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THORIUM DETERMINATION IN INTERCOMPARISON SAMPLES AND IN SOME ROMANIAN BUILDING MATERIALS BY GAMMA RAY SPECTROMETRY

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Abstract — Thorium content in zircon sand, thorium ore and a thorium liquid sample (EU Laboratories Network Intercomparison), as well as in some Romanian building materials: sand, wood, tufa, asbestos-cement, cement mill dust, coal fly ash, bricks, and tile (28 samples) was determined by gamma ray spectrometry. For the building materials, ^{226}Ra, ^{40}K and ^{137}Cs specific activities were also measured. The results were compared with the Romanian legal norms concerning the highest admissible levels for ^{232}Th, ^{226}Ra, and ^{40}K radioactivity, and to Th, U, and K concentration values previously determined in our laboratory on similar types of samples.

INTRODUCTION

The paper presents the results our laboratory has obtained in thorium analysis by gamma ray spectrometry on some mineral samples. ^{232}Th activity concentration was calculated from its decay products ^{228}Ac, ^{212}Pb, ^{212}Bi, and ^{208}Tl, assuming radioactive equilibrium among all ^{232}Th decay chain isotopes. By comparison, it should be mentioned that radioactive equilibrium does not exist within biological samples such as tissues because of the different metabolic behaviour of ^{232}Th decay radionuclides (e.g. ^{224}Ra and ^{228}Ra are largely transported from the liver to the bone, while ^{220}Rn enters the general circulation)[1].

Zircon sand, thorium ore and a thorium liquid sample were analysed in the framework of the European Commission Project 'Thematic Network on the Analysis of Thorium and its Isotopes in Workplace Materials' coordinated by the Health and Safety Laboratory (HSL), Sheffield, United Kingdom[2]. Sand, wood, tufa, asbestos-cement, cement mill dust, coal fly ash, tile, red and autoclaved cellular concrete (ACC) bricks collected from building material factories in different zones of Romania were investigated for natural and artificial radioactivity. The results were compared to the Romanian legal norms for maximum permissible ^{232}Th, ^{226}Ra, and ^{40}K activity concentrations in building materials[3].

Thorium content in ores (monazite) was previously analysed in our institutes by emanation, autoradiography with nuclear emulsions, and gamma spectrometry methods[4]. Moreover, Instrumental Neutron Activation Analysis (INAA) was used to determine Th and U concentration in Romanian zircon samples[5] and in some building materials (raw material for cement production, cement, furnace slag, phosphogypsum, cold compacted brick, and coal fly ash)[6,7]. Fission and/or alpha track methods were applied to determine U concentration in wood building materials (tree and rush)[8].

EXPERIMENTAL

Thorium nitrate solution containing ^{232}Th in equilibrium with its decay products and two thorium minerals (an ore and zircon sand) without any prior treatment were prepared as test samples by the Centre for Ionizing Radiation Metrology at the UK National Physical Laboratory (NPL), Teddington, England[2].

Building materials (28 samples) were collected from different factories in the southern half of Romania: coal fly ash from Deva and Paroseni (sub-bituminous coal-fired power plants), cement mill dust from Hoghiz and Fieni, and the other types of investigated building materials from Horezu, Targu Jiu, Rovinari, Slatina, and Craiova. The samples were collected during the summer of 1999, except for the cement mill dust from Hoghiz (April 1994) and Fieni (May 1995), as well as the coal fly ash from Deva (March 1995).

Sample preparation

Zircon sand and thorium ore intercomparison samples of 5.7326 ± 0.0003 g and 5.2800 ± 0.0003 g, respectively, were maintained inside sealed glass vessels of 2.5 cm diameter and 6 cm height. The liquid thorium intercomparison sample (10 ml in 2 M nitric acid solution) was diluted to 100 ml and put into a polyethylene pot (Sarpagan type, 7.2 cm diameter and 4 cm height).

The bulk building materials were air-dried, except for the wood samples which were dried in an oven at 60°C. Brick, tile, tufa and asbestos-cement samples were then ground and homogenised, while cement and coal fly ash powder, as well as the sand samples were only hom-

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ogenised in a mortar. Wood material was cut in pieces less than 5 mm each. Building material (30–150 g and 80–150 cm^3) was placed within Sarpagan polyethylene pots.

All samples were kept tightly closed in the pots for about one month to avoid losses of the gaseous ^{222}Rn (^{238}U series) and ^{220}Rn (^{232}Th series) in order to re-establish radioactive equilibrium from their precursors ^{226}Ra and ^{224}Ra, respectively.

Sample analysis

Gamma ray spectrometry was carried out using a HPGe (EG&G Ortec) detector of 2.3 keV FWHM at 1332.5 keV of ^{60}Co, and 30% relative efficiency, mounted in a low background shielding. Counting time varied between 4 and 27 h.

As calibration standards, water equivalent solid volume sources (^{133}Ba, ^{137}Cs, ^{152}Eu, and ^{241}Am) of 100 and 150 cm^3 prepared by the Radionuclide Metrology Laboratory (RML) of IFIN-HH[9,10], as well as $Th(NO_3)_4.5H_2O$ (p.a. Merck, Germany) for zircon sand and thorium ore samples (2.6306 g and 4.4748 g, respectively) were used. RML is legally, metrologically authorised to supply reference materials that are directly traceable to the national activity standard.

In addition, appropriate IAEA Reference Materials of geometry and densities similar to those of the investigated building materials were chosen as calibration standards. They consisted of: IAEA-373 (Chernobyl grass) for wood; IAEA-300 (Baltic Sea sediment) for ACC brick, coal fly ash, and tufa; IAEA-135 (Irish Sea sediment) for red brick and tile, sand, cement, and asbestos-cement samples.

Detection efficiency calibration curves were calculated for different building materials using certified activity concentration values of ^{134}Cs, ^{137}Cs, and ^{40}K in all the calibration standards considered and also of ^{241}Am and ^{232}Th in IAEA-135[11–13]. The self-absorption correction factors for samples relative to the calibration standards were determined by transmission measurements of gamma ray point sources.

The major chemical components of IAEA-135 sediment, are respectively the following: SiO_2 61.7%; Al_2O_3 9.3%; FeO 4.4%; $CaCO_3$ 11.2% and CaO 3.6%[13]. The major contents of mineral building materials lie within the following ranges: SiO_2 25–50% (coal fly ash, red brick and tile) and ~95% (sand); Al_2O_3 2–15%; Fe_2O_3 0.5–15% or Fe_3O_4 7–10% (cement); CaO 6–12% (coal fly ash, red brick and tile, ACC brick) and 35–40% (cement)[14].

Cellulose is the main constituent of the cell walls of plants and also of wood (beside the lignin).

RESULTS AND DISCUSSION

Table 1 shows the characteristic gamma rays taken into account and their absolute emission probabilities for ^{228}Ac, ^{212}Pb, ^{212}Bi, and ^{208}Tl radionuclides of the natural ^{232}Th series. The ^{208}Tl gamma ray emission probability in this table has been corrected for the ^{212}Bi decay branching ratio (BR A = 35.94%)[2].

Table 2 includes the ^{232}Th activity concentration by its decay products ^{228}Ac, ^{212}Pb, ^{212}Bi and ^{208}Tl in intercomparison samples (in $Bq.kg^{-1}$). The presence of the same radionuclides, save for ^{212}Bi, in building materials is given in Table 3. Tables 2 and 3 also contain the corresponding thorium mass concentration in $mg.kg^{-1}$ (1 g Th yields 4057.2 Bq[2]).

The activity concentrations of ^{226}Ra (by ^{214}Pb and ^{214}Bi decay products), ^{40}K, and ^{137}Cs measured in building materials are given in Table 4.

Overall uncertainty values in all the tables are calculated as squared roots of the sum of squared type A and type B components (k = 1). Type A uncertainties stem from sample and standard statistical counting; type B uncertainty values correspond to detection efficiency calibration (2–5%), self-absorption (<3%), and activity concentration certified for calibration standards (1.5–5%). Detection limits (3σ) for the non-measured elements are also shown in the tables.

As can be seen from Tables 2 and 3, a rather good agreement between the activity values was obtained for the measured ^{232}Th decay products in every investigated sample. ^{232}Th activity concentration was calculated as arithmetic (unweighted) mean of its progeny's activities.

For the intercomparison samples, the ^{232}Th results determined (Table 2) are in good agreement with the NPL target values of 551 ± 21 $Bq.kg^{-1}$ in zircon sand, 2494 ± 32 $Bq.kg^{-1}$ in thorium ore, and 10716 ± 102 $Bq.kg^{-1}$ in thorium nitrate solution (analyst/NPL ratios of 1.045, 0.99 and 0.97, respectively).

For the building materials, Th, U, and K concentrations obtained in the present work (Tables 3 and 4) are similar to those previously determined by INAA in cement, a cold compacted brick, and coal fly ash samples[6,7], as well as by fission and/or the alpha track method in wood[8] (Table 5). It was taken into account that 1 g of U and 1 g of K yield 12,358 Bq ^{238}U and 33.11 Bq ^{40}K, respectively.

Concerning the radioactivity levels in building materials, higher (by about 1.3–2 times) values were found for ^{232}Th in two of the red brick samples, and for ^{232}Th, ^{226}Ra, and ^{40}K in almost all tile samples compared with the Romanian legal norms. The accepted radioactivity levels are 53.3 $Bq.kg^{-1}$ for ^{232}Th, 100 $Bq.kg^{-1}$ for ^{226}Ra, and 832 $Bq.kg^{-1}$ for ^{40}K in red brick, as well as 32.2 $Bq.kg^{-1}$ for ^{232}Th, 32.6 $Bq.kg^{-1}$ for ^{226}Ra, and 466 $Bq.kg^{-1}$ for ^{40}K in tile[3].

CONCLUSIONS

The gamma ray spectrometry method could successfully be used in the thorium analysis of liquid and solid mineral samples, provided that the radioactive equilibrium between ^{232}Th and its decay products can be estab-

Table 1. Nuclear data for ^{228}Ac, ^{212}Pb, ^{212}Bi, and ^{208}Tl (^{232}Th radioactive series)[(2)].

Radionuclide	^{228}Ac	^{228}Ac	^{212}Pb	^{212}Bi	^{208}Tl
Energy (keV)	338.3	911.2	238.6	727.3	583.1
Gamma ray emission probability (%)	11.27	25.8	43.4	6.75	30.6

Table 2. ^{228}Ac, ^{212}Pb, ^{212}Bi, ^{208}Tl and ^{232}Th activity concentrations (Bq.kg^{-1}) and Th content (mg.kg^{-1}) in intercomparison samples.

Sample	^{228}Ac	^{212}Pb	^{212}Bi	^{208}Tl	^{232}Th	
					(Bq.kg^{-1})	(mg.kg^{-1})
Zircon sand	541 ± 18	595 ± 18	568 ± 41	599 ± 37	576 ± 14	142 ± 3
Thorium ore	2451 ± 76	2744 ± 123	2328 ± 123	2366 ± 66	2472 ± 47	609 ± 12
Liquid sample	10520 ± 569	10429 ± 643	11006 ± 596	9787 ± 535	10435 ± 294	2572 ± 72

Table 3. ^{228}Ac, ^{212}Pb, ^{208}Tl and ^{232}Th activity concentrations (Bq.kg^{-1}) and Th content (mg.kg^{-1}) in building materials.

Sample	^{228}Ac	^{212}Pb	^{208}Tl	^{232}Th	
				(Bq.kg^{-1})	(mg.kg^{-1})
Red brick, Horezu	38.3 ± 3.4	41.3 ± 3.7	39.3 ± 4.7	39.6 ± 2.3	9.8 ± 0.6
Red brick, Targu Jiu	87.4 ± 7.9	85.0 ± 4.2	83.6 ± 9.3	85.3 ± 4.3	21.0 ± 1.1
Red brick, Rovinari	117.5 ± 8.5	101.6 ± 7.8	104.8 ± 8.0	108.0 ± 4.7	26.6 ± 1.2
Red brick, Slatina	49.5 ± 3.7	45.5 ± 3.7	41.0 ± 2.9	45.3 ± 2.0	11.2 ± 0.5
Red brick, Craiova	50.1 ± 4.0	49.2 ± 4.5	50.0 ± 5.8	49.8 ± 2.8	12.3 ± 0.7
ACC brick, Targu Jiu	14.7 ± 3.7	12.2 ± 1.3	10.4 ± 1.3	12.4 ± 1.4	3.1 ± 0.3
ACC brick, Slatina	11.7 ± 3.5	15.3 ± 3.9	14.5 ± 2.0	13.8 ± 1.9	3.4 ± 0.5
ACC brick, Craiova	10.8 ± 1.8	12.8 ± 2.4	10.1 ± 1.7	11.2 ± 1.1	2.8 ± 0.3
Tile, Horezu	60.4 ± 3.0	56.8 ± 4.0	52.4 ± 3.1	56.5 ± 2.0	13.9 ± 0.5
Tile, Targu Jiu	52.3 ± 5.3	47.8 ± 3.1	49.6 ± 3.9	49.9 ± 2.4	12.3 ± 0.6
Tile, Rovinari	65.1 ± 3.3	71.7 ± 5.0	63.4 ± 3.2	66.7 ± 2.3	16.4 ± 0.6
Tile, Slatina	58.1 ± 4.0	60.3 ± 8.4	59.8 ± 8.9	59.4 ± 4.3	14.6 ± 1.1
Cement mill dust, Hoghiz	17.0 ± 3.6	15.2 ± 2.5	16.1 ± 3.0	16.1 ± 1.8	4.0 ± 0.4
Cement dust, Fieni	16.6 ± 3.7	14.6 ± 2.6	16.8 ± 2.0	16.0 ± 1.6	3.9 ± 0.4
Asbestos-cem., Horezu	10.1 ± 3.0	11.6 ± 2.5	10.6 ± 3.0	10.8 ± 1.6	2.7 ± 0.4
Asbestos-cem., Targu Jiu	10.7 ± 1.5	11.2 ± 1.5	10.4 ± 1.9	10.8 ± 0.9	2.7 ± 0.2
Asbestos-cem., Craiova	13.8 ± 3.1	12.7 ± 2.1	13.9 ± 2.0	13.5 ± 1.4	3.3 ± 0.3
Coal fly ash, Deva	103.9 ± 7.8	90.1 ± 7.2	96.1 ± 14.2	96.7 ± 5.9	23.8 ± 1.5
Coal fly ash, Paroseni	70.6 ± 8.4	82.8 ± 7.4	76.8 ± 5.4	76.7 ± 4.1	18.9 ± 1.0
Sand, Horezu	23.4 ± 4.2	17.6 ± 2.0	17.4 ± 2.3	19.5 ± 1.7	4.8 ± 0.4
Sand, Targu Jiu	30.5 ± 2.4	27.4 ± 2.3	28.7 ± 2.5	28.9 ± 1.4	7.1 ± 0.3
Sand, Rovinari	38.2 ± 4.6	29.8 ± 2.0	28.4 ± 3.0	32.1 ± 1.9	7.9 ± 0.5
Sand, Slatina	16.5 ± 2.2	13.6 ± 1.6	13.8 ± 1.6	14.6 ± 1.1	3.6 ± 0.3
Sand, Craiova	12.6 ± 1.5	16.6 ± 2.5	12.5 ± 1.6	13.9 ± 1.1	3.4 ± 0.3
Tufa, Horezu	12.9 ± 3.6	9.4 ± 3.1	7.1 ± 2.3	9.8 ± 1.8	2.4 ± 0.4
Wood, Horezu	<5.4	1.7 ± 1.4	<4.0	1.7 ± 1.4	0.42 ± 0.35
Wood, Targu Jiu	3.9 ± 3.4	1.8 ± 1.3	<3.6	2.9 ± 1.8	0.71 ± 0.44
Wood, Craiova	<5.6	1.7 ± 1.4	<4.7	1.7 ± 1.4	0.42 ± 0.35

lished. The method also makes it possible to analyse uranium and potassium contents in mineral samples (building materials, in particular) by measuring ^{238}U (in equilibrium with its radioactive progeny) and ^{40}K radioactivity.

Thorium concentrations determined by gamma ray spectrometry of thorium minerals and of some Romanian building materials are found to lie in a range from 0.42 ± 0.35 mg.kg^{-1} in wood to 24.4 ± 0.8 mg.kg^{-1} in red brick, and 643 ± 13 mg.kg^{-1} in thorium ore samples.

Table 4. ^{226}Ra, ^{40}K, and ^{137}Cs activity concentrations in building materials (Bq.kg^{-1}).

Sample	^{226}Ra	^{40}K	^{137}Cs
Red brick, Horezu	25.2 ± 2.4	588 ± 48	14.5 ± 1.7
Red brick, Targu Jiu	55.7 ± 5.0	727 ± 51	1.7 ± 0.8
Red brick, Rovinari	104.9 ± 4.1	760 ± 30	<0.8
Red brick, Slatina	21.7 ± 2.2	615 ± 25	<0.8
Red brick, Craiova	30.0 ± 2.1	655 ± 26	1.4 ± 0.6
ACC brick, Targu Jiu	6.2 ± 1.6	233 ± 13	4.3 ± 0.8
ACC brick, Slatina	5.0 ± 1.4	279 ± 17	<0.8
ACC brick, Craiova	12.4 ± 1.1	279 ± 14	4.1 ± 0.7
Tile, Horezu	37.7 ± 2.5	892 ± 33	8.0 ± 0.4
Tile, Targu Jiu	29.9 ± 2.2	706 ± 35	<0.9
Tile, Rovinari	59.2 ± 2.8	826 ± 37	<1.1
Tile, Slatina	55.4 ± 5.2	742 ± 52	<1.6
Cement mill dust, Hoghiz	<3.5	633 ± 30	3.9 ± 0.7
Cement mill dust, Fieni	<4.2	209 ± 23	1.7 ± 0.6
Asbestos-cement, Horezu	7.6 ± 1.8	46.5 ± 9.3	7.6 ± 0.5
Asbestos-cement, Targu Jiu	4.3 ± 1.1	46.6 ± 6.5	0.9 ± 0.5
Asbestos-cement, Craiova	8.9 ± 1.2	56.6 ± 9.0	7.7 ± 1.0
Coal fly ash, Deva	121.5 ± 8.0	729 ± 55	3.3 ± 1.6
Coal fly ash, Paroseni	113.7 ± 7.3	617 ± 37	<2.1
Sand, Horezu	5.5 ± 0.9	410 ± 21	1.3 ± 0.5
Sand, Targu Jiu	12.4 ± 0.7	662 ± 26	1.9 ± 0.4
Sand, Rovinari	10.9 ± 1.5	592 ± 21	3.2 ± 0.6
Sand, Slatina	3.4 ± 1.8	501 ± 18	2.7 ± 0.3
Sand, Craiova	<1.6	370 ± 22	1.1 ± 0.3
Tufa, Horezu	10.5 ± 2.4	180 ± 27	9.6 ± 0.9
Wood, Horezu	<6.7	140 ± 34	3.8 ± 0.8
Wood, Targu Jiu	<4.8	40.9 ± 33.7	14.3 ± 1.3
Wood, Craiova	<3.3	44.3 ± 35.4	9.7 ± 1.4

Table 5. Th, U, and K contents in building materials by INAA and by fission and/or alpha track method (mg.kg^{-1}).

Elem.	Cement[6]	Brick[6]	Coal fly ash[7]	Wood[8]
Th	(4.7 ± 0.1) – (5.9 ± 0.3)	15.9 ± 0.5	18.7 ± 0.9	na*
U	(1.6 ± 0.1) – (3.9 ± 0.2)	7.4 ± 0.4	7.7 ± 0.7	0.006 – 0.25
K	(3900 ± 400) – (6500 ± 400)	11700 ± 500	21100 ± 1100	na

*na–not analysed.

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