Research Article

Elemental Analysis and Natural Radioactivity Levels of Clay by Gamma Ray Spectrometer and Instrumental Neutron Activation Analysis

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Due to increased global demand for clay, the present work involves the use of INAA for elemental analysis and pollutants concentration in clay. The samples were collected from Aswan in South Egypt. The samples were irradiated using the thermal neutrons “at the TRIGA Mainz research reactor” and at a neutron flux “of $7 \times 10 \text{ n/cm s}$ ”. Twenty-six elements quantitatively and qualitatively were specified for the first time upon studying the samples. The elements determined are U, Th, Ta, Hf, Lu, Eu, Ce, Ba, Sn, Nb, Rb, Zn, Co, Fe, Cr, Sc, Sm, La, Yb, As, Ga, K, Mn, Na, Ti, and Mg. The concentrations of natural radionuclides ^{232}Th , ^{226}Ra , and ^{40}K were also calculated. Based on these concentrations, to estimate the exposure risk for using clay as raw materials in building materials, the radiation hazard indices such as radium equivalent activities, effective doses rate, and the external hazard indices have been computed. The obtained results were compared with analogous studies carried out in other countries and with the UNSCEAR reports.

1. Introduction

Due to increased global demand for clay and its industrial importance, for diversity of uses, it is considered as one of the leading minerals worldwide [1]. Instrumental neutron activation analysis INAA using HPGe detector coupled with a multichannel pulse height analyzer and optimum choice of irradiation and delay times may yield promising results and have been employed in a number of methods for the analysis of geochemical materials. The elemental content in different environmental media has been widely employed by INAA technique [2, 3]. Until now, there is no database for the constituent elements for clay. Therefore, our results can be considered as reference data for the Egyptian clay. Natural radionuclides research has contributed greatly to developing a quantitative understanding of the environmental performance. In order to attain an improved understanding of the environmental destiny of contaminant radionuclides, it is necessary to characterize not only the biogeochemical

properties of the radionuclides but also the expected biogeochemical processes occurring in the receiving environment [4, 5].

The present work dealt with measuring the elemental content of clay samples collected from Aswan, South Egypt, and shed more light on the activity concentrations of the naturally occurring radioactive materials (NORM) to assess the radiation hazard parameters due to using clay as building materials.

2. Experimental Technique

2.1. Samples Preparation. Clay samples were collected from Aswan, South Egypt. Each of the samples weighs about 1 kg and is then dried in an oven at about 105° to make sure that all the moisture has been removed. For elemental analysis using instrumental neutron activation analysis, the powder samples were sieved through a set of standard sieves with diameters ranging within 63–125 μm , and an electric

TABLE 1: Irradiation conditions for the elements determined.

Irradiation time	Counting time	Decay time	Elements
1 m	4 m	5 m	Ti, Mg
5 m	15 m	1 h	M, Na
6 h	1 h	2 d	U, Sm, La, As, Ga,
6 h	8 h	14 d	Th, Rb, Nb, Cr, Sc, Co, Fe, Zn, Sn, Hf, Eu, Ce, Lu, Yb, Ta, Ba

shaker was used to obtain homogeneous samples; the samples were irradiated using thermal neutrons. With regard to measurement of the natural radioactivity, each sample was grinded and homogenized and thereafter the powder clay samples were sieved through a 200-mesh sieves, “which is the optimum size when enriched in heavy minerals” to become homogenized powder [6]. The samples were weighed, Packed, and sealed in polyethylene Marinelli beakers, of 350 cm³ volume each, and then stored for 4 weeks to attain secular equilibrium with the short-lived daughters of ²³²Th and ²²⁶Ra and their long-lived parent radionuclides [7].

The activity concentrations of radionuclides were determined from the significant average energy lines of 609.3, 1120.3 and 1764.5 keV (²¹⁴Bi), 352.9 keV (²¹⁴Pb) for ²²⁶Ra, 1460.7 keV for ⁴⁰K and 968.9, 338.4 and 911.1 keV (²²⁸Ac) for ²³²Th series [8].

2.2. Instrumentation and Irradiations. Polyethylene capsules were filled with a hundred mg from powder clay samples and then irradiated with a Dolerite WSE and Microgabro PMS standard reference material with thermal neutrons “at the University of Mainz Triga research reactor (100 kWth) with a flux of 7×10^{11} n/cm² s”. The concentration of the elements determined in the irradiated samples was quantitatively specified by comparison with the activities of the reference materials [9, 10]. After appropriate cooling times, the data were collected to conduct different measurements [11]. The irradiation conditions for the elements determined were shown in Table 1.

The measuring of activity concentration for radionuclide in studied samples was defined using gamma ray spectrometer system by HPGe detector with an electronic circuit. The HPGe detector has specifications as a follows: energy resolution (FWHM) is 1.70 keV at 1.33 MeV ⁶⁰Co, Peak-to-Compton ratio ⁶⁰Co is 65.2, and relative efficiency is 29.2 at 1.33 MeV ⁶⁰Co. The analysis of results was accomplished by the Inter-Gamma Software that was generated by Intertechnique “Deutschland GmbH, Mainz, Germany” [12–17]. In all measurements, the electronic dead time is less than 10% and the Inter-Gamma Software has performed the correction automatically [2].

2.3. Estimation of Radiological Dose and Hazardous Indices

2.3.1. Radium Equivalent Activity (Ra_{eq}). The radium equivalent activity (Ra_{eq}) values in Bq/kg were obtained by using the following equation:

$$Ra_{eq} = C_{Ra} + C_{Th} \times 1.43 + C_K \times 0.077, \quad (1)$$

where C_K , C_{Th} , and C_{Ra} are the activity concentrations of ⁴⁰K, ²³²Th, and ²²⁶Ra in samples, respectively. The definition is based on the supposition that 130 Bq/kg of ⁴⁰K, 7 Bq/kg of ²³²Th, and 10 Bq/kg of ²²⁶Ra create the same gamma radiation exposure dose [18, 19].

2.3.2. Absorbed Dose Rate (D). The absorbed dose rate in air due to radionuclides at 1 m above the ground surface for the uniform distribution of ²²⁶Ra, ²³²Th, and ⁴⁰K was calculated according to guidelines supplied from UNSCEAR:

$$D = C_{Ra} \times 0.462 + C_{Th} \times 0.604 + C_K \times 0.0417, \quad (2)$$

where 0.462, 0.0417, and 0.604 nGy h⁻¹ per Bq/kg were the conversion factors that correspond to ²²⁶Ra (²³⁸U-series), ⁴⁰K, and ²³²Th [20, 21].

2.3.3. External Hazard Index (H_{ex}). The recommended value of absorbed dose rate is 1.5 mSv y⁻¹ [22, 23]. To limit the radiation dose value to this rate, the conservative model suggestion is based on infinitely thick walls, without doors and windows [24] to serve as a standard for the computation of index defined as external hazard index H_{ex} from the following relation:

$$H_{ex} = \frac{C_{Ra}}{740} + \frac{C_{Th}}{520} + \frac{C_K}{9620} \leq 1. \quad (3)$$

3. Results and Discussion

Twenty-six elements were identified in studied clay samples. The average concentration of the elements determined is listed in Table 2. The elements Ti, K, Cr, Ga, Na, Mg, Mn, Sm, As, Sc, La, Co, Rb, Nb, Sn, Ce, Fe, Ba, Eu, Lu, Yb, Hf, Ta, Zn, Th, and U were determined. The concentration for all elements was expressed in $\mu\text{g/g}$ except for Mn, Mg, Na, Fe, K, and Ti which were given in g/kg. In all other situations, the elements were measured by their most distinctive peaks, with lowest statistical errors and free of interference. The measurements accuracy has been estimated using the PMS and WSE analysis, for the standard reference materials. From the obtained results, we can say that INAA is an effective and successful means to supply valuable data for clay samples with a satisfying precision. The accuracy for most elements in present results is in the range of 10% of the reference values, and a good precision has been shown in most results [25, 26]. The activation converts ²³⁸U and ²³²Th into ²³⁹Np and ²³³Pa, respectively, by neutron capture and successive β -decay:

The feature γ -rays can be detected using γ -spectroscopy [27, 28].

TABLE 2: Clay composition and the average concentration of the elements calculated using INAA.

Element	Measured isotope	Half-life (T 1/2)	Energy: E_γ (keV)	Average concentration (ppm)	Statistical error (%)
Mg%	²⁷ Mg	9.5 m	1014	5.3	6.74
Na%	²⁴ Na	15 h	1369	26	0.26
K%	⁴² K	12.36 h	1525	6.9	6.87
Ti%	⁵¹ Ti	3.75 m	320	3.71	5.68
Mn%	⁵⁶ Mn	2.6 h	846	29	1.31
Fe%	⁵⁹ Fe	44.5 d	1099	0.84	2.60
Sc	⁴⁶ Sc	38.8 d	889	842	0.24
Cr	⁵¹ Cr	27.7 d	320	274	2.40
Co	⁶⁰ Co	5.3 y	1332	3.3	0.92
Zn	⁶⁵ Zn	244 d	115	0.1	5.80
Ga	⁷² Ga	14.1 h	834	1.18	11.63
As	⁷⁶ As	26.3 h	559	219	18.66
Rb	⁸⁶ Rb	18.7 d	1077	5.9	5.38
Nb	⁹⁵ Nb	34.98 d	766	1	2.91
Sn	¹¹⁷ Sn	13.6 d	158	15.11	20.6
Ba	¹³¹ Ba	11.8 d	496	0.14	9.90
La	¹⁴⁰ La	40.3 h	1596	183	1.48
Ce	¹⁴¹ Ce	32.5 d	145	18.4	1.76
Eu	¹⁵² Eu	13.3 y	1408	16.5	4.31
Sm	¹⁵³ Sm	46.3 h	103	106	0.89
Yb	¹⁶⁹ Yb	32 d	198	31.3	5.34
Lu	¹⁷⁷ Lu	161 d	208.4	77.4	4.69
Hf	¹⁸¹ Hf	42.4 d	428	9.8	2.60
Ta	¹⁸² Ta	114.43 d	1221	7.0	5.51
Th	²³³ Pa	27 d	312	12.6	3.08
U	²³⁹ NP	2.4 d	106	2.36	14.4

3.1. Assessment of Natural Radioactivity and Exposure Risk.

To estimate the exposure risk which naturally occurs as a result of the use of clay as raw materials in construction, the radiological indicators like the external hazard index H_{ex} , absorbed dose rate D , and radium equivalent activity Ra_{eq} and the specific activity concentrations of radionuclides in Bq/kg have been computed according to [19]. The obtained results were listed in Table 3. Average activity concentration of ⁴⁰K, ²³²Th, ²²⁶Ra, and Ra_{eq} in clay samples was 208, 28, 36, and 101 Bq/kg, respectively. These values are within the worldwide range of the activity concentration values of ²³²Th, ²²⁶Ra, and ⁴⁰K in soil and 30, 35, and 400 Bq/kg, respectively [21]. Up to our knowledge, there is no published world average activity concentration of natural radioactivity in clay deposits. All over the world clays deposits are widely used as a building material (e.g., bricks and ceramic industries). Their radioactivity content could be a source of dwelling internal and external radiation exposure. Ra_{eq} values were less than 370 Bq/kg, the maximum permissible activity concentration limit for building material. This value, 370 Bq/kg, is equivalent to maximum permissible limit [8, 29, 30].

The average activity concentrations of ²²⁶Ra, ²³²Th, ⁴⁰K, and Ra_{eq} in clay bricks and building materials, from twelve different countries, were given in Table 4 [31]. The average activity concentrations of natural radionuclides in Egyptian clay samples that could be used as a raw material for bricks industry were less than the average of all studies for ²²⁶Ra, ²³²Th, ⁴⁰K, and Ra_{eq} [32].

TABLE 3: Specific activities and radiological indices for the clay studied samples.

Sample number	²²⁶ Ra	²³² Th	⁴⁰ K	Ra_{eq}	D	H_{ex}
1	40 ± 3.1	12.5 ± 0.6	47 ± 6.9	62	28	0.2
2	49 ± 2.5	50 ± 2.5	241 ± 12.1	135	65	0.4
3	44 ± 3.2	43 ± 2.1	251 ± 12.6	108	50	0.3
4	45 ± 3.3	60 ± 3.3	283 ± 15	66	31	0.2
5	34 ± 2.4	45 ± 3.2	132 ± 10.0	103	49	0.3
6	36 ± 2.1	31 ± 1.8	167 ± 9.5	150	71	0.4
7	30 ± 1.5	21 ± 10	263 ± 13.1	78	38	0.2
8	30 ± 1.5	20 ± 10	279 ± 13.9	78	38	0.2
9	39 ± 2.5	18 ± 1.8	125 ± 6.3	75	34	0.2
10	35 ± 1.8	52 ± 2.6	136 ± 6.8	73	35	0.2
11	27 ± 1.4	21 ± 10	222 ± 11.1	104	40	0.2
12	39 ± 2.3	18 ± 0.8	240 ± 13.5	82	39	0.3
13	32 ± 1.6	30 ± 1.6	250 ± 12.5	86	41	0.2
14	38 ± 3.5	18 ± 2.8	260 ± 14.9	219	103	0.6
15	30 ± 2.4	29 ± 2.6	214 ± 11.7	97	46	0.3
16	38 ± 1.9	12 ± 0.6	245 ± 12.2	72	39	0.2
17	37 ± 1.9	07 ± 0.4	171 ± 8.6	156	74	0.5
18	31 ± 2.7	19 ± 2.0	210 ± 11.5	74	35	0.2
Min	30 ± 1.5	07 ± 0.4	47 ± 6.90	62	28	0.2
Max	49 ± 2.5	60 ± 3.3	279 ± 14	219	103	0.6
Average	36.3 ± 1.5	28.1 ± 0.8	208 ± 11	101	47.5	0.3

TABLE 4: Comparison of ^{226}Ra , ^{228}Ra , and ^{40}K and radiation hazard parameter in clay from around the world [31].

Country	^{226}Ra	^{232}Th	^{40}K	Ra_{eq}
Australia	41	89	681	220
China	41	52	717	171
Egypt	20	14	204	56
Finland	78	62	962	241
Greece	49	24	670	135
Germany	59	67	673	207
India	48	52	381	152
Netherlands	39	41	560	141
Sweden	96	127	962	352
Norway	104	62	1058	276
Sri Lanka	35	72	585	183
Egypt, present work	36	28	208	101

4. Conclusions

Twenty-six elements were quantitatively determined in the first time for clay samples collected from Aswan, South Egypt. The elements Ti, K, Cr, Ga, Na, Mg, Mn, Sm, As, Sc, La, Co, Ce, Sn, Rb, Nb, Fe, Ba, Eu, Lu, Yb, Ta, Zn, Th, and U were determined. From the obtained results, we can say that INAA is an effective and useful tool to provide good data for clay samples with a precision and satisfying accuracy. The average activity concentrations of natural radionuclides in Egyptian clay samples that could be used as a raw material for bricks industry were less than the recommended levels by UNSCEAR data for soil. It is hoped that our clay data are useful to those dealing with clay applications.

Competing Interests

The authors declare that they have no competing interests.

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