addition, gross alpha and beta radioactivity concentration in water, soil and sediment of the Bendimahi River and Lake Van, Turkey were measured by Zorer et al. [8]. People, especially in the spas are required to be very careful against radionuclides and radon gases because water has directly been drunk from source by them. Elevated levels of natural radionuclides in ground water are mainly associated with uranium and thorium bearing soil and rock minerals, or with uranium, thorium and radium deposits. The spa water arises from fault from the crack and it may contain a high percentage of radionuclides. Some of the radionuclides from these sources may be transferred to human beings through food chain or inhalation. Natural radioactivity is wide-spread in the earth's environment coming from Uranium (^{238}U) and Thorium (^{232}Th) series and Potassium (^{40}K), existing in various geological formations like soils, rocks, plants, water and air [9-14]. Uranium, naturally occurring heaviest radioactive toxic element is found in traces in almost all types of rocks, soils, sands and water [15].

The aim of this study is to determine the activity concentration of gross alpha and gross beta, radionuclide activity concentrations in the water of The Suleymanli thermae and The Ekinozu spa and to make the qualitative and quantitative analysis of the water in two places in Turkey (at The Suleymanli thermae and at Ekinozu spa).

2. EXPERIMENTAL

2.1. Qualitative and quantitative analysis of the water in The Suleymanli thermae and The Ekinozu spa

The geometry of the experimental set-up for annular source is shown in Figure 1. To obtain statistical sensitivity, the live time was selected as 5000s for each sample. All samples were sieved in 400 mesh. In this experimental set-up, 5.96 keV photons emitted by a 50 mCi ^{55}Fe annular radioactive sources and 59.5 keV photons emitted by a 100 mCi ^{241}Am annular radioactive sources were used. The fluorescence K X-rays from the sample were detected by using a collimated Ultra-LEGe detector having a thickness of 5 mm and an energy resolution of 0.150 keV at 5.96 keV. The output from the preamplifier, with a pulse pile-up rejection capability, was fed to a multi-channel analyzer interfaced with a personal computer provided with suitable software for data acquisition and peak analysis. The elemental concentrations in residue were determined using the following equation [16].

$$C_i = \frac{N_{ij}}{I_0 G \varepsilon_{ij} \beta_{ij} \sigma_{ij} t} \quad (1)$$

where C_i is the concentration of the element present in the sample, N_{ij} is the net counts/unit time for the ith group of X-rays of the jth element, I_0 is the intensity of incident photon, G is a geometric factor, ε_{ij} is the efficiency of the detector for the ith group of X-rays of the jth element, t is the sample mass in gcm-2, β_{ij} is the self-absorption correction factor for the target material, which accounts for the absorb and the emitted characteristic X-rays of the ith peak of the jth element. σ_{ij} is the theoretical X-ray fluorescence cross-section of the ith group of X-rays of the jth element. The product of $I_0G\varepsilon$, containing the terms related to the incident photon flux, geometrical factor and absolute efficiency of the X-ray detector, was determined by collecting the Kα and Kβ X-ray spectra of samples of Si, S, K, Ca and Ti for ^{55}Fe in the same geometry using the equation,

$$I_0 G \varepsilon_{Ki} = \frac{N_{Ki}}{\sigma_{Ki}\, \beta_{Ki}\, t_i} \ (i = \alpha, \beta) \quad (2)$$

where NKi is the measured intensity (area under the photopeak) corresponding to the Ki group of X-rays, I_0 is the intensity of the incident radiation, G is a geometrical factor, ε_{Ki} is the detection efficiency for the Ki group of X-rays and β_{Ki} is the self-absorption correction factor for the target material [17], which accounts for the absorption in the target of the incident photons and the emitted characteristic X-rays. Details regarding the detector efficiency were given in our earlier work [18]. In addition, the spectrum of Süleymanlı thermae and Ekinözü spa, given in Figures 2-4, have been obtained by using a ^{55}Fe and ^{241}Am radioactive sources, respectively, in the same geometry.

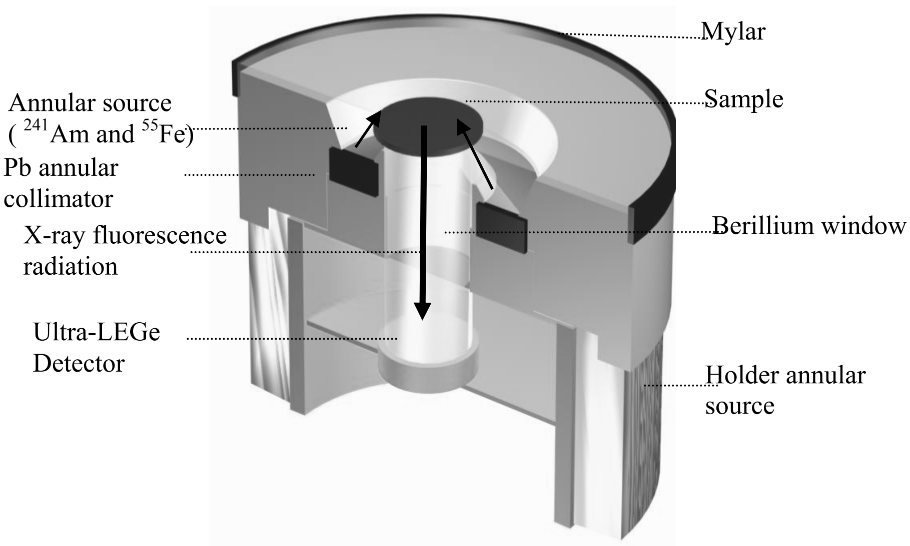

Figure 1. Experimental setup

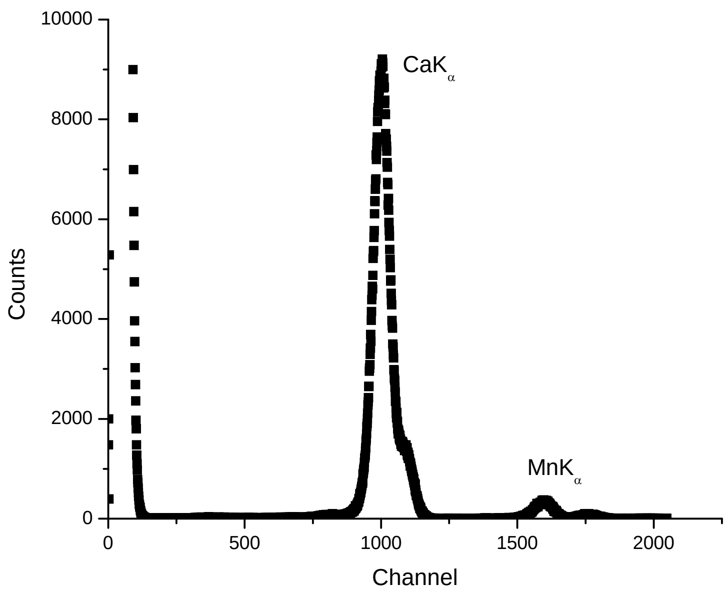

Figure 2. A typical spectrum of residue of The Ekinozu spa excited with ^{55}Fe radioactive source.

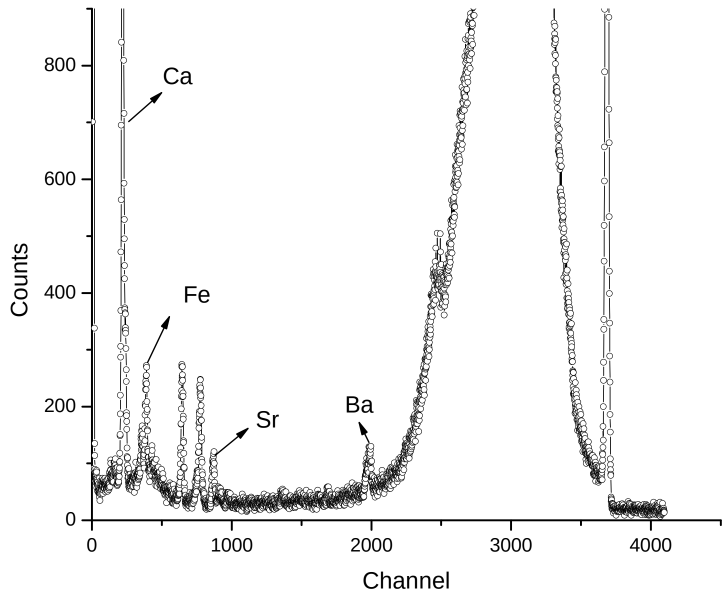

Figure 3. A typical spectrum of residue of Ekinozu spa excited with ^{241}Am radioactive source.

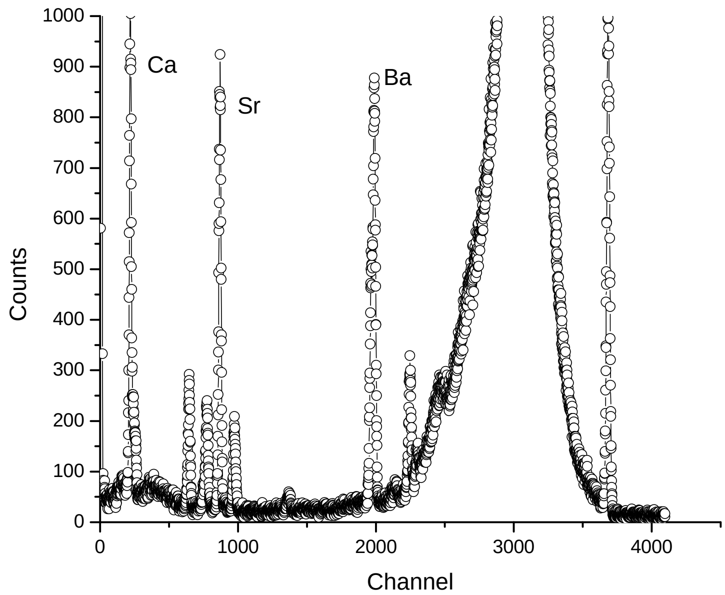

Figure 4. A typical spectrum of residue of The Suleymanli thermae excited with ^{241}Am radioactive source.

2.2. Measurement of Gross Alpha and Gross Beta Activity Concentrations

The water samples were taken from Süleymanlı thermae and Ekinözü spa. All of the samples were collected in one liter capacity, sterilized glass bottles. All the samples were prepared by evaporation, at low temperature. They were evaporated slowly at 70 ^{0}C to near dryness (approximately 2-3 ml). Then each sample was transferred quantitatively to an aluminium planchette and dried until precipitation is obtained. Each sample precipitation in planchette was directly applied to counting systems. The results were obtained by arithmetic means. The measurements of radioactivity level of all water samples were calculated by the KRIEGER method [19] using the gross-alpha and gross-beta counting system. The instrumentation used to count global-alpha activity was a ZnS(Ag) alpha-scintillator supported by a photomultiplier tube from NE Technology. The instrumentation used to count global-beta activity was a low-background beta scintillation counter (NE Technology, Inc.). Gross-alpha activity counting was performed by a lead shielding to protect from external radiation during gross-alpha and gross-beta activity measurements [20]. The counting time was 3000 seconds for gross-alpha and 1000 seconds for gross-beta activities for each counting period. Three counting periods were selected to determine total counts for each gross-alpha and gross-beta activity. The background was subtracted from the gross count to obtain the net counts for calculation. The gross-alpha and gross-beta activities were calculated using the following equations [20-22]

$$A_\alpha = (N^*\mathrm{ECF}) / 2.22 \quad (1)$$

$$A_\beta = (0.391^*R^*N_m) / N_0 \quad (2)$$

where A_α and A_β are the activities of alpha and beta in pCi, respectively, N is the sample of the net count per minute for alpha, ECF is the efficiency correction factor [23], R is the sample of the net count for beta per minute, N_m is the specific mass of the sample in mg/cm2, N_0 is the count corresponding to the specific activity which was determined from the standard calibration curve obtained using a KCl source [24]. The correlation co-efficient (r) of the curve was calculated to be 0.998. The calculation of the efficiency correction factor (ECF) for the determination of alpha-activity of the residue in the aluminium planchette is given by:

$$\mathrm{ECF} = 1 / (E^*T) \quad (3)$$

where the quantity of T is determined from the U_3O_8 self-absorption lines obtained in mg/cm2 and E is the absolute efficiency. Using the calculation of the standard deviation method for the radioactivity measurement, the uncertainty calculations were performed [25]. The accuracy was about 5% of the standard deviation.

2.3. Measurement of Radionuclide in the water of Süleymanlı thermae and Ekinözü spa

Gamma spectrometric system was used to measure the radionuclide in water of the samples taken from Süleymanlı thermae and Ekinözü spa. These measurements were obtained by using a low level gamma counting spectrometer including a 7.62 cm x7.62 cm NaI(TI) detector that is produced or manufactured by ORTEC Inc. The detector is connected to a multichannel pulse height analyzer (2048 channels). The necessary power for the detector as well as the acquisition of gamma spectra was achieved using an integrated spectroscopy system from ORTEC. The detector is surrounded by a 5 cm thick lead shield to smooth the background γ-radiation. The detector has a resolution of about 7.6% at 662 keV of ^{137Cs} which is capable of distinguishing the gamma ray energies used for the measurement. The photopeak at 1.460 MeV was used for the measurement of 40K while those at 1.760 MeV peak from ^{214}Bi and 2.614 MeV from ^{208}TI were used for the measurement of ^{226}Ra (^{232}U) and ^{232}Th, respectively. Concentration activities were calculated by using the following equation,

$$A_v(Bqkg^{-1}) = \frac{C}{\varepsilon P_\gamma M_S} \quad (1)$$

where C is count rate of gamma radiation (count/sec), ε is detector efficiency of gamma radiation (24%), P_γ is transition probability of gamma radiation and M_S is mass of samples (kg) [26-28].

3. RESULTS AND DISCUSSION

The gross alpha and beta activity concentrations and radionuclide activity concentrations in the water of the Süleymanlı thermae and the Ekinözü spa were measured. In addition, the water analyses have been done in Süleymanlı thermae and Ekinözü spa and obtained values are given in Table 1. Besides, the values of radionuclides in the samples were measured and obtained results are given in Table 2. In addition, obtained values of gross alpha and gross beta activity concentration are given in Table 3. In the water analysis of the Ekinözü spa, Ca, Fe, Sr and Ba elements were found, while in the water analysis of the Süleymanlı thermae, Ca, Sr, Ba and trace of Ag were found. Forte et al., [28] were used standart methods to measure radionuclide in drinking water and their results are given as tables and graphics. Besides, the natural gross radioactivity in various surface and tap waters were measured by Dogru and Canbazoglu, [20] and their results were compared with values of WHO and the Institution of Turkish Standards (ITS). In addition, Happel et al. [29] were measured gross alpha determination in salt rich water samples using an extraction chromatographic resin and LSC. The natural radioactivity in public drinking water quality assessment were measured by Yusof et al. [30] and their results were compared with WHO's results. The average activity reported for 90Sr in the drinking water samples was 0.52±0.07 Bq/L, which is lower than the maximum permissable level (MCL) of 1.11 Bq/L allowed by WHO. Moreover, the radioactivity in selected drinking water samples from Maryland was investigated by Outola et al. [31]. The values of gross alpha and beta of spring water used as spas in Spain were measured by Ródenas et al. [5]. Furthermore, the radioactivity properties and trace element contents of mineral waters in the Gümüşhane vicinity, Turkey, have been measured by Gültekin et al. [7]. As seen from Table 1, the obtained values were compared with the values of Ródenas et al. [5] and Gültekin et.al. [7].

Table 3 shows that mineral water has passed through the ore containing large amount of uranium-series radioisotope. Although the values of gross beta are found very low, the amount of potassium is found to be high. The reason for this may be that beta active radionuclides were screened by alpha emitted ones. Amostly the same outputs can be said for the water of Suleymanli thermae. Every year, approximately 5000-10000 people from various parts of the region come to The Ekinozu spa and stay here for one or two weeks. In this period, everyday they drink 4-5 liters of mineral water. People are doing this because they believe that mineral water cures their digestive system. On the other case,, every year, roughly 25000-30000 people from various parts of the region come to The Suleymanli thermae and stay here for one or two weeks. They use hot water in bath and pool. The baths and swimming pools are usually closed areas. Therefore, people may expose to some amount of radiation such as radon gas.

Table 1. The analysis of the water in the Suleymanli thermae and Ekinozu spa.

	%				
	Ca	**Fe**	**Sr**	**Ba**	**Ag**
Ekinözü thermae	37.380±2.056	0.002±0.0001	0.003±0.0002	0.009±0.0005	--
Süleymanlı spa	22.810±1.118	--	0.018±0.0 0	0.022±0.001	the quantity of trace

Table 2.The values of radionuclides in the water of the Suleymanli thermae and Ekinozu spa.

Measured values (Bq/kg)				World mean (Bq/kg)		
Radionuclide	^{232}Th	^{238}U	^{40}K	^{232}Th	^{238}U	^{40}K
Suleymanli thermae	83.6	140.4	208	25	25	370
Ekinozu spa	165	1087	2912			

Table 3. The values of gross alpha and gross beta in the water of Suleymanli thermae and Ekinozu spa

	Measured values		**Ródenas et. al. (2008)**		**Gültekin et al. (2005)**	
Samples	Gross alpha (Bq/L)	Gross beta (Bq/L)	Gross alpha (Bq/L)	Gross beta (Bq/L)	Gross alpha (Bq/L)	Gross beta (Bq/L)
Suleymanli thermae	0.108± 0.015	0.121±0.010	-	-	-	-
Ekinozu spa	0.299±0.084	0.072±0.008	LLD–16.95	LLD–60.14	0.122-0.78	0.067-0.401

LLD: lower limit of detection.

4. CONCLUSION

In this work, three different measurements were made in the water of the Süleymanlı thermae and the Ekinözü spa. These measurements are water analysis, radionuclide activity concentrations and the gross alpha-beta activity concentrations in the Süleymanlı thermae and the Ekinözü spa. As seen from Table 1, we found different concentrations of Ca, Fe, Sr and Ba in the water analysis of the Ekinözü spa and different concentrations of Ca, Sr, Ba and trace of Ag in the water analysis of the Süleymanlı thermae. Additionally, as seen from Table 2, the radionuclide activity concentrations in the water, the gross alpha and beta activity concentrations measurements were done by us.

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