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Radioactivity levels and concentrations of heavy elements in black sand

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Abstract. The radioactivity levels and concentrations of heavy elements in Langkawi black sand have been studied through gamma ray spectroscopy. Direct gamma counting was used for measuring the activity of the natural radionuclides uranium, thorium and potassium, and neutron activation analysis for detecting the presence of other heavy elements. Our results show the activity of uranium is 44.5 pCi g^{-1}, which is four times higher than that of thorium (11.6 pCi g^{-1}) and eight times that of potassium (5.5 pCi g^{-1}). Ytterbium, thorium, europium, cesium, antimony, scandium, gallium, iron, chromium, cobalt, cerium, arsenic, lanthanum, samarium and hafnium were detected; their concentrations range from 4.9 to 16072 ppm.

Abstrak. Aras keradioaktifan dan kepekatan unsur berat di pasir hitam telah dikaji secara spektroskopi sinar gamma. Penghitung terus gamma digunakan untuk penentuan keaktifan radionuklid semulajadi uranium, thorium dan kalium, dan analisa pengaktifan neutron untuk mengesan kehadiran unsur berat lain. Hasil kami menunjukkan bahawa aktifan uranium adalah 44.5 pCi g^{-1}, yang empat kali aktifan thorium (11.6 pCi g^{-1}) dan lapan kali aktifan kalium (5.5 pCi g^{-1}). Ytterbium, thorium, europium, cesium, antimoni, scandium, galium, iron, kromium, kobalt, sirium, arsenik, lanthanum, samarium and hafnium telah dikesan; julat kepekatan adalah 4.9 ke 16072 ppm.

Introduction

Radioactivity in the environment results from the decay of radionuclides that are present in the ground; the distribution of radionuclides in the ground has been well documented in the literature [1]. The main natural radionuclides include potassium, thorium and uranium. Although most of the gamma rays emitted by the nuclides are absorbed by the ground, those originating near the surface pose a health hazard, and the extent of human exposure to the radiations depends on factors such as air-flow pattern and time of exposure.

Our work is a study on the level of radioactivity in the black sand found at Pasir HItam beach on Langkawi Island (100° E and 6° N), Malaysia. The sand contains monazite ($CeLaYThPO_4$), a mixed phosphate salt of thorium and other heavy metals [2]. The Pasir Hitam (literally, black sand) beach stretches for almost two kilometers, and the sand is black owing to the high content of ilmenite ($FeTiO_3$). A study the natural radioactivity of the black sand may be of geological interest as a sand having an elemental concentration above 10 ppm indicates possible mineralisation. In this study, a direct gamma-ray counting method was used for the activity measurements whereas the concentration of heavy elements was determined by neutron activation analysis.

Experimental

The black sand (top 5 cm) was collected from four different sites on Pasir Hitam beach into plastic tubes (3 cm diameter, 15 cm long) that were cleaned with 10% nitric acid. The samples were then homogenised and air dried. Representative samples were used for the radioactivity measurements and for the analysis of heavy elements.

Direct gamma counting

The gamma ray spectra of the samples were recorded on a high-resolution HPGe gamma ray detector (20% efficiency) that was coupled to a PC-based multichannel analyser. The detector was maintained in vertical position inside a cylindrical 12-cm x 1 m lead shield. The resolution of ^{60}Co as measured by the FWHM at 1332 keV energy is 1.90 keV. The absolute efficiency of the detector was calibrated by standard sources and a standard reference material IAEA-368 (sediment), which took into account the geometry of the samples.

The samples were placed in sealed cylindrical 300 mL plastic containers and then set aside for four weeks to enable the radon gas in the U series to equilibrate with the other daughter nuclei. A series of measurements was performed by placing the sample approximately 10 cm from the detector. For each measurement, the observed counting rate was corrected for the background contribution. The counting time for all samples was 10 hours.

The radionuclides measured were ^{238}U, ^{232}Th and ^{40}K. The ^{226}Ra (or ^{238}U for samples at radioactive equilibrium) and ^{232}Th radioactivities were estimated from the 609.3 keV and 583.1 keV gamma lines of ^{214}Bi and ^{208}Tl, respectively. The ^{40}K radioactivity was determined by using the 1460 keV gamma line.

The equation for the specific activity is:

$A_S = C_a/\varepsilon * Pr * Ms$ (in Bq kg^{-1} units)

where

C_a = count rate of the analytical line
ε = detector efficiency of the specific line
Pr = absolute transition probability of gamma decay through the line, and
Ms = mass of the sample (kg)

In order to estimate the doses 1 m above ground,

$$D = aC$$

where

D = dose rate, mrad yr^{-1}
C = concentration, pCi g^{-1}, and
a = 17.8 for ^{238}U (+decay products) and 25.5 for ^{232}Th (+decay products) and 1.6 for ^{40}K.

Neutron Activation Analysis (NAA)

The sand samples were placed inside polyethylene vials (2/5 drag), sealed and then inserted into irradiation containers and irradiated with neutron fluxes of 4 x 10^{12} ncm^{-1}s^{-1} at the Malaysian Institute of Nuclear Technology (MINT) nuclear reactor TRIGA MK II. Irradiation time was set at 10 hours, with a cooling time of two weeks. The presence of heavy elements in the samples was deduced from the detection of of gamma rays emitted by induced radionuclide activities [3]. The method of comparison was used to calculate the concentration level of each element and the comparator used was SRM Coal Ash 1632a.

Results and Discussion

Table 1 shows the result of the activity measurements by the method of direct gamma counting that are expressed as pCi g^{-1}. Our results indicate the presence of natural radionucides; U, Th and K in Langkawi black sand. We observed that the activity of uranium is higher than the activities contributed by thorium and potassium. Generally, the percentage error from our measurements are relatively small between 5 - 7 per cent which are attributed from the counting statistics.

The second and third row of the table show the respective activity values obtained from Egyptian black sand [4] and sandstone [5]. The activity values obtained from our samples are greater than the activities of the other two types of sand. For instance, the activity of uranium in Langkawi black sand is more than 100 times higher than the activity found in sandstone and approximately 8 times greater than that of Egyptian black sand.

The last column of Table 1 show the exposure rate calculated for the three types of sand as expressed in microrad per hour. Again we observed that the rate derived from our black sand is higher almost 4 times greater than that of Egyptian sand and 30 times that of the normal sandstone. Table 2 shows the concentrations of heavy trace elements in Langkawi black sands as

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obtained by the method of instrumental neutron activation analysis.

Fifteen heavy elements; Yb, Tb, Eu, Cs, Sb, Sc, Ga, Fe, Cr, Co, Ce, As, La. Sm and Hf were detected by NAA with concentrations ranging from 5.4 ppm to as high as 16072 ppm dry weight. Our analysis have shown that Langkawi black sand contains considerable amount of europium, approximately 16 mg g^{-1} followed by hafnium and cerium. With this high concentration of heavy elements there is a possibility that mineral extraction can be carried out in future which on the other hand has to be weighed against the economic costs.

Langkawi black sand has been shown to contain naturally occuring radioisotopes ^{232}Th, ^{226}Ra and ^{40}K as well as several important heavy elements. The main radioactivity is contributed by uranium and the overall exposure rate was found to be small.

References

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Table 1. Activities of radionuclides expressed as pCi g^{-1}

	^{238}U (609 keV)	^{232}Th (583 keV)	^{40}K (1460 keV)	Exposure rate (μR h^{-1})
Langkawi black sand	44.5 ± 2.6	11.6 ± 0.6	5.5 ± 0.4125.1	
Egyptian black sand	5.2	9.8	1.8	39.4
Sandstone	0.4	0.7	9.1	4.3

Table 2. Concentrations of heavy elements in Langkawi black sand

Element	Induced radionucide	Half-life	Dominant photo emission (keV)	Concentration (ppm)
Yb	^{168}Yb	32 d	177	56.4±10.4
Tb	^{159}Tb	72 d	879	6.0±0.9
Eu	^{152}Eu	12.2 y	1408	16072±1205
Cs	^{134}Cs	2.07 y	796	5.4±0.84
Sb	^{122}5b	67.2 h	564	4.9±1.2
Sc	^{46}Sc	83 d	889	34.6±0.9
Ga	^{72}Ga	14 h	835	48.6±1.7
Fe	^{59}Fe	45 d	1099	34.3±4.6
Co	^{60}Co	5.24 y	1332	8.5±0.5
Ce	^{141}Ce	32.5 d	145	108±10
As	^{76}As	26.3 h	559	10.5±4.8
La	^{140}La	40.2 h	487	57.7±6.8
Sm	^{153}Sm	47 h	103	11.2±2.8
Hf	^{180}Hf	42.5d	482	172 ±25