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Determination of Natural and Artificial Radionuclides in Hot Water Spring Mud of Haymana-Ankara Spa (Turkey)

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γ-Ray spectrometric analysis was performed on hot water spring mud samples, collected from Haymana-Ankara (Turkey) Spa, a well known health resort in the middle of Anatolia. The contents of natural and artificial radionuclides (^{226}Ra, ^{235}U, ^{238}U, ^{228}Th, ^{232}Th, ^{40}K and ^{137}Cs) were determined. The results were compared with the radioactivity values of different Spas. γ-Isotopic analysis indicated that the maximum level concentration of the thermal mud samples for ^{226}Ra, ^{235}U, ^{238}U, ^{228}Th, ^{232}Th, ^{40}K and ^{137}Cs were (Bq/kg) 162, 7.4, 156, 75, 127, 66 and 1.6, respectively.

Key Words: γ-Isotopic analysis, Mud, Radionuclides, Spa.

INTRODUCTION

Haymana thermal Spa is 75 km away from the south-western part of the city of Ankara, Turkey. The faults cutting through the tertiary volcanistic rocks are observed in the area and the spring is classified as a volcanic hot spring. Haymana hot spring has been remained from Roman and Seljuk era and suitable for both bathing and drinking. It cures many diseases. The water has a temperature of 44 ºC and has healing characteristics on illness as rheumatism, skin, heart, circulation, respiration, gynaecological, nervous and muscle exhaustions. The spring water has positive effects on stomach, liver, gall and pancreas[1]. This beneficial hot mineral water has pH of 6.86 and contains bicarbonate, calcium, sodium and magnesium[1]. Physical chemical properties, ionic composition and radioactivity concentrations (gross-a, ^{222}Rn, ^{226}Ra, ^{238}U) of the thermal spring water were determined[1] in 1975. To our best of knowledge, no systematic study on the radioactivity levels of Haymana spring mud has been published, although the mud is used for therapy.

In this study, four composite mud samples, representing the mud nearby the hot spring source, the mud of the channel (the transportation channel from the source to Spa), the mud of the border of Spa and the mud of Spa were analyzed for their ^{226}Ra, ^{235}U, ^{238}U, ^{228}Th, ^{232}Th, ^{40}K and ^{137}Cs contents.

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EXPERIMENTAL

In this study 4 composite mud samples (*ca.* 0.5 kg each), representing the mud around the hot spring source (I), the transportation canal from source to Spa (II), border of Spa (III) and Spa (IV) were prepared, each, as mixtures of the same portions of 10 individual mud samples, collected each of the 4 mentioned areas of the Haymana Spa. The composite samples were dried (40 ºC) and then were homogenized and ground to fine powder of < 0.5 μm particle size. Prior to radiation measurement, the composite mud samples were kept in air-tight cylindrical acrylic plastic containers (1 mm wall thickness; 3 cm dia., 8 cm height) for *ca.* 40 d to ensure that ^{226}Ra and ^{232}Th attained radioactive equilibrium with respect to the daughters. Then the cup was placed directly on the HPGe detector for γ-ray spectrometry. The distance between sample and detector was 8.5 cm. The distance was kept constant for the full energy efficiency calibration.

γ-Isotopic analysis of these samples was carried out by using HPGe detector connected with standard fast electronics. The resolution FWHM was 1.8 keV at 1.33 MeV of ^{60}Co. The energy dependent efficiency calibration was done using a solid nuclide mixture of Amersham γ-reference material containing known activities of ^{109}Cd, ^{57}Co, ^{139}Ce, ^{113}Sn, ^{137}Cs, ^{88}Y and ^{60}Co. The peak analysis of the counted sample was made by using spectran AT software at PC. The spectra were collected for 2.5-10^5 seconds counting time. Estimated total error of the method was 10 % (at 95 % confidence level).

The specific radioactivity of the radionuclides present in the samples was evaluated from the neat peak areas of full-energy peaks after background subtraction and taking into account the detection efficiency of the system, the branching ratio of γ-transitions[2]. The values were given on dry weight basis and 2σ standard deviations.

The specific activity of ^{238}U was calculated from 609 keV line (transition of ^{214}Bi), for ^{226}Ra, γ-ray with energy of 186 keV was used. For the other radionuclides, radioactive equilibrium between ^{214}Bi and ^{226}Ra was assumed. There is a contribution to the intensity of the 186 keV line of about 10 % from the 185 keV line is the surer basis for the activity of ^{226}Ra. This line was used in this paper.

The levels of U and Th radionuclides were also determined by comparing with the IAEA-135 reference standard material of the International Atomic Energy Agency (IAEA). It contains ^{232}Th (36.9 Bq/kg), ^{238}U (30 Bq/kg), ^{226}Ra (23.9 Bq/kg), ^{137}Cs (1108 Bq/kg) and ^{40}K (560 Bq/kg). The results obtained by comparing with the mixture reference standards and by comparing with the IAEA-135 reference standard were found to be similar.

The quantitative analysis of the major elements of the composite mud sample (IV) obtained from Spa, was performed by EDXRF analysis using Spectro IQ-II EDXRF spectrometer. About 4 g of dry sample powder and 0.9 g WAX, which were homogenized by grinding 5 min using a mixer mill, was pressed into 31 mm diameter pellets by using stainless steel Spex evacuable dies and 25 tons hydraulic press, for quantitative analysis. The samples were analyzed for 180 s using an air

cooled low power Pd end window X-ray tube (25-50 kV) combined with HOPG crystal for monochromatization and polarization of the primary tube spectrum. A silicon drift detector (SDD) was used to collect the fluorescence radiation from the sample. The resolution of the SDD was better than 175 eV (for Mn K_α at an input count rate of 10000 cps). During the measurement the excitation area was flushed with helium gas. The accuracy of the analytical procedures was checked against the standard reference materials.

RESULTS AND DISCUSSION

The results of the chemical analysis for the major elements of the composite mud sample obtained from Spa (IV) were given in Table-1. The mineralogical analysis indicated that the sample was mainly composed of quartz (*ca.* 85 %) and contains kaolin and limestone. γ-Isotopic analysis results of the composite mud samples obtained around the hot spring source (I), from the transportation canal; from the source to Spa (II), from the border of Spa (III) and from Spa (IV), are tabulated in Table-2. The concentrations of U and Th, calculated from the obtained activities[3] are given in Table-3. Cesium is found to be between 1.2-1.6 Bq/kg except for the mud sample obtained from the border of Spa (III), which was below the detection limit (Table-2). The man-made radionuclide ^{137}Cs content is agreeing with those obtained from other spas[4,5]. The mud samples of Haymana Thermal spring show pretty high concentration of uranium especially in the composite mud sample of

TABLE-1
CHEMICAL ANALYSIS (%) OF THE MAJOR ELEMENTS OF HAYMANA SPA MUD (SAMPLE IV)*

SiO_2	85.0	TiO_2	0.500
Al_2O_3	9.0	K_2O	1.500
CaO	0.6	Ba	0.050
ΣFe_2O_3	1.1	Rb	0.020
MgO	0.7	Sr	0.200
Na_2O	0.4	Y	0.006
P_2O_5	0.2	LOI	1.200

*LOI = Loss on ignition.

TABLE-2
ACTIVITY CONCENTRATION OF (Bq/kg dry wt) HOT WATER SPRING MUD SAMPLES OF HAYMANA SPA*

Sample	^{226}Ra	^{228}Th	^{232}Th	^{235}U	^{238}U	^{137}Cs	^{40}K	Chemical composition
IV	162±16	75±8	127±13	7.4±0.9	156±15	1.6±0.5	66±6	Kaolin+quartz + limestone
III	96±10	33±3	59±6	5.0±0.5	113±12	BDL	55±4	Clay+ quartz
II	25±3	nm	20±2	nm	30±2	1.2±0.5	40±3	Grey clay+ quartz + schists
I	11±2	nm	10±1	nm	7±1	1.4±0.5	30±2	Clay + quartz

*Chemical composition was obtained by mineralogical analysis. BLD = Below detection limit (detection limit for ^{137}Cs = 1 Bq/kg), nm = not measured.

TABLE-3
CONCENTRATIONS OF URANIUM AND THORIUM (mg/kg)

Sample	^{232}Th	^{238}U
IV	30.83	12.75
III	14.32	9.23
II	2.42	0.57
I	4.85	2.45

Spa (IV). Uranium from soluble complexes under oxidic conditions particularly with carbonates and it can be transported by groundwater over long distance. Under reduction condition, ^{238}U precipitates from groundwater and is concentrated in secondary deposits[6,7]. Therefore probably the high uranium content could be related to the deposition of volatile activities are found to be lower than the other spa muds[4,5]. Nearly equal activities of ^{226}Ra and ^{238}U in all the investigated samples confirm the existing equilibrium between ^{238}U and his progenies.

Conclusion

In this study the contents of natural radionuclides and man made ^{137}Cs in hot water spring mud samples, used for radioactive mud therapy, collected from Haymana-Ankara (Turkey) Spa were analyzed. The maximum level concentration of the thermal mud samples for ^{226}Ra, ^{235}U, ^{238}U, ^{228}Th, ^{40}K and ^{137}Cs were (Bq/kg) 162, 7.4, 156, 75, 127, 66 and 1.6, respectively. Due to the alkaline origin of spring water, high value of ^{238}U specific activity is obtained, as expected. Nearly equal activities of ^{226}Ra and ^{238}U in all the investigated samples confirm the existing equilibrium between ^{238}U and his progenies. From the specific activities of ^{238}U and ^{232}Th, their total amounts were calculated. The values of uranium and thorium are found to be with in the range reported for different spas[4,5].

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