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Elemental analysis of marble used in Saudi Arabia by different nuclear analytical techniques

A. El-Taher [a,b,*], Awad A. Ibraheem [a,c], Salah Abdelkawy [c]

[a] Physics Department, Faculty of Science, Al-Azher University, Assuit 71452, Egypt
[b] Physics Department, Faculty of Science, Qassim University, Buraydah 51452, Saudi Arabia
[c] Physics Department, Faculty of Science, King Khalid University, Abha, Saudi Arabia

HIGHLIGHTS

- The instrumental neutron activation analysis technique was used for analysis of marble.
- The samples simultaneously irradiated by thermal neutrons in the TRIGA Mainz research reactor.
- Twenty eight major and trace elements have been determined

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ABSTRACT

Instrumental neutron activation analysis (INAA) and HPGe detector γ-spectroscopy were used to determine a total of 22 elements qualitatively and quantitatively for the first time from marble rock samples collected from local markets in Saudi Arabia. The elements determined are Mg, Ca, V, Na, Mn, As, La, Sm, U, Sc, Cr, Fe, Co, Zn, Sn, Ba, Ce, Eu, Yb, Lu, Hf, and Th. The samples were properly prepared together with their standard reference material and simultaneously irradiated by thermal neutrons at the TRIGA Mainz research reactor at a neutron flux of 7×10^{11} n/cm^2 s. XRF was also used. The concentrations of natural radionuclides ^{226}Ra, ^{232}Th and ^{40}K were also determined by gamma ray spectroscopy to estimate the radiological parameters such as radium equivalent activity, and the external hazard index was calculated to estimate the exposure risk from usage of marble as raw materials in construction. For the sake of comparison the results of concentration levels and radium equivalent activities are compared with similar studies carried out in other countries.

1. Introduction

The usage of marble as a construction material has expanded widely during the last decades. Natural radionuclides exist as impurities in building materials. The accumulation of these radionuclides, due to the application of marble as a building/construction material and as a lining on walls and floors in dwellings, could be a potential source for environmental pollution (Aslam et al., 2002; Tufail et al., 2000; Iqbal et al., 2000; Walley El-Dine et al., 2001). Exposure to ionizing radiation is generally regarded as undesirable at all levels, although no harmful effects are known to follow very low-level exposure (UNSCAIR, 2000). Recently, considerable attention has been given to low-level exposure arising from naturally occurring radionuclides, particularly ^{238}U, ^{232}Th and ^{40}K. The reason for the current interest is due to the fact that external radiation exposures from naturally occurring radionuclides contribute, on average, about 10% of the average annual dose to the human body from all radiation sources (UNSCAIR, 2000). Few attempts were carried out in Saudi Arabia to estimate the natural radioactivity levels in building materials (Al-Saleh and Al-Berzan, 2007).

Because of its polished surface and its availability in a variety of attractive colors, marble is widely used as a building/construction material. It is mostly used as a lining on walls and floors in dwellings. The presence of other minerals in marble gives it a variety of attractive colors. Therefore, the aim of the present paper was to assess the elemental content in marble by instrumental neutron activation analysis and X-ray fluorescence and in addition, to assess the levels of ^{226}Ra, ^{232}Th and ^{40}K to estimate the radium equivalent activities (Ra eq) which is related to the external γ-dose rate. For the sake of comparison the results of concentration levels and radiation equivalent activities are compared with similar studies carried out in other countries.

* Corresponding author. Present address: Physics Department, College of Science, Qassim University, P.O. 6644, 51452 Buryadh, Kingdom of Saudi Arabia.
E-mail address: Atef_Eltaher@hotmail.com (A. El-Taher).

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2. Experimental technique

2.1. Sampling and sample preparation

Marble samples used in Saudi Arabia have been collected from local markets for investigation. The samples each about 1 kg in weight, were dried in an oven at about 105 °C to ensure that moisture is completely removed. For X-ray fluorescence, 8 g from the powdered sample and 1.6 g of wax were pressed under 300 N/cm^2 pressure to produce discs with 4 cm diameter. These discs were then measured by XRF (El-Taher, 2007). For elemental analysis by instrumental neutron activation analysis, the powdered samples were sieved using a standard set of sieves to a diameter range of less than 125 μm and greater than 63 μm. Each powdered sample was homogenized using an electric shaker. The samples then were irradiated by thermal neutrons. For determination of the natural radionuclides the samples were crushed, homogenized, and sieved through a 200 mesh, which is the optimum size when enriched in heavy minerals. Weighted samples were placed in a polyethylene beaker of 350 cm^3 volume each. The beakers were completely sealed for 4 weeks to reach secular equilibrium where the rate of decay of the daughters becomes equal to that of the parent. The gamma transmissions used for activity calculations are 352.9 (^{214}Pb), 609.3, 1120.3 and 1764.5 keV (^{214}Bi) for ^{226}Ra (^{238}U) series, 338.4, 911.1 and 968.9 keV (^{228}Ac) for ^{232}Th series and 1460.7 keV for ^{40}K (El-Taher, 2010a).

2.2. Instrumentation and irradiations

INAA achieves a qualitative and quantitative analysis of the unknown samples by irradiating them with neutrons through the (n, γ) reaction and detecting the emitted γ rays from the resulting radioactive nuclides after irradiation. Qualitative analysis can be achieved by the analysis of γ lines in the γ spectrum detected and registered by a (HPGe) detector and its associated electronic circuit (El-Taher, 2010b). Polyethylene capsules were filled with 100 mg of powder samples and then irradiated with a standard reference material with thermal neutrons at the university of Mainz Triga research reactor (100 kWth) with a flux of 7×10^{11} n/cm^2 s. The elemental content of our samples were quantitatively determined by comparison with the activities of Dolerite WSE and Microgabro PMS reference materials (El-Taher, 2010c, 2010d). The data were collected for various measurements after appropriate cooling times (Kernchemie, 1989). Table 1 shows the irradiation cycles and the elements determined.

The gamma-ray spectrometer used consists of a HPGe detector with its electronic circuit. The detector has the following specifications: energy resolution (FWHM) at 1.33 MeV Co-60 is 1.70 keV, peak to compton ratio Co-60 is 65.2, relative efficiency at 1.33 MeV Co-60 is 29.2%, energy resolution (FWHM) at 0.122 MeV Co-57 is 686 eV, and bias voltage is +2000 dc. The detector is connected to the following components: preamplifier, amplifier, ADC converter and MCA. The measurements were performed and analyzed using the Intergamma Software produced by Intertechnique Deutschland GmbH, Mainz, Germany. The electronic dead time in all measurements was less than 10% and was automatically corrected by the Intergamma software.

Table 1
Irradiation cycles, cooling and counting times and elements determined.

Irradiation time	Cooling time	Measuring time	Elements determined
1min	5 min	4 min	Mg, Ca, V
5 min			Na, Mn
6 h	2 d	1 h	As, La, Sm, U
6 h	14 d	8 h	Sc, Cr, Fe, Co, Zn, Sn, Ba, Ce, Eu, Yb, Lu, Hf, Th

3. Results and discussion

All the elements, under investigation in the present work, were calculated by means of multiple activities induced by (n, γ) reactions, since some of the radionuclides measured exhibit more than one prominent gamma line. In all other cases the elements were determined by their most prominent peaks, free of interference and with lower statistical errors. The accuracy and reproducibility were evaluated by the analysis of replicates of the WSE and PMS geo-standard reference materials. Twentytwo elements were identified. The elements determined with their concentrations are shown in Table 2. The average concentration values are expressed in μg/g for all elements except for Na, Mn, Mg, Ca and Fe which are given in units of g/kg.

Quantitative analysis was carried out for each isotope by comparing the activities from the most favorable peaks in the gamma spectra of samples with those of the standard reference material. In such an analysis the highest-energy peaks were usually used, as in the case of ^{59}Fe,^{140}La, ^{60}Co and ^{46}Sc, since these peaks normally had less interference than the lower-energy peaks due to the Compton effect. In some cases, low-energy gamma lines had to be used to determine some elements, since these radionuclides have no high energy peak, as in the case of ^{141}Ce and ^{153}Sm. Another reason to use a low-energy peak is because of interferences associated with the high-energy peaks due to the complex spectra of irradiated marble as in case of ^{181}Hf, where its high-energy line of 482 keV interferes with the 487 keV gamma line of ^{140}La. Scandium is the most favorable element to be determined by INAA, due to the 100% abundance of its single stable nuclide. In addition to its 100% branching ratio of the measured gamma lines at 889.4 keV and 1120.5 keV, it has a convenient half-life of 83.8 days (El-Taher et al., 2003, 2004).

Six rare earth elements were determined in all marble samples. The elements determined are La, Ce, Sm, Eu, Yb and Lu. The selection of photopeaks for the analysis is briefly discussed below for each element. For lanthanum, the high abundance photopeak of ^{140}La at 1596 keV was used, which is free of interference. The

Table 2
The average elemental concentrations of marble determined by INAA.

Element	Activation product	Energy (keV)	t 1/2	Average	Statistical error %
Na%	^{24}Na	1369	15 h	0.01	7.37
Mg%	^{27}Mg	1014	9.5 min	1.5	6.74
Ca%	^{49}Ca	3984	8.7 min	3.71	15.68
Mn%	^{56}Mn	846	2.6 h	0.01	1.31
Fe%	^{59}Fe	1099	44.5 d	3.93	4.62
Sc	^{46}Sc	889	38.8 d	0.41	1.8
Cr	^{51}Cr	320	27.7 d	376	1.96
V	^{52}V	1434	3.4 min	0.47	11.71
Co	^{60}Co	1332	5.3 y	0.58	6.25
Zn	^{65}Zn	115	244 d	23.5	7.78
As	^{76}As	559	26.3 h	4.94	12.76
Sn	^{117}Sn	158	13.6 d	328	20.6
Ba	^{131}Ba	496	11.8 d	34.2	20.59
La	^{140}La	1596	40.3 h	2.76	13.81
Ce	^{141}Ce	145	32.5 d	7.24	6.31
Eu	^{152}Eu	1408	13.3 y	0.1	15.28
Sm	^{153}Sm	103	46.3 h	1.09	6.19
Yb	^{169}Yb	198	32 d	0.85	9.09
Lu	^{177}Lu	208.4	161 d	0.06	10.69
Hf	^{181}Hf	428	42.4 d	0.37	10.46
Th	^{233}Pa	312	27 d	0.18	17.36
U	^{239}NP	106	2.4 d	1.68	15.66