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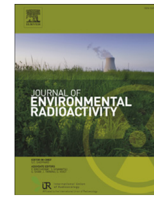

First intercomparison among laboratories involved in COST Action-TU1301 "NORM4Building": Determination of natural radionuclides in ceramics

Gerti Xhixha [a, b, *], José Antonio Trinidad [c], Catalina Gascó [c], Fabio Mantovani [d, e]

[a] *Legnaro National Laboratory - National Institute of Nuclear Physics (INFN), Via dell'Università, 2 - 35020 Legnaro, Padova, Italy*
[b] *Department of Physics, Faculty of Natural Sciences, University of Tirana, Blv. Zogu I, 1001 Tirana, Albania*
[c] *Unit of Environmental Radioactivity and Radiological Surveillance, CIEMAT, Avda de la Complutense, 40 - 28040 Madrid, Spain*
[d] *Departments of Physics and Earth Sciences, University of Ferrara, Via Saragat, 1 - 44122 Ferrara, Italy*
[e] *INFN Ferrara Section, National Institute of Nuclear Physics (INFN), Via Saragat 1, 44122 Ferrara, Italy*

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ABSTRACT

This work describes the outcomes of the COST Action-TU1301 "NORM4Building" intercomparison on the determination of natural radioactivity in ceramics. Twenty-two laboratories involved in the intercomparison are evaluated for their performance using robust statistics. The reference values of ^{226}Ra (^{214}Bi and ^{214}Pb) are determined to be 122 ± 11 Bq kg^{-1} and 124 ± 14 Bq kg^{-1}, respectively and in secular equilibrium in the uranium chain while the reference values of ^{232}Th (^{228}Ac) is determined to be 61 ± 6 Bq kg^{-1} and that of ^{40}K was determined to be 955 ± 40 Bq kg^{-1}. Although the aim of the exercise was to determine the activity concentration of ^{226}Ra, ^{232}Th and ^{40}K and evaluation of the "Activity Concentration Index", laboratories were asked to report complete characterization of natural radionuclides. The results of this exercise pointed out a good performance among laboratories since the percentage of the acceptable results were above 90% for the radionuclides of interest. Based on these results, considering the systematic rejection of the results reported from a few laboratories we emphasize the need for quality control procedures.

1. Introduction

The depletion of energy resources and raw materials has a huge impact on the construction industry. Recycling of secondary materials -such as industrial residues-to develop new construction materials is becoming a challenge. The COST Action TU1301 "NORM for Building materials (NORM4Building)" aims to motivate the collaboration of scientists, industries and regulators to gather knowledge, experiences and technologies, and to stimulate research on the reuse of residues containing enhanced concentrations of natural radionuclides (NORM) while considering the impact on both external gamma exposure of population and indoor air quality.

According to the European Council Directive 2013/59/Euratom (2013), the reference level applying to indoor external exposure to gamma radiation emitted by building materials, in addition to outdoor external exposure, should be less than 1 mSv y^{-1}. The directive proposed a screening tool, for conservatively controlling the radiological hazards due to building materials, using the **A**ctivity **C**oncentration **I**ndex (ACI) calculated with the Eq. (1):

$$ACI = \frac{C_{Ra-226}}{300} + \frac{C_{Th-232}}{200} + \frac{C_{K-40}}{3000} \leq 1 \quad (1)$$

where C_{Ra-226}, C_{Th-232} and C_{K-40} are the activity concentrations in Bq/kg for radium (equivalent to uranium under secular equilibrium conditions), thorium and potassium, respectively.

The laboratories involved in the COST Action TU1301 "NORM4-Building" faced the problem of the quality control on the determination of natural radionuclides in building materials, following other exercises (Tuo et al., 2010; Anagnostakis et al., 2004). To address this issue two actions are proposed: promoting the necessity of including building materials in the future worldwide intercomparison exercises by the institutions in charge and

* Corresponding author. Department of Physics, Faculty of Natural Sciences, University of Tirana, Blv. Zogu I, 1001 Tirana, Albania.
E-mail address: xhixha@fe.infn.it (G. Xhixha).

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stimulating laboratories to perform quality control measurements. Regarding the last purpose, within the NORM4Building COST Action TU1301, the Department of Physics (University of Ferrara - Italy) and the Unit of Environmental Radioactivity and Radiological Surveillance (CIEMAT - Spain) cooperated to organize the intercomparison exercise on the determination of natural radionuclides in ceramics. The aim of this exercise was to determine the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K (considered in the calculation of the "Activity Concentration Index"), as a screening tool for conservatively controlling the radiological hazards due to building materials. The participating laboratories (see Table 1) have reported results on the methods and amount of sample used, number of determinations, activity concentration, combined uncertainty, etc. Several conclusions can be drawn regarding the choice of the analytical procedures, radionuclides, and gamma energy, the performance of participating laboratories and the calculation and interpretation of the activity concentration index.

2. Materials and methods

2.1. Preparation of the material

Ceramic tiles (Grès porcellanato) used as building material were collected from an Italian factory. The ceramics are manufactured by using clay, sand, kaolin and feldspar as raw materials and baking them at 1100–1300 °C. The bulk material was crushed, milled and homogenized as <1 mm particle size. The dry mass content of the material was measured at 90 °C at a controlled temperature furnace for six sample aliquots for 24 h, and was found to be <0.4%.

The homogeneity of the material was assessed using gamma ray spectrometry measurements (Xhixha et al., 2013, 2015) on a series of measurements. The statistical uncertainty for 1 h of counting time were found to be less or comparable with the standard deviations. The count rates for the most intense gamma lines for ^{234m}Pa (1001.0 keV at 0.85%), ^{214}Pb (351.9 keV at 35.6%), ^{214}Bi (609.3 keV at 45.5%), ^{228}Ac (911.2 keV at 26.2%), ^{212}Pb (238.6 keV at 43.6%), ^{212}Bi (727.3 keV at 6.65%), ^{208}Tl (583.2 keV at 30.5%) and ^{40}K (1460.8 keV at 10.5%) are reported in Appendix A. Therefore, the bulk material (ceramics) can be considered sufficiently homogeneous for the intended purpose of the intercomparison, i.e. determination of natural radionuclides.

The bulk material -approximately 500 g-was packaged and sealed in polyethylene bottles, then dispatched to the 22 participant laboratories in April 2015, as a milestone of the COST Action TU1301 "NORM4Building". As the particle size distribution was not determined, it was recommended to mix the material before opening the bottle in order to overcome segregation effects due to storage or transportation. Moreover, no additional information was given to the laboratories on the chemical composition of the material, in order to do routine determination on self-absorption corrections. As the activity concentrations were asked to be reported based on dry weight, the dry weight was proposed to be determined at the time of the measurement.

2.2. Performance evaluation and z-scores

The selection of the reference value and the assessment of the performance of each participant laboratory in this intercomparison exercise were accomplished according to ISO/IEC Guide 43-1 (1997). There are several methods for establishing the reference value when a non-certified material is used. Following the recommendations of the international standard (ISO 13528, 2005), we adopt robust statistical methods based on the median and Robust Standard Deviation (RDS). In particular the laboratory performance evaluation criteria are defined by the Z_{Score} test:

$$Z_{Score} = \frac{x_{Lab} - x_M}{RSD} \tag{2}$$

where, for a fixed isotope, x_{Lab} is the measurement reported by each laboratory, x_M is the median of all measurements and RSD = 1.5 · MAD (Median Absolute Deviation). The established acceptance criteria for evaluating the exercise performance are $|Z_{Score}| \leq 2$ "*acceptable*", $2 < |Z_{Score}| \leq 3$ "*warning*", and $|Z_{Score}| \geq 3$ "*non-acceptable*".

3. Results and discussions

In this intercomparison exercise, 22 laboratories were involved, reporting 216 data (67.5% of the total expected data). However, the goal of the exercise on the determination of natural radionuclides

Table 1
Participating countries and institutions in the 1st intercomparison exercise on natural radionuclides in ceramics.

Country	Organization
Albania	Institute of Applied Nuclear Physics, University of Tirana
Belgium	Nuclear Technology - Faculty of Engineering Technology, University of Hasselt
Belgium	SCK CEN Belgian Nuclear Research Centre
Croatia	Institute for Medical research and occupational Health Radiation Protection Unit
Denmark	DTU Nutech, Technical University of Denmark
Estonia	Institute of Physics, University of Tartu
France	IRSN Institut de Radioprotection et de Sureté Nucléaire
Germany	IAF - Radioökologie GmbH
Greece	National Technical University of Athens
Hungary	Institute of Radiochemistry and Radioecology, University of Pannonia
Hungary	Social Organization for Radioecological Cleanliness
Italy	Department of Physics and Earth Sciences - University of Ferrara
Italy	Instituto Superiore di Sanità
Netherlands	NRG
Poland	Silesian Centre for Environmental Radioactivity, GIG
Portugal	Instituto Superior Técnico (IST), Campus Tecnologico e Nuclear (CTN), Universidade de Lisboa
Slovenia	ZVD Zavod za varstvo pri delu d.o.o.
Spain	CIEMAT-Servicio de Protección Radiológica
Spain	CIEMAT-Unidad de Radiactividad Ambiental y Vigilancia Radiólogica
Spain	University of Huelva
Spain	University of Salamanca
Spain	University Autónoma de Barcelona
USA	Nuclear Engineering Teaching Lab, University of Texas

for estimating the activity concentration index was fully accomplished. The activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K were determined by gamma-ray spectrometry measurements using High-Purity Germanium (HPGe) detectors (11 laboratories), Reverse Electrode Germanium (REGe) detectors (2 laboratories), Broad Energy Germanium (BEGe) detectors (6 laboratories), Gamma-X Germanium (GM-X) detectors (2 laboratories) and only one laboratory used $LaBr_3$:Ce detector. The size of ceramic samples ranged from 30 g to 564 g. The spectrum analysis was usually performed using commercial software with proper attenuation, geometry and coincidence summing corrections. All the results of the intercomparison exercise are summarized in Appendix B. Some results of selected radionuclides for uranium series, thorium series and ^{40}K are discussed in this article as they are of greater interest in the intercomparison exercise and the number of participants was enough to allow such assessment, while the results on other reported radionuclides with scarce laboratories participation are shown and commented in Appendix B.

For the uranium series, the activity concentrations of ^{226}Ra, ^{214}Pb and ^{214}Bi were determined, among other radionuclides (Fig. 1). The reference values of the activity concentration of ^{226}Ra, ^{214}Pb and ^{214}Bi are determined to be 125 ± 11 Bq kg^{-1}, 122 ± 11 Bq kg^{-1} and 124 ± 14 Bq kg^{-1}, respectively. In Table B-1 (Appendix B) the reference values on ^{234}Th and ^{210}Pb confirm the secular equilibrium within the reported uncertainty of uranium series. Out of the 17 laboratories that reported the activity concentration of ^{226}Ra, only 41% used the gamma energy of 186 keV (^{226}Ra), while the others either determined the activity concentration using ^{214}Pb and/or ^{214}Bi or did not specify the method used. According to the evaluation criteria of the intercomparison exercise, the percentage of acceptable scores is 88%. In total 21 laboratories reported the activity concentration of ^{214}Pb, determined by using the gamma energy of 295 keV (24% of laboratories), 352 keV (33% of laboratories), both of them (29% of laboratories) and the rest did not report this information. According to the evaluation criteria of the intercomparison exercise, the percentage of acceptable scores is 90%. For this reason, ^{214}Pb was selected for determining the activity concentration of ^{226}Ra that appears in the activity concentration index (ACI). The activity concentration of ^{214}Bi was reported by 20 laboratories, when most of them determined it by using the gamma energy of 609 keV. Only 15% of laboratories declared that used 1120 keV gamma energy for the determination of the activity concentration of ^{214}Bi. According to the evaluation criteria of the intercomparison exercise, the percentage of acceptable scores is 90%.

For the thorium series the activity concentrations of ^{228}Ac, ^{212}Pb and ^{208}Tl were determined, among other radionuclides (Fig. 2). The reference values of the activity concentration of ^{228}Ac, ^{212}Pb and ^{208}Tl are determined to be 61 ± 6 Bq kg^{-1}, 64 ± 6 Bq kg^{-1} and 24 ± 5 Bq kg^{-1}, respectively. The activity concentration of ^{228}Ra (reference value 62 ± 3 Bq kg^{-1}) is generally determined by gamma-ray spectrometry measurements using the ^{228}Ac gamma energies. However, only 8 laboratories reported ^{228}Ra activity concentrations (therefore the performance was not evaluated), while 20 laboratories reported the activity concentration of ^{228}Ac. The activity concentration was determined by using the gamma energy of 911 keV, 338 keV or both of them. According to the evaluation criteria of the intercomparison exercise, the percentage of acceptable scores is 100%. The activity concentration of ^{212}Pb was reported by 19 laboratories, most of them determined the activity concentration by means of 239 keV gamma ray. Approximately 10% of laboratories overestimated the activity concentration of ^{212}Pb, therefore the percentage of acceptable scores is 90%. On the other hand, 19 laboratories reported the activity concentration of ^{208}Tl. Most of the laboratories used the 583 keV gamma energy for the determination of its activity concentration. Considering the performance of the above-mentioned radionuclides, we observe a greater number of laboratories overestimating the activity

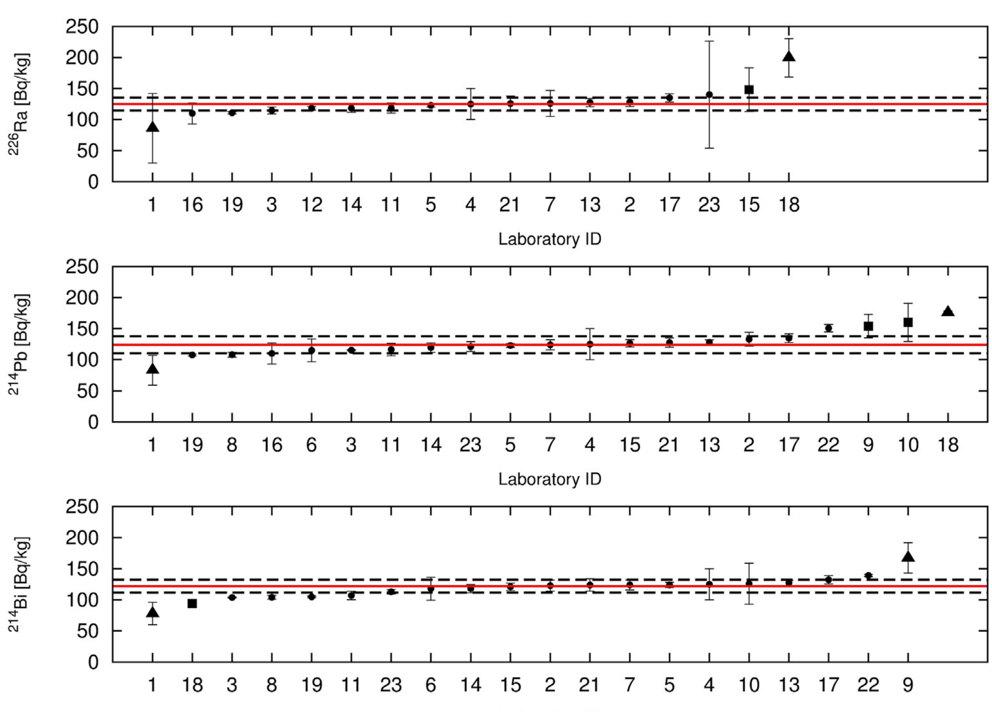

Fig. 1. The activity concentrations of ^{226}Ra, ^{214}Pb and ^{214}Bi measured in ceramic samples. Symbols express the Z-score: acceptable (circle), warning (squares) and non-acceptable (triangles). The red line and the dotted black line correspond to the median and robust standard deviation respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

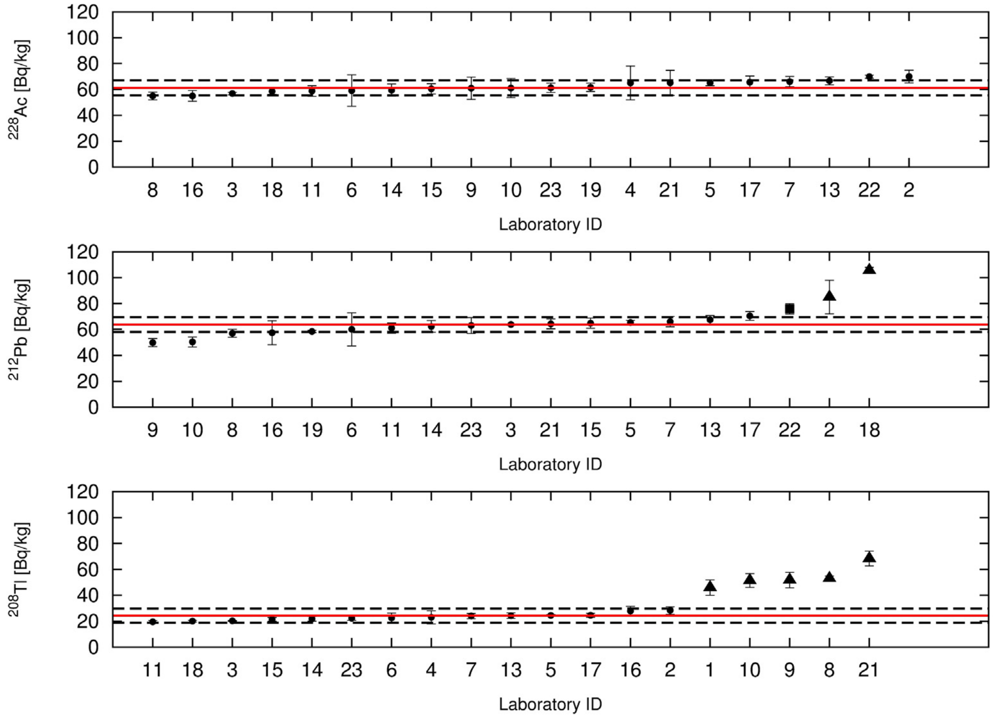

Fig. 2. The activity concentrations of ^{228}Ac, ^{212}Pb and ^{208}Tl measured in ceramic samples. Symbols express the Z-score: acceptable (circle), warning (squares) and non-acceptable (triangles). The red line and the dotted black line correspond to the median and robust standard deviation respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

concentration of ^{208}Tl (26% of them). This result is affected by the fact that at least half of these laboratories reported the activity concentration of ^{208}Tl in equilibrium with ^{232}Th, without taking into account the branching ratio in the natural series. Therefore, the percentage of acceptable scores are about 87%.

The activity concentration of ^{40}K was reported by all 22 laboratories (Fig. 3) with a reference value of 955 ± 40 Bq kg^{-1}. All of them used the gamma ray spectrometry technique for the determination of the activity concentration through the 1460 keV gamma energy. According to the evaluation criteria of the intercomparison exercise, described above, the percentage of acceptable scores is 91%. However, the results for ^{40}K were not fully

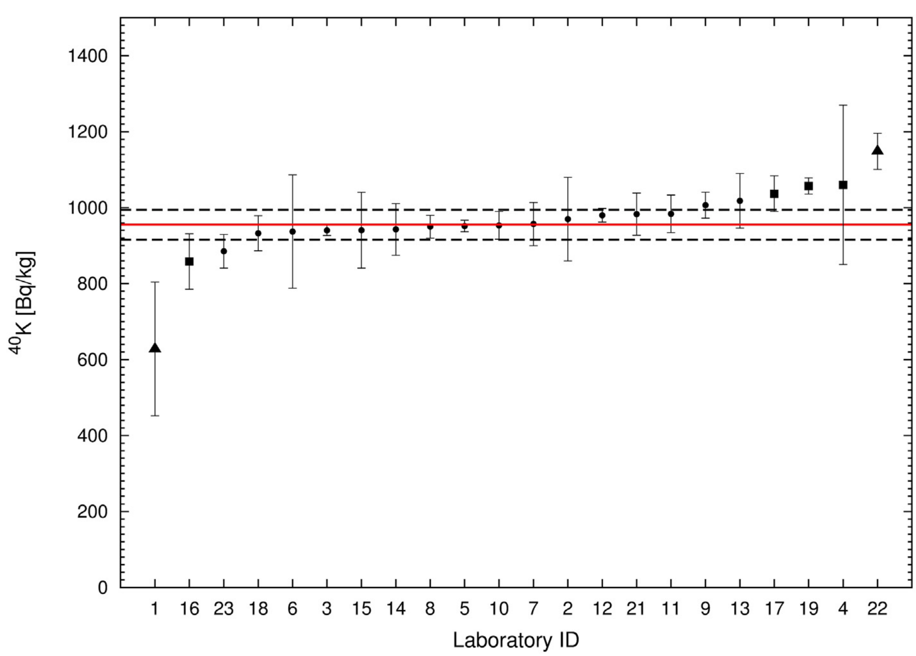

Fig. 3. The activity concentrations of ^{40}K measured in ceramic samples. Symbols express the Z-score: acceptable (circle), warning (squares) and not-acceptable (triangles). The red line and the dotted black line correspond to the median and robust standard deviation respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

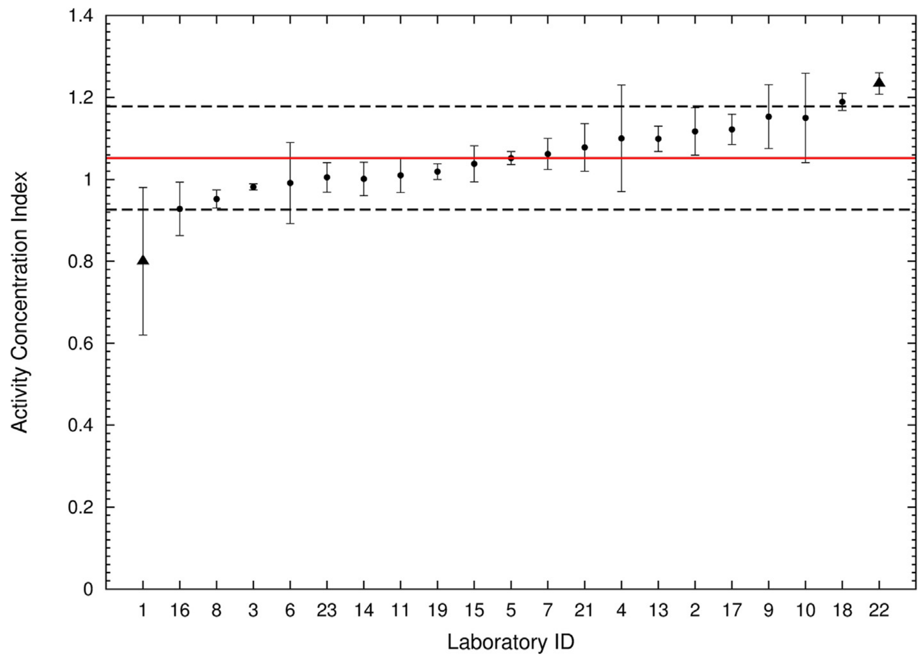

Fig. 4. The activity concentration index calculated for the ceramic samples. Symbols express the Z-score: acceptable (circle), warning (squares) and non-acceptable (triangles). The red line and the dotted black line correspond to the median and robust standard deviation respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

satisfactory, considering that is an "easy to be measured" radionuclide.

The activity concentration of radionuclides having the better agreement among laboratories were ^{228}Ac for ^{232}Th series, and ^{214}Pb and ^{214}Bi for ^{238}U series. For ^{40}K, a single gamma energy can only measure its activity concentration and no other radionuclides or energies can be chosen. The percentage of acceptable scores are 100% for ^{232}Th, 90% for ^{238}U and 91% for ^{40}K: considering the abovementioned radionuclides as the best candidates for reliable characterization of their respective radioactive series. These results were then used to calculate the activity concentration index as reported in Fig. 4.

As demonstrated in this intercomparison exercise, the performance of the laboratories for the determination of natural radionuclides was satisfactory. However, very few laboratories did not use appropriate calibration as systematically shown by their results. The median of the index was 1.05 ± 0.13 (k = 1). Attention must be focused on the interpretation of such results. According to the Council Directive 2013/59/Euratom (2013) an activity concentration index value of 1 can be used as a conservative screening tool for identifying materials that may cause the reference level of 1 mSv y^{-1} to be exceeded. In this case, prior to make a decision, the calculation of dose is needed taking into account other factors such as density, thickness of the material as well as factors relating to the type of building and the intended use of the material (bulk or superficial) (Nuccetelli et al., 2015).

4. Conclusions

This is the first intercomparison on determination of natural radionuclides in Italian ceramics (Grès porcellanato) organized in the framework of COST Action-TU1301 "NORM4Building" involving 22 European laboratories which performed 216 gamma-ray spectrometry measurements of activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K.

For the uranium series the activity concentrations of ^{226}Ra, ^{214}Pb and ^{214}Bi the percentage of acceptable scores are 88%, 90% and 90% respectively. Concerning the thorium series, the percentage of acceptable scores for ^{228}Ac is 100%, while 10% of the laboratories overestimate the values of ^{212}Pb and 13% of the laboratories overestimate or reported in equilibrium with ^{232}Th the activity concentration of ^{208}Tl. It is surprising to note that a non-negligible 9% of the measurements of ^{40}K single gamma decay are evaluated as non-acceptable. Considering the systematic rejection of the results reported from a few laboratories, we conclude that they may not use appropriate calibration; therefore, there is a need for quality assurance measures. The choice of gamma energies in each case was found to be appropriate for the determination of the activity concentration of radionuclides.

As demonstrated from the performance of laboratories involved in the intercomparison, the percentage of acceptable scores obtained was higher than 85% regarding the radionuclides of interest for the calculation of the activity concentration index, which shows a median of 1.05 ± 0.13. Considering the recommendations of Council Directive 2013/59/Euratom (2013), this is a typical border line value which requires a detailed study (Nuccetelli et al., 2015) including other contributions (e.g. density, thickness, use of the material, etc.) to the dose.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvrad.2016.03.007.

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