NUKLEONIKA 2000;45(4):243–247

ORIGINAL PAPER

A modified method for the determination of radioactive isotopes in building raw and construction materials with multichannel gamma spectrometry

**Witold A. Charewicz,
Adam Żebrowski,
Władysław Walkowiak,
Beata Borek**

Abstract A modified method is presented for the determination of natural and artificial isotopes in building raws and materials using multichannel gamma-ray spectrometry. A procedure is given for the preparation of standards as well as for the determination of radioisotopes content in typical building raws and/or materials. Results of these determinations were compared with those from standard, tri-channel gamma spectrometry described in Instruction No. 234/95 [2] issued by the Institute of Building Technology in Warsaw, Poland.

Key words building materials • multichannel gamma-ray spectrometry • radioactive isotopes

W. A. Charewicz✉, A. Żebrowski, W. Walkowiak, B. Borek
Institute of Inorganic Chemistry and Metallurgy
of Rare Elements,
Wrocław University of Technology,
23 Smoluchowskiego Str., 50-370 Wrocław, Poland,
Tel./Fax: +4871/ 3284330,
e-mail: charewicz@ichn.ch.pwr.wroc.pl

Received: 10 January 2000, Accepted: 8 September 2000

Introduction

From among radiation affecting people today especially important is the ionizing radiation of natural radioactive isotopes from soil, rocks, air, and waters as well as from cosmic radiation. The greatest contribution to the total dose of this ionizing radiation comes from radon, particularly from the ^{222}Rn isotope, which is a daughter isotope of ^{226}Ra. Therefore, since radon and other natural radioactive isotopes present in building raws and materials create a hazard for people working or residing in buildings, Poland established limits in concentrations of natural radioisotopes for building raws and materials [7].

The three most important radioactive isotopes among those present in building raws and materials are ^{40}K, ^{238}U with uranium-radium series isotopes, and ^{232}Th with thorium series isotopes. The contribution of natural uranium-actinium series isotopes to natural radiation is not considered due to very low concentrations of the mother isotope ^{235}U. Radioactive decay of the above isotopes produces alpha, beta, and gamma radiation. Concentrations of these radioisotopes in the Earth's crust and in building materials determine the dose of natural radiation both outside and inside of buildings. Concentration of ^{226}Ra (the daughter isotope of ^{238}U) is crucial because its daughter isotope ^{222}Rn easily penetrates into places of permanent residence for people. The isotope ^{40}K (half-life time 1.28×10^9 years) is the only radioactive isotope among the three constituents of natural potassium (0.012%). The isotope ^{238}U (half-life time 4.51×10^9 years) consist of 99.77% of natural uranium. The total content of uranium in the Earth's crust is about 2.4 ppm, mainly as uranium containing

minerals (uranite, carnotite) and as traces in other minerals and rocks. ^{238}U undergoes alpha decay and is responsible for the initiation of the uranium-radium series isotopes.

^{232}Th, the only one natural isotope of thorium, undergoes alpha decay with a half-life time of 1.41×10^{10} and initiates the thorium series isotopes. The content of thorium in the Earth's crust amounts to approximately 12 ppm. The spectra of gamma radiation from these series isotopes cover the energy range from several tenths of keV up to 2.62 MeV. From the point of view of radiological protection the most important is the content of Ra-226 and Ra-228 isotopes rather than the mother radionuclides U-238 and/or Th-232. A shift of radiation equilibrium within the uranium-radium and thorium series may result from mining of building raws as well as from technological processes involving fabrication of building materials both from mineral and secondary sources (ashes, slags, etc.).

Production of building materials does not generally involve chemical operations leading to the release of any isotope-member of the uranium-radium series isotopes. Therefore, the only possible release of a radioactive isotope during production of building materials involves gaseous radon originally trapped in pores of the processed raw material. On the other hand, where secondary building raws are concerned, the probability of a disturbance in radiation equilibrium results from the nature of industrial processes (metallurgical, etc.) from which these secondary raws originate. Almost all the products of ^{226}Ra decay have short lives. Therefore, radiation equilibrium is achieved quickly. Reequilibration between ^{226}Ra and ^{222}Rn reaches 94% after 7 days. Consequently, the concentration of ^{226}Ra in building materials could be determined by measuring the activity of its gamma-emitting daughters after only 7 days of equilibration. In thorium series isotopes, the equilibrium between ^{232}Th and ^{228}Th is fundamental to determine ^{232}Th.

The radioactivity of ^{40}K, uranium-radium, and thorium series isotopes in building raws and materials vary within a wide range depending on the sort and origin of the source materials (Table 1). The concentration of radioactive isotopes in building walls, ceilings, and floors determines, in turn, the dose of radiation in a region and/or in a country.

An estimation of the radiation hazard originating in building raws and materials can be based by comparing the contents of radioactive isotopes in such materials with their average contents in Earth's crust. The isotopes ^{222}Rn (half-life time 3.82 day) and ^{220}Rn (half-life time 55 s) with their daughter isotopes, when present in the air of a dwelling, result in the risk of internal contamination. These gaseous radioactive isotopes emanate from solid materials, and therefore, when breathed into the lung cause internal irradiation by means of the strongly ionizing alpha particles. The actual concentration of radon in the air inside buildings depends on several factors, e.g. the rate of radon diffusion into the building interior from its base, tightness of its foundations and walls, ventilation, etc. Another important factor is the radium content in the building materials used in floors, walls, and ceilings. Therefore, the determination of radium concentration in a given building material provides the basis to qualify, which material should be used in the building materials industry. In addition to natural radioactive isotopes, also the artificial ones such as ^{137}Cs (half-life time 30 years) should be considered, which were introduced into the environment from radioactive contamination [6].

In 1980 the Ministry of Building and Building Materials Industry, the Central Laboratory of Radiological Protection and the Ministry of Health and Social Welfare have issued a compulsory regulation of validation/certification of building raws and materials [1]. Detailed regulations and procedures were published in Instruction No. 234/95 issued by the Institute of Building Technology in Warsaw (ITB) [2].

Two criteria for evaluating building raws and materials, to be used in buildings destined for permanent residence, have been established:
– the condition limiting the hazard of exposition of the entire body to gamma radiation, in which the concentrations of potassium ^{40}K (S_K), radium ^{226}Ra (S_{Ra}), and thorium ^{228}Th (S_{Th}) in [Bq/kg] are expressed as:

$$F_1 = 0.00027S_K + 0.0027S_{Ra} + 0.0043S_{Th} \quad (1)$$

$$f_{1,\,max} = F_1 + \Delta F_1 \le 1 \quad (2)$$

– the condition limiting ^{226}Ra concentration in a building material because of emanation of ^{222}Rn from walls, ceilings, and bases:

$$F_2 = S_{Ra} \quad (3)$$

$$f_{2,\,max} = F_2 + \Delta F_2 \le 185 \text{ Bq/kg} \quad (4)$$

where: ΔF_1 and ΔF_2 are the absolute errors at a confidence level of 0.95.

Evaluation of a building raw or material is considered to be positive, if both of these criteria are met simultaneously. If the actual values of $f_{1,max}$ and/or $f_{2,max}$ for a given material exceed their limits by no more than 20%, such a raw can be used for the production of building materials but only after adequate dilution with other, radioactive-free ingredients. If $f_{1,max}$ and/or $f_{2,max}$ exceed the limits by more than 20% the material can be, for example, utilised in road construction.

The determination procedure for radioactive isotopes elaborated by the Institute of Building Technology assumes the equilibrium status between the ^{226}Ra and ^{214}Bi isotopes. Measurement is based on the determination of concentrations of ^{40}K, ^{226}Ra, and ^{228}Th. Radiation of these radioisotopes is registered in three channels of a tri-channel gamma spectrometer with a NaI(Tl) scintillation detector. The method itself is a comparative one since the intensity of gamma radiation is analysed separately for a sample and for three volumetric standards of potassium, radium, and thorium. Generally, the ITB method seems to provide a relatively simple and efficient way of determining the natural

radioactive isotopes in building raws and materials. Nevertheless, this method has certain weaknesses. First, it is not suitable for materials in which radioactive equilibrium is non existent between the heavier natural radioisotopes. Secondly, it is designed for natural radioactive isotopes exclusively. Consequently, the possible presence of an artificial radioisotope in the sample could not be detected. In order to eliminate the above weaknesses two procedures were advanced to determine radioactive isotopes in raws and materials using multichannel gamma-ray spectrometry [5, 6]. These procedures allow to determine both natural and artificial radioisotopes. A method for evaluating solid angles was presented elsewhere [6]. Solid angles, which depend on the energy of gamma quanta [3], were estimated by determining the coefficients of absorption of gamma radiation *vs.* energy. The fundamental weakness of this method is the necessity to determinate the absorption curve for each material within the range of radiation energy from 50 to 2000 keV.

We now present a modified method for the determination of radioactive isotopes (both natural and artificial) in building raw and/or construction materials to replace the above procedure.

Experimental

Procedure

The method is based on procedures and calculations used for determining concentrations of radioactive isotopes in atmospheric air which involve the absorption of air aerosols. In order to perform a quantitative radioanalysis, the adequate standards must be calibrated. Such standards should be made from materials of identical or very similar physical properties. Thus, we can neglect coefficients of absorption of gamma radiation in both the sample and standard.

The activity (A) of a radioisotope is given by the equation:

$$A = N(E)/F(E) \cdot n \cdot t \quad (5)$$

where: N(E) – number of counts (background substracted) of gamma quanta of energy E; F(E) – the absolute detection efficiency of a detector; n – the probability of emission of the gamma quantum of energy E; t – time of measurement.

The absolute counting efficiency F(E) is calculated from equation (6) using the results of standards measurements:

$$F(E) = N_s(E)/A_s \cdot n \cdot t_s \quad (6)$$

where: $N_s(E)$ – number of counts (background substracted) of gamma quanta of energy E in a standard; A_s – activity of a standard source [Bq]; n – as in equation (5); t_s – time of standard measurement.

Thus, determination of coefficients is possible by correlating the detection efficiency and the energy of gamma quanta. Consequently, calculation of the detection efficiency becomes possible for the given energy of gamma radiation. Therefore, both natural and artificial radioactive isotopes can be determined in a sample.

Measurements were made with a multichannel gamma spectrometer (Nuclear Data Inc.) type ND-76 with a germanium (HPGe) detector. Its parameters as well as sample detector geometry are given elsewhere [6]. A total of 4096 channels has covered the range of quanta energy from 50 to 2000 keV.

Preparation of standards

Radiometric standards of building raws and materials were prepared from the following base components: brick, slag, sand, gypsum, ash, and gravel. Sand and gravel were mixed before use, because of their similar compositions (SiO_2). Samples of these base materials were taken from different places:
brick – 100 class from the "Biała" brick-kiln (Nysa), 150 class from the "Leszczyna" brick-kiln (Kłodzko), 200 class from the "Cerabud" (Krotoszyn); slag – from the heat/power station (Wrocław), the heat/power station (Wrocław-Popowice), the power station "Turów" (Turoszów); sand – from the river sand (Odra), river sand (Mietków), mined sand (Mękarzowice); gravel – from Paczków, Mietków and Wrocław-Popowice; gypsum – from the gypsum boards (Nida-Gips), filling gypsum (Nida-Gips); ash – fly ash from the "Opole" power station, blocks: 3, 5, and 16.

Samples of these materials were ground and screened in order to separate fractions (104, 74, 46 and 37 μm) corresponding to the granulation of spectrometric standards used to prepare working standards of building raws and materials. A base component of the standard of a given building raw or materi-

Material	Concentration [Bq/kg]			The rate of absorbed dose in air [mSv/year]
	^{40}K	^{226}Ra	^{232}Th	
Sand	37-666	7.0-81.4	7.4-103.6	0.09-1.16
Gravel	37-666	3.7-55.5	3.7-62.9	0.05-0.82
Gypsum	7-370	11.1-22.2	7.4-18.5	0.11-0.33
Phosphogypsum	37-370	18.5-1480.0	7.4-25.9	0.24-5.83
Fly ash	252-1773	7.4-610.5	7.4-310.8	0.17-4.76
Slag	37-2227	18.5-510.6	7.4-429.2	0.13-5.26

Table 1. Ranges of concentrations of natural radioactive isotopes in selected building raws [2].

Table 2. Selected peaks of gamma-radioactive isotopes.

Isotope	Series	Energy [keV]	Quantum yield
Th-234	U-Ra	63.29	0.038
Ac-228	Th	129.03	0.029
Ac-228	Th	209.39	0.041
Pb-212	Th	238.58	0.436
Ac-228	Th	338.42	0.124
Pb-214	U-Ra	351.87	0.371
Ac-228	Th	463.10	0.046
B-214	U-Ra	609.31	0.461
Ac-228	Th	911.16	0.290
Bi-214	U-Ra	934.04	0.032
Bi-214	U-Ra	1120.27	0.150
Bi-214	U-Ra	1377.66	0.040
K-40	-	1460.83	0.107
Bi-214	U-Ra	1764.49	0.159

al was made by mixing three (for gypsum – two) source base materials. The base component of each building raw and material prepared in this way for two hours was divided into two parts. One part was mixed with spectrometric standards supplied by the IAEA (Vienna): RGU-1, RGTh-1, and RGK-1 (400 μgU/g, 800 μgTh/g, and 44.8% ^{40}K, respectively) to produce the final standards. The amounts of standards did not exceed 10 wt.% of the mass of the base components. Therefore, the difference self absorption in RGU-1 and RGTh-1 standards, and in the measured samples may be neglected. The second part was preserved in order to measure the background spectrum to be subtracted from the spectra of the final standards. As a result, the net radioactivities of measured sources were determined. Samples (ca. 50 g) were placed in a measuring cylinder made from Plexiglas and thereafter, gamma spectra for each case were taken for 24 hours.

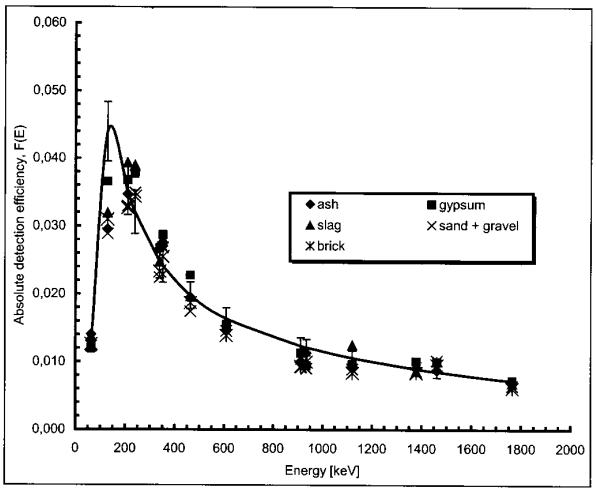

Fig. 1. The absolute detection efficiency *vs.* photon energy for some building raws/materials. (Solid line represents the mean value).

Total errors of the measurements were at the level of one standard deviation value. Nevertheless, certain lack of homogeneity in the prepared standards and the procedure of substracting, the measured spectra may be a additional source of errors.

Results and discussion

The gamma spectra were first analysed qualitatively in order to choose the peaks corresponding to energies covering the whole measuring range from 50 to 2000 keV. The criteria of choosing these peaks were the following:
– the peak can be ascribed to only one isotope exclusively,
– a sufficiently high quantum yield which allows to detect the peak even at low content of an isotope.
The peaks and corresponding isotopes are given in Table 2. The values of absolute detection efficiency for each peak list-

Table 3. Results of radiometric analysis of heat-resisting brick (A) and gravel (B) samples.

Isotope	Energy [keV]	Multichannel spectroscopy		Tri-channel spectrometry (AZAR-90)	
		A	B	A	B
		Concentration [Bq kg^{-1}]			
^{40}K	1460.83	238±24	1092.4±120.5	222.41±95.00	802.16±79.09
^{226}Ra	63.29 (Th-234)	-			
	186.00 (Ra-226)	1301±26			
	351.87 (Pb-214)	1350±12			
	609.31 (Bi-214)	1282±14	43.8±3.8	1095.50±66.29	67.29±12.02
	934.04 (Bi-214	1183±65			
	1120.27 (Bi-214)	1125±29			
	1377.66 (Bi-214)	1321±65			
	1764.49 (Bi-214)	994±20			
^{228}Th	129.03 (Ac-228)	-			
	209.39 (Ac-228)	173±25			
	238.58 (Pb-212)	218±3			
	338.42 (Ac-228)	261±10	49.4±14.6	258.70±18.64	24.79±4.11
	463.10 (Ac-228)	338±31			
	583.02 (Tl-208)	97±11			
	860.30 (Tl-208)	111±39			
	911.16 (Ac-228)	270±12			
^{137}Cs	661.62	Not detected	18.1±1.3	Not detected	Not detected

Table 4. Comparison of evaluation criteria $f_{1, max}$, $f_{2, max}$ (eqs. 2 and 4) of heat-resisting brick (A) and gravel (B) samples determined with multichannel and tri-channel gamma-spectrometry.

			Multichannel spectrometry	
Coefficient	AZAR-90		S_{K-40} (1460.83 keV), S_{Ra-226} (1120 keV), S_{Th-228} (911 keV)	
	A	B	A	B
$f_{1, max}$	4.36	0.50	4.40	0.60
$f_{2, max}$	1161.79	67.29	1154	43.8

ed in Table 2 were calculated from equation (4). Then, the following dependence was evaluated from these values using the computational procedure GENIE-2000 (Canberra) [4]:

$$\log F(E) = A \cdot E + B + C/E + D/E^2 \quad (7)$$

where: $A = -2.02\times10^{-4}$, $B = -1.86$, $C = 1.36\times10^{2}$, $D = -8.71\times10^{3}$.

Application of equation (7) is illustrated in Fig. 1.
The concentrations of ^{40}K, ^{226}Ra, and ^{228}Th isotopes were determined in the heat-resisting brick and gravel (Złoty Stok) samples with the above elaborated methodology; thereafter, results were compared with those of similar measurements with a standard tri-channel spectrometer AZAR-90 (Table 3). For certain energies (corresponding to the lowest discrepancy of results) the evaluation criteria ($f_{1, max}$ and $f_{2, max}$) were calculated (Table 4).

Conclusions

Satisfactory agreement exists between the concentrations of natural gamma-emitters determined by our modified methodology and the standard tri-channel spectrometry recommended by ITB, while the best agreement for the evaluation criteria $f_{1, max}$ and $f_{2, max}$ was achieved at the peaks 1120 keV and 911 keV of Ra-226 and Th-228, respectively. This methodology also allows to determine artificial gamma radioisotopes (e.g. Cs-137), which is of special importance in areas contamineted by a nuclear accident (e.g. Chernobyl, Ukraine). Contrary to the procedures described above [6], the present methodology does not require the determination of absorption coefficients for each measured material. On the other hand, the mixing procedure for the components of radiometric standards of building raws/materials seem to effect the final accuracy of our radiometric measurements. The major weaknesses of the proposed methodology are the costly apparatus (a multichannel spectrometer with a semiconductor detector) and a relatively long time of determination.

References

1. Brunarski L, Biernacka M, Gwiazdowski B, Krawczyk M, Mamont-Cieśla K, Żak A (1980) Guiding rules of investigating of the natural radioactivity of building raws and materials. Instruction ITB No. 234
2. Brunarski L, Biernacka M, Krawczyk M, Mamont-Cieśla K, Żak A (1995) Guiding rules of investigating of the natural radioactivity of building raws and materials. Instruction ITB No. 234/95
3. Frączkiewicz R, Walkowiak W (1992) Calculations of an effective solid angle including self-absorption correction applied to gamma-ray spectrometry analysis of natural samples. Nucl Instrum Meth Phys Res B 71:434-440
4. Genie-2000 Spectroscopy System (1997) Customization Tools, Canberra Industries
5. Kalita S (1984) Determination of natural radioactive impurities in some raw materials and building materials by gamma spectrometry. Institute of Nuclear Physics and Technique, Academy of Mining and Metallurgy, Kraków, No. 186/I
6. Walkowiak W, Żebrowski A (1995) Determination of radioactive isotopes in building raws and materials with the multichannel gamma-radiation spectrometry. Postępy Techniki Jądrowej 38;3:5-15
7. Żak A, Biernacka M, Jagielak J, Lipiński P (1993) Investigations of radioactivity of building raws and materials. Nukleonika 38;4:51-63