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Radiochemical Characterization of Phosphogypsum for Engineering Use

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ABSTRACT

The new phosphogypsum (PG) waste management policy allowed to reduce the negative environmental impact of this residue by finding better alternatives uses with an extremely limited radiological impact. Building material could be one of these alternatives that could lead to the production of final products with good mechanical properties and very limited radionuclides content. The optimization of the radioactive levels in the building materials when PG is used for its production requires the previous knowledge of the content of naturally occurring radionuclides in the PG waste. This article aims the radioactive characterization of two different PG sources (from Spain (Fertiberia S.A., Huelva) and Tunisia (Sfax), before being incorporated in building materials. For this purpose, the natural selected radionuclides content belonging to uranium and thorium decay series and ^{40}K was determined, by means of two different methods: i) gamma spectrometry with high-purity germanium detectors and ii) laser-induced kinetic phosphorimetry (KPA-11 Chemcheck Instruments Inc., Richland, WA). Also, the semiquantitative chemical composition, the mineralogical study and the morphological aspect of the PG samples were analysed. The results obtained from both techniques show that ^{226}Ra and ^{210}Po are the main source of the radioactivity in both studied PG samples. However, PG samples from Tunisia present low natural radionuclide levels (30.7 $Bq \cdot kg^{-1}$ average value for ^{238}U, 188 $Bq \cdot kg^{-1}(^{226}Ra)$, 163 $Bq \cdot kg^{-1}(^{210}Pb)$, 12.4 $Bq \cdot kg^{-1}$ (^{232}Th) compared to the level of natural radionuclides in PG samples from Huelva (102 $Bq \cdot kg^{-1}$ average value for ^{238}U, 520 $Bq \cdot kg^{-1}(^{226}Ra)$, 881 $Bq \cdot kg^{-1}(^{210}Pb)$ and 8 $Bq \cdot kg^{-1}$ (^{232}Th). Both PG fulfil European Commission Recommendation (ECR) for the maximum activity concentrations of naturally-occurring radionuclides for industrial by product used in building materials in the European Union.

Keywords: Phosphogypsum, Radionuclides Analysis, Phosphate Industry, Gamma Spectrometry, TENORM

1. Introduction

Phosphogypsum (PG) is an industrial residue from processing phosphate rock using the "wet acid" process to produce the phosphoric acid (H_3PO_4) in fertilizer plants (Equation (1)), which currently accounts for over 90% of phosphoric acid production.

$$Ca_5F(PO_4)_3 + 5H_2SO_4 + 10H_2O$$
$$\rightarrow 3H_3PO_4 + 5CaSO_4 \cdot 2H_2O + HF \quad (1)$$
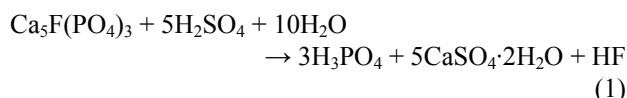
This process is economic however it results in the generation of a large amount of PG (for every ton of phosphoric acid produced, about 5 tons of PG are yielded). The worldwide generation is estimated to be around 100 - 280 Mt per year [1,2]. PG consists principally of

calcium sulphate ($CaSO_4 \cdot 2H_2O$) but also contains a high level of impurities such as phosphates, fluorides and sulphates, naturally occurring radionuclides, heavy metals, and other trace elements.

Nowadays, PG represents one of the most serious problems faced by the phosphate industry, since commercial uses, in manufacturing gypsum board and Portland cement and in agricultural fertilisers or soil stabilisation amendments, consume less than 15% of the worldwide generation of PG. The remaining 85% is disposed of without any treatment and usually dumped in large stockpiles exposed to weathering processes, occupying considerable land areas and causing serious environmental contamination of soils, water and the atmosphere, particularly in coastal regions [3]. The main prob-

lem associated with the storage of PG is considered to be the relatively high levels of natural uranium-series radionuclides, naturally present in the phosphate rock and which provoke a negative environmental impact and many restrictions on the use of this residue. Depending on the quality of the phosphate rock source, PG can contain as much as 60 times the levels normally found prior to processing. Previous study performed by Bolivar [4] showed that about 80% of the ^{226}Ra, 90% of the ^{210}Po and 20% of the ^{238}U and ^{234}U originally present in the phosphate rock remain in PG. Furthermore, the most important source of PG radioactivity is reported to be ^{226}Ra [5]. ^{226}Ra produces radon gas (^{222}Rn), which has a short half-life of 3.8 days, an intense radiation capacity, and causes significant damage to internal organs [6]. Thus the potential problem of PG piles is the emanation of ^{222}Rn from the alpha-decay of ^{226}Ra, a radionuclide classified by the USEPA as a Group human carcinogen, whose common presence in PG led to the regulation of PG disposal under the National Emission Standards for Hazardous Air Pollutants (NESHAP) and the National Emission Standards for Radon Emission from PG Stacks [7]. The United States Environmental Protection Agency (USEPA) classified PG as a "Technologically Enhanced Naturally Occurring Radioactive Material" (TENORM) [6] and PG exceeding 370 Bq/kg of radioactivity has been banned from all uses by the EPA since 1992. The maximum regulatory limit of ^{222}Rn exhalation (the flux density of ^{222}Rn gas entering the atmosphere from the surface of a ^{226}Ra-bearing material) established by the EPA [8] is 0.74 Bq/m^2/s.

In Huelva (Spain), PG stacks located on salt marshes contain about 100 Mt of PG (area of approx. 1200 ha with average height of 5 m) and are generally not completely watertight or even covered with any inert material, leading to a local gamma radiation level between 5 and 38 times the normal rate (0.74 Bq/m^2/s) [9]. The same situation is observed in Sfax (Tunisia), where PG is accumulated in two enormous warehouses situated at the coastal strip of the urban area, the first one is 12 m high and covers an area of 40 ha, and the other one, 30 m high, covers an area of 60 ha.

The present study was conducted to determine the natural selected radionuclides content belonging to uranium and thorium decay series and ^{40}K in the two different PG sources mentioned above, using two different methods.

2. Material and Methods

The PG samples used in this study came from a fertiliser factory in Sfax city, Tunisia and from Fertiberia S.A., Huelva, Spain.

The semiquantitative chemical composition of the PG samples was identified by an X-ray fluorescence analyser (Philips model PW-1404 sequential wavelength dispersion unit). Mineral species were determined by X-ray diffraction (Siemens model D5000, with a Cu tube and LiF monochromator). The morphological aspect of the PG was analysed using scanning electron microscopy (SEM) (Joel model JXA-840) with energy dispersive spectroscopy (EDS). Natural selected radionuclides belonging to uranium and thorium decay series and ^{40}K present in PG samples have been quantified as shown in the **Figure 1**.
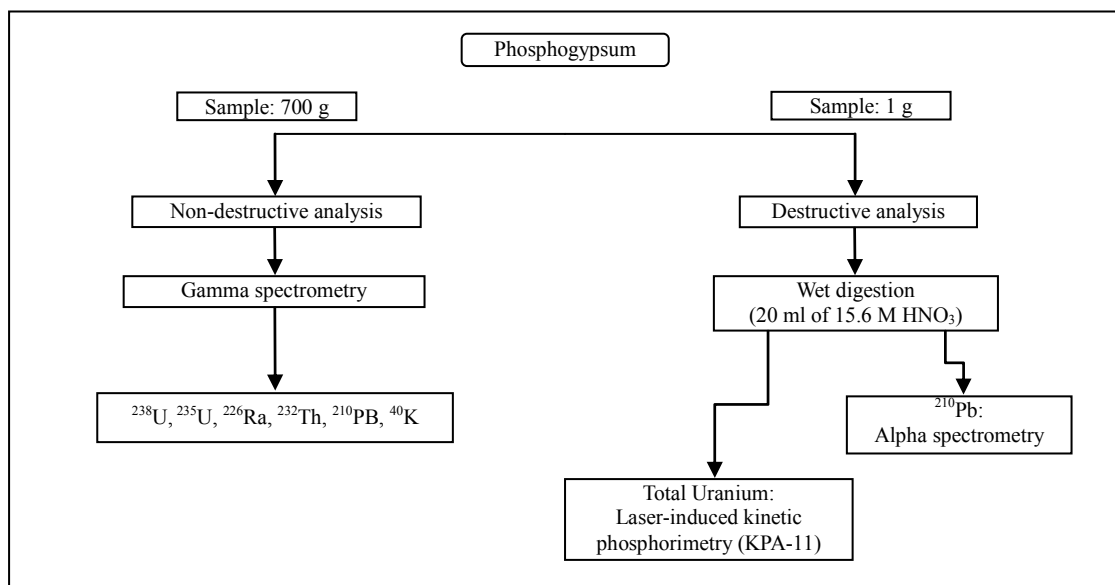

Figure 1. Scheme of radionuclides quantification procedure.

Uranium: the uranium content in the samples was determined using two different methods: 1) Direct measurements by gamma spectrometry with high-purity germanium detectors and 2) Laser-induced kinetic phosphorimetry. The direct measurements were carried out on 700-g aliquots of the samples packed in standard marinelli beakers. The ^{238}U activity concentration was determined through the photopeaks of its immediate decay product, ^{234}Th (63 and 92.5 keV), whereas ^{235}U was measured directly from its 143.8 and 163.4 keV gamma-ray peaks. Concerning Laser-induced kinetic phosphorimetry technique, 1 g of the sample was completely digested in 15.6 mol·l^{-1} HNO$_3$ and the measurements were performed using a kinetic phosphorescence analyzer (KPA-11) (Chemcheck Instruments Inc., Richland, WA) [10]. In order to compare the results obtained by both techniques, the total uranium concentration obtained by Laser-induced kinetic phosphorimetry, expressed in µg·g^{-1}, were then converted to the activity concentration of each uranium isotope. Theoretical values of the isotopic composition of natural uranium (99.3% ^{238}U, 0.72% ^{235}U, and 5.5·10^{-3}% ^{234}U) and the specific activities of these isotopes in natural uranium (Bq·g^{-1}) were used for this purpose [11].

Polonium: the polonium activity concentration in the both samples was determined by alpha spectrometry, following the ^{210}Po separation procedure described in the **Figure 2** [12]. An aliquot of 1 g was digested in a hot plate at a controlled temperature ($< 90°$C), using 8 mol·l^{-1} HNO$_3$. Polonium-209 standard dissolution was added to the dissolved samples as a tracer to estimate the recovery of the whole process. The polonium isotopes were self-deposited on silver disks following Flynn's method [13].
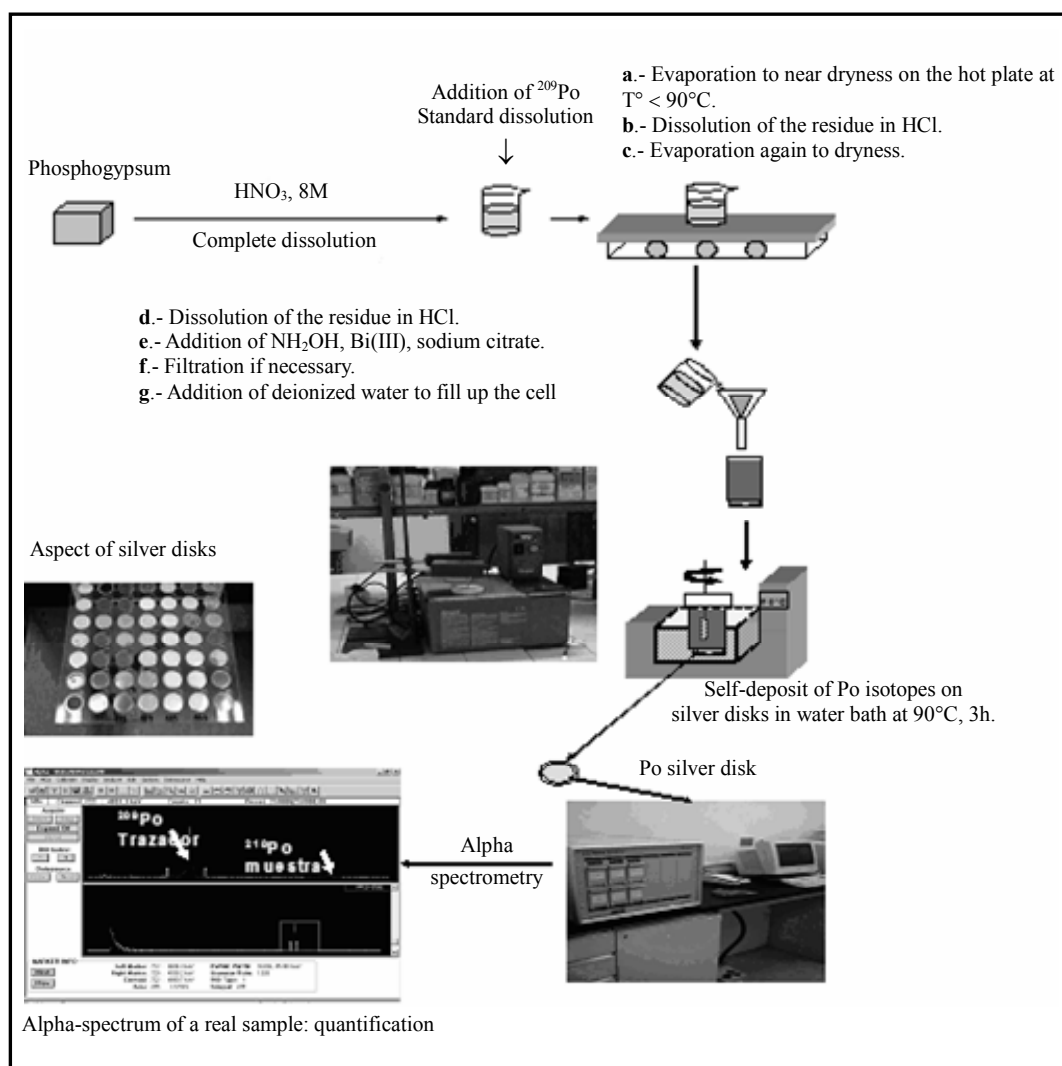

a.- Evaporation to near dryness on the hot plate at T° $< 90°$C.
b.- Dissolution of the residue in HCl.
c.- Evaporation again to dryness.

Addition of ^{209}Po Standard dissolution

Phosphogypsum

HNO$_3$, 8M

Complete dissolution

d.- Dissolution of the residue in HCl.
e.- Addition of NH$_2$OH, Bi(III), sodium citrate.
f.- Filtration if necessary.
g.- Addition of deionized water to fill up the cell

Aspect of silver disks

Self-deposit of Po isotopes on silver disks in water bath at 90°C, 3h.

Po silver disk

Alpha spectrometry

Alpha-spectrum of a real sample: quantification

Figure 2. Scheme of ^{210}Po separation procedure.

[226]Ra, [232]Th, ^{210}Pb and [40]K: the concentrations of these radionuclides were quantified by gamma spectrometry analysis using an HPGe detector. The detector was shielded from external radiation by an iron wall (15 cm thickness). The emission gamma spectrum was analyzed using Genie-2000 application software. To ensure radioactive equilibrium between [226]Ra and its short lived decay products, the samples (700 g aliquot) were packed in standard marinelli beakers, hermetically sealed and stored for about four weeks prior to counting. The concentration of [226]Ra and [232]Th was estimated from their daughters gamma-ray photopeaks, [214]Bi (609 keV) and [228]Ac (911.2 keV, 969.0 keV) respectively. [210]Pb and [40]K were measured directly from their gamma-ray emissions at 46.5 keV and 1460.8 keV respectively. The minimum detectable activity limit (DL) was also calculated.

3. Results and Discussion

3.1. Phosphogypsum Characterization

The chemical composition of both type of PG sample is summarised in **Table 1**. The data shows that sulphate (expressed as SO_3), CaO, SiO_2 and P_2O_5 are the major elements (50.7, 41.24, 1.38 and 1.2%, respectively) for Tunisian PG, and 52.6, 42.82, 2.72 and 0.7, respectively for Spanish PG.

The **Figure 3** reports the powder X-ray diffraction pattern of PG samples. As shown, Spanish PG presents two maximum intensity diffraction peaks corresponding to gypsum ($CaSO_4 \cdot 2H_2O$) (JCPDS 33-0311) and bassanite ($CaSO_4 \cdot 1/2H_2O$), while the main diffraction peaks of the Tunisian PG corresponds to gypsum ($CaSO_4 \cdot 2H_2O$).

The morphological study of PG sample using SEM, illustrated in **Figure 4**, shows two different sections of the sample. The micrographs reveal a homogeneous and prismatic PG piling arrangement and a well-defined crystalline structure with a majority of orthorhombic shaped crystals [14]. Similar results can be observed in the study performed by Miloš and Dragan [15], in which they reported that the marked crystal structure of PG indicates that PG presents a more complex composition than natural gypsum (characterized by a poorly expressed crystalline structure), which may eventually influence its chemical behaviour.

3.2. Natural Radionuclide Concentrations

The results of the natural radioactivity concentration analyses of each one of the PG samples by the two techniques employed for this purpose (gamma spectrometry and laser-induced kinetic phosphorimetry) are listed in **Tables 2** and **3**. The average activity concentration of [238]U, [226]Ra, [210]Po, [232]Th and [40]K in Tunisian PG samples are 30.7, 188, 194, 12.4 and 13 Bq·kg^{-1}, respectively, while in Spanish PG samples are 102, 520, 820, 8 and 39 Bq·kg^{-1}, respectively. We can deduce that [226]Ra and [210]Po are the main source of the radioactivity in both PG

Table 1. The major element composition (wt%) of PG samples.

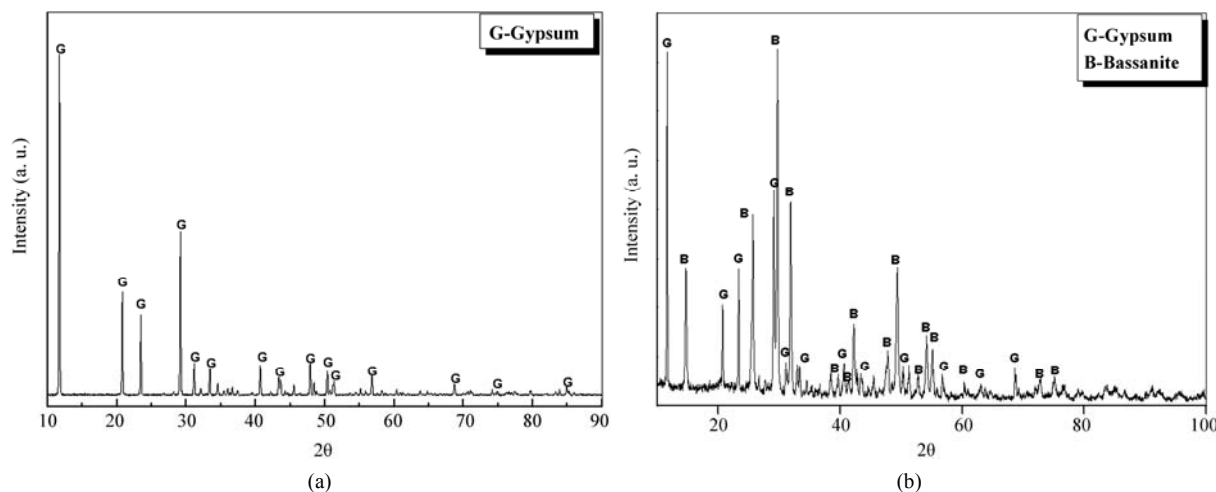| Element (Wt%)	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	SO$_3$	Na$_2$O	P$_2$O$_5$	F$^-$
PG (Tunisia)	41.24	1.38	0.11	0.09	0.02	50.7	0.59	1.2	4.9
PG (Spain)	42.82	2.72	0.40	0.22	0.07	52.6	0.24	0.7	-

Figure 3. X-ray pattern of phosphogypsum: (a) from Tunisia and (b) from Spain. Intensities in arbitrary units (a. u.).
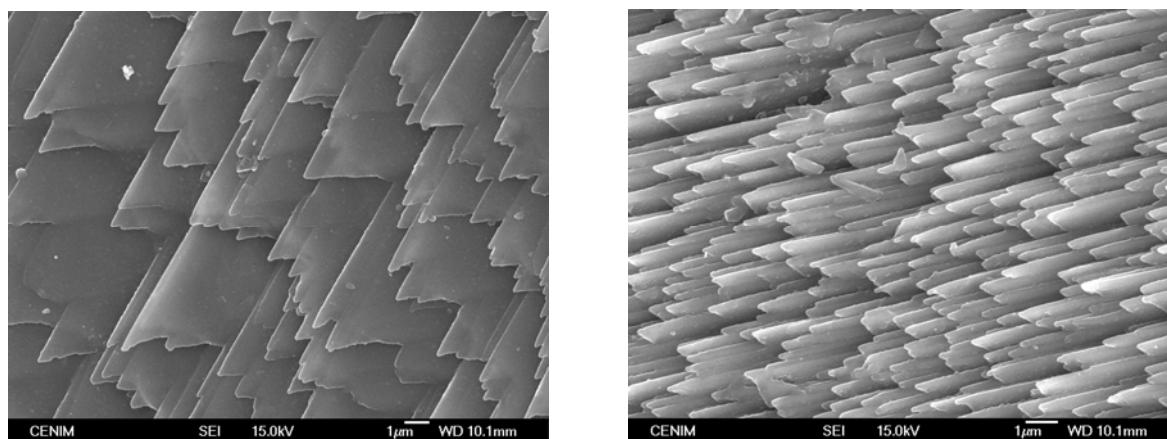
Figure 4. SEM micrographs of two different sections of a PG sample (15 keV).

Table 2. Uranium activity ratio in PG from Spain and Tunisia, expressed in Bq·kg^{-1} (± 2 s), by means of phosphorimetry and gamma spectrometry techniques.

Sample	U (Phosphorimetry)			U (Gamma spectrometry) (DL)[*]	
	^{238}U	^{234}U	^{235}U	^{238}U(^{234}Th)	^{235}U
PG (Tunisia)	30.7	31.6	1.4	27 ± 4.9 (40)*	< 6.5 *
PG (Spain)	102 ± 1	105 ± 5	4.7 ± 0.2	81 ± 28	8 ± 3 (20) *

[*]DL. Detection Limit

Table 3. Natural radionuclide activity ratio of the 238 Uranium-series (226Ra, 210Pb and 210Po in this case in radioactive equilibrium), 232 Th and 40 K expressed in Bq·kg^{-1} (± 2 s) in PG from Spain and Tunisia.

Sample	^{226}Ra(^{214}Bi)	^{210}Pb	^{210}Po	^{40}K	^{232}Th(^{228}Ac)
PG (Tunisia)	188 ± 9.5	163 ± 81	194 ± 78	< 13.5	12.4 ± 1.4
PG (Spain)	520 ± 23	881 ± 58	820 ± 43	< (39) *	8 ± 2

[*]DL. Detection Limit

samples. The results obtained were compared to those reported in other world regions (**Table 4**) [5,9,16,17]. It is found that a special attention is drawn to the low natural radionuclide levels present in the PG samples from Tunisia (30.7 for ^{238}U, 188 (^{226}Ra), 194 (^{210}Po), 12.4 (^{232}Th) and 13 Bq·kg^{-1} (^{40}K)). Furthermore, these values are lower than those of the average worldwide activity concentration of ^{238}U, ^{232}Th, and ^{40}K (50, 50 and 500 Bq·kg^{-1}, respectively) [18]. This different content may be attributed to the nature of the phosphate rock, the depth of sampling [19] and differences in the industrial process applied to obtain phosphoric acid. Natural radioactivity in the different phases of the production system has recently been analysed by Bolivar *et al.* [20] showing that Pb, Ra and to a certain extent Th isotopes are exclusively supplied by the phosphate rock and remain associated to the PG particles, while uranium decreases according to the number of washings of the PG.

The data showed that the both studied PG samples (Tunisian and Spanish) fulfil European Commission Recommendation for the maximum activity concentrations of naturally-occurring radionuclides in common buildings materials and industrial by-products used for building materials in the EU [21]. This finding could make possible the use of the studied PG as building material.

Concerning the measurement techniques used in this study, it found that the use of gamma spectrometry for uranium determination allows the analysis of a more representative aliquot of the whole sample than in the case of the KPA technique. KPA has a lower detection limit (sensitivity) and better uncertainty (6%), but due to the limitations of wet digestion until total dissolution and chemical interferences, only 1 g can be analysed. Nevertheless, the results obtained from both techniques are in good agreement.

Table 4. Activity concentrations of different types of phosphogypsum samples analyzed, in Bq kg^{-1} [5,9,16,17].

Origen	^{238}U	^{226}Ra	^{210}Pb	^{210}Po	^{230}Th
Spain [9]	220	670	520	-	8.2
China [16]	15d	85	82	82	-
Indonesia [16]	43	473	480	450	-
India [16]	60	510	490	420	-
Egypt [17]	140	459	323	-	8.3
Florida [5]	130	1140	1370	1030	113
Australia [5]	10	500	-	-	-
Sweden [5]	390	15	-	-	-

4. Conclusions

The sensitivity of the analytical methods is good enough to detect the radionuclides existing in both types of samples.

For uranium quantification, the gamma spectrometry allows the analysis of a more representative aliquot of the whole sample than in the case of the KPA technique. However; KPA has a lower detection limit (sensitivity) and better uncertainty (6%).

The PG samples from Tunisia present a low natural radionuclide levels (30.7 Bq·kg^{-1} for ^{238}U, 188 Bq·kg^{-1} (^{226}Ra), 163 Bq·kg^{-1} (^{210}Pb), 12.4 Bq·kg^{-1} (^{232}Th)) compared to the level of PG samples from Huelva (102 Bq·kg^{-1} for ^{238}U, 520 Bq·kg^{-1} (^{226}Ra), 881 Bq·kg^{-1} (^{210}Pb) and 8 Bq·kg^{-1} (^{232}Th). In both cases, the values are below the maximum activity concentrations limits of naturally-occurring radionuclides in common buildings materials and industrial by-products used for building materials in the EU, recommended by the European Commission.

5. Acknowledgements

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